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(12) United States Patent
Shibanuma et al.**(10) Patent No.: US 7,186,469 B2**
(45) Date of Patent: *Mar. 6, 2007**(54) BATHOPHENANTHROLINE COMPOUND
AND EL DEVICE****(75) Inventors:** Tetsuo Shibanuma, Kanagawa (JP);
Yasunori Kijima, Tokyo (JP);
Nobutoshi Asai, Kanagawa (JP);
Shinichiro Tamura, Kanagawa (JP)**(73) Assignee:** Sony Corporation, Tokyo (JP)**(*) Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 62 days.This patent is subject to a terminal dis-
claimer.**(21) Appl. No.:** 10/798,820**(22) Filed:** Mar. 11, 2004**(65) Prior Publication Data**

US 2004/0265626 A1 Dec. 30, 2004

Related U.S. Application Data**(63)** Continuation of application No. 09/704,968, filed on
Nov. 2, 2000, now Pat. No. 6,972,334.**(30) Foreign Application Priority Data**

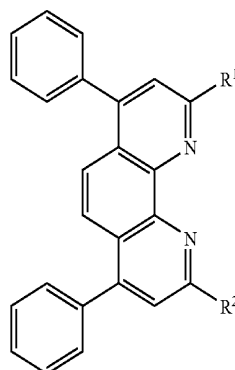
Nov. 2, 1999 (JP) P11-312071

(51) Int. Cl.**H01L 51/54** (2006.01)**H05B 33/12** (2006.01)**(52) U.S. Cl.** 428/690; 428/917; 313/504;
313/506; 257/E51.05**(58) Field of Classification Search** None
See application file for complete search history.**(56) References Cited****U.S. PATENT DOCUMENTS**3,951,833 A 4/1976 Juda et al.
5,077,142 A 12/1991 Sakon et al.
5,262,526 A 11/1993 Sasamoto et al.
6,524,728 B1 * 2/2003 Kijima et al. 428/690**FOREIGN PATENT DOCUMENTS**EP 0564224 10/1993
WO WO99/53724 10/1999**OTHER PUBLICATIONS**Sugihara, H. et al.; "Lithium Ion-Selective Electrodes Based on
1,10-Phenanthroline Derivatives," *Analytical Sciences*, Oct. 1993,
vol. 9, pp. 593-597.
Case, F. et al. "Substituted 1, 10-Phenanthrolines, VIII. 2-and
3-Phenyl Derivatives," *Journal of Organic chemistry*, Oct. 1955,
vol. 20, pp. 1330-1336.
Dietrich-Buchecker, C.O., "Direct Synthesis of Disubstituted Aro-
matic Polyimine Chelates," *Tetrahedron Letters*, 1982, vol. 23 No.
50, pp. 5291-5294.Dietrich-Buchecker, C.O., "Interlocked Macrocyclic Ligands: A
Catenand Whose Rotation of One Ring Into The Other is Precluded
By Bulky Substituents," *Tetrahedron Letters*, 1986, vol. 27, No. 20,
pp. 2257-2260.

* cited by examiner

Primary Examiner—Marie Yaminitzky*(74) Attorney, Agent, or Firm*—Sonnenschein Nath &
Rosenthal LLP**(57) ABSTRACT**A novel bathophenanthroline compound of the general for-
mula [I] or [II] is provided

General Formula [I]:



General Formula [II]:

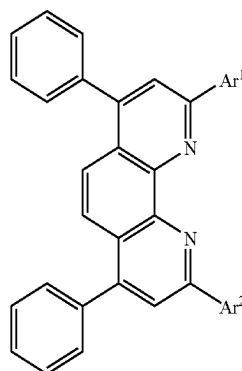
wherein R¹ and R² may be the same or different and
independently represent a linear, branched or cyclic, satu-
rated or unsaturated hydrocarbon group, or a substituted or
unsubstituted, saturated or unsaturated hydrocarbon group
provided that at least one of R¹ and R² has at least two
carbon atoms, and wherein Ar¹ and Ar² may be the same or
different and independently represent a substituted or unsub-
stituted aryl group. A process for preparing the compound is
also provided wherein bathophenanthroline and an organo-
lithium compound are subjected to nucleophilic substitution
reaction to obtain the compound of the above formula [I] or
[II].**24 Claims, 7 Drawing Sheets**

