



(12) 发明专利

(10) 授权公告号 CN 101488562 B

(45) 授权公告日 2011. 10. 12

(21) 申请号 200810188965. 2

H01L 51/46(2006. 01)

(22) 申请日 2008. 12. 31

C09K 11/06(2006. 01)

(30) 优先权数据

10-2007-0141997 2007. 12. 31 KR

(56) 对比文件

WO 2004055130 A1, 2004. 07. 01, 全文.

CN 1816556 A, 2006. 08. 09, 全文.

(73) 专利权人 葛来西雅帝史派有限公司

地址 韩国首尔

US 20040124769 A1, 2004. 07. 01, 说明书第

0033-0097 段及 0173 段.

(72) 发明人 金贤 阴盛镇 赵英俊 权赫柱

金奉玉 金圣珉 尹胜洙

EP 1394235 A1, 2004. 03. 03, 说明书摘要、第

0082-0085 段.

(74) 专利代理机构 上海专利商标事务所有限公

司 31100

审查员 刘颖洁

代理人 陈哲锋

(51) Int. Cl.

H01L 51/50(2006. 01)

H01L 51/54(2006. 01)

H01L 51/42(2006. 01)

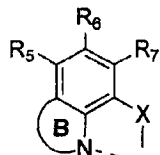
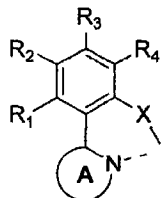
权利要求书 3 页 说明书 145 页 附图 1 页

(54) 发明名称

采用电致发光化合物的电致发光器件

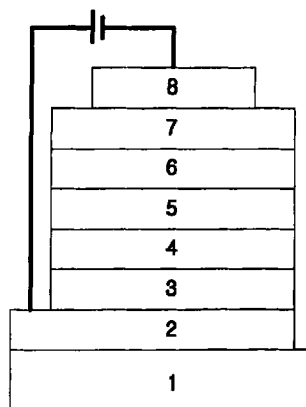
(57) 摘要

本发明涉及一种电致发光器件。更具体地说,本发明所述的电致发光器件包括第一电极;第二电极;和至少一个插入所述第一电极和所述第二电极之间的有机层;而所述有机层包含一种或多种由化学式(1)代表的有机电致发光化合物作为主体材料:化学式 $1L^1L^2M(Q)_y$;其中,配体 L^1 和 L^2 独立地选自以下结构:



其中,

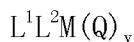
M代表二价金属或三价金属;当M是二价金属时y是0,而当M是三价金属时y是1;Q代表(C6-C60)芳氧基或三(C6-C60)芳基甲硅烷基,且Q的芳氧基或三芳基甲硅烷基可被(C1-C60)烷基或(C6-C60)芳基进一步取代。本发明的电致发光器件具有出色的色纯度和发光效率。



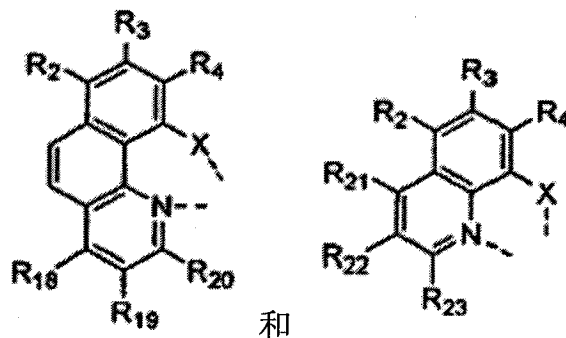
1. 一种电致发光器件,其包括第一电极;第二电极;和至少一个插入所述第一电极和所述第二电极之间的有机层,所述有机层包含电致发光区,所述电致发光区包含:

i) 一种或多种由化学式 (1) 代表的主体化合物,

化学式 1



其中,配体 L^1 和 L^2 独立地选自以下结构:



其中, M 代表二价或三价金属;

当 M 是二价金属时 y 是 0, 而当 M 是三价金属时 y 是 1;

Q 代表 (C6-C60) 芳氧基或三 (C6-C60) 芳基甲硅烷基, 且 Q 的芳氧基或三芳基甲硅烷基可被 (C1-C60) 烷基或 (C6-C60) 芳基进一步取代;

X 代表 O、S 或 Se;

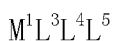
R_2 至 R_4 独立地代表氢, (C1-C60) 烷基, 卤素, 具有卤素取代基的 (C1-C60) 烷基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基; 或者它们各自可通过亚烷基或亚烯基与相邻取代基相连而形成稠环;

R_2 至 R_4 的芳基或杂芳基, 或者通过亚烷基或亚烯基与相邻取代基相连而形成的稠环可被选自下组的一个或多个取代基进一步取代: (C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基; 和

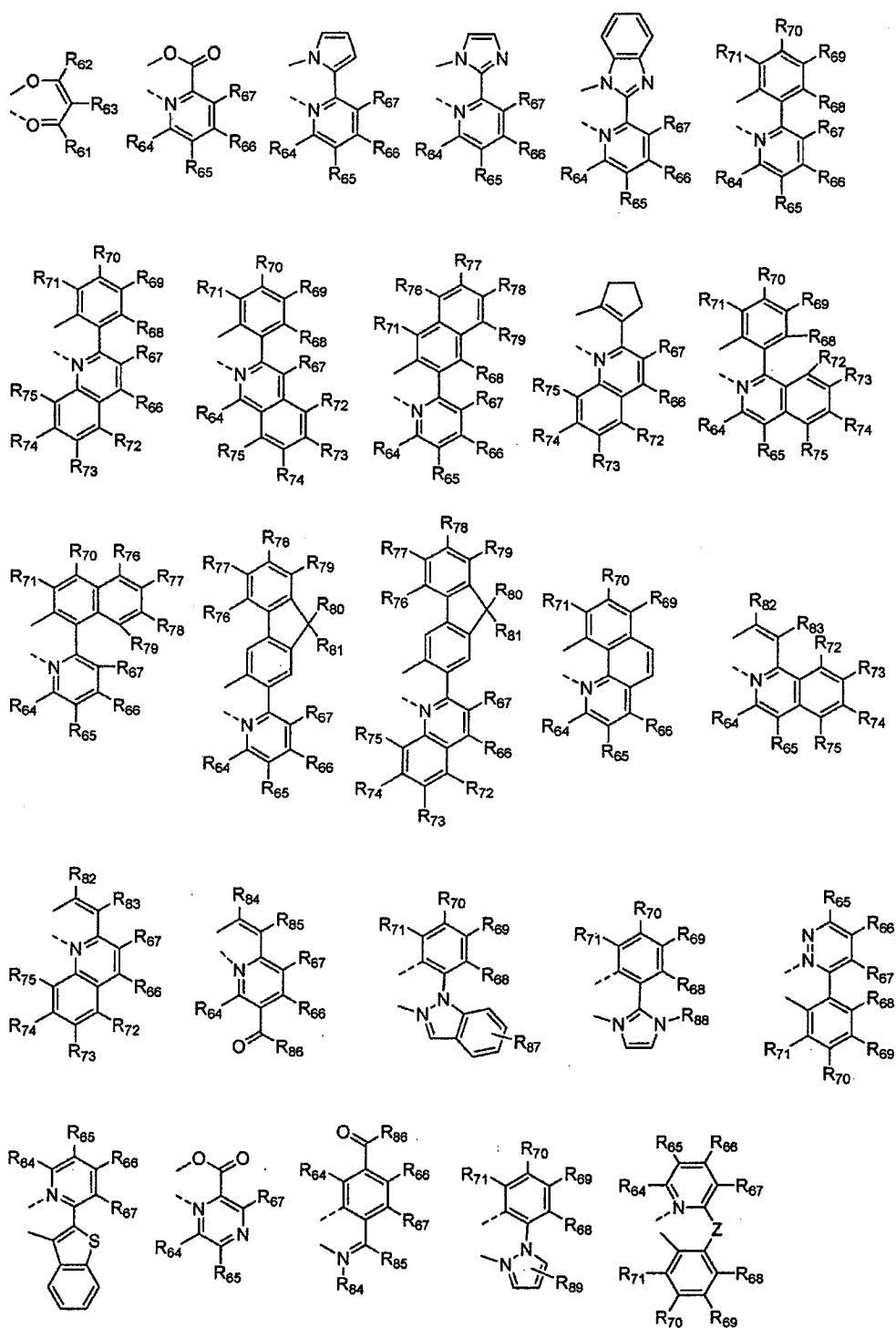
R_{18} 至 R_{23} 独立地代表氢, (C1-C60) 烷基, 卤素, 具有卤素取代基的 (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基或二 (C6-C30) 芳基氨基; 或者 R_{13} 至 R_{16} 和 R_{17} 至 R_{20} 各自可通过亚烷基或亚烯基与相邻取代基相连而形成稠环; 且所述稠环可被一个或多个选自下组的取代基进一步取代: (C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基; 以及

ii) 一种或多种由化学式 (2) 代表的电致发光掺杂剂:

化学式 2



其中, M^1 选自周期表的第 7、8、9、10、11、13、14、15 和 16 列, 配体 L^3 、 L^4 和 L^5 独立地选自以下结构:



其中, R_{61} 至 R_{63} 独立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, 有 (C1-C60) 烷基取代基或没有 (C1-C60) 烷基取代基的 (C6-C60) 芳基, 或卤素;

R_{64} 至 R_{79} 独立地代表氢, (C1-C60) 烷基, (C1-C30) 烷氧基, (C3-C60) 环烷基, (C2-C30) 烯基, (C6-C60) 芳基, 单或二 (C1-C30) 烷基氨基, 单或二 (C6-C30) 芳基氨基, SF_5 , 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 氰基或卤素; R_{70} 至 R_{76} 各自可通过 (C2-C12) 亚烷基或 (C2-C12) 亚烯基与相邻取代基

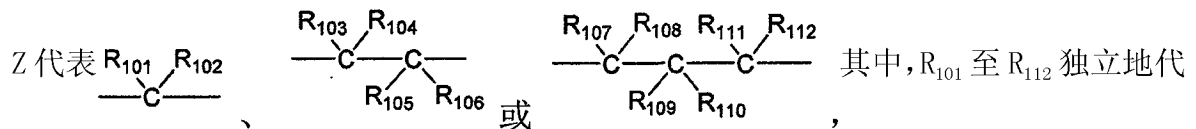
相连而形成稠环或多个稠环； R_{64} 至 R_{79} 的烷基、环烷基、烯基或芳基，或者由 R_{70} 和 R_{76} 通过亚烷基或亚烯基连接而形成的稠环或多个稠环可被选自以下的一个或多个取代基进一步取代：(C1-C60) 烷基，(C6-C60) 芳基和卤素；

R_{80} 至 R_{83} 独立地代表氢，有卤素取代基或没有卤素取代基的 (C1-C60) 烷基，或者有 (C1-C60) 烷基取代基或没有 (C1-C60) 烷基取代基的 (C6-C60) 芳基；

R_{84} 和 R_{85} 独立地代表氢，直链或支链 (C1-C60) 烷基，(C6-C60) 芳基或卤素，或者 R_{84} 和 R_{85} 可通过有稠环或没有稠环的 (C3-C12) 亚烷基或 (C3-C12) 亚烯基连接而形成脂环或者单环或多环的芳环；而烷基、芳基或者通过 (C3-C12) 亚烷基或 (C3-C12) 亚烯基连接而形成的脂环或者单环或多环的芳环可被一个或多个选自下组的取代基进一步取代：有卤素取代基或没有卤素取代基的直链或支链 (C1-C60) 烷基，(C1-C30) 烷氧基，卤素，三 (C1-C30) 烷基甲硅烷基，三 (C6-C30) 芳基甲硅烷基和 (C6-C60) 芳基；

R_{86} 代表 (C1-C60) 烷基，(C6-C60) 芳基，(C5-C60) 杂芳基或卤素；

R_{87} 至 R_{89} 独立地代表氢，(C1-C60) 烷基，(C6-C60) 芳基或卤素，且 R_{86} 至 R_{89} 的烷基或芳基可被卤素或 (C1-C60) 烷基进一步取代；和



表氢，有卤素取代基或没有卤素取代基的 (C1-C60) 烷基，(C1-C30) 烷氧基，卤素，(C6-C60) 芳基，氰基或 (C5-C60) 环烷基，或者 R_{101} 至 R_{112} 各自可通过亚烷基或亚烯基与相邻取代基相连而形成 (C5-C7) 螺环或 (C5-C9) 稠环，或者它们可通过亚烷基或亚烯基与 R_{67} 或 R_{68} 相连而形成 (C5-C7) 稠环。

2. 如权利要求 1 所述的电致发光器件，其特征在于，所述有机层包含一种或多种选自下组的化合物：芳基胺化合物和苯乙烯基芳基胺化合物。

3. 如权利要求 1 所述的电致发光器件，其特征在于，所述有机层包含一种或多种选自下组的金属：第四和第五周期过渡金属第 1 列和第 2 列的金属，镧系金属，和 d- 过渡元素。

4. 如权利要求 1 所述的电致发光器件，其为有机显示器，该显示器在其有机层中还包含电致发光峰波长不超过 560nm 的化合物。

5. 如权利要求 1 所述的电致发光器件，其特征在于，还原性掺杂剂和有机物的混合区，或者氧化性掺杂剂和有机物的混合区被置于一对电极中的一个电极或两个电极的内表面上。

6. 如权利要求 1 所述的电致发光器件，其特征在于，所述电致发光区内电致发光掺杂剂对主体的掺杂浓度为 1-20 重量%。

采用电致发光化合物的电致发光器件

[0001] 发明领域

[0002] 本发明涉及包含电致发光化合物的电致发光器件。

[0003] 发明背景

[0004] 在显示器件中,电致发光器件(EL器件)是自发光型显示器件,与LCD相比具有宽视角、极佳对比以及快速响应速率的优点。

[0005] 根据形成发射层的材料和发光机制可将EL器件分成无机EL器件和有机EL器件。其中,有机EL器件的发光效率、色纯度和操作电压较佳,并可方便地实现全色显示。

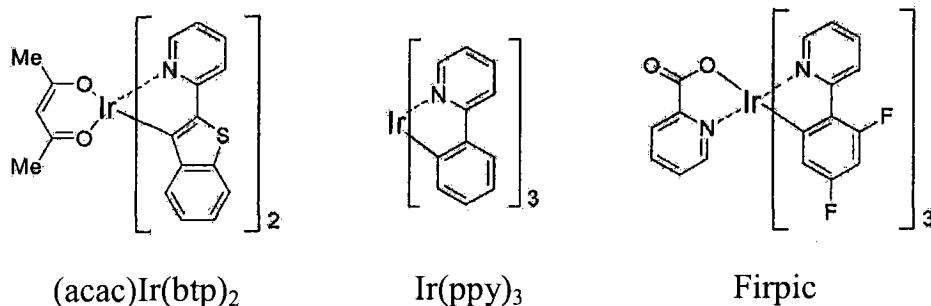
[0006] 同时,Eastman Kodak在1987年首先研制了一种有机EL器件[Appl. Phys. Lett. 51,913,1987],该器件使用低分子量芳香族二胺作为形成EL层的材料以及铝配合物。

[0007] 可根据功能将EL材料分成主体材料和掺杂剂材料。通常已知具有最佳EL性能的器件结构可用通过将掺杂剂掺入主体中制成的EL层制造。最近,迫切需要开发出具有高性能和长寿命的有机EL器件,考虑到中型到大型OLED面板所需的EL性能,尤其迫切需要开发出与传统EL材料相比具有好得多的EL性能的材料。对主体材料(作为固态溶剂和能量输送器)而言,所需性能为高纯度和能够在真空中气相沉积的合适分子量。此外,玻璃转化温度和热分解温度应足够高以确保热稳定性。此外,主体材料应具有高电化学稳定性以提供较长寿命。容易形成与其他相邻材料的高粘附性但没有层间迁移的无定形薄膜。

[0008] 在OLED(有机发光二极管)中,决定发光效率的最重要因素是电致发光材料的种类。迄今,虽然荧光材料被广泛用于电致发光材料,但考虑电致发光机理,磷光材料的发展是将发光效率理论上提高至4倍的最好方法之一。

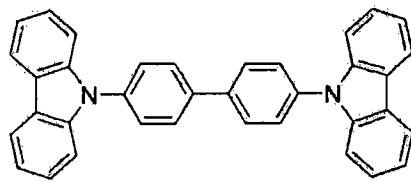
[0009] 到目前为止,已知铱(III)配合物被广泛用作磷光材料,包括(acac)Ir(btp)₂, Ir(ppy)₃和Firpic,分别作为红,绿和蓝色磷光材料。特别的,大量磷光材料最近在日本,欧洲和美国被研究,并预期对进一步改进的磷光材料的研究。

[0010]

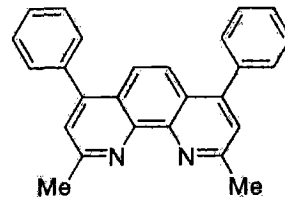


[0011] 迄今,作为用于磷光发光材料的主体材料,4,4'-N,N'-二咔唑-联苯(CBP)是广泛已知的,并且已经开发了采用空穴阻挡层(如BCP和BALq)的高效率的OLED。East-North Pioneer(日本)等公司报道,使用二(2-甲基-8-喹啉代(quinolinato))(对-苯基苯酚)铝(III)(BALq)及其衍生物作为磷光材料的主体开发出高性能OLED。

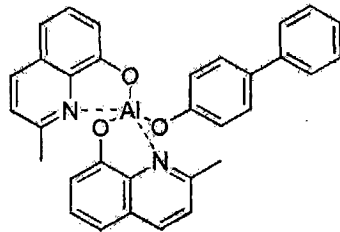
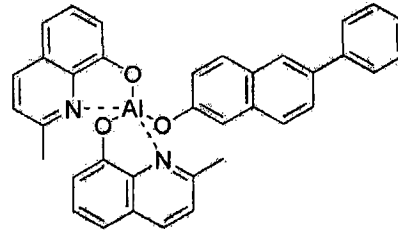
[0012]



CBP



BCP

Alq₃Alq₃

[0013] 考虑到发光特性,现有技术中的材料是有利的,但它们具有低的玻璃转化温度和差的热稳定性,从而使得这些材料在高温真空气相沉积过程中倾向于发生转变。有机电致发光器件中,定义能效 = $(\pi / \text{电压}) \times \text{电流效率}$ 。因此,能效与电压成反比,为了使 OLED 具有较低的能耗,能效应该更高。实际上,采用磷光电致发光 (EL) 材料的 OLED 与采用荧光 EL 材料的 OLED 相比,表现出明显更高的电流效率 (cd/A)。然而,若采用常规的材料像 Alq₃ 和 BCP 作为磷光 EL 材料的主体材料,在能效 (lm/w) 方面并没有显著的优势,因为相对于采用荧光材料的 OLED 需要较高的操作电压。

[0014] 通常,有机电致发光器件主要是由阳极 / 有机 EL 层 / 阴极构成的层叠结构,适当具有空穴注入传输层和电子注入层;例如,目前已知的结构为阳极 / 空穴注入层 / 空穴传输层 / 有机 EL 层 / 阴极;阳极 / 空穴注入层 / 空穴传输层 / 有机 EL 层 / 电子注入层 / 阴极;和阳极 / 空穴注入层 / 空穴传输层 / 有机 EL 层 / 电子传输层 / 电子注入层 / 阴极,等等。

[0015] 这些层叠型器件的电子注入层或电子传输层可采用各种有机化合物。这些化合物包括轻金属配合物,典型为三(8-羟基喹啉)铝 (Alq₃),噁二唑,三唑,苯并咪唑,苯并噁唑,苯并噻唑,等等,但从 EL 亮度、耐久性等方面看来它们不能令人完全满意。其中,Alq₃ 据称是最优选的化合物,其具有极佳稳定性和高电子亲和力。然而,当将其用于蓝色电致发光器件时,荧光会由于激子扩散而会使色纯度恶化。

[0016] 如上所述,电致发光器件最近商业化突飞猛进,表现为获得的薄型 EL 器件具有在低施加电压下高亮度、EL 波长多样化且响应迅速,同时,低功率消耗也是高效能和长寿命器件所必需的。

[0017] 发明概述

[0018] 因此,本发明的目的是提供一种电致发光器件,其包括第一电极;第二电极;和至少一个插入所述第一电极和所述第二电极之间的有机层;其中,所述有机层包含二价金属或三价金属配合物作为主体材料,其中掺有各种电致发光掺杂剂。

[0019] 本发明的另一个目的是提供一种具有极佳发光效率、高色纯度、低操作电压和良好使用期的电致发光器件。

[0020] 具体地说,本发明的电致发光器件包括第一电极;第二电极;和至少一个插入所述第一电极和所述第二电极之间的有机层;该有机层包含一种或多种由化学式 (1) 代表的

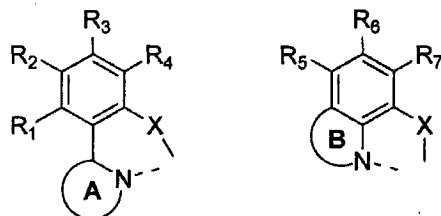
有机电致发光化合物作为主体材料：

[0021] 化学式 1

[0022] $L^1L^2M(Q)_y$

[0023] 其中，配体 L^1 和 L^2 独立地选自以下结构：

[0024]



[0025] 其中，M 代表二价金属或三价金属；

[0026] 当 M 是二价金属时 y 是 0，而当 M 是三价金属时 y 是 1；

[0027] Q 代表 (C6-C60) 芳氧基或三 (C6-C60) 芳基甲硅烷基，且 Q 的芳氧基或三芳基甲硅烷基可被 (C1-C60) 烷基或 (C6-C60) 芳基进一步取代；

[0028] X 代表 O、S 或 Se；

[0029] 环 A 和环 B 独立地代表 5-元或 6-元杂芳环，或与 (C6-C60) 芳环稠合的 5-元或 6-元杂芳环；环 A 可与 R_1 形成化学键从而形成稠环，且环 A 或环 B 可被选自下组的一个或多个取代基进一步取代：(C1-C60) 烷基，卤素，被卤素取代的 (C1-C60) 烷基，(C6-C60) 芳基，(C4-C60) 杂芳基，三 (C1-C30) 烷基甲硅烷基，二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基，三 (C6-C30) 芳基甲硅烷基，二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基；

[0030] R_1 至 R_7 独立地代表氢，(C1-C60) 烷基，卤素，具有卤素取代基的 (C1-C60) 烷基，三 (C1-C30) 烷基甲硅烷基，二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基，三 (C6-C30) 芳基甲硅烷基，(C6-C60) 芳基，(C4-C60) 杂芳基，二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基；或者它们各自可通过亚烷基或亚烯基与相邻取代基相连而形成稠环；和

[0031] 环 A 或环 B 上要被取代的芳基或杂芳基，或者 R_1 至 R_7 的芳基或杂芳基，或者通过亚烷基或亚烯基与相邻取代基相连而形成的稠环可被选自下组的一个或多个取代基进一步取代：(C1-C60) 烷基，卤素，氰基，具有卤素取代基的 (C1-C60) 烷基，(C3-C60) 环烷基，(C1-C30) 烷氧基，(C6-C60) 芳基，(C4-C60) 杂芳基，三 (C1-C30) 烷基甲硅烷基，二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基，三 (C6-C30) 芳基甲硅烷基，二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基。

[0032] 附图简述

[0033] 图 1 是 OLED 的横截面视图。

[0034] 发明详述

[0035] 参考附图，图 1 是 OLED 的截面图，该 OLED 包括玻璃 1，透明电极 2，空穴注入层 3，空穴传输层 4，电致发光层 5，电子传输层 6，电子注入层 7 和 Al 阴极 8。

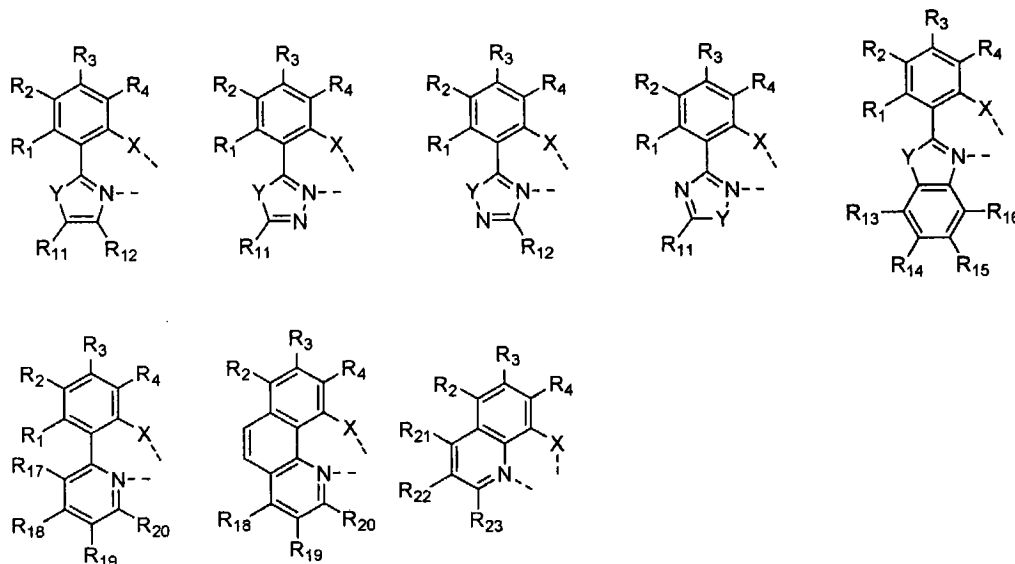
[0036] 这里所述的术语“烷基”或“烷氧基”包括直链和支链的烷基或烷氧基。

[0037] 这里所述的术语“杂芳环”指的是包含一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元芳香基团，包括，例如吡咯、吡唑、噁唑、异噁唑、噻唑、异噻唑、咪唑、噁二唑、噻二唑、吡啶、吡嗪、嘧啶和哒嗪。与 (C6-C30) 芳环稠合的 5-元或 6-元杂芳环的特别的例子包

括吡啶、苯并噁唑、苯并噻唑、苯并咪唑、二氮杂萘、喹啉、喹唑啉、噌啉、咪唑、菲啶、吡啶、喹啉和异喹啉。环 A 优选自噁唑、噻唑、咪唑、噁二唑、噻二唑、苯并噁唑、苯并噻唑、苯并咪唑、吡啶和喹啉。

[0038] 配体 L^1 和 L^2 独立地选自以下结构：

[0039]



[0040] 其中, X, R_1 , R_2 , R_3 和 R_4 按照化学式 (1) 中定义；

[0041] Y 代表 O、S 或 NR_{24} ；

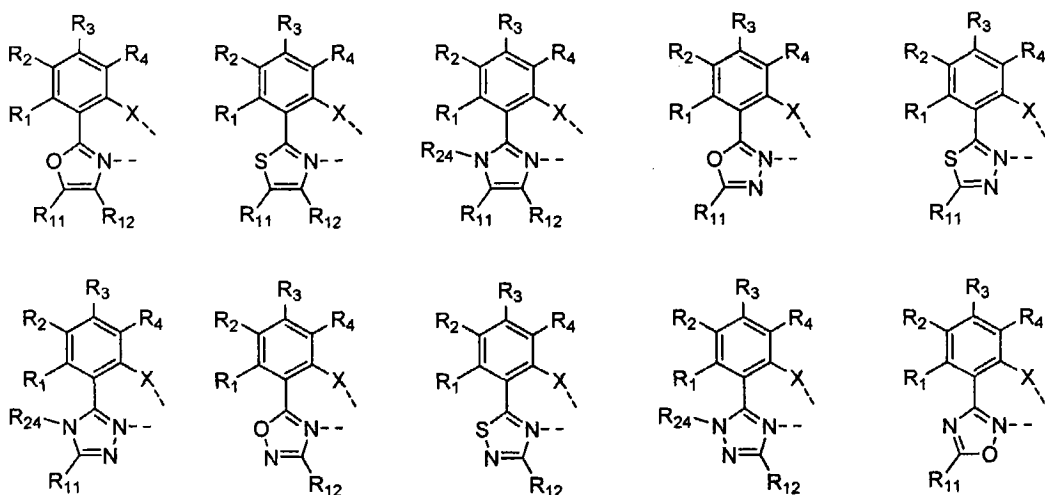
[0042] R_{11} 至 R_{23} 独立地代表氢, (C1-C60) 烷基, 卤素, 具有卤素取代基的 (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基或二 (C6-C30) 芳基氨基；或者 R_{13} 至 R_{16} 和 R_{17} 至 R_{20} 各自可通过亚烷基或亚烯基与相邻取代基相连而形成稠环；且所述稠环可被一个或多个选自下组的取代基进一步取代：(C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基；

[0043] R_{24} 代表 (C1-C60) 烷基或 (C6-C60) 芳基；和

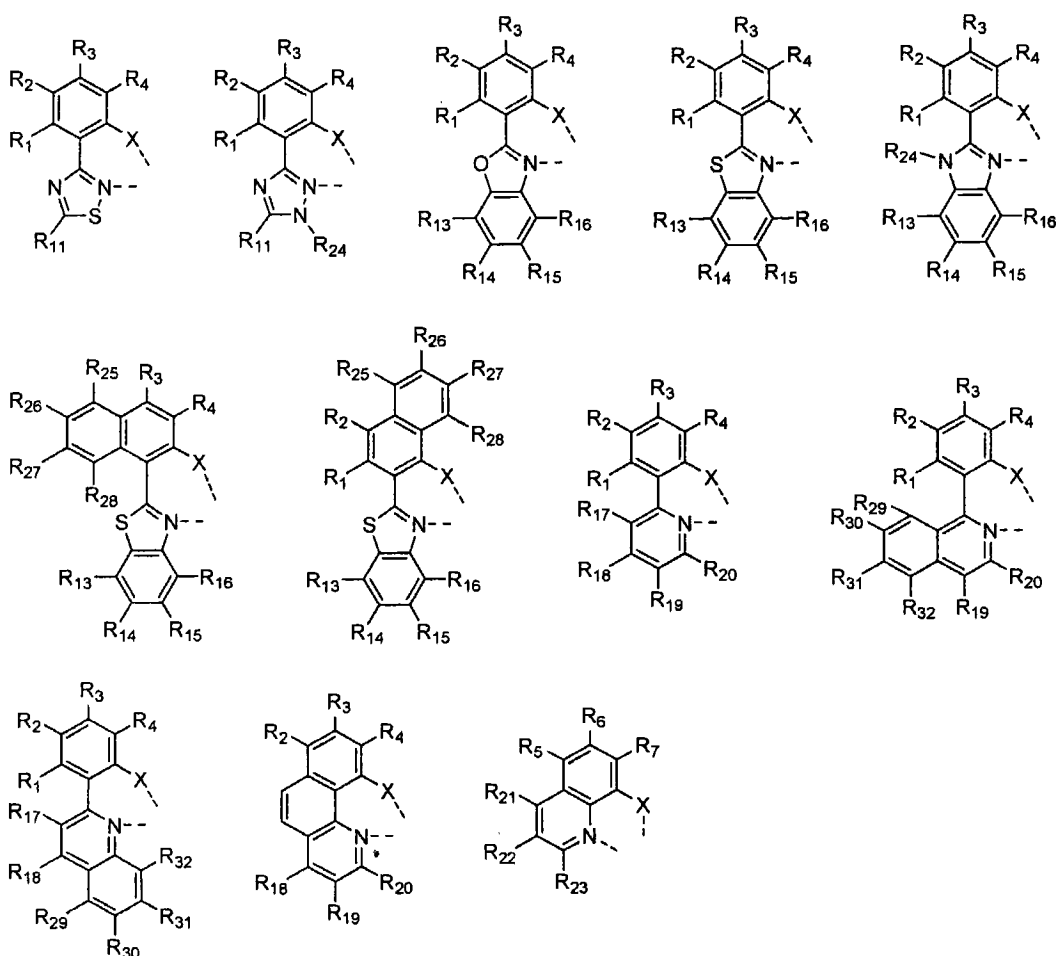
[0044] R_{11} 至 R_{24} 的芳基或杂芳基可被一个或多个选自下组的取代基进一步取代：(C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基。

[0045] 配体 L^1 和 L^2 独立地选自以下结构：

[0046]



[0047]



[0048] 其中, X 如化学式 (1) 中所定义;

[0049] R₁ 至 R₇ 独立地代表氢, (C1-C60) 烷基, 卤素, 具有卤素取代基的 (C1-C60) 烷基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 二 (C1-C30) 烷基氨基或二 (C6-C30) 芳基氨基;

[0050] R₁₁ 至 R₂₃ 独立地代表氢, (C1-C60) 烷基, 卤素, 具有卤素取代基的 (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基或二 (C6-C30) 芳基氨基;

[0051] R₂₄ 代表 (C1-C60) 烷基, (C6-C60) 芳基或 (C4-C60) 杂芳基;

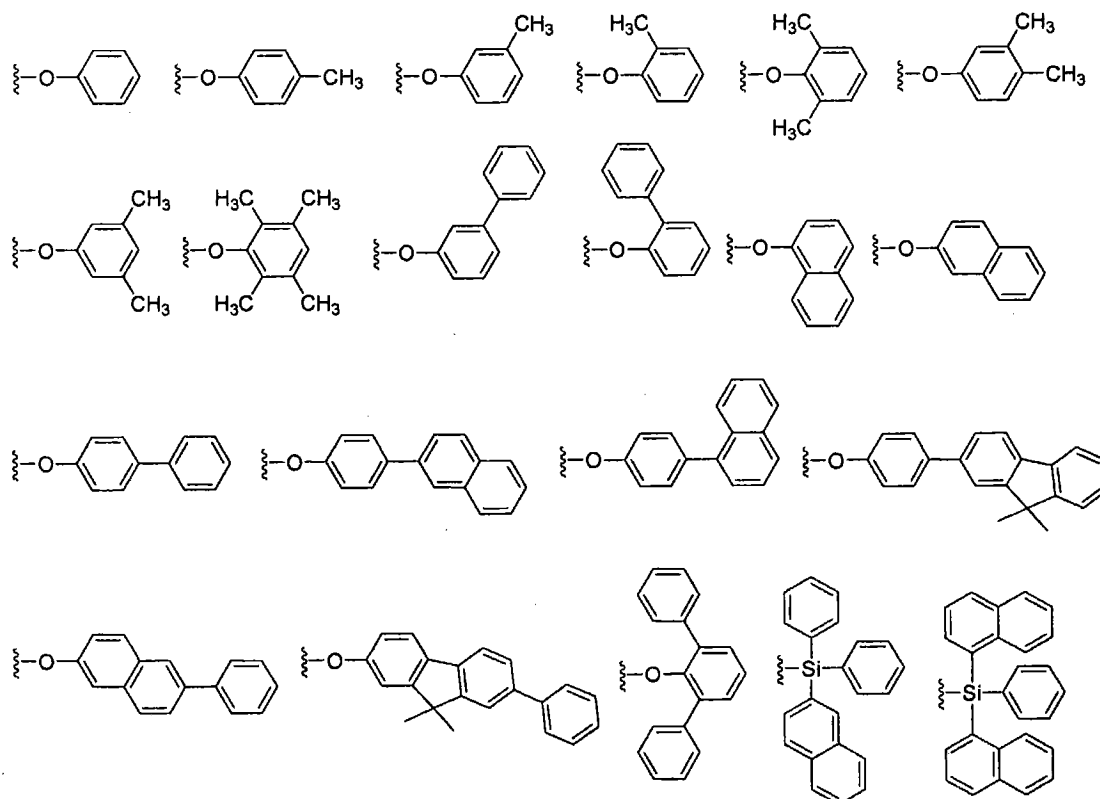
[0052] R_{25} 至 R_{32} 独立地代表氢, (C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基或二 (C6-C30) 芳基氨基;

[0053] R_1 至 R_7 、 R_{11} 至 R_{23} 、 R_{24} 以及 R_{25} 至 R_{32} 的芳基或杂芳基可被一个或多个选自下组的取代基进一步取代: (C1-C60) 烷基, 卤素, 氰基, 具有卤素取代基的 (C1-C60) 烷基, (C3-C60) 环烷基, (C1-C30) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基, 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 二 (C1-C30) 烷基氨基和二 (C6-C30) 芳基氨基; 和

[0054] 所述烷基可以是直链或支链的。

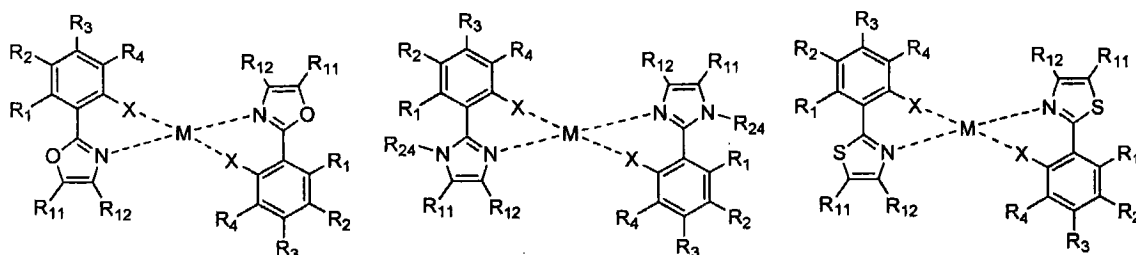
[0055] 在化学式 (1) 中, M 代表选自 Be、Zn、Mg、Cu 或 Ni 的二价金属或者选自 Al、Ga、In 或 B 的三价金属; Q 选自以下结构:

[0056]

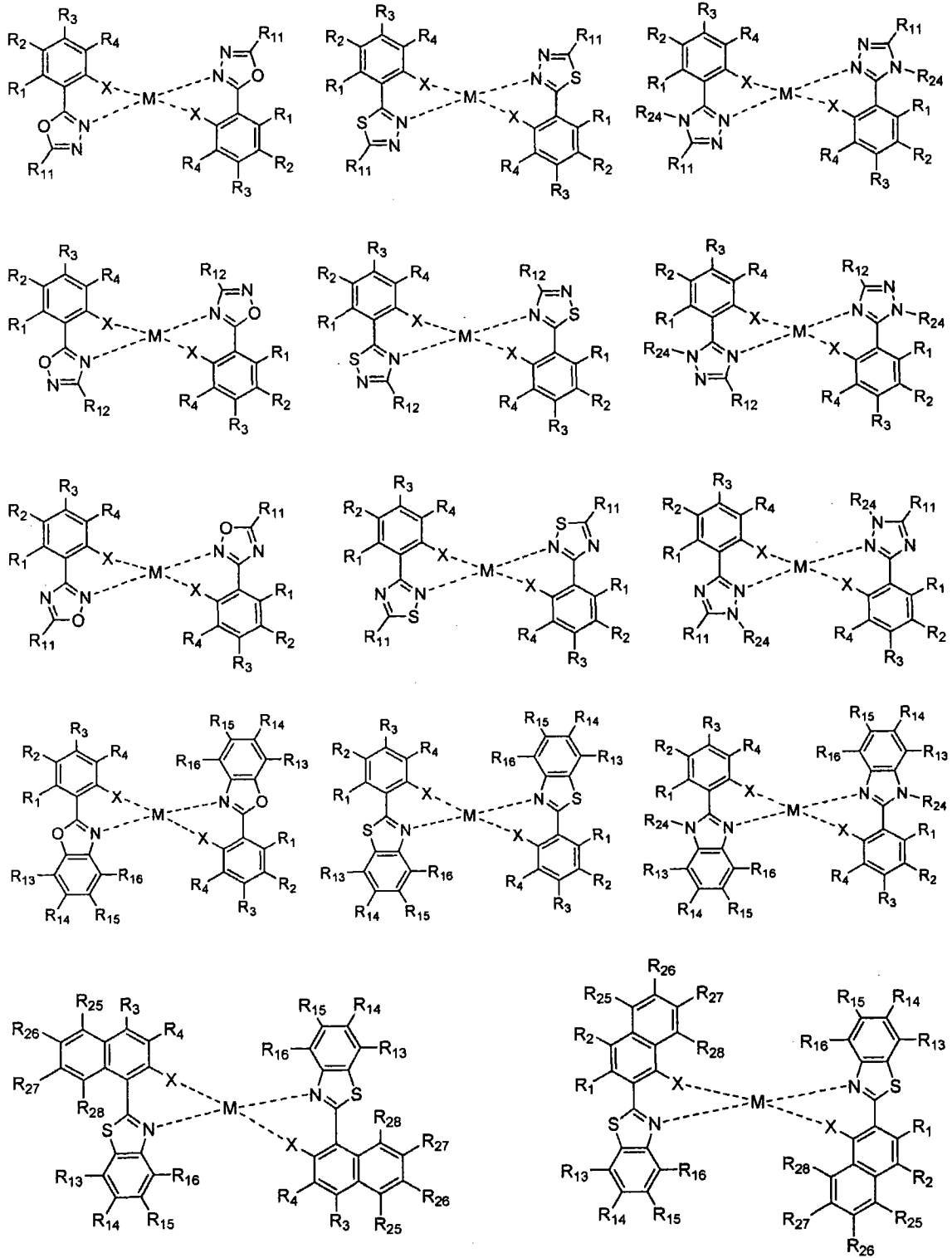


[0057] 当 M 是二价金属时, 由化学式 (1) 代表的化合物的例子具体包括以下化合物, 但不限于此:

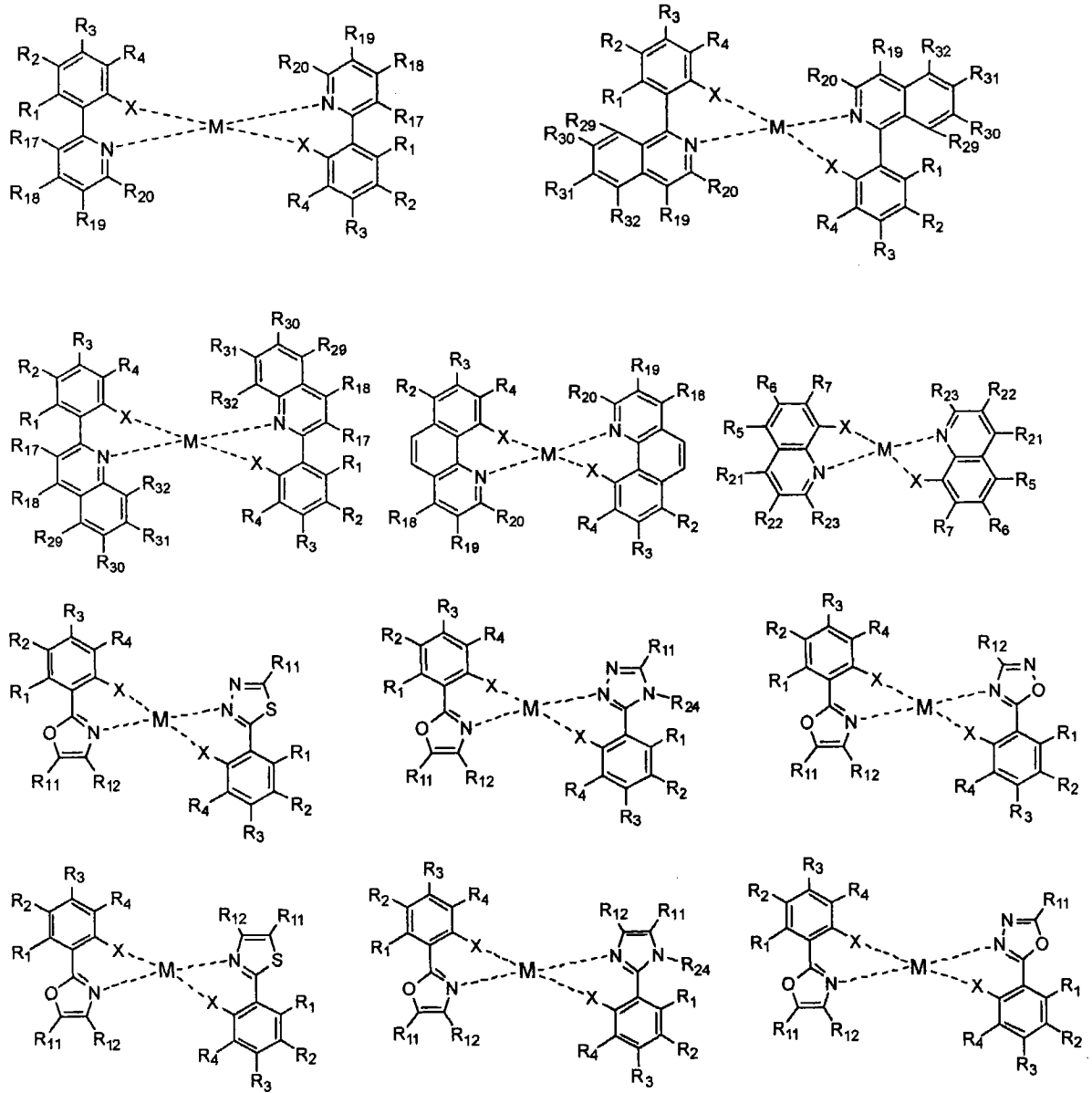
[0058]



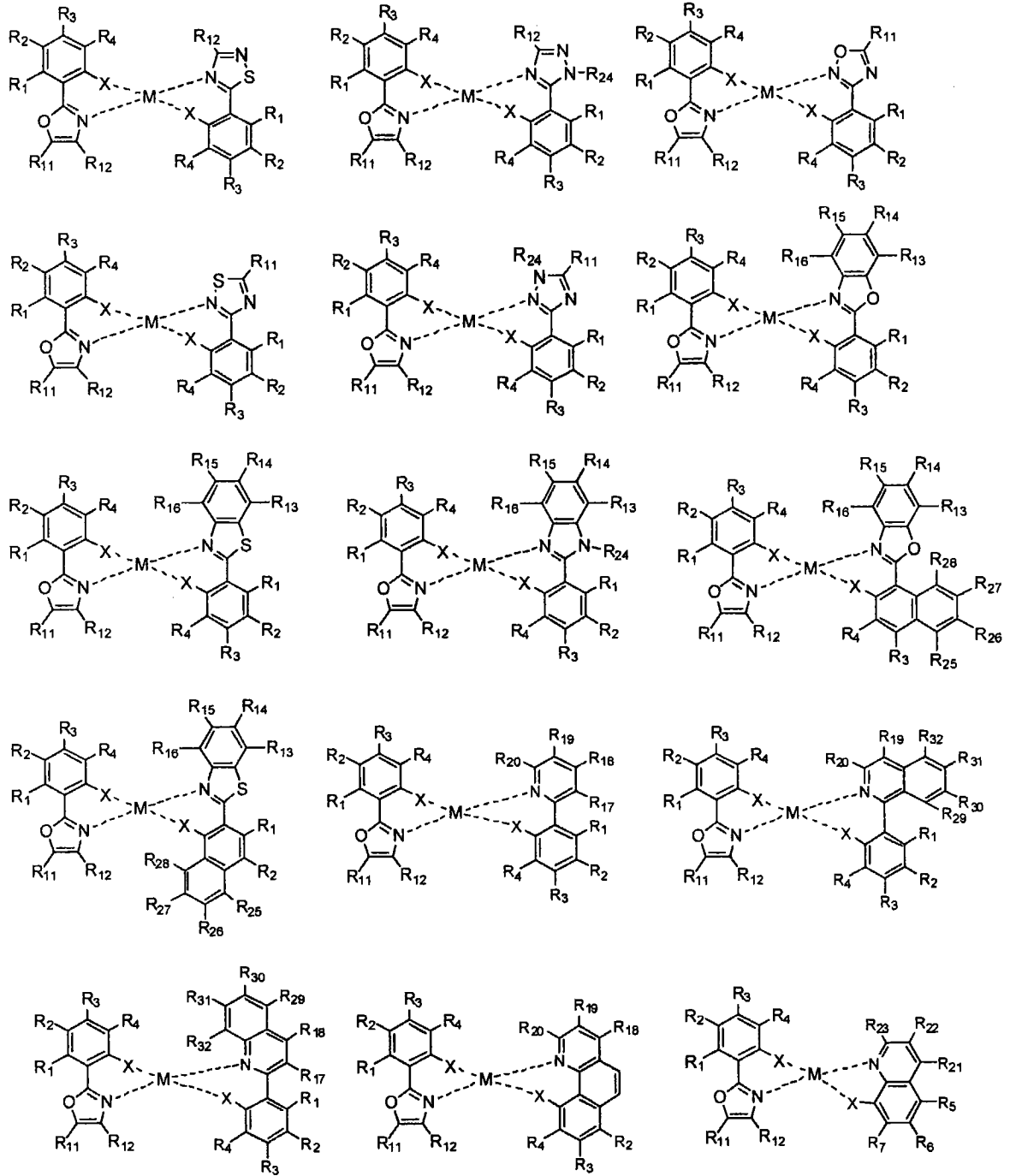
[0059]



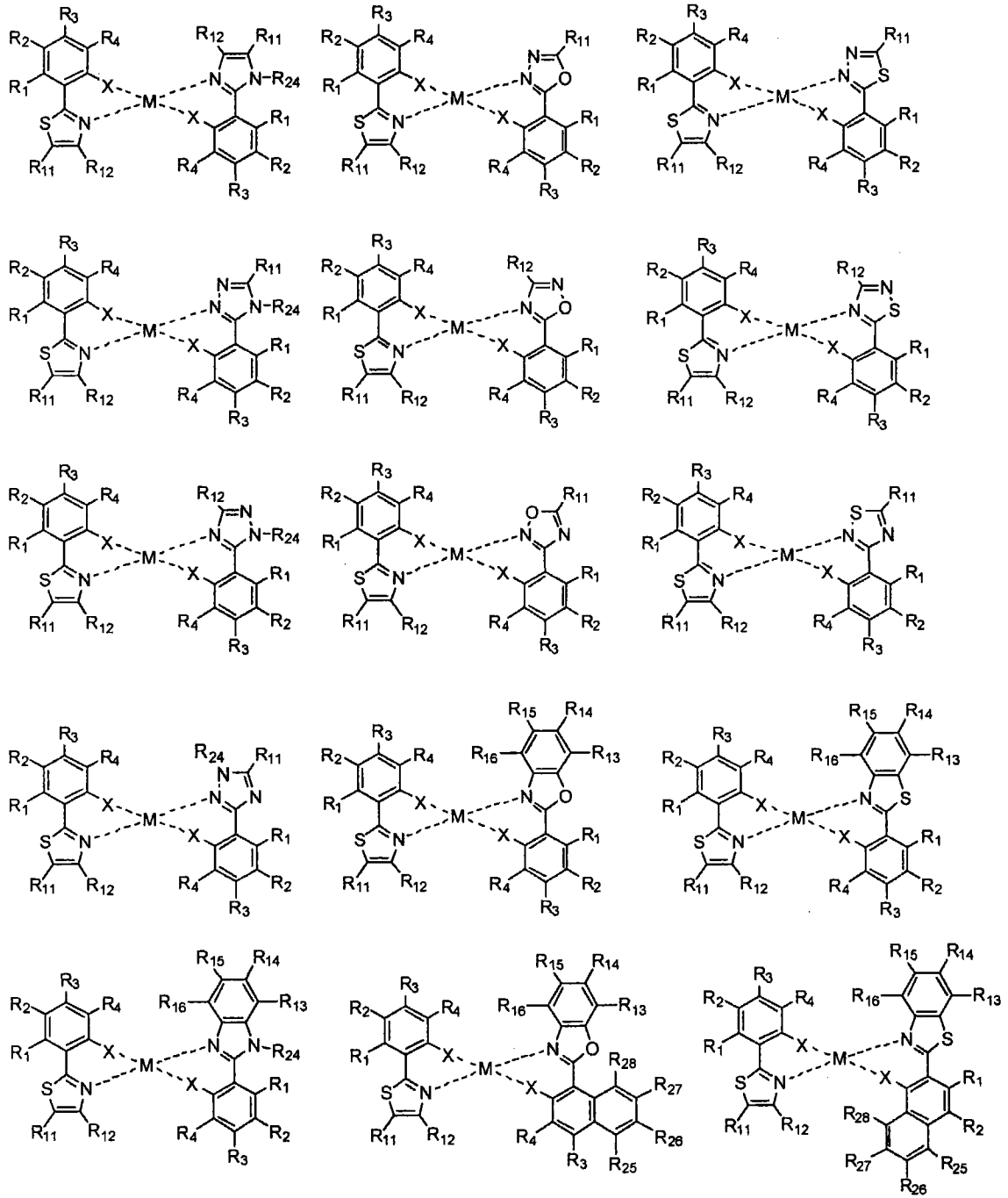
[0060]



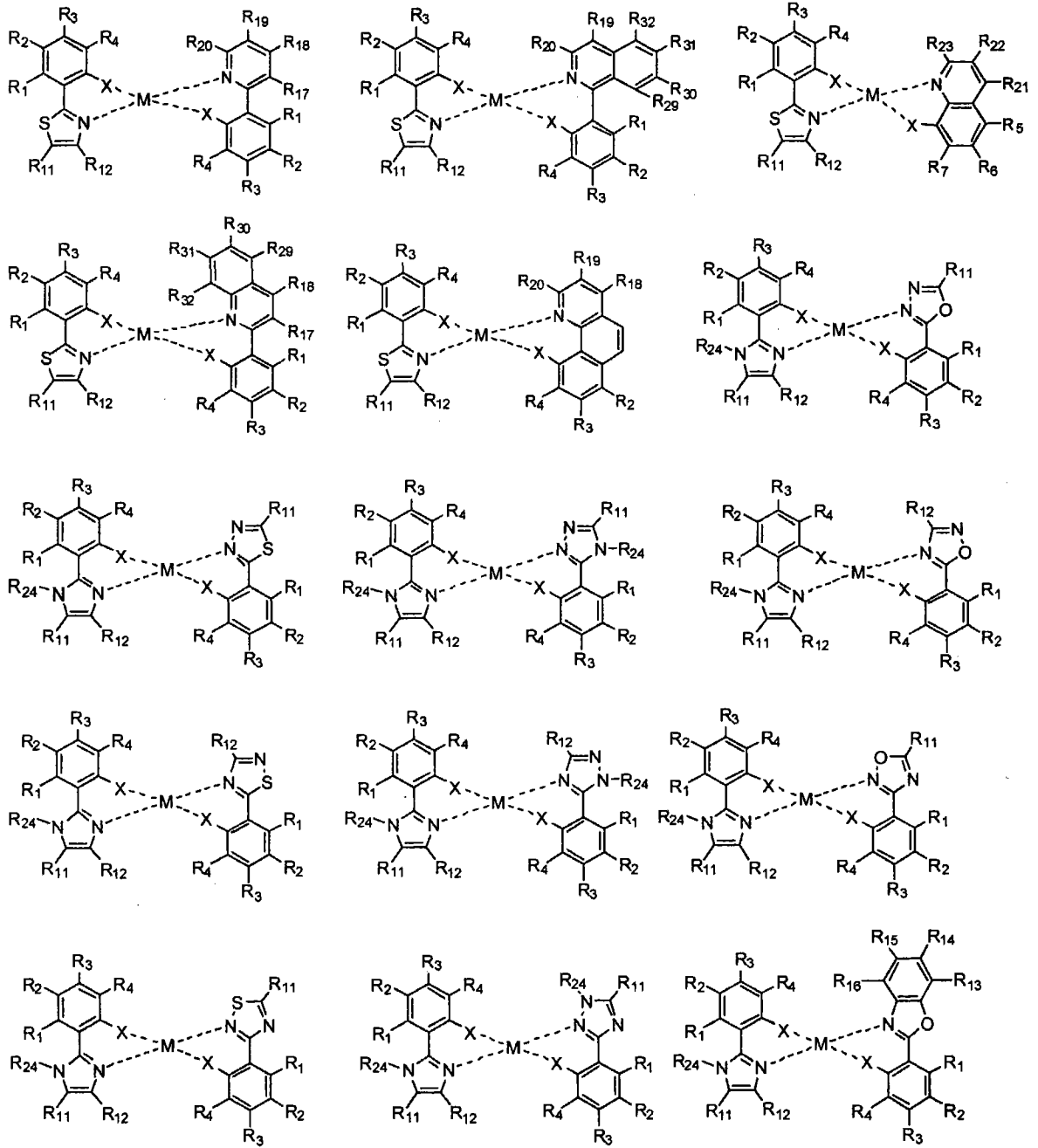
[0061]