FIG. 1

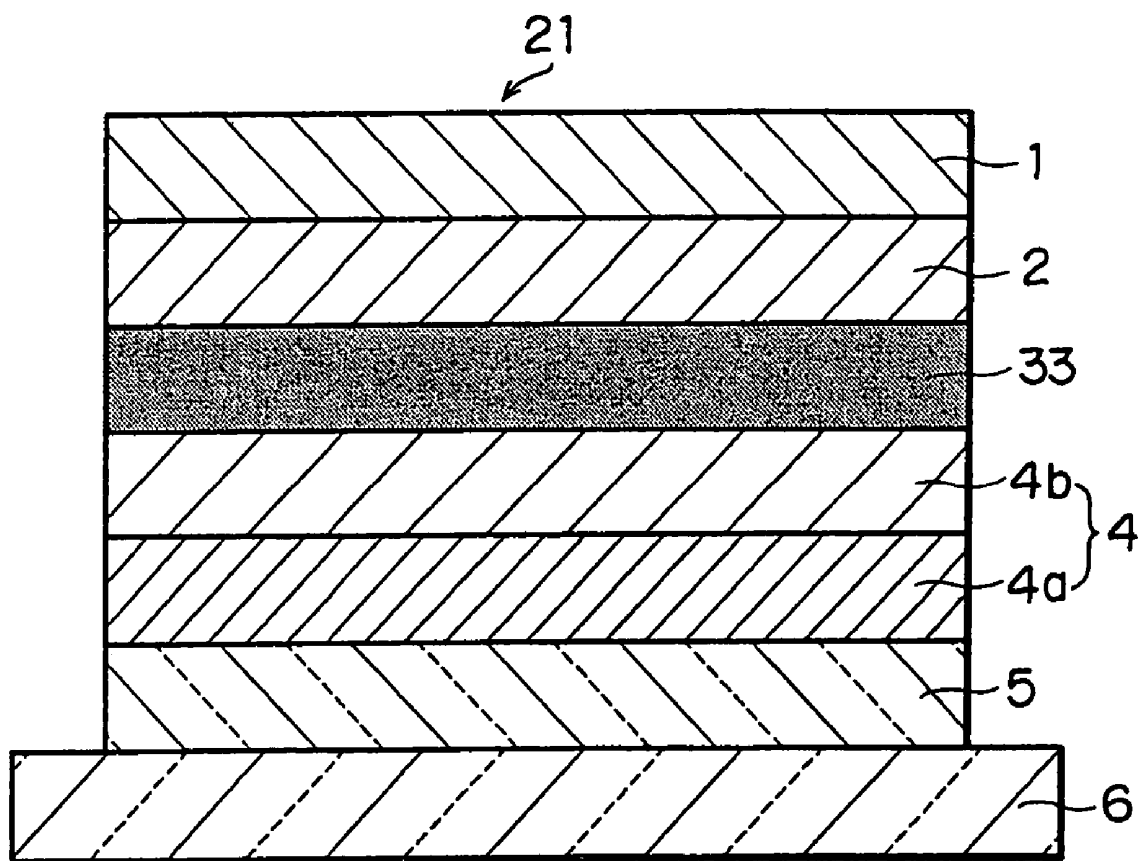


FIG. 2

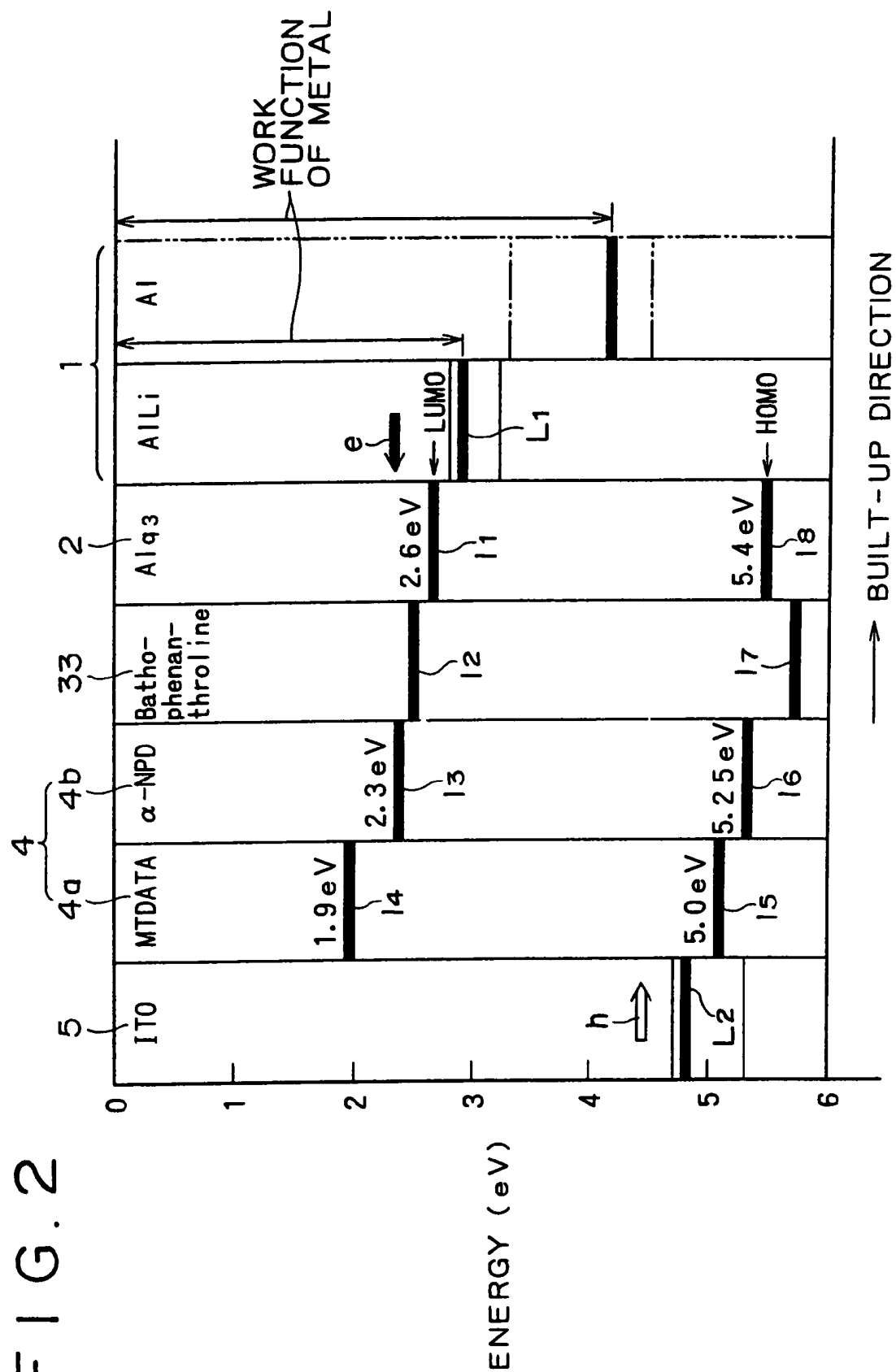


FIG. 3

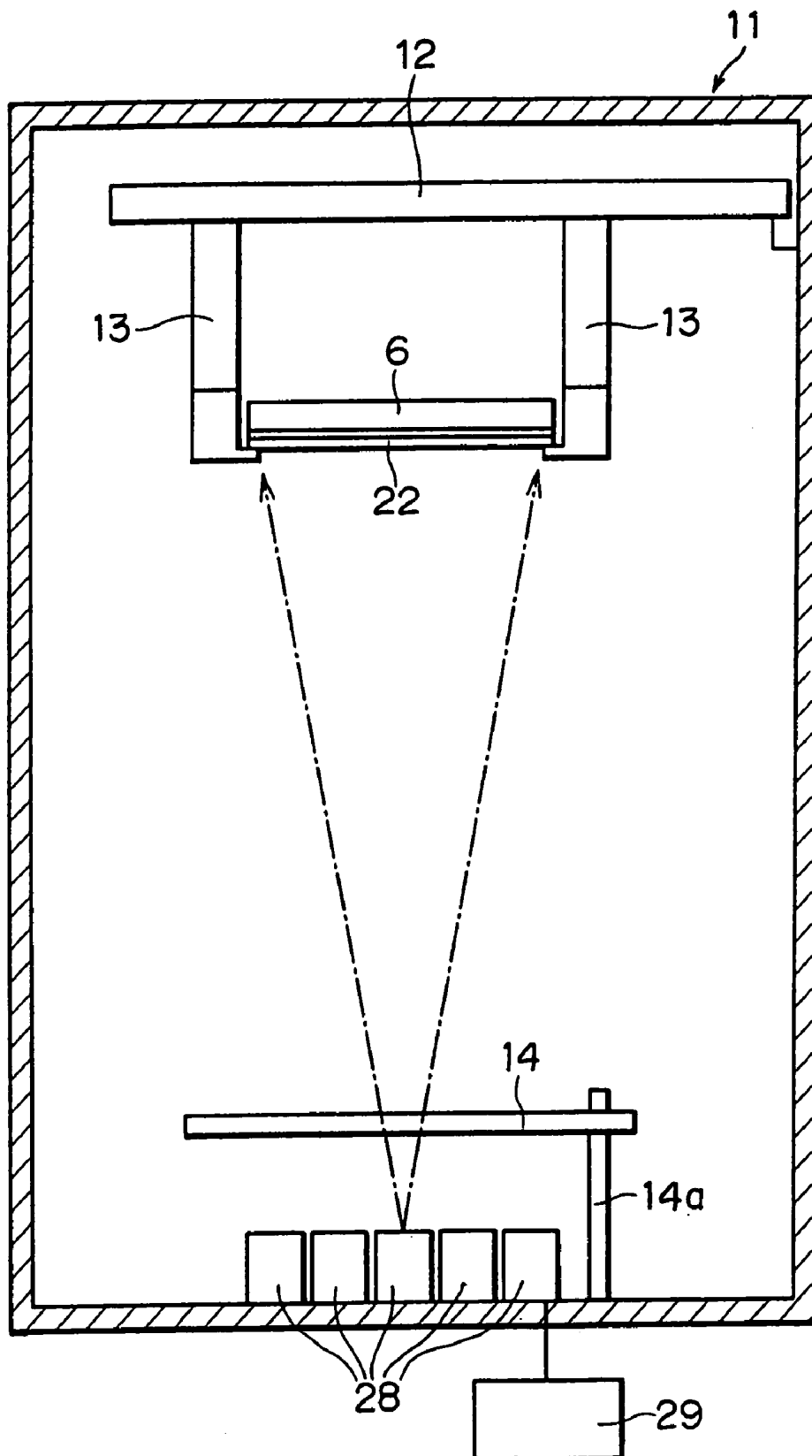


FIG. 4

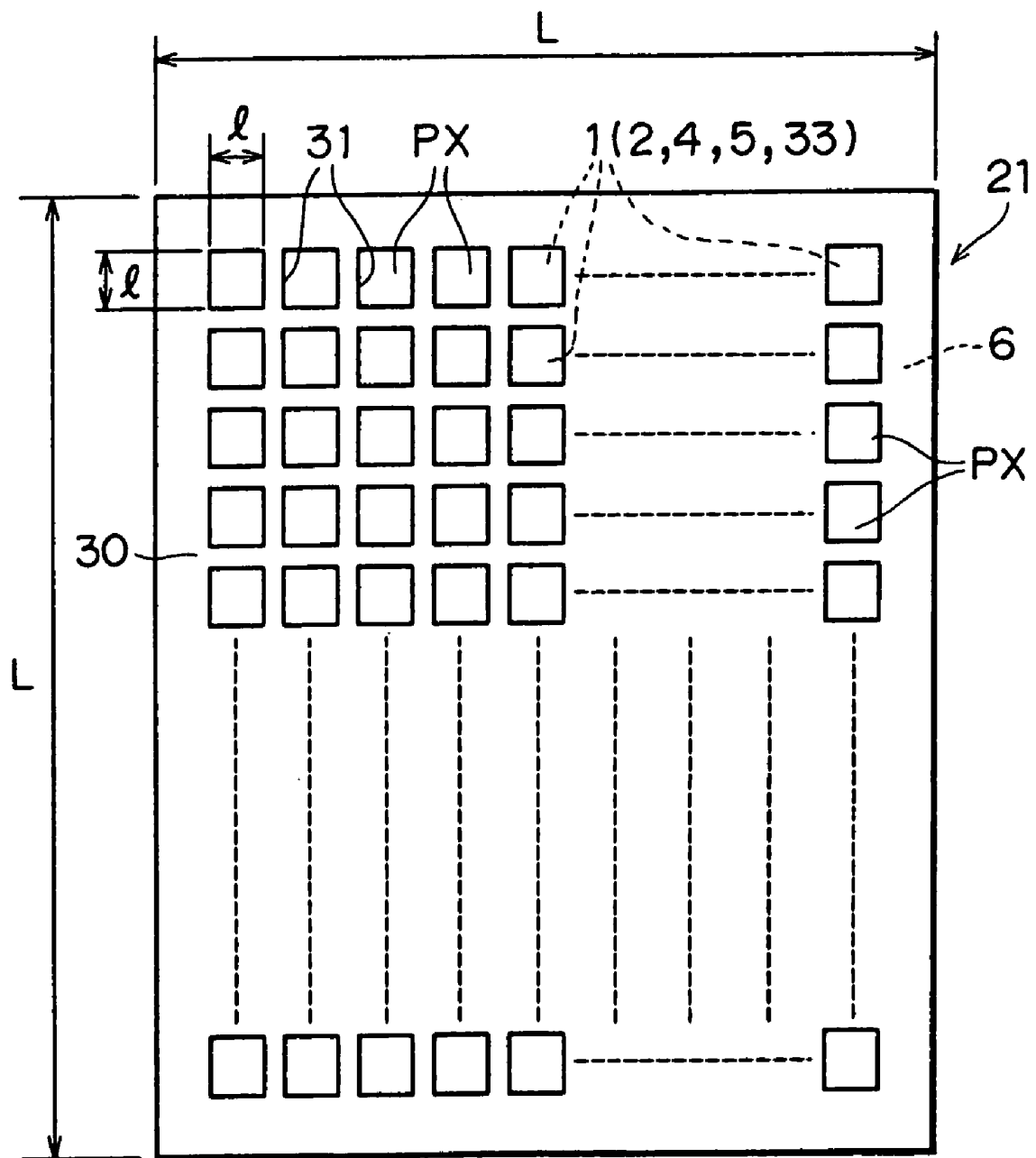


FIG. 5

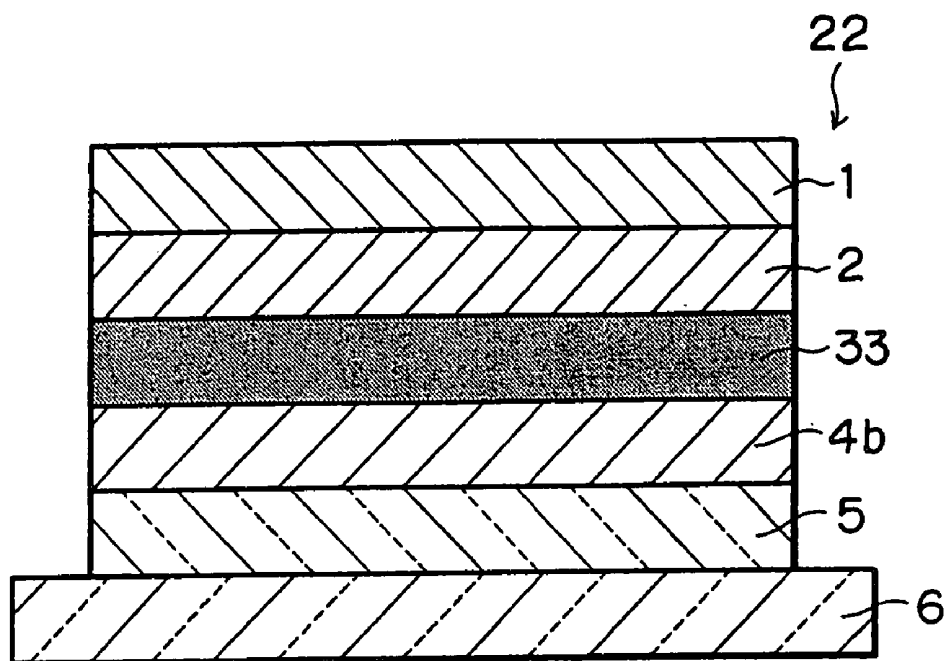


FIG. 6

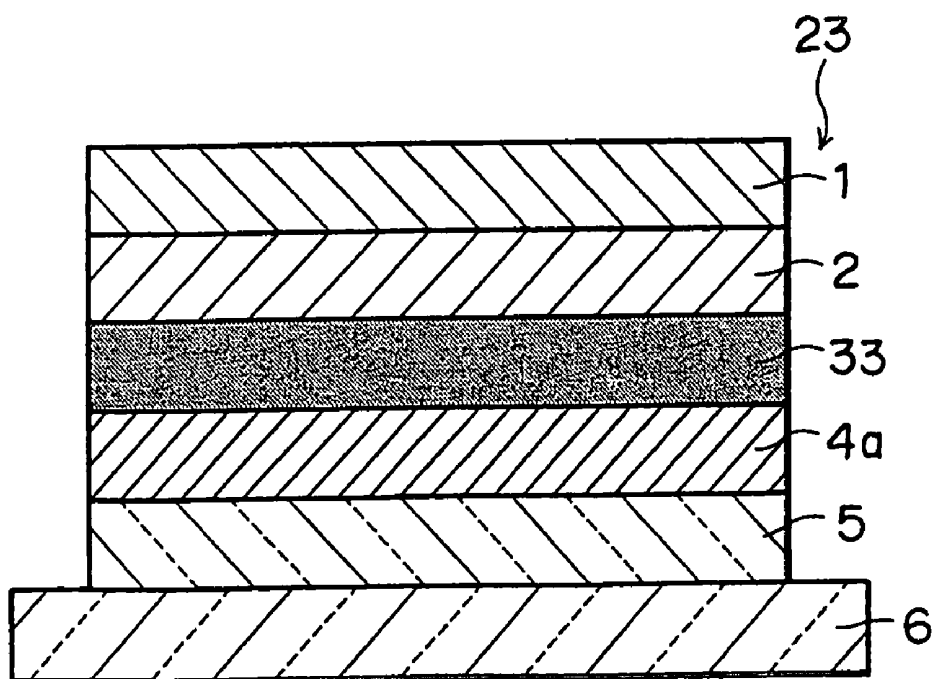


FIG. 7

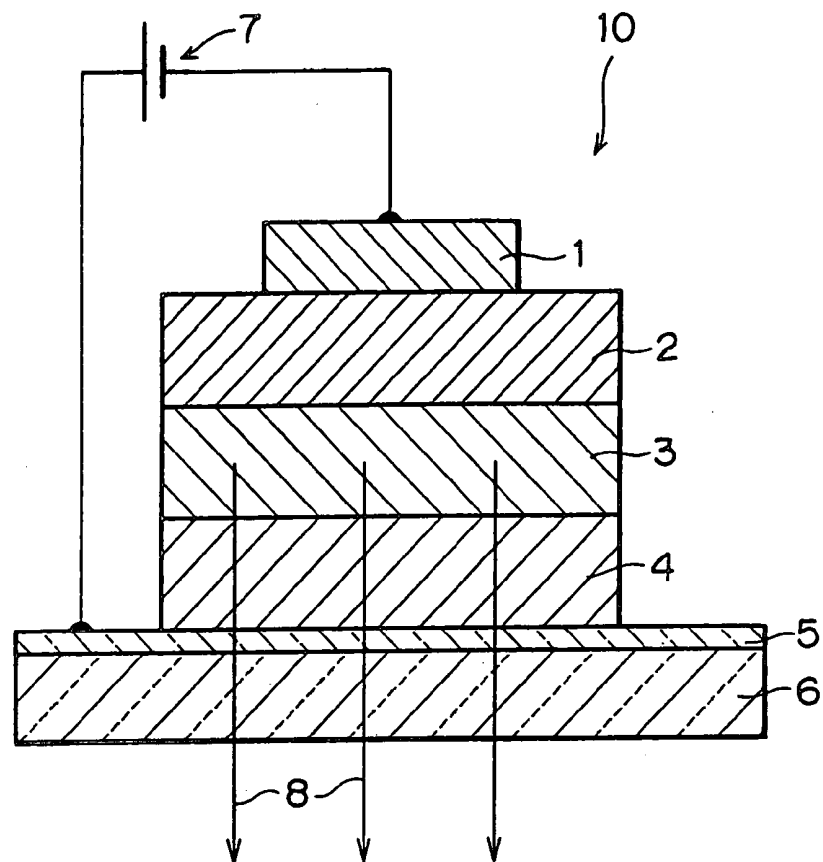


FIG. 8

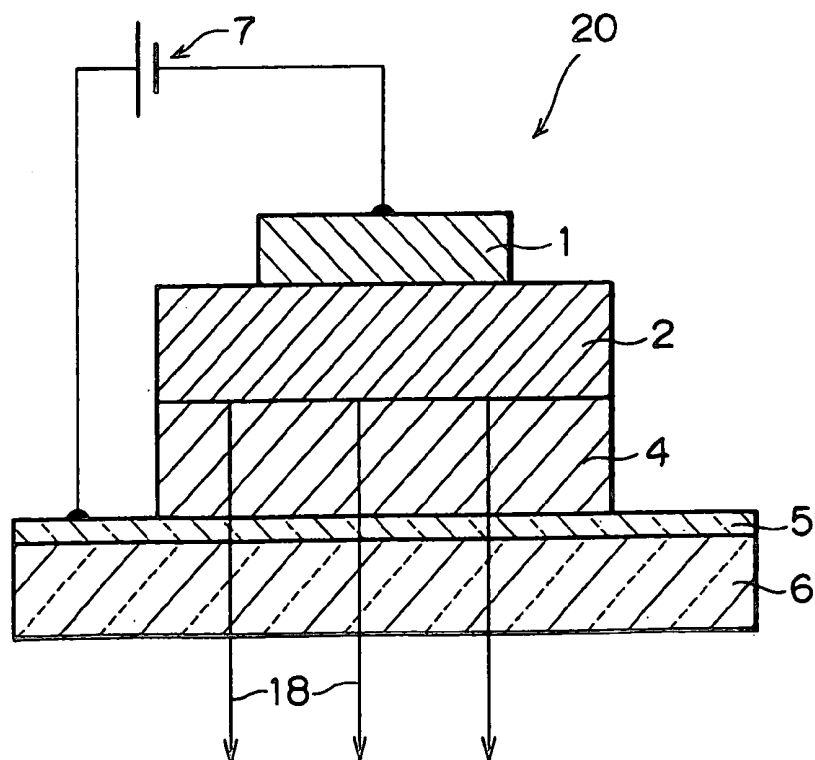
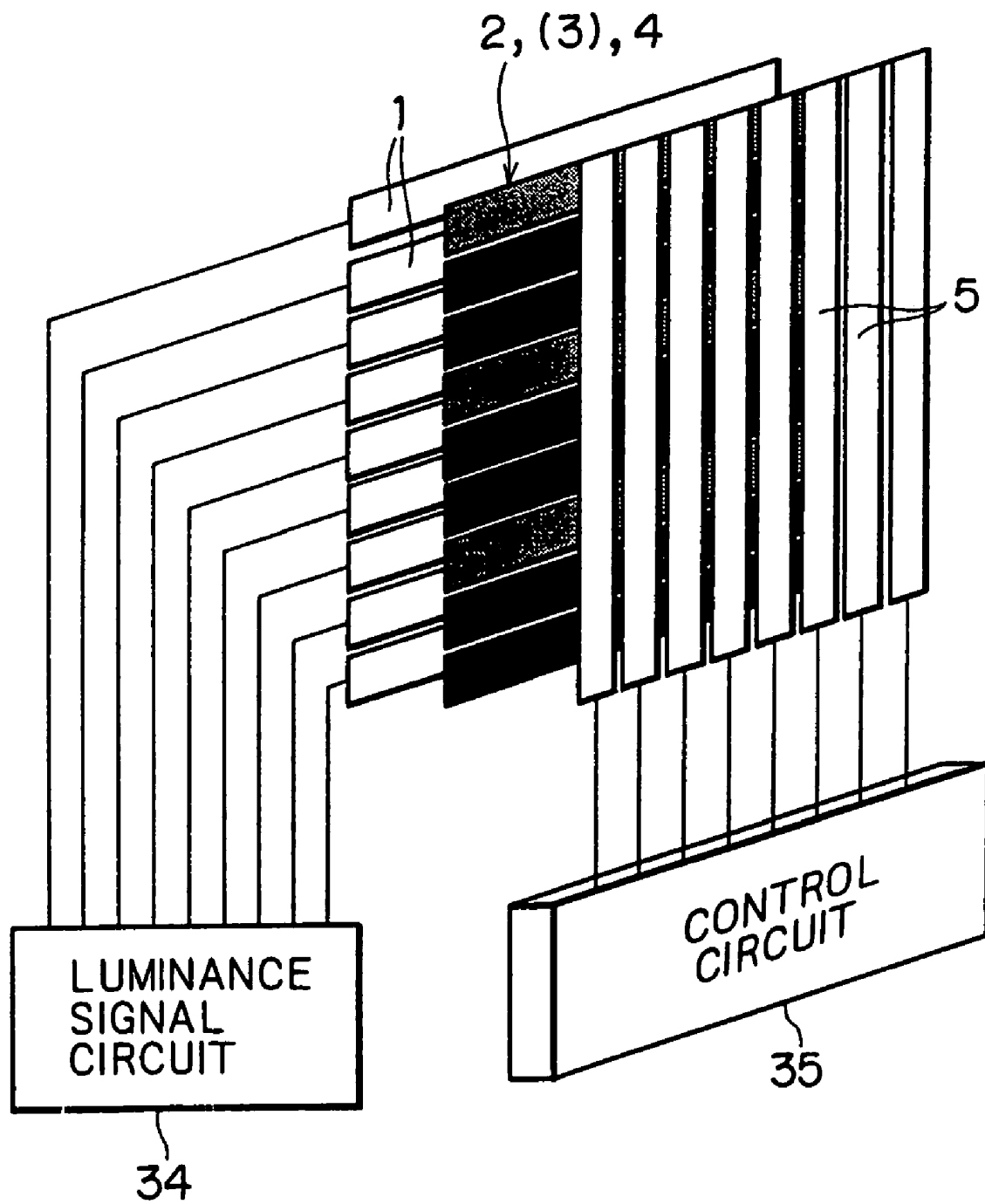


FIG. 9



BATHOPHENANTHROLINE COMPOUND AND EL DEVICE

This application is a continuation of prior application Ser. No. 09/704,968, filed Nov. 2, 2000, now U.S. Pat. No. 6,972,334, incorporated herein by reference to the extent permitted by law.

BACKGROUND OF THE INVENTION

This invention relates to a bathophenanthroline compound, which is adapted for use in an organic electroluminescent device (e.g. an organic electroluminescent device suitable as a display device or a light-emitting device such as a spontaneous light flat display, especially an organic electroluminescent color display using an organic thin film as an electroluminescent layer), and also a process for preparing the compound.

In recent years, importance of interfaces between human beings and machines including multimedia-oriented commercial articles is exalted. For more comfortable and more efficient machine operations, it is necessary to retrieve information from an operated machine without failure simply, instantaneously and in an adequate amount. To this end, studies have been made on various types of display devices or displays.

As machines are now miniaturized, there is an increasing demand, day by day, for miniaturization and thinning of display devices. For instance, there is an inconceivable development with respect to the miniaturization of lap top-type information processors of the all-in-one type such as notebook-size personal computers, notebook-size word processors and the like. This, in turn, entails a remarkable technical innovation on liquid crystal displays for use as a display device for the processor.

Nowadays, liquid crystal displays are employed as an interface of a diversity of articles and have wide utility in the fields not only of lap top-type information processors, but also of articles for our daily use including small-sized television sets, watches, desk-top calculators and the like.

These liquid crystal displays have been studied as a key of display devices, which are used as the interface connecting a human being and a machine and cover small-sized to large capacitance display devices while making use of the feature that liquid crystals are low in drive voltage and power consumption. However, liquid crystal displays have the problems that they do not rely on spontaneous light and thus need a greater power consumption for back light drive than for liquid crystal drive, with the result that a service time is shortened when using a built-in battery, thus placing a limitation on their use. Moreover, the liquid crystal display has another problem that it has such a narrow angle of field as not to be suitable for use as a large-sized display device.

Furthermore, the liquid crystal display depends on the manner of display using the orientation of liquid crystal molecules, and this is considered to bring about a serious problem that its contrast changes depending on the angle even within an angle of field.

From the standpoint of drive systems, an active matrix system, which is one of drive systems, has a response speed sufficient to deal with a motion picture. However, since a TFT (thin film transistor) drive circuit is used, a difficulty is involved in making a large screen size owing to the pixel defects, thus being disadvantageous in view of the reduction in cost.

In the liquid crystal display, a simple matrix system, which is another type of drive system, is not only low in cost,

but also relatively easy in making a large screen size. However, this system has the problem that its response speed is not enough to deal with a motion picture.

In contrast, a spontaneous light display device is now under study such as on a plasma display device, an inorganic electroluminescent device, an organic electroluminescent device and the like.

The plasma display device employs plasma emission in a low pressure gas for display and is suited for the purposes of a large size and large capacitance, but has the problem on thinning and costs. In addition, an AC bias of high potential is required for its drive, and thus, the display is not suitable as a portable device.

The inorganic electroluminescent device has been put on the market as a green light emission display. Like the plasma display device, an AC bias drive is essential, for which several hundreds of volts are necessary, thus not being of practical use.

In this connection, however, emission of three primaries including red (R), green (G) and blue (B) necessary for color display has been succeeded due to the technical development. Since inorganic materials are used for this purpose, it has been difficult to control emission wavelengths depending on the molecular design or the like. Thus, it is believed that full color display is difficult.

On the other hand, the electroluminescent phenomenon caused by organic compounds has been long studied ever since there was discovered a luminescent or emission phenomenon wherein carriers are injected into the single crystal of anthracene capable of emitting a strong fluorescence in the first part of 1960s. However, such fluorescence is low in brightness and monochronous in nature, and the single crystal is used, so that this emission has been made as a fundamental investigation of carrier injection into organic materials.

However, since Tang et al. of Eastman Kodak have made public an organic thin film electroluminescent device of a built-up structure having an amorphous luminescent or emission layer capable of realizing low voltage drive and high brightness emission in 1987, extensive studies have been made, in various fields, on the emission, stability, rise in brightness, built-up structure, manner of fabrication and the like with respect to the three primaries of R, G and B.

Furthermore, diverse novel materials have been prepared with the aid of the molecular design inherent to an organic material. At present, it starts to conduct extensive studies on applications, to color displays, of organic electroluminescent devices having excellent characteristic features of DC low voltage drive, thinning, and spontaneous light emission and the like.

The organic electroluminescent device (which may be sometimes referred to as organic EL device hereinafter) has a film thickness of 1 μm or below. When an electric current is charged to the device, the electric energy is converted to a light energy thereby causing luminescence to be emitted in the form of a plane. Thus, the device has an ideal feature for use as a display device of the spontaneous emission type.

FIG. 7 shows an example of a known organic EL device. An organic EL device 10 includes, on a transparent substrate 6 (e.g. a glass substrate), an ITO (indium tin oxide) transparent electrode 5, a hole transport layer 4, an emission layer 3, an electron transport layer 2, and a cathode 1 (e.g. an aluminium electrode) formed in this order, for example, by a vacuum deposition method.

A DC voltage 7 is selectively applied between the transparent electrode 5 serving as an anode and the cathode 1, so that holes serving as carriers charged from the transparent

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electrode **5** are moved via the hole transport layer **4**, and electrons charged from the cathode **1** are moved via the electron transport layer **2**, thereby causing the re-combination of the electrons-holes. From the site of the re-combination, light **8** with a given wavelength is emitted and can be observed from the side of the transparent substrate **6**.

The emission layer **3** may be made of a light-emitting substance such as, for example, anthracene, naphthalene, phenanthrene, pyrene, chrysene, perylene, butadiene, coumarin, acridine, stilbene and the like. This may be contained in the electron transport layer **2**.

FIG. **8** shows another example of an organic EL device. In an organic EL device **20**, the emission layer **3** as in FIG. **7** is omitted and, instead, such a light-emitting substance as mentioned above is contained in the electron transport layer **2**, and thus, the organic EL device **20** is so arranged as to emit light **18** having a given wavelength from an interface between the electron transport layer **2** and the hole transport layer **4**.

FIG. **9** shows an application of the organic EL device. More particularly, a built-up body of the respective organic layers (including the hole transport layer **4**, and the emission layer **3** or the electron transport layer **2**) is interposed between the cathode **1** and the anode **5**. These electrodes are, respectively, provided in the form of stripes that are intersected in the form of a matrix. In this state, a signal voltage is applied to in time series by means of a luminance signal circuit **34** and a shift register-built in control circuit **35** so that light is emitted at a number of intersected points (pixels), respectively.

Such an arrangement as set out above is usable not only as a display, but also as an image reproducing apparatus. It will be noted that if the striped pattern is provided for the respective colors of R, G and B, there can be obtained a full color or a multi-color arrangement.

In a display device made of a plurality of pixels using the organic EL device, emitting organic thin film layers **2**, **3** and **4** are usually sandwiched between the transparent electrode **5** and the metal electrode **1**, and emission occurs at the side of the transparent electrode **5**.

For use as constituting materials of the organic EL device, attention has now been drawn to organic luminescent materials and carrier transport materials suitable for use in combination with the organic luminescent materials. The advantages of these organic materials reside in that their optical and electrical properties can be controlled to some extent through the molecular design thereof. When an organic luminescent material having a given light emission and a carrier transport material suited therewith are used in combination, efficient light emission is ensured. Accordingly, there can be realized a full color organic EL device wherein primaries of R, G and B are emitted using the respective luminescent materials.

In some case, such an organic EL device as set out above may have such a structure that a hole transport layer serves also as a luminescent element. In this device structure, it is essential to provide a carrier transport layer that is able to efficiently transport electrons and block holes. However, organic materials that satisfy the above requirement and the efficient manufacture of these materials have never been found yet.

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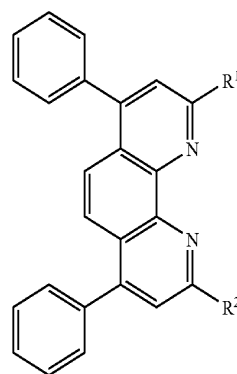
SUMMARY OF THE INVENTION

An object of the invention is to provide a novel organic material, which is suitable for use as a carrier transport material capable of efficiently transporting electrons and blocking holes.

Another object of the invention is to provide a process for preparing such an organic compound as mentioned above in an efficient manner.

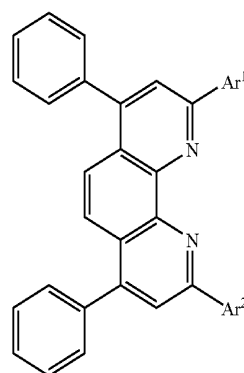
According to an aspect of the invention, there is provided a bathophenanthroline compound of the following general formula [I] or [II]

General Formula [I]:



wherein R^1 and R^2 may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group, or a substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R^1 and R^2 has at least two carbon atoms, or

General Formula [II]:

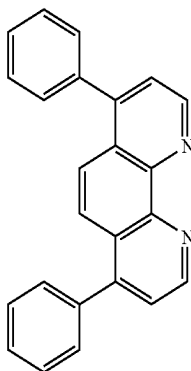


wherein Ar^1 and Ar^2 may be the same or different and independently represent a substituted or unsubstituted aryl group.

The bathophenanthroline compound of the invention can control carrier transportability depending on the type of substituent introduced into the molecule, and can thus be utilizable as a carrier transport material of various types of organic EL devices. The compounds have high glass transition point and high melting point and are stable electrically, thermally and/or chemically. In addition, the compounds are sublimable in nature, which is advantageous in

$$\text{R}^3\text{—Li} \text{ or } \text{R}^4\text{—Li}$$
$$\text{Ar}^3\text{—Li or Ar}^4\text{—Li}$$

General Formula [IV]:



BRIEF DESCRIPTION OF THE DRAWINGS

In the general formula [III], Ar¹ and Ar² independently represent a substituted or unsubstituted aryl group. Specific examples include a phenyl group, a 1-naphthyl group, a 2-anthryl group, a 9-anthryl group, a 2-fluorenyl group, a 4-quinolyl group, a pyridyl group, a 3-pyridinyl group, a 2-pyridinyl group, a 3-furyl group, a 2-furyl group, a 3-thienyl group, a 2-oxazolyl group, a 2-thiazolyl group, a 2-benzoxazolyl group, a 2-benzothiazolyl group, a 2-benzothiazolyl group, a 4-methylphenyl group, a 3-methylphenyl group, a 2-methylphenyl group, a 2,3-dimethylphenyl group, a 2,4-dimethylphenyl group, a 2,5 -dimethylphenyl group, a 2,6-dimethylphenyl group, a 3,4-dimethylphenyl group, a 3,5-dimethylphenyl group, a 2,3,4-trimethylphenyl group, a 2,3,5-trimethylphenyl group, a 2,3,6-trimethylphenyl group, a 3,4,5 -trimethylphenyl group, a 4-ethylphenyl group, a 3-ethylphenyl group, a 2-ethylphenyl group, a 2,3-diethylphenyl group, a 2,4-diethylphenyl group, a 2,5-diethylphenyl group, a 2,6-diethylphenyl group, a 3,4-diethylphenyl group, a 3,5-diethylphenyl group, a 2,3,4-triethylphenyl group, a 2,3,5-triethylphenyl group, a 2,3,6-

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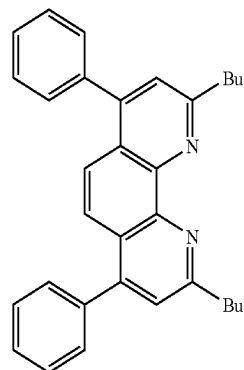
triethylphenyl group, a 3,4,5-triethylphenyl group, a 4-n-propylphenyl group, a 4-isopropylphenyl group, a 2-isopropylphenyl group, a 4-n-butylphenyl group, a 4-isobutylphenyl group, a 4-sec-butylphenyl group, a 4-tert-butylphenyl group, a 3-tert-butylphenyl group, a 2-tert-butylphenyl group and the like although not limited to those mentioned above.

Specific examples of the bathophenanthroline compound of the invention includes those mentioned below as Compound Nos. 1 to 178, but these compounds should not be construed as limitation thereof. In the specific compounds, Me represents a methyl group, Et represents an ethyl group, Pr represents a propyl group, and Bu represents a butyl group.

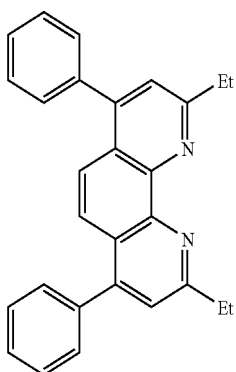
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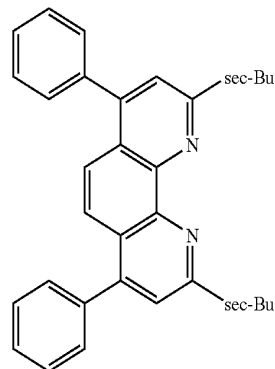
Compound No. 4



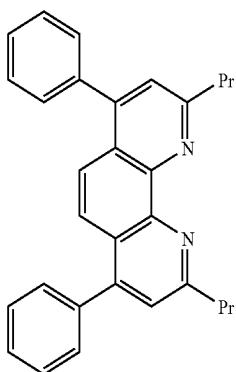
Compound No. 1



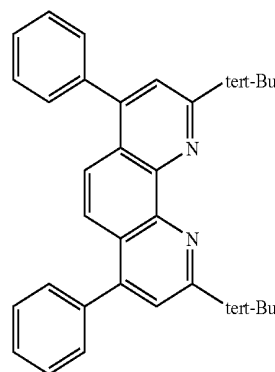
Compound No. 5



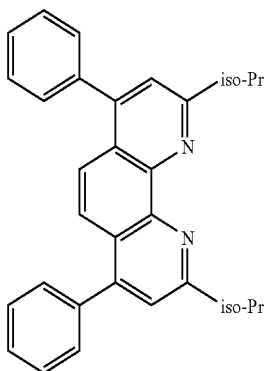
Compound No. 2



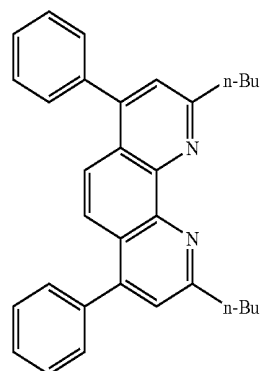
Compound No. 6



Compound No. 3

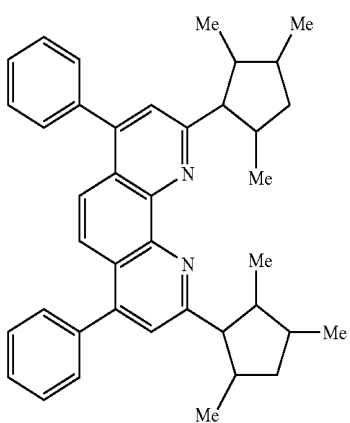
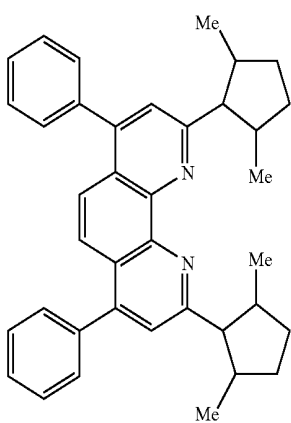
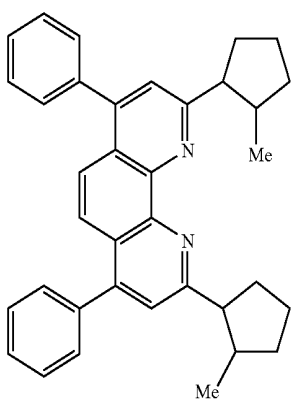
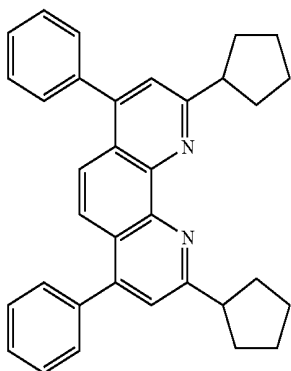


Compound No. 7



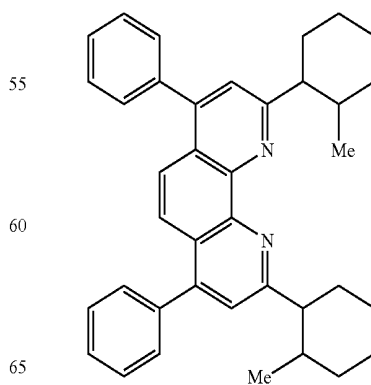
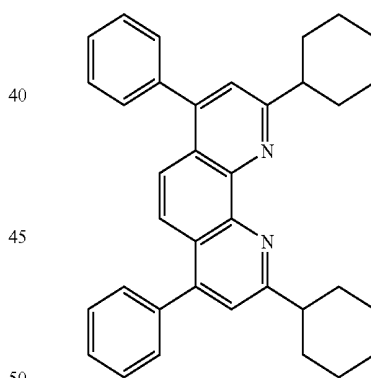
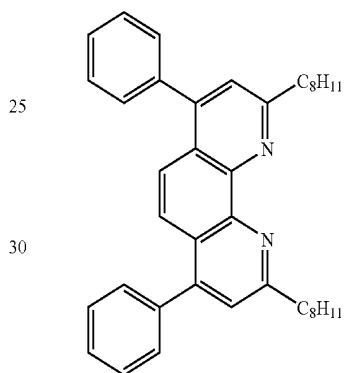
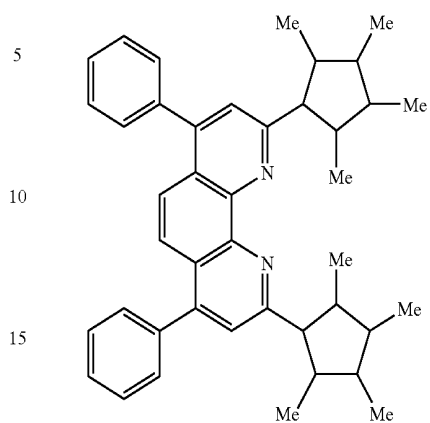
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-continued



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Compound No. 8

Compound No. 12

Compound No. 9

Compound No. 13

Compound No. 10

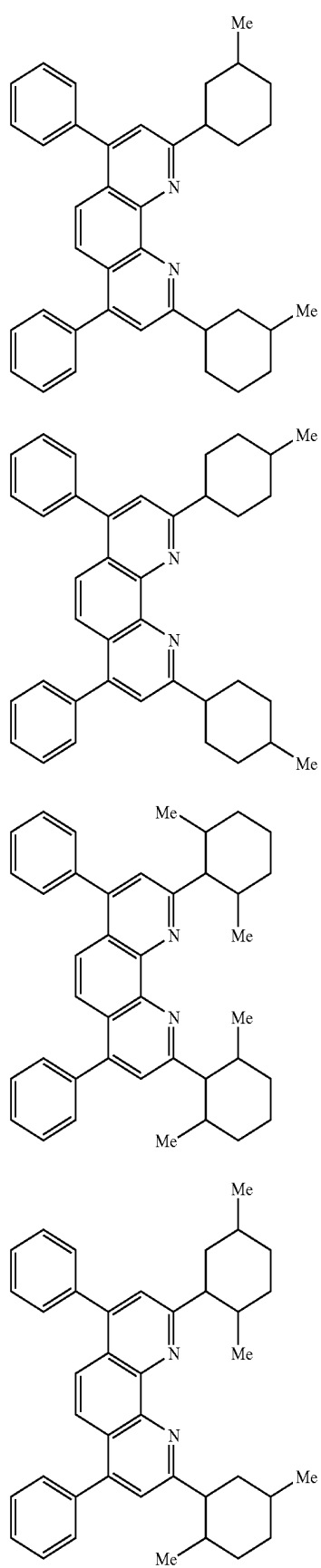
Compound No. 14

Compound No.11

Compound No. 15

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-continued

Compound No. 16

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Compound No. 17

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Compound No. 18

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Compound No. 19

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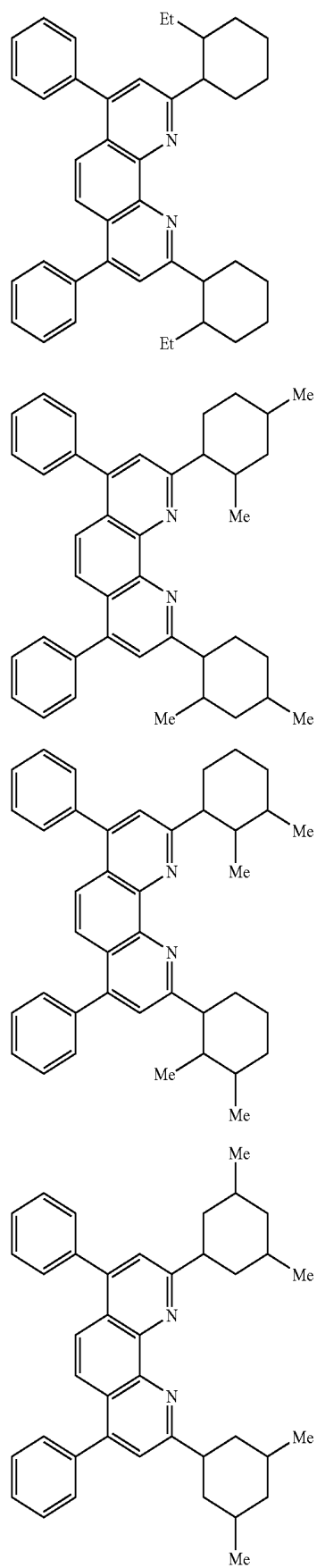
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Compound No. 20

Compound No. 21

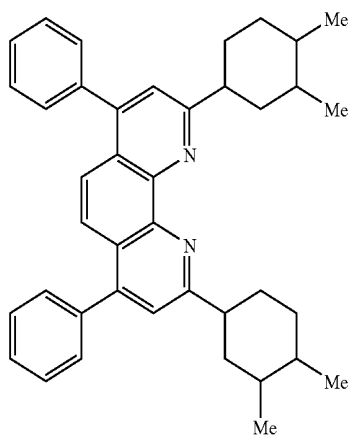
Compound No. 22

Compound No. 23



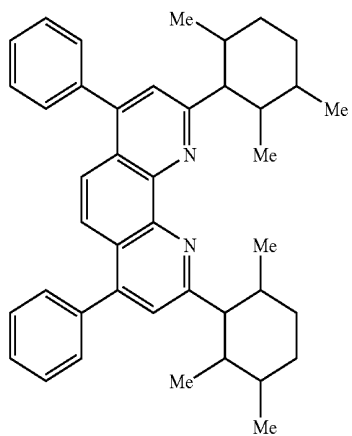
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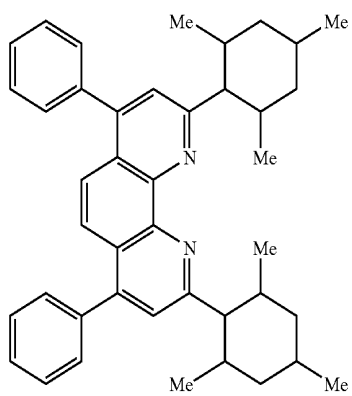
Compound No. 24

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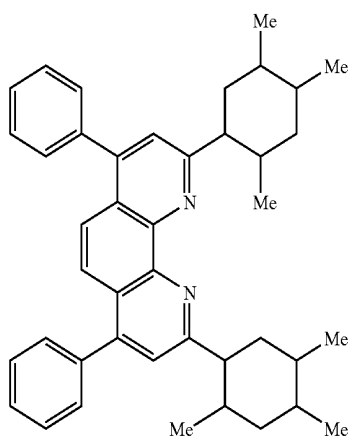
Compound No. 25

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Compound No. 26

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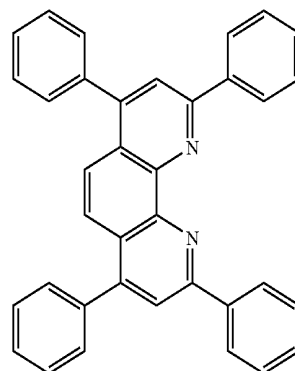


Compound No. 27

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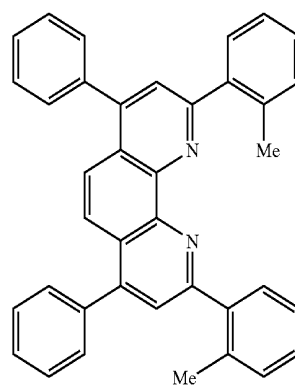
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Compound No. 28

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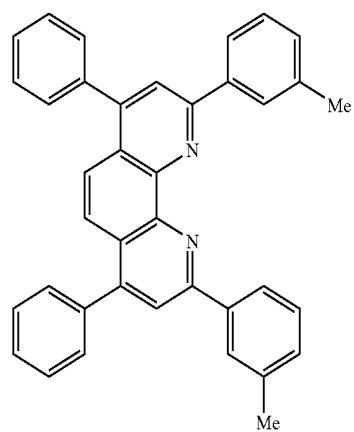
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Compound No. 29

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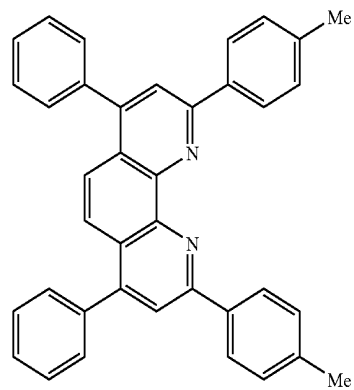
Compound No. 30

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Compound No. 31

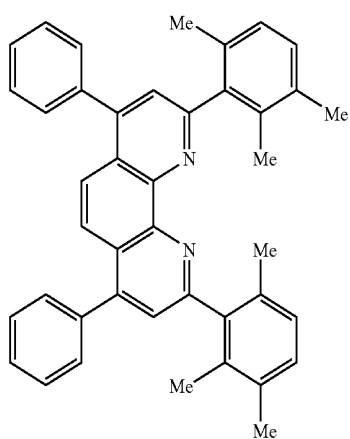
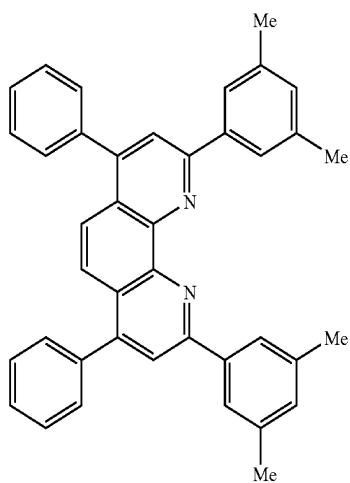
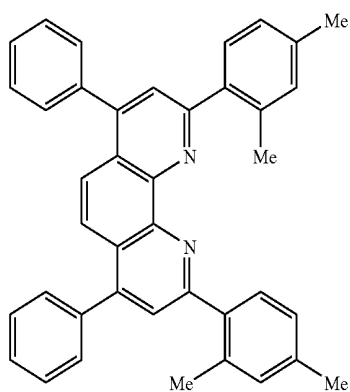
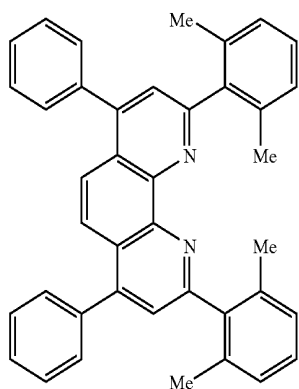
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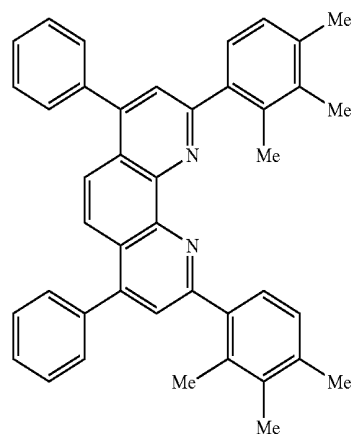


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Compound No. 32

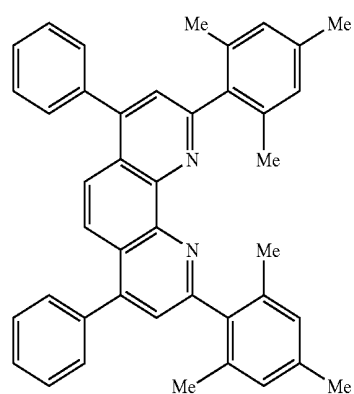
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Compound No. 33

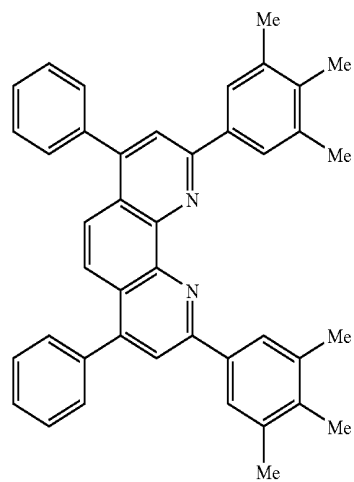
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Compound No. 34

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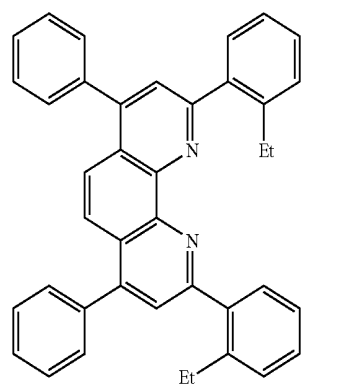


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Compound No. 37

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Compound No.38

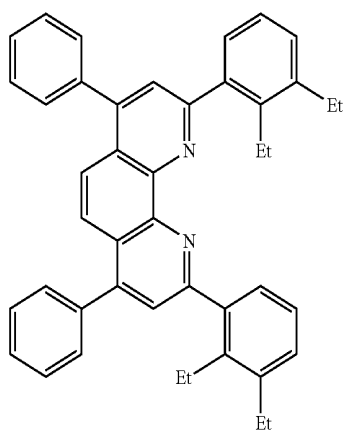
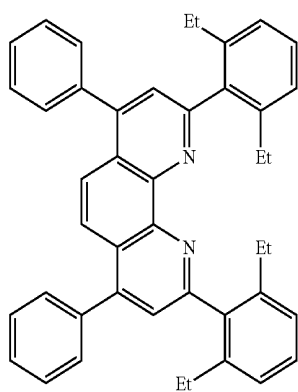
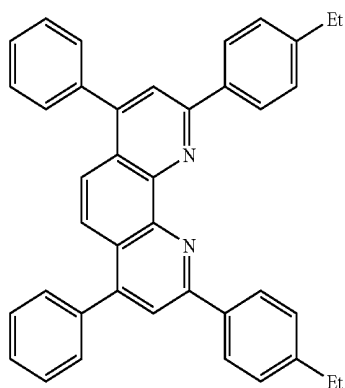
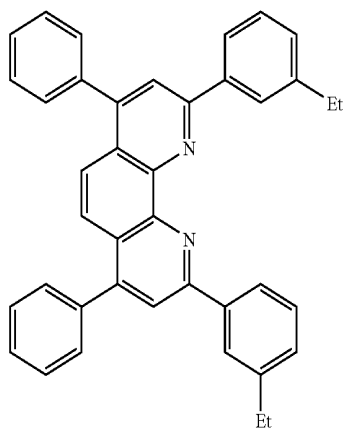
Compound No.39

Compound No.40

Compound No.41

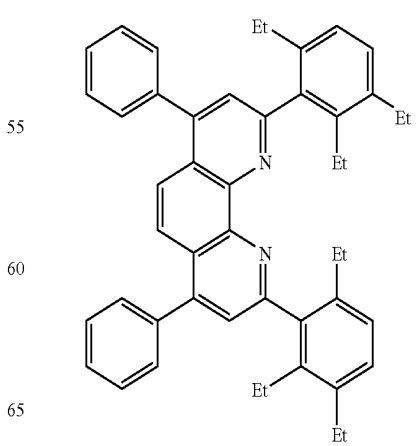
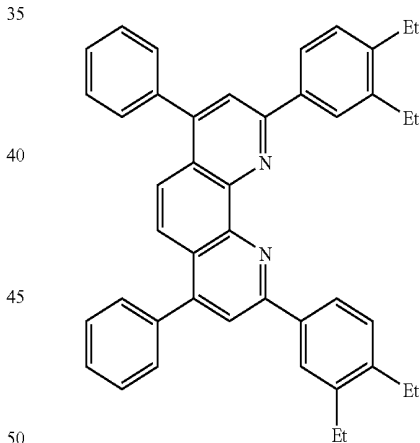
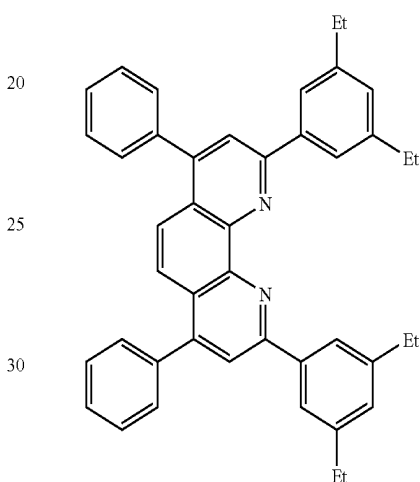
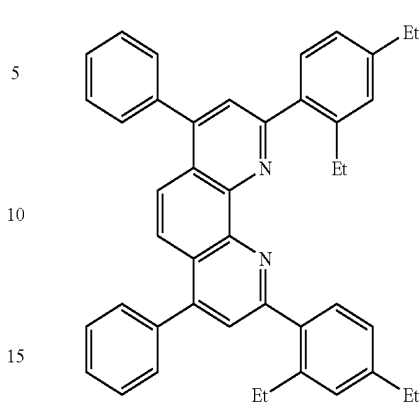
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Compound No.42

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Compound No.43

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Compound No.44

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Compound No.45

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Compound No.46

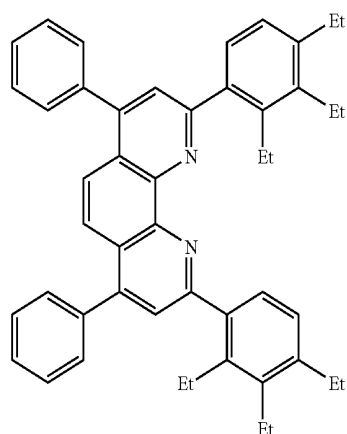
Compound No.47

Compound No.48

Compound No.49

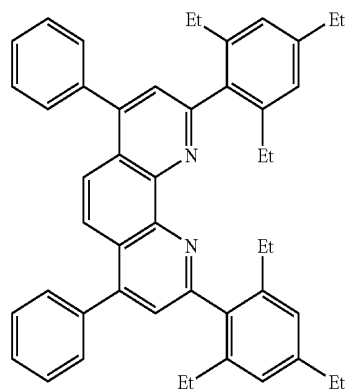
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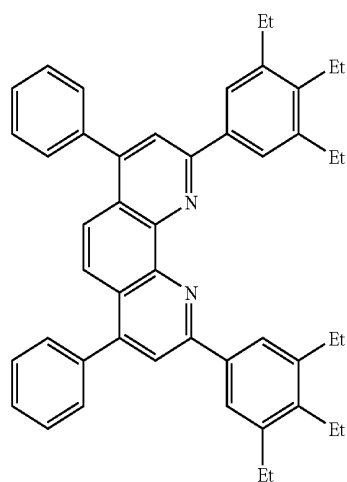
Compound No.50

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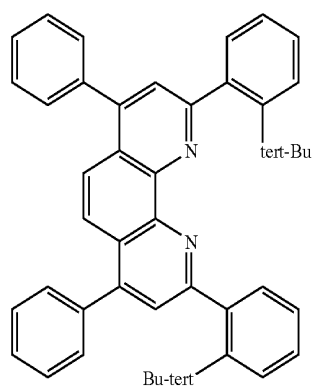
Compound No.51

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Compound No.52

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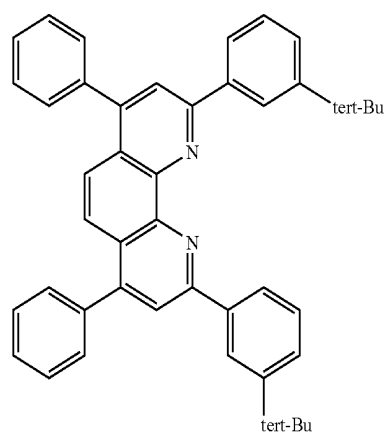


Compound No.53

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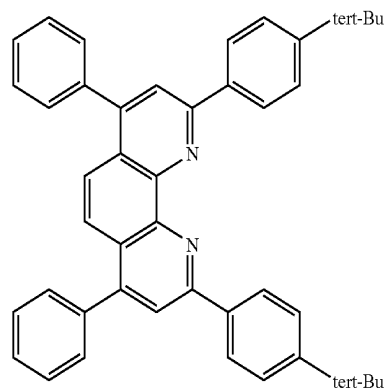
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Compound No.54

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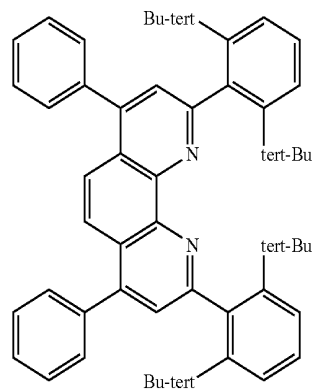
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Compound No.55

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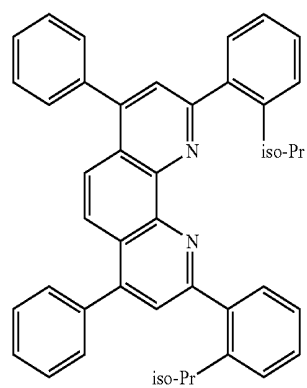


Compound No.56

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Compound No.57

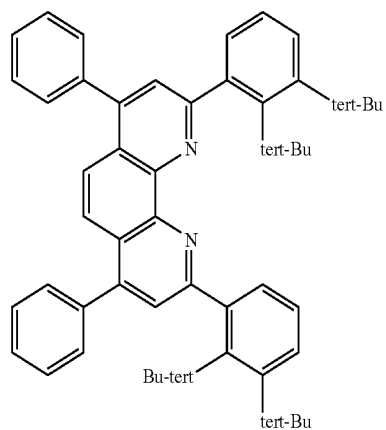
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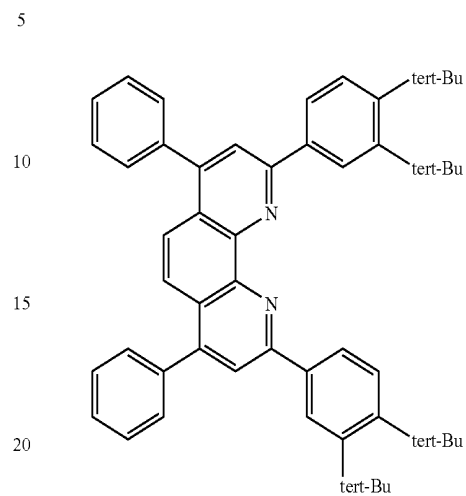
Compound No.58



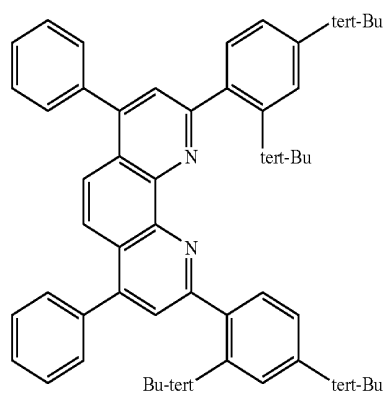
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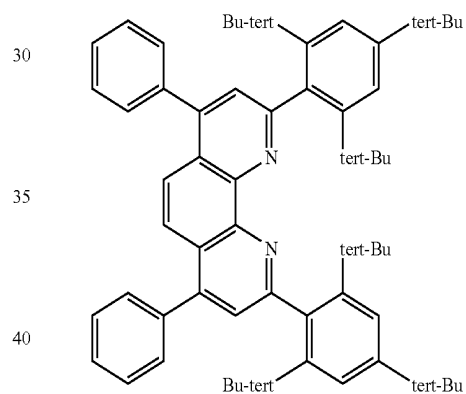
Compound No.61