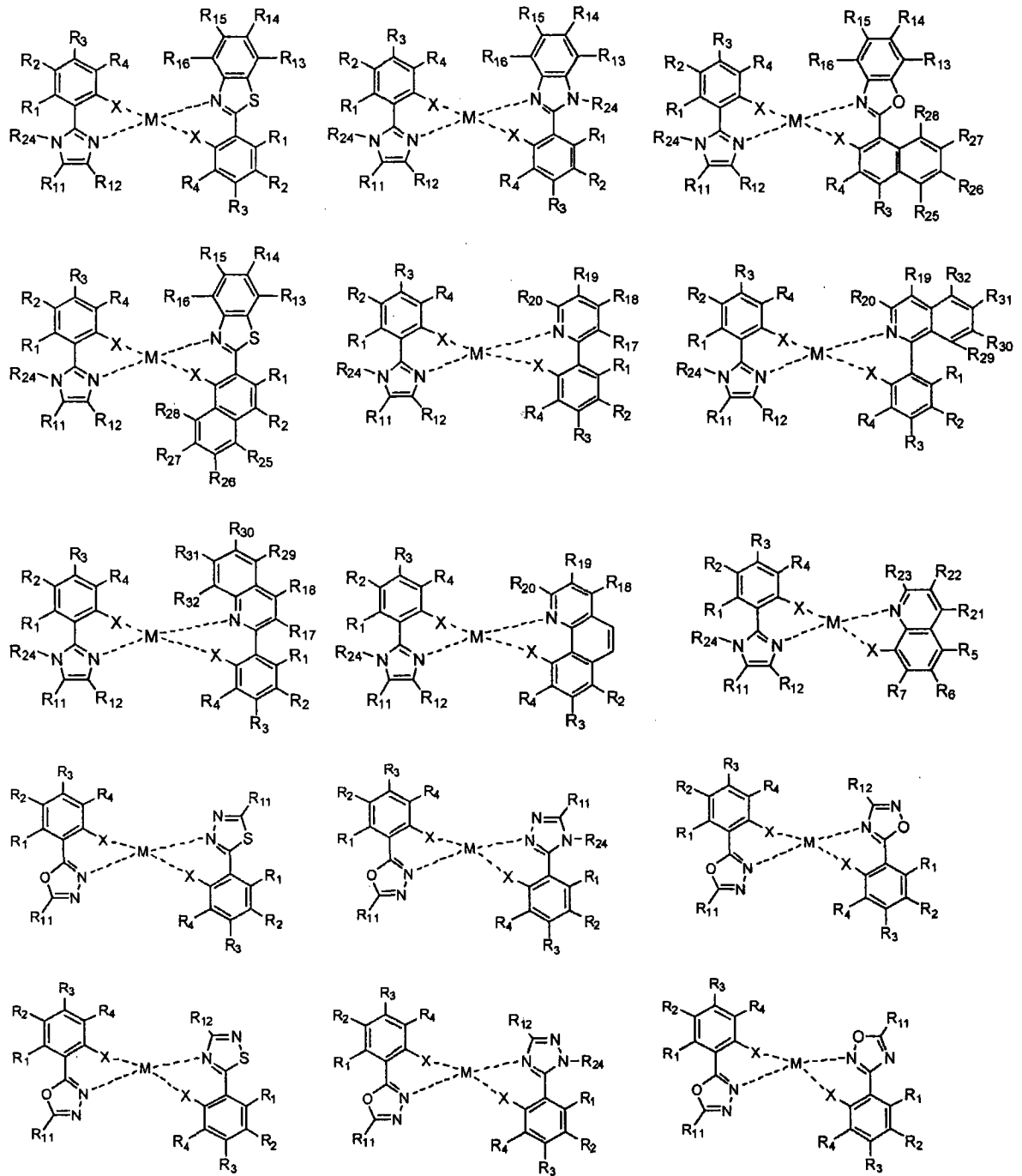
[0062]



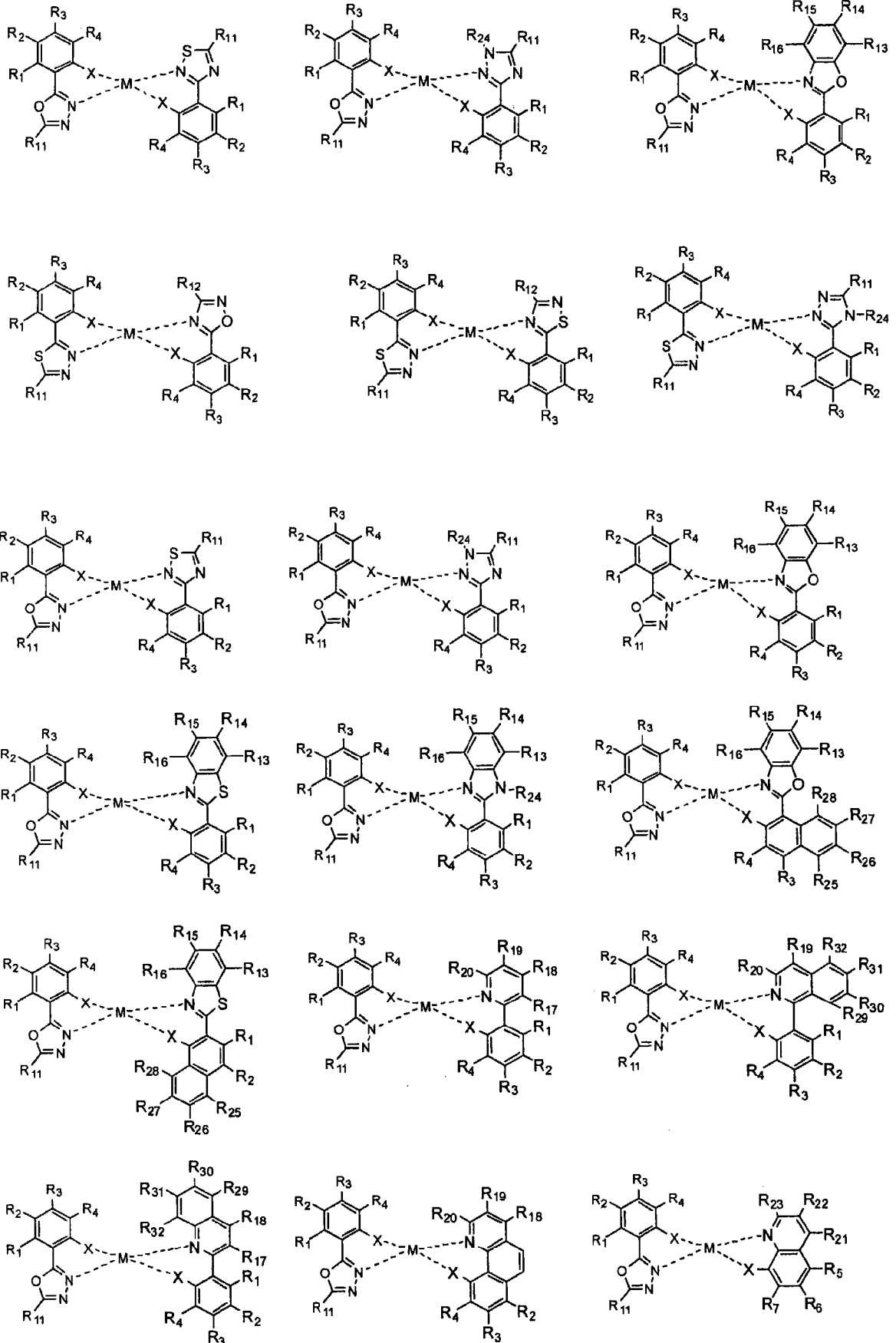
[0063]



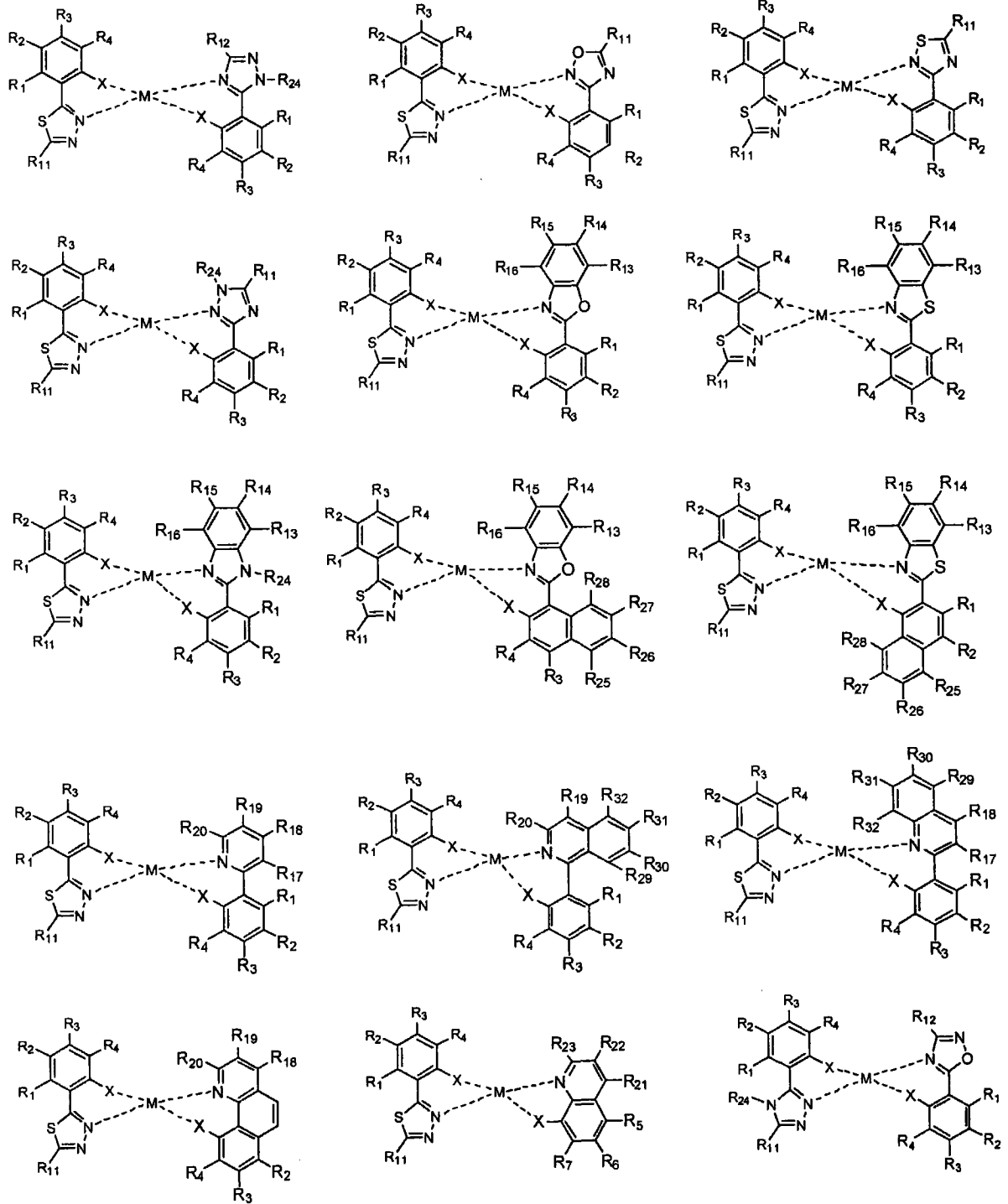
[0064]



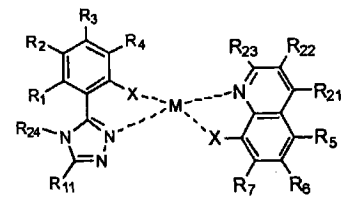
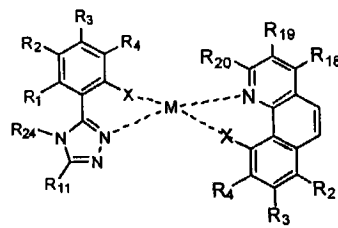
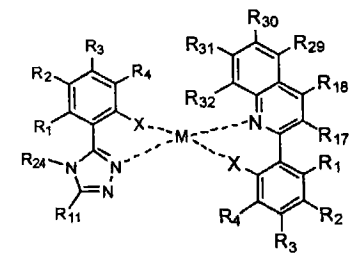
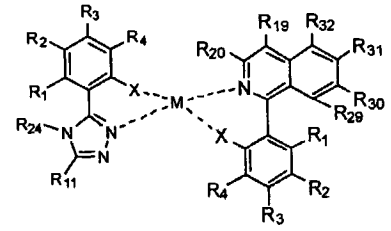
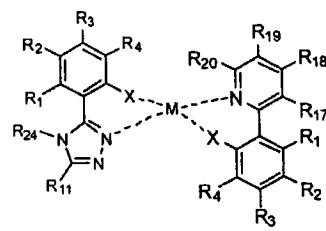
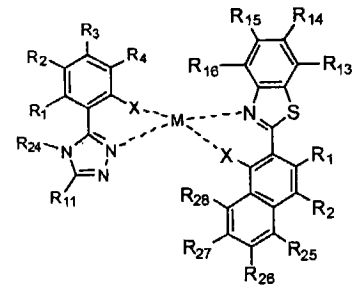
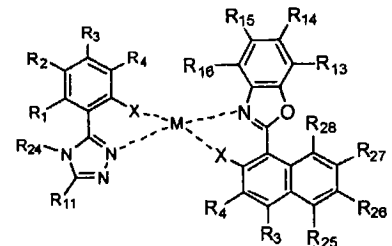
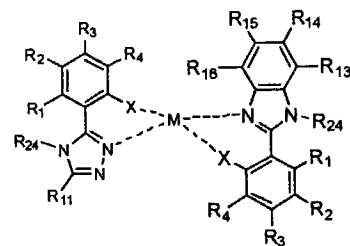
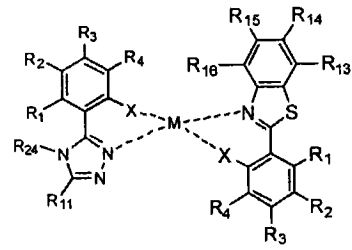
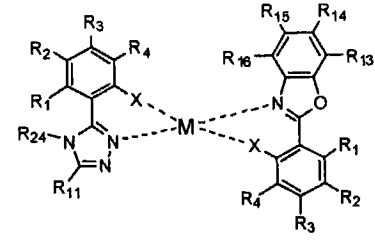
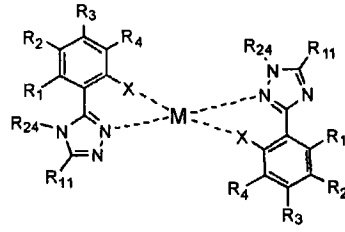
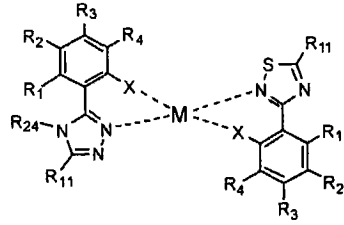
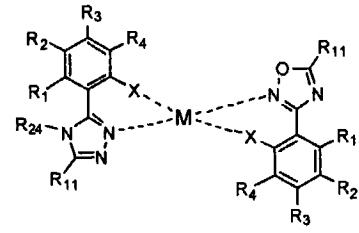
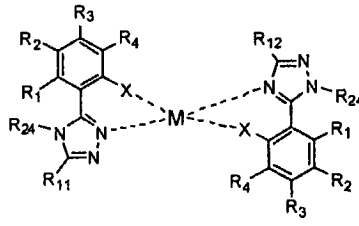
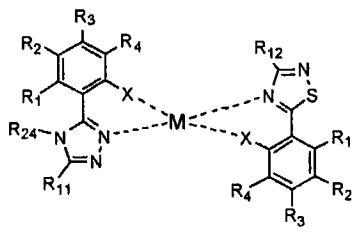
[0065]



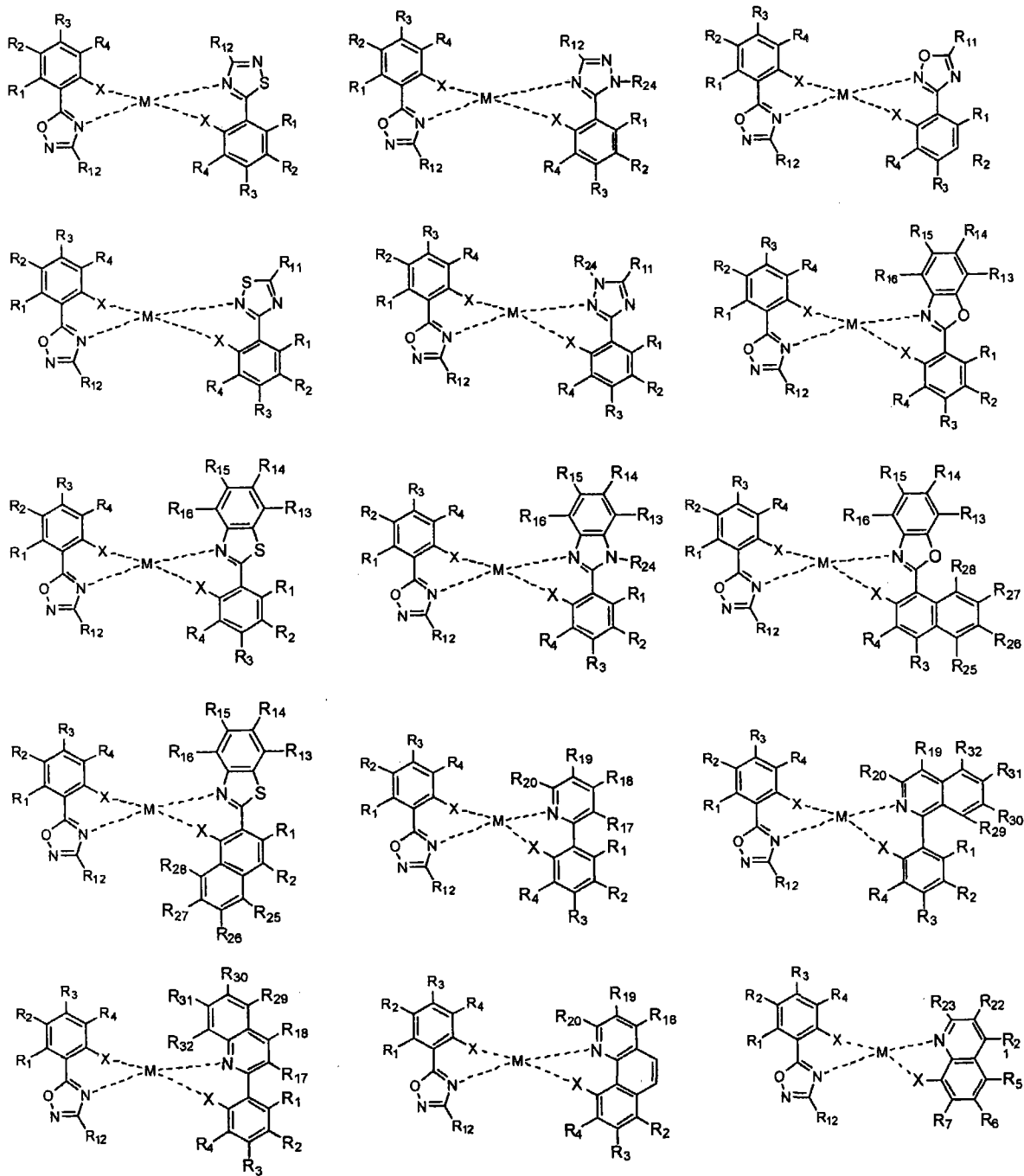
[0066]



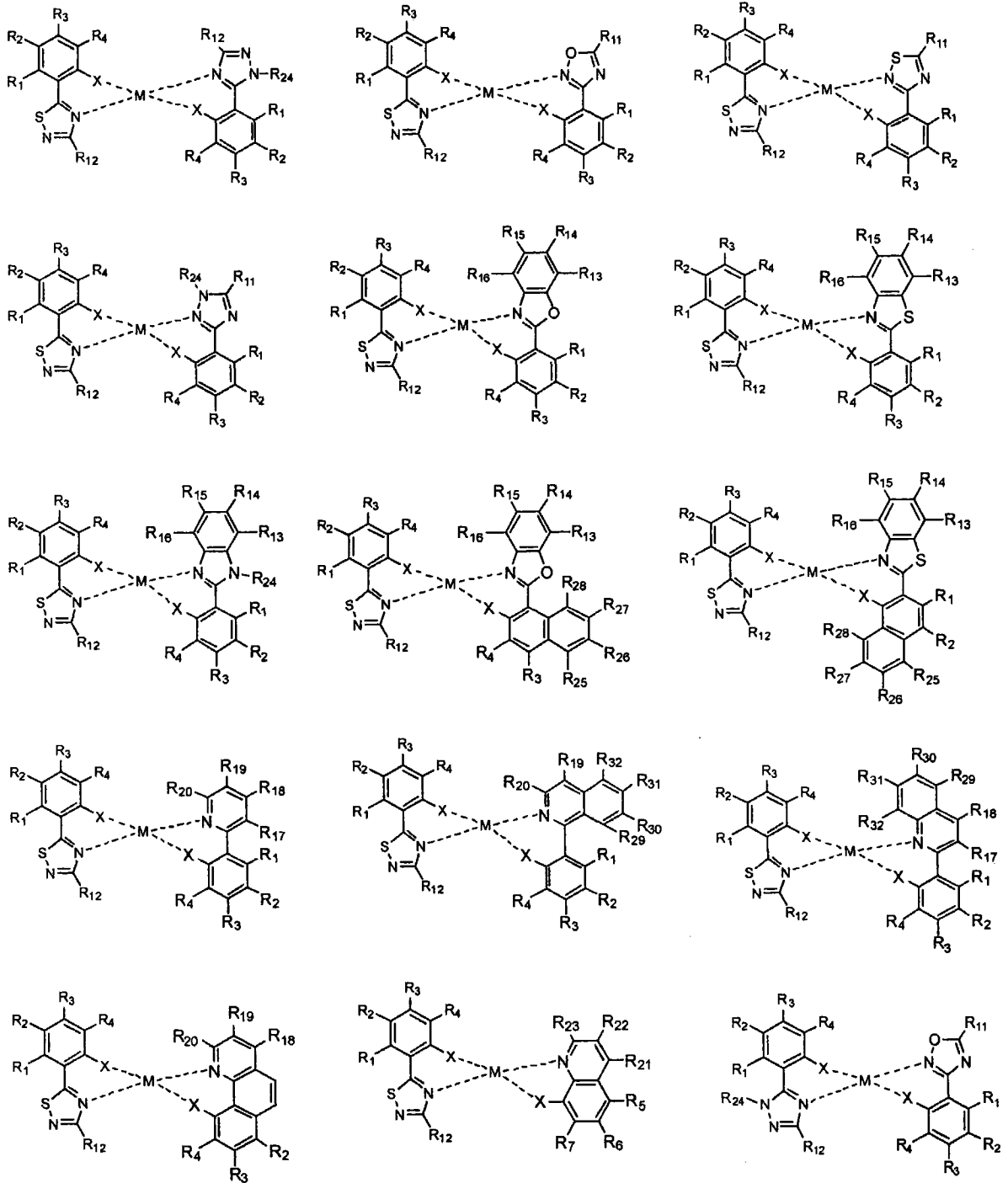
[0067]



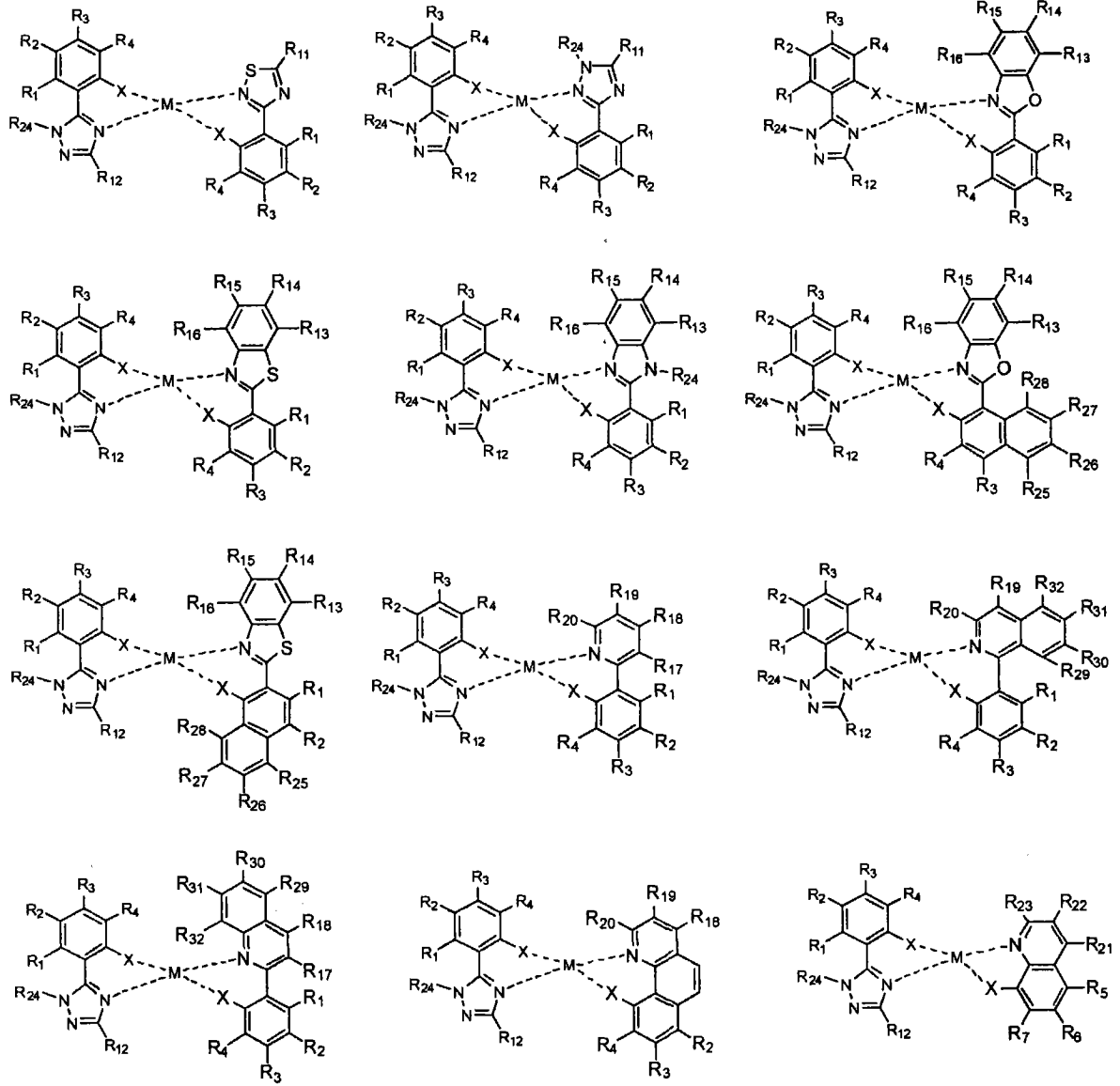
[0068]



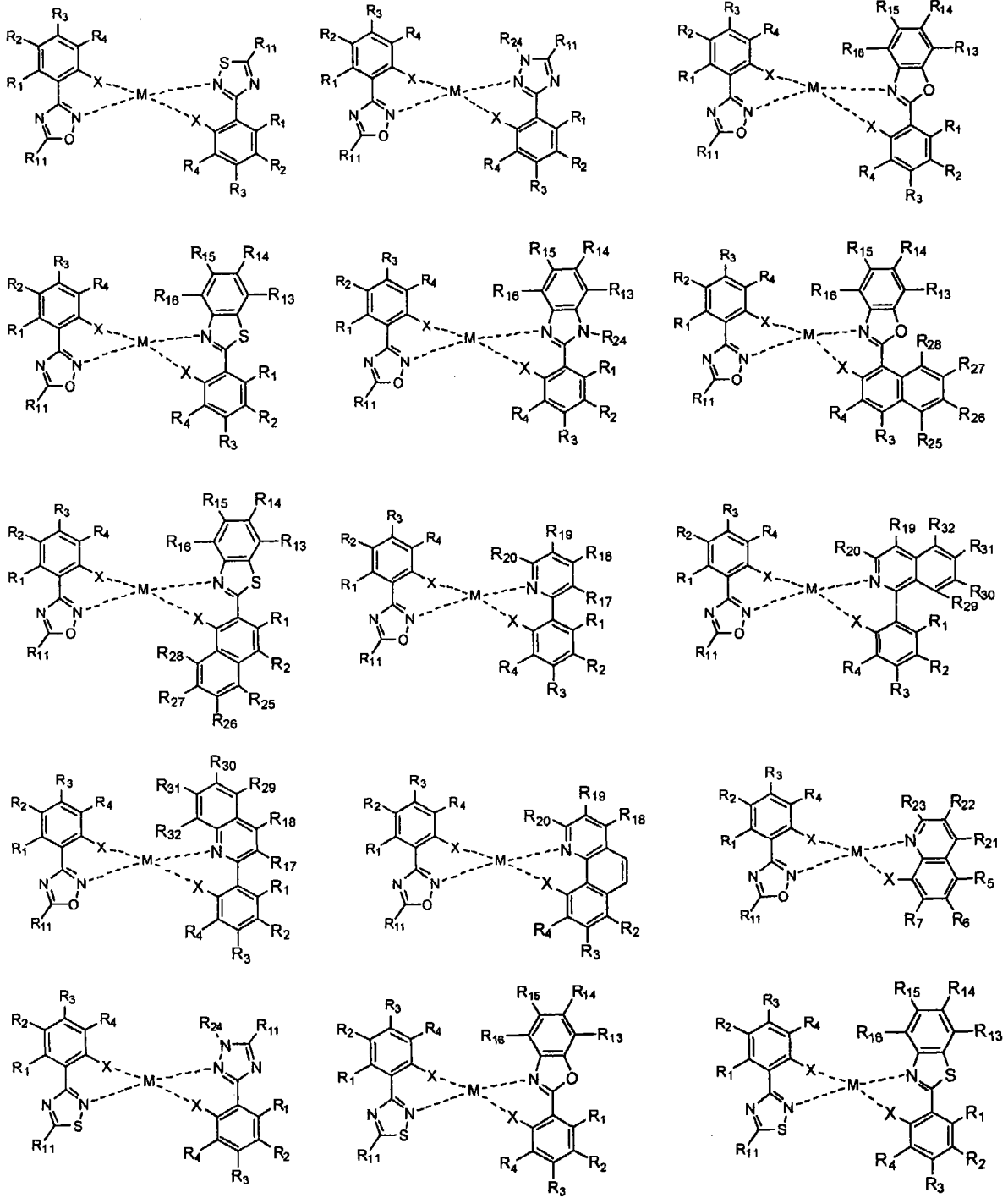
[0069]



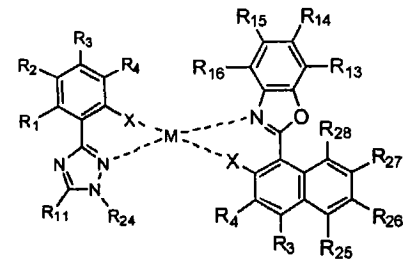
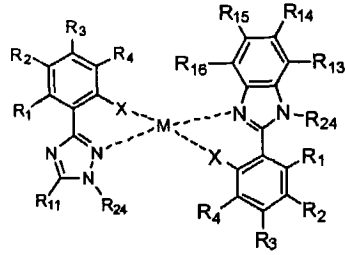
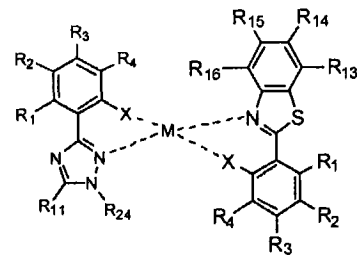
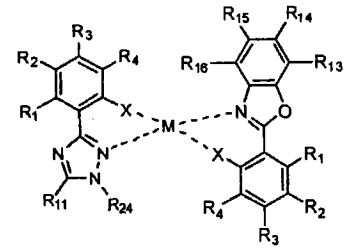
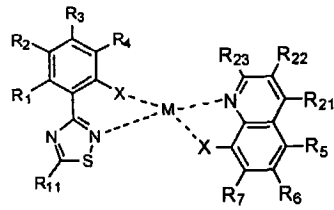
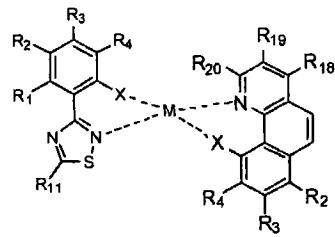
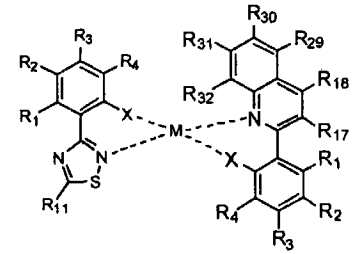
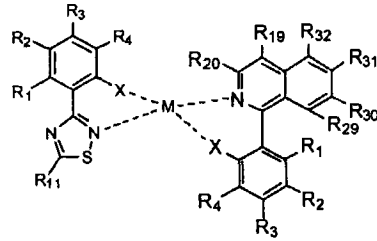
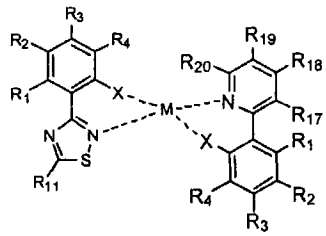
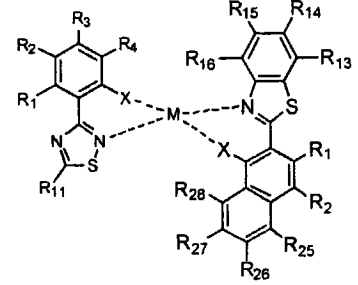
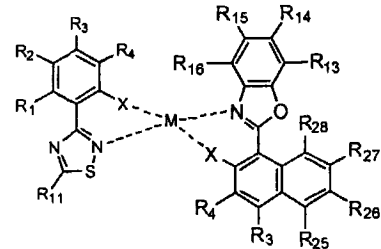
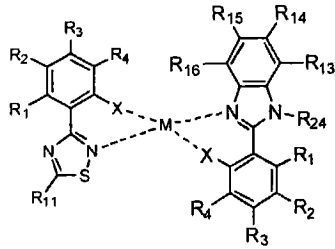
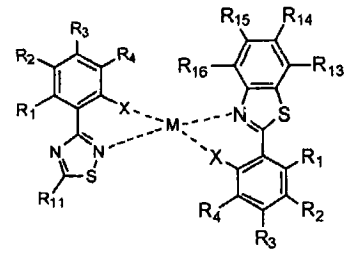
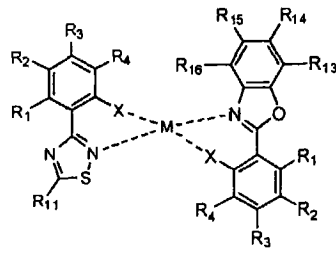
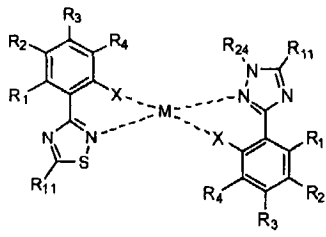
[0070]



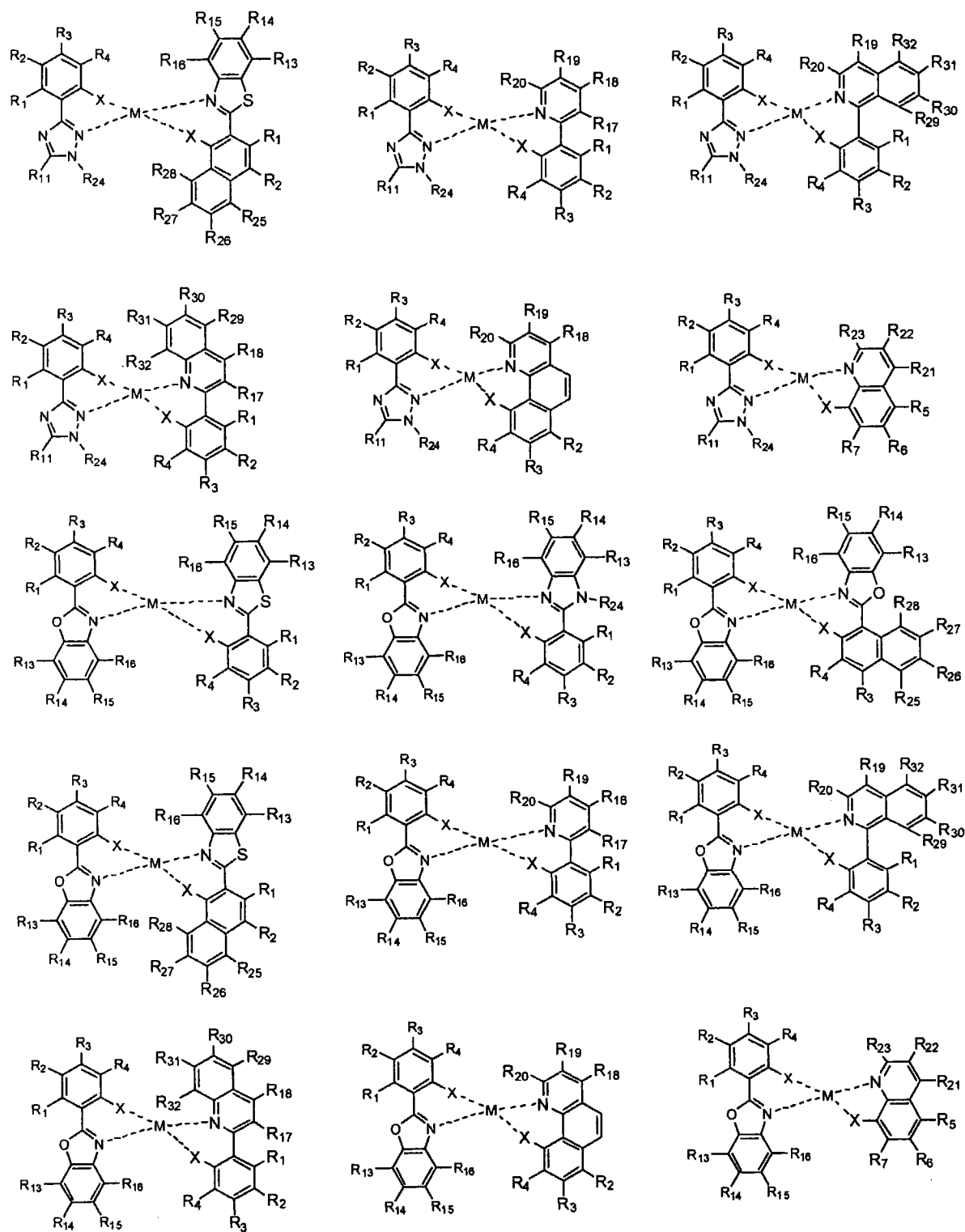
[0071]



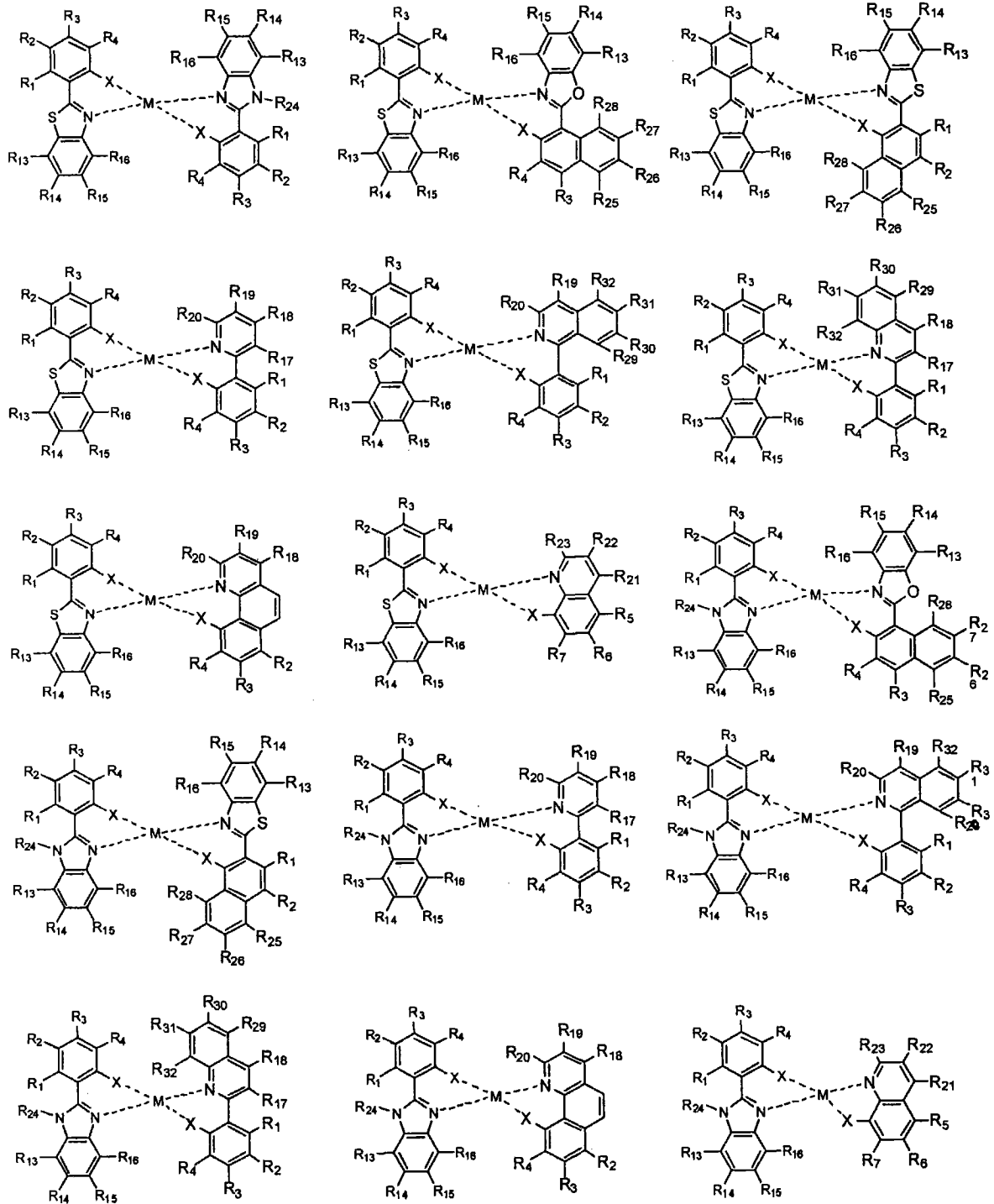
[0072]



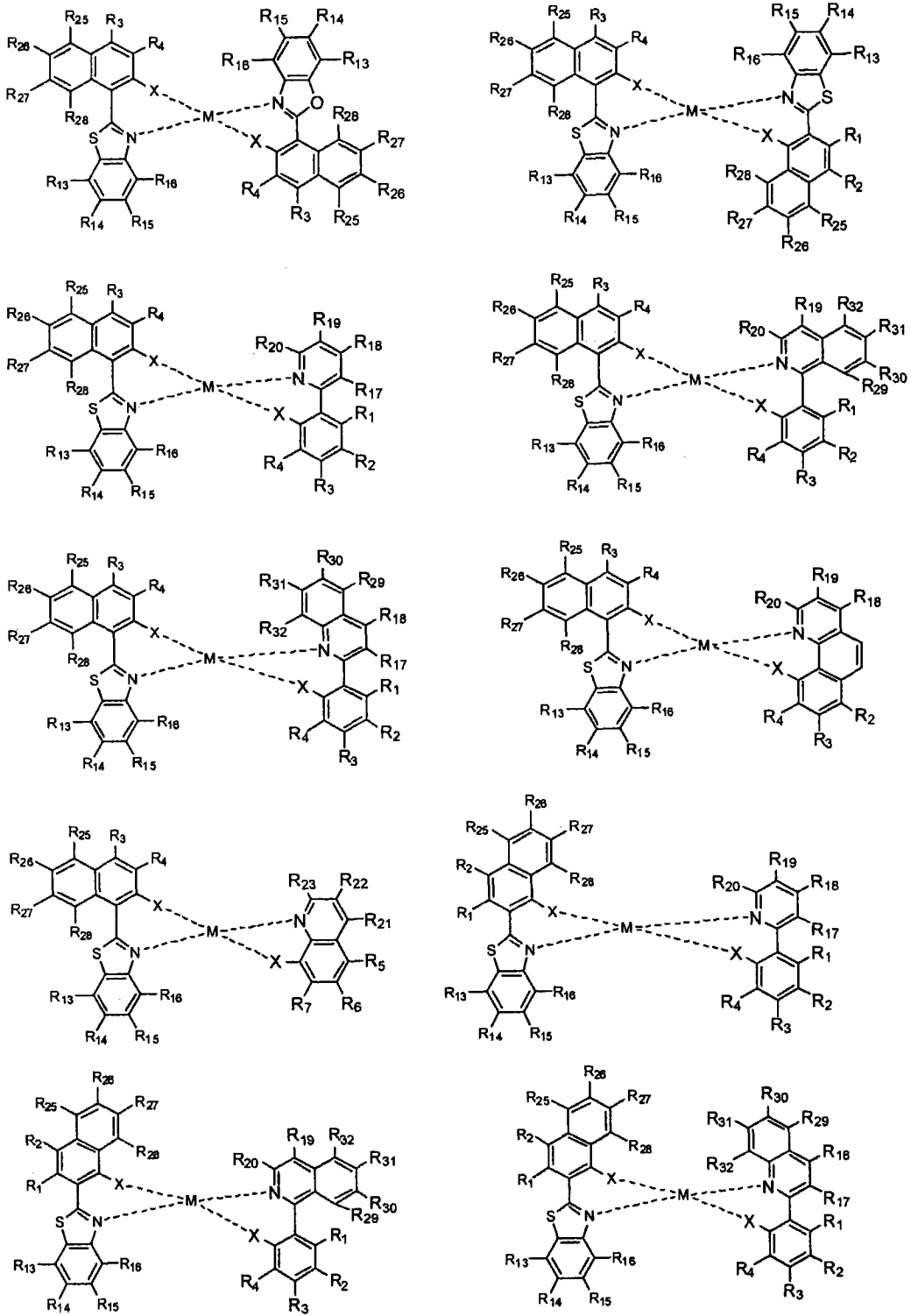
[0073]



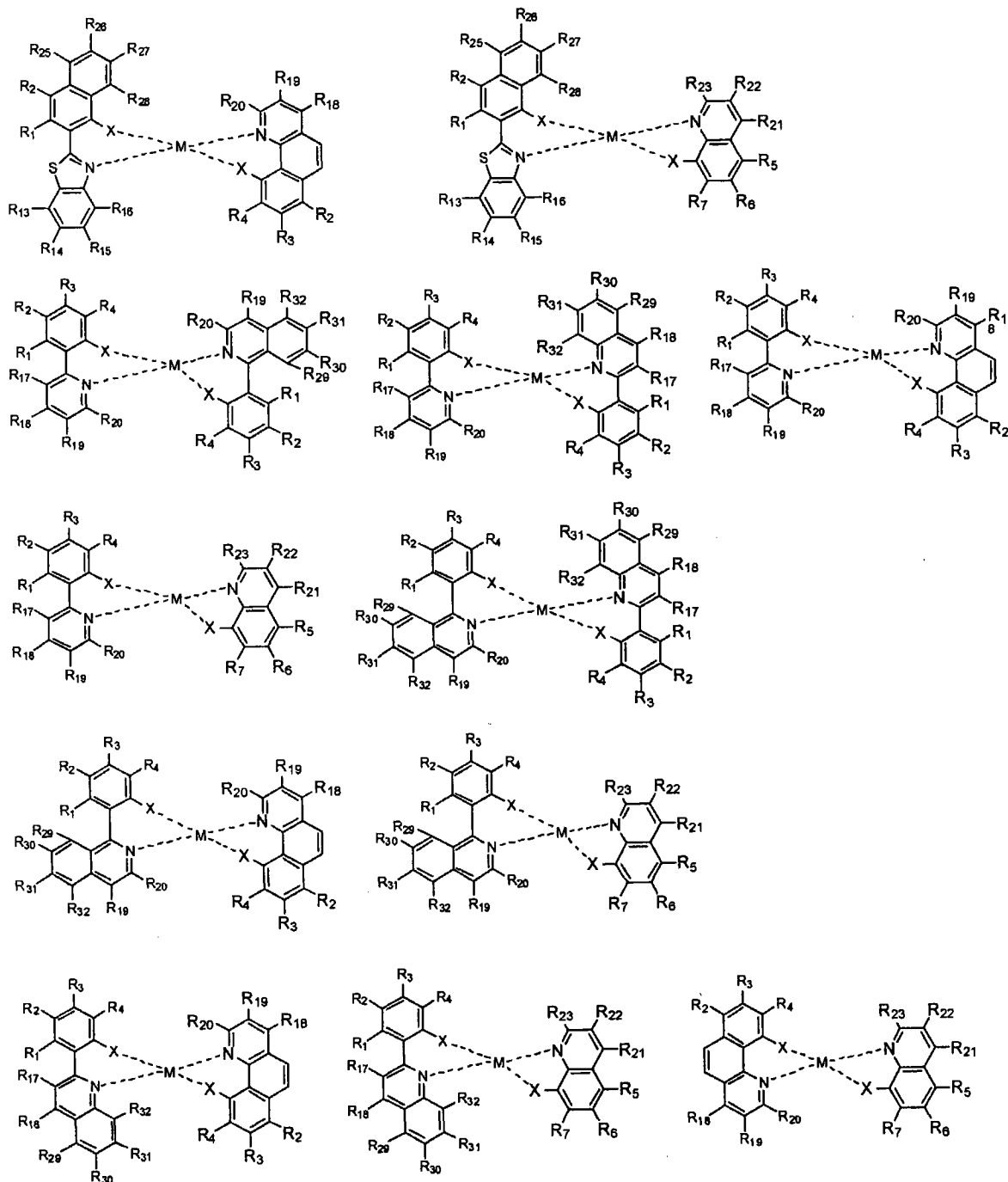
[0074]



[0075]



[0076]



[0077] 其中, X 代表 O、S 或 Se ;M 代表 Be、Zn、Mg、Cu 或 Ni ;

[0078] R₁ 至 R₇ 独立地代表氢, 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟, 氯, 三氟甲基, 全氟乙基, 三氟乙基, 全氟丙基, 全氟丁基, 三甲基甲硅烷基, 三乙基甲硅烷基, 三丙基甲硅烷基, 三(叔丁基)甲硅烷基, 叔丁基二甲基甲硅烷基, 二甲基苯基甲硅烷基, 三苯基甲硅烷基, 苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 咪唑基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基, 苯并噁唑基, 二甲基氨基, 二乙基氨基或二苯基氨基 ;

[0079] R₁₁ 至 R₂₃ 独立地代表氢, 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟,

氯,三氟甲基,全氟乙基,三氟乙基,全氟丙基,全氟丁基,三甲基甲硅烷基,三乙基甲硅烷基,三丙基甲硅烷基,三(叔丁基)甲硅烷基,叔丁基二甲基甲硅烷基,二甲基苯基甲硅烷基,三苯基甲硅烷基,苯基,联苯基,萘基,蒽基,芴基,吡啶基,喹啉基,呋喃基,苯硫基,噻唑基,咪唑基,噁唑基,苯并呋喃基,苯并噻唑基,苯并咪唑基,苯并噁唑基,二甲基氨基,二乙基氨基或二苯基氨基;