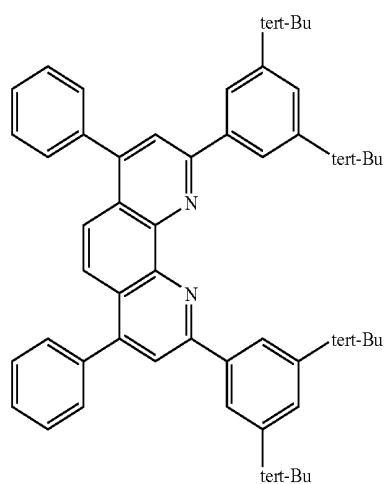
Compound No.59



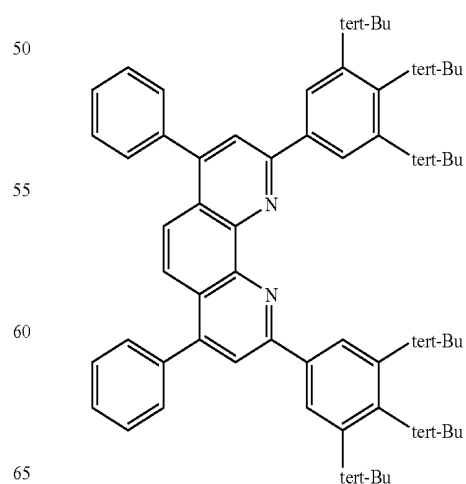
Compound No.62



Compound No.60

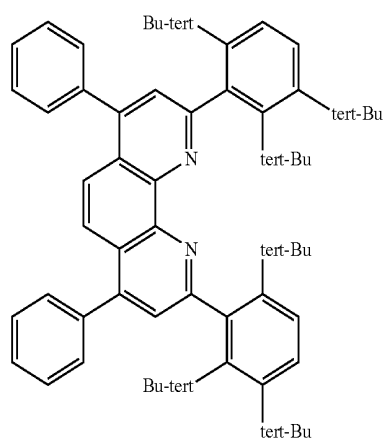


Compound No.63



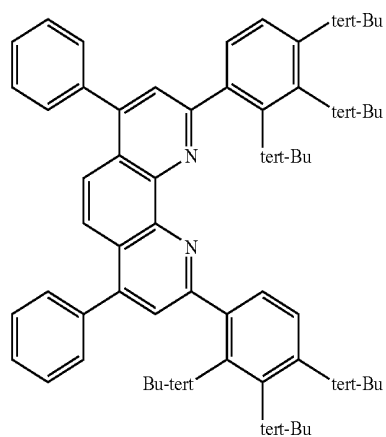
23

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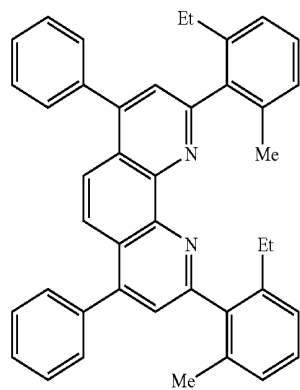


Compound No.64

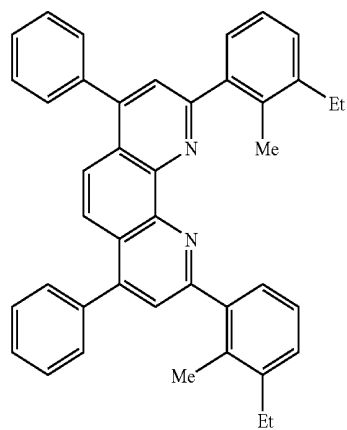
Compound No.65



Compound No.66

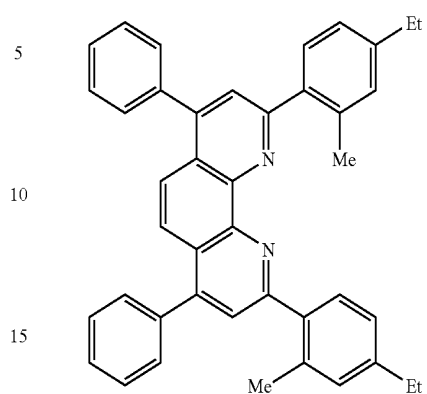


Compound No.67

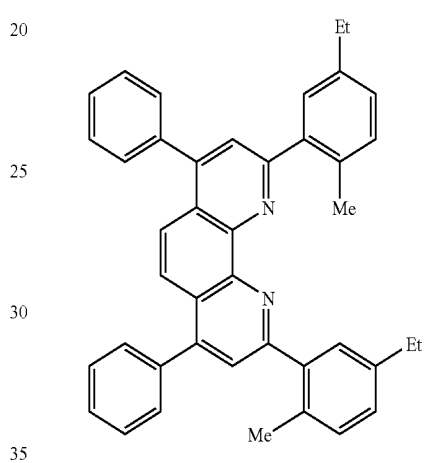


24

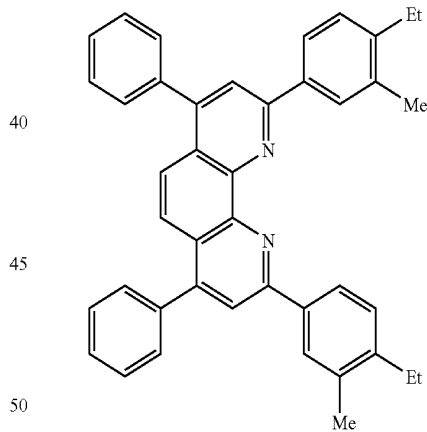
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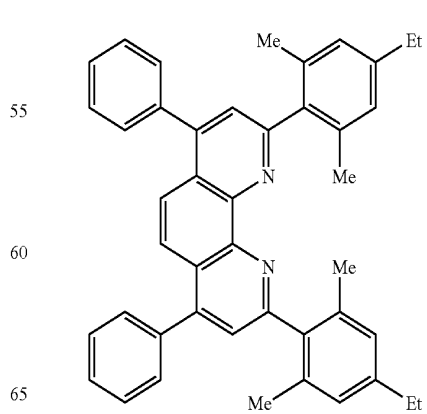
Compound No.68



Compound No.69



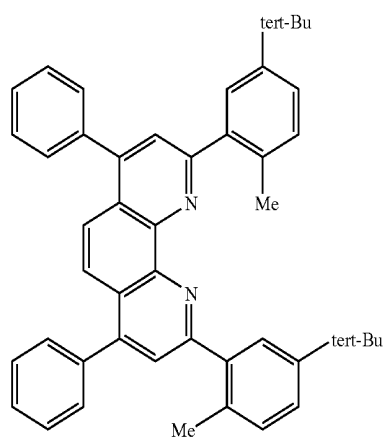
Compound No.70



Compound No.71

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Compound No. 72

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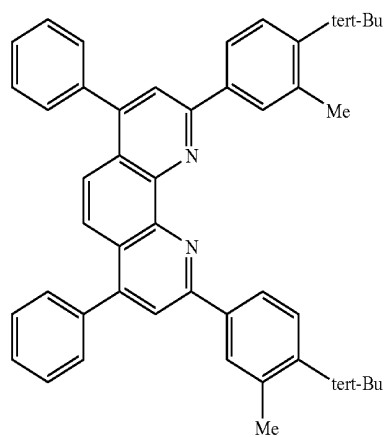
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Compound No. 73



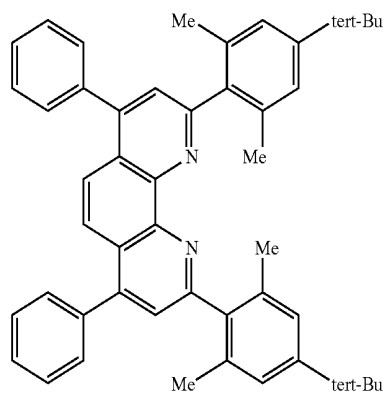
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Compound No. 74



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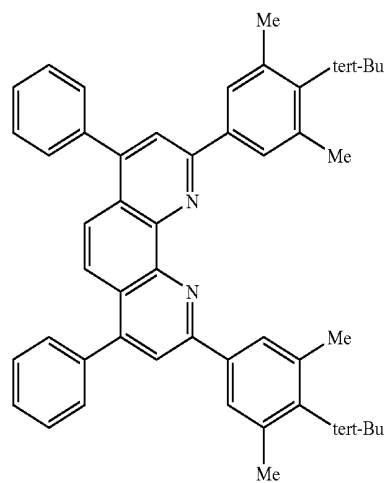
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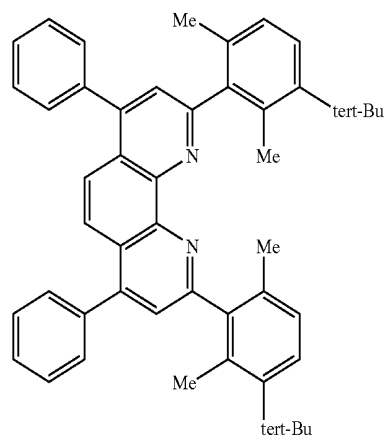
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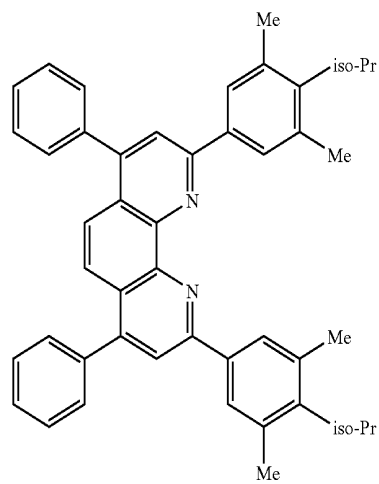
Compound No. 75



Compound No. 76

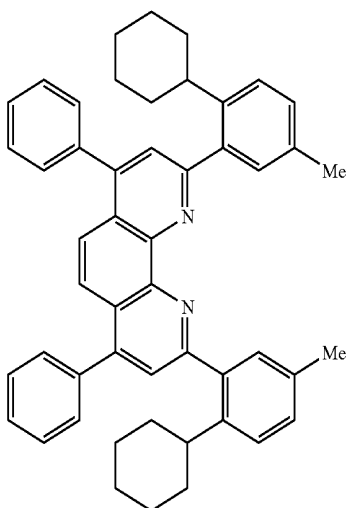
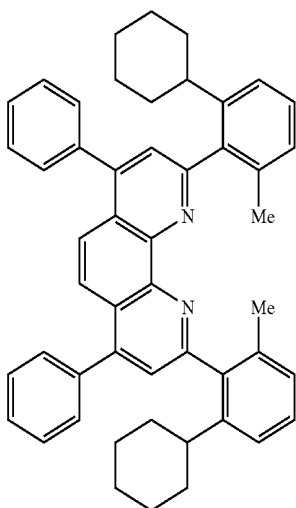
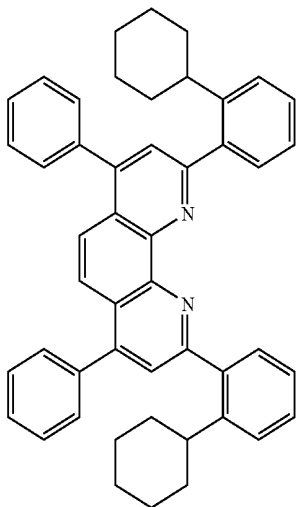


Compound No. 77



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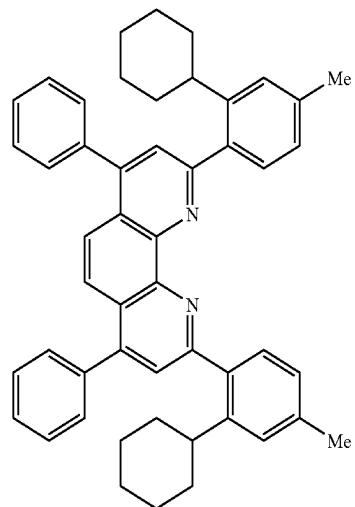
Compound No. 78

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Compound No. 81

Compound No. 79

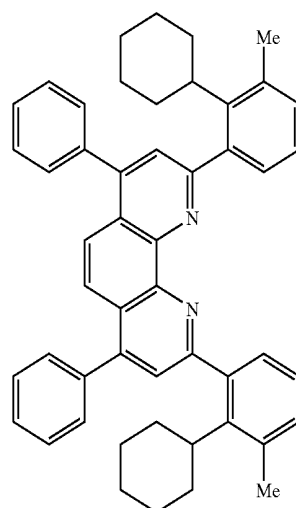
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Compound No. 82

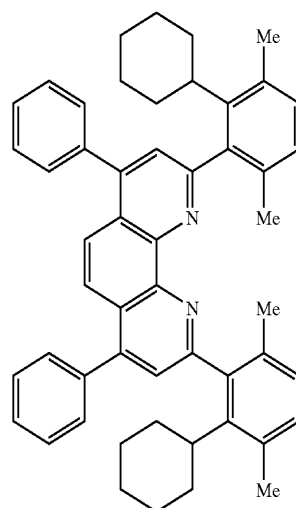
Compound No. 80

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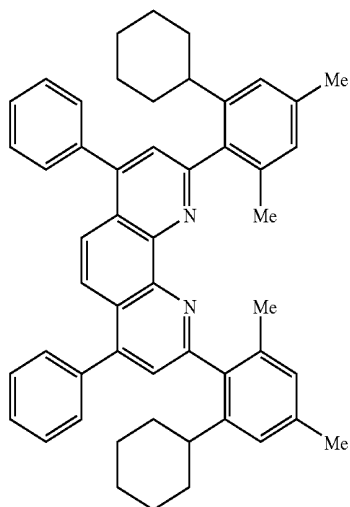
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Compound No. 83

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Compound No. 84

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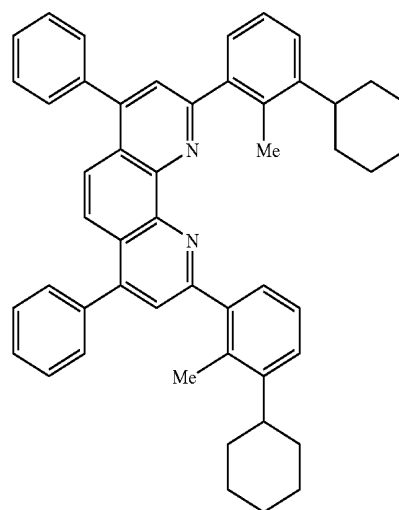
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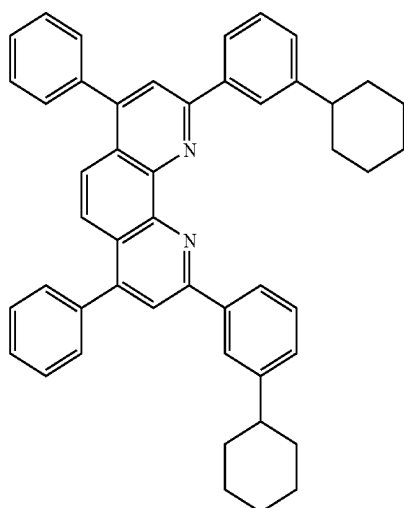
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Compound No. 87

Compound No. 85

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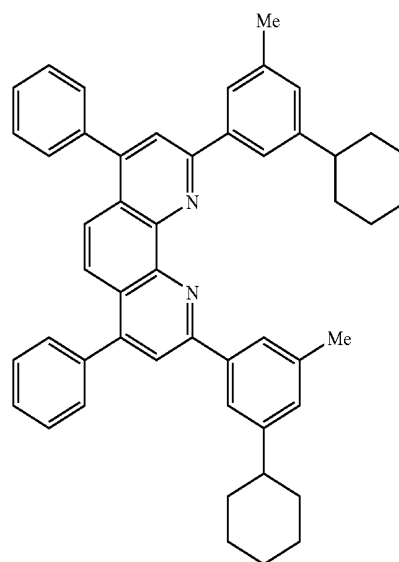
Compound No. 88

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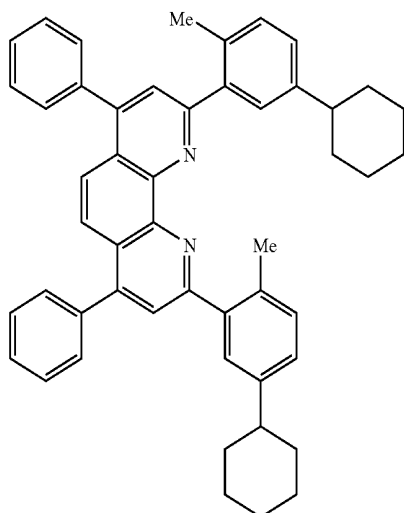
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Compound No. 86

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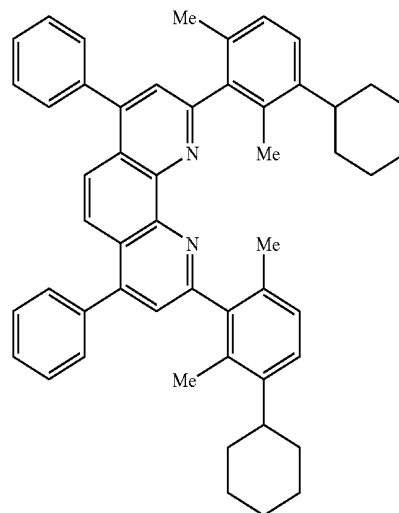


Compound No. 89

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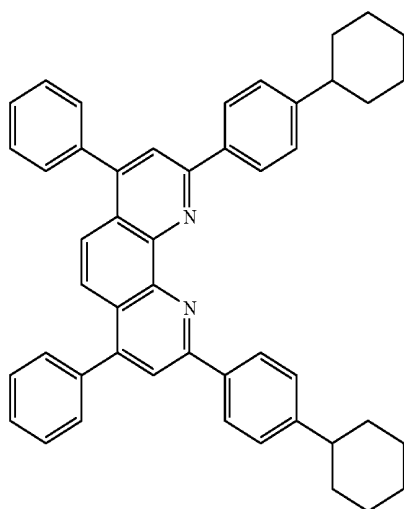
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Compound No. 90



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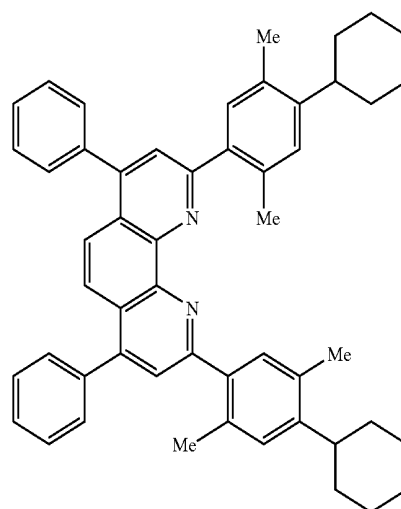
Compound No. 93

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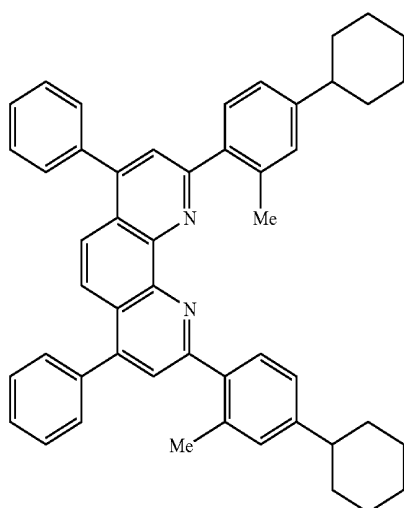
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Compound No. 91

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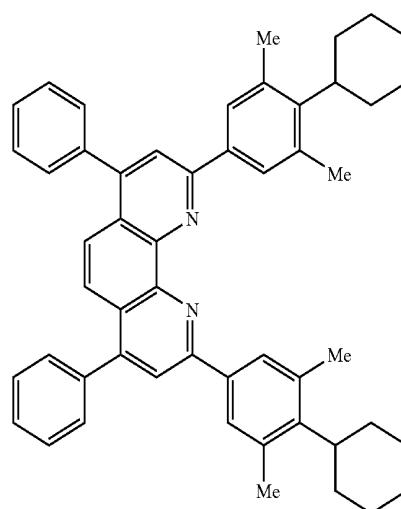
Compound No. 94

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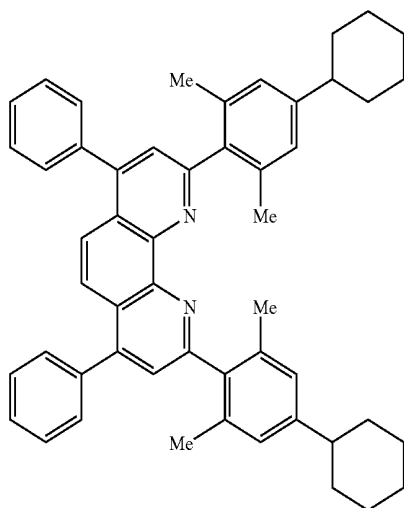
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Compound No. 92

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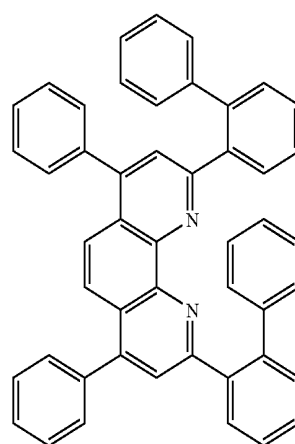


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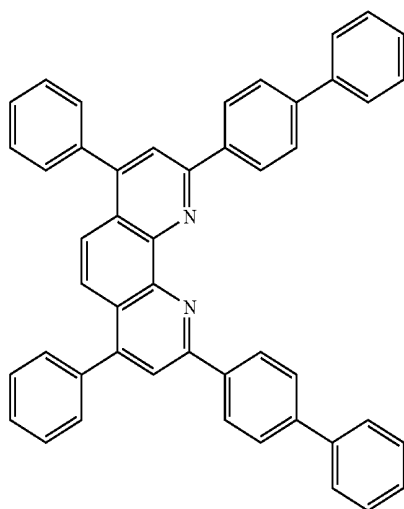
Compound No. 95



33

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Compound No. 96



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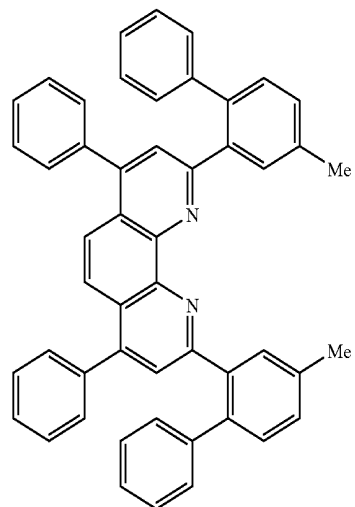
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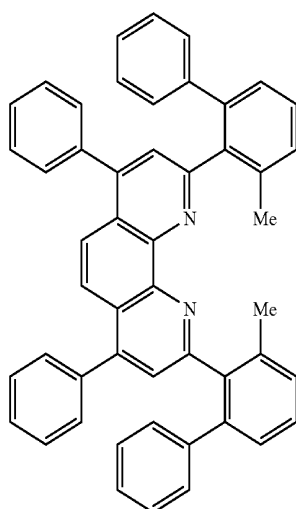
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Compound No. 99



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Compound No. 97



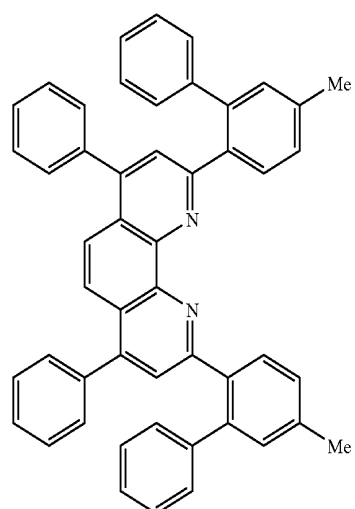
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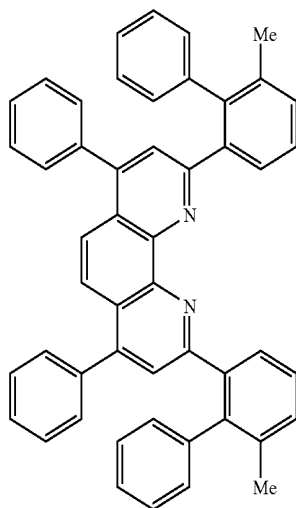
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Compound No. 100



Compound No. 98



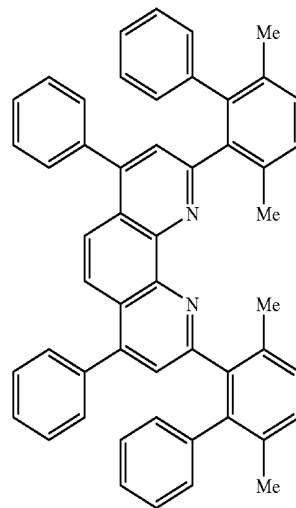
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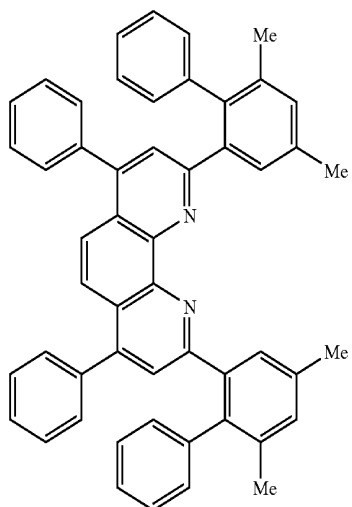
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Compound No. 101



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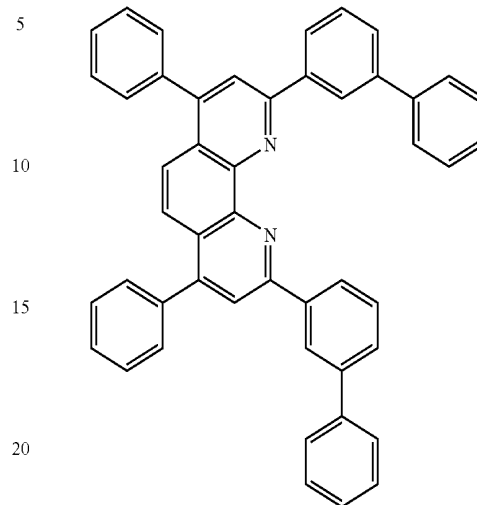
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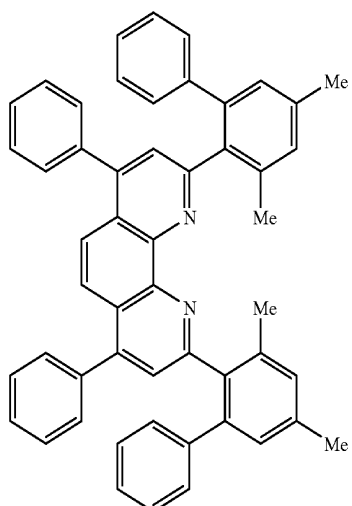
Compound No. 102

36

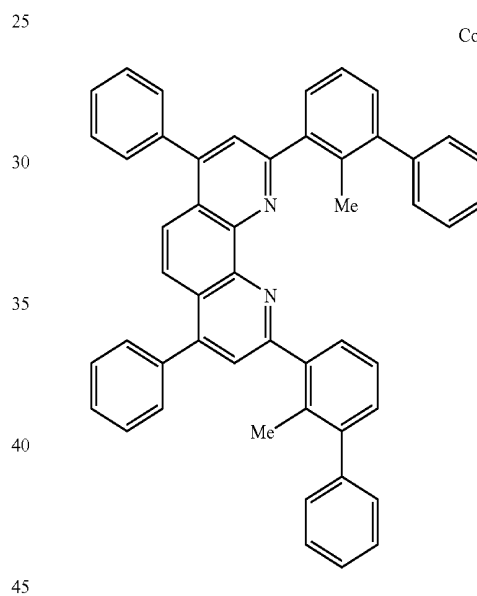
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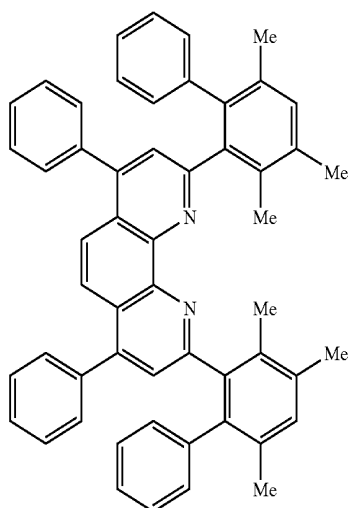
Compound No. 105



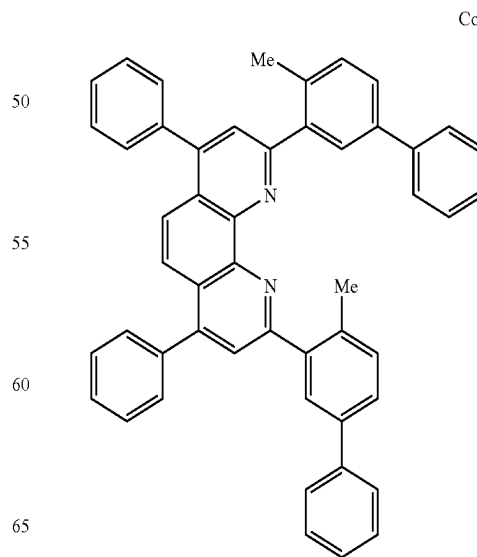
Compound No. 103



Compound No. 106



Compound No. 104

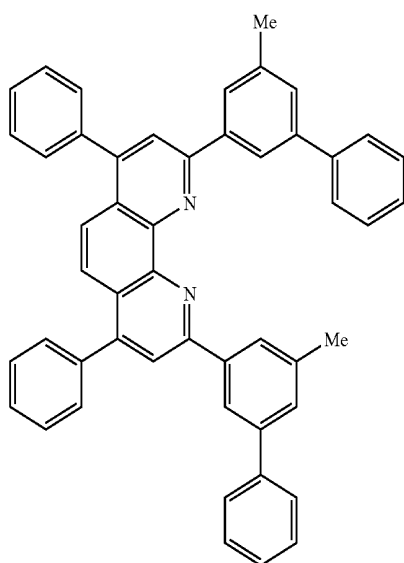


Compound No. 107

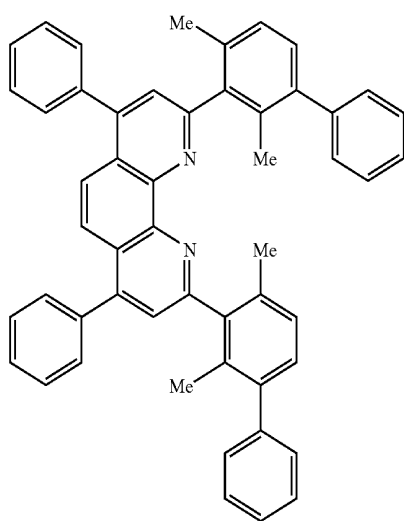
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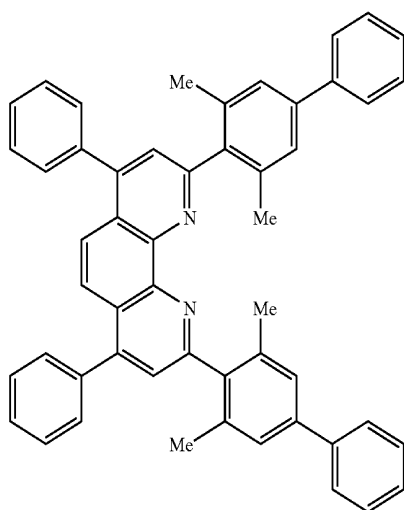
Compound No. 108



Compound No. 109



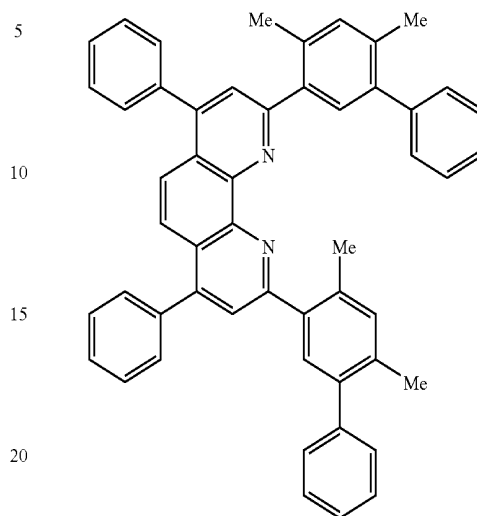
Compound No. 110



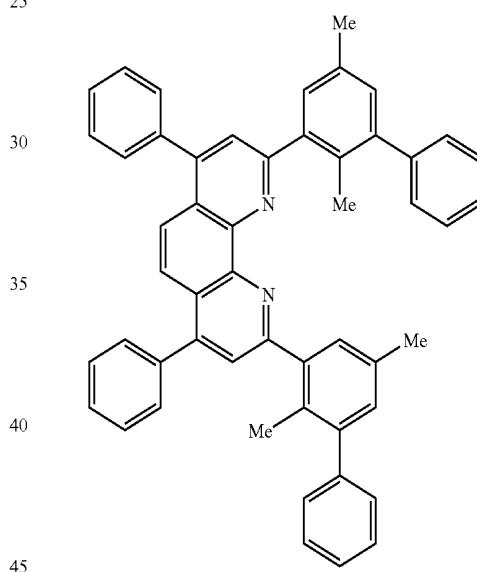
38

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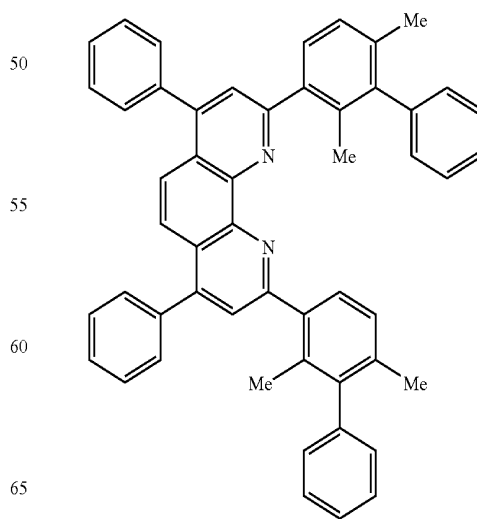
Compound No. 111



Compound No. 112



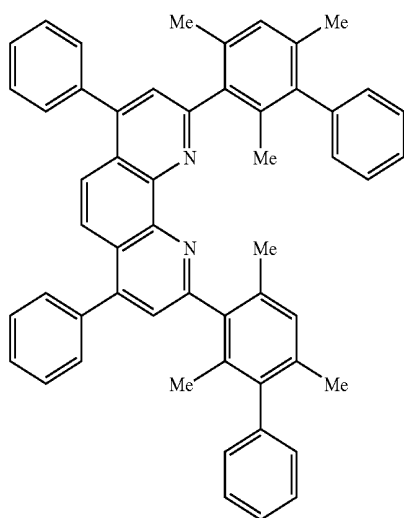
Compound No. 113



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Compound 114



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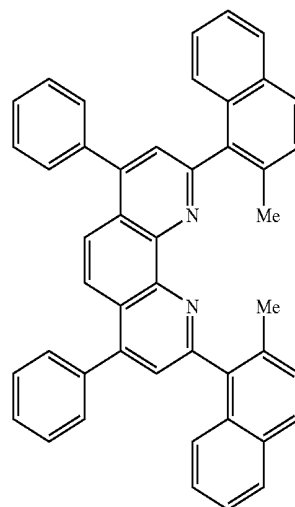
Compound No. 117

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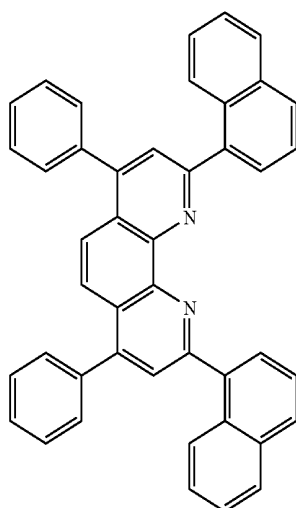
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Compound No. 115



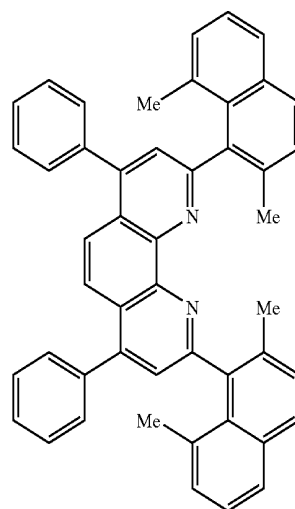
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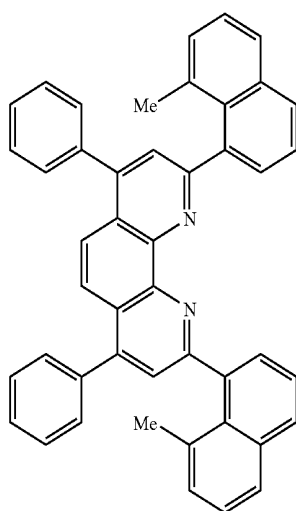
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Compound No. 118



Compound No. 116



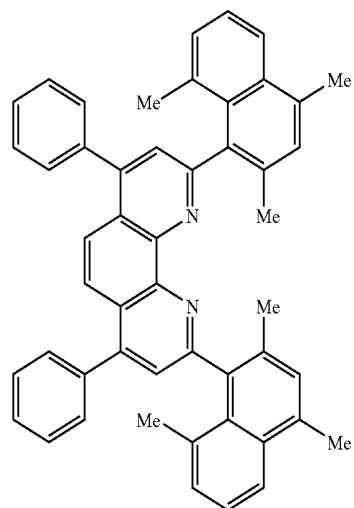
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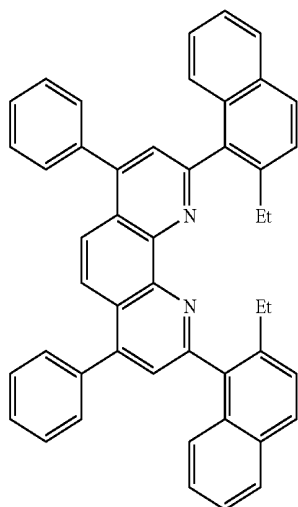
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Compound No. 119



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Compound No. 120

42

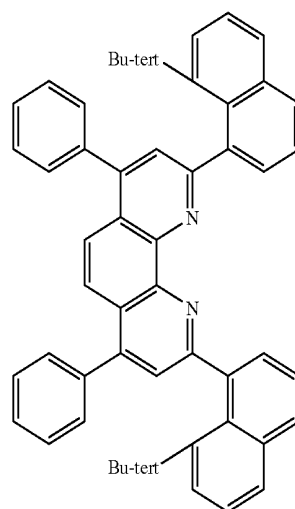
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Compound No. 123

Compound No. 121

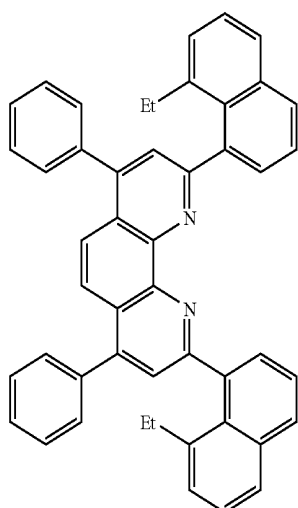
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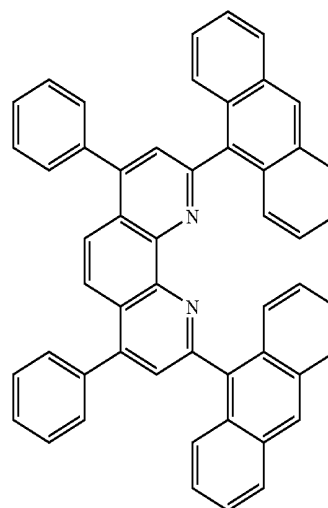
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Compound No. 124



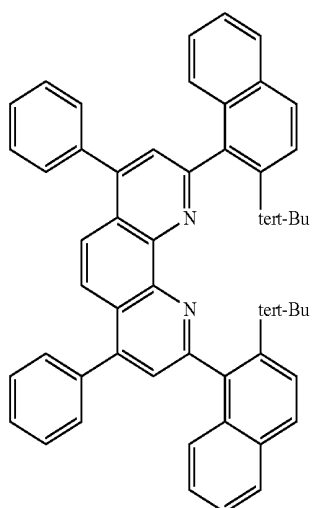
Compound No. 122

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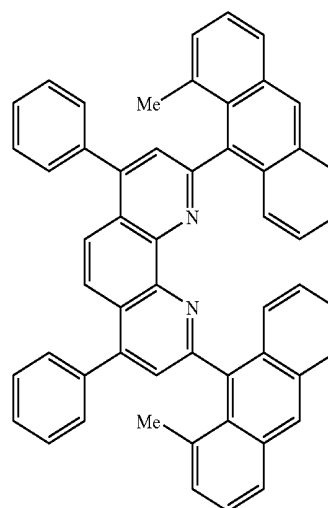
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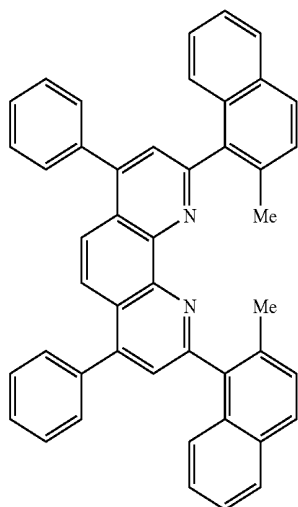


Compound No. 125



43

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Compound No. 126

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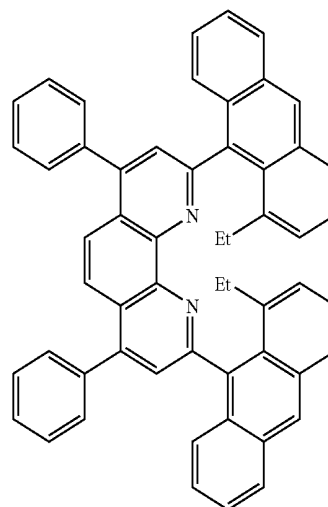
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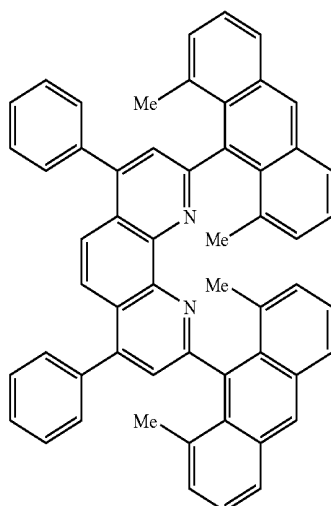
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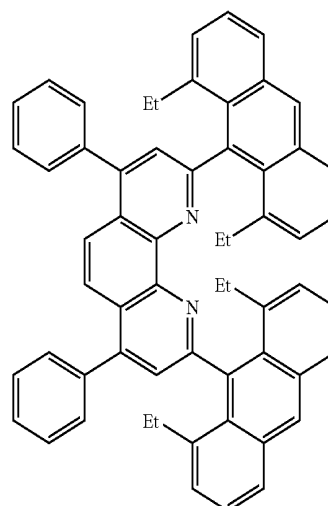
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Compound No. 127

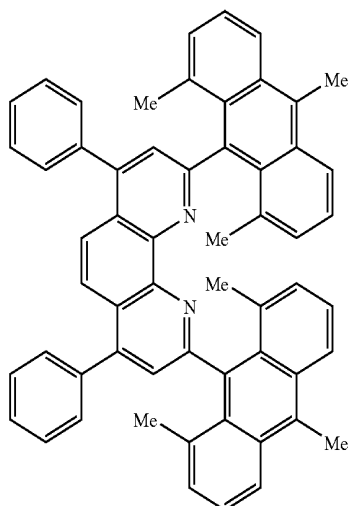


Compound No. 130

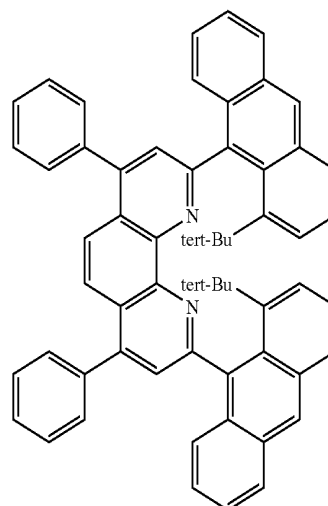


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Compound No. 128



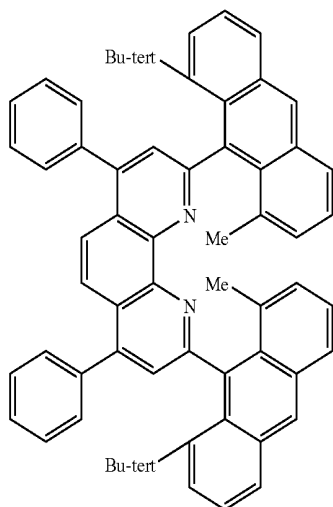
Compound No. 131



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-continued



Compound No. 132

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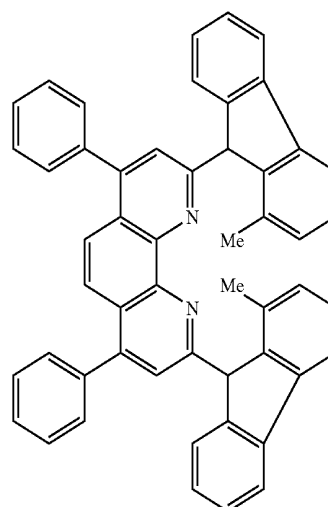
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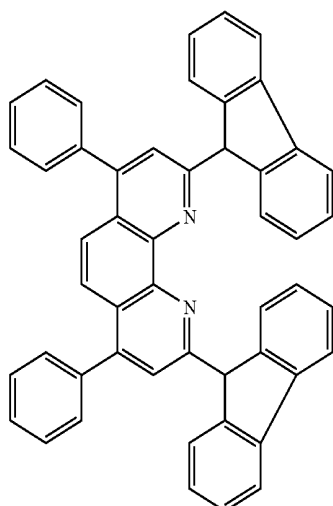
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Compound No. 135

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Compound No. 133



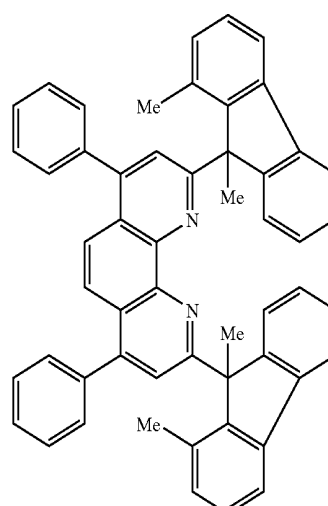
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Compound No. 136



Compound No. 134

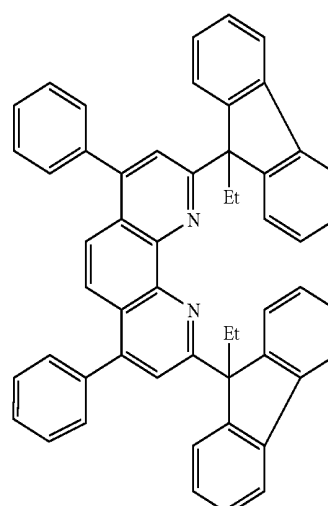
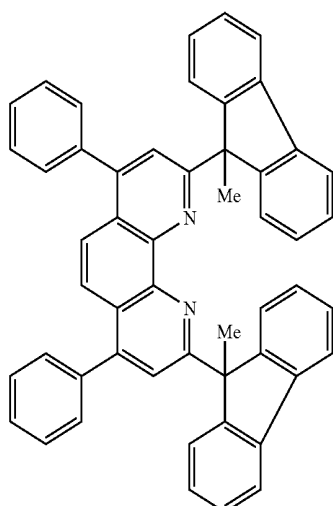
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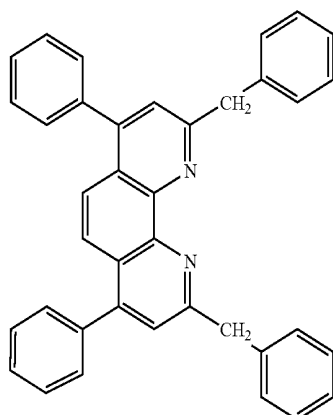
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Compound No. 137



47

-continued

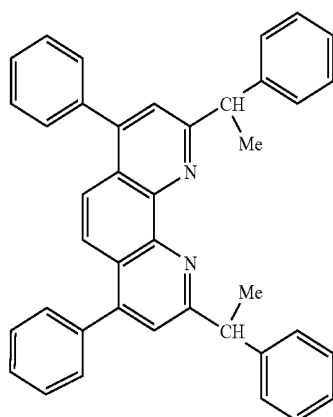


Compound No. 138

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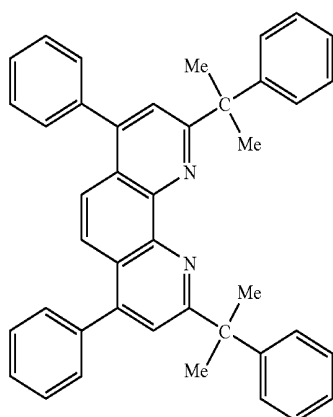
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Compound No. 139