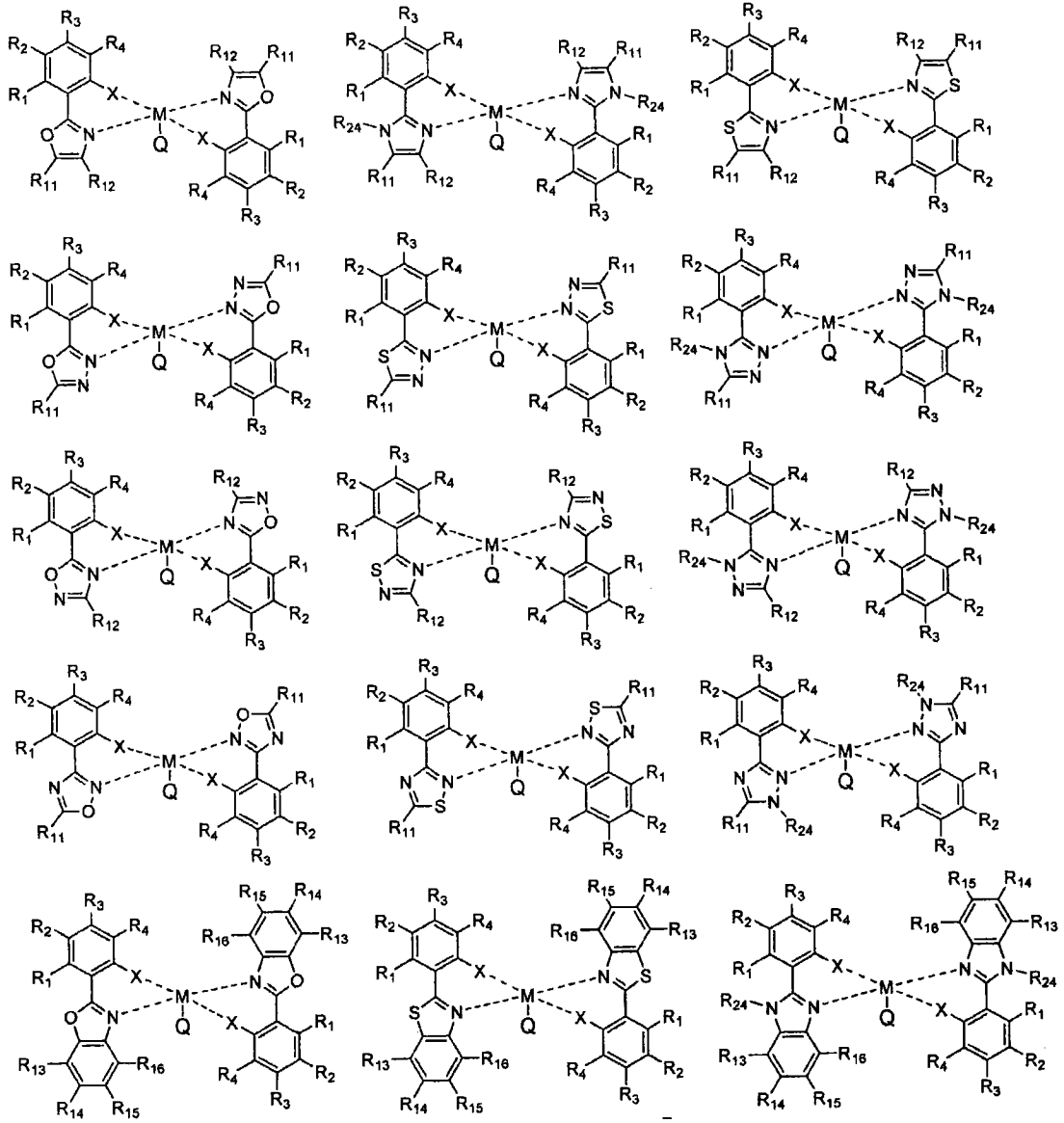
[0080] R_{24} 代表甲基,乙基,正丙基,异丙基,正丁基,异丁基,叔丁基,正戊基,异戊基,正己基,正庚基,正辛基,2-乙基己基,正壬基,癸基,十二烷基,十六烷基,苯基,联苯基,萘基,蒽基或芴基;

[0081] R_{25} 至 R_{32} 独立地代表氢,甲基,乙基,正丙基,异丙基,正丁基,异丁基,叔丁基,正戊基,异戊基,正己基,正庚基,正辛基,2-乙基己基,正壬基,癸基,十二烷基,十六烷基,氟,氯,氰基,三氟甲基,全氟乙基,三氟乙基,全氟丙基,全氟丁基,环丙基,环丁基,环戊基,环己基,环庚基,环辛基,甲氧基,乙氧基,丁氧基,己氧基,苯基,联苯基,萘基,蒽基,芴基,吡啶基,喹啉基,呋喃基,苯硫基,噻唑基,咪唑基,噁唑基,苯并呋喃基,苯并噻唑基,苯并咪唑基,苯并噁唑基,三甲基甲硅烷基,三乙基甲硅烷基,三丙基甲硅烷基,三(叔丁基)甲硅烷基,叔丁基二甲基甲硅烷基,二甲基苯基甲硅烷基,三苯基甲硅烷基,二甲基氨基,二乙基氨基或二苯基氨基;和

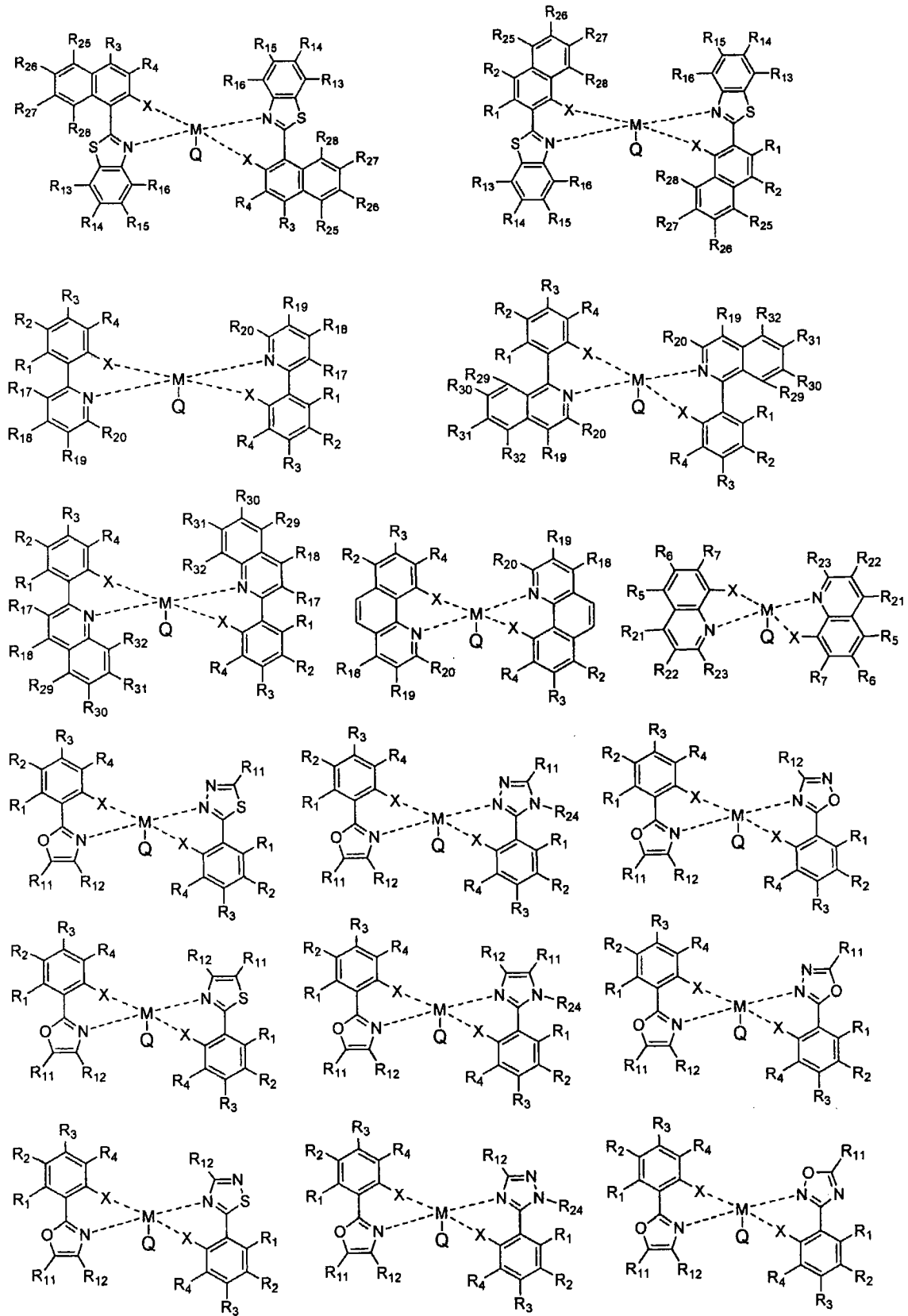
[0082] R_1 至 R_7 、 R_{11} 至 R_{23} 、 R_{24} 以及 R_{25} 至 R_{32} 的苯基,联苯基,萘基,蒽基,芴基,吡啶基,喹啉基,呋喃基,苯硫基,噻唑基,咪唑基,噁唑基,苯并呋喃基,苯并噻唑基,苯并咪唑基或苯并噁唑基可被一个或多个选自下组的取代基进一步取代:甲基,乙基,正丙基,异丙基,正丁基,异丁基,叔丁基,正戊基,异戊基,正己基,正庚基,正辛基,2-乙基己基,正壬基,癸基,十二烷基,十六烷基,氟,氯,氰基,三氟甲基,全氟乙基,三氟乙基,全氟丙基,全氟丁基,环丙基,环丁基,环戊基,环己基,环庚基,环辛基,甲氧基,乙氧基,丁氧基,己氧基,苯基,联苯基,萘基,蒽基,芴基,吡啶基,喹啉基,呋喃基,苯硫基,噻唑基,咪唑基,噁唑基,苯并呋喃基,苯并噻唑基,苯并咪唑基,苯并噁唑基,三甲基甲硅烷基,三乙基甲硅烷基,三丙基甲硅烷基,三(叔丁基)甲硅烷基,叔丁基二甲基甲硅烷基,二甲基苯基甲硅烷基,三苯基甲硅烷基,二甲基氨基,二乙基氨基和二苯基氨基。

[0083] 当 M 是三价金属时,本发明所述由化学式 (1) 代表的化合物的例子具体包括以下化合物,但不限于此:

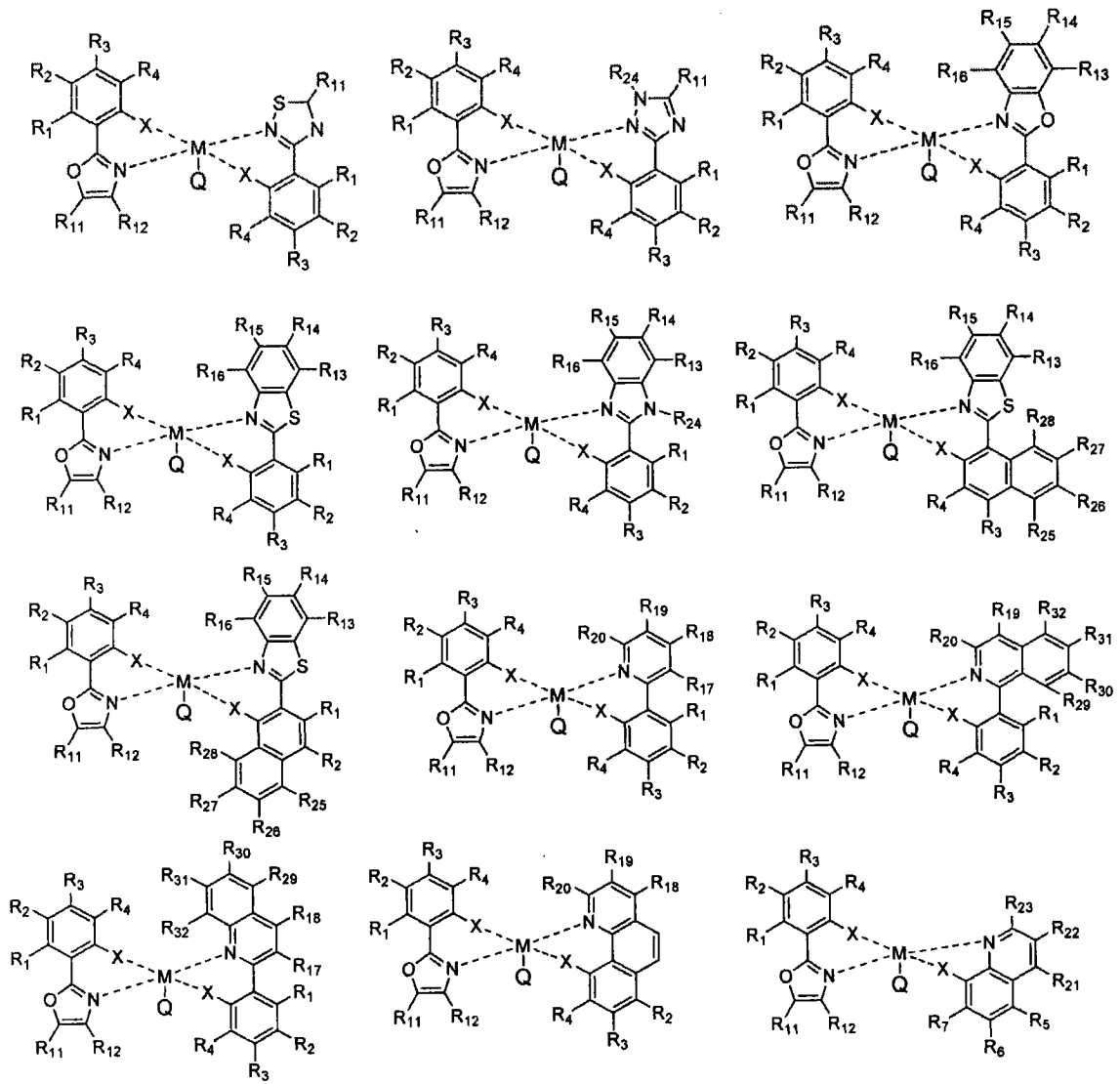
[0084]



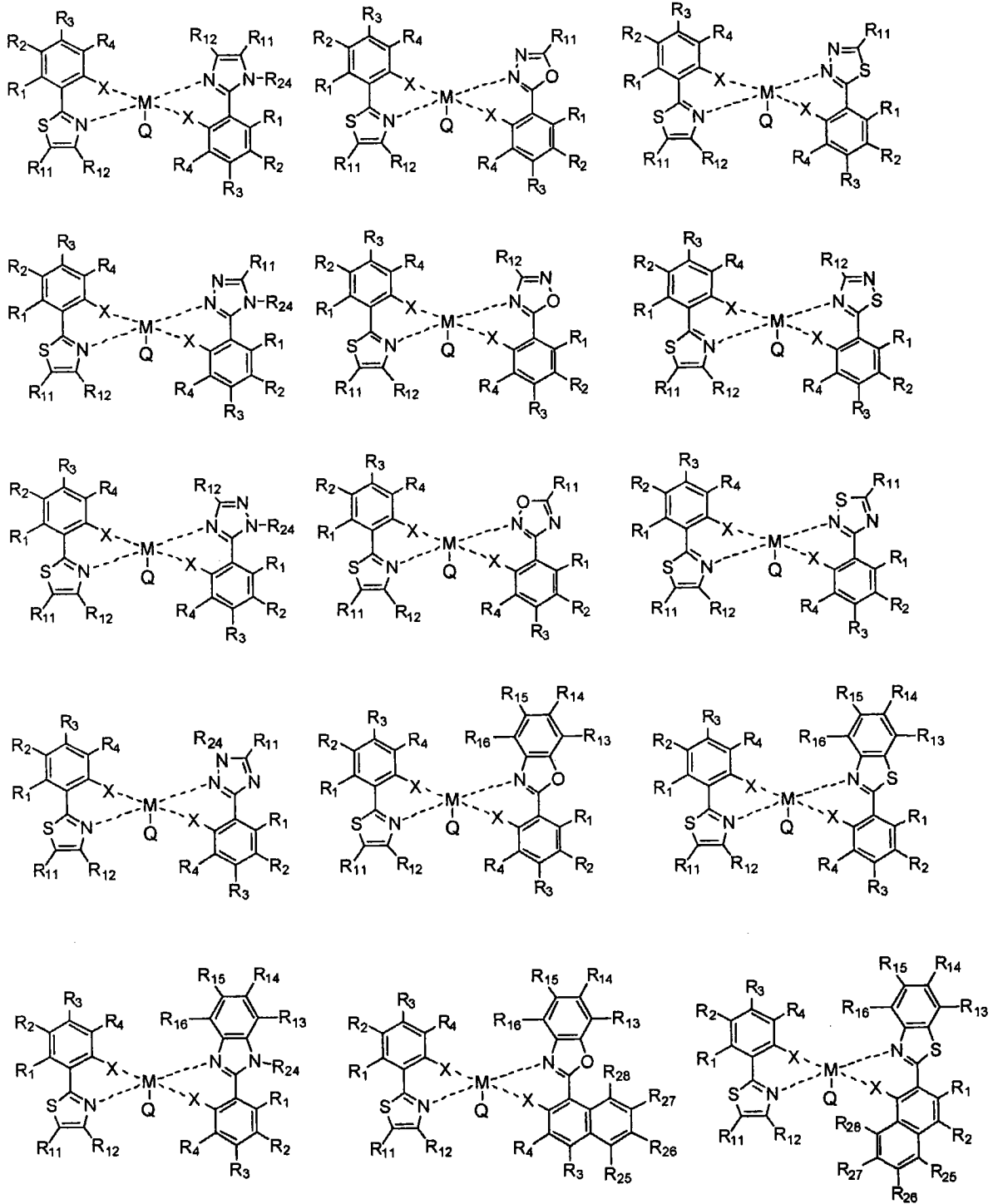
[0085]



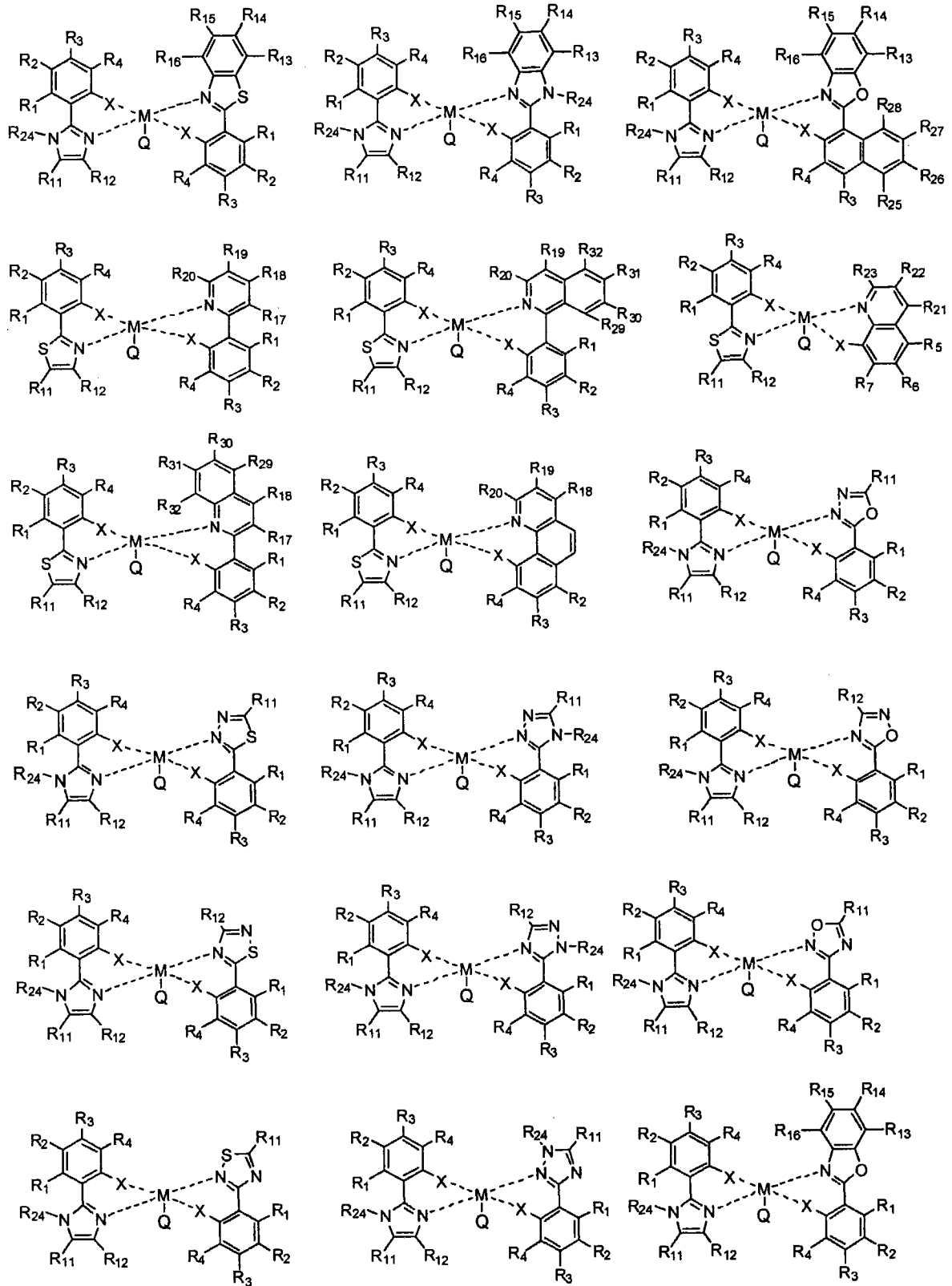
[0086]



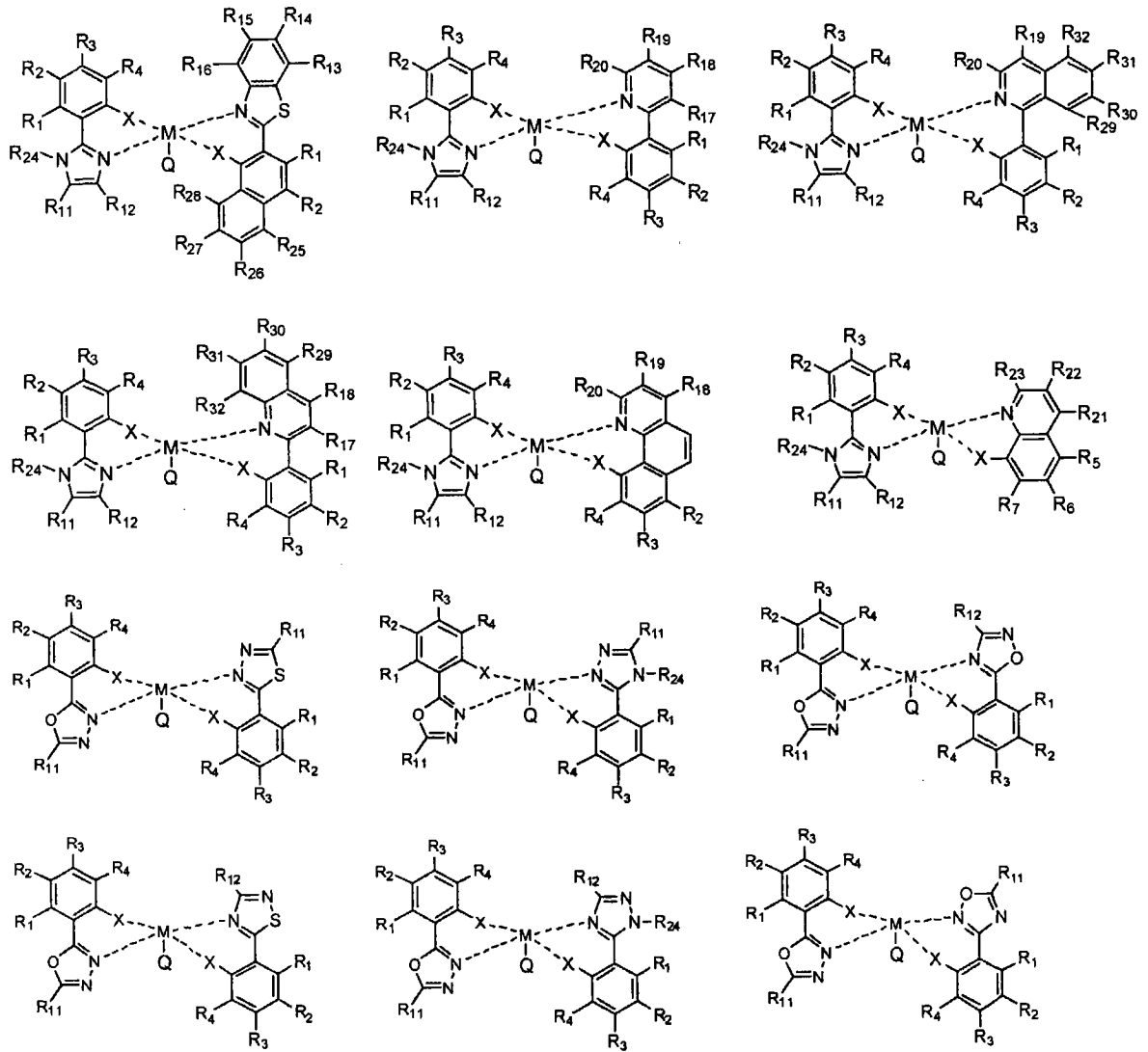
[0087]



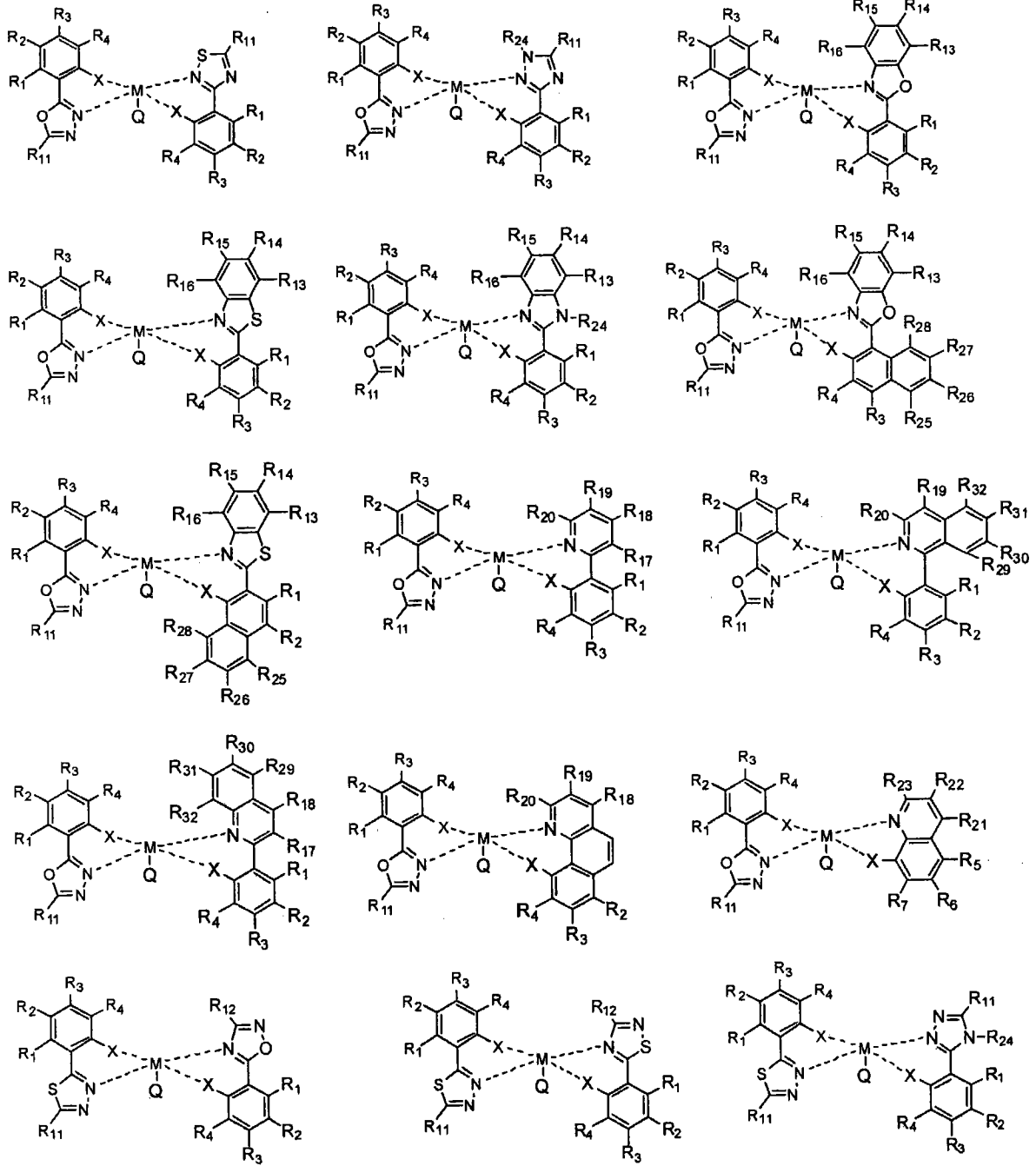
[0088]



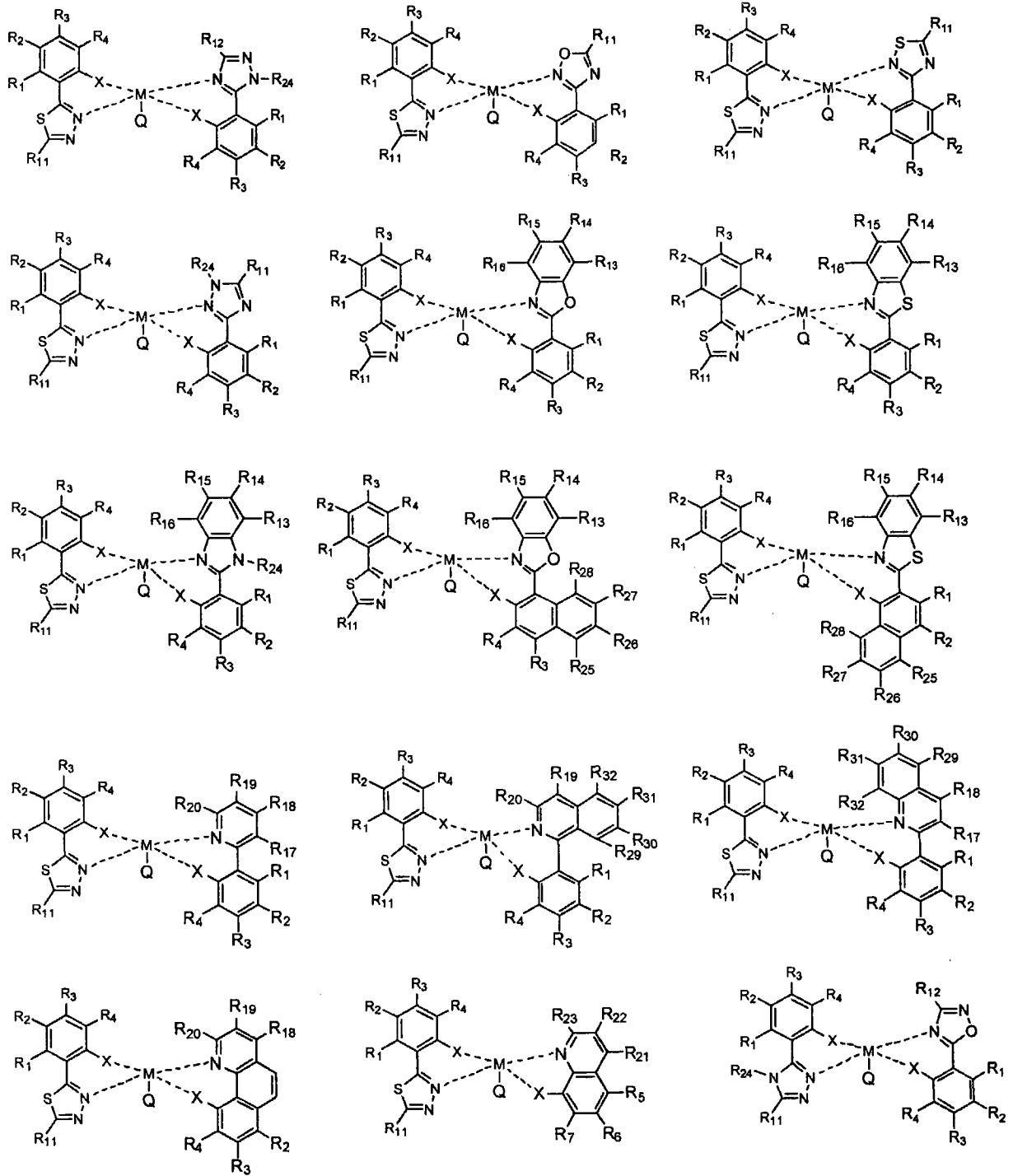
[0089]



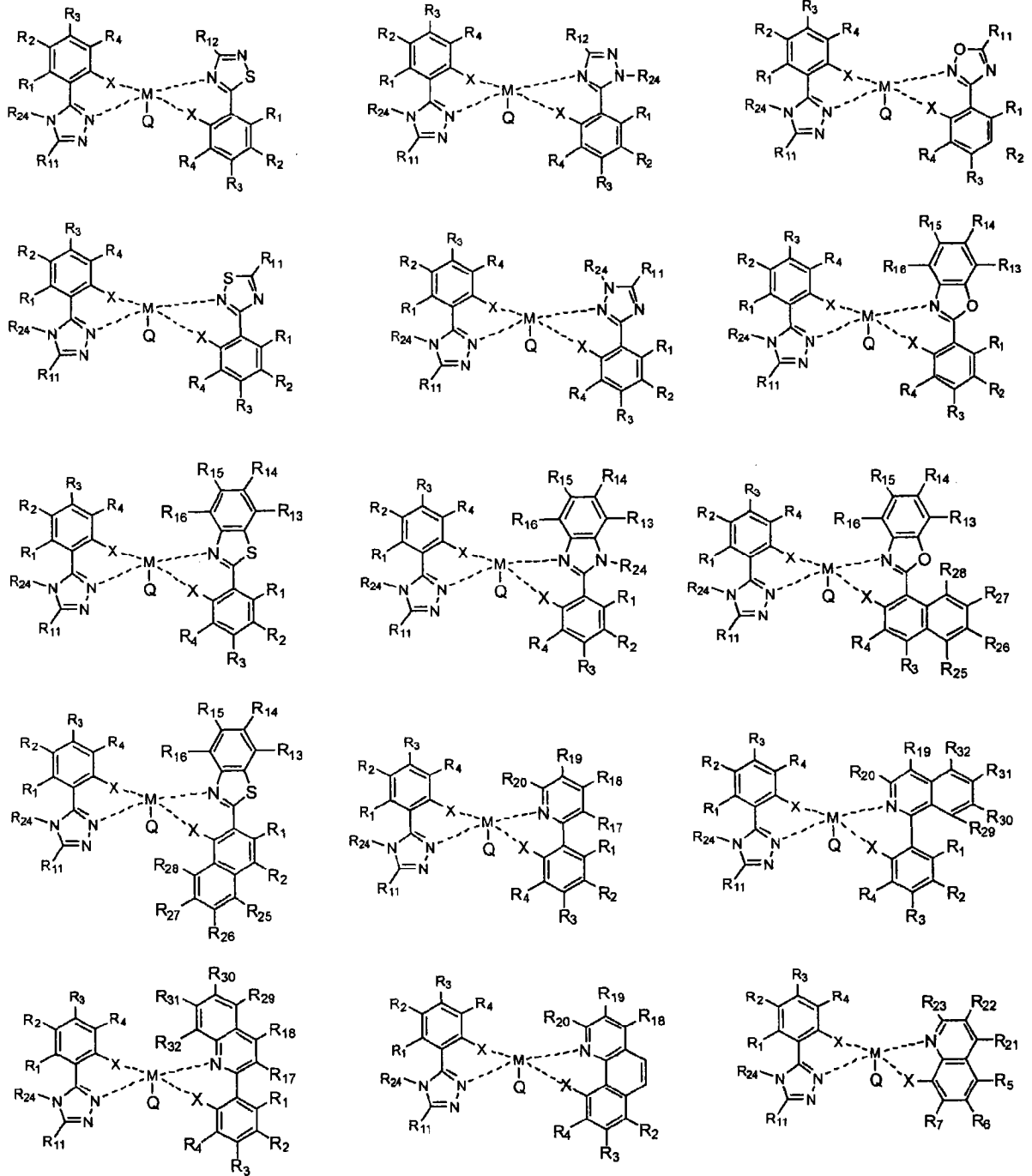
[0090]



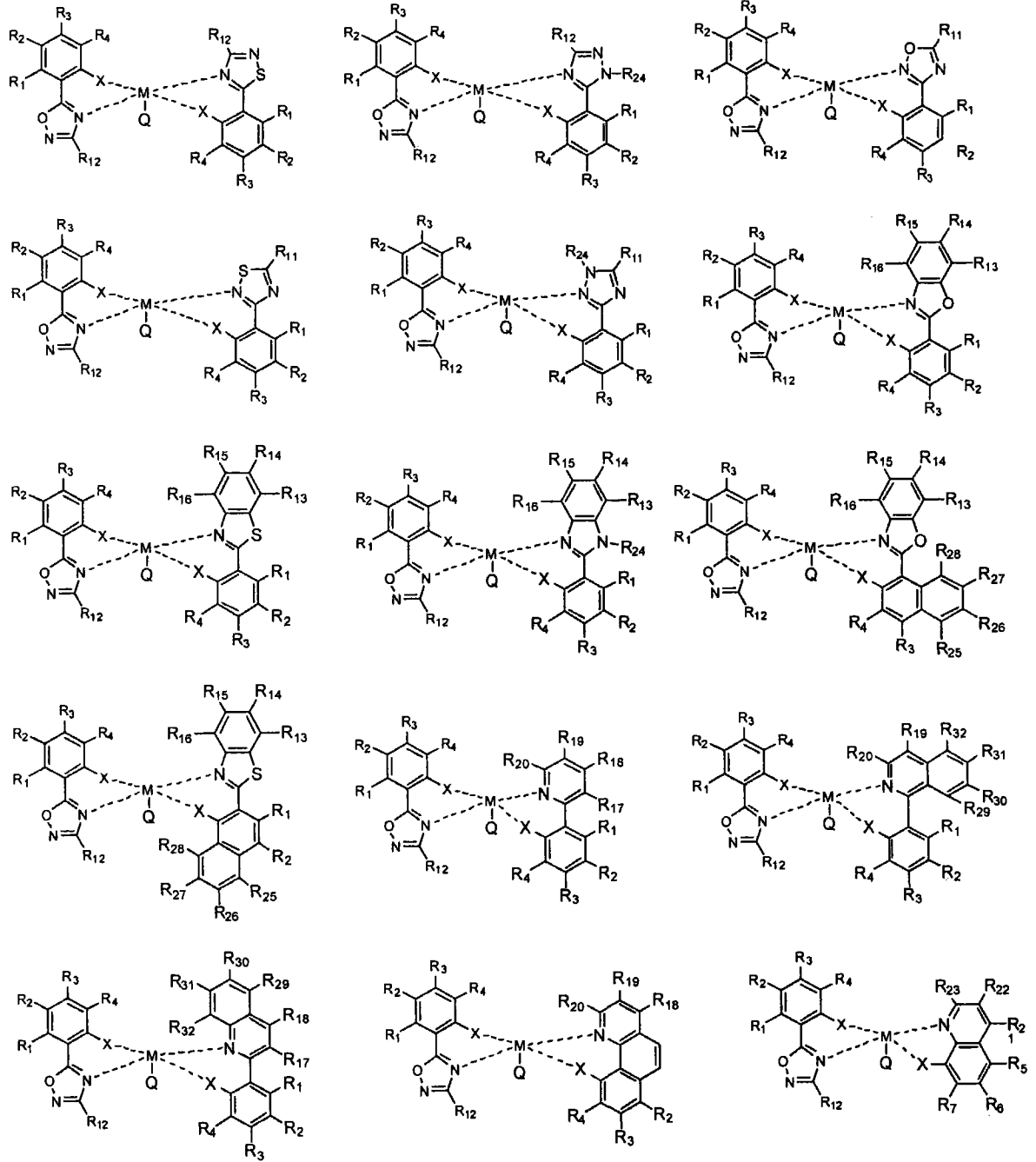
[0091]



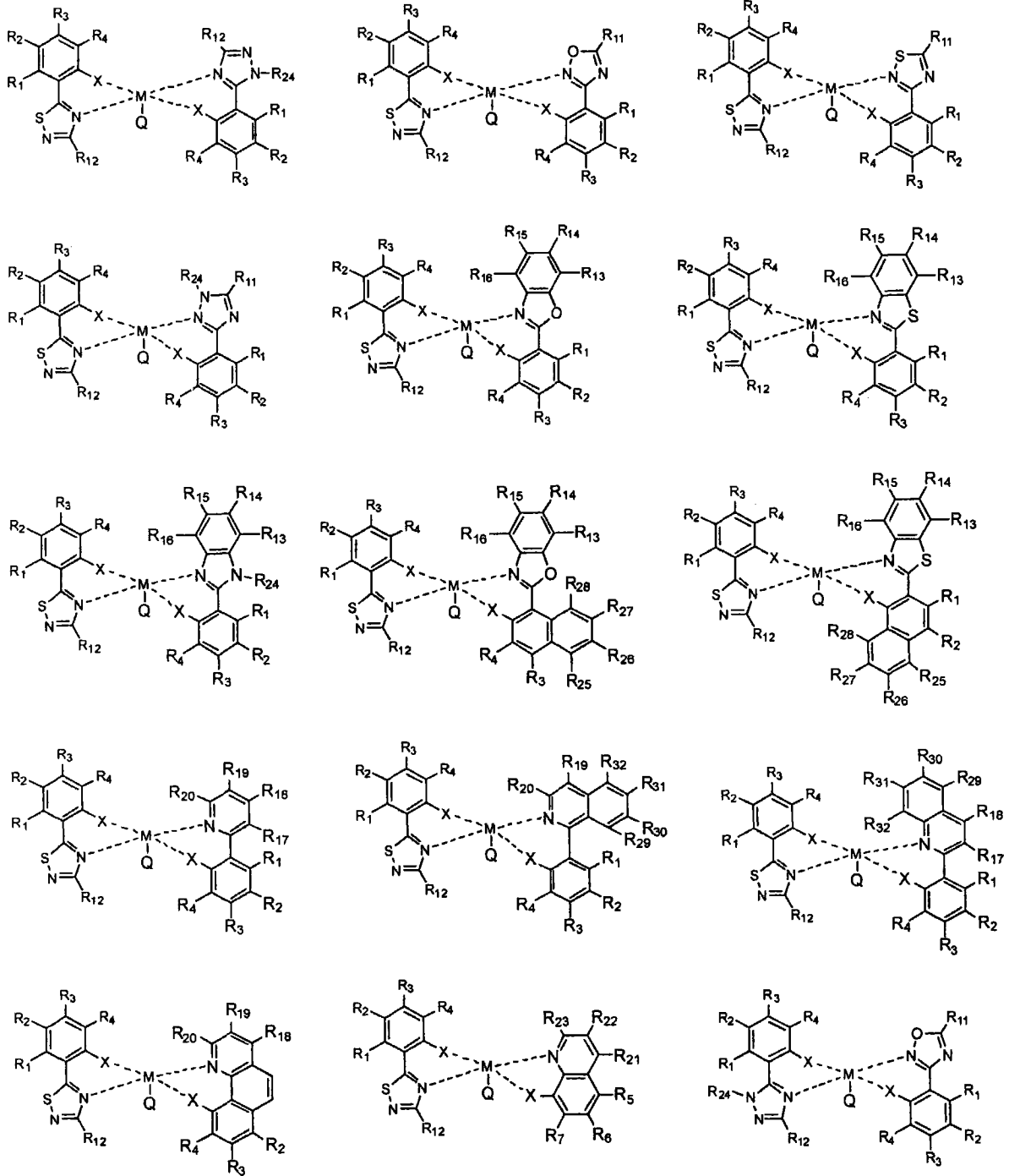
[0092]



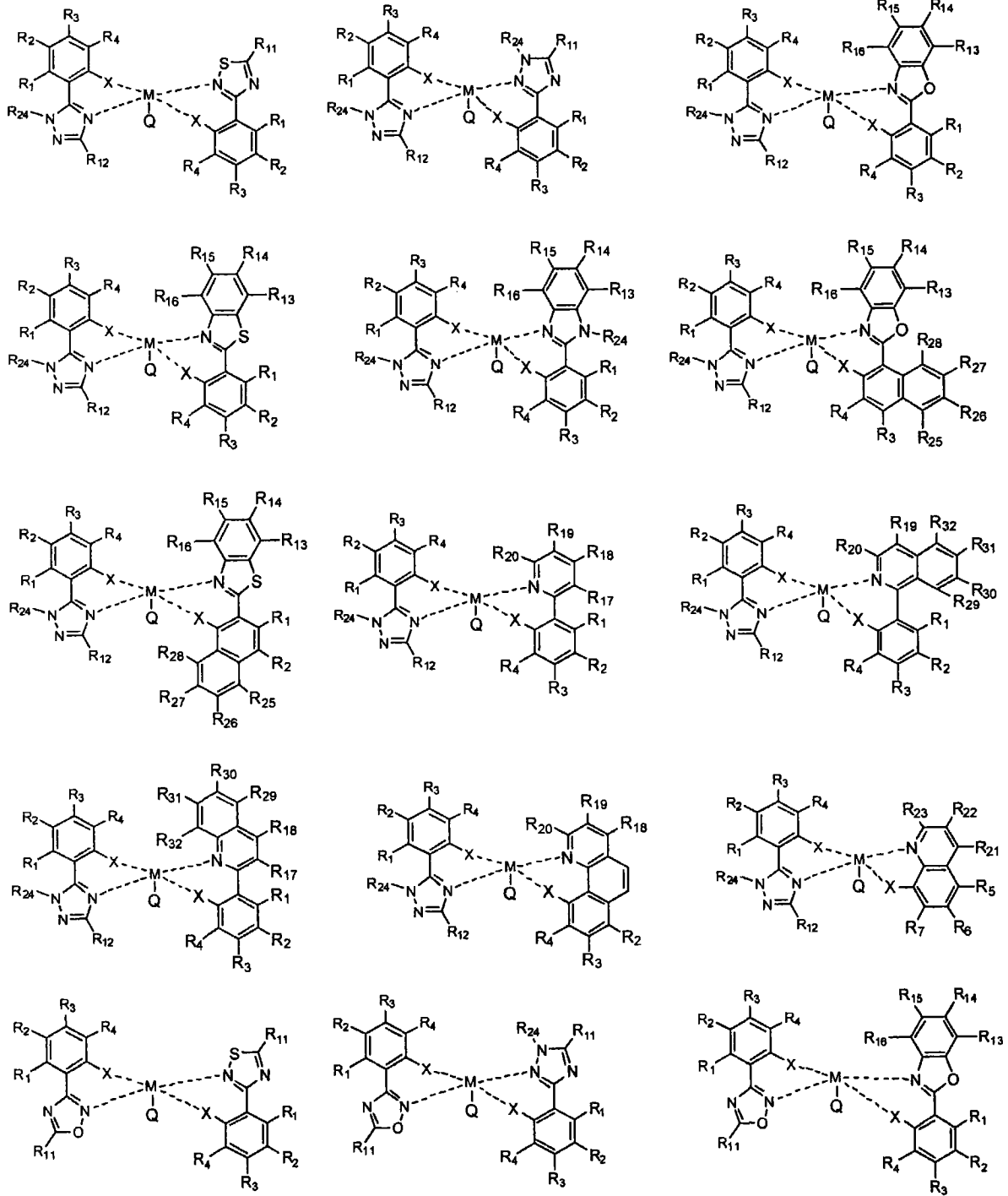
[0093]



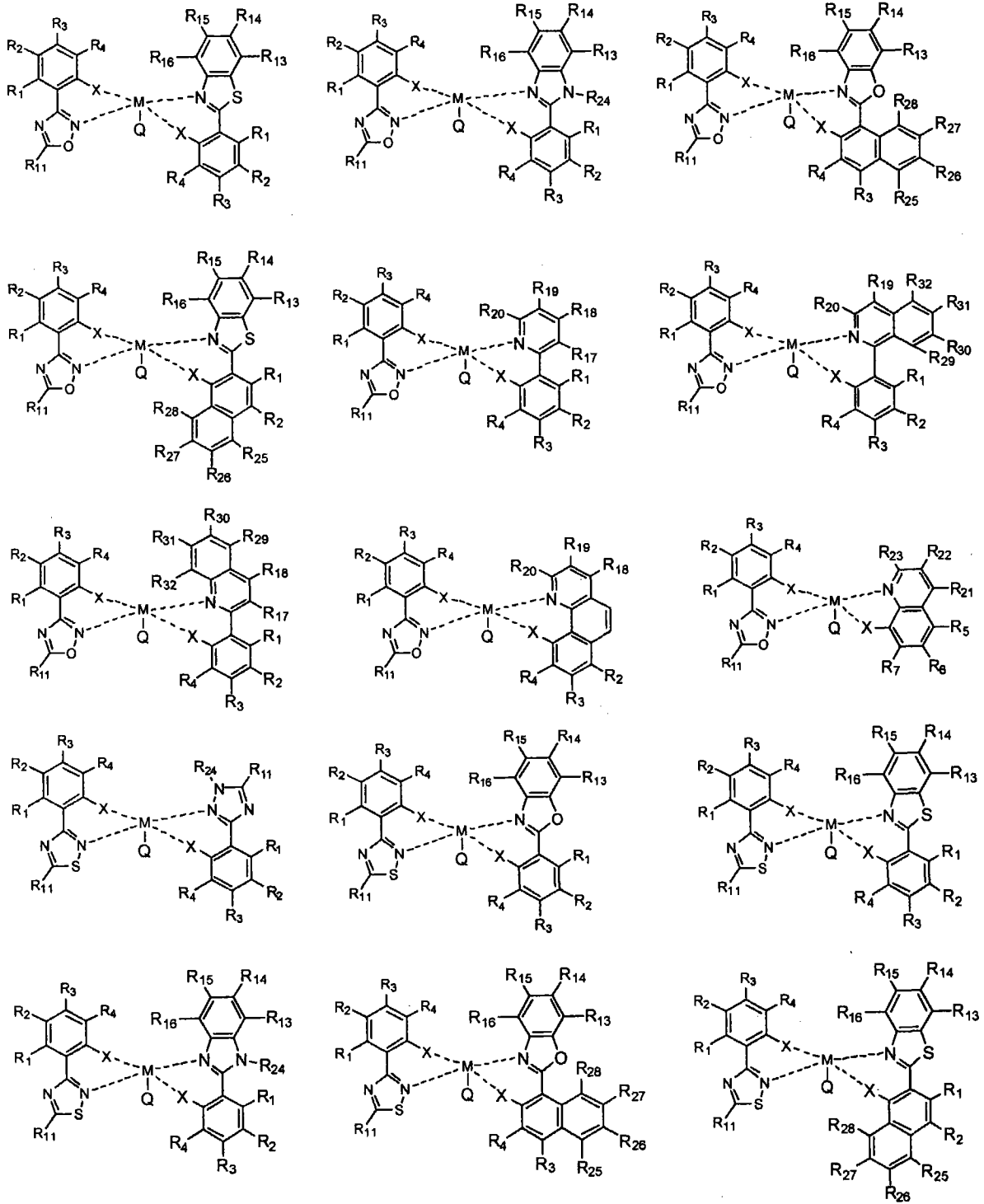
[0094]



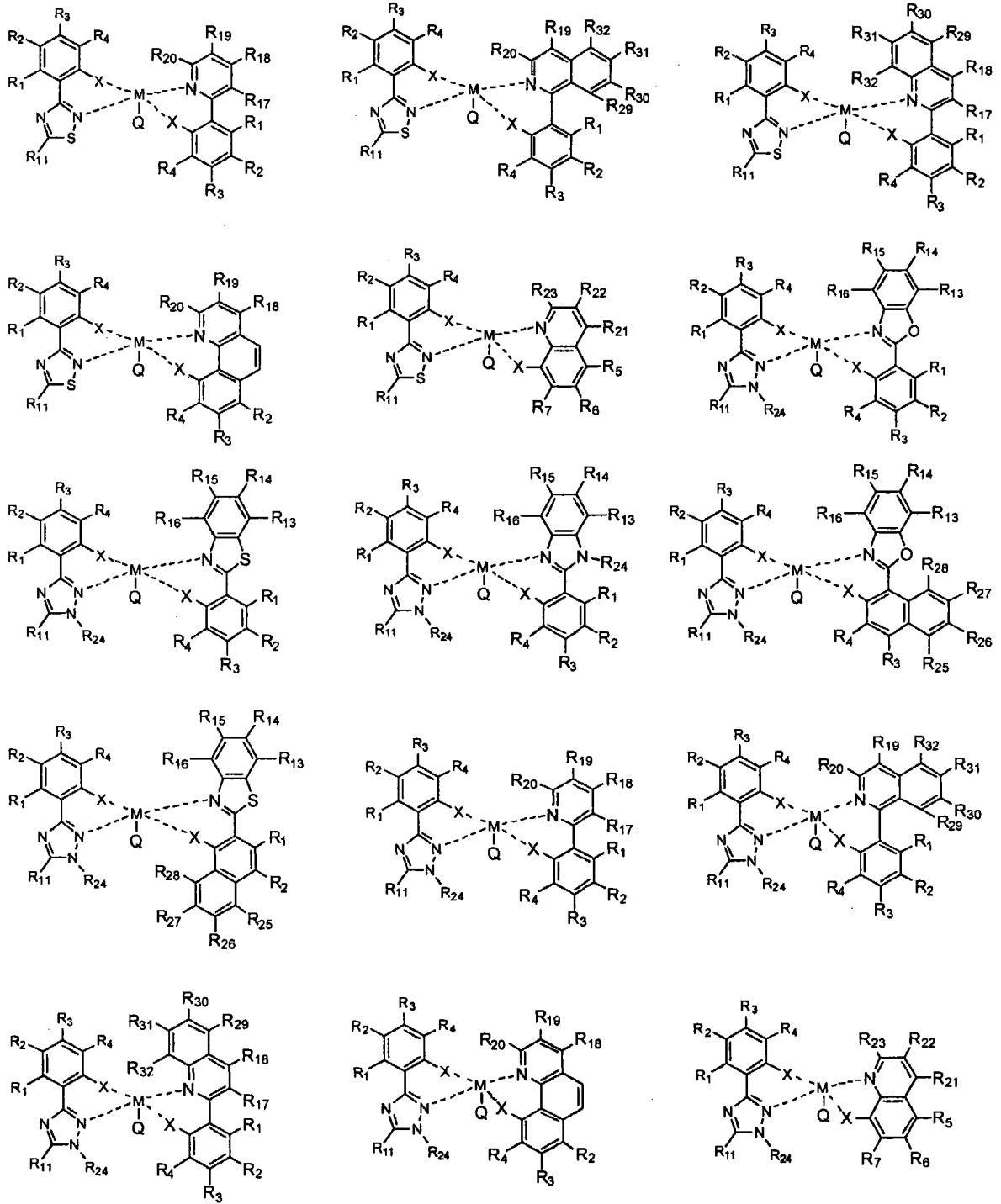
[0095]