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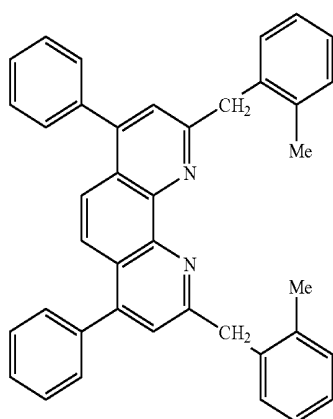


Compound No. 140

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Compound No. 141

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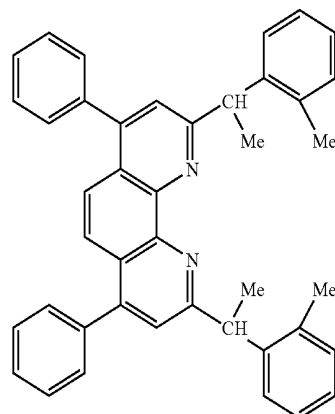
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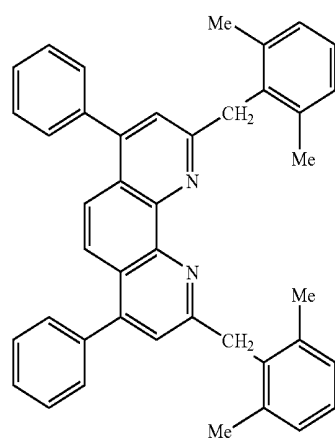
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48

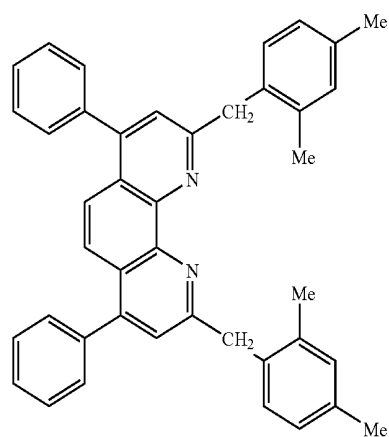
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Compound No. 142



Compound No. 143

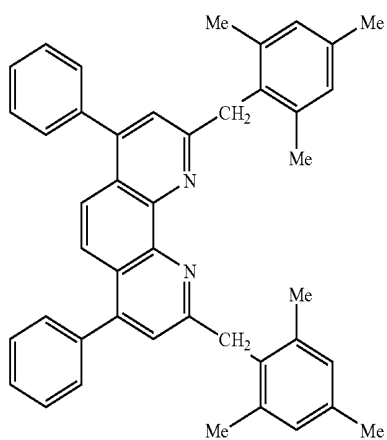


Compound No. 144

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-continued

Compound No. 145



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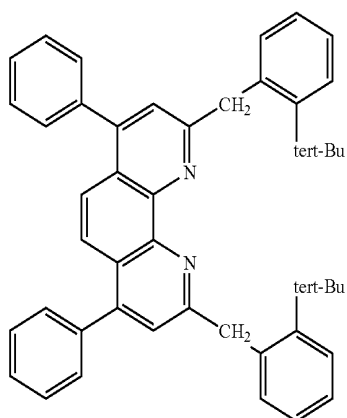
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Compound No. 146



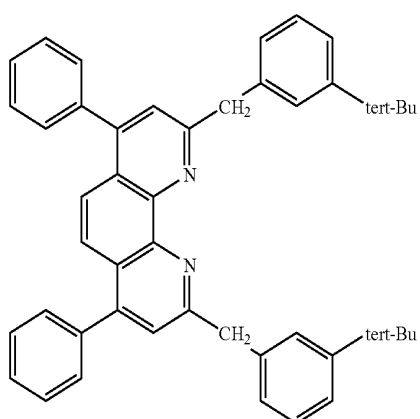
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Compound No. 147



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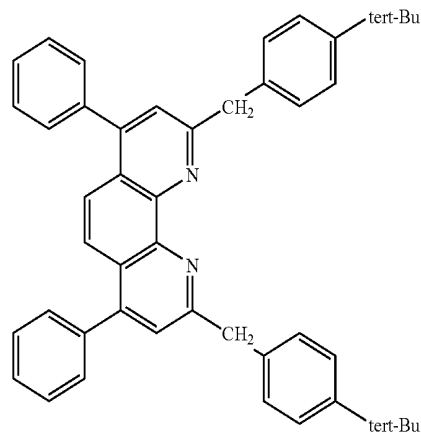
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-continued

Compound No. 148



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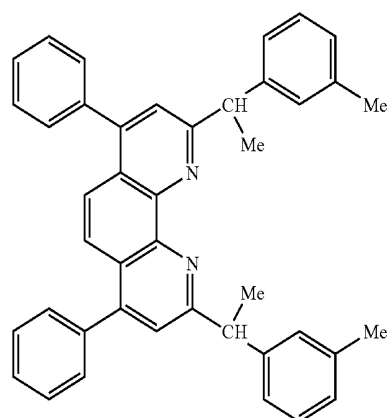
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Compound No. 149



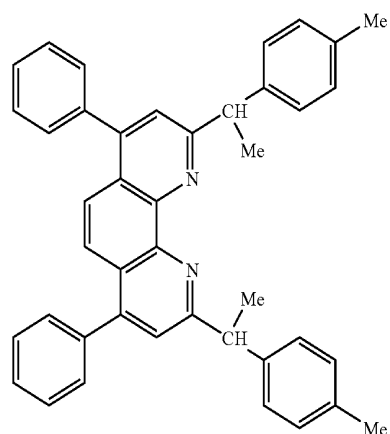
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Compound No. 150



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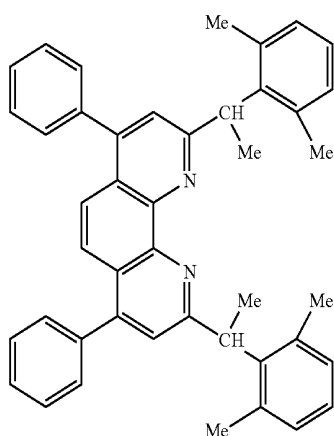
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-continued



Compound No. 151

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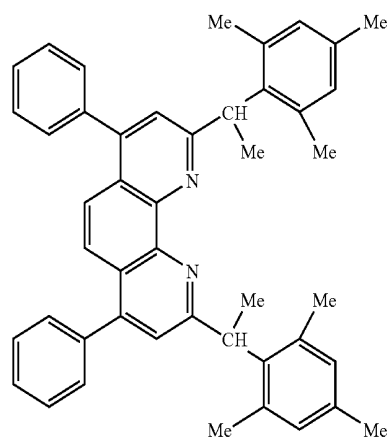
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-continued



Compound No. 154

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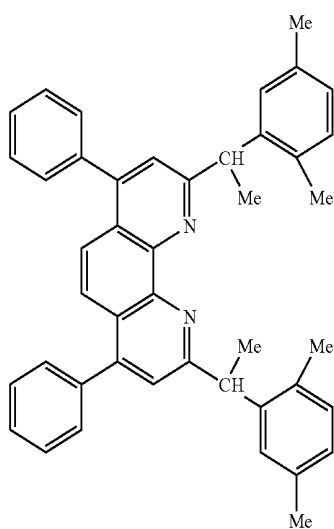
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Compound No. 152

Compound No. 155



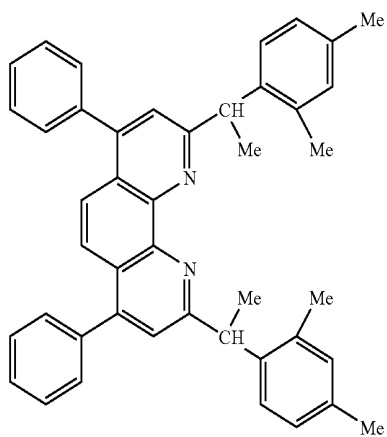
Compound No. 153

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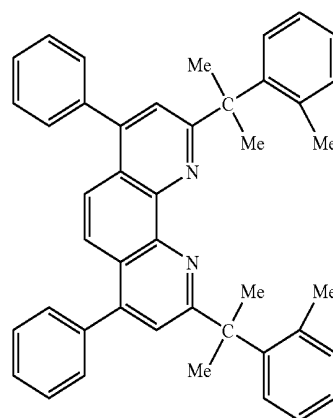
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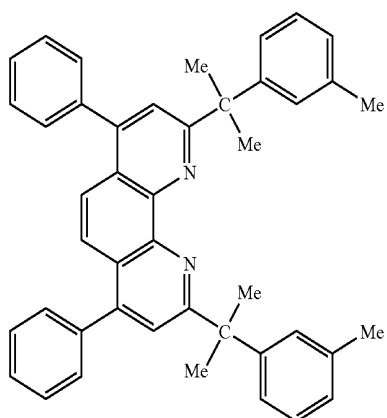
Compound No. 156



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-continued

Compound No. 157



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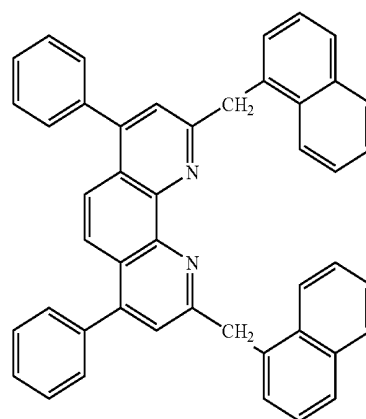
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Compound No. 160



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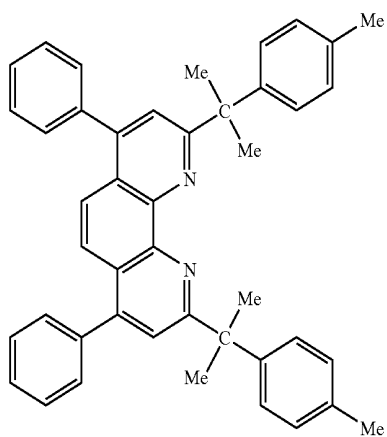
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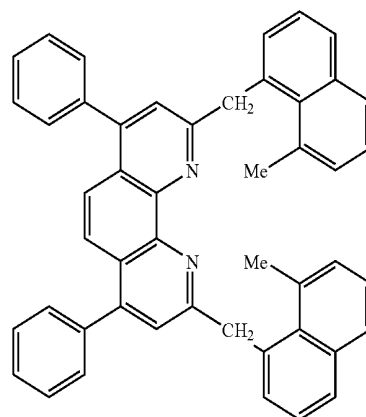
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Compound No. 158



Compound No. 161



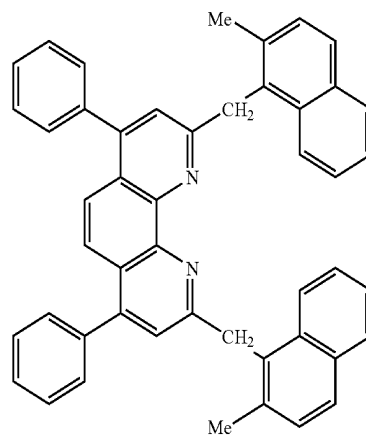
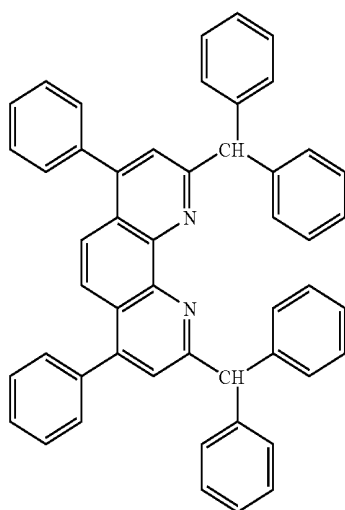
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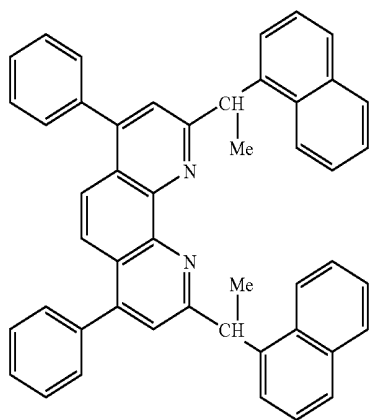
Compound No. 162



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-continued

Compound No. 163



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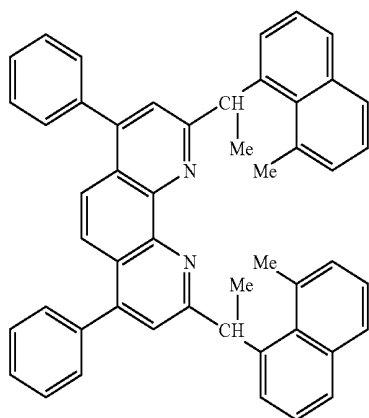
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Compound No. 164



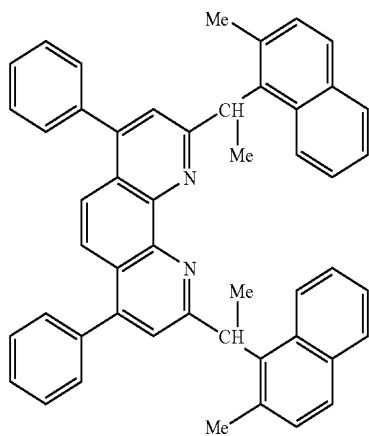
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Compound No. 165



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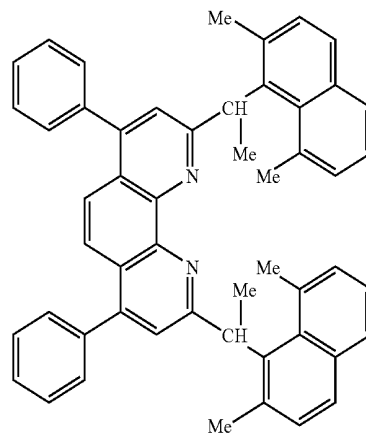
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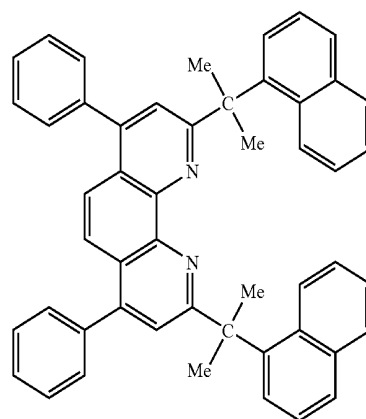
56

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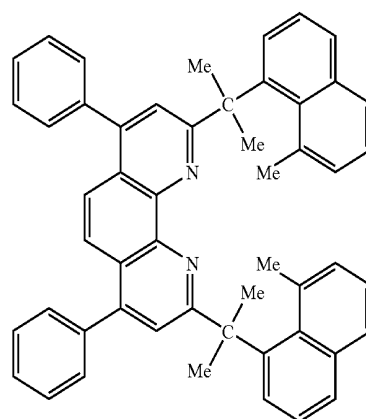
Compound No. 166



Compound No. 167



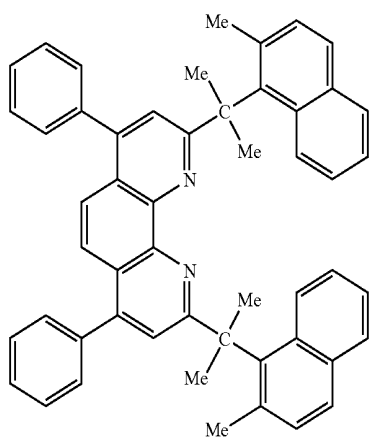
Compound No. 168



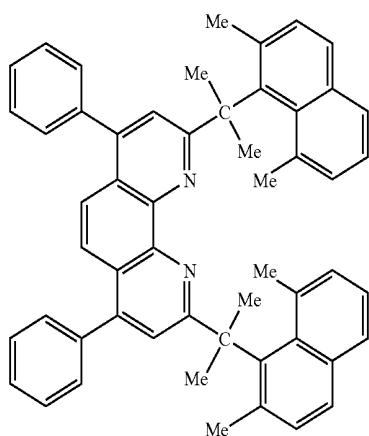
57

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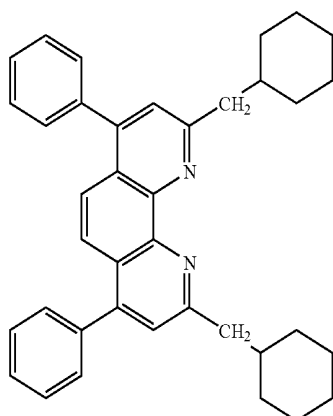
Compound No. 169



Compound No. 170



Compound No. 171



58

-continued

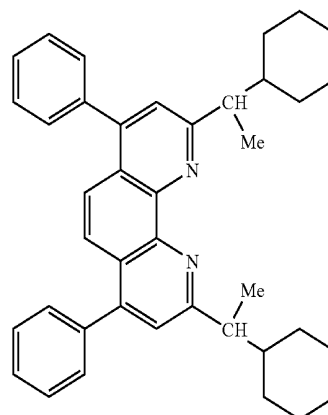
Compound No. 172

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Compound No. 173

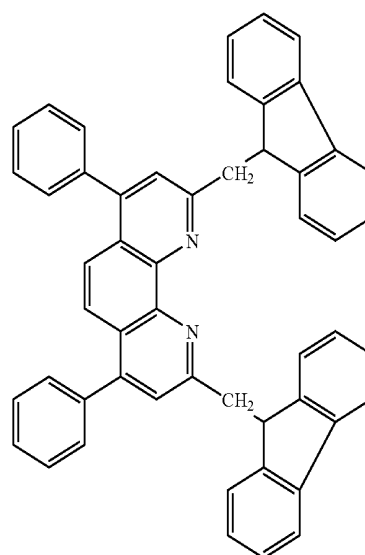
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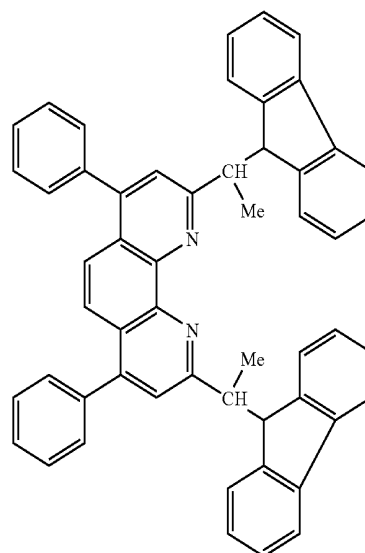
Compound No. 174

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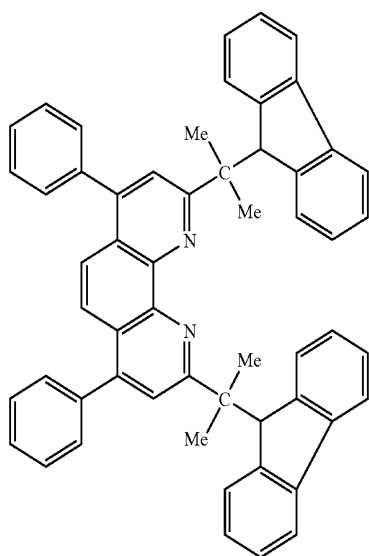
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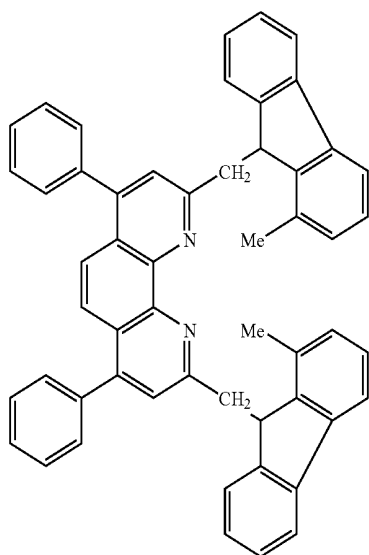
59

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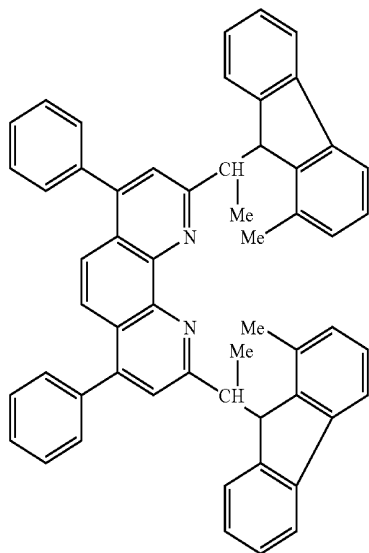
Compound No. 175



Compound No. 176



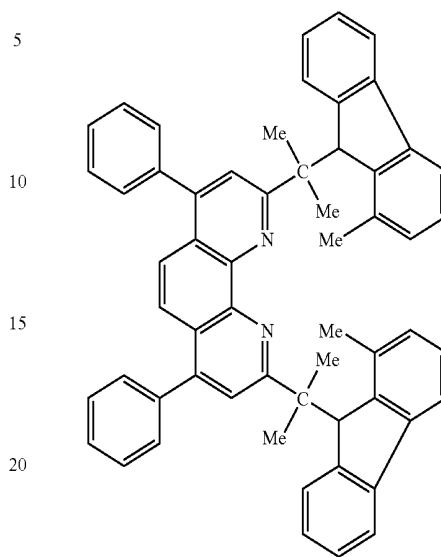
Compound No. 177



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Compound No. 178



Preferred embodiments of the invention wherein bathophenanthroline compounds of the invention are, respectively, applied to an organic EL device are described.

<First Embodiment>

FIG. 1 is a schematic sectional view showing an essential part of an organic EL device capable of emitting blue luminescence according to the first embodiment of the invention.

In this embodiment, a transparent electrode, made of ITO (indium tin oxide) or Zn-doped indium oxide, is formed on a glass substrate 6 by sputtering or vacuum deposition, followed by successively forming a hole transporting luminescent layer 4a hole transporting luminescent layer 4b, a hole-blocking layer 33 containing a bathophenanthroline (derivative) compound of the afore-indicated general formula, an electron transport layer 2, and a cathode electrode 1 in this order according to a vacuum deposition technique to form an organic EL device (organic EL device) 21 made of the amorphous organic thin films.

This organic EL device 21 has such an arrangement that the hole transport layer 4 serves also as a luminescent layer, and this fundamental structure is likewise employed in other embodiments described hereinafter.

The feature of the organic EL device 21 of this embodiment resides in that the bathophenanthroline derivative-containing layer 33 is interposed, as a hole-blocking layer, between the hole transport layer 4 and the electron transport layer 2, so that the re-combination of electrons-holes is promoted in the hole transport layer 4, at which luminescence is emitted, and/or luminescence is also emitted from the bathophenanthroline derivative-containing layer 33.

FIG. 2 schematically shows the built-up structure of the organic EL device of this embodiment in FIG. 1 as a band model.

In FIG. 2, the thick lines (L_1 , L_2) indicated at the cathode 1 made of Al and Al—Li (aluminium-lithium,) and the ITO transparent electrode 5 layer, respectively, mean approximate work functions of the respective metals. In the respective layers between the electrodes, upper thick lines l_1 , l_2 , l_3 and l_4 and numerical values thereof indicate the lowest unoccupied molecular orbital (LUMO) levels, and lower thick lines l_5 , l_6 , l_7 and l_8 and numerical values thereof

indicate the highest occupied molecular orbital (HOMO) levels, respectively. It is to be noted that the energy levels in FIG. 2 are shown only by way of example and may widely vary depending on the types of materials.

In the organic EL device, as shown in FIG. 2, the holes h charged from the transparent electrode 5 serving as an anode are moved via the hole transport layer 4. On the other hand, electrons e charged from the metal electrode 1 serving as a cathode are moved via the electron transport layer 2. The electrons-holes are re-combined in the hole transporting luminescent layer, at which luminescence is emitted.

The electrons e charged from the metal electrode 1 serving as a cathode has the tendency of moving toward a lower energy level, and can arrive at the hole transporting luminescent layers 4b, 4a via the lowest unoccupied molecular orbital (LUMO) levels l_1 to l_4 of the respective layers in the order of the metal electrode 1, electron transport layer 2, hole-blocking layer 33, hole transporting luminescent layer 4b and hole transporting luminescent layer 4a.

On the other hand, the holes h charged from the ITO transparent electrode 5 serving as an anode has the tendency of moving toward a higher energy level, and can move to the electron transport layer 2 via the highest occupied molecular orbital (HOMO) levels l_5 to l_7 of the respective layers in the order of the hole transporting luminescent layer 4a, hole transporting luminescent layer 4b and hole-blocking layer 33.

However, as shown in FIG. 2, the highest occupied molecular orbital (HOMO) level l_8 of the electron transport layer 2 is lower in energy than the highest occupied molecular orbital (HOMO) level l_7 of the hole-blocking layer 33. This makes it difficult that the charged holes h moves from the hole-blocking layer 33 toward the electron transport layer 2, and thus, they are filled in the hole-blocking layer 33.

Eventually, the holes h filled in the hole-blocking layer 33 promote the re-combination of electrons-holes at the hole transport layer 4, thereby permitting the luminescent materials of the hole transporting luminescent layers 4a, 4b or the hole transport layer 4 to emit luminescence or light.

In this way, the provision of the hole-blocking layer 33 effectively controls the transport of the holes h in the hole-blocking layer 33 so that the electron-hole re-combination in the hole transport layer 4 is efficiently caused. Thus, light with a specific wavelength (blue) is emitted in the form of light emission mainly from the hole transporting luminescent layer 4b, adjoining to the hole-blocking layer 33, of the light-emitting hole transporting luminescent layers 4a, 4b, to which emission from the hole transporting luminescent layer 4a is added.

Fundamentally, the electron-hole re-combination takes place in the respective layers including the electron transport layer 2 and the hole transport layer 4 as resulting from the charge of electrons from the cathode electrode 1 and the charge of holes from the anode electrode 5. Accordingly, in the absence of such a hole-blocking layer 33 as set out above, the electron-hole re-combination occurs at the interface between the electron transport layer 2 and the hole transport layer 4 so that light emission with a long wavelength alone is obtained. However, when the hole-blocking layer 33 as in this embodiment is provided, it is enabled to promote blue light emission while permitting the luminescent substance-containing hole transport layer 4 as an emission region.

As set out above, the hole-blocking layer 33 is provided to control the transport of the holes h. To this end, it is sufficient that the highest occupied molecular orbital

(HOMO) level of the hole-blocking layer 33 is not higher than the HOMO level that is lower in energy between the HOMO levels of the hole transporting luminescent layer 4b and the electron transport layer 2, and that the lowest unoccupied molecular orbital (LUMO) level of the hole-blocking layer 33 is not lower than the LUMO level that is lower in energy and is not higher than the LUMO level that is higher in energy, between the LUMO levels of the hole transporting luminescent layer 4b and the electron transport layer 2. Thus, the invention is not limited to such an arrangement as set out before.

In the practice of the invention, the energy levels may not always be within such ranges as defined before, and the bathophenanthroline compound-containing layer per se may emit light or luminescence. In addition, the hole-blocking layer may be made of a built-up structure including a plurality of layers.

The hole-blocking layer 33 may be formed of the bathophenanthroline derivative and/or other material, and its thickness may be changed within a range permitting its function to be maintained. More particularly, the thickness is preferably within a range of 1 Å to 1,000 Å (0.1 nm to 100 nm). If the thickness is too small, the hole blocking ability becomes incomplete, so that the re-combination region is liable to extend over the hole transport layer and the electron transport layer. On the contrary, when the thickness is too large, light emission may not occur due to the increase in film resistance.

The organic EL device 21 is made by use of a vacuum deposition apparatus 11 shown in FIG. 3. The apparatus 11 has therein a pair of support means 13 fixed below an arm 12. A stage mechanism (not shown) is provided between the fixed support means 13 so that a transparent glass substrate 6 can be turned down and a mask 22 can be set as shown. Below the glass substrate 6 and the mask 22, a shutter 14 supported with a shaft 14a is provided, below which a given number of deposition sources 28 are further provided. The deposition sources are heated by means of a resistance heating system using an electric power supply 29. For the heating, an EB (electron beam) heating system may also be used, if necessary.

In this apparatus, the mask 22 is for pixels, and the shutter 14 is for deposition materials. The shutter 14 is able to rotate about the shaft 14a and has the function of intercepting a deposition stream of a material depending on the sublimation temperature of the deposition material.

FIG. 4 is a plan view showing a specific example of the organic EL device fabricated by use of the vacuum deposition apparatus. More particularly, ITO transparent electrodes 5 each with a size of 2 mm×2 mm are vacuum deposited on a glass substrate 6 with a size, L, of 30 mm×30 mm by means of the vacuum deposition apparatus in a thickness of about 100 nm, followed by vacuum deposition of SiO₂ 30 over the entire surface thereof and etching in a given pixel pattern to form a multitude of openings 31. In this way, the transparent electrodes 5 are, respectively, exposed. Thereafter, the respective organic layers 4, 33, 2 and a metal electrode 1 are successively formed through a deposition mask 22 of SiO₂ on each 2 mm×2 mm emission region (pixel) PX.

Using the vacuum deposition apparatus 11, a large-sized pixel may be singly formed, aside from the device having a multitude of pixels as shown in FIG. 4.

In this way, when the organic layer 33 is formed in order to improve the efficiency of the electron-hole re-combinations in the emission region, there can be obtained an organic EL device that is stable and high in brightness, can be driven

at a low voltage and has the hole transporting luminescent layer **4**. As will be described in more detail, it is enabled to obtain a brightness of not smaller than 10,000 cd/m² by DC drive and a peak brightness, calculated as DC, of not smaller than 55,000 cd/M² by pulse drive at a duty ratio of 1/10 with respect to blue light emission.

The transparent electrode, organic hole transport layer, organic hole-blocking layer, organic electron transport layer and metal electrode of the electroluminescent device may, respectively, have a built-up structure made of a plurality of layers.

The respective organic layers of the electroluminescent device may be formed not only by vacuum deposition, but also other film-forming techniques using sublimation or vaporization, or a technique of spin coating, casting or the like.

The hole transporting luminescent layer of the electroluminescent device may be formed by co-deposition of a small amount of molecules in order to control emission spectra of the device, and may be, for example, an organic thin film containing a small amount of an organic substance such as a perylene derivative, a coumarin derivative or the like.

Usable hole transport materials include, aside from benzidine or its derivatives, styrylamine or its derivatives and triphenylmethane or its derivatives, porphyrin or its derivatives, triazole or its derivatives, imidazole or its derivatives, oxadiazole or its derivatives, polyarylethanes or derivatives thereof, phenylenediamine or its derivatives, arylamines or derivatives thereof, oxazole or its derivatives, anthracene or its derivatives, fluorenone or its derivatives, hydrazone or its derivatives, stilbene or its derivatives, or heterocyclic conjugated monomers, oligomers, polymers and the like such as polysilane compounds, vinylcarbazole compounds, thiophene compounds, aniline compounds and the like.

More particularly, mention is made of α -naphthylphenyldiamine, porphyrin, metal tetraphenylporphyrins, metal naphthalocyanines, 4,4',4''-trimethyltriphenylamine, 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine, N,N,N',N'-tetrakis(p-tolyl)-p-phenylenediamine, N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl, N-phenylcarbazole, 4-di-p-tolylaminostilbene, poly(paraphenylenevinylene), poly(thiophenevinylene), poly(2,2'-thienylpyrrole) and the like, although not limited thereto.

Usable electron transport materials include quinoline or its derivatives, perylene or its derivatives, bistyryl or its derivatives, pyrazine or its derivatives, and the like.

More specifically, mention is made, for example, of 8-hydroxyquinoline aluminium, anthracene, naphthalene, phenanthrene, pyrene, chrysene, perylene, butadiene, coumarin, acridine, stilbene, or derivatives thereof.

The materials used as the anode electrode or cathode electrode of the electroluminescent device are not limitative in types.

The cathode electrode material should preferably be made of a metal whose work function from a vacuum level of an electrode material is small in order to efficiently charge electrons. There may be used, aside from an aluminium-lithium alloy, low work function metals such as, for example, aluminium, indium, magnesium, silver, calcium, barium, lithium and the like, singly or in the form of alloys with other metals for enhancing the stability thereof.

In order to take out organic electroluminescence from the side of the anode electrode, ITO is used as a transparent anode electrode in examples appearing hereinafter. Nevertheless, there may be used electrode materials, which have a great work function from the vacuum level of an anode electrode material and include, for example, gold, a stannic

oxide-antimony mixture, a zinc oxide-aluminium mixture or the like, so as to efficiently charge holes.

The substrate **2** may not be limited to a glass substrate, but may be made of an opaque material. More particularly, there may be used, for example, a silicon substrate, a Cr substrate, or a substrate made of glass, on which a metal is formed by vacuum deposition. Where a substrate made of an opaque material is used, it is preferred that the upper surface of an organic EL device (i.e. the side of the cathode electrode) is formed of a transparent or translucent material so that electroluminescence is picked out to outside. ITO may be used for this purpose, for example.

There can be made an organic EL device for full color or multi-color, which is capable of emission of primaries of R, G and B, by proper choice of luminescent materials, not to mention an organic EL device for monochrome. Besides, the organic EL device of the invention is usable not only for display, but also for light source along with its application to other optical use.

It will be noted that the organic EL device may be sealed with germanium oxide or the like so as to enhance, the stability thereof by suppressing the influence of oxygen or the like in air, or may be driven under conditions drawn to vacuum.

<Second Embodiment>

FIG. **5** is a schematic sectional view showing an essential part of an organic EL device according to a second embodiment of the invention. An organic EL device **22** of this embodiment differs from that of FIG. **1** in that the hole transporting luminescent layer **4b** is formed on the ITO transparent electrode **5** so that the hole transporting luminescent layer is formed as a single layer.

<Third Embodiment>

FIG. **6** is a schematic sectional view showing an essential part of an organic EL device according to a third embodiment of the invention.

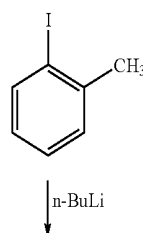
An organic EL device **23** of this embodiment differs from that of FIG. **1** in that a hole transport layer (serving also as a hole transporting luminescent layer) **4a** is formed on the ITO transparent electrode **5**, and thus, the hole transporting luminescent layer is formed as a single layer, like the second embodiment.

The invention is more particularly described by way of examples.

EXAMPLE 1

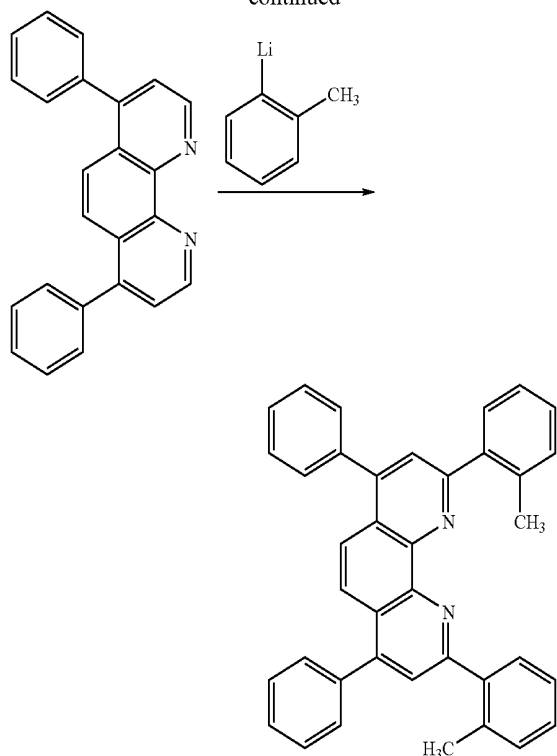
Preparation of 2,9-di(2-methylphenyl)bathophenanthroline

The reaction sequence is shown below



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-continued



n-Butyl lithium (1.6 M n-hexane solution, 17.0 ml, 26.8 mmol) was gradually dropped in an n-hexane solution (40 ml) of 2-iodotoluene (5.84 g, 26.4 mmol) at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was separated by filtration, followed by washing of the resulting white solid with n-hexane (40 ml×3 times). A toluene solution (50 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether/toluene (3:1) solution (20 ml) of the resulting white solid, followed by agitation at room temperature for 16 hours.

60 ml of iced water was added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform 4:1→2:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (1.01 g, yield: 49.5%) as light yellow crystals.

The product was identified through ¹H-NMR (solvent: chloroform) and FAB-MS measurements.

¹H-NMR: 2.70 (m, 6H, CH₃—Ar—), 7.25–7.75 (s, 18H, aromatic), 7.80 (s, 2H, aromatic), 7.90 (s, 2H, aromatic)

MS: m/s (relative intensity) 512 (M⁺, 100)

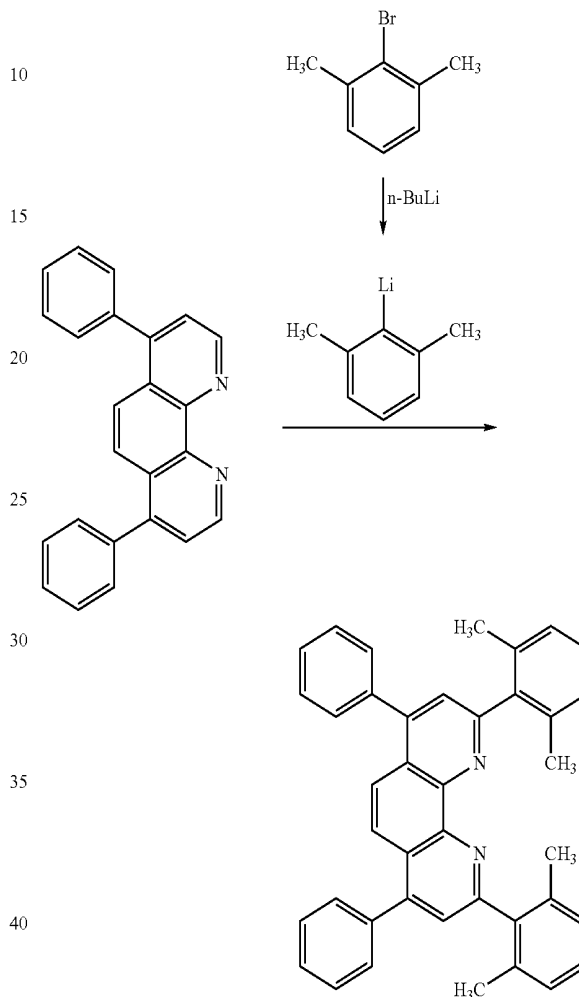
The visible light absorption maximum wavelength of a tetrahydrofuran (THF) solution of the product was at 297 nm, with a fluorescent wavelength being at 390 nm.

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EXAMPLE 2

Preparation of
2,9-di(2,6-dimethylphenyl)-bathophenanthroline

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 60.2 ml, 96.3 mmol) was gradually dropped in an n-hexane/anhydrous diethyl ether (10:1) solution (110 ml) of 2-bromo-m-xylene (17.8 g, 96.3 mmol) at room temperature. After completion of the dropping, the reaction solution was heated under reflux for 2 hours and further agitated at room temperature for 16 hours, and the resultant product was separated by filtration, followed by washing of the resulting white solids with n-hexane (50 ml×3 times). A toluene solution (80 ml) of bathophenanthroline (5.09 g, 15.3 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting white solids. After completion of the dropping, the solution was heated under reflux for 2 hours and agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chro-

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matography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (2.00 g, yield: 39.4%) as light yellow crystals.

The product was identified through ¹H-NMR and FAB-MS measurements.

¹H-NMR: 2.25 (m, 12H, CH₃—Ar—), 7.05–7.25 (s, 6H, aromatic), 7.35–7.70 (s, 12H, aromatic), 7.95 (s, 2H, aromatic)

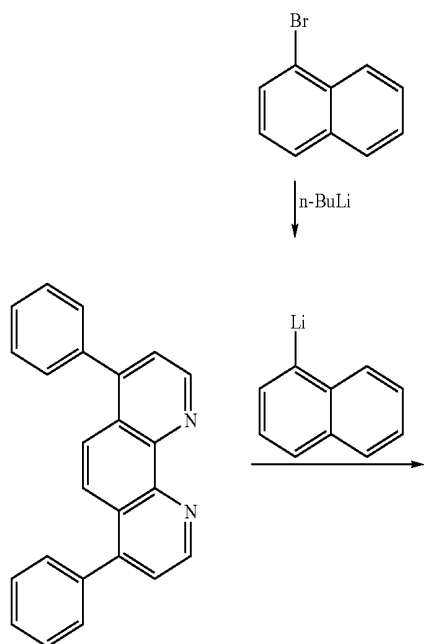
MS: m/s (relative intensity) 540 (M⁺, 100)

The visible light absorption maximum wavelength of a THF solution of the product was at 286 nm, with a fluorescent wavelength being at 380 nm.

EXAMPLE 3

Preparation of 2,9-dinaphthyl-bathophenanthroline

The reaction sequence is shown below



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n-Butyl lithium (1.6 M n-hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0° C., in an n-hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromonaphthalene (5.01 g, 24.4 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the residue was washed with n-hexane (40 ml×3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (1.38 g, yield: 68.2%).

The product was identified through ¹H-NMR and FAB-MS measurements.

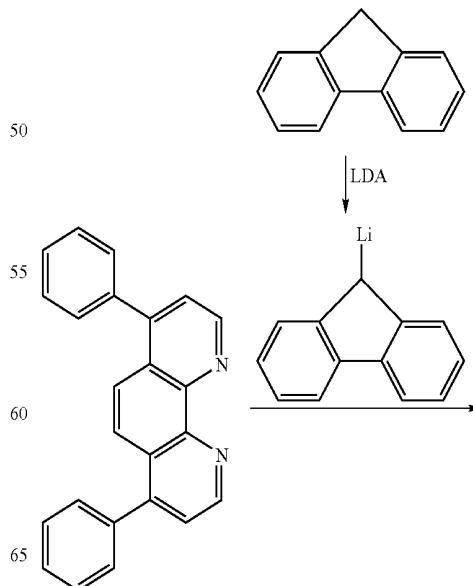
¹H-NMR: 7.30–8.00 (s, 24H, aromatic), 8.32 (s, 2H, aromatic), 8.68 (s, 2H, aromatic)

MS: m/s (relative intensity) 584 (M⁺, 100)

EXAMPLE 4

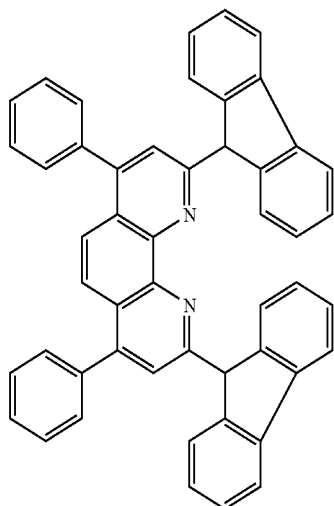
Preparation of 2,9-difluorenyl-bathophenanthroline

The reaction sequence is shown below



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-continued



Lithium diisopropylamine (LDA) (1.89 g, 17.4 mmol) was added to a THF solution (30 ml) of fluorene (4.16 g, 25.0 mmol) and agitated at room temperature for 16 hours. Thereafter, the THF and diisopropylamine were removed by distillation under reduced pressure. A toluene solution (60 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in an anhydrous diethyl ether solution (20 ml) of the resultant yellow solids at room temperature. After the dropping, the reaction solution was heated under reflux for 2 hours and agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (1.38 g, yield: 68.2%).

The product was identified through ¹H-NMR and FAB-MS measurements.

¹H-NMR: 4.51 (m, 2H, Ar—CH₂—Ar), 7.30–7.78 (s, 28H, aromatic), 7.81 (s, 2H, aromatic)

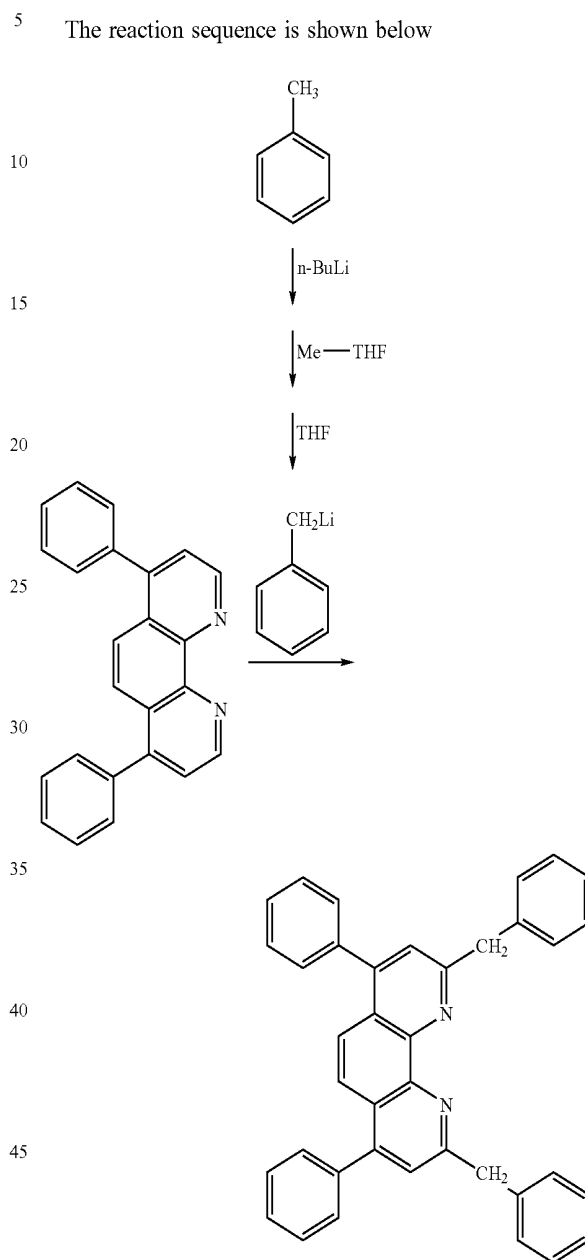
MS: m/s (relative intensity) 660 (M⁺, 100)

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EXAMPLE 5

Preparation of 2,9-dibenzyl-bathophenanthroline

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in anhydrous toluene (2.24 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was further added to the solution at -22° C. in 20 minutes. Thereafter, THF (1.06 g, 14.7 mmol) was added to in 30 minutes, followed by agitation at 6 to 10° C. for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in the resultant reaction solution. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed

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organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (0.88 g, yield: 43.3%).

The product was identified through ¹H-NMR and FAB-MS measurements.

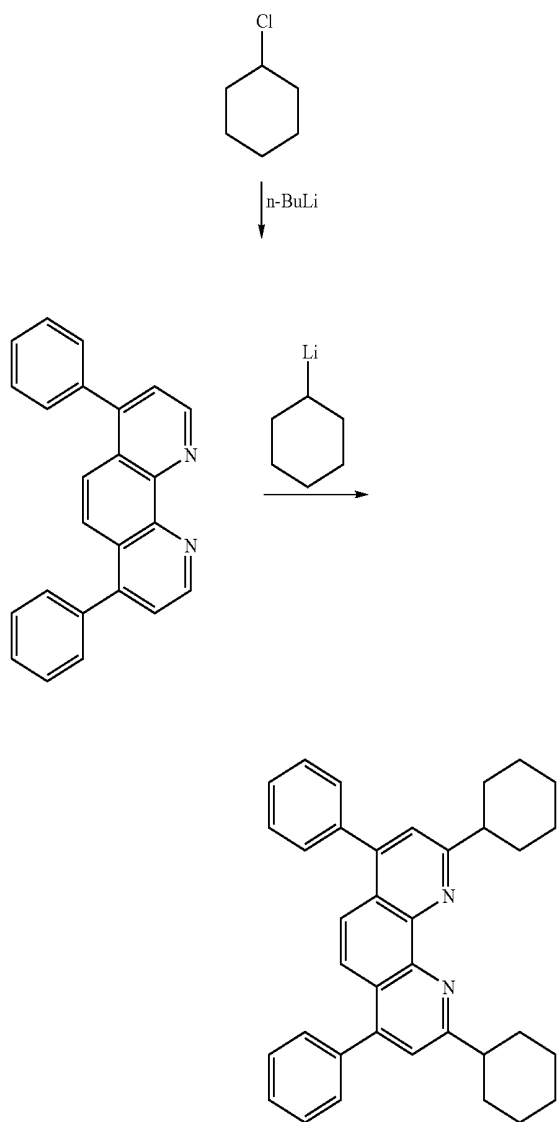
¹H-NMR: 4.68 (m, 4H, —CH₂—Ar), 7.28–7.78 (s, 22H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 512 (M⁺, 100)

EXAMPLE 6

Preparation of
2,9-dicyclohexyl-bathophenanthroline

The reaction sequence is shown below



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n-Butyl lithium (1.6 M n-hexane solution, 36.3 ml, 58.0 mmol) was gradually dropped, at room temperature, in an n-hexane/anhydrous diethyl ether (10:1) solution (50 ml) of chlorocyclohexane (3.00 g, 25.0 mmol). After completion of the dropping, the reaction solution was further agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the resulting white solids were washed with n-hexane (50 ml×3 times). A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (10 ml) of the resulting white solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (0.98 g, yield: 48.3%).