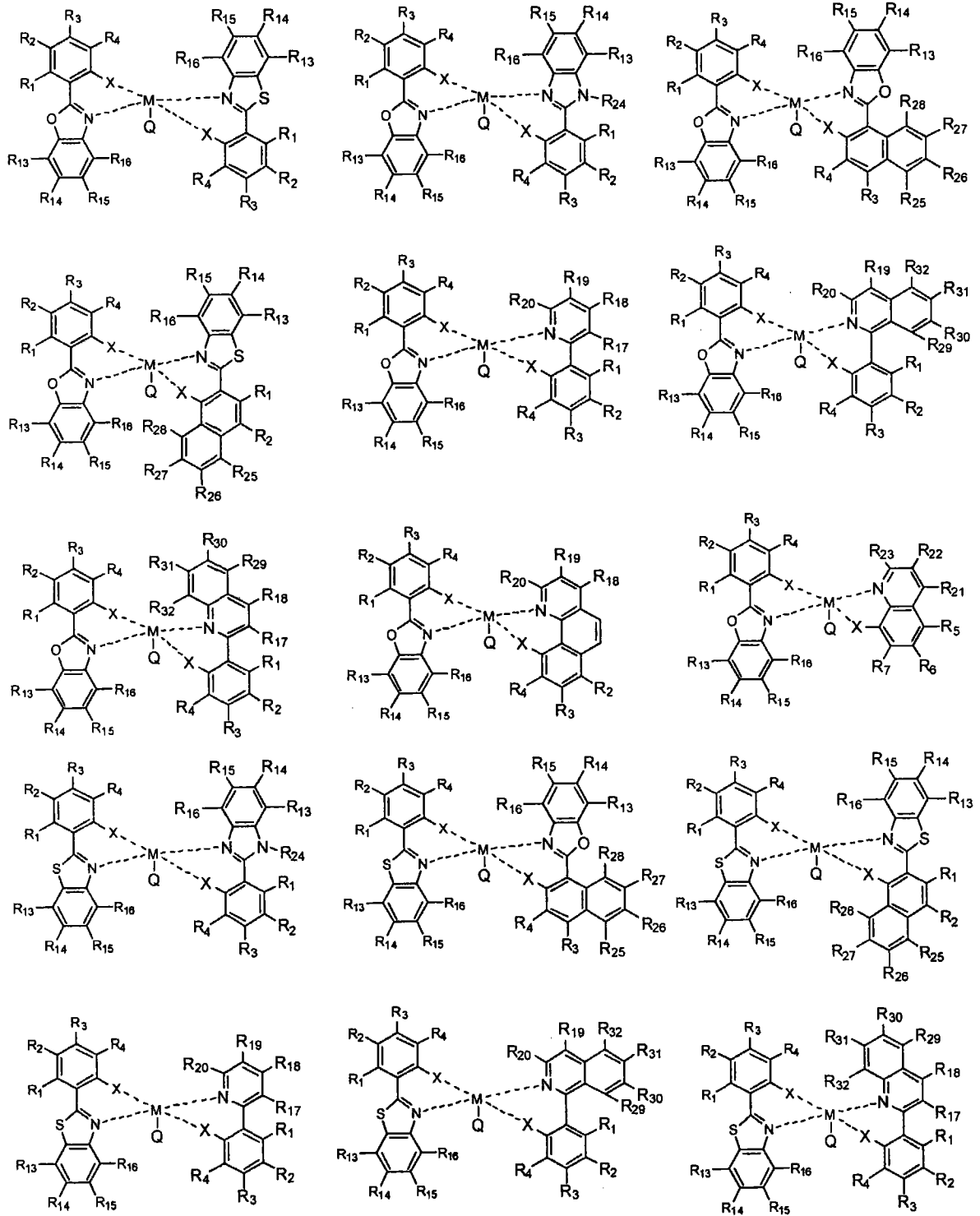
[0096]



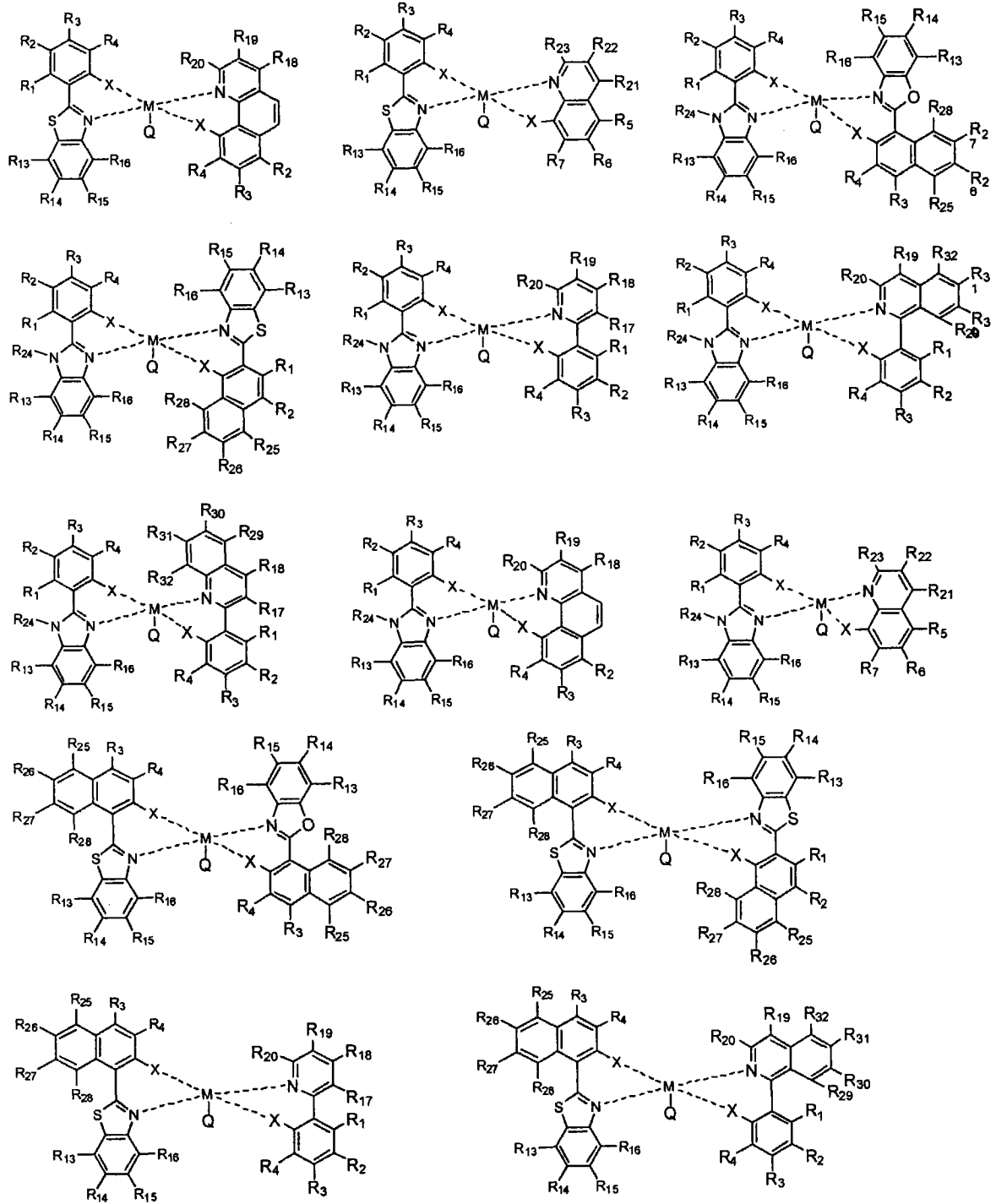
[0097]



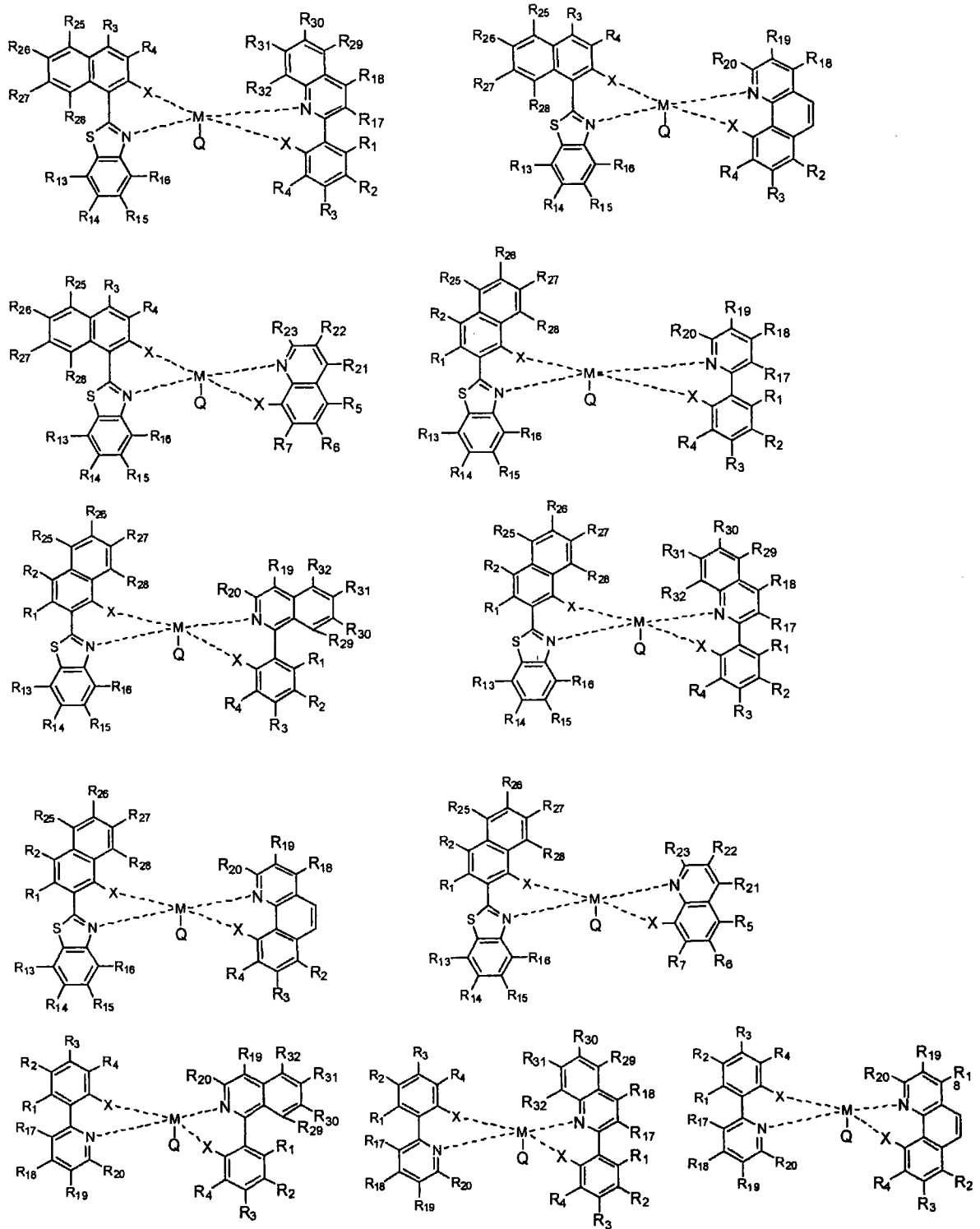
[0098]



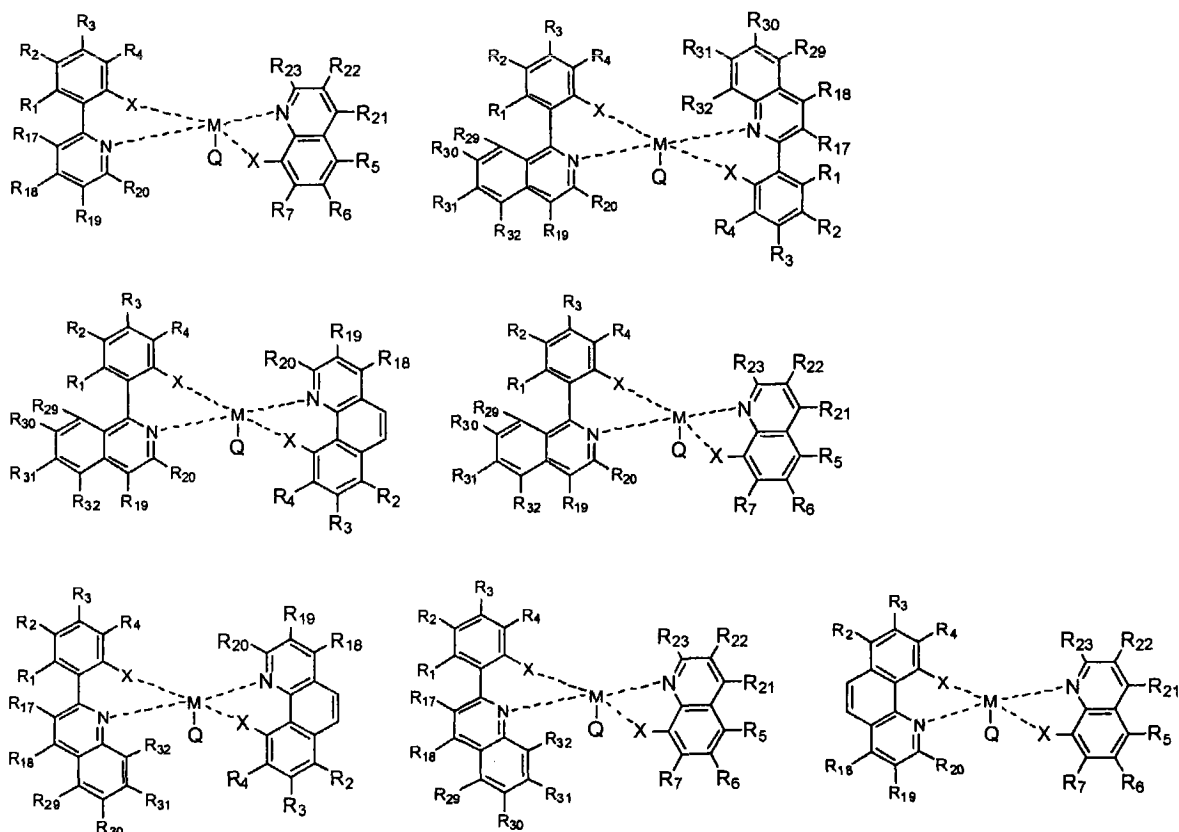
[0099]



[0100]



[0101]



[0102] 其中, X 代表 O、S 或 Se ;M 代表 Al、Ga、In 或 B ;Q 代表 (C6-C60) 芳氧基或三 (C6-C60) 芳基甲硅烷基, Q 的芳氧基和三芳基甲硅烷基可被 (C1-C60) 烷基或 (C6-C60) 芳基进一步取代 ;

[0103] R_1 至 R_7 独立地代表氢, 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟, 氯, 三氟甲基, 全氟乙基, 三氟乙基, 全氟丙基, 全氟丁基, 三甲基甲硅烷基, 三乙基甲硅烷基, 三丙基甲硅烷基, 三(叔丁基)甲硅烷基, 叔丁基二甲基甲硅烷基, 二甲基苯基甲硅烷基, 三苯基甲硅烷基, 苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 咪唑基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基, 苯并噁唑基, 二甲基氨基, 二乙基氨基或二苯基氨基 ;

[0104] R_{11} 至 R_{23} 独立地代表氢, 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟, 氯, 三氟甲基, 全氟乙基, 三氟乙基, 全氟丙基, 全氟丁基, 三甲基甲硅烷基, 三乙基甲硅烷基, 三丙基甲硅烷基, 三(叔丁基)甲硅烷基, 叔丁基二甲基甲硅烷基, 二甲基苯基甲硅烷基, 三苯基甲硅烷基, 苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 咪唑基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基, 苯并噁唑基, 二甲基氨基, 二乙基氨基或二苯基氨基 ;

[0105] R_{24} 代表甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 苯基, 联苯基, 萘基, 蒽基或芴基 ;

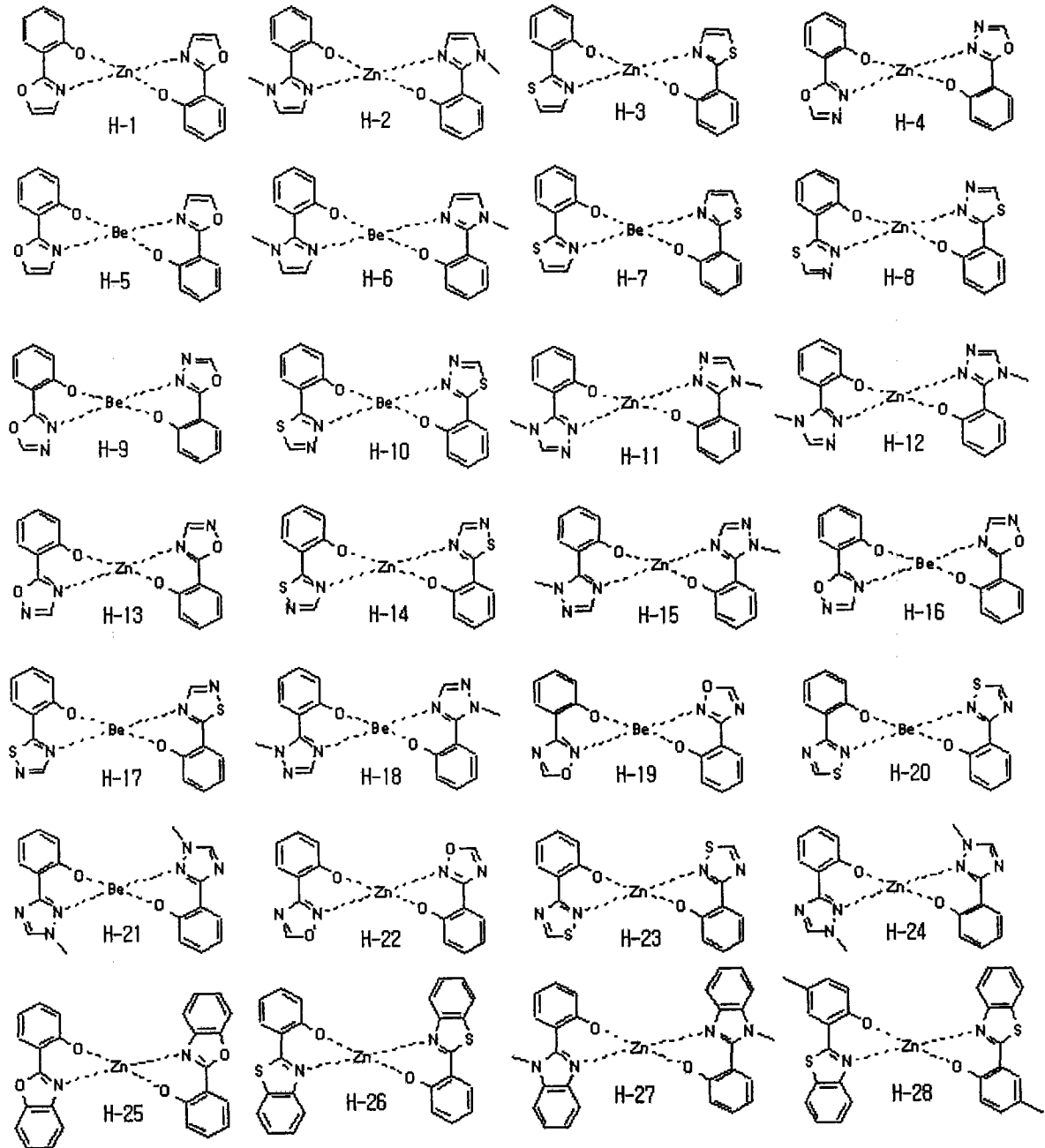
[0106] R_{25} 至 R_{32} 独立地代表氢, 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟,

氯, 氰基, 三氟甲基, 全氟乙基, 三氟乙基, 全氟丙基, 全氟丁基, 环丙基, 环丁基, 环戊基, 环己基, 环庚基, 环辛基, 甲氧基, 乙氧基, 丁氧基, 己氧基, 苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基, 苯并噁唑基, 三甲基甲硅烷基, 三乙基甲硅烷基, 三丙基甲硅烷基, 三(叔丁基)甲硅烷基, 叔丁基二甲基甲硅烷基, 二甲基苯基甲硅烷基, 三苯基甲硅烷基, 二甲基氨基, 二乙基氨基或二苯基氨基;

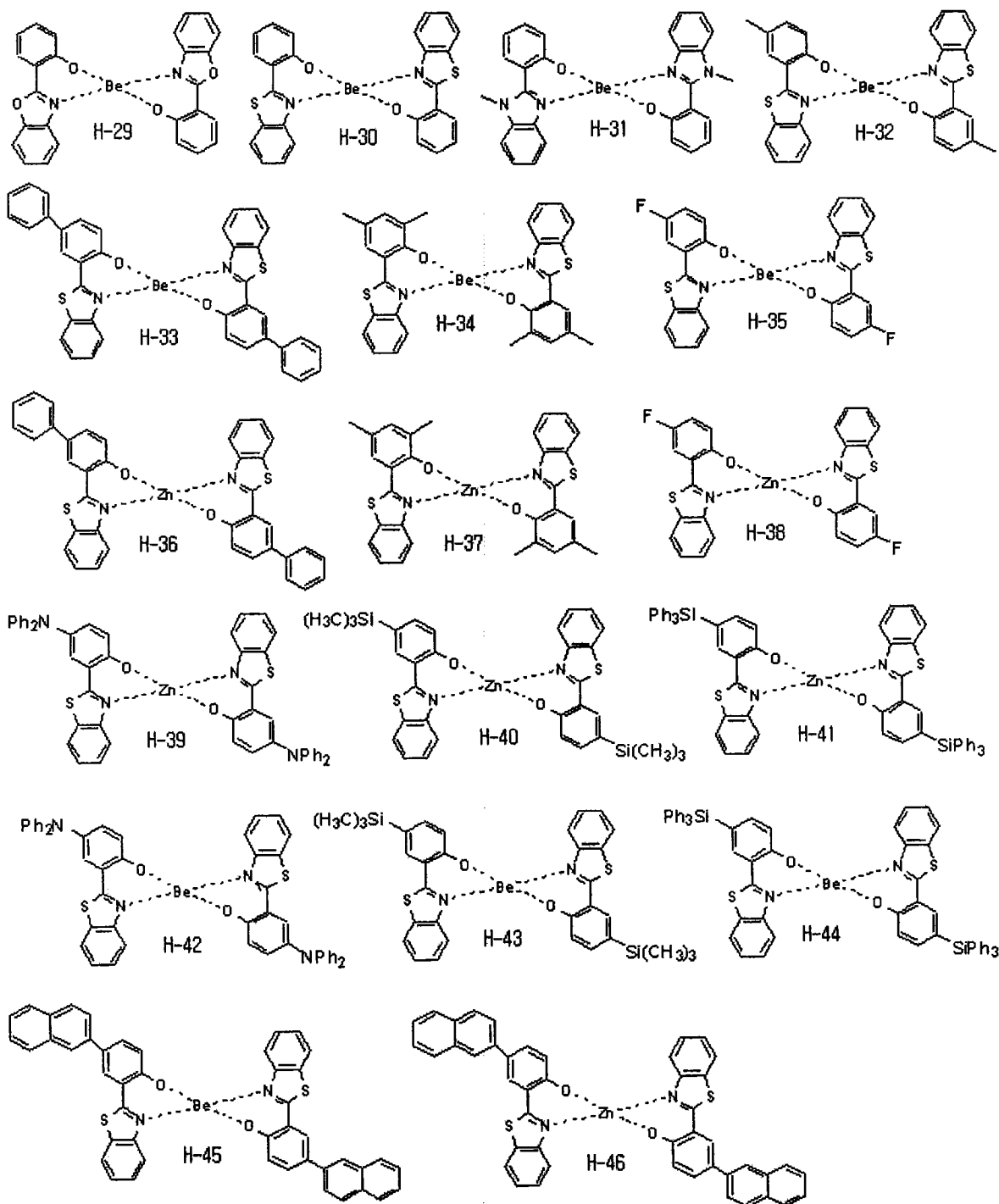
[0107] R_1 至 R_7 、 R_{11} 至 R_{23} 、 R_{24} 以及 R_{25} 至 R_{32} 的苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基或苯并噁唑基可被一个或多个选自下组的取代基进一步取代: 甲基, 乙基, 正丙基, 异丙基, 正丁基, 异丁基, 叔丁基, 正戊基, 异戊基, 正己基, 正庚基, 正辛基, 2-乙基己基, 正壬基, 癸基, 十二烷基, 十六烷基, 氟, 氯, 氰基, 三氟甲基, 全氟乙基, 三氟乙基, 全氟丙基, 全氟丁基, 环丙基, 环丁基, 环戊基, 环己基, 环庚基, 环辛基, 甲氧基, 乙氧基, 丁氧基, 己氧基, 苯基, 联苯基, 萘基, 蒽基, 芴基, 吡啶基, 喹啉基, 呋喃基, 苯硫基, 噻唑基, 咪唑基, 噁唑基, 苯并呋喃基, 苯并噻唑基, 苯并咪唑基, 苯并噁唑基, 三甲基甲硅烷基, 三乙基甲硅烷基, 三丙基甲硅烷基, 三(叔丁基)甲硅烷基, 叔丁基二甲基甲硅烷基, 二甲基苯基甲硅烷基, 三苯基甲硅烷基, 二甲基氨基, 二乙基氨基和二苯基氨基。

[0108] 本发明所述由化学式 (1) 代表的化合物优选选自以下化合物, 但不限于此:

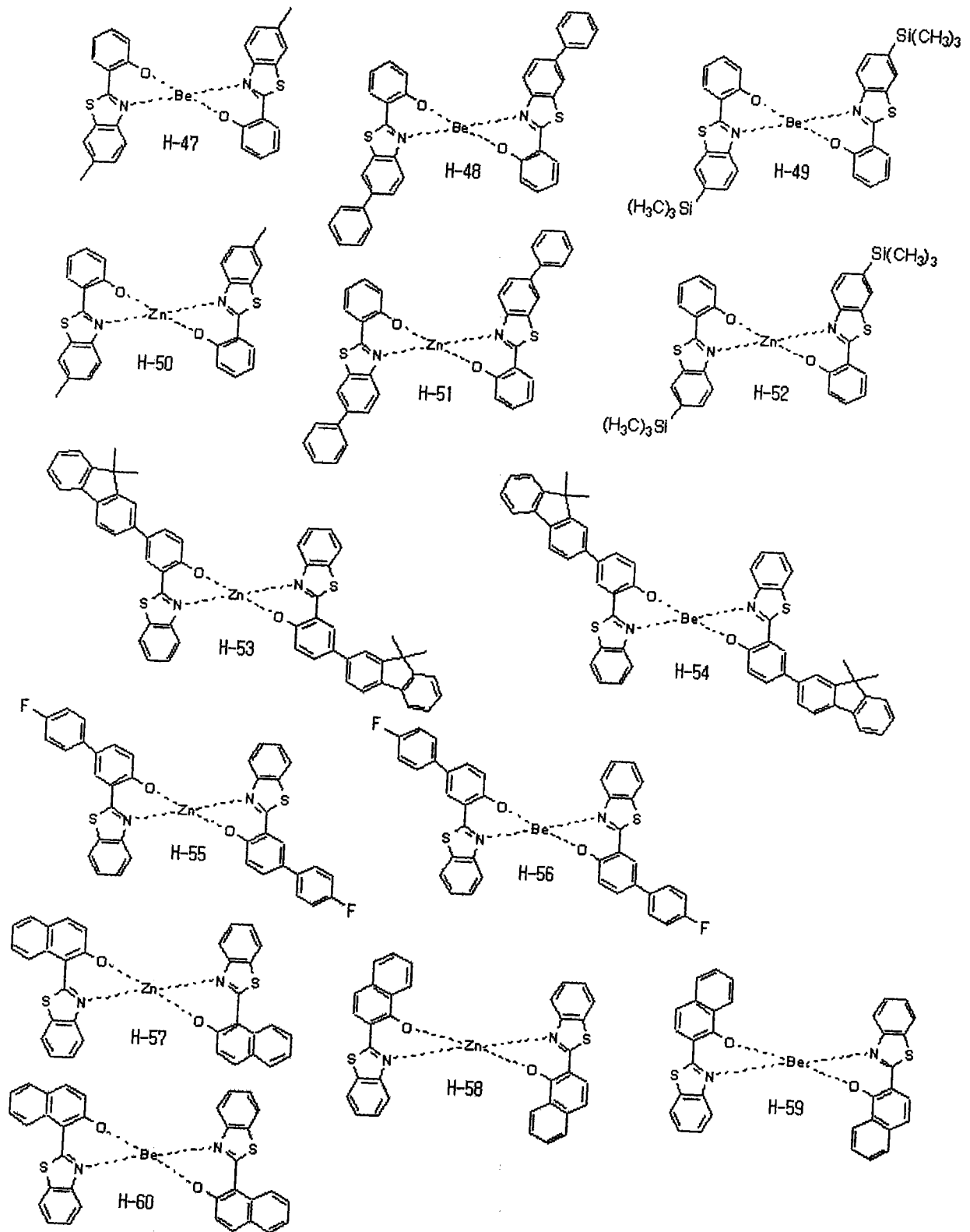
[0109]



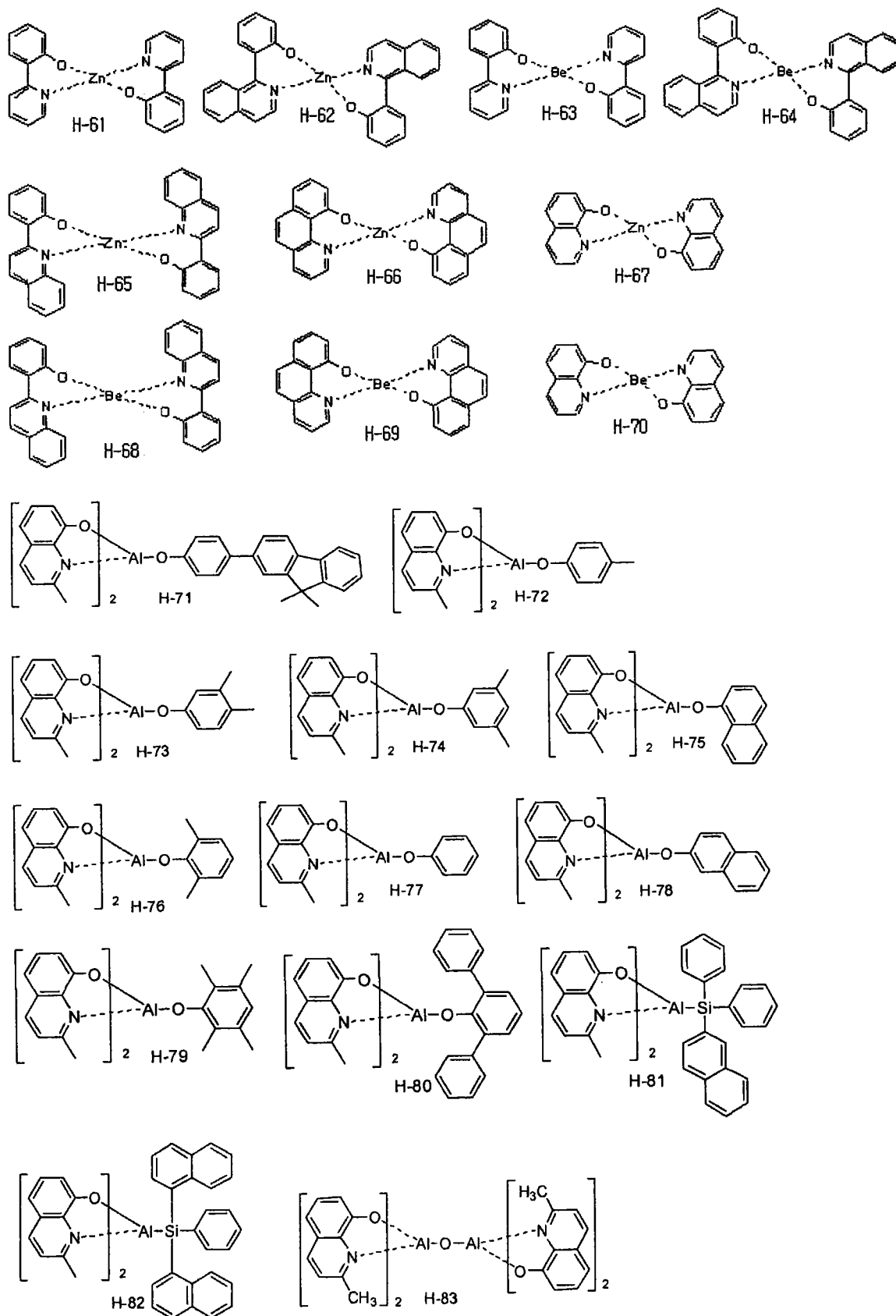
[0110]



[0111]



[0112]



[0113] 本发明的电致发光器件的特征在于,所述有机层包含电致发光层,其包含一种或多种由化学式(1)代表的电致发光化合物作为电致发光主体,以及含量为1-20重量%的一种或多种电致发光掺杂剂。对用于本发明的电致发光器件的电致发光掺杂剂没有特别限

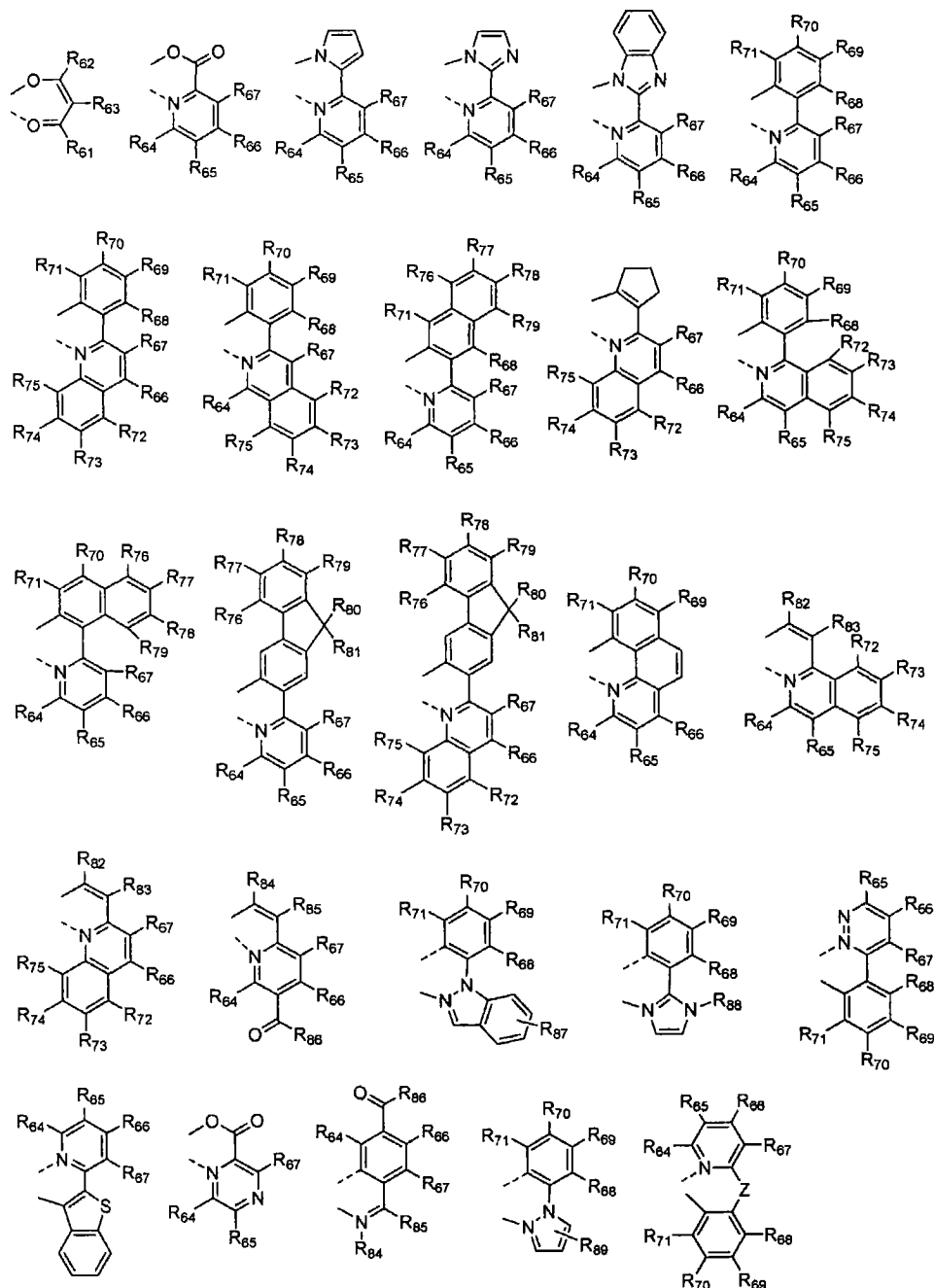
制,但其例子可以是由化学式 (2) 代表的化合物

[0114] 化学式 2

[0115] $M^1L^3L^4L^5$

[0116] 其中, M^1 选自周期表的第 7、8、9、10、11、13、14、15 和 16 列, 而配体 L^3 、 L^4 和 L^5 独立选自以下结构:

[0117]



[0118] 其中, R_{61} 至 R_{63} 独立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, 有 (C1-C60) 烷基取代基或没有 (C1-C60) 烷基取代基的 (C6-C60) 芳基, 或卤素;

[0119] R_{64} 至 R_{79} 独立地代表氢, (C1-C60) 烷基, (C1-C30) 烷氧基, (C3-C60) 环烷基, (C2-C30) 烯基, (C6-C60) 芳基, 单或二 (C1-C30) 烷基氨基, 单或二 (C6-C30) 芳基氨基, SF_5 , 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲

硅烷基, 氰基或卤素; R_{70} 至 R_{76} 各自可通过 (C2-C12) 亚烷基或 (C2-C12) 亚烯基与相邻取代基相连而形成稠环或多个稠环; 而 R_{64} 至 R_{79} 的烷基、环烷基、烯基或芳基, 或者 R_{70} 和 R_{76} 通过亚烷基或亚烯基连接而形成的稠环或多个稠环可被选自以下的一个或多个取代基进一步取代: (C1-C60) 烷基, (C6-C60) 芳基和卤素;

[0120] R_{80} 至 R_{83} 独立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, 或者有 (C1-C60) 烷基取代基或没有 (C1-C60) 烷基取代基的 (C6-C60) 芳基;

[0121] R_{84} 和 R_{85} 独立地代表氢, 直链或支链 (C1-C60) 烷基, (C6-C60) 芳基或卤素, 或者 R_{84} 和 R_{85} 可通过有稠环或没有稠环的 (C3-C12) 亚烷基或 (C3-C12) 亚烯基连接而形成脂环或者单环或多环的芳环; 而烷基、芳基或者通过 (C3-C12) 亚烷基或 (C3-C12) 亚烯基连接而形成的脂环或者单环或多环的芳环可被一个或多个选自下组的取代基进一步取代: 有或卤素取代基没有卤素取代基的直链或支链 (C1-C60) 烷基, (C1-C30) 烷氧基, 卤素, 三 (C1-C30) 烷基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基和 (C6-C60) 芳基;

[0122] R_{86} 代表 (C1-C60) 烷基, (C6-C60) 芳基, (C5-C60) 杂芳基或卤素;

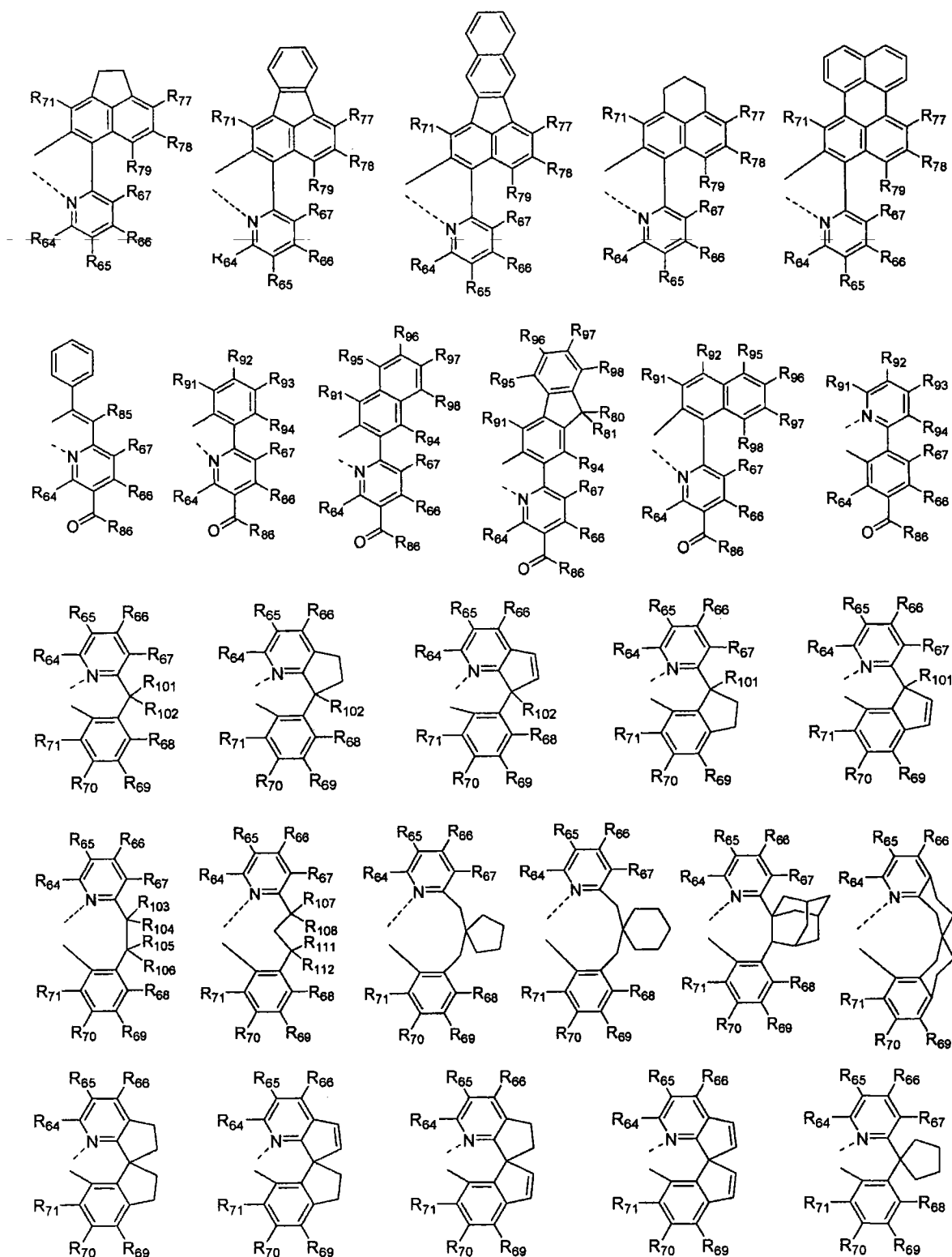
[0123] R_{87} 至 R_{89} 独立地代表氢, (C1-C60) 烷基, (C6-C60) 芳基或卤素, 且 R_{86} 至 R_{89} 的烷基或芳基可被卤素或 (C1-C60) 烷基进一步取代; 和

[0124] Z 代表 $\begin{array}{c} R_{101} \quad R_{102} \\ \diagdown \quad / \\ C \\ / \quad \backslash \end{array}$ 、 $\begin{array}{c} R_{103} \quad R_{104} \\ \diagdown \quad / \\ C \quad C \\ / \quad \backslash \quad / \quad \backslash \\ R_{105} \quad R_{106} \end{array}$ 或 $\begin{array}{c} R_{107} \quad R_{108} \quad R_{111} \quad R_{112} \\ \diagdown \quad / \quad \diagdown \quad / \\ C \quad C \quad C \\ / \quad \backslash \quad / \quad \backslash \\ R_{109} \quad R_{110} \end{array}$ 其中, R_{101} 至 R_{112} 独

立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, (C1-C30) 烷氧基, 卤素, (C6-C60) 芳基, 氰基或 (C5-C60) 环烷基, 或者 R_{101} 至 R_{112} 各自可通过亚烷基或亚烯基与相邻取代基相连而形成 (C5-C7) 螺环或 (C5-C9) 稠环, 或者它们可通过亚烷基或亚烯基与 R_{67} 或 R_{68} 相连而形成 (C5-C7) 稠环。

[0125] 在化学式 (2) 中, M' 可选自 Ir, Pt, Pd, Rh, Re, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au 或 Ag, 而化学式 (2) 所示化合物的配体 L^3 、 L^4 和 L^5 可独立地选自以下结构, 但不限于此。

[0126]



[0127] 其中, R_{64} 至 R_{79} 独立地代表氢, (C1-C60) 烷基, (C1-C30) 烷氧基, (C3-C60) 环烷基, (C2-C30) 烯基, (C6-C60) 芳基, 单或二 (C1-C30) 烷基氨基, 单或二 (C6-C30) 芳基氨基, SF_5 , 三 (C1-C30) 烷基甲硅烷基, 二 (C1-C30) 烷基 (C6-C30) 芳基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基, 氰基或卤素;

[0128] R_{64} 至 R_{79} 的烷基、环烷基、烯基或芳基可被一个或多个选自下组的取代基进一步取代: (C1-C60) 烷基, (C6-C60) 芳基和卤素;

[0129] R_{80} 和 R_{81} 独立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, 或者

有 (C1-C60) 烷基取代基或没有 (C1-C60) 烷基取代基的 (C6-C60) 芳基；

[0130] R_{85} 独立地代表氢, 直链或支链 (C1-C60) 烷基, (C6-C60) 芳基或卤素; 且 R_{85} 的烷基或芳基可被选自下组的一个或多个取代基进一步取代: 直链或支链的有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, (C1-C30) 烷氧基, 卤素, 三 (C1-C30) 烷基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基和 (C6-C60) 芳基;

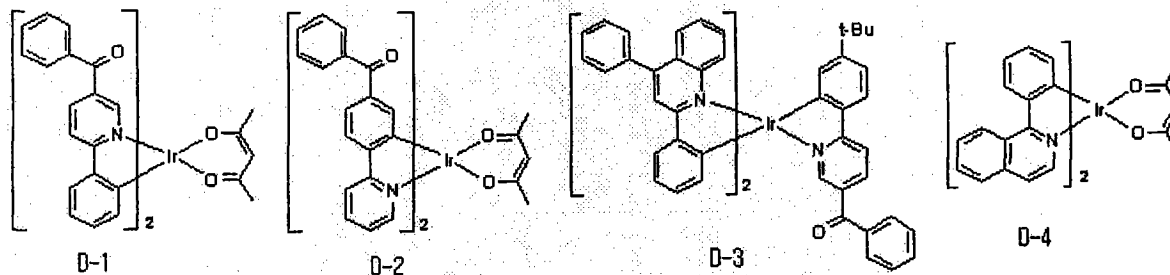
[0131] R_{86} 代表 (C1-C60) 烷基, (C6-C60) 芳基或卤素; 且 R_{86} 的烷基或芳基可被卤素或 (C1-C60) 烷基进一步取代;

[0132] R_{91} 至 R_{98} 独立地代表氢, 有卤素取代基或没有卤素取代基的直链或支链 (C1-C60) 烷基, (C1-C30) 烷氧基, 卤素, 三 (C1-C30) 烷基甲硅烷基, 三 (C6-C30) 芳基甲硅烷基或 (C6-C60) 芳基; 和

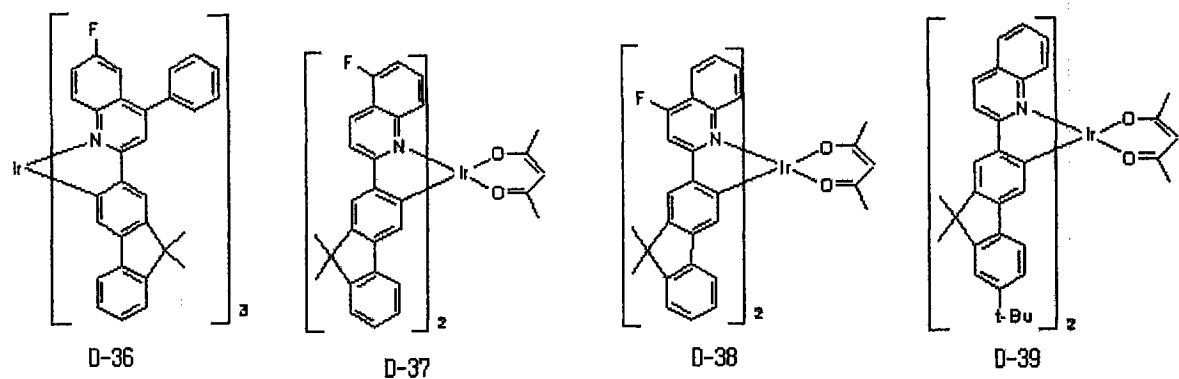
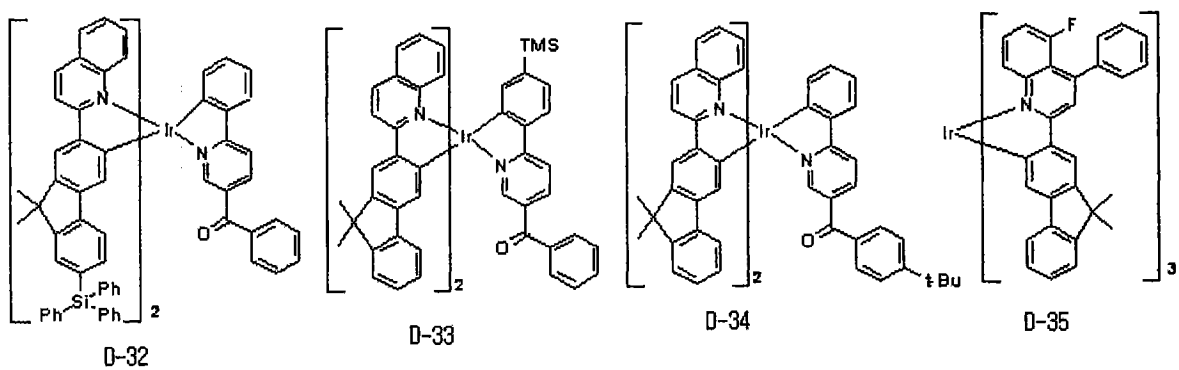
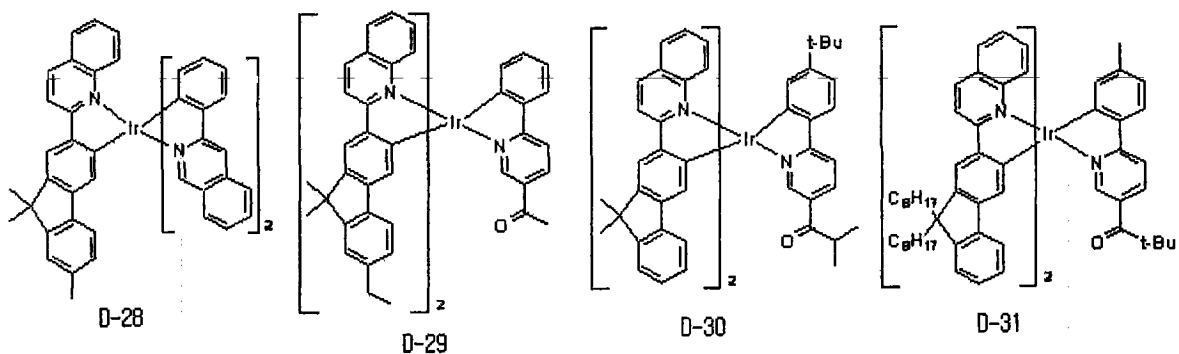
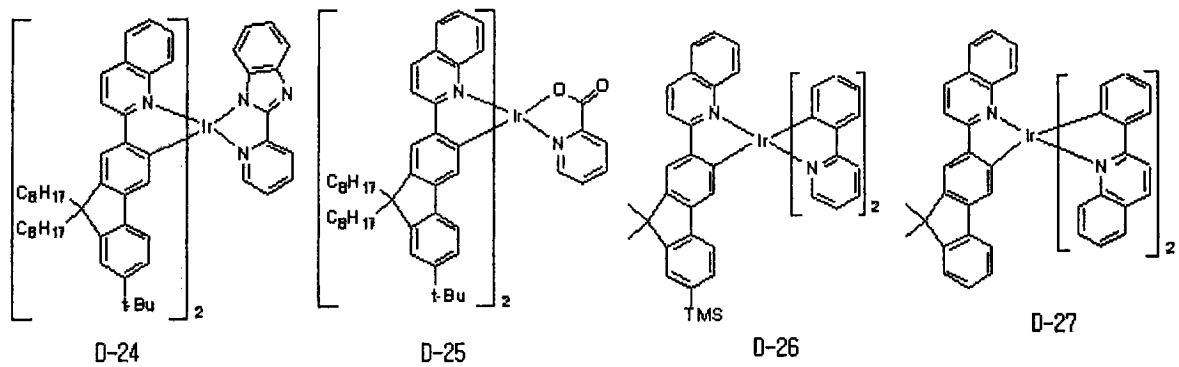
[0133] R_{101} 至 R_{108} , R_{111} 和 R_{112} 独立地代表氢, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, (C1-C30) 烷氧基, 卤素, (C6-C60) 芳基, 氰基或 (C5-C60) 环烷基。

[0134] 由化学式 (2) 代表的掺杂剂化合物的例子包括由以下结构式之一代表的化合物, 但不限于此。

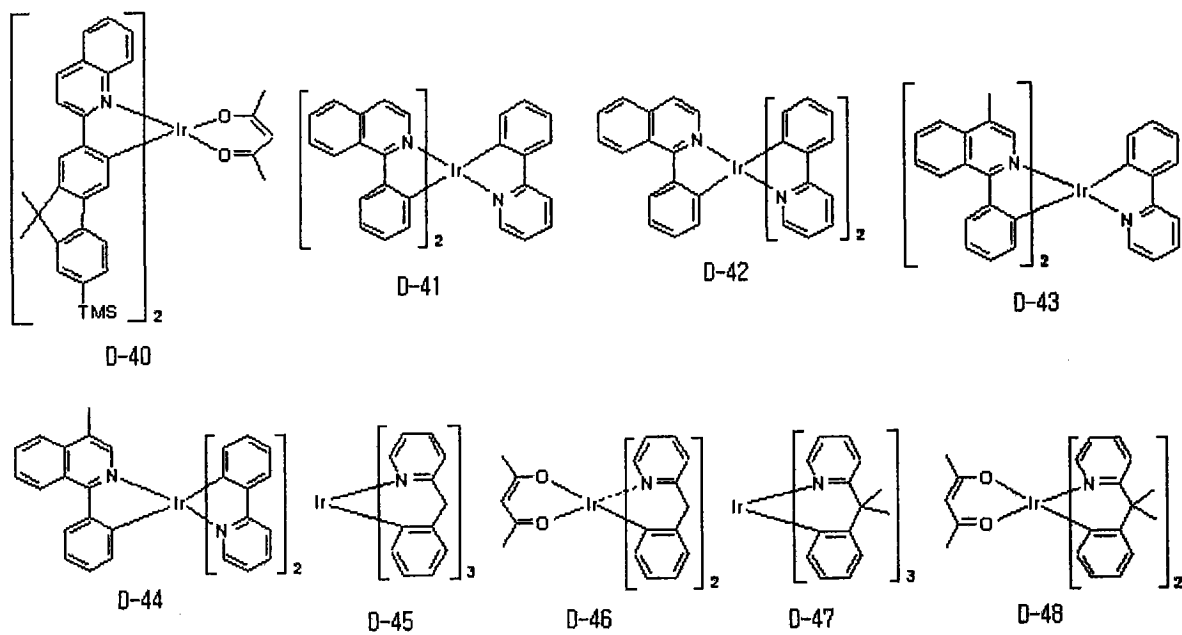
[0135]



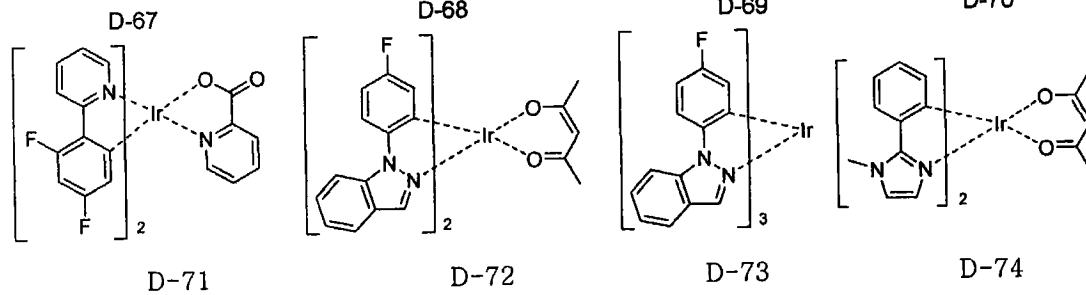
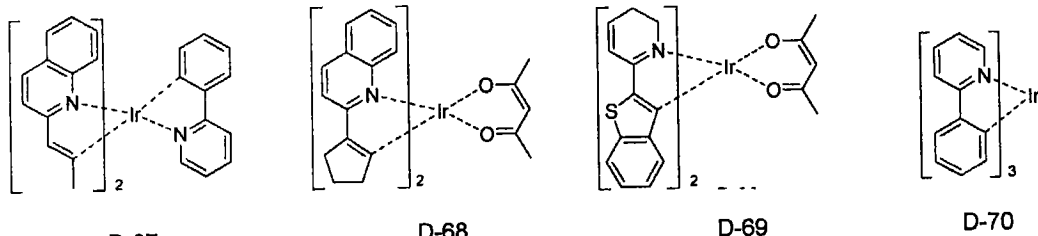
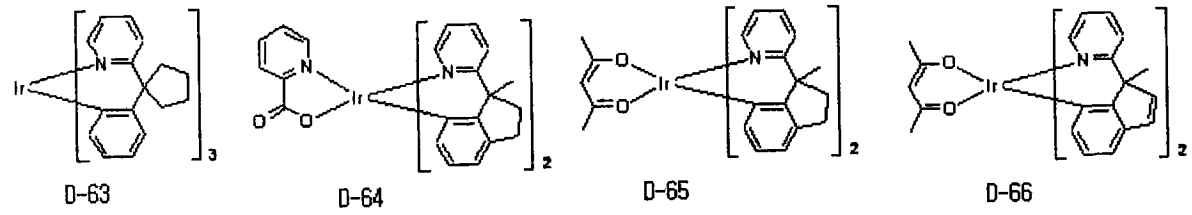
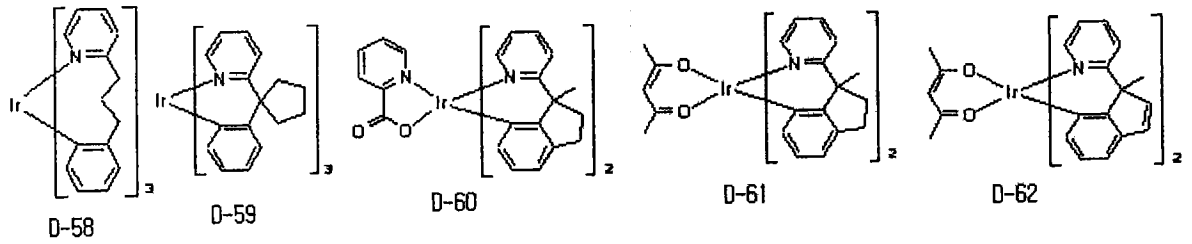
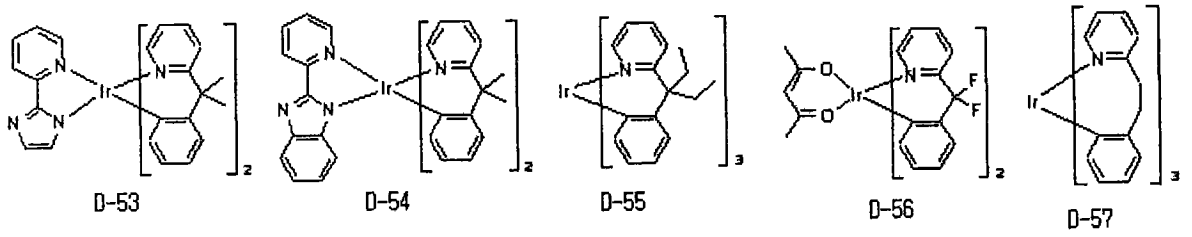
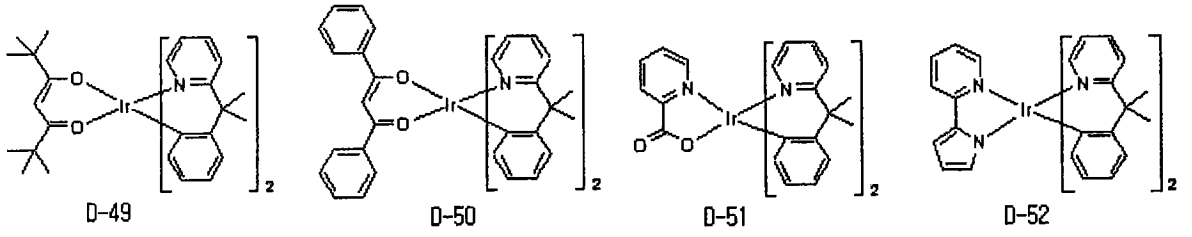
[0136]



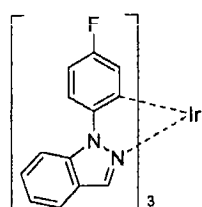
[0138]



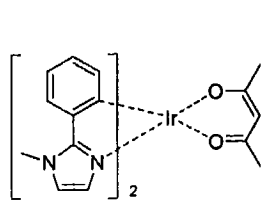
[0139]



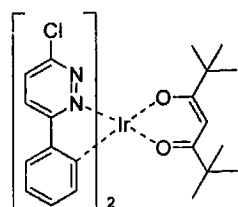
[0140]



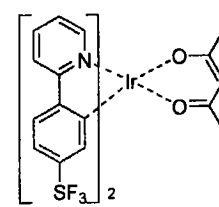
D-75



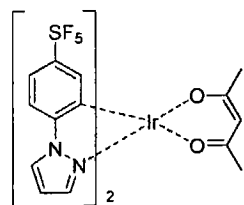
D-76



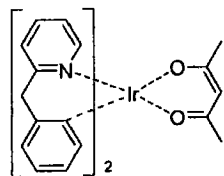
D-77



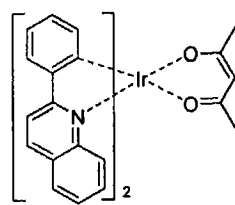
D-78



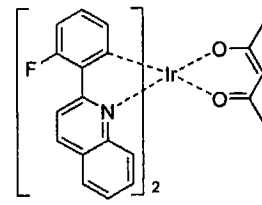
D-79



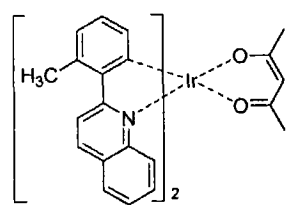
D-80



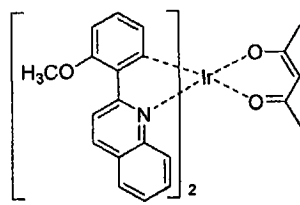
D-81



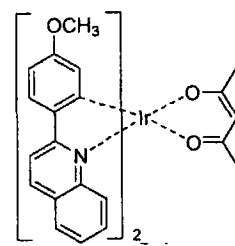
D-82



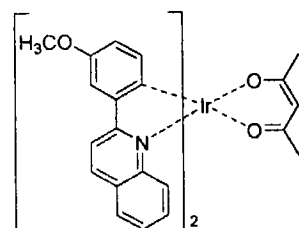
D-83



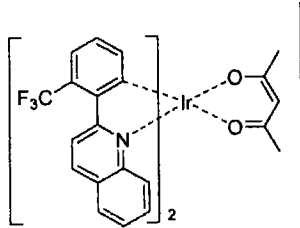
D-84



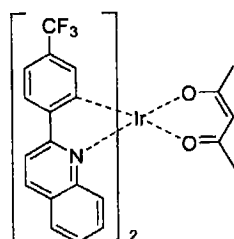
D-85



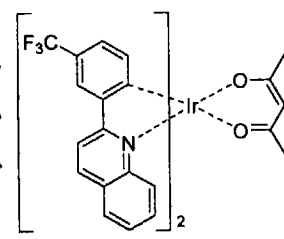
D-86



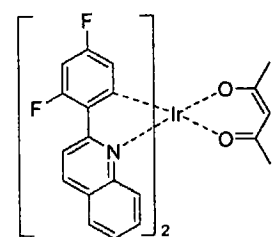
D-87



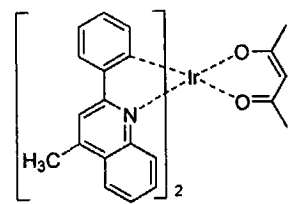
D-88



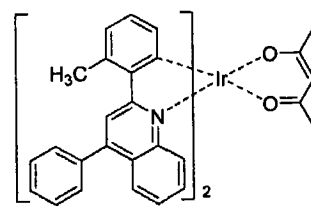
D-89



D-90

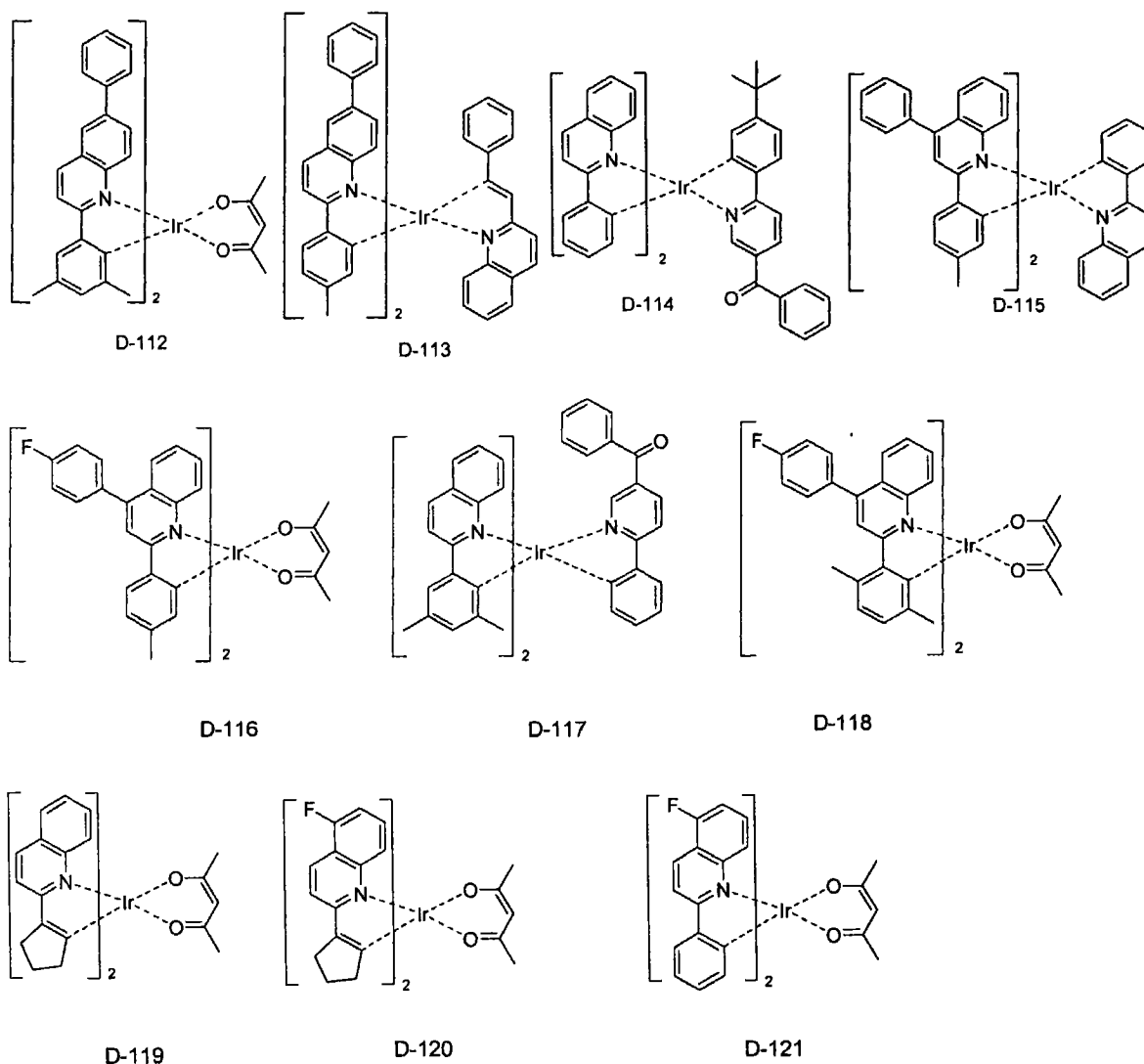


D-91



D-92

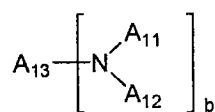
[0141]



[0143] 本发明的有机电致发光器件还可包含一种或多种选自芳基胺化合物和苯乙烯基芳基胺化合物的化合物以及由化学式 (1) 表示的有机电致发光化合物。芳基胺或苯乙烯基芳基胺化合物的例子包括由化学式 (3) 代表的化合物,但不限于此:

[0144] 化学式 3

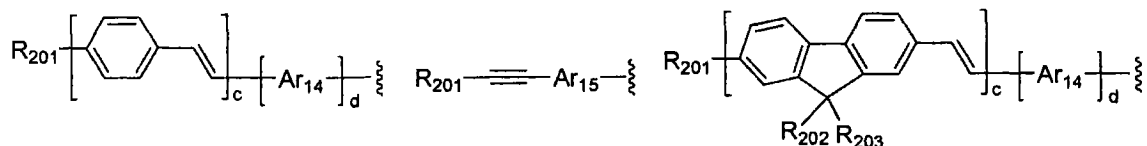
[0145]



[0146] 其中, Ar_{11} 和 Ar_{12} 独立地代表 (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, (C6-C60) 芳基氨基, (C1-C60) 烷基氨基, 含有一个或多个选自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, 或 (C3-C60) 环烷基, 或者 Ar_{11} 和 Ar_{12} 可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基连接而形成脂环或者单环或多环的芳环;

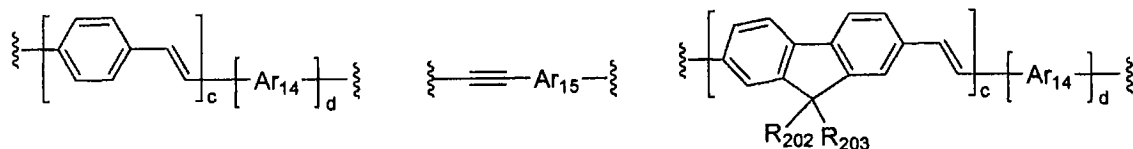
[0147] 当 b 是 1 时, Ar_{13} 代表 (C6-C60) 芳基, (C4-C60) 杂芳基, 或由以下结构式之一代表的取代基:

[0148]



[0149] 当 b 是 2 时, Ar_{13} 代表 (C6-C60) 亚芳基, (C4-C60) 杂亚芳基, 或由以下结构式之一代表的取代基:

[0150]



[0151] 其中, Ar_{14} 和 Ar_{15} 独立地代表 (C6-C60) 亚芳基或 (C4-C60) 杂亚芳基;

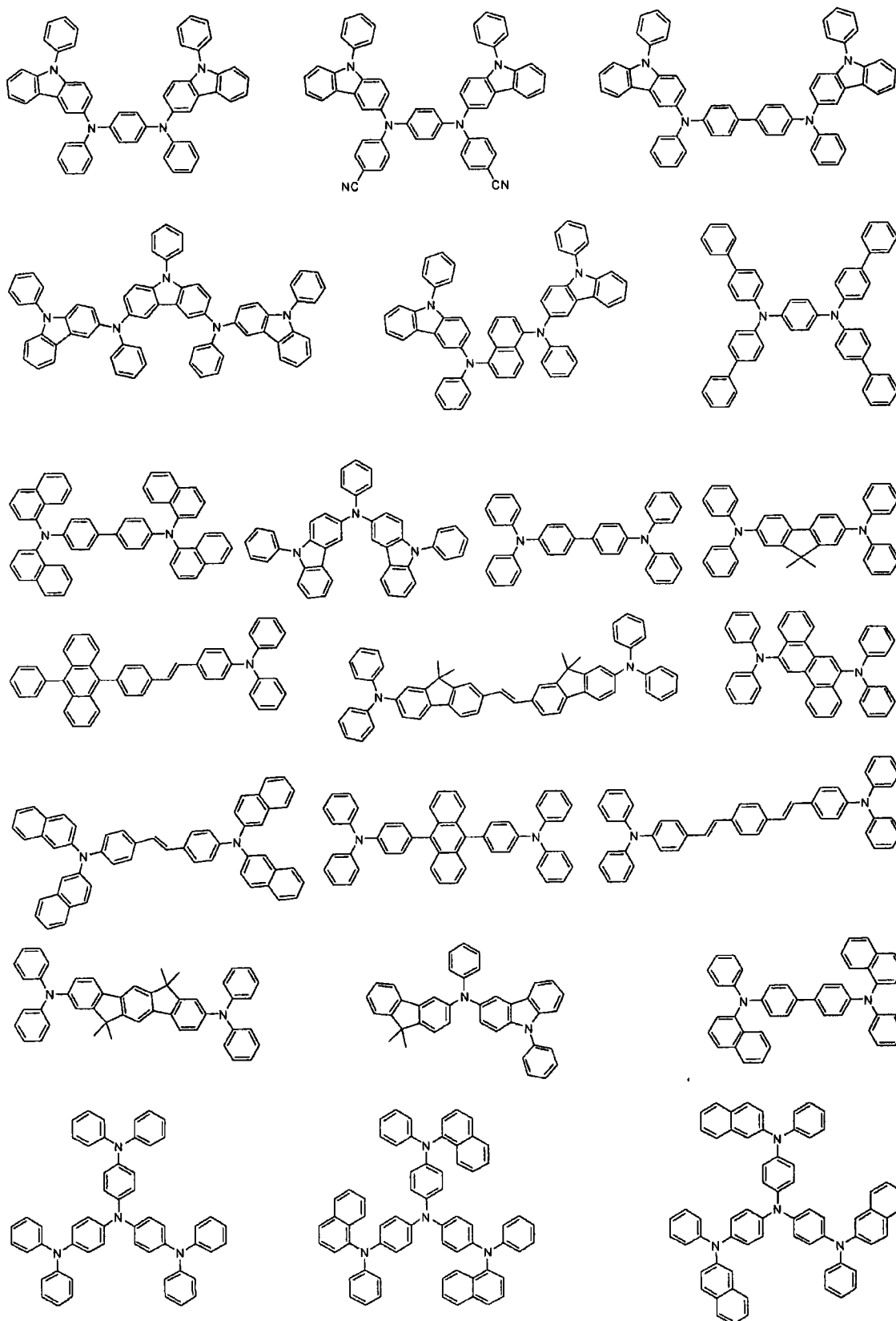
[0152] R_{201} 至 R_{203} 独立地代表氢, 氘, (C1-C60) 烷基或 (C6-C60) 芳基;

[0153] c 是 1-4 的整数, d 是整数 0 或 1; 和

[0154] Ar_{11} 和 Ar_{12} 的烷基, 芳基, 杂芳基, 芳基氨基, 烷基氨基, 环烷基或杂环烷基, 或者 Ar_{13} 的芳基, 杂芳基, 亚芳基或杂亚芳基, 或者 Ar_{14} 和 Ar_{15} 的亚芳基或杂亚芳基, 或者 R_{201} 至 R_{203} 的烷基或芳基可被一个或多个选自下组的取代基进一步取代: 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C6-C60) 芳氧基, (C1-C60) 烷氧基, (C6-C60) 芳硫基, (C1-C60) 烷硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基和羟基。

[0155] 所述芳基胺化合物和苯乙烯基芳基胺化合物的例子更具体包括以下化合物, 但不限于此。

[0156]



[0157] 在本发明的有机电致发光器件中,所述有机层还包含一种或多种选自下组的金属:第四和第五周期过渡金属第1列和第2列的有机金属,镧系金属,和d-过渡元素,以及由化学式(1)代表的有机电致发光化合物。有机层可同时包含电致发光层和电荷发生层。

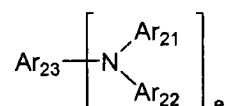
[0158] 本发明可得到具有独立发光模式的像素结构的电致发光器件,其包括有机电致发

光器件,该器件包含同时平行图案化的化学式(1)的化合物作为子像素(sub-pixel),和一个或多个含有一种或多种金属化合物的子像素,所述金属化合物选自:Ir, Pt, Pd, Rh, Re, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au 和 Ag。

[0159] 此外,可形成有机显示器,该显示器的有机层中还包含一种或多种选自电致发光峰波长不超过 560nm 的化合物,以及上述有机电致发光化合物。电致发光峰波长不超过 560nm 的化合物的例子包括由化学式(4)-(9)之一所代表的化合物,但不限于此。

[0160] 化学式 4

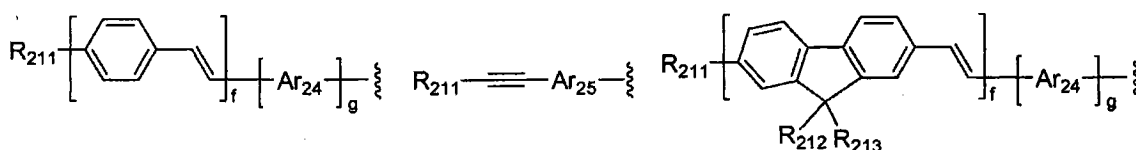
[0161]



[0162] 在化学式(4)中,Ar₂₁和Ar₂₂独立地代表(C1-C60)烷基,(C6-C60)芳基,(C4-C60)杂芳基,(C6-C60)芳基氨基,(C1-C60)烷基氨基,含有一个或多个选自N、O或S的杂原子的5-元或6-元杂环烷基,或(C3-C60)环烷基,或者Ar₂₁和Ar₂₂可通过有稠环或没有稠环的(C3-C60)亚烷基或(C3-C60)亚烯基连接而形成脂环或者单环或多环的芳环;

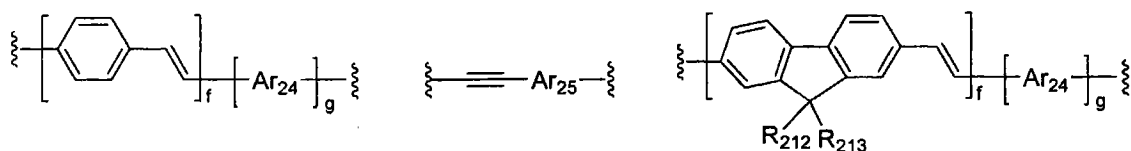
[0163] 当e是1时,Ar₂₃代表(C6-C60)芳基,(C4-C60)杂芳基,或由以下结构式之一代表的取代基:

[0164]



[0165] 当e是2时,Ar₂₃代表(C6-C60)亚芳基,(C4-C60)杂亚芳基,或由以下结构式之一代表的取代基:

[0166]



[0167] 其中,Ar₂₄和Ar₂₅独立地代表(C6-C60)亚芳基或(C4-C60)杂亚芳基;

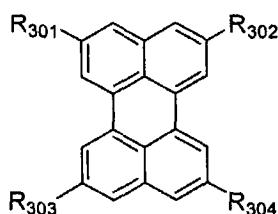
[0168] R₂₁₁至R₂₁₃独立地代表氢,氘,(C1-C60)烷基或(C6-C60)芳基;

[0169] f是1-4的整数,g是整数0或1;和

[0170] Ar₂₁和Ar₂₂的烷基,芳基,杂芳基,芳基氨基,烷基氨基,环烷基或杂环烷基,或者Ar₂₃的芳基,杂芳基,亚芳基或杂亚芳基,或者Ar₂₄和Ar₂₅的亚芳基或杂亚芳基,或者R₂₁₁至R₂₁₃的烷基或芳基可被一个或多个选自下组的取代基进一步取代:氘,卤素,(C1-C60)烷基,(C6-C60)芳基,(C4-C60)杂芳基,含有一个或多个选自N、O或S的杂原子的5-元或6-元杂环烷基,(C3-C60)环烷基,三(C1-C60)烷基甲硅烷基,二(C1-C60)烷基(C6-C60)芳基甲硅烷基,三(C6-C60)芳基甲硅烷基,金刚烷基,(C7-C60)二环烷基,(C2-C60)烯基,(C2-C60)炔基,氰基,(C1-C60)烷基氨基,(C6-C60)芳基氨基,(C6-C60)芳基(C1-C60)烷基,(C6-C60)芳氧基,(C1-C60)烷氧基,(C6-C60)芳硫基,(C1-C60)烷硫基,(C1-C60)烷氧基羰基,(C1-C60)烷基羰基,(C6-C60)芳基羰基,羧基,硝基和羟基。

[0171] 化学式 5

[0172]

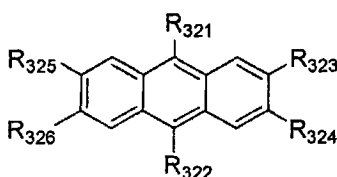


[0173] 在化学式 (5) 中, R_{301} 至 R_{304} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, (C1-C60) 烷氧基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, 羧基, 硝基或羟基, 或者 R_{301} 至 R_{304} 中的每一个可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环;

[0174] R_{301} 至 R_{304} 的烷基, 烯基, 炔基, 环烷基, 杂环烷基, 芳基, 杂芳基, 芳基甲硅烷基, 烷基甲硅烷基, 烷基氨基或芳基氨基, 或者通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成的脂环或单环或多环的芳环可被一个或多个选自下组的取代基进一步取代: 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, (C1-C60) 烷氧基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, 羧基, 硝基和羟基。

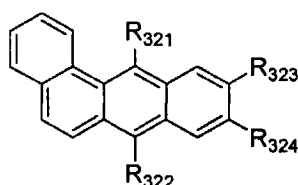
[0175] 化学式 6

[0176]



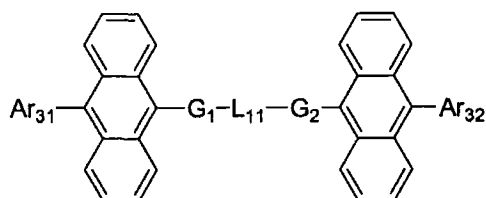
[0177] 化学式 7

[0178]



[0179] 化学式 8

[0180]



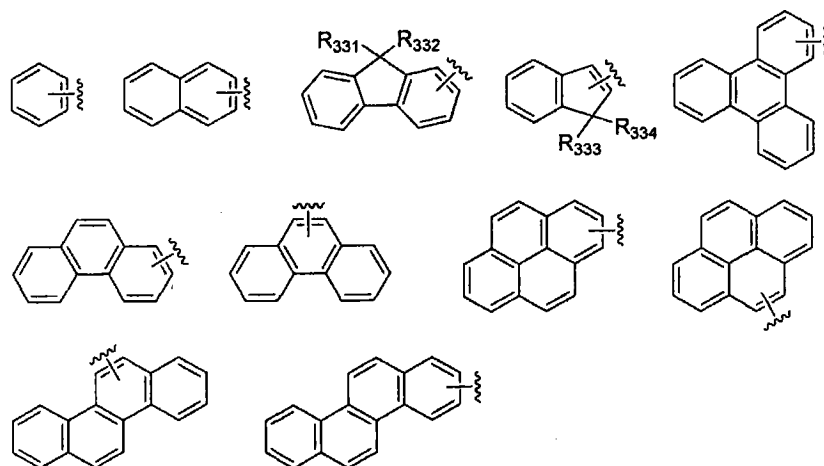
[0181] 在化学式 (6) 至 (8) 中, R_{321} 和 R_{322} 独立地代表 (C6-C60) 芳基, (C4-C60) 杂芳基或含有一个或多个选自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, 或 (C3-C60) 环烷基, 且 R_{321} 和 R_{322} 的芳基或杂芳基可被一个或多个选自下组的取代基进一步取代: 氘, (C1-C60) 烷基, 卤代 (C1-C60) 烷基, (C1-C60) 烷氧基, (C3-C60) 环烷基, (C6-C60) 芳基, (C4-C60) 杂芳基, 卤素, 氰基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基和三 (C6-C60) 芳基甲硅烷基;

[0182] R_{323} 至 R_{326} 独立地代表氢, 氘, (C1-C60) 烷基, (C1-C60) 烷氧基, 卤素, (C4-C60) 杂芳基, (C5-C60) 环烷基或 (C6-C60) 芳基, 且 R_{323} 至 R_{326} 的杂芳基, 环烷基或芳基可被选自下组的一个或多个取代基进一步取代: 氘, 有卤素取代基或没有卤素取代基的 (C1-C60) 烷基, (C1-C60) 烷氧基, (C3-C60) 环烷基, 卤素, 氰基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基和三 (C6-C60) 芳基甲硅烷基;

[0183] G_1 和 G_2 独立地代表化学键或 (C6-C60) 亚芳基, 该 (C6-C60) 亚芳基没有取代基或有一个或多个选自下组的取代基: (C1-C60) 烷基, (C1-C60) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基和卤素;

[0184] Ar_{31} 和 Ar_{32} 代表 (C4-C60) 杂芳基或选自以下结构的芳基:

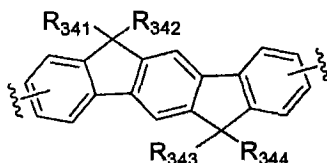
[0185]



[0186] Ar_{31} 和 Ar_{32} 的芳基或杂芳基可被一个或多个选自下组的取代基进一步取代: 氘, (C1-C60) 烷基, (C1-C60) 烷氧基, (C6-C60) 芳基和 (C4-C60) 杂芳基;

[0187] L_{11} 代表 (C6-C60) 亚芳基, (C4-C60) 杂亚芳基或由以下结构代表的化合物:

[0188]



[0189] L_{11} 的亚芳基或杂亚芳基可被一个或多个选自下组的取代基进一步取代: 氘,

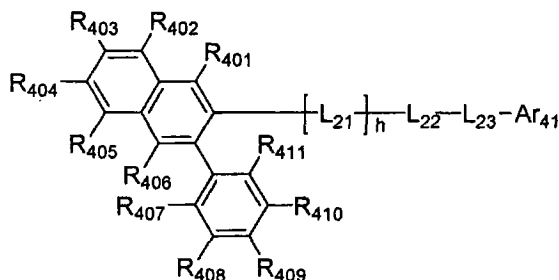
(C1-C60) 烷基, (C1-C60) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基和卤素;

[0190] R_{331} 至 R_{334} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基或 (C6-C60) 芳基, 或者它们各自可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环;

[0191] R_{341} 至 R_{344} 独立地代表氢, 氘, (C1-C60) 烷基, (C1-C60) 烷氧基, (C6-C60) 芳基, (C4-C60) 杂芳基或卤素, 或者它们各自可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环。

[0192] 化学式 9

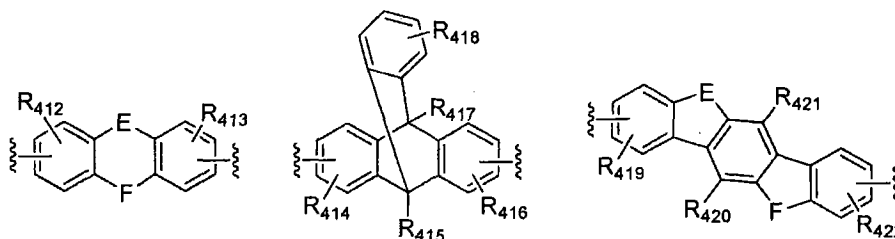
[0193]



[0194] 在化学式 9 中,

[0195] L_{21} 代表 (C6-C60) 亚芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂亚芳基, 或选自以下结构的二价基团:

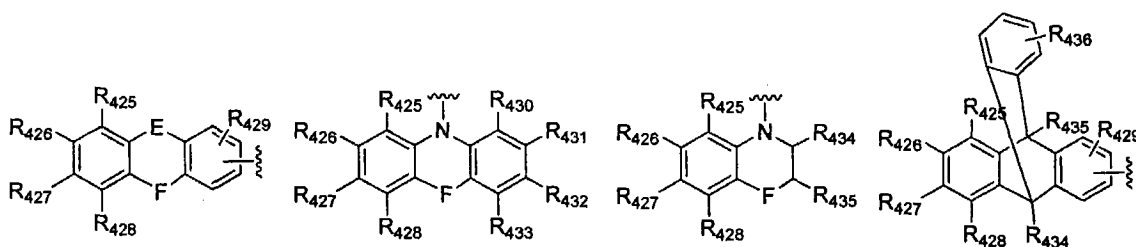
[0196]



[0197] L_{22} 和 L_{23} 独立地代表化学键, (C1-C60) 亚烷氧基, (C1-C60) 亚烷硫基, (C6-C60) 亚芳氧基, (C6-C60) 亚芳硫基, (C6-C60) 亚芳基, 或含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂亚芳基;

[0198] Ar_{41} 代表 $NR_{423}R_{424}$, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 金刚烷基, (C7-C60) 二环烷基, 或选自以下结构的取代基:

[0199]



[0200] 其中, R_{401} 至 R_{411} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代 (thiomorpholino), 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 三

(C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基或羟基, 或者 R_{401} 至 R_{411} 中的每一个可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环;

[0201] R_{412} 至 R_{422} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代, 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基或羟基, 或者 R_{412} 至 R_{422} 中的每一个可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环;

[0202] R_{423} 和 R_{424} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代, 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基或羟基, 或者 R_{423} 和 R_{424} 可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基连接而形成脂环或者单环或多环的芳环;

[0203] R_{425} 至 R_{436} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代, 含有一个或多个选自 N、O 或 S 的杂原子的 5-元或 6-元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基或羟基, 或者 R_{425} 至 R_{436} 中的每一个可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基与相邻取代基相连而形成脂环或者单环或多环的芳环;

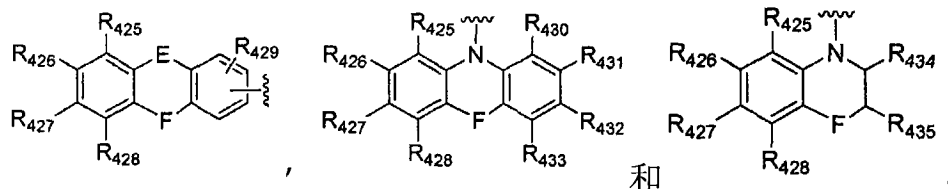
[0204] E 和 F 独立地代表化学键, $-(CR_{437}R_{438})_i-$, $-N(R_{439})-$, $-S-$, $-O-$, $-Si(R_{440})(R_{441})-$, $-P(R_{442})-$, $-C(=O)-$, $-B(R_{443})-$, $-In(R_{444})-$, $-Se-$, $-Ge(R_{445})(R_{446})-$, $-Sn(R_{447})(R_{448})-$, $-Ga(R_{449})-$ 或 $-(R_{450})C=C(R_{451})-$;

[0205] R_{437} 至 R_{451} 独立地代表氢, 氘, 卤素, (C1-C60) 烷基, (C6-C60) 芳基, 含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代, 含有一个或多个选

自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基或羟基, 或者 R_{437} 和 R_{438} , R_{440} 和 R_{441} , R_{445} 和 R_{446} , R_{447} 和 R_{448} , 以及 R_{450} 和 R_{451} 可通过有稠环或没有稠环的 (C3-C60) 亚烷基或 (C3-C60) 亚烯基连接而形成脂环或者单环或多环的芳环;

[0206] L_{21} 至 L_{23} 的亚芳基或杂亚芳基, Ar_{41} 的芳基或杂芳基, 或者 R_{401} 至 R_{411} 、 R_{412} 至 R_{422} 、 R_{423} 、 R_{424} 、 R_{425} 至 R_{436} 以及 R_{437} 至 R_{451} 的烷基, 芳基, 杂芳基, 杂环烷基, 环烷基, 三烷基甲硅烷基, 二烷基芳基甲硅烷基, 三芳基甲硅烷基, 烯基, 炔基, 烷基氨基或芳基氨基可独立地被一个或多个选自下组的取代基进一步取代: 氘, 卤素, (C1-C60) 烷基, 卤代 (C1-C60) 烷基, (C6-C60) 芳基, 有 (C6-C60) 芳基取代基或没有 (C6-C60) 芳基取代基的含有一个或多个选自 N、O 或 S 的杂原子的 (C3-C60) 杂芳基, 吗啉代, 硫代吗啉代, 含有一个或多个选自 N、O 或 S 的杂原子的 5- 元或 6- 元杂环烷基, (C3-C60) 环烷基, 三 (C1-C60) 烷基甲硅烷基, 二 (C1-C60) 烷基 (C6-C60) 芳基甲硅烷基, 三 (C6-C60) 芳基甲硅烷基, 金刚烷基, (C7-C60) 二环烷基, (C2-C60) 烯基, (C2-C60) 炔基, 氰基, (C1-C60) 烷基氨基, (C6-C60) 芳基氨基, (C6-C60) 芳基 (C1-C60) 烷基, (C1-C60) 烷氧基, (C1-C60) 烷硫基, (C6-C60) 芳氧基, (C6-C60) 芳硫基, (C1-C60) 烷氧基羰基, (C1-C60) 烷基羰基, (C6-C60) 芳基羰基, 羧基, 硝基, 羟基,

[0207]

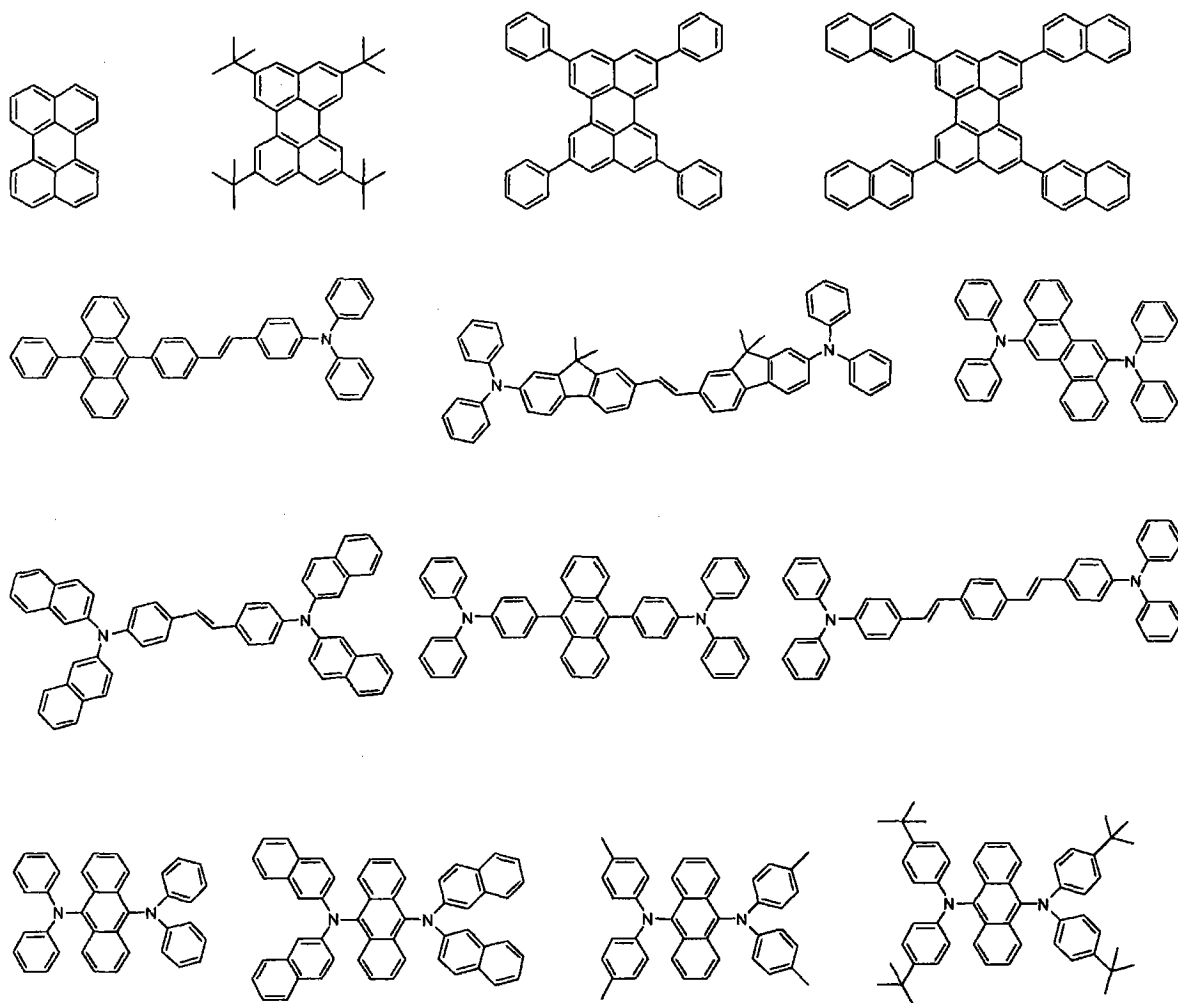


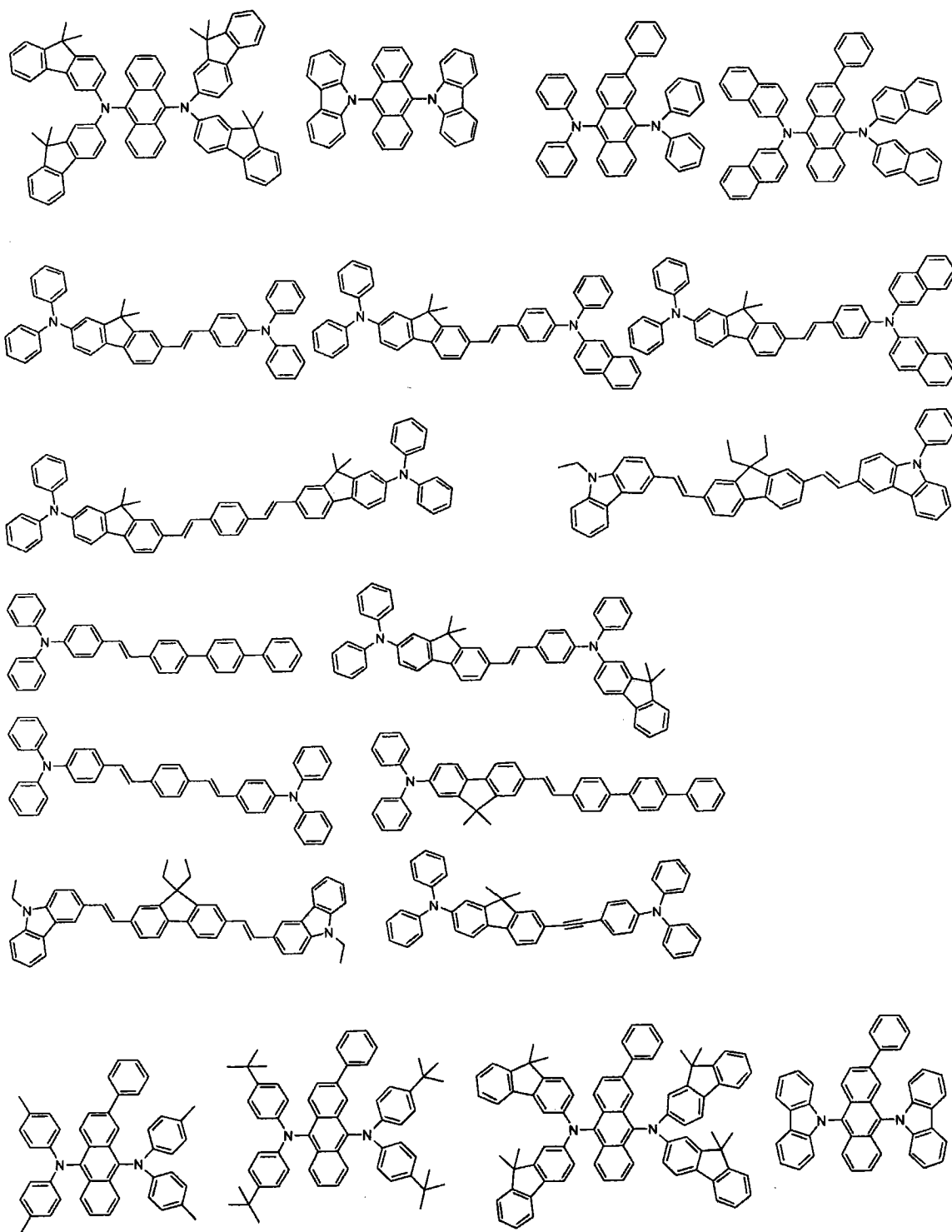
[0208] h 是 1-4 的整数 ; 和

[0209] i 是 1-4 的整数。

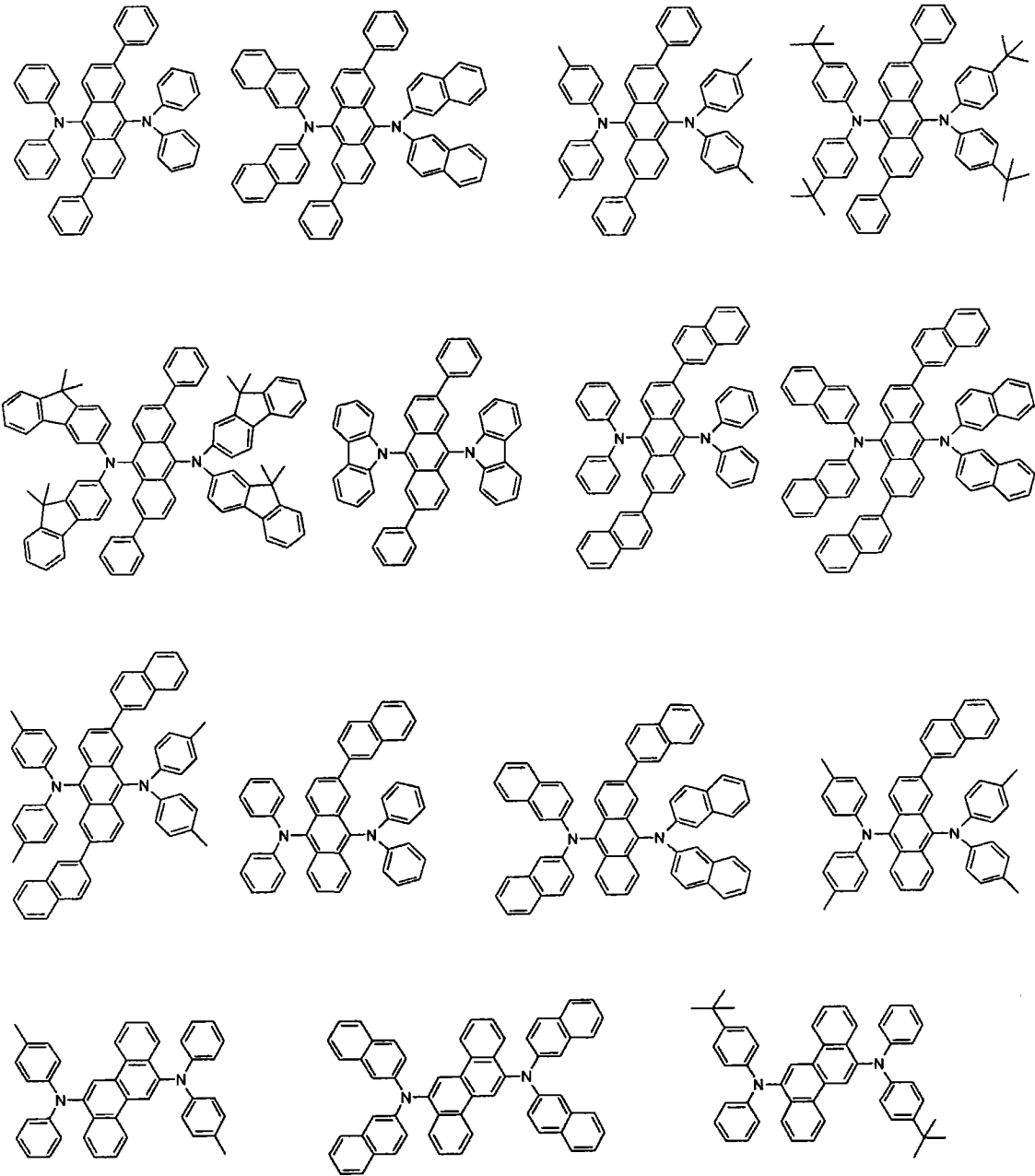
[0210] 电致发光峰波长不超过 560nm 的化合物的例子包括以下化合物, 但不限于此。

[0211]

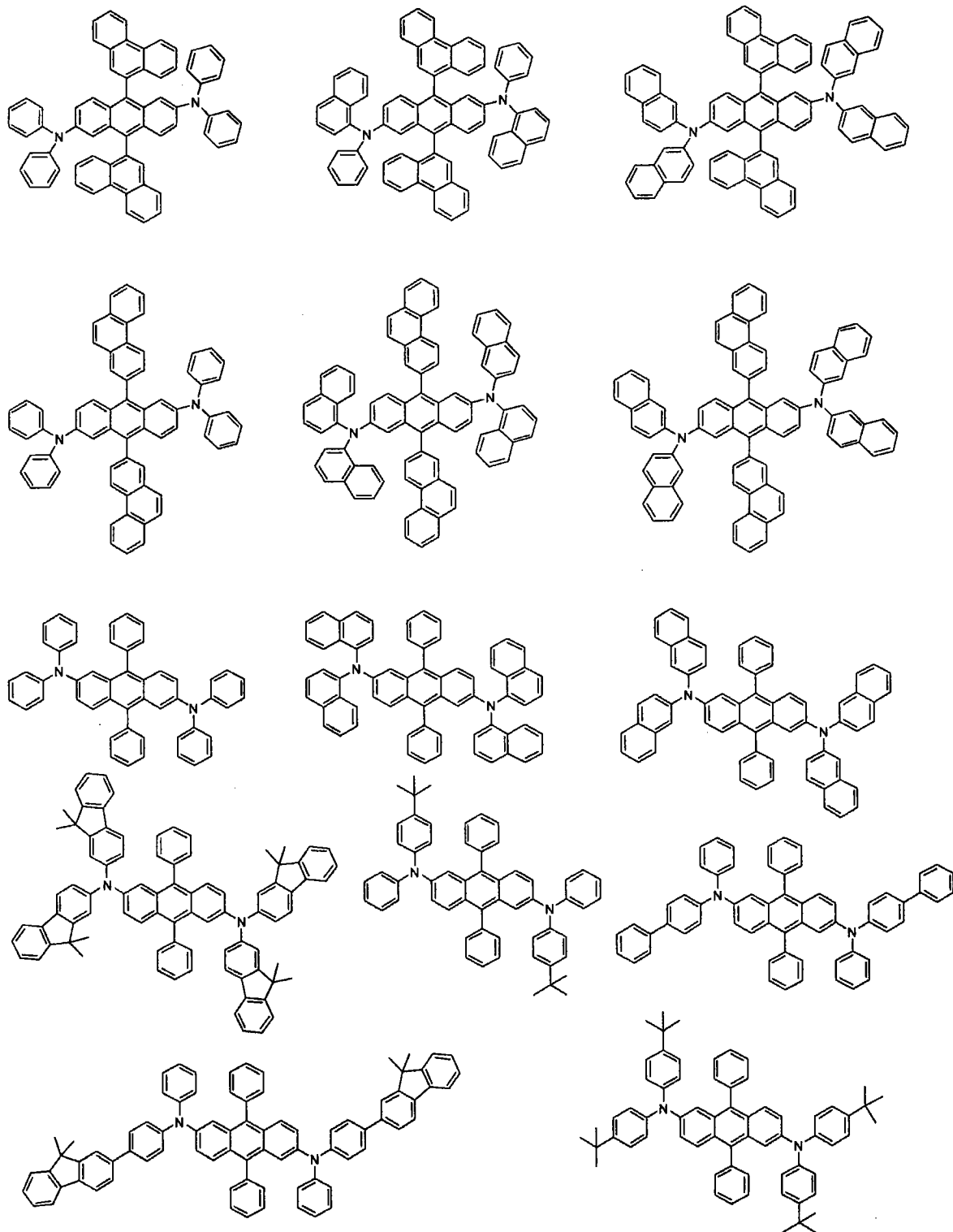




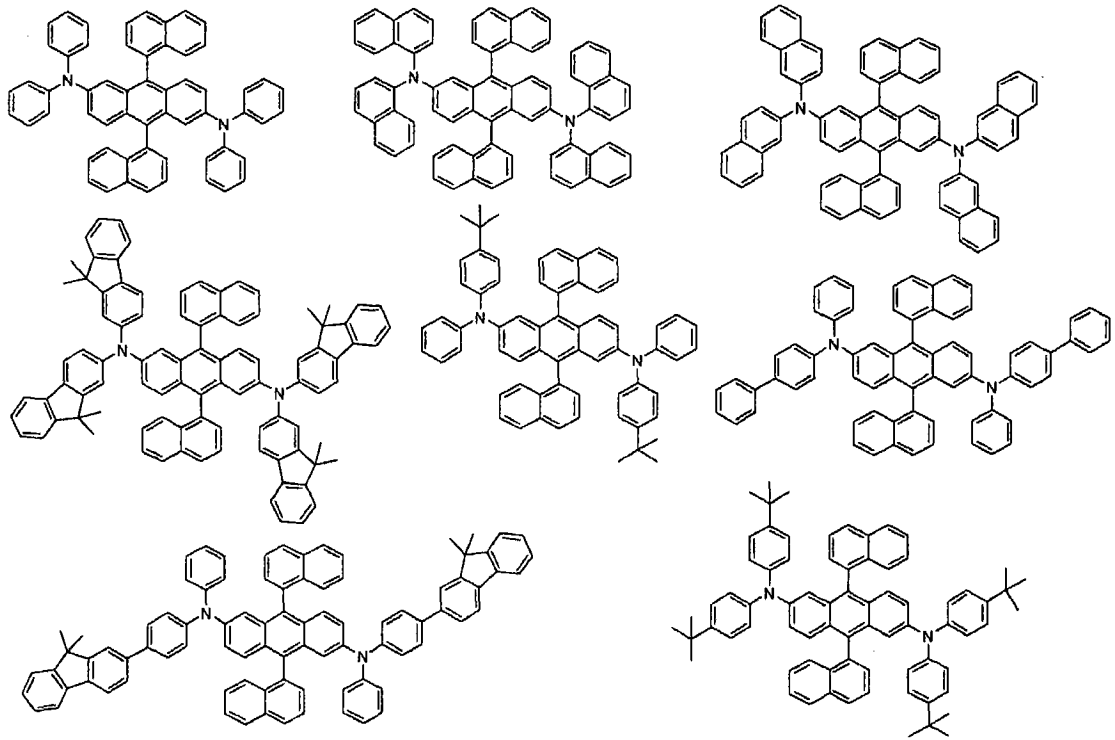
[0213]



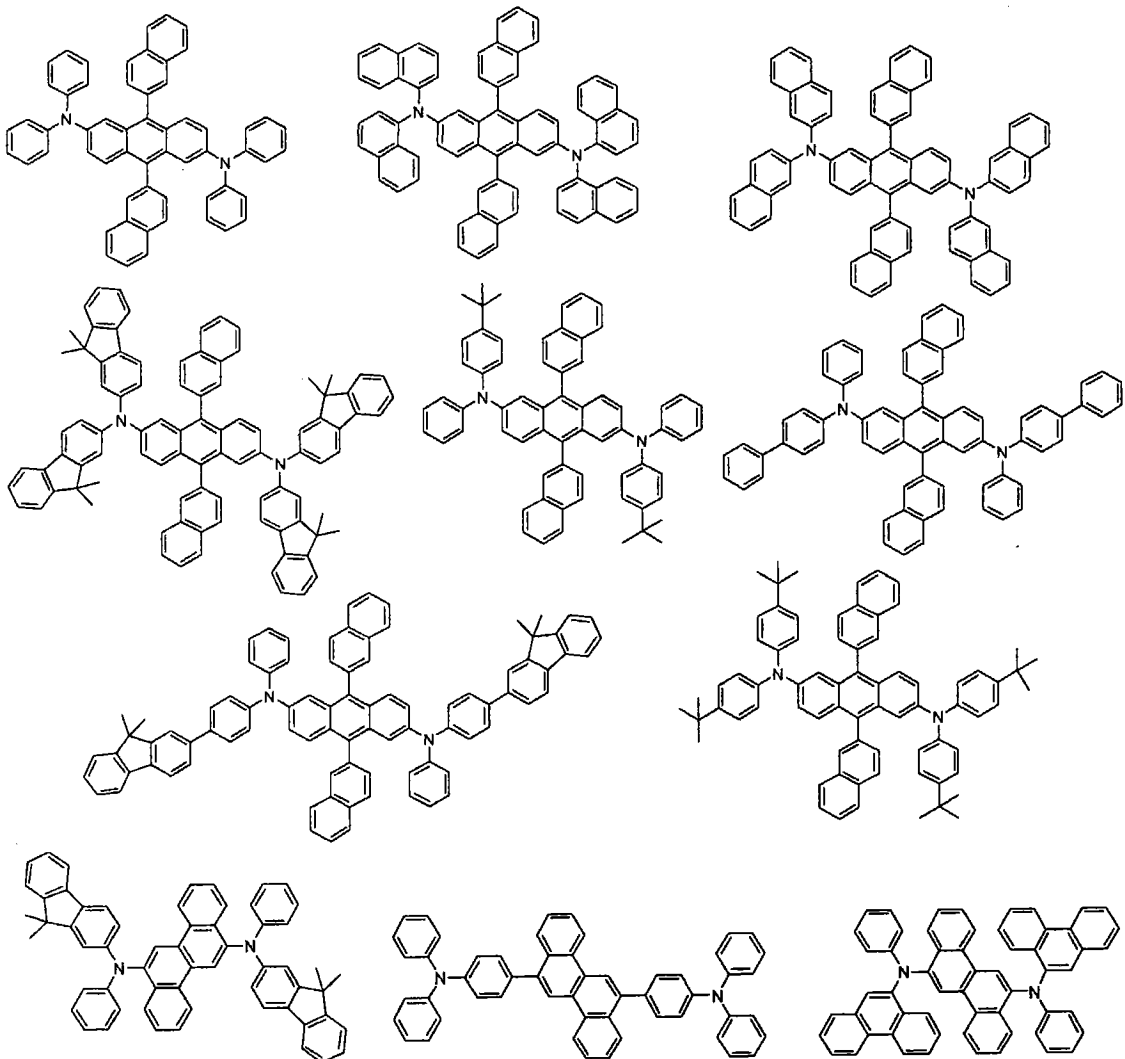
[0214]



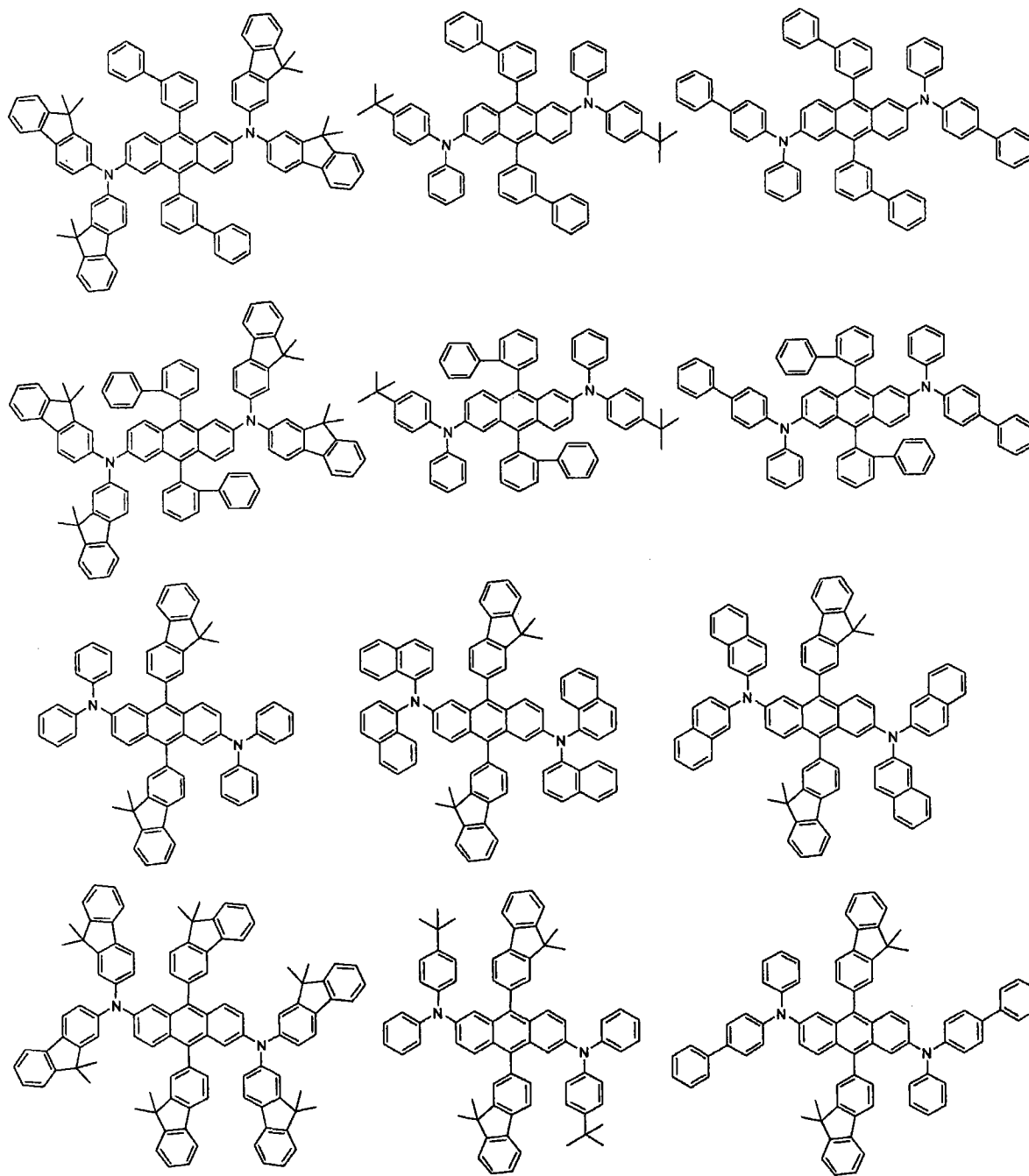
[0215]



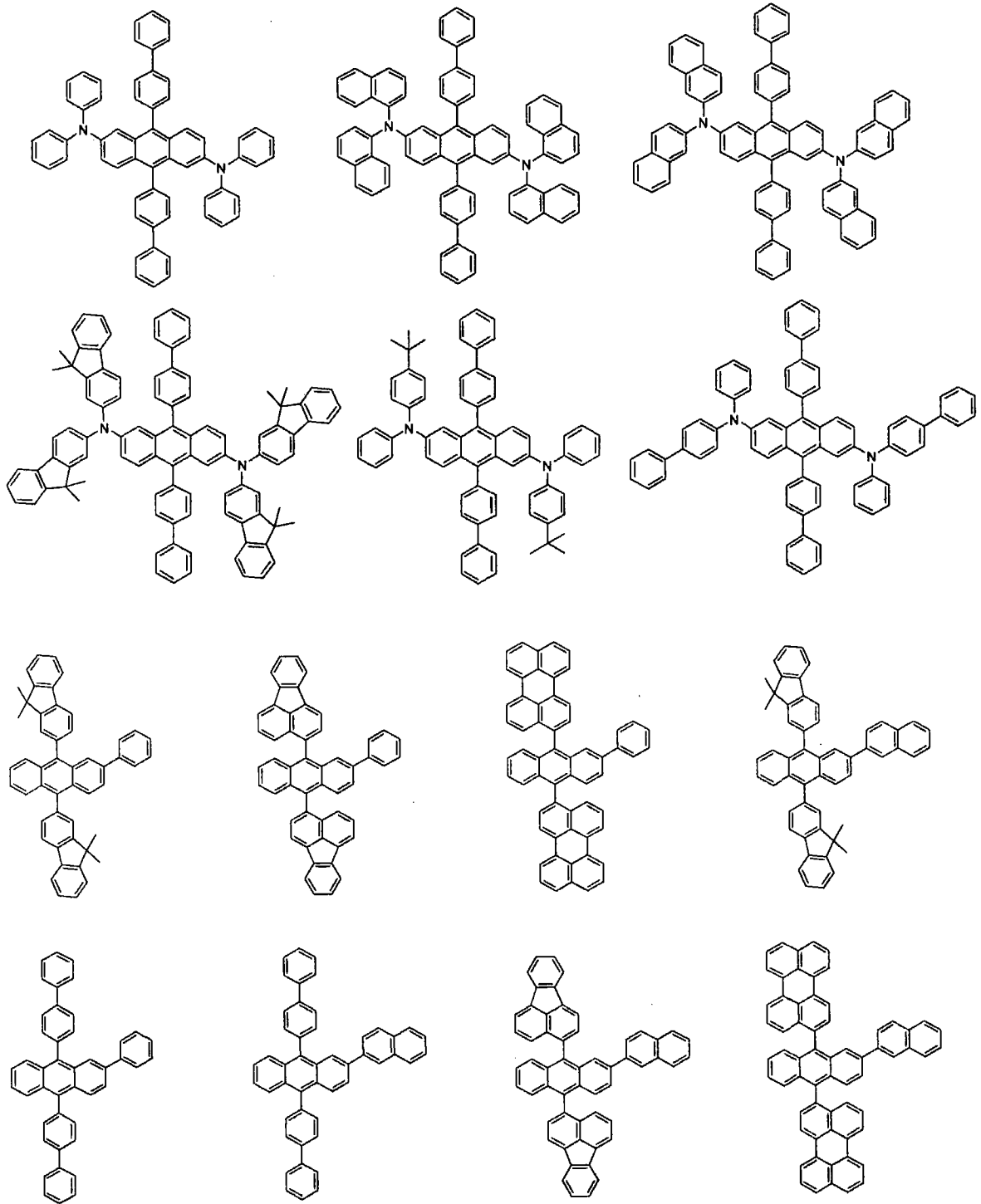
[0216]



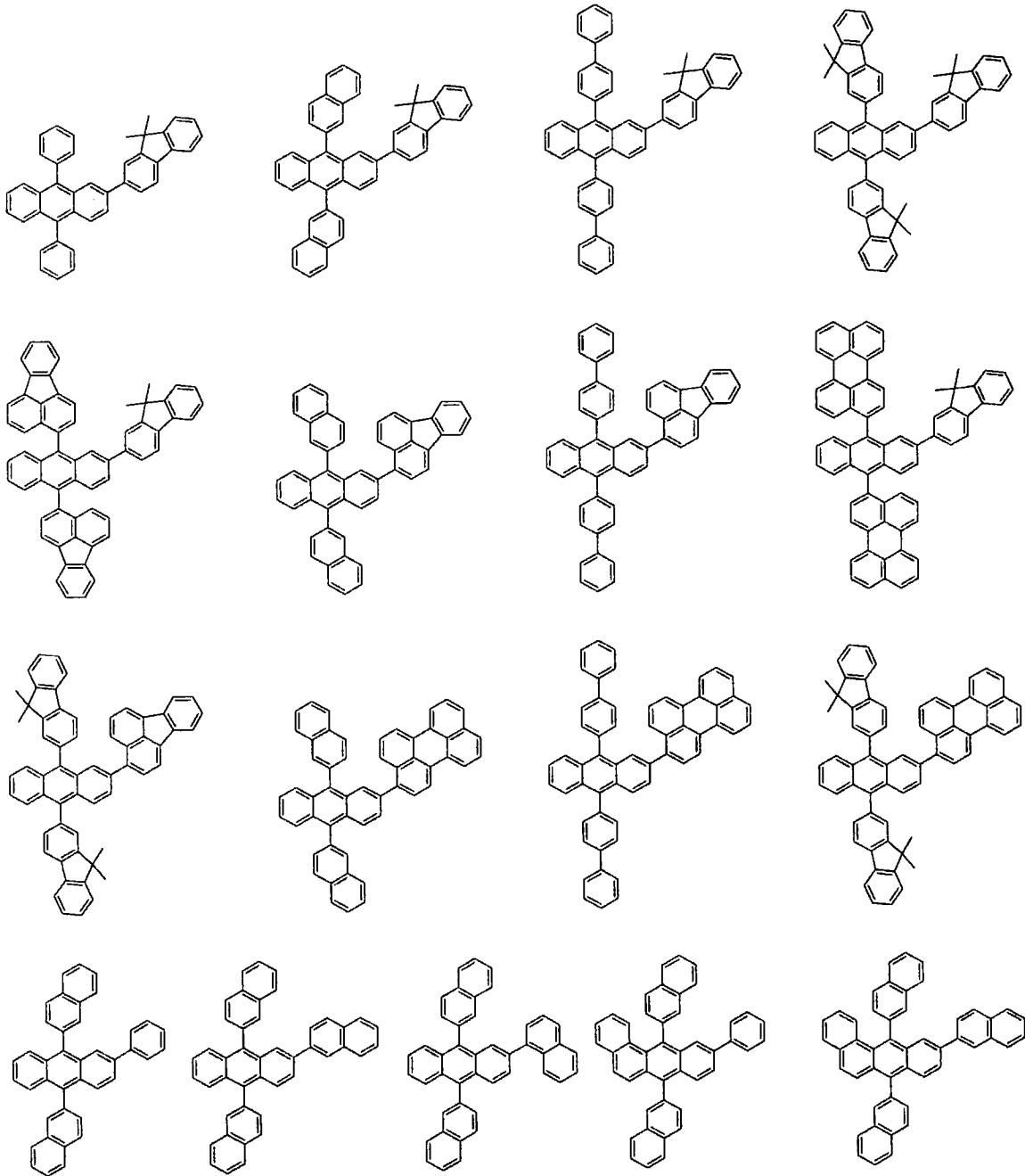
[0217]



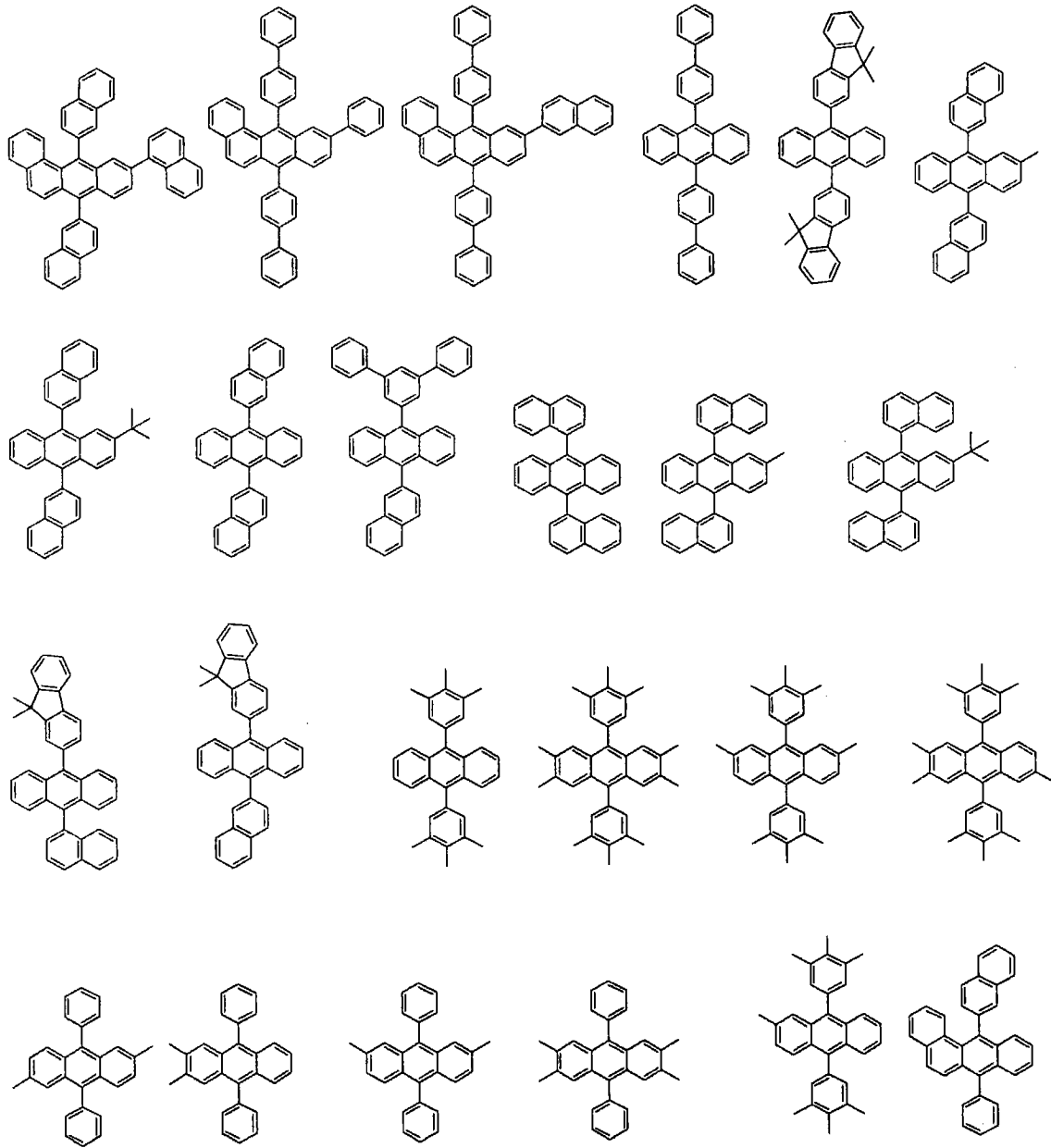
[0218]



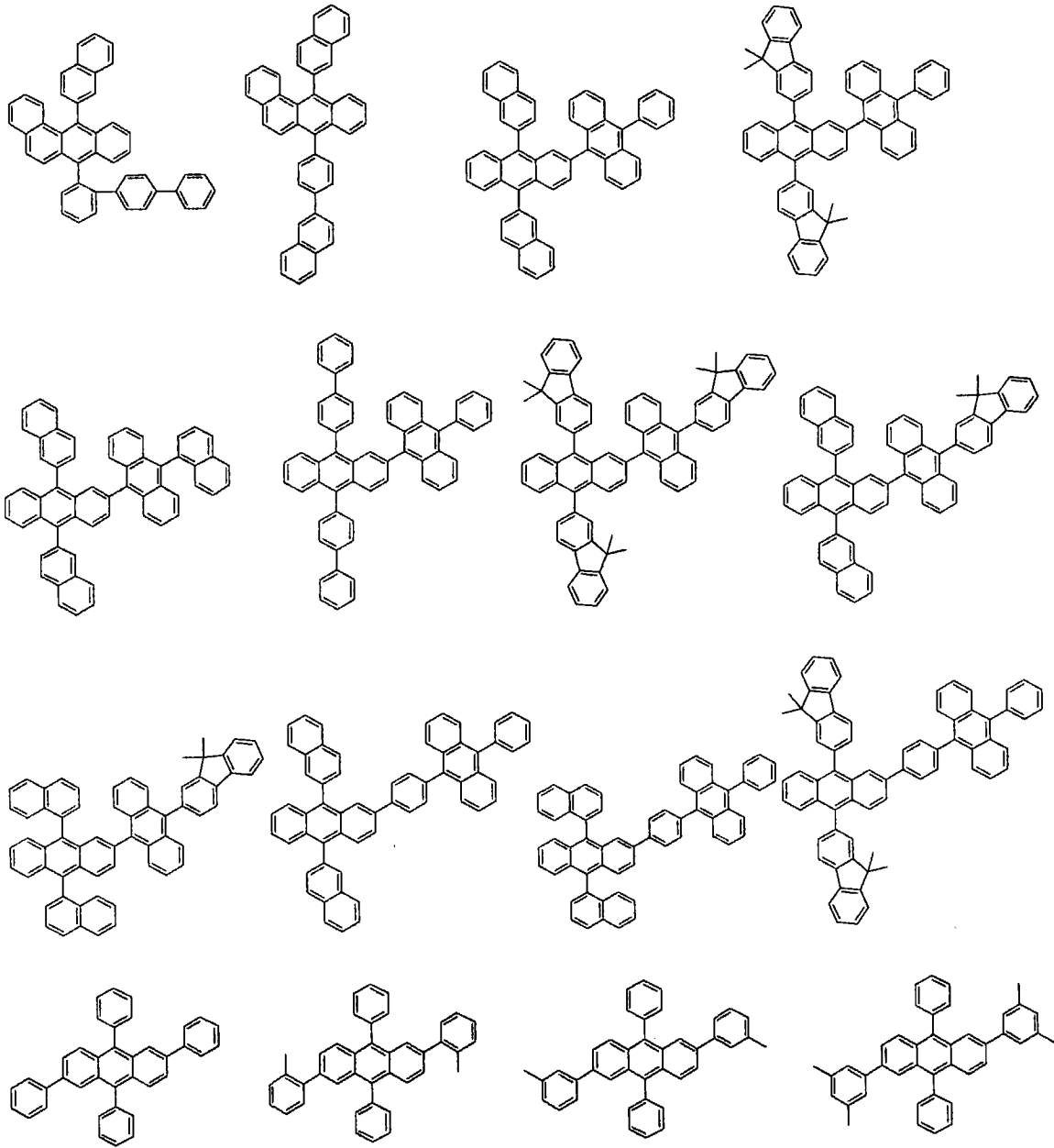
[0219]



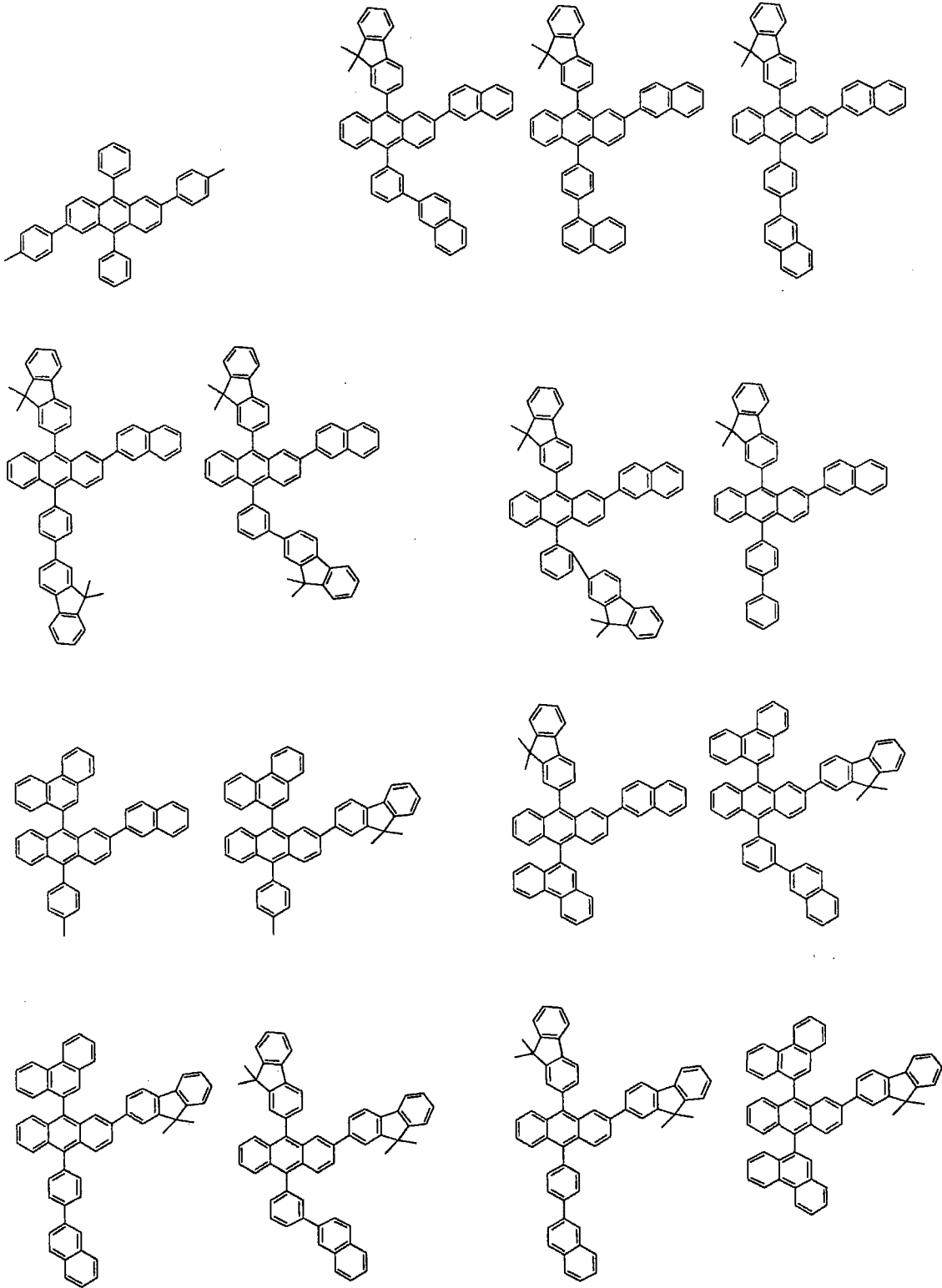
[0220]



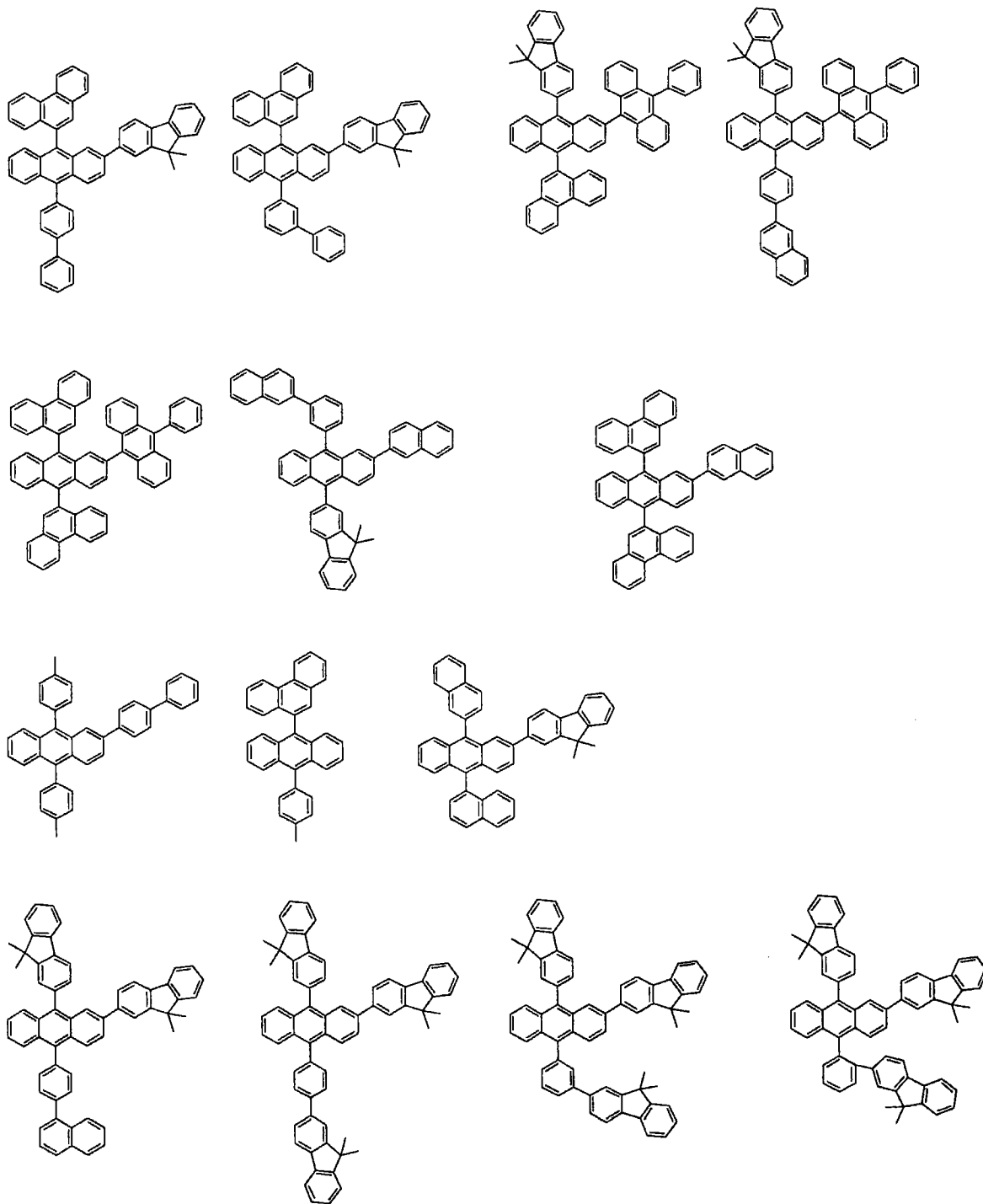
[0221]



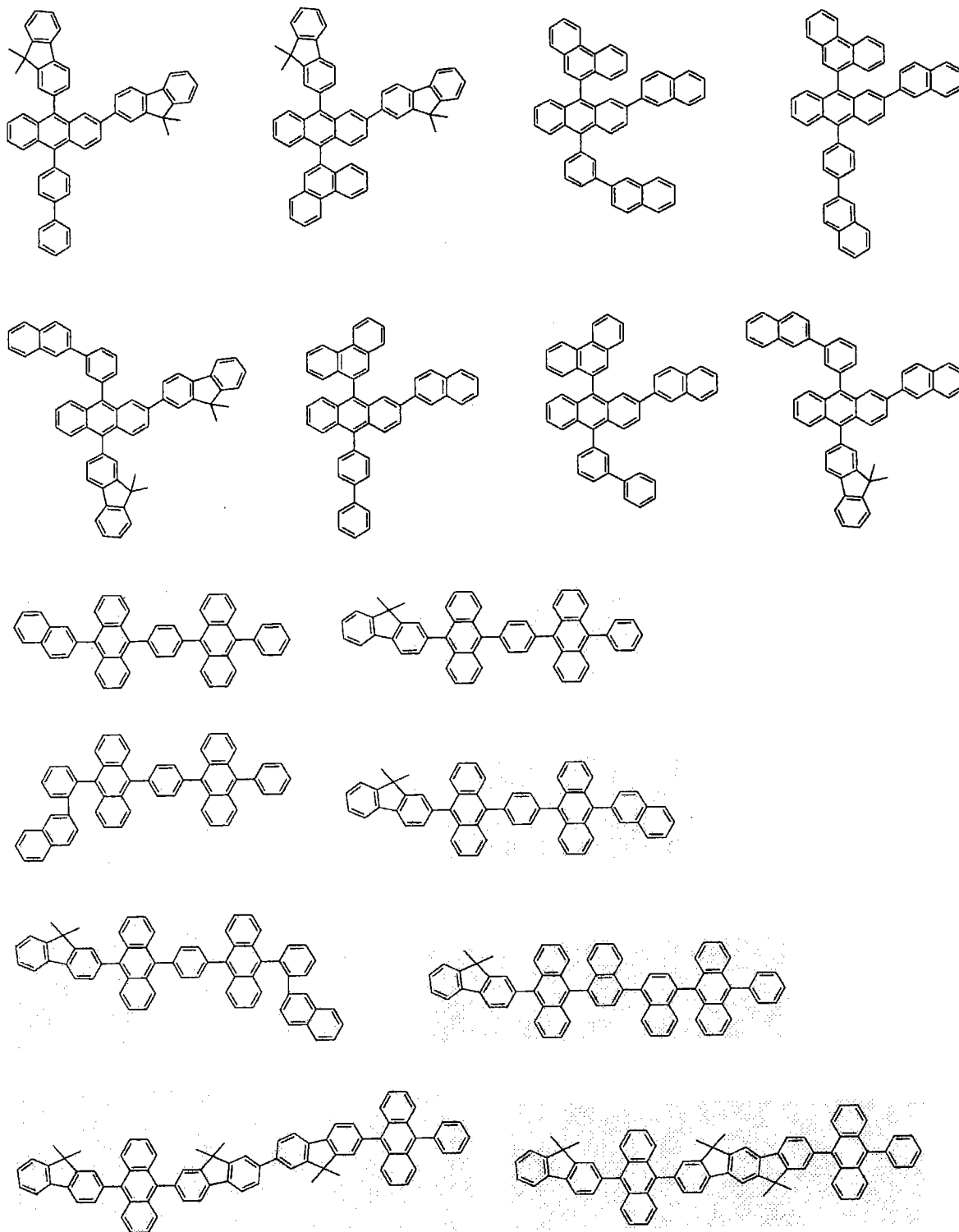
[0222]



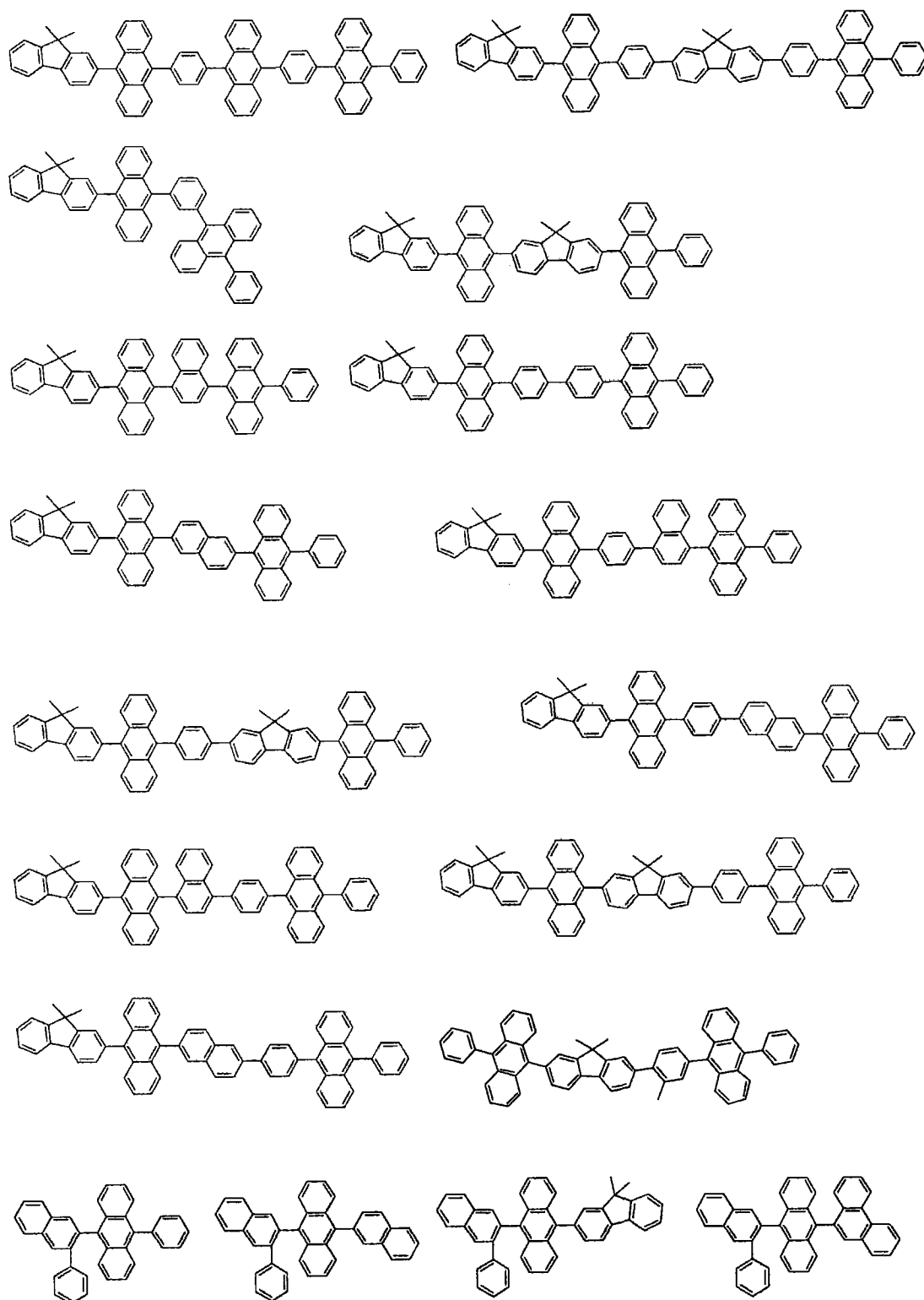
[0223]



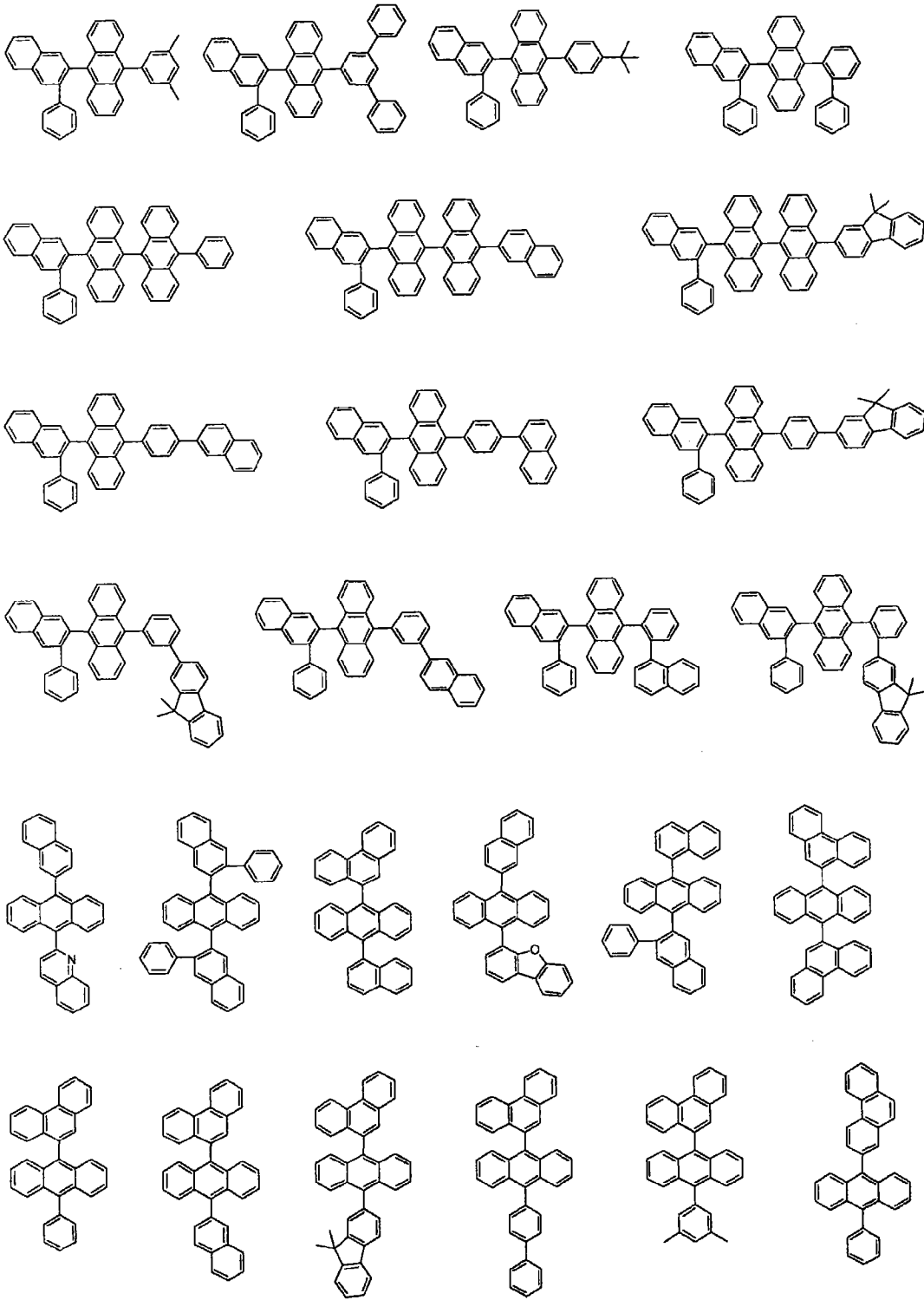
[0224]



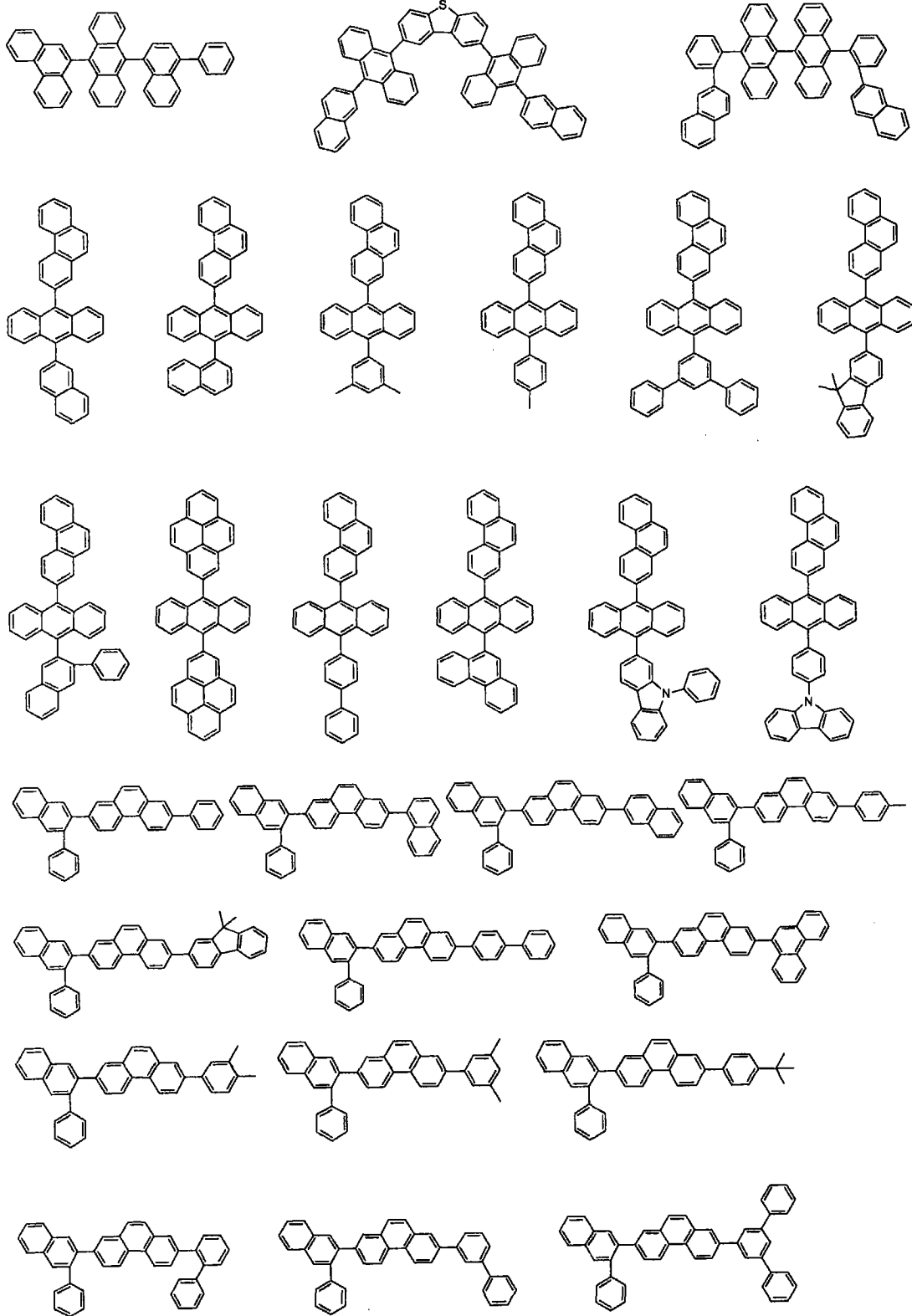
[0225]



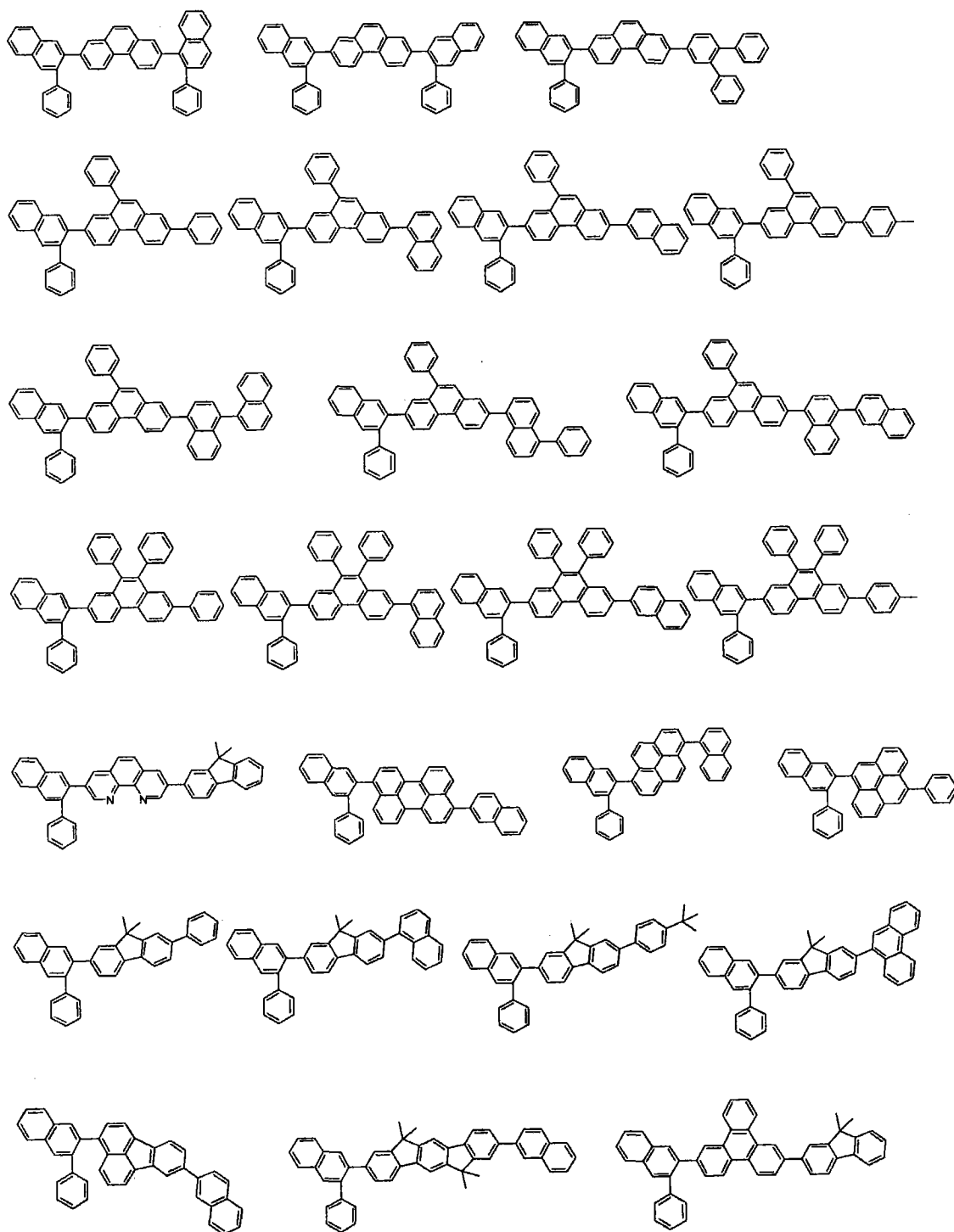
[0226]



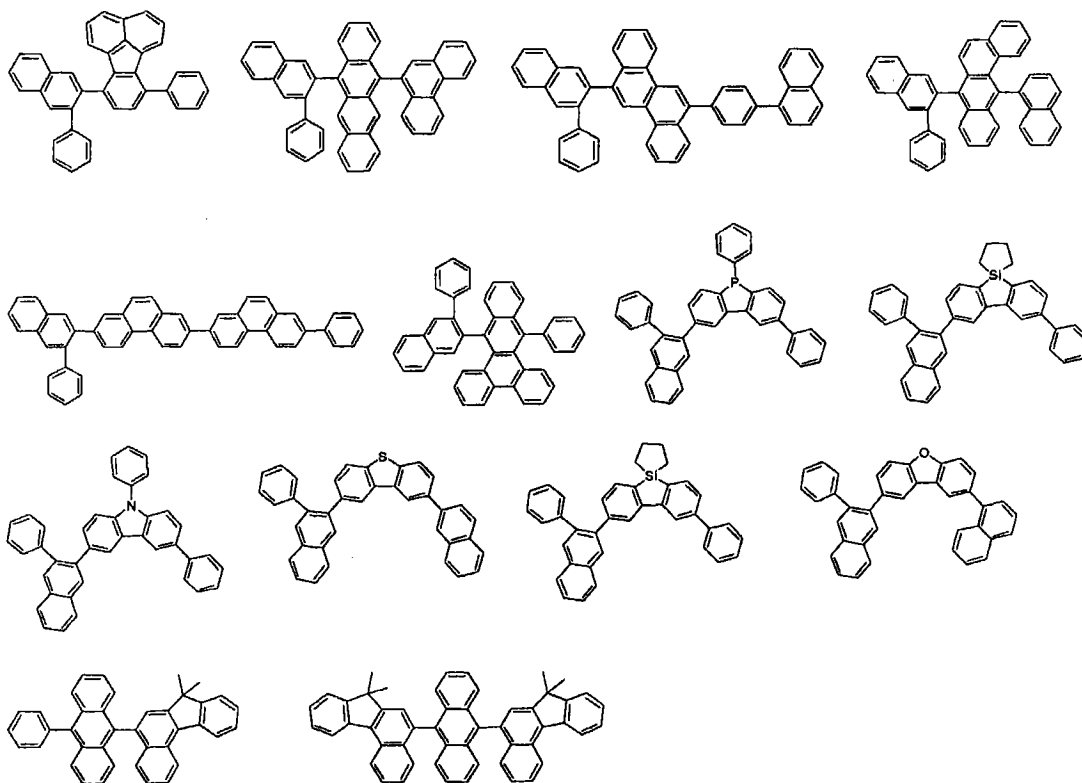
[0227]



[0228]



[0229]



[0230] 在本发明的有机电致发光器件中,优选在一对电极的至少一侧的内表面上放置一个或多个选自以下的层(以下称为“表面层”):氧属化物(chalcogenide)层、金属卤化物层和金属氧化物层。具体地说,优选将硅和金属铝(包括氧化物)的氧属化物层置于EL中间层的阳极表面上,并将金属卤化物层或金属氧化物层置于EL中间层的阴极表面上。其结果是在操作时能获得稳定性。

[0231] 氧属化物的例子优选包括 SiO_x ($1 \leq x \leq 2$), AlO_x ($1 \leq x \leq 1.5$), SiON , SiAlON 等等。金属卤化物的例子优选包括 LiF , MgF_2 , CaF_2 , 稀土金属氟化物等等。金属氧化物的例子优选包括 Cs_2O , Li_2O , MgO , SrO , BaO , CaO 等等。

[0232] 在本发明的有机电致发光器件中,还优选在如此制得的一对电极的至少一个表面上设置电子传输化合物和还原性掺杂剂的混合区,或者空穴传输化合物和氧化性掺杂剂的混合区。因此,电子传输化合物被还原成阴离子,从而有助于电子从混合区注入并传输到EL中间层。此外,由于空穴传输化合物被氧化形成阳离子,故而有助于空穴从混合区注入并传输到EL中间层。优选的氧化性掺杂剂包括各种路易斯酸和受体化合物。优选的还原性掺杂剂包括碱金属、碱金属化合物、碱土金属、稀土金属,以及它们的混合物。

[0233] 本发明的电致发光器件具有极佳的发光效率、良好色纯度、且在较低操作电压下有非常好的操作寿命。

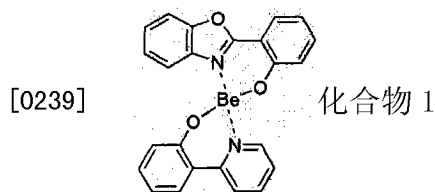
[0234] 最佳实施方式

[0235] 将参考制备例和实施例进一步描述本发明,以阐述本发明的新型电致发光器件的发光特性,但提供这些实施例仅是为了更好地理解本发明而并非试图通过任何方式对本发明的范围进行限制。

[0236] 制备例

[0237] 制备例 1-18 描述于韩国专利登记号 0684109。

[0238] [制备例 1] 制备化合物 (1)

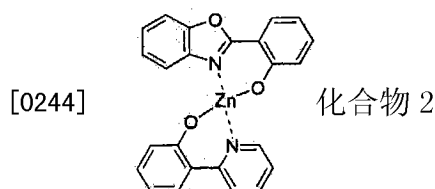


[0240] 将 2-吡啶-2-基-苯酚 (1.0g, 5.84mmol) 溶于甲醇 (50mL) 并在其中加入 1M 氢氧化钠水溶液 (10mL)。在此混合物中加入溶于甲醇水溶液 (甲醇 7mL : 水 3mL) 的四水合硫酸铍 (1.05g, 5.93mmol) 溶液, 并将所得混合物室温搅拌 2 小时。之后在其中缓慢加入溶于甲醇 (50mL) 的 2-羟基-苯基苯并噁唑 (1.54g, 7.30mmol)。将反应混合物室温再搅拌 2 小时, 然后升温至 50℃。搅拌 10 小时后滤出产生的沉淀, 用水 (50mL) 和丙酮 (50mL) 洗涤, 并干燥以获得标题化合物, 化合物 (1) (0.80g, 2.04mmol, 产率 : 34%)。

[0241] MS/FAB : 391 (实测值), 391.43 (计算值)

[0242] EA : C 73.55%, H 4.59%, N 7.05%, O 12.41%

[0243] [制备例 2] 制备化合物 (2)

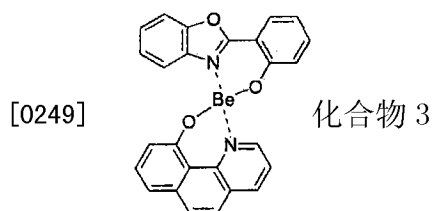


[0245] 将 2-吡啶-2-基-苯酚 (1.0g, 5.84mmol) 溶于甲醇 (50mL) 并在其中加入 1M 氢氧化钠水溶液 (10mL)。在此混合物中逐滴加入溶于甲醇 (10mL) 的醋酸锌 (0.95g, 5.18mmol) 溶液, 并将所得混合物室温搅拌 2 小时。之后在其中缓慢加入溶于甲醇 (50mL) 的 2-羟基-苯基苯并噁唑 (1.50g, 7.10mmol)。再将反应混合物室温搅拌 10 小时。然后滤出产生的沉淀, 用水 (50mL) 和丙酮 (50mL) 洗涤, 并干燥以获得标题化合物, 化合物 (2) (0.72g, 1.61mmol, 产率 : 27%)。

[0246] MS/FAB : 447 (实测值), 447.79 (计算值)

[0247] EA : C 64.22%, H 4.01%, N 6.05%, O 10.95%

[0248] [制备例 3] 制备化合物 (3)

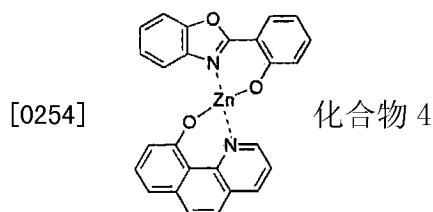


[0250] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 10-羟基苯并 [h] 喹啉 (1.48g, 7.58mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (3) (0.35g, 0.84mmol, 产率 14%)

[0251] MS/FAB : 415 (实测值), 415.46 (计算值)

[0252] EA : C 75.02%, H 4.27%, N 6.64%, O 11.65%

[0253] [制备例 4] 制备化合物 (4)

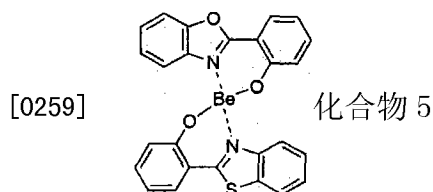


[0255] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 10-羟基苯并[h]喹啉 (1.48g, 7.58mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (104) (0.52g, 1.10mmol, 产率 19%)

[0256] MS/FAB : 471 (实测值), 471.81 (计算值)

[0257] EA : C 66.08%, H 3.79%, N 5.84%, O 10.30%

[0258] [制备例 5] 制备化合物 (5)

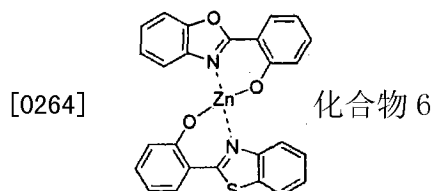


[0260] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 2-羟基-苯基苯并噁唑 (1.72g, 7.57mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (5) (0.96g, 2.15mmol, 产率 37%)

[0261] MS/FAB : 447 (实测值), 447.52 (计算值)

[0262] EA : C 69.68%, H 4.01%, N 6.16%, O 10.85%, S 7.05%

[0263] [制备例 6] 制备化合物 (6)

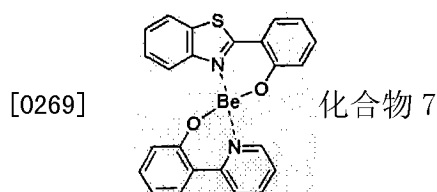


[0265] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 2-羟基-苯基苯并噁唑 (1.72g, 7.57mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (6) (1.36g, 2.70mmol, 产率 46%)

[0266] MS/FAB : 503 (实测值), 503.88 (计算值)

[0267] EA : C 61.88%, H 3.54%, N 5.46%, O 9.73%, S 6.26%

[0268] [制备例 7] 制备化合物 (7)

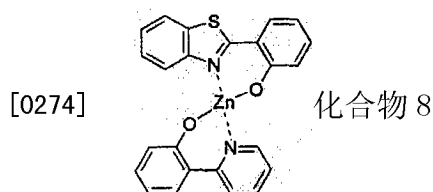


[0270] 采用 2-羟基-苯基苯并噁唑 (1.32g, 5.80mmol), 2-吡啶-2-基-苯酚 (1.30g, 7.59mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (107) (0.59g, 1.45mmol, 产率 25%)。

[0271] MS/FAB : 407 (实测值), 407.50 (计算值)

[0272] EA :C 70.64%, H 4.35%, N 6.76%, O 7.96%, S 7.75%

[0273] [制备例 8] 制备化合物 (8)

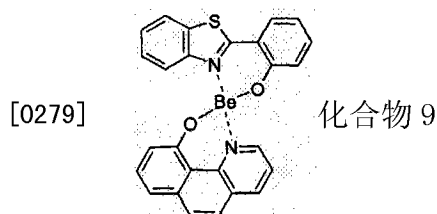


[0275] 采用 2-羟基-苯基苯并噻唑 (1.32g, 5.80mmol), 2-吡啶-2-基-苯酚 (1.30g, 7.59mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (8) (0.83g, 1.79mmol, 产率 31%)

[0276] MS/FAB :463 (实测值), 463.86 (计算值)

[0277] EA :C 62.04%, H 3.82%, N 5.98%, O 7.02%, S 6.83%

[0278] [制备例 9] 制备化合物 (9)

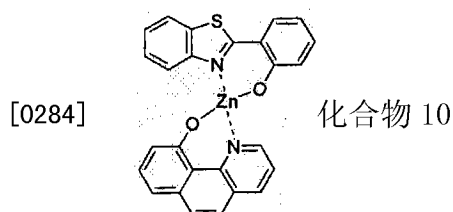


[0280] 采用 2-羟基-苯基苯并噻唑 (1.32g, 5.80mmol), 2-羟基苯并[h]喹啉 (1.48g, 7.58mmol) 替代 2-羟基-苯基苯并噻唑, 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (9) (0.98g, 2.27mmol, 产率 39%)。

[0281] MS/FAB :431 (实测值), 431.52 (计算值)

[0282] EA :C 72.22%, H 4.10%, N 6.40%, O 7.62%, S 7.33%

[0283] [制备例 10] 制备化合物 (10)

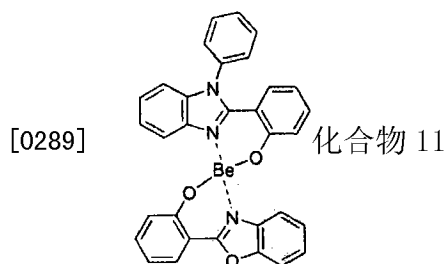


[0285] 采用 2-羟基-苯基苯并噻唑 (1.32g, 5.80mmol), 10-羟基苯并[h]喹啉 (1.48g, 7.58mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 4 所述的相同方法以获得标题化合物, 化合物 (10) (1.22g, 2.50mmol, 产率 43%)。

[0286] MS/FAB :487 (实测值), 487.88 (计算值)

[0287] EA :C 63.93%, H 3.65%, N 5.64%, O 6.70%, S 6.44%

[0288] [制备例 11] 制备化合物 (11)

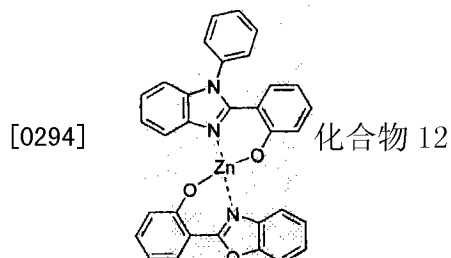


[0290] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (2.17g, 7.58mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (11) (0.56g, 1.11mmol, 产率 19%)

[0291] MS/FAB : 506 (实测值), 506.57 (计算值)

[0292] EA : C 75.67%, H 4.50%, N 8.20%, O 9.68%

[0293] [制备例 12] 制备化合物 (12)

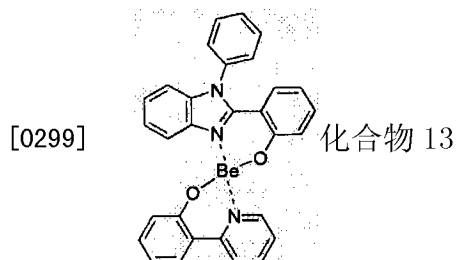


[0295] 采用 2-羟基-苯基苯并噁唑 (1.23g, 5.82mmol), 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (2.17g, 7.58mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (12) (0.72g, 1.28mmol, 产率 22%)

[0296] MS/FAB : 562 (实测值), 562.93 (计算值)

[0297] EA : C 68.16%, H 4.05%, N 7.36%, O 8.68%

[0298] [制备例 13] 制备化合物 (13)

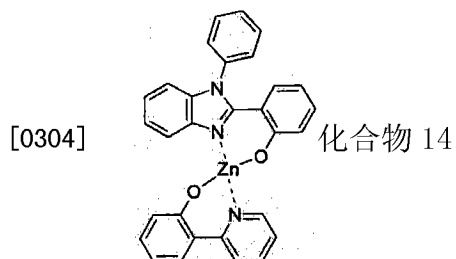


[0300] 采用 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (1.67g, 5.83mmol), 2-吡啶-2-基-苯酚 (1.30g, 7.59mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (13) (0.84g, 1.80mmol, 产率 31%)

[0301] MS/FAB : 466 (实测值), 466.55 (计算值)

[0302] EA : C 77.08%, H 4.87%, N 8.90%, O 6.98%

[0303] [制备例 14] 制备化合物 (14)

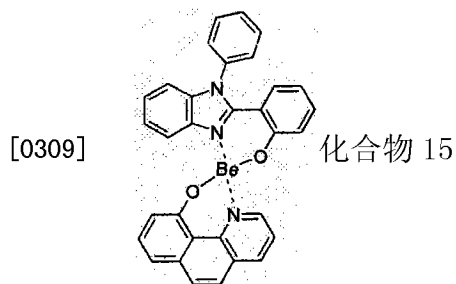


[0305] 采用 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (1.67g, 5.83mmol), 2-吡啶-2-基-苯酚 (1.30g, 7.59mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (14) (0.88g, 1.68mmol, 产率 29%)

[0306] MS/FAB : 522 (实测值), 522.91 (计算值)

[0307] EA :C 68.81%, H 4.33%, N 7.92%, O 6.32%

[0308] [制备例 15] 制备化合物 (15)

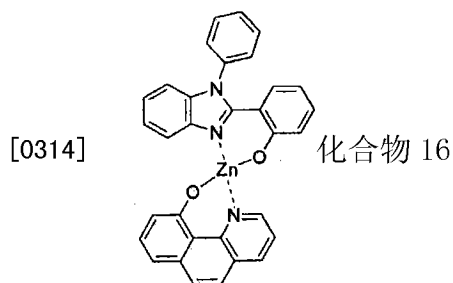


[0310] 采用 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (1.67g, 5.83mmol), 10-羟基苯并[h]喹啉 (1.50g, 7.68mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (15) (0.53g, 产率 9%)

[0311] MS/FAB :490 (实测值), 490.57 (计算值)

[0312] EA :C 78.20%, H 4.68%, N 8.42%, O 6.70%

[0313] [制备例 16] 制备化合物 (16)

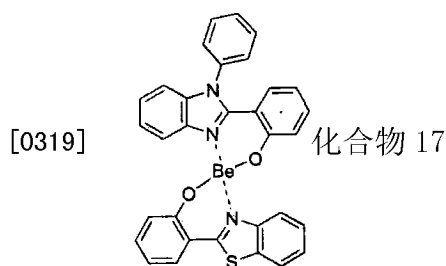


[0315] 采用 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (1.67g, 5.83mmol), 10-羟基苯并[h]喹啉 (1.50g, 7.68mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (16) (0.42g, 0.77mmol, 产率 13%)

[0316] MS/FAB :546 (实测值), 546.93 (计算值)

[0317] EA :C 70.13%, H 4.16%, N 7.58%, O 5.98%

[0318] [制备例 17] 制备化合物 (17)

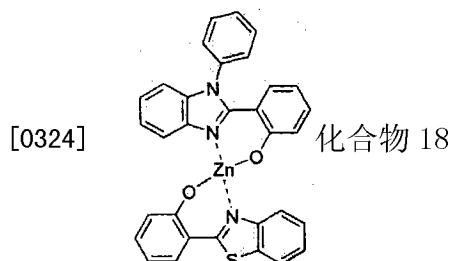


[0320] 采用 2-羟基-苯基苯并噻唑 (1.32g, 5.80mmol), 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (2.17g, 7.58mmol) 和四水合硫酸铍 (1.05g, 5.93mmol), 重复制备例 1 所述的相同方法以获得标题化合物, 化合物 (17) (0.64g, 1.22mmol, 产率 21%)。

[0321] MS/FAB :522 (实测值), 522.64 (计算值)

[0322] EA :C 73.42%, H 4.34%, N 7.97%, O 6.25%, S 6.04%

[0323] [制备例 18] 制备化合物 (18)



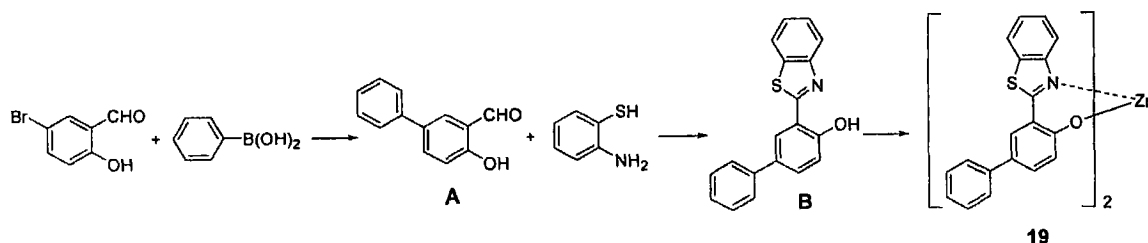
[0325] 采用 2-羟基-苯基苯并噻唑 (1.32g, 5.80mmol), 2-(1-苯基-1H-苯并咪唑-2-基)-苯酚 (2.17g, 7.58mmol) 和醋酸锌 (0.95g, 5.18mmol), 重复制备例 2 所述的相同方法以获得标题化合物, 化合物 (18) (0.94g, 1.62mmol, 产率 28%)

[0326] MS/FAB : 578 (实测值), 578.99 (计算值)

[0327] EA : C 66.22%, H 3.94%, N 7.16%, O 5.70%, S 5.49%

[0328] [制备例 19] 制备化合物 (19)

[0329]



[0330] 制备化合物 A

[0331] 将 5-溴-2-羟基苯甲醛 (20.0g, 99.5mmol)、苯基硼酸 (13.4g, 109.5mmol) 和三苯基膦四钯 (0) ($\text{Pd}(\text{PPh}_3)_4$) (5.8g, 5.0mmol) 溶于二甲基乙二醇 (200mL) 和乙醇 (100mL) 中, 在其中加入 2M 碳酸钾水溶液 (132mL), 将所得混合物于 90℃ 回流搅拌 4 小时。反应结束后在反应混合物中加入水 (100mL) 以猝灭反应。混合物然后用乙酸乙酯 (200mL) 萃取, 将萃取液减压干燥。通过硅胶层析柱纯化 (正己烷 : MC = 1 : 5) 得到化合物 (A) (12.0g, 61.0mmol)。

[0332] 制备化合物 (B)

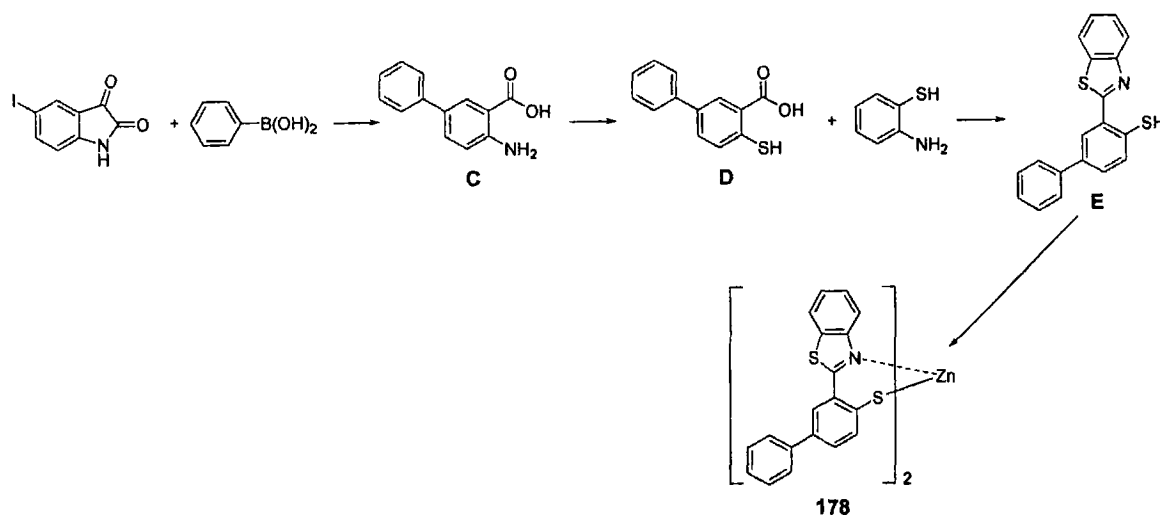
[0333] 将 2-氨基苯硫醇 (3.8g, 30.2mmol) 和化合物 (A) (5.0g, 25.2mmol) 溶于 1,4-二噁烷 (12mL), 并将混合物于 100℃ 加压搅拌 12 小时。当反应结束时将反应混合物冷却至室温, 并用二氯甲烷 (100mL) 和水 (100mL) 萃取。萃取液然后减压干燥, 并将残余物通过硅胶柱层析 (正己烷 : MC = 3 : 1) 纯化以获得化合物 (B) (4.5g, 4.8mmol)。

[0334] 制备化合物 (19)

[0335] 将化合物 (B) (4.5g, 14.8mmol) 和氢氧化钠 (0.6g, 14.8mmol) 溶于乙醇 (100mL)。将搅拌该溶液 30 分钟后缓慢加入 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.8g, 8.2mmol), 并将所得混合物室温搅拌 12 小时。当反应结束时, 反应混合物依次用水 (200mL)、乙醇 (200mL) 和己烷 (200mL) 洗涤, 并减压干燥以获得标题化合物 (19) (4.5g, 6.7mmol, 45%)。

[0336] [制备例 20] 制备化合物 (178)

[0337]



[0338] 制备化合物 (C)

[0339] 将 5-碘代二氢吡咯-2,3-二酮 (10.0g, 36.6mmol) 和苯基硼酸 (5.4g, 43.9mmol) 溶于乙二醇 (dimethylene glycol) (600mL)。在此溶液中加入三苯基膦四钯 (0) ($\text{Pd}(\text{PPh}_3)_4$) (2.1g, 1.8mmol) 和 2M 碳酸氢钠水溶液 (120mL)。回流条件下搅拌混合物 12 小时,并在反应结束时除去溶剂。在残余物中加入 5% 氢氧化钠水溶液 (120mL) 并室温搅拌所得混合物。水溶液用二氯甲烷萃取并收集水层。加入 30% 过氧化氢水溶液 (120mL) 之后将温度升至 50°C 并搅拌 30 分钟。冷却至室温后缓慢加入 1N 盐酸水溶液以将水溶液调至 pH4。然后减压过滤产生的固体并干燥以获得化合物 (C) (5.5g, 26.0mmol)。

[0340] 制备化合物 (D)

[0341] 将化合物 (C) (7.1g, 33.3mmol) 溶于水 (18mL) 和浓盐酸 (7mL) 中,并室温搅拌该溶液。10 分钟后将温度降至 0°C 并在其中缓慢加入溶于水 (10mL) 的硝酸钠 (NaNO_3) (2.3g, 33.3mmol)。然后搅拌所得混合物同时维持温度在 0°C。在另一个反应容器内将九水合硫化钠 ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) (9.6g, 39.9mmol) 和硫 (1.3g, 39.9mmol) 溶于水 (10mL),并在其中加入 10M 氢氧化钠水溶液 (4mL)。将该混合物加入 0°C 的反应混合物中,使所得混合物升至室温并搅拌直到不再有任何气体产生。当反应结束时加入浓盐酸直到有固体出现,减压过滤混合物。将所得固体加入碳酸氢钠 (NaHCO_3) 水溶液 (85mL),并在回流下搅拌混合物 20 分钟并冷却至室温。除去不溶性固体 (杂质) 后在水溶液中加入浓盐酸以再次形成固体。将减压过滤获得的固体加入乙醇 (30mL) 中,并回流搅拌混合物 20 分钟。除去不溶性固体 (杂质) 并浓缩滤液。在其中加入锌 (2.2g, 33.3mmol) 和冰醋酸 (30mL) 并回流搅拌所得混合物 48 小时。当反应结束时,反应混合物冷却至室温,将收集的固体加入 5M 氢氧化钠水溶液 (63mL),并回流搅拌混合物 30 分钟。除去不溶性固体 (杂质) 后分小份加入浓盐酸以酸化水溶液。然后收集产生的固体并加入到乙醇 (20mL) 中。回流搅拌 30 分钟后除去不溶性固体 (杂质) 并浓缩滤液以获得化合物 (D) (1.8g, 7.6mmol)。

[0342] 制备化合物 (E)

[0343] 在反应容器内将化合物 (D) (5.0g, 21.7mmol), 2-氨基苯硫醇 (2.1mL, 19.5mmol) 和多磷酸 (20g) 于 140°C 回流搅拌 24 小时。当反应结束时,将反应混合物冷却至室温,并缓慢加入饱和氢氧化钠水溶液以调节 pH 至中性。然后减压过滤产生的固体以获得固体产物。该固体用乙醇洗涤并干燥以得到化合物 (E) (5.4g, 17.1mmol)。

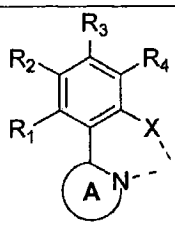
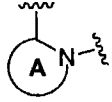

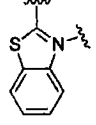

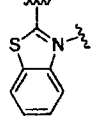

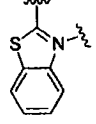

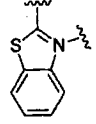

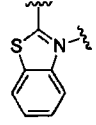

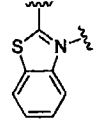

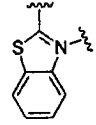

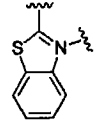
[0344] 制备化合物 (178)

[0345] 将化合物 (E) (5.0g, 15.6mmol) 和氢氧化钠 (0.6g, 15.6mmol) 溶于乙醇 (100mL) 并搅拌该溶液 30 分钟。在其中缓慢加入 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.9g, 8.7mmol), 室温搅拌所得混合物 12 小时。之后将混合物依次用水 (200mL)、乙醇 (200mL) 和己烷 (200mL) 洗涤并减压干燥以获得标题化合物, 化合物 (178) (7.1g, 10.1mmol, 65%)。

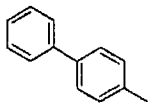
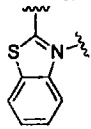
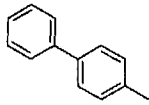
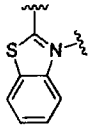
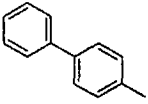
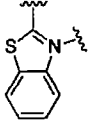
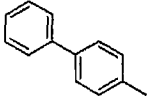
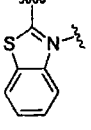
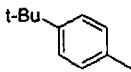
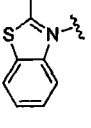
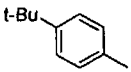
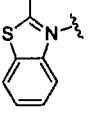
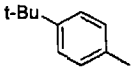
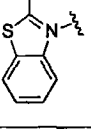
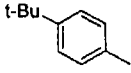
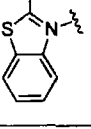
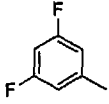
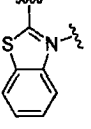
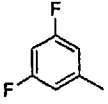
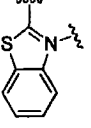
[0346] 根据与制备例 19 和 20 相同的方法制备了表 1 中列出的化合物 19-336, 其 ^1H NMR 和 MS/FAB 数据列于表 2。表 1 所列化合物是含有二价金属 M 的化合物。

[0347] 表 1

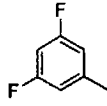
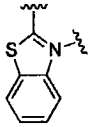
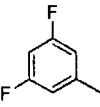
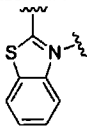
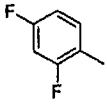
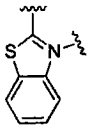
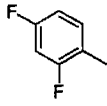
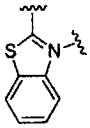
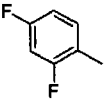
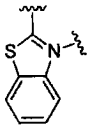
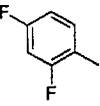
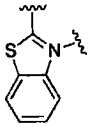
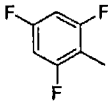
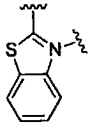
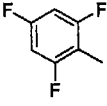
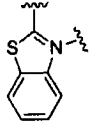
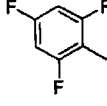
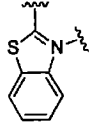
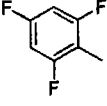
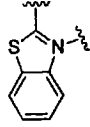
[0348]

L ¹ L ² M						
 $L^1 = L^2 =$						
化合物 编号	R ₁	R ₂	R ₃	R ₄		X
19	H		H	H		O Zn
20		H	H	H		O Zn
21	H	H		H		O Zn
22	H	H	H			O Zn
23	H		H	H		O Zn
24	H	H		H		O Zn
25	H	H	H			O Zn
26		H	H	H		O Zn


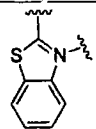

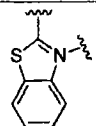

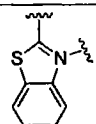

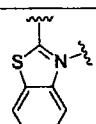
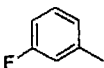
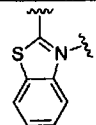
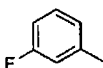
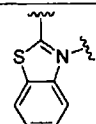
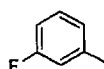
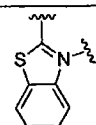
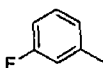
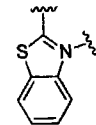

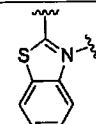

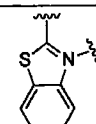
[0349]

27	H		H	H		O	Zn
28		H	H	H		O	Zn
29	H	H		H		O	Zn
30	H	H	H			O	Zn
31	H	H		H		O	Zn
32	H		H	H		O	Zn
33	H	H		H		O	Zn
34		H	H	H		O	Zn
35	H	H		H		O	Zn
36	H		H	H		O	Zn

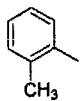
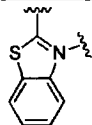
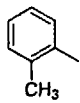
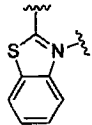
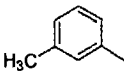
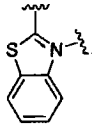
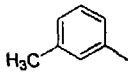
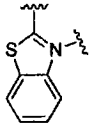
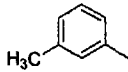
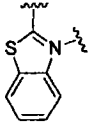
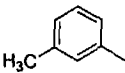
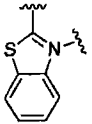
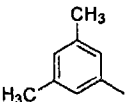
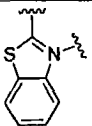
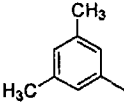
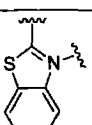
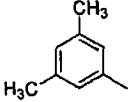
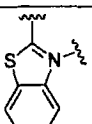
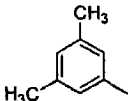
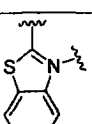
[0350]

37	H	H	H			O	Zn
38		H	H	H		O	Zn
39	H		H	H		O	Zn
40	H	H	H			O	Zn
41	H	H		H		O	Zn
42		H	H	H		O	Zn
43		H	H	H		O	Zn
44	H		H	H		O	Zn
45	H	H	H			O	Zn
46	H	H		H		O	Zn

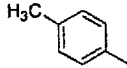
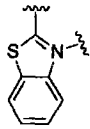
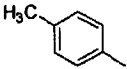
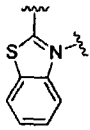
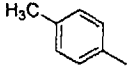
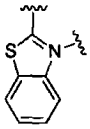
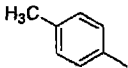
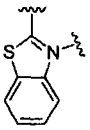
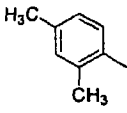
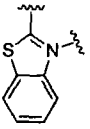
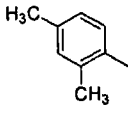
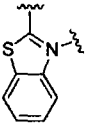
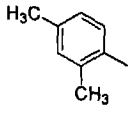
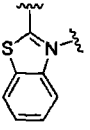
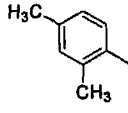
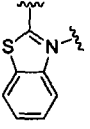
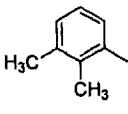
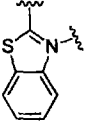
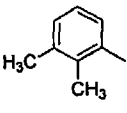
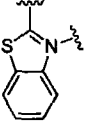
[0351]

47		H	H	H		O	Zn
48	H		H	H		O	Zn
49	H	H		H		O	Zn
50	H	H	H			O	Zn
51	H		H	H		O	Zn
52	H	H		H		O	Zn
53	H	H	H			O	Zn
54		H	H	H		O	Zn
55	H		H	H		O	Zn
56	H	H		H		O	Zn

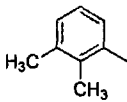
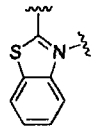
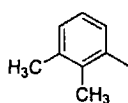
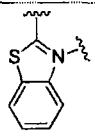
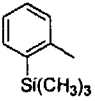
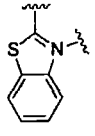
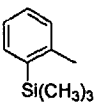
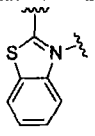
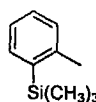
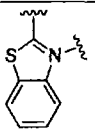
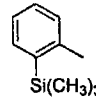
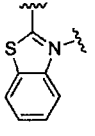
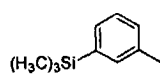
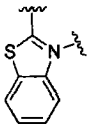
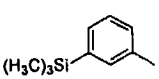
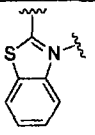
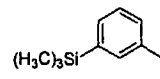
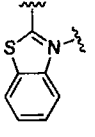
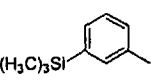
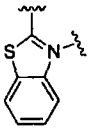
[0352]

57		H	H	H		O	Zn
58	H	H	H			O	Zn
59	H		H	H		O	Zn
60	H	H		H		O	Zn
61	H	H	H			O	Zn
62		H	H	H		O	Zn
63		H	H	H		O	Zn
64	H		H	H		O	Zn
65	H	H		H		O	Zn
66	H	H	H			O	Zn

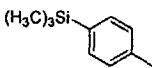
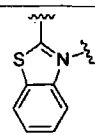
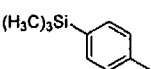
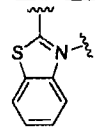
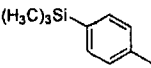
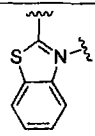
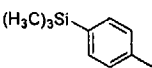
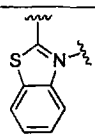
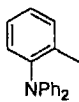
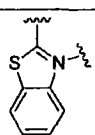
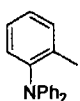
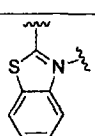
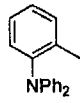
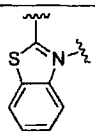
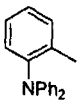
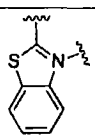
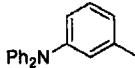
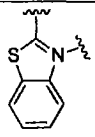
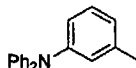
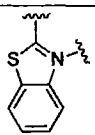
[0353]

67	H		H	H		O	Zn
68	H	H		H		O	Zn
69		H	H	H		O	Zn
70	H	H	H			O	Zn
71	H	H		H		O	Zn
72	H		H	H		O	Zn
73		H	H	H		O	Zn
74	H	H	H			O	Zn
75	H		H	H		O	Zn
76	H	H		H		O	Zn

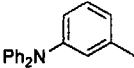
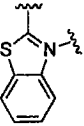
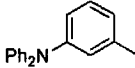
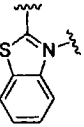
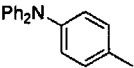
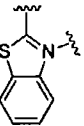
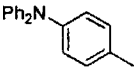
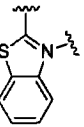
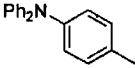
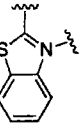
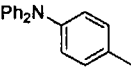
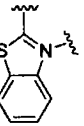
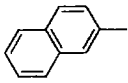
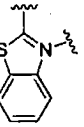
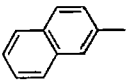
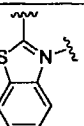
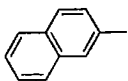
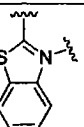
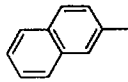
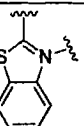
[0354]

77		H	H	H		O	Zn
78	H	H	H			O	Zn
79		H	H	H		O	Zn
80	H	H		H		O	Zn
81	H		H	H		O	Zn
82	H	H	H			O	Zn
83	H		H	H		O	Zn
84	H	H		H		O	Zn
85	H	H	H			O	Zn
86		H	H	H		O	Zn

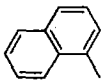
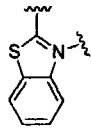
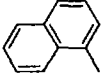
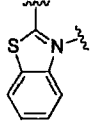
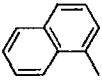
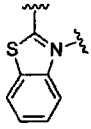
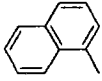
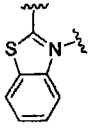
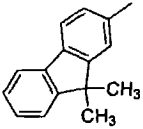
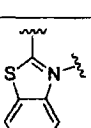
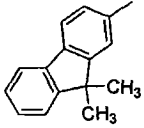
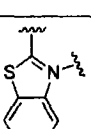
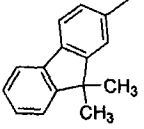
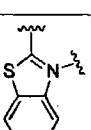
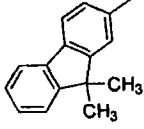
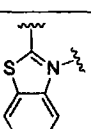
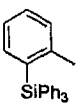
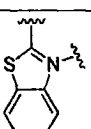
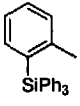
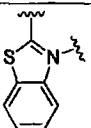
[0355]

87	H		H	H		O	Zn
88		H	H	H		O	Zn
89	H	H		H		O	Zn
90	H	H	H			O	Zn
91	H	H		H		O	Zn
92	H		H	H		O	Zn
93	H	H	H			O	Zn
94		H	H	H		O	Zn
95		H	H	H		O	Zn
96	H		H	H		O	Zn


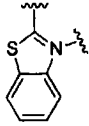

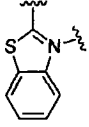
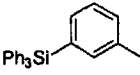
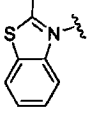
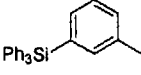
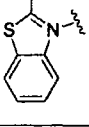
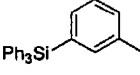
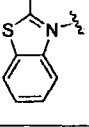
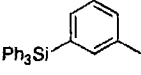
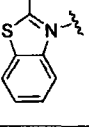
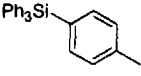
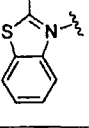
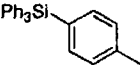
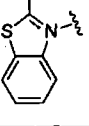
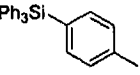
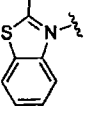
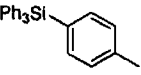
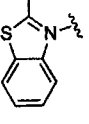
[0356]

97	H	H		H		O	Zn
98	H	H	H			O	Zn
99	H	H		H		O	Zn
100	H		H	H		O	Zn
101	H	H	H			O	Zn
102		H	H	H		O	Zn
103	H		H	H		O	Zn
104	H	H		H		O	Zn
105		H	H	H		O	Zn
106	H	H	H			O	Zn

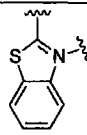
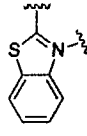
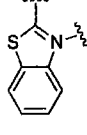
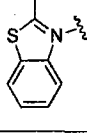
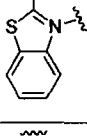
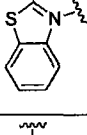
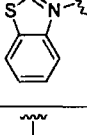
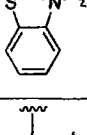
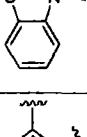
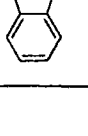
[0357]

107	H	H		H		O	Zn
108	H	H	H			O	Zn
109	H		H	H		O	Zn
110		H	H	H		O	Zn
111	H		H	H		O	Zn
112	H	H		H		O	Zn
113		H	H	H		O	Zn
114	H	H	H			O	Zn
115	H		H	H		O	Zn
116	H	H		H		O	Zn

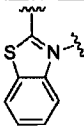
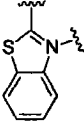
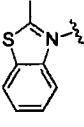
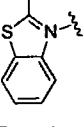
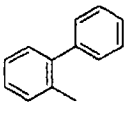
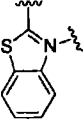
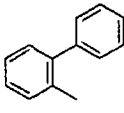
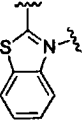
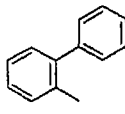
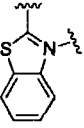
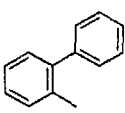
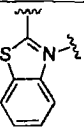
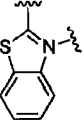
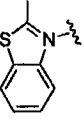
[0358]

117		H	H	H		O	Zn
118	H	H	H			O	Zn
119	H	H		H		O	Zn
120	H	H	H			O	Zn
121	H		H	H		O	Zn
122		H	H	H		O	Zn
123		H	H	H		O	Zn
124	H		H	H		O	Zn
125	H	H		H		O	Zn
126	H	H	H			O	Zn


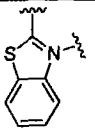

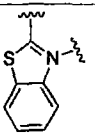
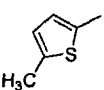
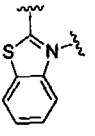
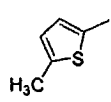
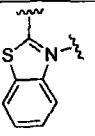

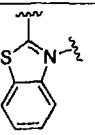

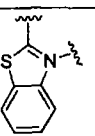
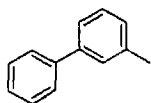
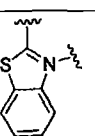
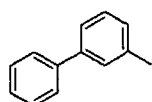
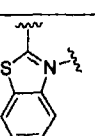
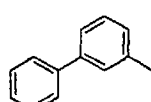
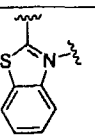
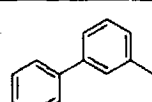
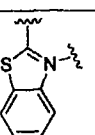
[0359]

127	H	H	-CH ₃	H		O	Zn
128	H	-CH ₃	H	H		O	Zn
129	H	H	H	-CH ₃		O	Zn
130	-CH ₃	H	H	H		O	Zn
131	H	-CH ₃	H	-CH ₃		O	Zn
132	-CH ₃	H	-CH ₃	H		O	Zn
133	H	-CH ₃	-CH ₃	H		O	Zn
134	H	H	-CH ₃	-CH ₃		O	Zn
135	-CH ₃	-CH ₃	H	H		O	Zn
136	-CH ₃	H	H	-CH ₃		O	Zn

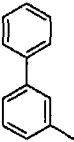
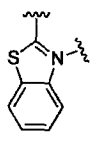
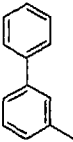
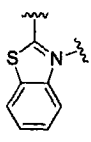
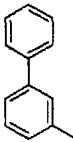
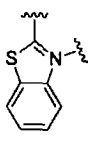
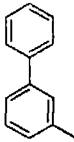
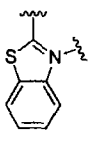
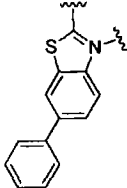
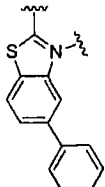
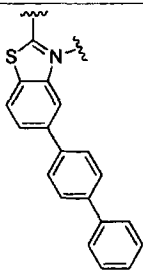
[0360]

137	$-\text{C}(\text{CH}_3)_3$	H	H	H		O	Zn
138	H	$-\text{C}(\text{CH}_3)_3$	H	H		O	Zn
139	H	H	$-\text{C}(\text{CH}_3)_3$	H		O	Zn
140	H	H	H	$-\text{C}(\text{CH}_3)_3$		O	Zn
141		H	H	H		O	Zn
142	H	H		H		O	Zn
143	H	H	H			O	Zn
144	H		H	H		O	Zn
145	H	$-\text{C}(\text{CH}_3)_3$	H	$-\text{CH}_3$		O	Zn
146	H	$-\text{CH}_3$	H	$-\text{C}(\text{CH}_3)_3$		O	Zn

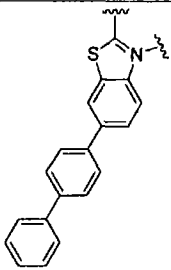
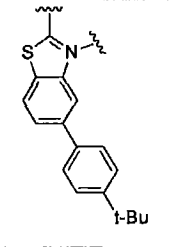
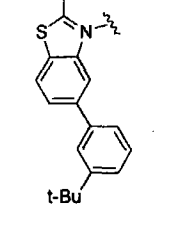
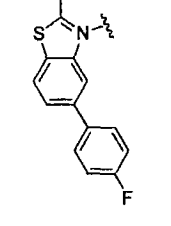
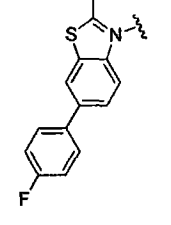
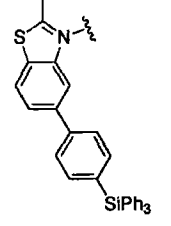
[0361]

147	H		H	H		O	Zn
148	H	H		H		O	Zn
149	H		H	H		O	Zn
150	H	H		H		O	Zn
151	H		H	-CH ₃		O	Zn
152	H	-CH ₃	H			O	Zn
153		H	H	H		O	Zn
154	H		H	H		O	Zn
155	H	H		H		O	Zn
156	H	H	H			O	Zn

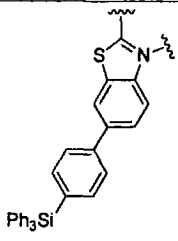
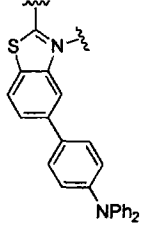
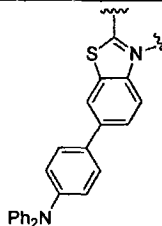
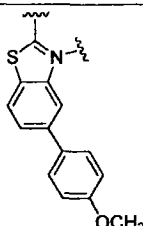
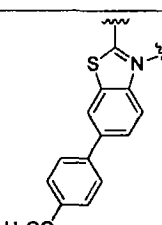
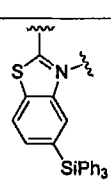
[0362]

157	H	H		H		O	Zn
158	H		H	H		O	Zn
159	H	H	H			O	Zn
160		H	H	H		O	Zn
161	H	H	H	H		O	Zn
162	H	H	H	H		O	Zn
163	H	H	H	H		O	Zn

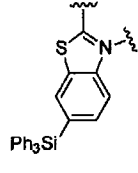
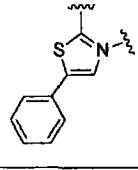

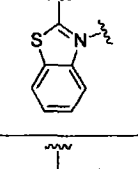

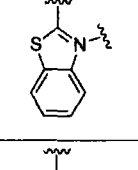

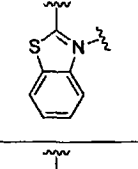

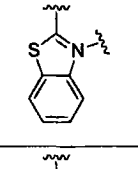
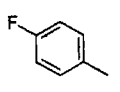
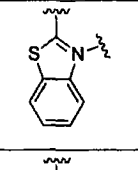
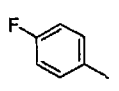
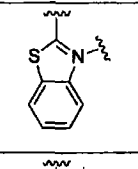
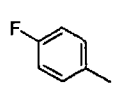
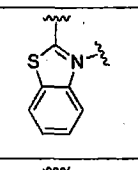
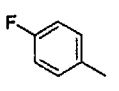
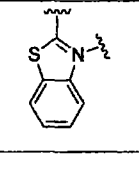
[0363]

164	H	H	H	H		O	Zn
165	H	H	H	H		O	Zn
166	H	H	H	H		O	Zn
167	H	H	H	H		O	Zn
168	H	H	H	H		O	Zn
169	H	H	H	H		O	Zn

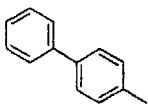
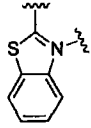
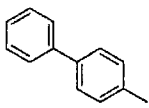
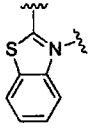
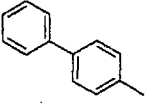
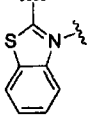
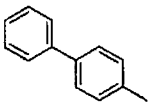
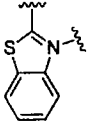
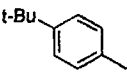
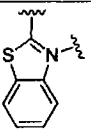
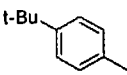
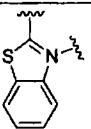
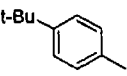
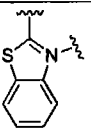
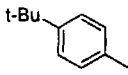
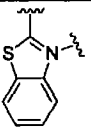
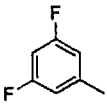
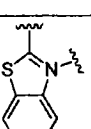
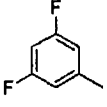
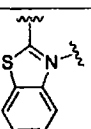
[0364]

170	H	H	H	H		O	Zn
171	H	H	H	H		O	Zn
172	H	H	H	H		O	Zn
173	H	H	H	H		O	Zn
174	H	H	H	H		O	Zn
175	H	H	H	H		O	Zn

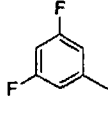
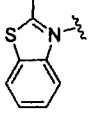
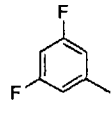
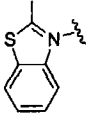
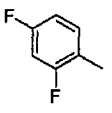
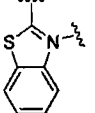
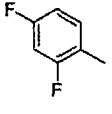
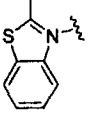
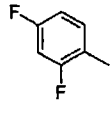
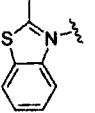
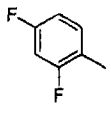
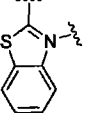
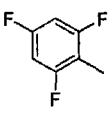
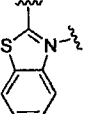
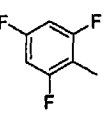
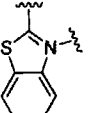
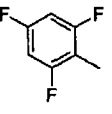
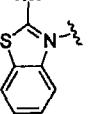
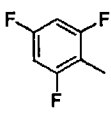
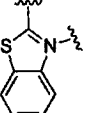
[0365]

176	H	H	H	H		O	Zn
177	H	H	H	H		O	Zn
178	H		H	H		S	Zn
179		H	H	H		S	Zn
180	H	H		H		S	Zn
181	H	H	H			S	Zn
182	H		H	H		S	Zn
183	H	H		H		S	Zn
184	H	H	H			S	Zn
185		H	H	H		S	Zn


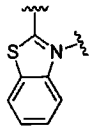

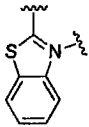

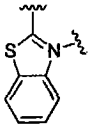

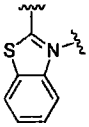
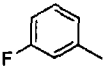
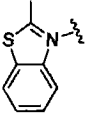
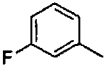
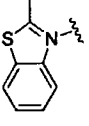
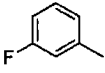
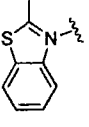
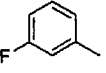
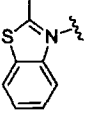

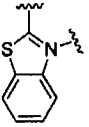

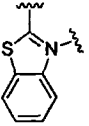
[0366]

186	H		H	H		S	Zn
187		H	H	H		S	Zn
188	H	H		H		S	Zn
189	H	H	H			S	Zn
190	H	H		H		S	Zn
191	H		H	H		S	Zn
192	H	H		H		S	Zn
193		H	H	H		S	Zn
194	H	H		H		S	Zn
195	H		H	H		S	Zn

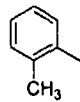
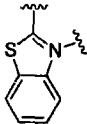
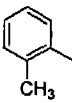
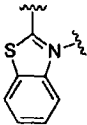
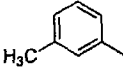
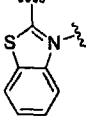
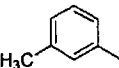
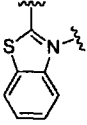
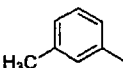
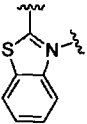
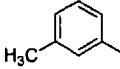
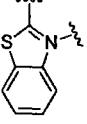
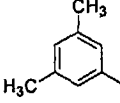
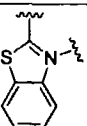
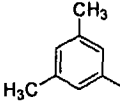
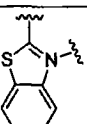
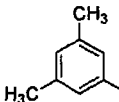
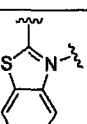
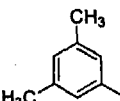
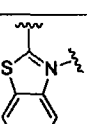
[0367]

196	H	H	H			S	Zn
197		H	H	H		S	Zn
198	H		H	H		S	Zn
199	H	H	H			S	Zn
200	H	H		H		S	Zn
201		H	H	H		S	Zn
202		H	H	H		S	Zn
203	H		H	H		S	Zn
204	H	H	H			S	Zn
205	H	H		H		S	Zn

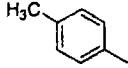
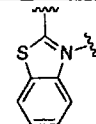
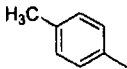
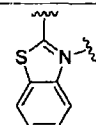
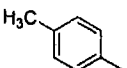
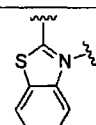
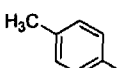
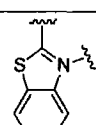
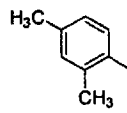
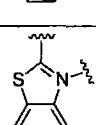
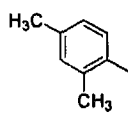
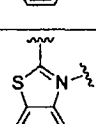
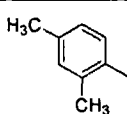
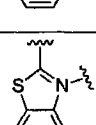
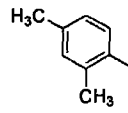
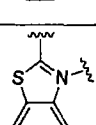
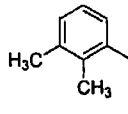
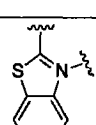
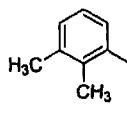
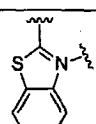
[0368]

206		H	H	H		S	Zn
207	H		H	H		S	Zn
208	H	H		H		S	Zn
209	H	H	H			S	Zn
210	H		H	H		S	Zn
211	H	H		H		S	Zn
212	H	H	H			S	Zn
213		H	H	H		S	Zn
214	H		H	H		S	Zn
215	H	H		H		S	Zn

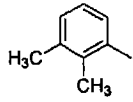
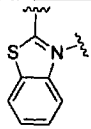
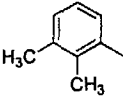
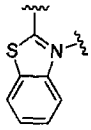
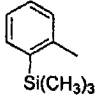
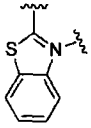
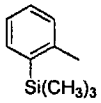
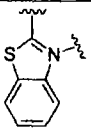
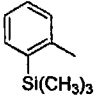
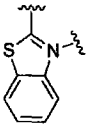
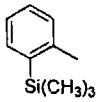
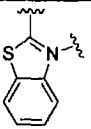
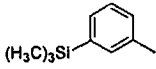
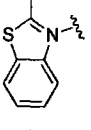
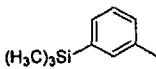
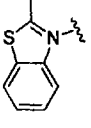
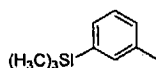
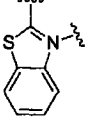
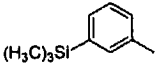
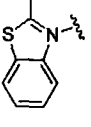
[0369]

216		H	H	H		S	Zn
217	H	H	H			S	Zn
218	H		H	H		S	Zn
219	H	H		H		S	Zn
220	H	H	H			S	Zn
221		H	H	H		S	Zn
222		H	H	H		S	Zn
223	H		H	H		S	Zn
224	H	H		H		S	Zn
225	H	H	H			S	Zn

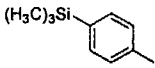
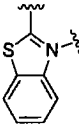
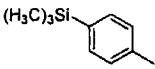
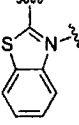
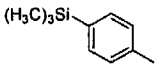
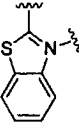
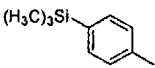
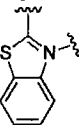
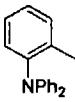
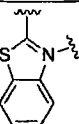
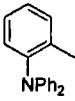
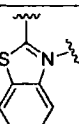
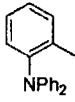
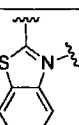
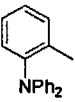
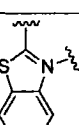
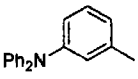
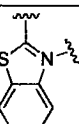
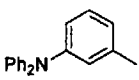
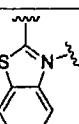
[0370]

226	H		H	H		S	Zn
227	H	H		H		S	Zn
228		H	H	H		S	Zn
229	H	H	H			S	Zn
230	H	H		H		S	Zn
231	H		H	H		S	Zn
232		H	H	H		S	Zn
233	H	H	H			S	Zn
234	H		H	H		S	Zn
235	H	H		H		S	Zn

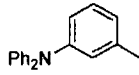
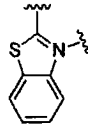
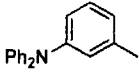
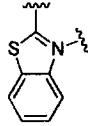
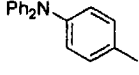
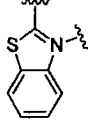
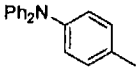
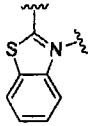
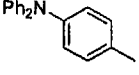
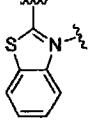
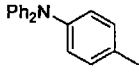
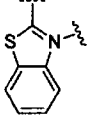
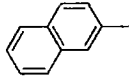
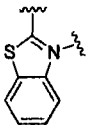
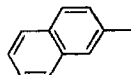
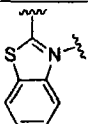
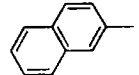
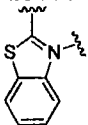
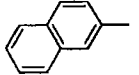
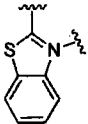
[0371]

236		H	H	H		S	Zn
237	H	H	H			S	Zn
238		H	H	H		S	Zn
239	H	H		H		S	Zn
240	H		H	H		S	Zn
241	H	H	H			S	Zn
242	H		H	H		S	Zn
243	H	H		H		S	Zn
244	H	H	H			S	Zn
245		H	H	H		S	Zn

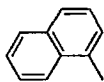
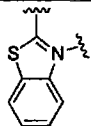
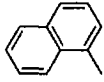
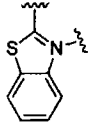
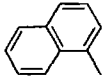
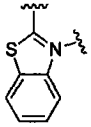
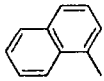
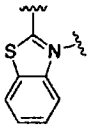
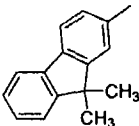
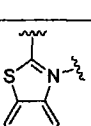
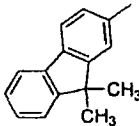
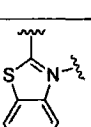
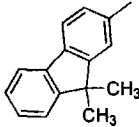
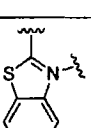
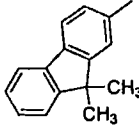
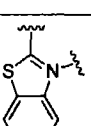

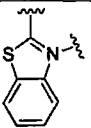

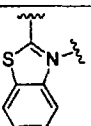
[0372]

246	H		H	H		S	Zn
247		H	H	H		S	Zn
248	H	H		H		S	Zn
249	H	H	H			S	Zn
250	H	H		H		S	Zn
251	H		H	H		S	Zn
252	H	H	H			S	Zn
253		H	H	H		S	Zn
254		H	H	H		S	Zn
255	H		H	H		S	Zn


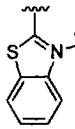

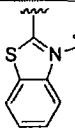
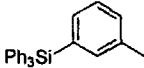
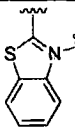
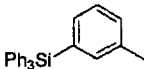
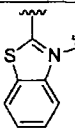
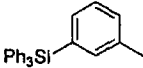
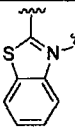
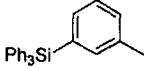
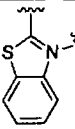
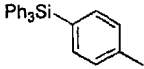
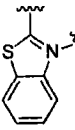
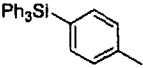
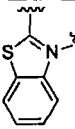
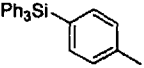
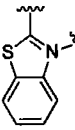
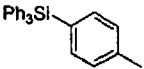
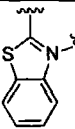
[0373]

256	H	H		H		S	Zn
257	H	H	H			S	Zn
258	H	H		H		S	Zn
259	H		H	H		S	Zn
260	H	H	H			S	Zn
261		H	H	H		S	Zn
262	H		H	H		S	Zn
263	H	H		H		S	Zn
264		H	H	H		S	Zn
265	H	H	H			S	Zn

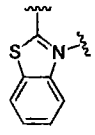
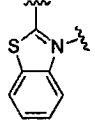
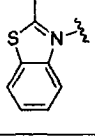
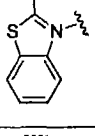
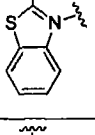
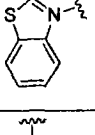
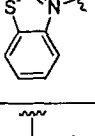
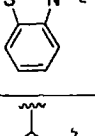
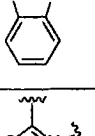
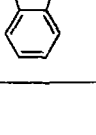
[0374]

266	H	H		H		S	Zn
267	H	H	H			S	Zn
268	H		H	H		S	Zn
269		H	H	H		S	Zn
270	H		H	H		S	Zn
271	H	H		H		S	Zn
272		H	H	H		S	Zn
273	H	H	H			S	Zn
274	H		H	H		S	Zn
275	H	H		H		S	Zn

[0375]

276		H	H	H		S	Zn
277	H	H	H			S	Zn
278	H	H		H		S	Zn
279	H	H	H			S	Zn
280	H		H	H		S	Zn
281		H	H	H		S	Zn
282		H	H	H		S	Zn
283	H		H	H		S	Zn
284	H	H		H		S	Zn
285	H	H	H			S	Zn


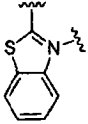

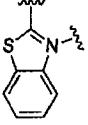

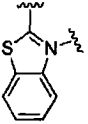

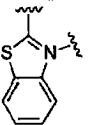

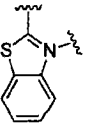

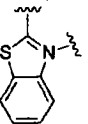
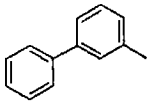
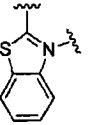
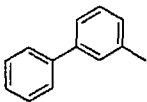
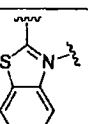
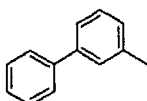
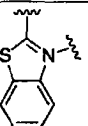
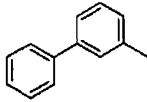
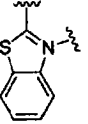
[0376]

286	H	H	-CH ₃	H		S	Zn
287	H	-CH ₃	H	H		S	Zn
288	H	H	H	-CH ₃		S	Zn
289	-CH ₃	H	H	H		S	Zn
290	H	-CH ₃	H	-CH ₃		S	Zn
291	-CH ₃	H	-CH ₃	H		S	Zn
292	H	-CH ₃	-CH ₃	H		S	Zn
293	H	H	-CH ₃	-CH ₃		S	Zn
294	-CH ₃	-CH ₃	H	H		S	Zn
295	-CH ₃	H	H	-CH ₃		S	Zn

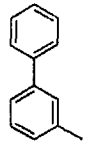
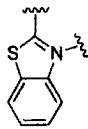
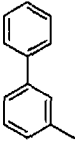
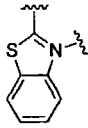
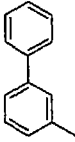
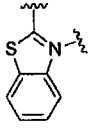
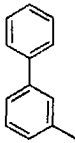
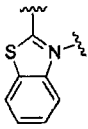
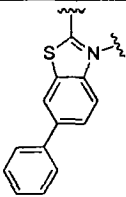
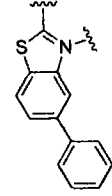
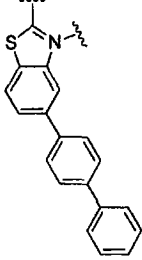
[0377]

296	$-\text{C}(\text{CH}_3)_3$	H	H	H		S	Zn
297	H	$-\text{C}(\text{CH}_3)_3$	H	H		S	Zn
298	H	H	$-\text{C}(\text{CH}_3)_3$	H		S	Zn
299	H	H	H	$-\text{C}(\text{CH}_3)_3$		S	Zn
300		H	H	H		S	Zn
301	H	H		H		S	Zn
302	H	H	H			S	Zn
303	H		H	H		S	Zn
304	H	$-\text{C}(\text{CH}_3)_3$	H	$-\text{CH}_3$		S	Zn
305	H	$-\text{CH}_3$	H	$-\text{C}(\text{CH}_3)_3$		S	Zn

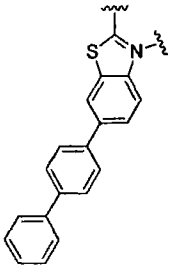
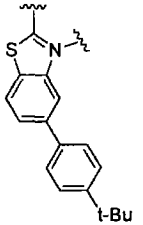
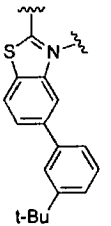
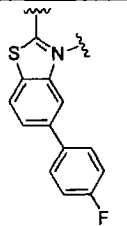
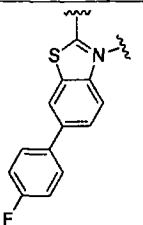
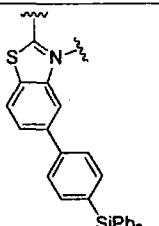
[0378]

306	H		H	H		S	Zn
307	H	H		H		S	Zn
308	H		H	H		S	Zn
309	H	H		H		S	Zn
310	H		H	-CH ₃		S	Zn
311	H	-CH ₃	H			S	Zn
312		H	H	H		S	Zn
313	H		H	H		S	Zn
314	H	H		H		S	Zn
315	H	H	H			S	Zn

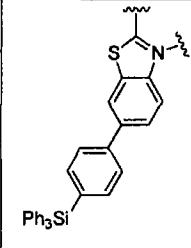
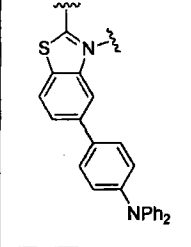
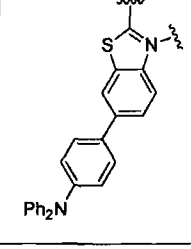
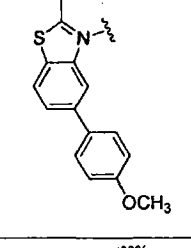
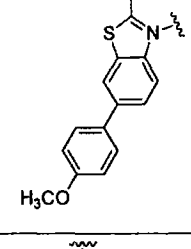
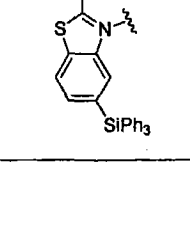
[0379]

316	H	H		H		S	Zn
317	H		H	H		S	Zn
318	H	H	H			S	Zn
319		H	H	H		S	Zn
320	H	H	H	H		S	Zn
321	H	H	H	H		S	Zn
322	H	H	H	H		S	Zn

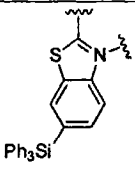
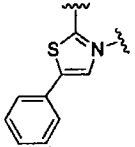
[0380]

323	H	H	H	H		S	Zn
324	H	H	H	H		S	Zn
325	H	H	H	H		S	Zn
326	H	H	H	H		S	Zn
327	H	H	H	H		S	Zn
328	H	H	H	H		S	Zn

[0381]

329	H	H	H	H		S	Zn
330	H	H	H	H		S	Zn
331	H	H	H	H		S	Zn
332	H	H	H	H		S	Zn
333	H	H	H	H		S	Zn
334	H	H	H	H		S	Zn

[0382]

335	H	H	H	H		S	Zn
336	H	H	H	H		S	Zn

[0383] 表2

[0384]

化合物 编号	¹ H NMR (CDCl ₃ , 200 MHz)	MS/FAB	
		实测值	理论值
19	$\delta = 6.85$ (d, 2H), 7.22-7.32 (m, 8H), 7.48-7.55 (m, 10H), 8.12-8.23 (dd, 4H)	668.1	670.1
21	$\delta = 6.85$ (m, 2H), 7.27-7.38 (m, 8H), 7.54-7.67 (m, 14H), 8.13-8.25 (m, 4H)	668.1	670.1
23	$\delta = 6.85$ (m, 2H), 7.27-7.32 (m, 8H), 7.48-7.55 (m, 18H), 8.12-8.23 (m, 4H)	704.0	706.1
25	$\delta = 7.03$ -7.10 (m, 8H), 7.37 (m, 2H), 7.46-7.55 (m, 8H), 8.12-8.25 (m, 4H)	704.0	706.1
27	$\delta = 6.85$ (m, 2H), 7.27-7.32 (m, 8H), 7.48-7.55 (m, 18H), 8.12-8.23 (m, 4H)	820.1	822.3
29	$\delta = 7.05$ (m, 2H), 7.10 (m, 2H), 7.22 (m, 2H), 7.32-7.37 (m, 6H), 7.46-7.56 (m, 16H), 8.12 (d, 2H), 8.23 (d, 2H)	820.1	822.3
32	$\delta = 1.34$ (s, 18H), 6.85 (m, 2H), 7.27 (m, 2H), 7.35-7.40 (m, 8H), 7.53-7.56 (m, 6H), 8.12-8.23 (dd, 4H)	780.2	782.3
33	$\delta = 1.34$ (s, 18H), 7.01-7.10 (m, 4H), 7.35-7.40 (m, 10H), 7.55 (m, 4H), 8.14-8.25 (m, 4H)	780.2	782.3
36	$\delta = 6.64$ (m, 2H), 6.85 (m, 2H), 6.96 (m, 4H), 7.27 (m, 2H), 7.53-7.55 (m, 6H), 8.24-8.25 (m, 4H)	740.0	742.1

[0385]

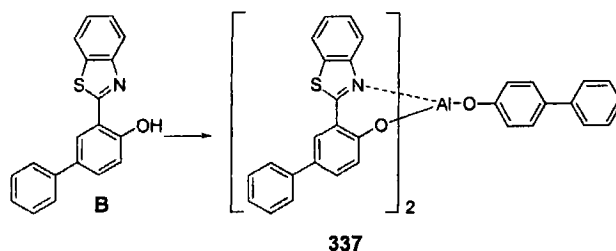
39	$\delta = 6.74-6.85$ (m, 6H), 7.27 (m, 2H), 7.44 (m, 2H), 7.53-7.55 (m, 6H), 8.12-8.23 (m, 4H)	740.0	742.1
44	$\delta = 6.51$ (m, 4H), 6.85 (m, 2H), 7.27 (m, 2H), 7.52-7.54 (m, 6H), 8.12 (m, 2H), 8.24 (m, 2H)	776.0	778.1
99	$\delta = 6.46-6.52$ (m, 12H), 6.62 (m, 4H), 7.01 (m, 12H), 7.23 (m, 4H), 7.37 (m, 2H), 7.55 (m, 4H), 8.12 (m, 2H), 8.23 (m, 2H)	1002.2	1004.5
100	$\delta = 6.46-6.52$ (m, 12H), 6.62 (m, 4H), 6.85 (m, 2H), 7.01 (m, 8H), 7.23-7.27 (m, 6H), 7.53-7.55 (m, 6H), 8.23-8.25 (m, 4H)	1002.2	1004.5
103	$\delta = 6.85$ (m, 2H), 7.27-7.32 (m, 6H), 7.52-7.56 (m, 8H), 7.67-7.73 (m, 6H), 7.89 (m, 2H), 8.12-8.23 (m, 4H)	768.1	770.2
109	$\delta = 6.85$ (m, 2H), 7.27-7.38 (m, 8H), 7.54-7.67 (m, 14H), 8.13-8.25 (m, 4H)	768.1	770.2
111	$\delta = 1.67$ (s, 12H), 7.27-7.28 (m, 4H), 7.38 (m, 2H), 7.55-7.60 (m, 10H), 7.77 (m, 2H), 7.84-7.90 (m, 4H), 8.13-8.25 (m, 4H)	900.2	902.4
124	$\delta = 6.85$ (m, 2H), 7.27 (m, 2H), 7.36 (m, 18H), 7.53-7.60 (m, 26H), 8.15-8.25 (m, 4H)	1184.2	1186.9
125	$\delta = 7.01$ (s, 2H), 7.10 (m, 2H), 7.36-7.37 (m, 20H), 7.54-7.60 (m, 24H), 8.12 (d, 2H), 8.24 (d, 2H)	1184.2	1186.9
161	$\delta = 6.79-6.88$ (m, 4H), 7.05 (m, 2H), 7.22-7.32 (m, 8H), 7.48 (m, 4H), 7.77 (m, 2H), 8.29-8.34 (m, 4H)	668.1	670.1
162	$\delta = 6.79-6.88$ (m, 4H), 7.05 (m, 2H), 7.22-7.32 (m, 8H), 7.48 (m, 4H), 7.77 (m, 2H), 8.18 (m, 2H), 8.45 (m, 2H)	668.1	670.1
163	$\delta = 7.79$ (m, 2H), 6.88 (m, 2H), 7.05 (m, 2H), 7.31-7.32 (m, 8H), 7.48-7.54 (m, 12H), 7.77 (m, 2H), 8.18 (m, 2H), 8.43 (m, 2H)	820.1	822.3
164	$\delta = 6.78-6.80$ (m, 4H), 7.04 (m, 2H), 7.22 (m, 2H), 7.31-7.32 (m, 6H), 7.48-7.54 (m, 12H), 7.77 (m, 2H), 8.30-8.33 (m, 4H)	820.1	822.3
165	$\delta = 1.36$ (s, 18H), 6.78-6.89 (m, 4H), 7.05 (m, 2H), 7.31-7.40 (m, 10H), 7.78 (m, 2H), 8.20 (m, 2H), 8.50 (m, 2H)	780.2	782.3
166	$\delta = 1.34$ (s, 18H), 6.70 (m, 2H), 6.88 (m, 2H), 7.07 (m, 2H), 7.31-7.40 (m, 10H), 7.77 (m, 2H), 8.28-8.32 (m, 4H)	780.2	782.3
167	$\delta = 6.80-6.90$ (m, 4H), 7.03-7.05 (m, 6H), 7.31 (m, 2H), 7.46 (m, 4H), 7.77 (m, 2H), 8.18 (m, 2H), 8.45 (m, 2H)	704.0	706.1
168	$\delta = 6.80-6.90$ (m, 4H), 7.03-7.08 (m, 6H),	704.0	706.1

[0386]

	7.31(m, 2H), 7.46(m, 4H), 7.77(m, 2H), 8.29-8.34(m, 4H)		
169	δ = 6.79(m, 2H), 6.88(m, 2H), 7.05(m, 2H), 7.31-7.36(m, 20H), 7.54-7.60(m, 20H), 7.77(m, 2H), 8.18(m, 2H), 8.46(m, 2H)	1184.2	1186.9
170	δ = 6.79(m, 2H), 6.88(m, 2H), 7.05(m, 2H), 7.31-7.36(m, 20H), 7.54-7.60(m, 20H), 7.77(m, 2H), 8.30-8.34(m, 4H)	1184.2	1186.9
171	δ = 6.46-6.52(m, 12H), 6.62(m, 4H), 6.79(m, 2H), 6.88(m, 2H), 7.01-7.05(m, 10H), 7.23-7.31(m, 6H), 7.77(m, 2H), 8.18(m, 2H), 8.46(m, 2H)	1002.2	1004.5
172	δ = 6.46-6.52(m, 12H), 6.62(m, 4H), 6.79-6.88(m, 4H), 7.01-7.05(m, 10H), 7.23(m, 4H), 7.31(m, 2H), 7.77(m, 2H), 8.30-8.34(m, 4H)	1002.2	1004.5
178	δ = 8.23(d, 2H), 8.13(d, 2H), 7.55-7.20(m, 20H)	700.1	700.0
191	δ = 1.34(s, 18H), 7.28-7.30(m, 4H), 7.35-7.40(m, 4H), 7.54(m, 6H), 8.12(m, 2H), 8.23(m, 2H)	814.1	812.1
194	δ = 6.64(m, 2H), 6.96(m, 4H), 7.32-7.38(m, 4H), 7.55(m, 4H), 8.12(m, 2H), 8.23(m, 2H)	773.9	771.9
223	δ = 2.35(s, 12H), 6.82(d, 2H), 7.09(s, 4H), 7.28-7.30(m, 4H), 7.55(m, 6H), 8.15-8.24(m, 4H)	758.0	756.1
259	δ = 6.46-6.52(m, 12H), 6.62(m, 4H), 7.02(m, 8H), 7.24-7.30(m, 8H), 7.56(m, 6H), 8.13(t, 2H), 8.23(t, 2H)	1035.1	1034.2
283	δ = 7.30-7.36(m, 22H), 7.54-7.60(m, 26H), 8.12(m, 2H), 8.24(m, 2H)	1219.2	1216.3
287	δ = 2.34(s, 6H), 6.86(m, 2H), 7.12(d, 4H), 7.57(m, 4H), 8.13-8.25(m, 4H)	577.9	575.9
291	δ = 2.36(s, 12H), 6.70(s, 2H), 6.85(s, 2H), 7.55(m, 4H), 8.14-8.25(m, 4H)	606.0	604.5
311	δ = 2.36(s, 6H), 7.08(s, 4H), 7.22(m, 2H), 7.32(m, 4H), 7.48(m, 8H), 8.20(m, 4H)	730.0	728.4
320	δ = 7.06-7.10(m, 4H), 7.24-7.32(m, 10H), 7.48(m, 4H), 7.77(m, 2H), 8.29-8.34(m, 4H)	702.1	700.1
336	δ = 7.06-7.12(m, 4H), 7.22-7.34(m, 10H), 7.48(m, 4H), 8.00(s, 2H)	601.9	599.9

[0387] [制备例 3] 制备化合物 (337)

[0388]

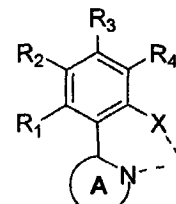
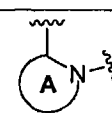

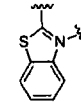
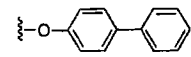

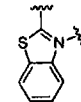
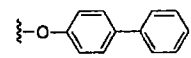

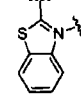
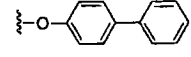

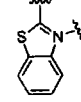
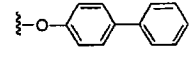
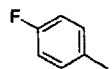
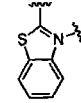
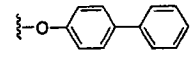
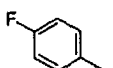
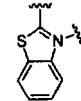
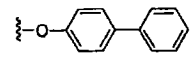


[0389] 将化合物 (B) (4.5g, 14.8mmol) 和异丙醇铝 (3.0g, 14.8mmol) 溶于氯仿 (50mL)/异丙醇 (150mL), 并于 60℃ 搅拌溶液 3 小时。当溶液变得澄清时在其中加入 4-苯基苯酚 (3.0g, 17.8mmol), 并于 80℃ 回流搅拌所得混合物 3 小时。然后在其中加入化合物 (B) (4.5g, 14.8mmol) 并回流搅拌混合物 12 小时。当反应结束时, 将反应混合物冷却至室温, 通过减压过滤收集产生的固体。该固体依次用异丙醇 (500mL)、甲醇 (300mL) 和乙醚 (250mL) 洗涤以获得标题化合物 (337) (3.8g, 7.6mmol, 51%)。

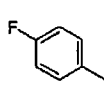
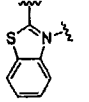
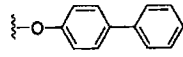
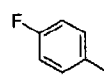
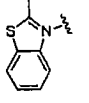
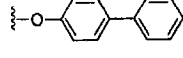
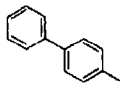
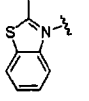
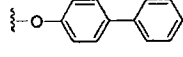
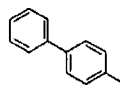
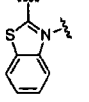
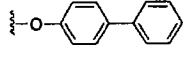
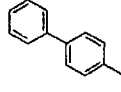
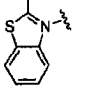
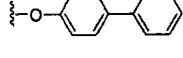
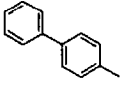
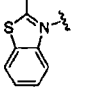
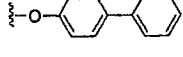
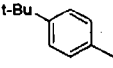
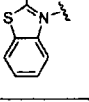
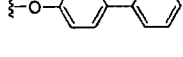
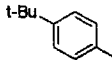
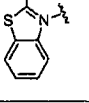
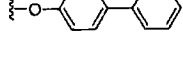
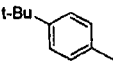
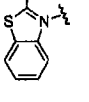
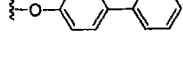
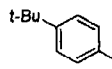
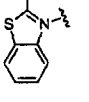
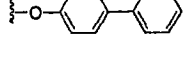
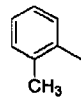
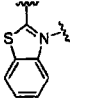
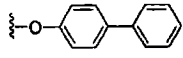
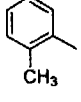
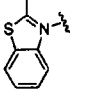
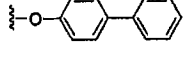
[0390] 根据与制备例 21 相同的方法制备了表 3 中列出的化合物 337-426, 其 ¹H NMR 和 MS/FAB 数据列于表 4。表 3 所列化合物是含有三价金属 M 的化合物。

[0391] 表 3



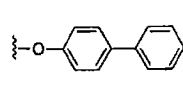


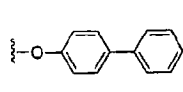


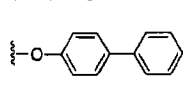


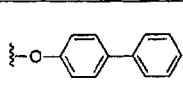


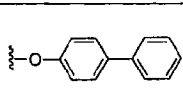


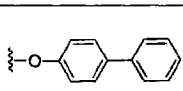
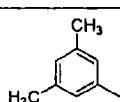
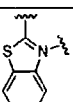
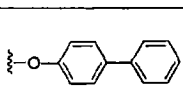
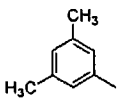
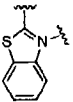
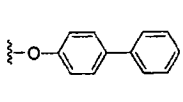
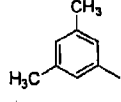
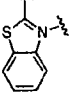
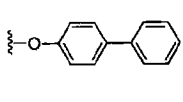
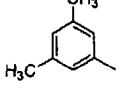
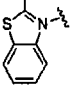
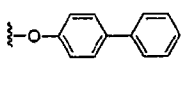
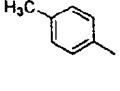

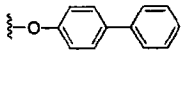
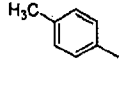

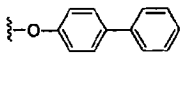
[0392]

L ¹ L ² M(Q) _y									
 L ¹ = L ² =							M	Q	y
编号	R ₁	R ₂	R ₃	R ₄		X			
337	H		H	H		O	Al		1
338		H	H	H		O	Al		1
339	H	H		H		O	Al		1
340	H	H	H			O	Al		1
341	H		H	H		O	Al		1
342	H	H		H		O	Al		1

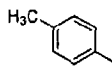
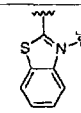
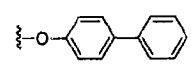
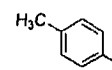
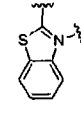
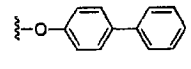
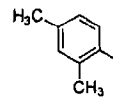
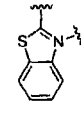
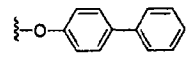
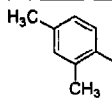
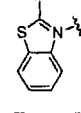
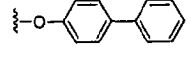
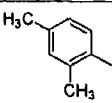
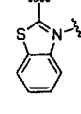
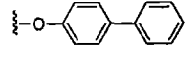
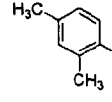
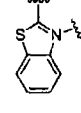
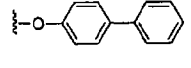
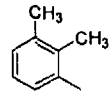
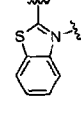
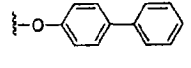
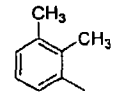
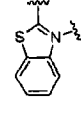
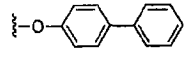
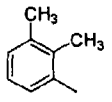
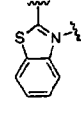
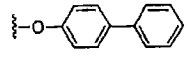
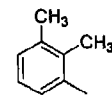
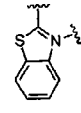
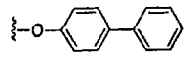
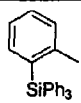
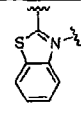
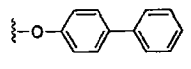
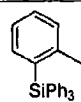
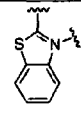
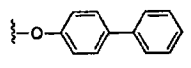
[0393]

343	H	H	H			O	Al		1
344		H	H	H		O	Al		1
345	H		H	H		O	Al		1
346		H	H	H		O	Al		1
347	H	H		H		O	Al		1
348	H	H	H			O	Al		1
349	H	H		H		O	Al		1
350	H		H	H		O	Al		1
351	H	H		H		O	Al		1
352		H	H	H		O	Al		1
353	H		H	H		O	Al		1
354	H	H		H		O	Al		1

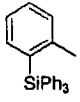
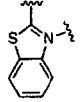
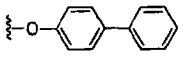
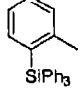
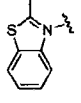
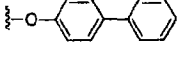
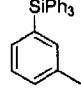
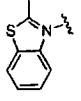
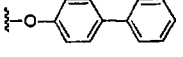
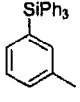
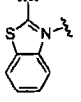
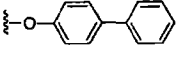
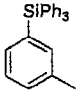
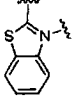
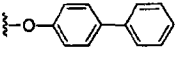
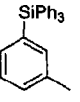
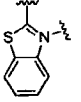
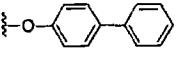
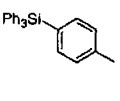
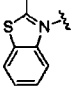
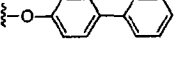
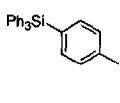
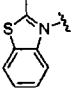
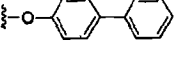
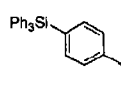
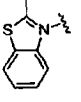
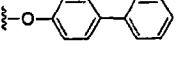
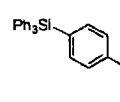
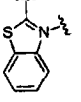
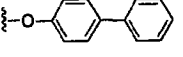
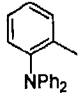
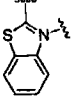
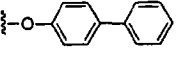
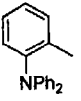
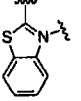
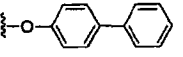
[0394]

355		H	H	H		O	Al		1
356	H	H	H			O	Al		1
357	H		H	H		O	Al		1
358	H	H		H		O	Al		1
359	H	H	H			O	Al		1
360		H	H	H		O	Al		1
361		H	H	H		O	Al		1
362	H		H	H		O	Al		1
363	H	H		H		O	Al		1
364	H	H	H			O	Al		1
365	H		H	H		O	Al		1
366	H	H		H		O	Al		1



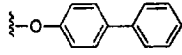
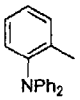
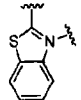
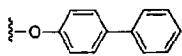



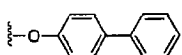


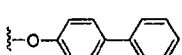
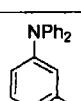
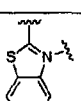
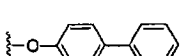
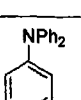
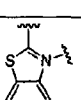
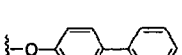
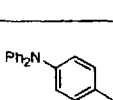
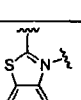
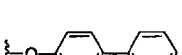
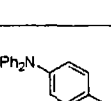
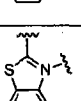

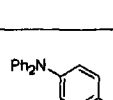
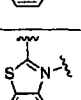

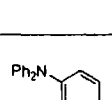
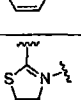

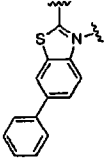

[0395]

367		H	H	H		O	Al		1
368	H	H	H			O	Al		1
369	H	H		H		O	Al		1
370	H		H	H		O	Al		1
371		H	H	H		O	Al		1
372	H	H	H			O	Al		1
373	H		H	H		O	Al		1
374	H	H		H		O	Al		1
375		H	H	H		O	Al		1
376	H	H	H			O	Al		1
377	H		H	H		O	Al		1
378	H	H		H		O	Al		1

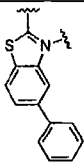
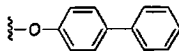
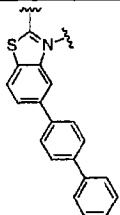
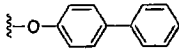
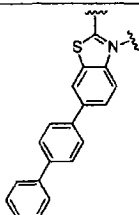
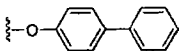
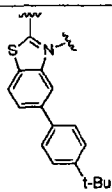
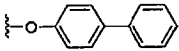
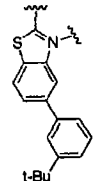
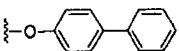
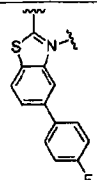
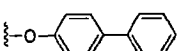
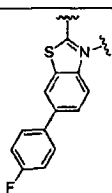
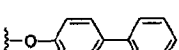
[0396]

379		H	H	H		O	Al		1
380	H	H	H			O	Al		1
381	H	H		H		O	Al		1
382	H	H	H			O	Al		1
383	H		H	H		O	Al		1
384		H	H	H		O	Al		1
385		H	H	H		O	Al		1
386	H		H	H		O	Al		1
387	H	H		H		O	Al		1
388	H	H	H			O	Al		1
389	H	H		H		O	Al		1
390	H		H	H		O	Al		1

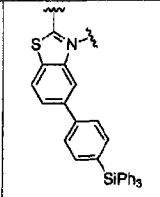
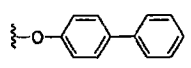
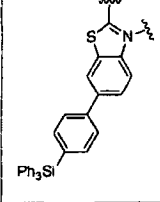
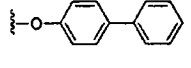
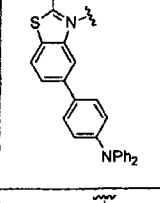
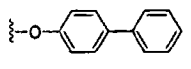
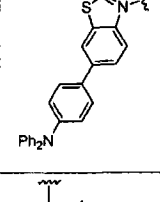
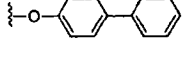
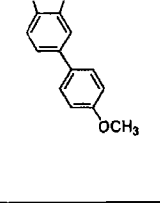
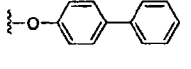
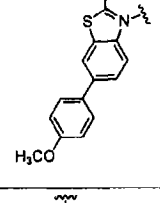
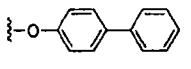
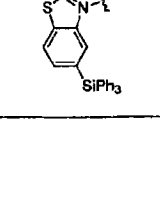
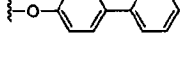
[0397]

391	H	H	H			O	Al		1
392		H	H	H		O	Al		1
393		H		H		O	Al		1
394	H		H	H		O	Al		1
395	H	H		H		O	Al		1
396	H	H	H			O	Al		1
397	H	H		H		O	Al		1
398	H		H	H		O	Al		1
399	H	H	H			O	Al		1
400		H	H	H		O	Al		1
401	H	H	H	H		O	Al		1

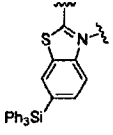
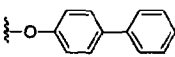
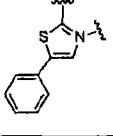
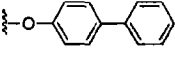
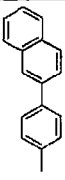
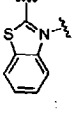
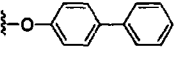
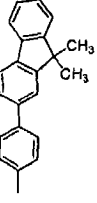
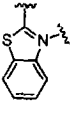
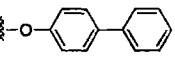
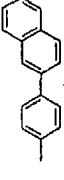
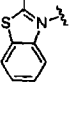
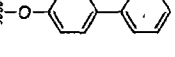
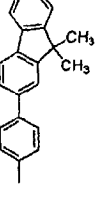
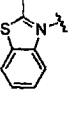
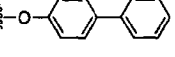

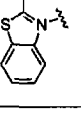
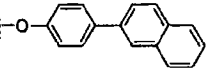

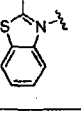
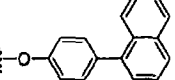

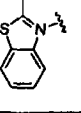
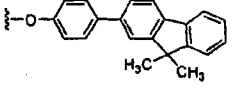
[0398]

402	H	H	H	H		O	Al		1
403	H	H	H	H		O	Al		1
404	H	H	H	H		O	Al		1
405	H	H	H	H		O	Al		1
406	H	H	H	H		O	Al		1
407	H	H	H	H		O	Al		1
408	H	H	H	H		O	Al		1


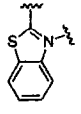
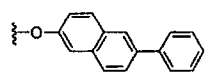

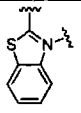
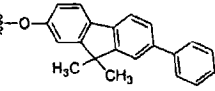
[0399]

409	H	H	H	H		O	Al		1
410	H	H	H	H		O	Al		1
411	H	H	H	H		O	Al		1
412	H	H	H	H		O	Al		1
413	H	H	H	H		O	Al		1
414	H	H	H	H		O	Al		1
415	H	H	H	H		O	Al		1

[0400]

416	H	H	H	H		O	Al		1
417	H	H	H	H		O	Al		1
418	H		H	H		O	Al		1
419	H		H	H		O	Al		1
420	H	H		H		O	Al		1
421	H	H		H		O	Al		1
422	H		H	H		O	Al		1
423	H		H	H		O	Al		1
424	H		H	H		O	Al		1

[0401]

425	H		H	H		O	Al		1
426	H		H	H		O	Al		1

[0402] 表 4

[0403]

化合物 编号	$^1\text{H NMR}(\text{CDCl}_3, 200 \text{ MHz})$	MS/FAB	
		实测值	理论值
337	$\delta = 6.79-6.85(\text{m}, 4\text{H}), 7.27-7.32(\text{m}, 18\text{H}), 7.48-7.56(\text{m}, 12\text{H}), 8.12-8.25(\text{m}, 4\text{H})$	801.2	800.2
340	$\delta = 6.79-6.85(\text{m}, 4\text{H}), 7.03(\text{m}, 4\text{H}), 7.22-7.32(\text{m}, 7\text{H}), 7.46-7.56(\text{m}, 12\text{H}), 8.14-8.25(\text{m}, 4\text{H})$	837.2	836.2
350	$\delta = 1.37(\text{s}, 18\text{H}), 6.79-6.90(\text{m}, 4\text{H}), 7.22-7.40(\text{m}, 15\text{H}), 7.48-7.55(\text{m}, 8\text{H}), 8.14-8.25(\text{m}, 4\text{H})$	913.3	912.3
359	$\delta = 2.37(\text{s}, 6\text{H}), 6.79(\text{d}, 2\text{H}), 6.94-7.02(\text{m}, 4\text{H}), 7.20-7.32(\text{m}, 15\text{H}), 7.48-7.55(\text{m}, 6\text{H}), 8.15-8.23(\text{m}, 4\text{H})$	829.2	828.2
362	$\delta = 2.38(\text{s}, 12\text{H}), 6.79-6.84(\text{m}, 6\text{H}), 7.09(\text{s}, 4\text{H}), 7.19-7.34(\text{m}, 7\text{H}), 7.48-7.54(\text{m}, 8\text{H}), 8.13-8.26(\text{m}, 4\text{H})$	857.2	856.2
365	$\delta = 2.24(\text{s}, 6\text{H}), 6.85(\text{m}, 4\text{H}), 7.12(\text{m}, 4\text{H}), 7.28-7.32(\text{m}, 11\text{H}), 7.49-7.55(\text{m}, 8\text{H}), 8.21(\text{m}, 4\text{H})$	829.2	828.2
398	$\delta = 6.46-6.52(\text{m}, 12\text{H}), 6.62(\text{m}, 4\text{H}), 6.80(\text{m}, 4\text{H}), 7.01(\text{m}, 8\text{H}), 7.20-7.33(\text{m}, 11\text{H}), 7.50-7.54(\text{m}, 8\text{H}), 8.10-8.20(\text{m}, 4\text{H})$	1135.3	1134.3

[0404]

401	$\delta = 6.79$ (m, 4H), 6.88 (m, 2H), 7.05 (m, 2H), 7.20-7.35 (m, 13H), 7.48 (m, 6H), 7.77 (m, 2H), 8.29-8.34 (m, 4H)	800.9	800.1
416	$\delta = 6.79$ (m, 4H), 6.88 (m, 2H), 7.05 (m, 2H), 7.22 (m, 1H), 7.31-7.36 (m, 11H), 7.48-7.54 (m, 14H), 7.83 (m, 2H), 8.33 (dd, 2H), 8.46 (m, 2H)	1165.5	1164.2
417	$\delta = 6.79$ (m, 4H), 6.88 (m, 2H), 7.05 (m, 2H), 7.22-7.32 (m, 13H), 7.48 (m, 6H), 8.01 (s, 2H)	700.8	700.1
422	$\delta = 6.79-6.85$ (m, 4H), 7.21-7.33 (m, 12H), 7.50- 7.55 (m, 11H), 7.67-7.73 (m, 3H), 7.89 (s, 1H), 8.12-8.23 (m, 4H)	851.1	850.1
423	$\delta = 6.79-7.85$ (m, 4H), 7.25-7.38 (m, 13H), 7.49- 7.67 (m, 14H), 8.13-8.21 (m, 4H)	851.1	850.1
424	$\delta = 1.67$ (s, 6H), 6.79-6.85 (m, 4H), 7.22-7.38 (m, 12H), 7.49-7.56 (m, 12H), 7.77 (d, 1H), 7.84- 7.90 (m, 2H), 8.12 (m, 2H), 8.23 (m, 2H)	917.0	916.2
425	$\delta = 6.85$ (m, 2H), 6.97-6.98 (m, 2H), 7.23-7.32 (m, 11H), 7.48-7.62 (m, 15H), 7.85 (d, 1H), 8.13- 8.25 (m, 4H)	850.9	850.1
426	$\delta = 1.68$ (s, 6H), 6.85 (t, 3H), 7.02 (d, 1H), 7.22-7.32 (m, 11H), 7.48-7.67 (m, 14H), 7.77 (d, 1H), 7.90 (d, 1H), 8.13-8.26 (m, 4H)	917.0	916.2

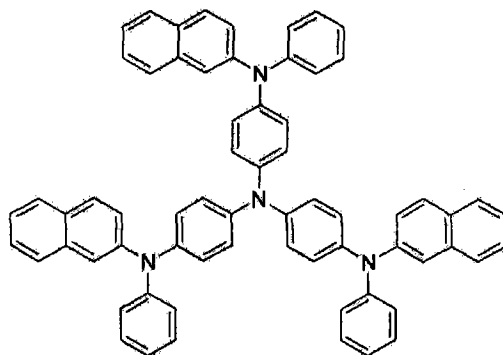
[0405] [实施例 1] 制造 OLED

[0406] 采用本发明的红色磷光化合物制造 OLED 器件。

[0407] 首先,采用三氯乙烯,丙酮,乙醇和蒸馏水,对用玻璃制造的用于 OLED(由三星康宁公司(Samsung Corning)制造)(1)的透明电极 ITO 薄膜(15 Ω /□)(2)进行超声波清洗,继而,在使用前,贮存于异丙醇中。

[0408] 然后,将 ITO 基片置于真空气相沉积装置的基板折叠器(folder)上,将 4,4',4''-三(N,N-(2-萘基)-苯胺)三苯胺(2-TNATA)置于真空气相沉积装置的槽(cell)中,然后抽真空至室内为 10⁻⁶ 托。在该槽上施加电流以蒸发 2-TNATA,因此,在 ITO 基片上产生厚度为 60nm 的空穴注入层(3)的气相沉积层。

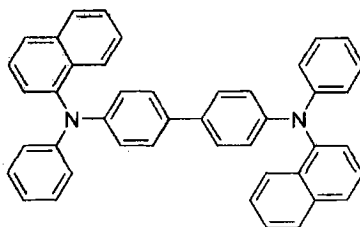
[0409]



2-TNATA

[0410] 接着,在该真空气相沉积装置的另一个槽中加入 N,N' -双(α -萘基)- N,N' -二苯基-4,4'-二胺(NPB),在该槽上施加电流以蒸发 NPB,因此,在空穴注入层上形成厚度为 20nm 的空穴传输层(4)的气相沉积层。

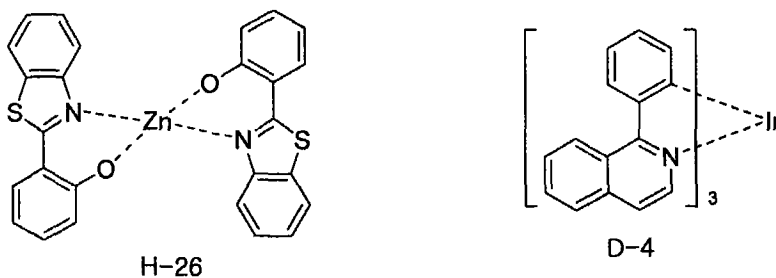
[0411]



NPB

[0412] 在所述真空气相沉积装置的另一个槽中加入本发明的电致发光主体材料(H-26),并再在又一个槽内加入本发明的红色磷光化合物(化合物D-4)。使上述两种物质以不同速率蒸发以进行掺杂,从而在空穴传输层上气相沉积 30nm 厚的电致发光层(5)。基于主体重量,掺杂浓度优选为 4-10 重量%。

[0413]

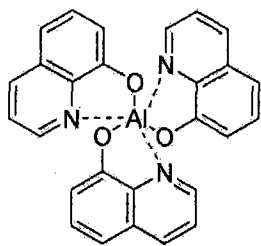


H-26

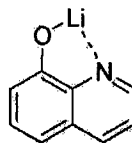
D-4

[0414] 接着,将三(8-羟基喹啉)铝(III)(Alq)通过气相沉积,形成厚度为 20nm 的电子传输层(6),羟基喹啉锂(lithium quinolate)(Liq)(其结构示于下面)通过气相沉积,形成厚度为 1-2nm 的电子注入层(7)。然后,通过另一个真空气相沉积装置,气相沉积以 150nm 厚度的 Al 阴极(8),制备得到 OLED。

[0415]



Alq



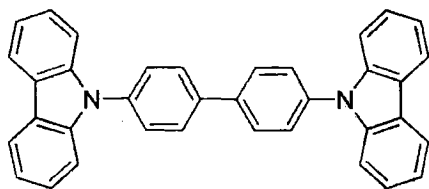
Liq

[0416] [对比例 1] 采用常规磷光主体材料制造 OLED

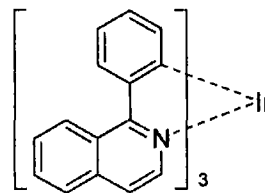
[0417] 按照实施例 1 所述的相同方法形成空穴注入层和空穴传输层之后,如下所述气相沉积电致发光层。

[0418] 在所述真空气相沉积装置的另一个槽内加入 4,4'-N,N'-二咔唑-联苯基 (CBP) 作为电致发光主体材料,并再在另一个槽内加入本发明的红色磷光化合物 (化合物 D-4)。使上述两种物质以不同速率蒸发以进行掺杂,从而在空穴传输层上气相沉积 30nm 厚的电致发光层 (5)。以 CBP 重量为基准,掺杂浓度优选为 4-10 重量%。

[0419]



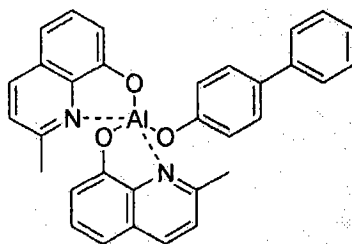
CBP



D-4

[0420] 接着,根据与 NPB 相同的方法,将双 (2-甲基-8-羟基喹啉) (对-苯基苯酚) 铝 (III) (BA1q) 气相沉积在电致发光层上作为空穴阻挡层 (blocking layer),然后将三 (8-羟基喹啉) 铝 (III) (Alq) 气相沉积为 20nm 厚度的电子传输层 (6)。之后,将羟基喹啉锂 (Liq) 气相沉积为 1-2nm 厚度的电子注入层 (7),并采用另一个真空气相沉积装置气相沉积 150nm 厚度的 Al 阴极 (8),从而制备得到 OLED。

[0421]



BA1q

[0422] [实验例 1] 测定制得的 OLED 的性能

[0423] 为检测 OLED 的性能,在 10mA/cm² 条件下,测量实施例 1 中包含本发明所述电致发光化合物的 OLED 和对比例 1 中包含常规电致发光材料的 OLED 的发光效率,结果示于表 5。

[0424] 表 5

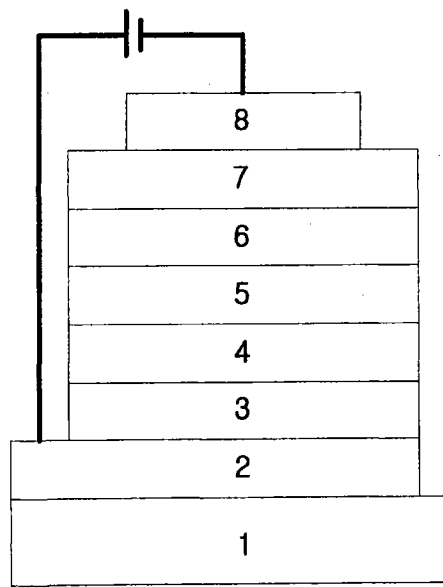
[0425]

材料	主体	空穴阻挡层	EL 颜色	操作电压	最大发光效率 (cd/A)
D-4	H-26	-	红	7.5	7.8
D-6	H-25	-	红	7.3	12.6
D-10	H-28	-	红	7.5	8.4
D-112	H-30	-	红	7.3	9.0
D-113	H-36	-	红	7.1	11.4
0-114	H-57	-	红	7.2	7.2
D-115	H-58	-	红	7.0	11.6
D-116	H-59	-	红	7.1	10.5
D-117	H-78	-	红	7.4	13.6
D-118	化合物 19	-	红	7.1	11.1
D-119	化合物 128	-	红	7.4	12.3
D-120	化合物 133	-	红	7.3	11.3
D-121	化合物 286	-	红	7.1	11.7
化合物 (D-4)	OBP	BA1q	红	8.3	6.5

[0426] 通过采用本发明所述主体和掺杂剂能够制得最高效率为 12.6cd/A 的高效红色磷光 EL 器件。当采用的本发明的主体未使用空穴阻挡层时,制得的 OLED 的效率相当于或者高于采用常规磷光 EL 主体 CBP 制得的器件。

[0427] 本发明所述器件能将操作电压降低 0.9-4.7V 下显著降低 OLED 的功率消耗。

[0428] 如果采用本发明大量制造 OLED,还可缩短大量制造的时间从而更有利于商业化。



专利名称(译)	采用电致发光化合物的电致发光器件		
公开(公告)号	CN101488562B	公开(公告)日	2011-10-12
申请号	CN200810188965.2	申请日	2008-12-31
申请(专利权)人(译)	葛来西雅帝史派有限公司		
当前申请(专利权)人(译)	葛来西雅帝史派有限公司		
[标]发明人	金贤 阴盛镇 赵英俊 权赫柱 金奉玉 金圣珉 尹胜洙		
发明人	金贤 阴盛镇 赵英俊 权赫柱 金奉玉 金圣珉 尹胜洙		
IPC分类号	H01L51/50 H01L51/54 H01L51/42 H01L51/46 C09K11/06		
CPC分类号	H01L51/0084 C09K11/06 C09K2211/1003 C09K2211/1007 C09K2211/1011 C09K2211/1029 C09K2211/1033 C09K2211/1044 C09K2211/1048 C09K2211/1051 C09K2211/1059 C09K2211/186 C09K2211/188 H01L51/0077 H01L51/0085 H01L51/5016 H05B33/14 Y02E10/549		
代理人(译)	陈哲锋		
审查员(译)	刘颖洁		
优先权	1020070141997 2007-12-31 KR		
其他公开文献	CN101488562A		
外部链接	Espacenet SIPO		

摘要(译)

本发明涉及一种电致发光器件。更具体地说，本发明所述的电致发光器件包括第一电极；第二电极；和至少一个插入所述第一电极和所述第二电极之间的有机层；而所述有机层包含一种或多种由化学式(1)代表的有机电致发光化合物作为主体材料：化学式 $1L_1L_2M(Q)_y$ ；其中，配体 L_1 和 L_2 独立地选自以下结构：其中， M 代表二价金属或三价金属；当 M 是二价金属时 y 是0，而当 M 是三价金属时 y 是1； Q 代表(C6-C60)芳氧基或三(C6-C60)芳基甲硅烷基，且 Q 的芳氧基或三芳基甲硅烷基可被(C1-C60)烷基或(C6-C60)芳基进一步取代。本发明的电致发光器件具有出色的色纯度和发光效率。