The product was identified through ¹H-NMR and FAB-MS measurements.

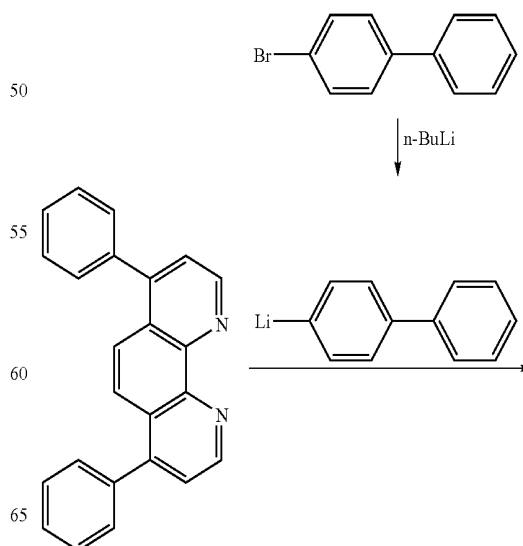
¹H-NMR: 0.80–2.45 (m, 20H, —CH₂—CH₂—CH₂—CH₂—), 3.20 (m, 2H, —CH—Ar), 7.25–7.75 (s, 12H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 496 (M⁺, 100)

EXAMPLE 7

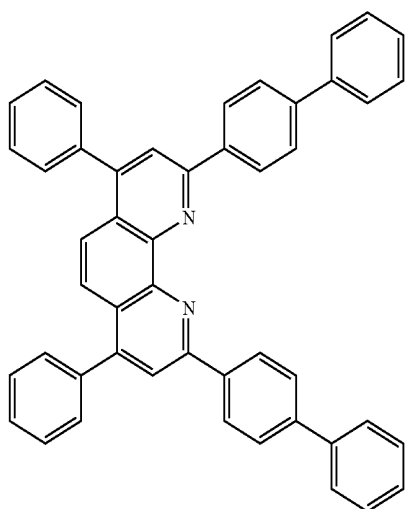
Preparation of 2,9-dibiphenyl-bathophenanthroline

The reaction sequence is shown below



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-continued



n-Butyl lithium (1.6 M n-hexane solution, 17.0 ml, 27.2 mmol) was gradually dropped, at room temperature, in an n-hexane/anhydrous diethyl ether (10:1) solution (110 ml) of 4-bromobiphenyl (6.33 g, 27.2 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the resulting white solids were washed with n-hexane (50 ml×3 times). A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (20 ml) of the resulting white solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (0.76 g, yield: 37.4%).

The product was identified through ¹H-NMR and FAB-MS measurements.

¹H-NMR: 7.25–7.78 (s, 26H, aromatic), 7.81 (s, 2H, aromatic), 8.32 (s, 4H, aromatic)

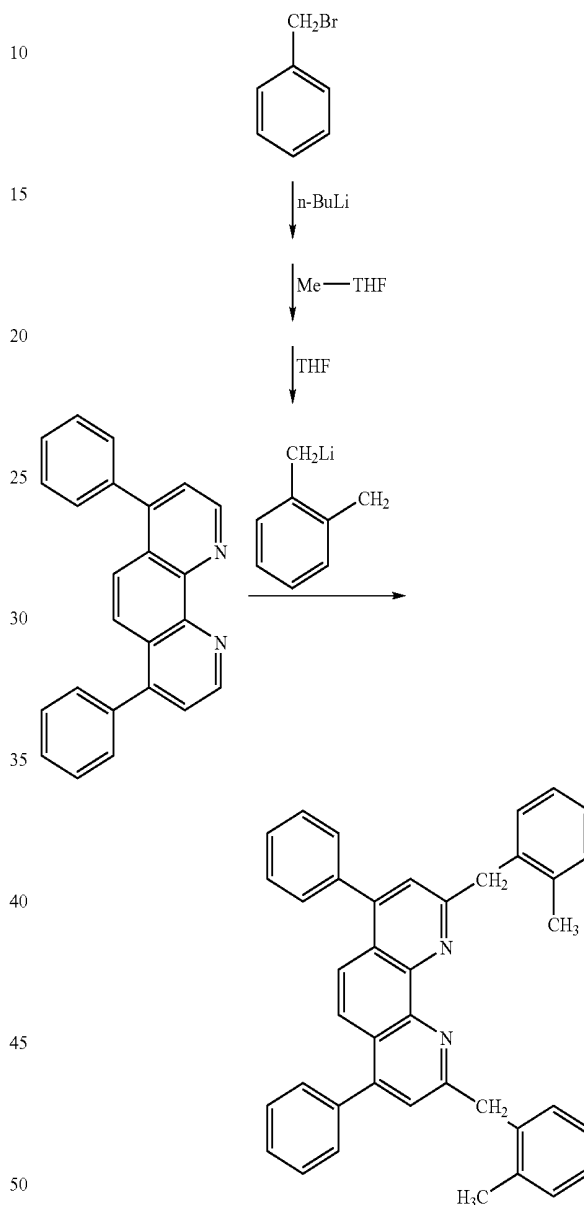
MS: m/s (relative intensity) 636 (M⁺, 100)

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EXAMPLE 8

Preparation of 2,9-di(2-methylbenzyl)-bathophenanthroline

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in α-bromo-o-xylene (4.91 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was added in 20 minutes at -22° C., after which THF (1.06 g, 14.7 mmol) was further added in 30 minutes, followed by further agitation at 6 to 10° C. for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in the resultant reaction solution at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previ-

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ously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (0.72 g, yield: 35.4%).

The product was identified through $^1\text{H-NMR}$ and FAB-MS measurements.

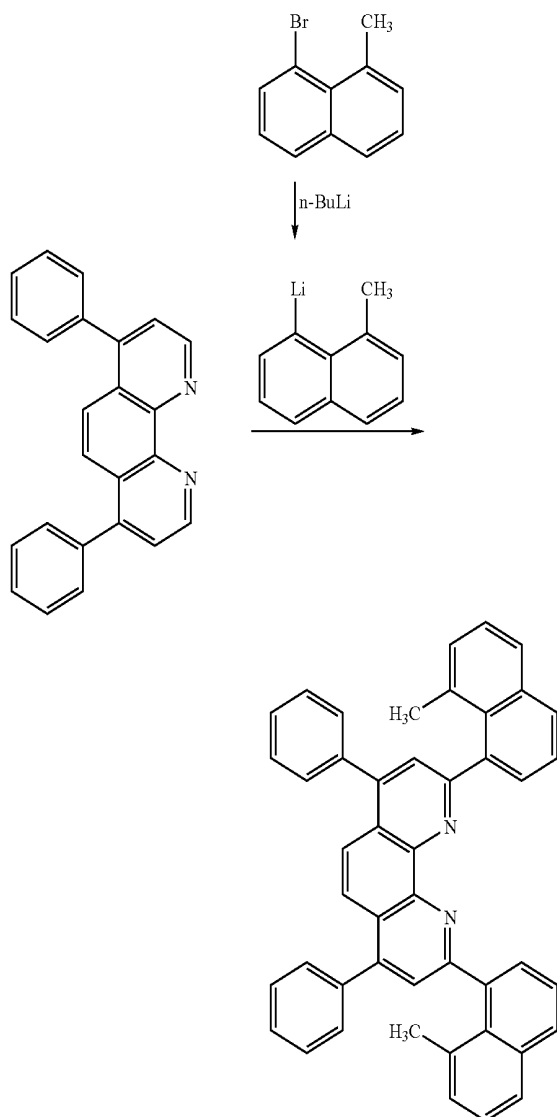
$^1\text{H-NMR}$: 2.35 (m, 6H, $\text{CH}_3\text{—Ar—}$), 4.65 (m, 4H, $\text{CH}_2\text{—Ar—}$), 7.25–7.78 (s, 20H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 540 (M^+ , 100)

EXAMPLE 9

Preparation of
2,9-di(8-methylnaphthyl)-bathophenanthroline

The reaction sequence is shown below



76

n-Butyl lithium (1.6 M n-hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0°C ., in an n-hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromo-8-methylnaphthalene (5.34 g, 24.4 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the residue was washed with n-hexane (40 ml×3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (1.30 g, yield: 64.0%).

The product was identified through $^1\text{H-NMR}$ and FAB-MS measurements.

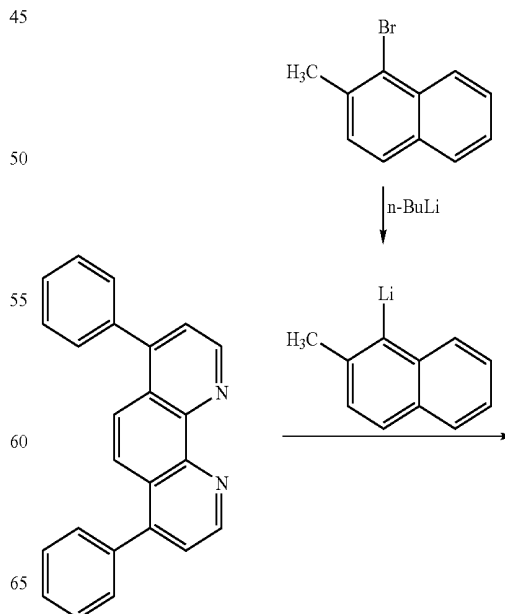
$^1\text{H-NMR}$: 2.60 (m, 6H, $\text{CH}_3\text{—Ar—}$), 7.30–7.81 (s, 22H, aromatic), 7.81 (s, 2H, aromatic), 8.25 (s, 2H, aromatic)

MS: m/s (relative intensity) 612 (M^+ , 100)

EXAMPLE 10

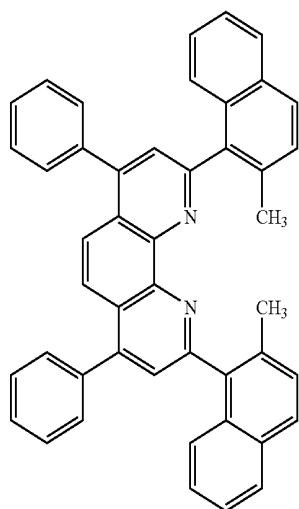
Preparation of 2,9-di
(2-methylnaphthyl)-bathophenanthroline

The reaction sequence is shown below



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-continued



n-Butyl lithium (1.6 M n-hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0° C., in an n-hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromo-2-methylnaphthalene (5.34 g, 24.4 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the residue was washed with n-hexane (40 ml×3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (1.20 g, yield: 59.1%).

The product was identified through ¹H-NMR and FAB-MS measurements.

¹H-NMR: 2.80 (m, 6H, CH₃—Ar—), 7.25–7.78 (s, 24H, aromatic), 7.81 (s, 2H, aromatic)

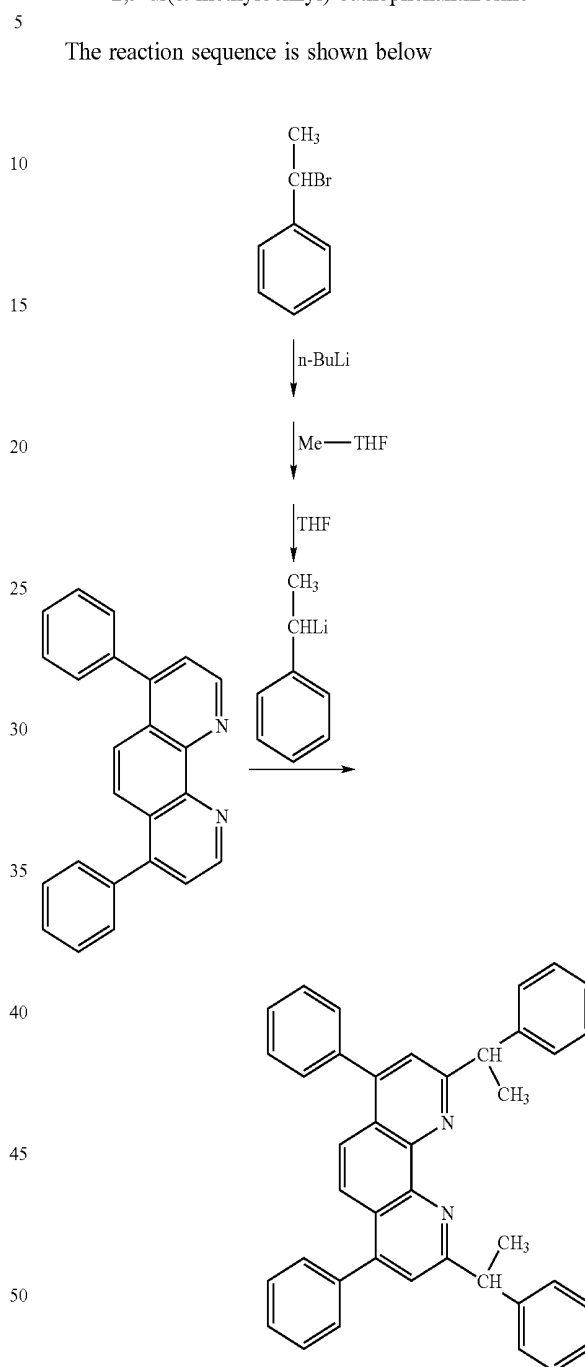
MS: m/s (relative intensity) 612 (M⁺, 100)

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EXAMPLE 11

Preparation of
2,9-di(α-methylbenzyl)-bathophenanthroline

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in 1-bromo-1-phenylethane (4.91 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was added in 20 minutes at -22° C., after which THF (1.06 g, 14.7 mmol) was further added in 30 minutes, followed by further agitation at 6 to 10° C. for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in the resultant reaction solution at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The

aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform=8:1→4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane=2:1) to obtain the intended compound (0.83 g, yield: 40.9%).

The product was identified through ¹H-NMR and FAB-MS measurements.

¹H-NMR: 2.40 (m, 6H, CH₃—Ar—), 4.64 (m, 2H, —CH—Ar—), 7.25–7.78 (s, 22H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 540 (M⁺, 100)

As will be appreciated from the foregoing, the bathophenanthroline compounds of the invention can control, for example, carrier transportability depending on the type of substituent to be introduced into the molecule, thus permitting one to utilize them as a carrier transport material of various types of organic EL devices. Moreover, these compounds have high glass transition point and melting point and are thus stable electrically, thermally and/or chemically. In addition, the compounds are sublimable in nature, thus leading to the advantage that they are readily formed as a uniform amorphous film according to a vacuum deposition process. The bathophenanthroline compound of the invention can be efficiently prepared through nucleophilic substitution reaction using an organolithium compound.

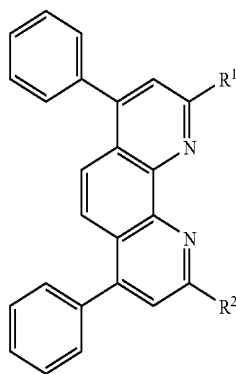
What is claimed is:

1. An electroluminescent device comprising a first electrode, a second electrode, an electron transport layer, a hole transport layer, and a hole-blocking layer,

wherein,

(a) the hole-blocking layer is distinct from the electron transport layer, and

(b) the hole-blocking layer comprises a compound of formula (I):



wherein R¹ and R² are independently selected from the group consisting of an ethyl group, an n-propyl group, an isopropyl group, a n-butyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an iso-pentyl group, a neopentyl group, a tert-pentyl group, a cyclopentyl group, a methylcyclopentyl group, a dimethylcyclopentyl group, a trimethylcyclopentyl group, a

formula (I)

tetramethylcyclopentyl group, an n-hexyl group, a 2-ethylbutyl group, a 3,3-dimethylbutyl group, a cyclohexyl group, a methylcyclohexyl group, a dimethylcyclohexyl group, a trimethylcyclohexyl group, an ethylcyclohexyl group, a diethylcyclohexyl group, a triethylcyclohexyl group, a 2-ethylhexyl group, an n-nonyl group, an n-decyl group, an n-dodecyl group, an n-tetradecyl group, an n-hexadecyl group, a benzyl group, a phenethyl group, an α-methylbenzyl group, an α,α-dimethylbenzyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a furfuryl group, a 2-methylbenzyl group, a 3-methylbenzyl group, a 4-methylbenzyl group, a 4-ethylbenzyl group, a 4-isopropylbenzyl group, a 4-tert-butylbenzyl group, a 4-n-hexylbenzyl group, a 4-nonylbenzyl group, and a 3,4-dimethylbenzyl group.

2. The electroluminescent device of claim 1, wherein at least one of the electrodes comprises a material which is one of transparent and translucent.

3. The electroluminescent device of claim 2, wherein at least one of the electrodes comprises indium tin oxide (ITO).

4. The electroluminescent device of claim 1, wherein the hole transporting layer is luminescent.

5. The electroluminescent device of claim 1 wherein: the brightness of the device is at least 10,000 cd/m².

6. A display device comprising the electroluminescent device of claim 5.

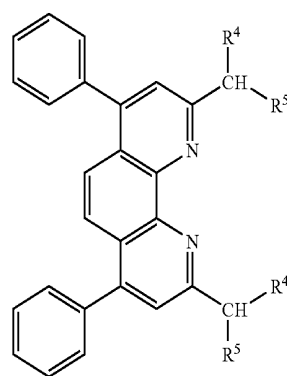
7. An electroluminescent device comprising a first electrode, a second electrode, an electron transport layer, a hole transport layer, and a hole-blocking layer,

wherein,

(a) the hole-blocking layer is distinct from the electron transport layer, and

(b) the hole-blocking layer comprises a compound of formula (II):

wherein:



formula (II)

R⁴ is selected from the group consisting of hydrogen and methyl and R⁵ is selected from the group consisting of methyl, cyclohexyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, naphthyl, methyl-naphthyl, dimethylnaphthyl, fluorenyl, methylfluorenyl and dimethylfluorenyl; or

each of R⁴ and R⁵ is phenyl.

8. The electroluminescent device of claim 7, wherein at least one of the electrodes comprises a material which is one of transparent and translucent.

9. The electroluminescent device of claim 8, wherein at least one of the electrodes comprises indium tin oxide (ITO).

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10. The electroluminescent device of claim 7, wherein the hole transporting layer is luminescent.

11. The electroluminescent device of claim 7 wherein: the brightness of the device is at least 10,000 cd/m².

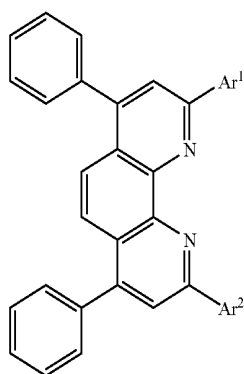
12. A display device comprising the electroluminescent device of claim 11.

13. An electroluminescent device comprising a first electrode, a second electrode, an electron transport layer, a hole transport layer, and a hole-blocking layer,

wherein,

(a) the hole-blocking layer is distinct from the electron transport layer, and

(b) the hole-blocking layer comprises a compound of formula (III):



wherein Ar¹ and Ar² may be the same or different and are independently selected from the group consisting of a 2-anthryl group, a 4-quinolyl group, a pyridyl group, a 3-pyridynyl group, a 2-pyridynyl group, a 3-furyl group, a 2-furyl group, a 3-thienyl group, a 2-oxazolyl group, a 2-thiazolyl group, a 2-benzoxazolyl group, a 2-benzothiazolyl group, a 2-benzimidazolyl group, a propylphenyl group, an isopropylphenyl group, a butylphenyl group, an isobutylphenyl group, a sec-butylphenyl group, a tert-butylphenyl group.

14. The electroluminescent device of claim 13, wherein one of the electrodes comprises a material which is one of transparent and translucent.

15. The electroluminescent device of claim 14, wherein at least one of the electrodes comprises indium tin oxide (ITO).

16. The electroluminescent device of claim 13, wherein the hole transporting layer is luminescent.

17. The electroluminescent device of claim 13 wherein: the brightness of the device is at least 10,000 cd/m².

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18. A display device comprising the electroluminescent device of claim 17.

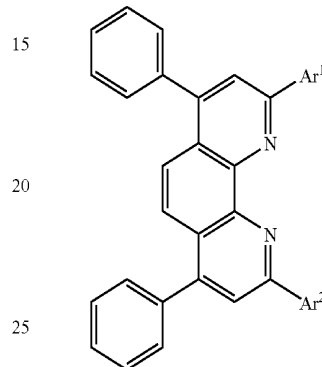
19. An electroluminescent device comprising a first electrode, a second electrode, an electron transport layer, a hole transport layer, and a hole-blocking layer,

wherein,

(a) the hole-blocking layer is distinct from the electron transport layer, and

(b) the hole-blocking layer comprises a compound of formula (V):

formula (III)



wherein Ar¹ and Ar² may be the same or different and independently represent an aryl group, and

Ar¹ and Ar² are selected from the group consisting of a 1-naphthyl group, a 9-anthryl group, a 2-fluorenyl group, a methylphenyl group, a dimethylphenyl group, a trimethylphenyl group, an ethylphenyl group, a diethylphenyl group, a triethylphenyl group, a tert-butylphenyl group, a cyclohexylphenyl group, a phenylphenyl group.

20. The electroluminescent device of claim 19, wherein at least one of the electrodes comprises a material which is one of transparent and translucent.

21. The electroluminescent device of claim 20, wherein at least one of the electrodes comprises indium tin oxide (ITO).

22. The electroluminescent device of claim 20, wherein the hole transporting layer is luminescent.

23. The electroluminescent device of claim 19 wherein: the brightness of the device is at least 10,000 cd/m².

24. A display device comprising the electroluminescent device of claim 23.

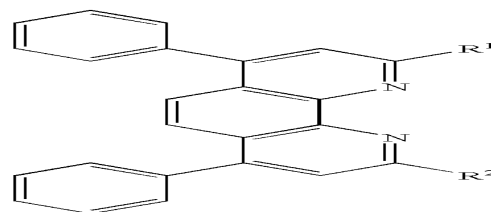
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专利名称(译)	Bathophenanthroline化合物和EL器件		
公开(公告)号	US7186469	公开(公告)日	2007-03-06
申请号	US10/798820	申请日	2004-03-11
[标]申请(专利权)人(译)	SHIBANUMA TETABUO 木岛安则 浅井信敏 田村SHINICHIRO		
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当前申请(专利权)人(译)	JOLED INC.		
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发明人	SHIBANUMA, TETSUO KIJIMA, YASUNORI ASAI, NOBUTOSHI TAMURA, SHINICHIRO		
IPC分类号	H01L51/54 H05B33/12 C07D471/04 H01L51/30 H01L51/50		
CPC分类号	C07D471/04 H01L51/0072 H01L51/0052 H01L51/0058 Y10S428/917 H01L51/0081 H01L51/5012 H01L2251/308		
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外部链接	Espacenet USPTO		

摘要(译)

提供了通式[I]或[II]的新型红菲咯啉化合物 其中R¹和R²可以相同或不同并且独立地表示直链, 支链或环状, 饱和或不饱和烃基, 或取代或未取代的饱和或不饱和烃基, 条件是R¹和R²中的至少一个具有至少两个碳原子, 其中Ar¹和Ar²可以相同或不同, 并且独立地表示取代或未取代的芳基。还提供了制备该化合物的方法, 其中将红菲咯啉和有机锂化合物进行亲核取代反应, 得到上式[I]或[II]的化合物。

General Formula [I]:



General Formula [II]:

