(19) 대한민국특허청(KR)
(12) 등록특허공보(B1)

(45) 공고일자 2014년02월11일
(11) 등록번호 10-1359701
(24) 등록일자 2014년01월29일

(51) 국제특허분류(Int. Cl.)
C09K 11/06 (2006.01)
(21) 출원번호 10-2008-0123423
(22) 출원일자 2008년12월05일
심사청구일자 2011년11월08일
(65) 공개번호 10-2010-0064815
(43) 공개일자 2010년06월15일
(56) 선행기술조사문헌
KR1020040057862 A*
KR1020070115588 A*
US20070009758 A1*
*는 심사관에 의하여 인용된 문헌

(73) 특허권자
엘지디스플레이 주식회사
서울특별시 영등포구 여의대로 128(여의도동)
(72) 발명자
이승재
서울특별시 송파구 백제고분로50길 15-15, 2층 204호 (방이동)
송인범
경기 의정부시 회룡로105번길 30, 101동 1209호 (호원동, 쌍용아파트)
(뒷면에 계속)
(74) 대리인
특허법인네이트

전체 청구항 수 : 총 4 항 심사관 : 오세주

(54) 발명의 명칭 **청색 형광 물질 및 이를 이용한 유기전계발광소자**

(57) 요 약

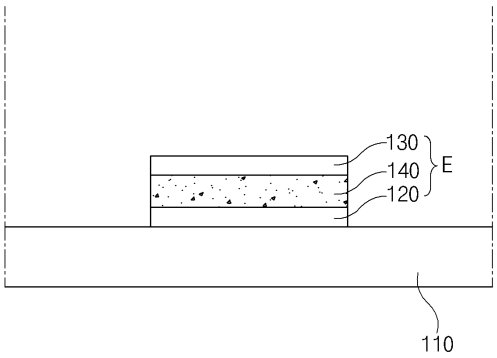
본 발명은 청색 형광 물질 및 이를 이용한 유기전계발광소자에 관한 것이다.

본 발명에 있어서, 청색 형광 물질은 6-플루오로페닐아민 유도체가 1,6-파이렌에 치환된 구조에서 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 중 적어도 두개와 질소에는 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되어, 색순도와 발광효율 및 발광수명이 향상되는 것이 특징이다.

또한, 6-플루오로페닐아민 유도체가 1,6-파이렌에 치환된 구조에서 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 및 질소 중 적어도 하나는 중수소(D)로 치환된 방향족 그룹에서 선택되는 물질로 치환되고, 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 중 적어도 두개는 수소, 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되며, 질소에는 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되어, 색순도와 발광효율 및 발광수명이 향상되는 것을 특징으로 한다.

또한, 페닐아민 유도체가 1,6-파이렌에 치환된 구조에서, 질소의 제 1 페닐기에는 플로린, 시아닌, 트리플로로메틸기 중 적어도 어느 하나가 치환되고, 제 2 페닐기에는 적어도 두개의 아릴기가 치환되어 색순도와 발광효율 및 발광수명이 향상되는 것을 특징으로 한다.

대 표 도 - 도2



(72) 발명자

김중근

경기 김포시 풍무로 232, 101동 701호 (사우동, 길훈4차아파트)

김도한

경기도 고양시 일산서구 강선로 71, 704동 1002호 (주엽동, 강선마을)

박춘건

서울특별시 관악구 난곡로46길 19, 101호 (신림동)

오형윤

경기도 고양시 일산동구 경의로 333, 505동 903호 (마두동, 백마마을)

빈종관

경기도 여주군 가남면 금당리길 92

이경훈

경기도 고양시 일산서구 강성로 62, 907동 401호 (주엽동, 강선마을)

정현철

경상남도 하동군 양보면 감당리 1002

유동희

서울 마포구 독막로 145, 110동 102동 (창전동, 서강쌍용예가)

조남성

경기도 고양시 일산동구 숲속마을2로 25, 602동 1203호 (풍동, 숲속마을)

박종현

서울 송파구 올림픽로45길 11, 1동 1502호 (풍납동, 극동아파트)

유인선

경기 파주시 월롱면 엘지로 245, 정다운마을 104동 1209호 (파주LCD산업단지)

박태한

서울특별시 구로구 고척로41길 24 (고척동)

차순욱

경기도 고양시 일산동구 노루목로 100, 212동 1704호 (장항동, 호수마을)

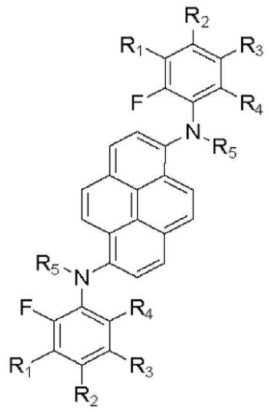
특허청구의 범위

청구항 1

전자 또는 정공을 전달할 수 있는 호스트물질과;

하기 화학식1로 표시되는 도펀트 물질을 포함하는 청색 형광 물질.

화학식1



(상기 화학식1에서, R1, R2, R3, R4 중 2개는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택되고 서로 동일하며, 나머지는 수소이며, R5는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택된다.)

청구항 2

제 1 항에 있어서,

상기 방향족 그룹은 페닐(phenyl), 바이페닐(biphenyl), 나프틸(naphthyl), 페난스렌(phenanthrene), 터페닐(terphenyl), 플루오레닐(fluorenyl)에서 선택되고, 상기 방향족 그룹의 치환체는 메틸(methyl), 에틸(ethyl), 프로필(propyl), 이소프로필(i-propyl), 터셔리부틸(tert-butyl), 실릴(silyl) 그룹, 플루오린(fluorine)에서 선택되는 것을 특징으로 하는 청색 형광 물질.

청구항 3

제 1 항에 있어서,

상기 이형고리 그룹은 퓨란(furan), 티오펜(thiophene), 피롤(pyrrole), 피리딘(pyridine), 피리미딘(pyrimidine)에서 선택되는 것을 특징으로 하는 청색 형광 물질.

청구항 4

삭제

청구항 5

삭제

청구항 6

삭제

청구항 7

삭제

청구항 8

삭제

청구항 9

삭제

청구항 10

제 1 전극과;

상기 제 1 전극과 마주보는 제 2 전극과;

상기 제 1 및 제 2 전극 사이에 위치하며, 정공주입층, 정공수송층, 발광물질층, 전자수송층, 전자주입층을 포함하고, 상기 발광물질층은 제 1항 내지 제 3항 중 어느 하나를 포함하는 것을 특징으로 하는 유기전계발광소자.

명 세 서

발명의 상세한 설명

기 술 분 야

[0001] 본 발명은 청색 형광 물질 및 이를 사용하는 유기전계발광소자에 관한 것이다. 보다 구체적으로, 본 발명은 발광효율과 색순도가 높고 향상된 수명을 갖는 청색 형광 물질 및 이를 포함하여 이루어지는 유기전계발광소자에 관한 것이다.

배 경 기 술

[0002] 최근 표시장치의 대형화에 따라 공간 점유가 적은 평면표시소자의 요구가 증대되고 있는데, 이러한 평면표시소자 중 하나로서 유기발광다이오드(organic light emitting diode: OLED)라고도 불리는 유기전계발광소자의 기술이 빠른 속도로 발전하고 있으며, 이미 여러 시제품들이 발표된 바 있다.

[0003] 유기 전계 발광 소자는 전자 주입 전극(음극) 과 정공 주입 전극(양극) 사이에 형성된 발광물질층에 전하를 주입하면 전자와 정공이 쌍을 이룬 후 소멸하면서 빛을 내는 소자이다. 플라스틱 같은 휠 수 있는(flexible) 투명 기판 위에도 소자를 형성할 수 있을 뿐 아니라, 플라즈마 디스플레이 패널(Plasma Display Panel)이나 무기 전계발광(EL) 디스플레이에 비해 낮은 전압에서 (10V이하) 구동이 가능하고, 또한 전력 소모가 비교적 적으며, 색감이 뛰어나다는 장점이 있다. 또한 유기 전계 발광(EL) 소자는 녹색, 청색, 적색의 3가지 색을 나타낼 수가 있어 차세대 풍부한 색 디스플레이 소자로 많은 사람들의 많은 관심의 대상이 되고 있다. 여기서 유기전계발광소자를 제작하는 과정을 간단히 살펴보면,

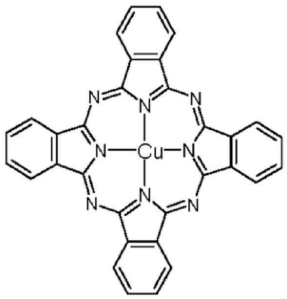
[0004] (1) 먼저, 투명기판 위에 인듐-틴-옥사이드(indium tin oxide; ITO)와 같은 물질을 증착하여 양극(anode)을 형성한다.

[0005] (2) 상기 양극 상에 정공주입층(HIL:hole injecting layer)을 형성한다. 정공주입층은 주로 하기 화학식1-1로 표시되는 구리 프탈로시아닌 (copper phthalocyanine(CuPc))을 10nm 내지 30nm 두께로 증착하여 형성된다.

[0006] (3) 다음, 상기 정공주입층 상에 정공수송층(HTL: hole transport layer)을 형성한다. 이러한 정공수송층은 4,4'-비스(bis)[N-(1-나프틸(naphtyl))-N-페닐아미노(phenylamino)]-바이페닐(biphenyl) (NPB)을 30nm 내지 60nm 정도 증착하여 형성된다.

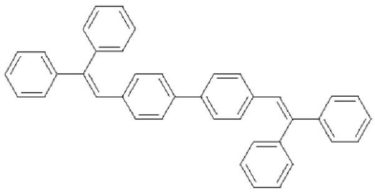
[0007] (4) 다음, 상기 정공수송층 상에 발광물질층 (EML: emitting material layer)을 형성한다. 상기 발광물질층은 호스트(host)와 도펀트(dopant)로 이루어지며, 하기 화학식1-2로 표시되는 DPVBi를 호스트 물질로 하고, 하기 화학식1-3으로 표시되는 BD-a를 도펀트로 1~10% 농도로 첨가하여, 20~40nm 정도 증착한다.

[0008] 화학구조식1-1



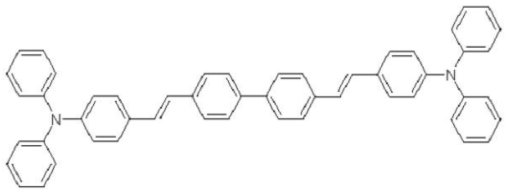
[0009]

[0010] 화학구조식1-2



[0011]

[0012] 화학구조식1-3



[0013]

[0014] (5) 다음, 상기 발광물질층 상에 전자수송층(ETL:electron transport layer) 및 전자주입층(EIL: electron injecting layer)을 연속적으로 형성한다. 이때, 상기 전자수송층은 tris(8-hydroxy-quinolate)aluminum (Alq3)로 이루어진다. 전자수송층과 전자주입층의 이중층 구조 대신에, 전자주입 운송층을 형성할 수 있다.

[0015] (6) 다음, 상기 전자주입층 상에 음극(cathode)을 형성하고, 마지막으로 상기 음극 상에 보호막을 형성한다.

[0016] 상기와 같은 구조에 있어 발광물질층은 청색, 녹색, 적색을 구현하여, 풀컬러의 화상을 구현하게 된다.

[0017] 유기 발광 다이오드의 유기 발광층을 형성하기 위한 다양한 유기 화합물이 알려져 있으며, 예를 들면, 미국특허 제6,455,720호는 2,2-(디아릴)비닐포스핀 (2,2-(Diarlyl)vinylphosphine) 화합물을 개시하고 있고, 미국특허 제 20070292714호는 중심부는 파이렌(pyrene) 구조를 가지며, 디페닐아민기(diphenylamino)가 말단에 치환된 청색 발광 화합물을 개시하고 있다. 또한 대한민국 특허공개 제2002-0070333호는 중심부는 디페닐안트라센 구조를 가지며, 아릴기가 말단에 치환된 청색 발광 화합물을 개시하고, 대한민국 특허공개 제2007-0023335호는 디파이렌 스피로(dipyrene-spiro)계 청색 발광 화합물을 개시하고 있다.

[0018] 하지만 수명, 발광효율 및 휘도가 충분하지 않다는 문제점이 있었다. 이는 도 1에 도시된 바와 같이, 청색의 색순도가 낮아서 진한 청색 구현이 어렵기 때문이며, 천연색의 풀컬러 디스플레이를 구현하는데 문제가 있다. 높은 전류 발광효율(Cd/A)을 얻기 위해서는 내부양자효율이 우수하여야 되나 높은 순도의 청색(CIE색좌표 y값이 작아질수록) 물질을 얻기 어려운 문제가 있다.

발명의 내용

해결 하고자하는 과제

[0019] 본 발명은 고색순도, 고휘도를 구현하고 발광수명이 향상되며 저전압 구동이 가능한 유기전계발광소자용 청색 형광물질을 제공하고자 한다.

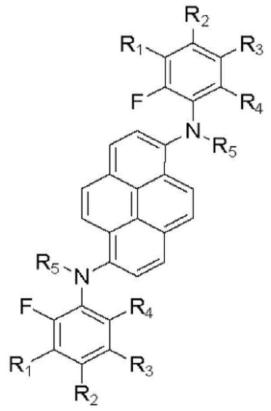
[0020] 또한, 상기 청색 형광물질을 이용하여 고색순도 및 고휘도의 영상을 구현할 수 있고 또한 제품 수명이 향상된

유기전계발광소자를 제공하고자 한다.

과제 해결수단

[0021] 상기한 과제를 해결하기 위해, 본 발명은 전자 또는 정공을 전달할 수 있는 호스트물질과; 하기 화학식으로 표시되는 도펀트 물질을 포함하는 청색 형광 물질을 제공한다.

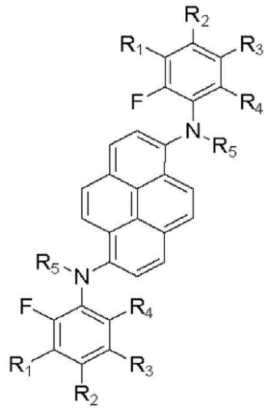
[0022] 화학식

[0023] 

[0024] (상기 화학식에서, R1, R2, R3, R4 중 적어도 2개는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택되고, R5는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택된다.)

[0025] 또한, 본 발명은 전자 또는 정공을 전달할 수 있는 호스트물질과; 하기 화학식으로 표시되는 도펀트 물질을 포함하는 청색 형광 물질을 제공한다.

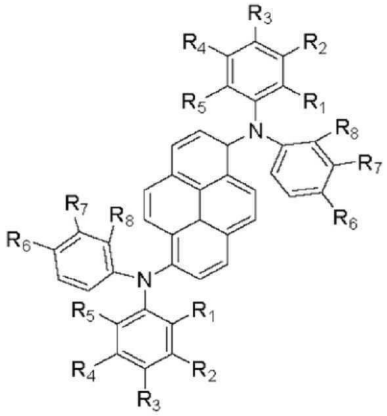
[0026] 화학식

[0027] 

[0028] (상기 화학식1에서, R1, R2, R3, R4, R5 중 적어도 하나는 중수소로 치환된 방향족 그룹에서 선택되고, R1, R2, R3, R4 중 적어도 두개는 수소, 치환 또는 비치환된 방향족 그룹 또는 이형고리 그룹에서 선택되며, R5는 치환 또는 비치환된 방향족 그룹 또는 이형고리 그룹에서 선택된다.)

[0029] 또한, 본 발명은 전자 또는 정공을 전달할 수 있는 호스트물질과; 하기 화학식으로 표시되는 도펀트 물질을 포함하는 청색 형광 물질을 제공한다.

[0030] 화학식



[0031]

[0032] (상기 화학식1에서, 상기 R1, R2, R3, R4, R5 각각은 수소, C1~C6까지의 알킬기, C6 이상의 치환 또는 비치환된 아릴기 중에서 선택되고, 이중 적어도 두 개는 C6 이상의 치환 또는 비치환된 아릴기에서 선택되며, 상기 R6, R7, R8 각각은 수소, C1~C6까지의 알킬기, C6이상의 치환 또는 비치환된 아릴기, 플로린, 시아닌, 트리플로로메틸기 중에서 선택되며, 이중 적어도 하나는 플로린, 시아닌, 트리플롤로메틸기에서 선택된다.)

효 과

[0033] 본 발명의 청색 형광 물질은 고색순도, 고휘도를 구현하고 발광수명이 향상되는 효과를 갖는다.

[0034] 또한, 상기 청색 형광물질을 이용하는 유기전계발광소자는 고색순도 및 고휘도의 영상을 구현할 수 있고 또한 제품 수명이 향상되는 효과를 갖는다.

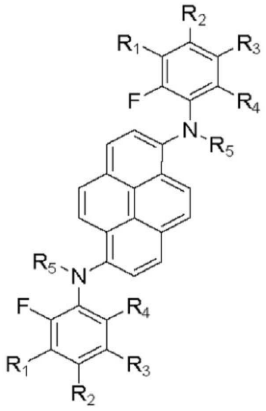
발명의 실시를 위한 구체적인 내용

[0035] 이하, 본 발명에 따른 청색 형광 물질의 구조 및 그 합성예와, 이를 이용한 유기전계발광소자에 대해 설명한다.

[0036] - 제 1 실시예-

[0037] 본 발명의 제 1 실시예에 따른 청색 형광 물질은 6-플루오로페닐아민 유도체가 1,6-파이렌에 치환된 구조에서 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 중 적어도 두개와 질소에는 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되어, 색순도와 발광효율 및 발광수명이 향상되는 것이 특징이며, 하기 화학식2로 표시된다.

[0038] 화학식2



[0039]

[0040] 여기서, R1, R2, R3, R4 중 적어도 2개는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택되고, R5는 치환 또는 비치환된 방향족 그룹, 이형고리 그룹에서 선택된다.

[0041] 보다 구체적으로 상기 화학식2에서 R1, R2, R3, R4, R5 각각은 페닐(phenyl), 바이페닐(biphenyl),

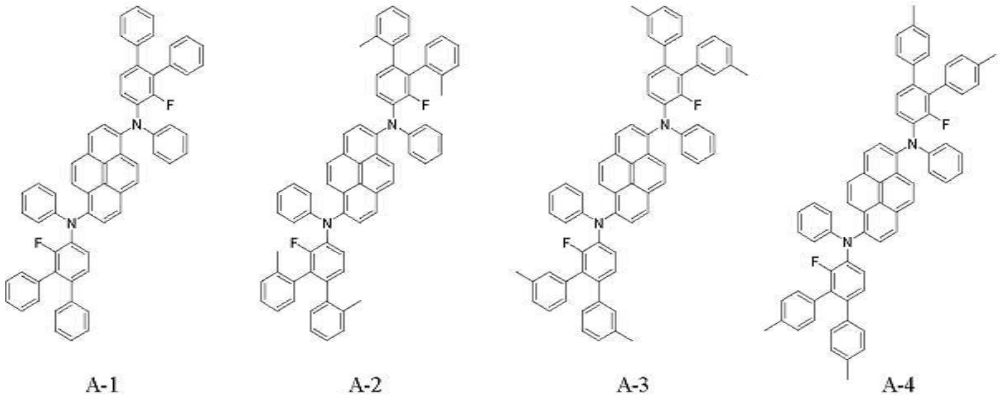
나프틸(naphthyl), 페난스렌(phenanthrene), 터페닐(terphenyl), 플루오레닐(fluorenyl) 등 방향족 그룹과 이들의 치환체 등으로부터 선택될 수 있다. 또한, 상기 화학식2에서 R1, R2, R3, R4, R5 각각은 퓨란(furan), 티오펜(thiophene), 피롤(pyrrole), 피리딘(pyridine), 피리미딘(pyrimidine) 등 이형고리 그룹으로부터 선택될 수 있다.

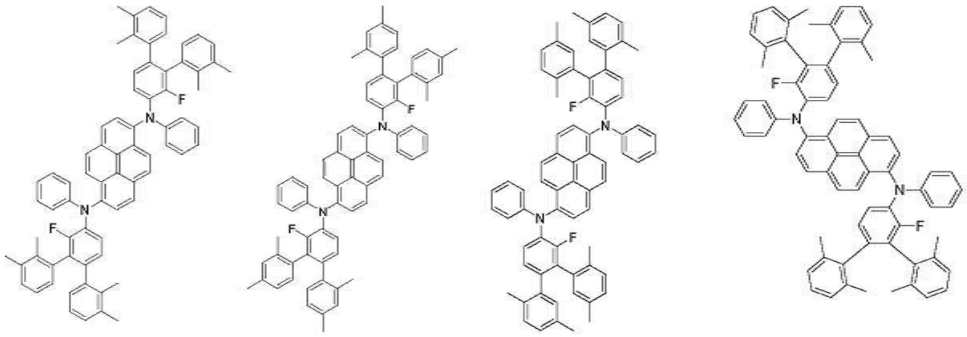
[0042] 방향족 그룹의 치환체는 메틸(methyl), 에틸(ethyl), 프로필(propyl), 이소프로필(i-propyl), 터셔리부틸(tert-butyl) 등과 같은 C1~C6 의 알킬(alkyl) 그룹, 시아노(cyano) 그룹, 실릴(silyl) 그룹, 플루오린(fluorine)에서 선택될 수 있다.

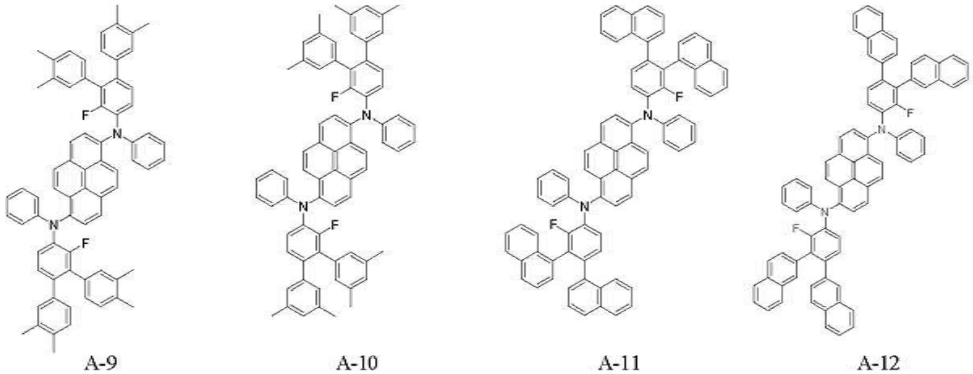
[0043] 제 1 실시예에서는 파이렌(pyrene) 중심부에 치환 또는 비치환된 방향족 그룹 또는 이형고리 그룹을 적어도 두 개 포함하는 6-플루오로페닐아민기를 도입하고, 아민기에 치환 또는 비치환된 방향족 그룹, 이형고리 그룹을 도입하여 발광효율 및 색순도가 높고 수명이 향상된 것을 특징으로 하는 청색 형광물질을 제공한다.

[0044] 결과적으로, 상기 화학식2는 하기 화학식3에 표시된 다수의 물질 중 어느 하나이다. 설명의 편의를 위해 각 물질에 A-1 내지 A-282의 번호를 부여하였다.

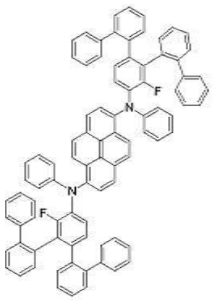
[0045] 화학식3

[0046] 
A-1 A-2 A-3 A-4

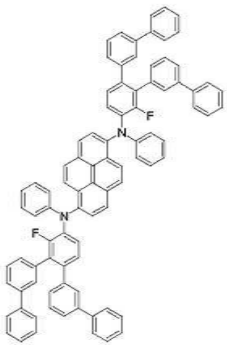
[0047] 
A-5 A-6 A-7 A-8

[0048] 
A-9 A-10 A-11 A-12

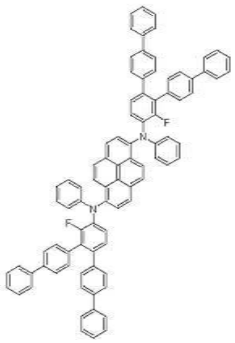
[0049]



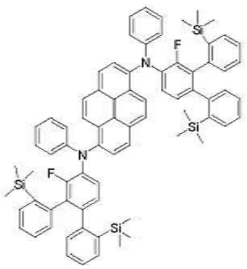
A-13



A-14

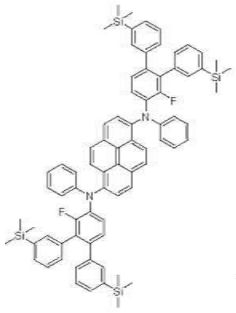


A-15

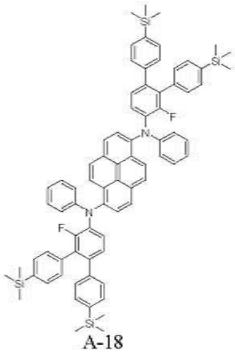


A-16

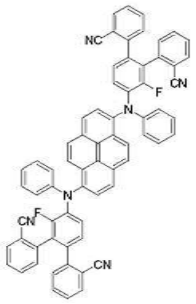
[0050]



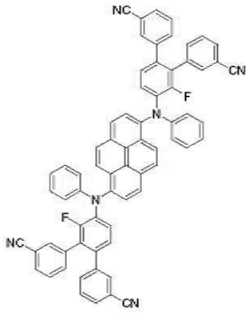
A-17



A-18

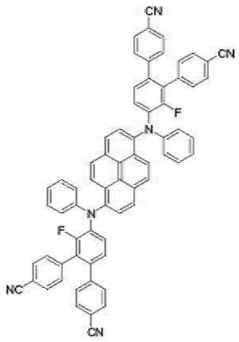


A-19

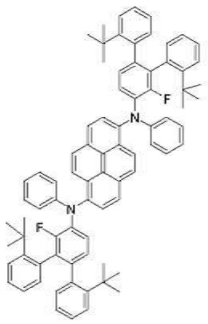


A-20

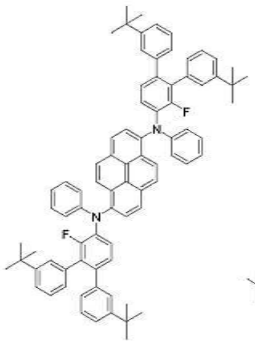
[0051]



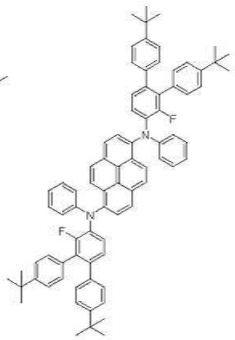
A-21



A-22

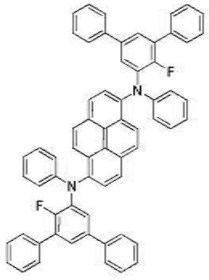


A-23

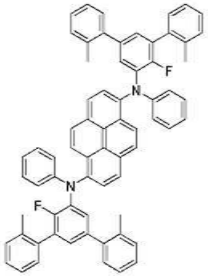


A-24

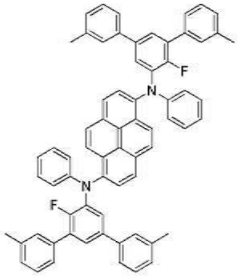
[0052]



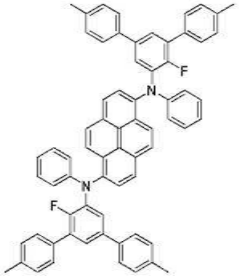
A-25



A-26

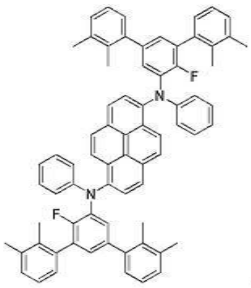


A-27

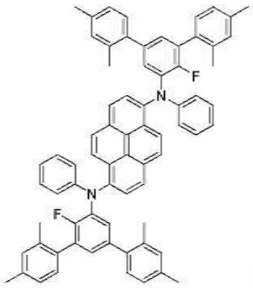


A-28

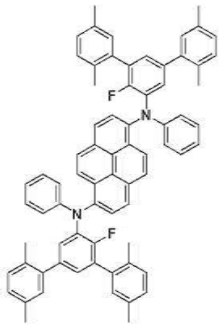
[0053]



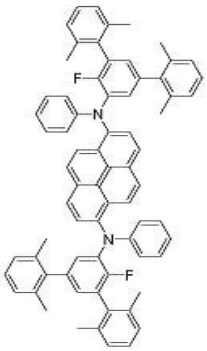
A-29



A-30

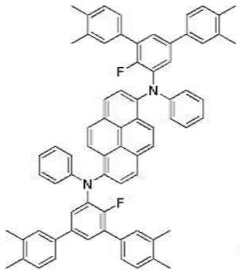


A-31

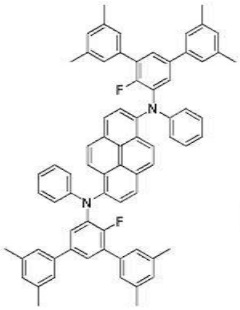


A-32

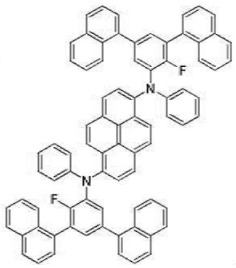
[0054]



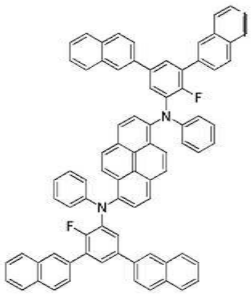
A-33



A-34

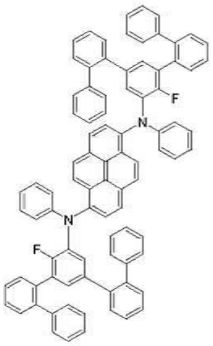


A-35

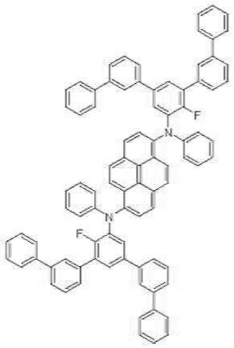


A-36

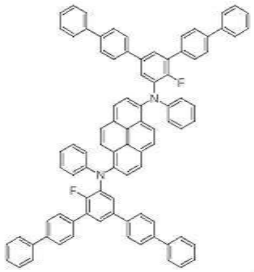
[0055]



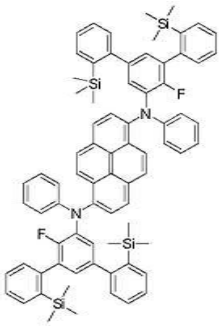
A-37



A-38

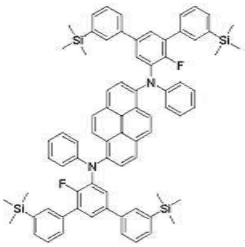


A-39

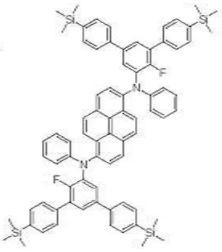


A-40

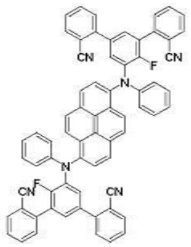
[0056]



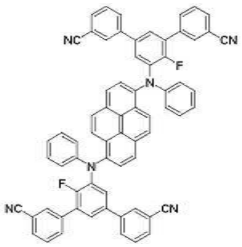
A-41



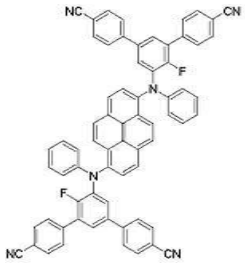
A-42



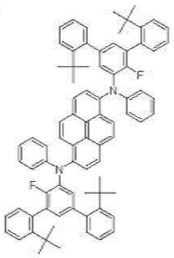
A-43



A-44

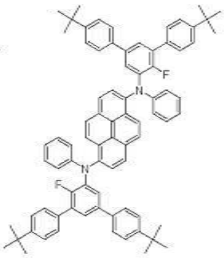


A-45



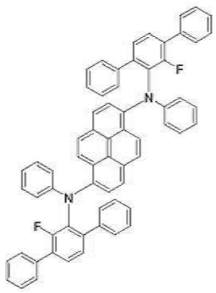
A-46

A-47

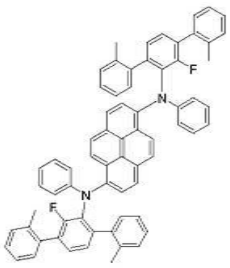


A-48

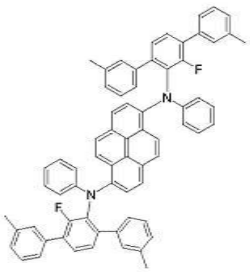
[0057]



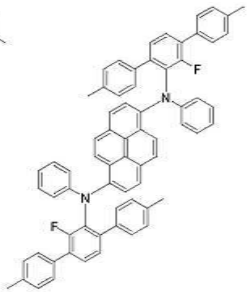
A-49



A-50

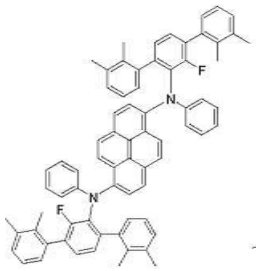


A-51

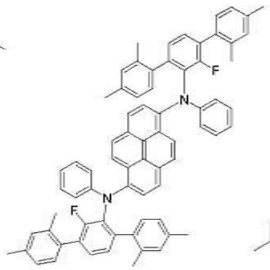


A-52

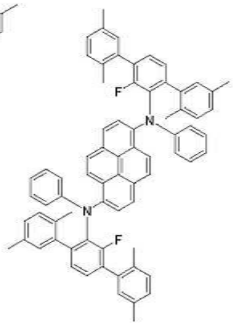
[0058]



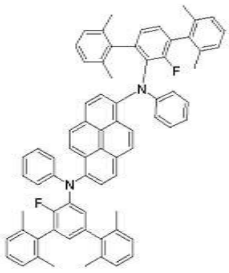
A-53



A-54

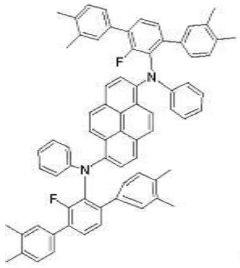


A-55

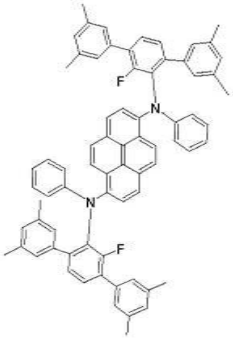


A-56

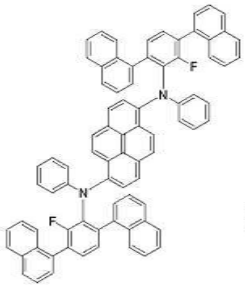
[0059]



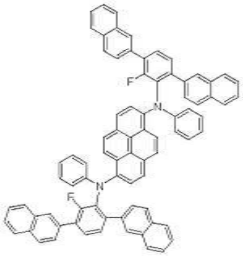
A-57



A-58



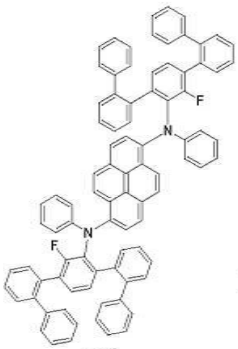
A-59



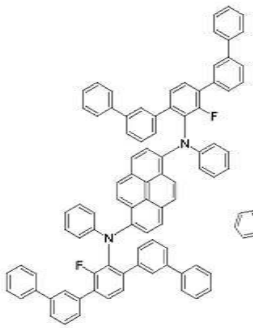
A-60

[0060]

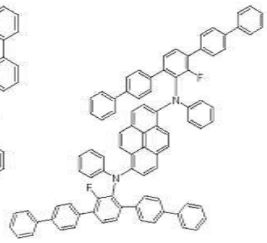
[0061]



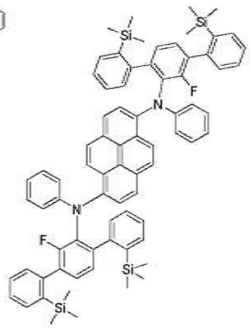
A-61



A-62

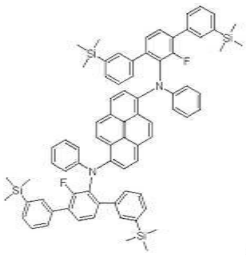


A-63

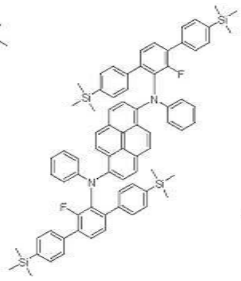


A-64

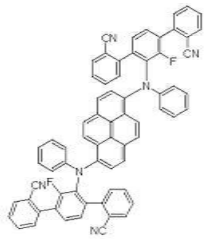
[0062]



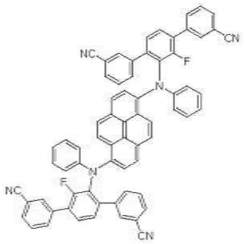
A-65



A-66

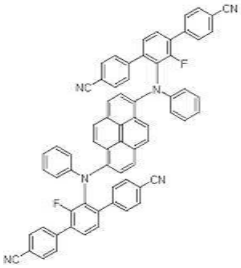


A-67

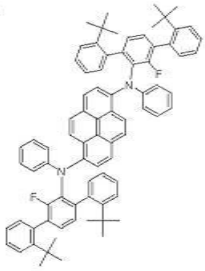


A-68

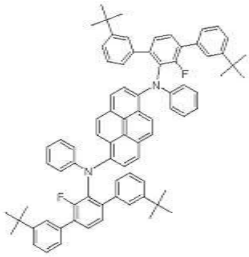
[0063]



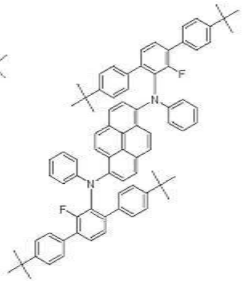
A-69



A-70

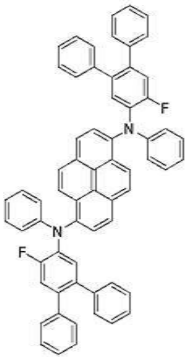


A-71

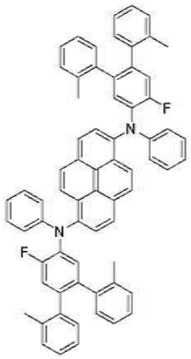


A-72

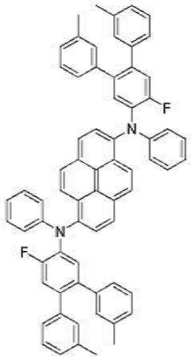
[0064]



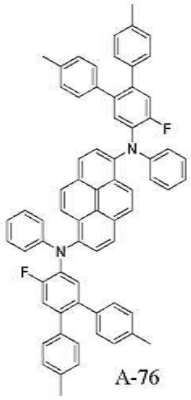
A-73



A-74

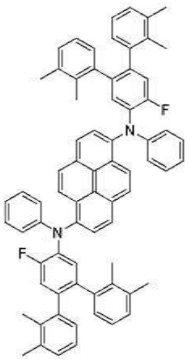


A-75

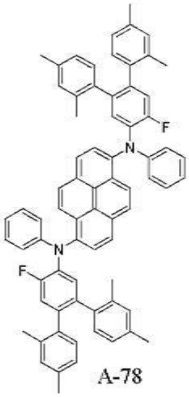


A-76

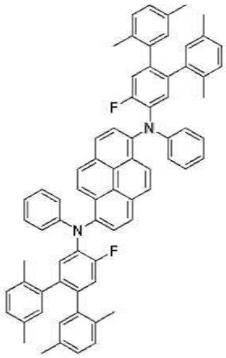
[0065]



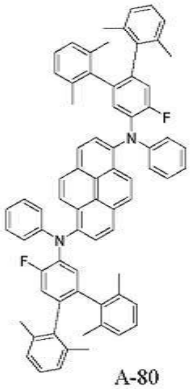
A-77



A-78

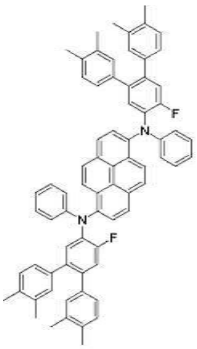


A-79

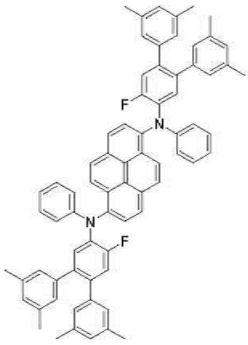


A-80

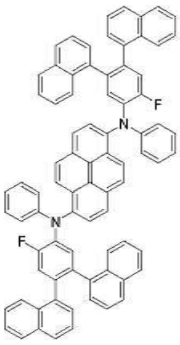
[0066]



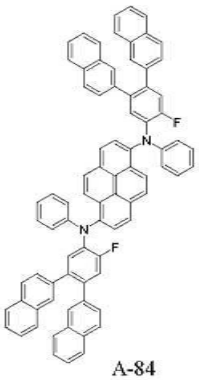
A-81



A-82

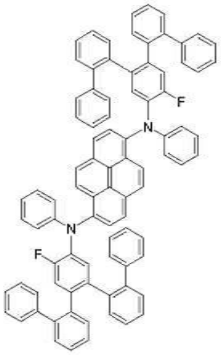


A-83

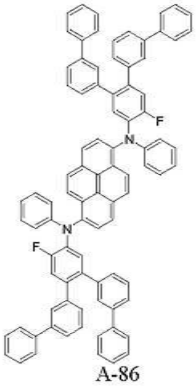


A-84

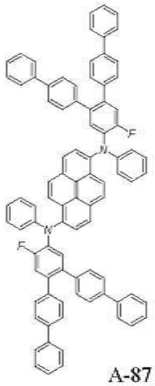
[0067]



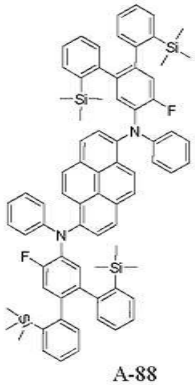
A-85



A-86

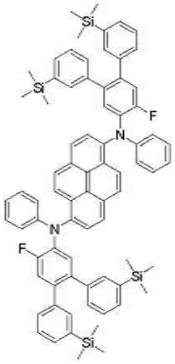


A-87

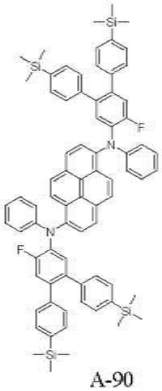


A-88

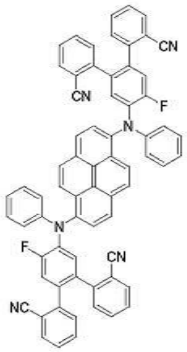
[0068]



A-89



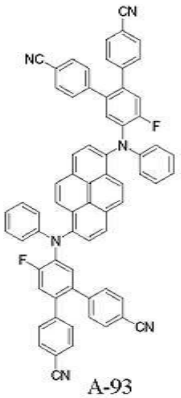
A-90

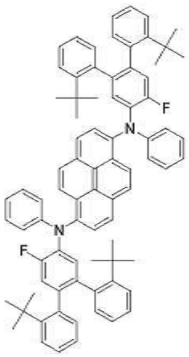


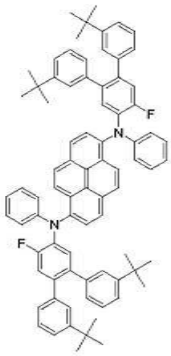
A-91

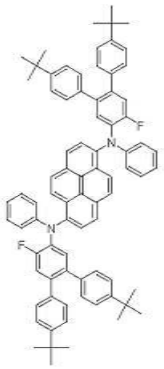
A-92

[0069]

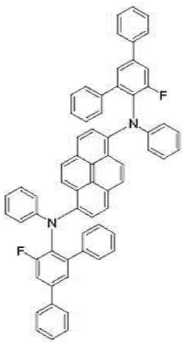

A-93

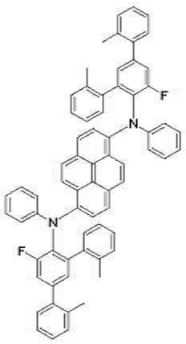

A-94

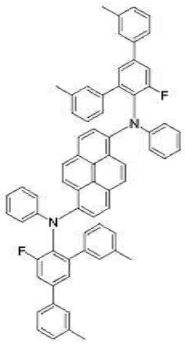

A-95

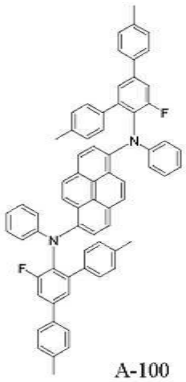

A-96

[0070]

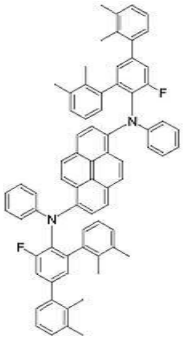

A-97

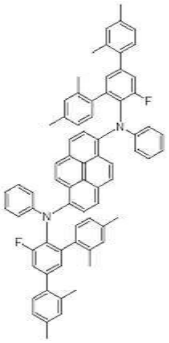

A-98

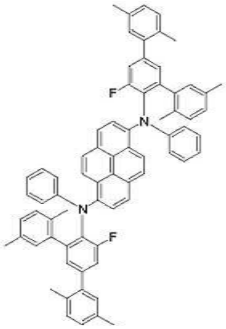

A-99

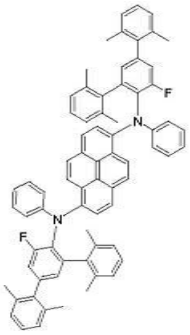

A-100

[0071]

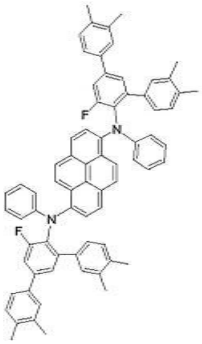

A-101

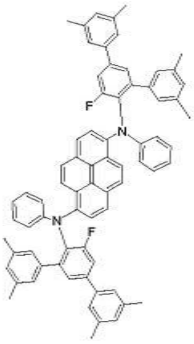

A-102

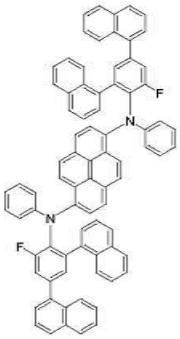

A-103

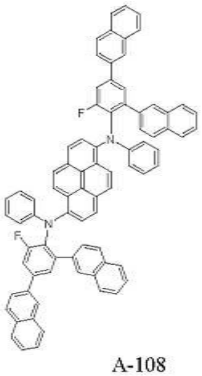

A-104

[0072]

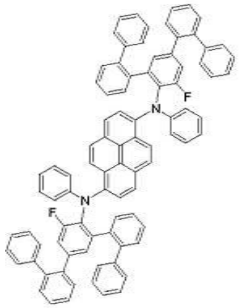

A-105


A-106

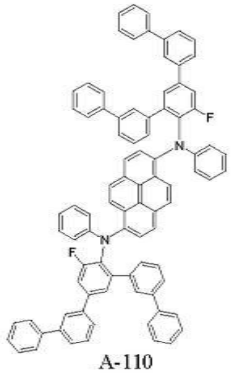

A-107


A-108

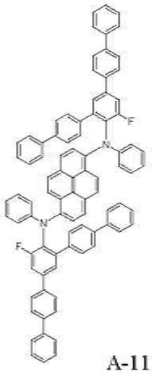
[0073]



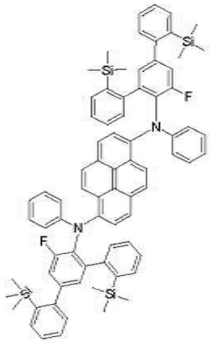
A-109



A-110

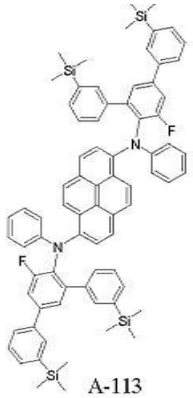


A-111

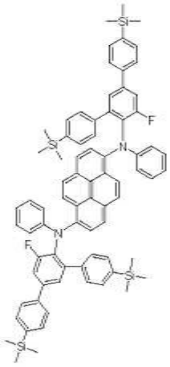


A-112

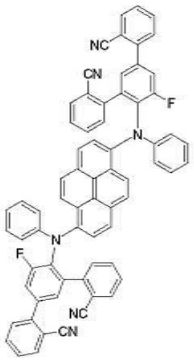
[0074]



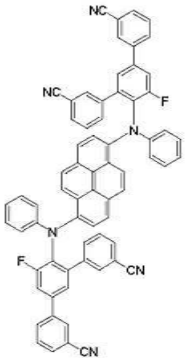
A-113



A-114

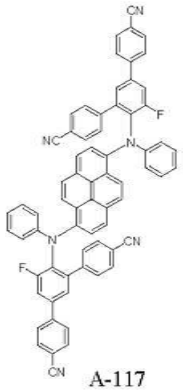


A-115

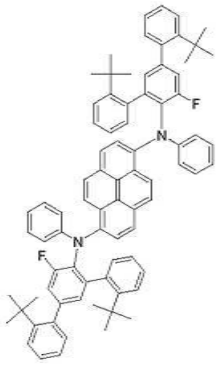


A-116

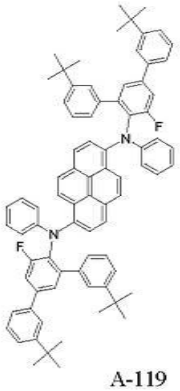
[0075]



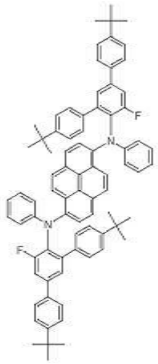
A-117



A-118

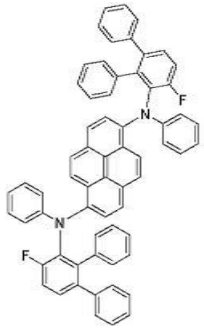


A-119

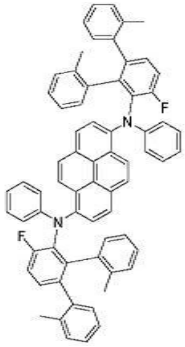


A-120

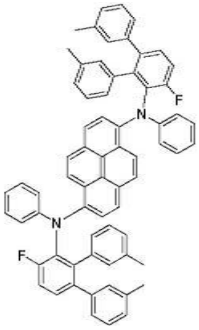
[0076]



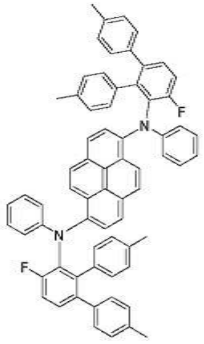
A-121



A-122

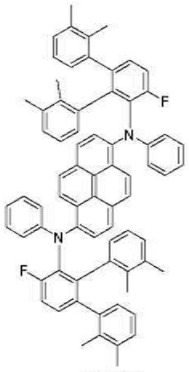


A-123

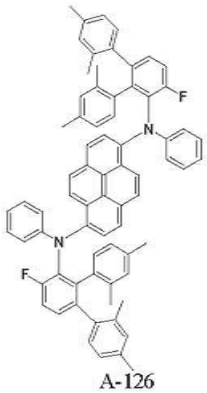


A-124

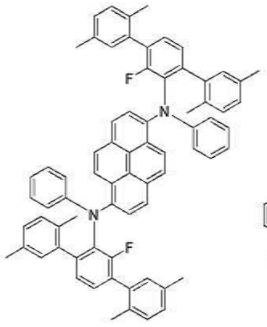
[0077]



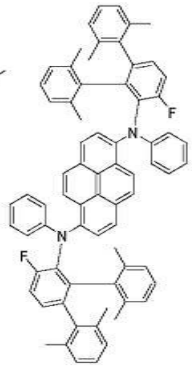
A-125



A-126

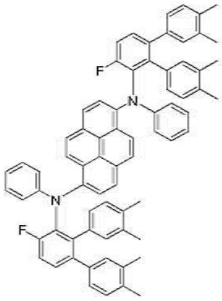


A-127

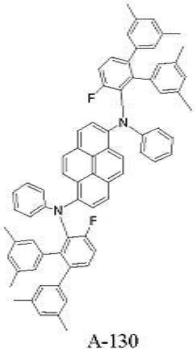


A-128

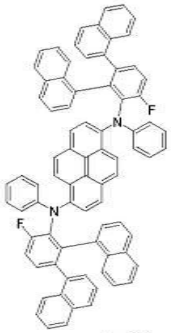
[0078]



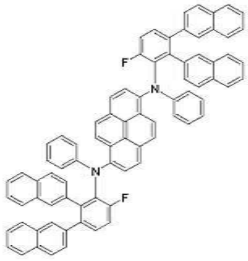
A-129



A-130

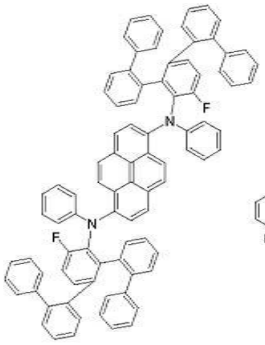


A-131

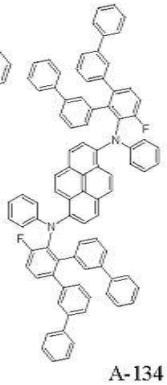


A-132

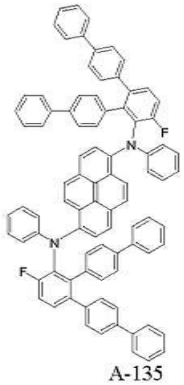
[0079]



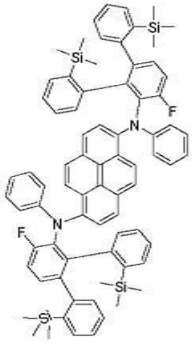
A-133



A-134

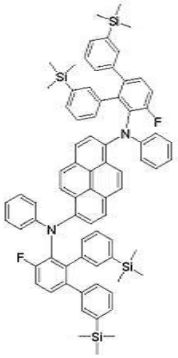


A-135

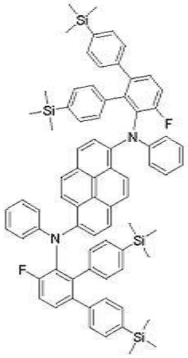


A-136

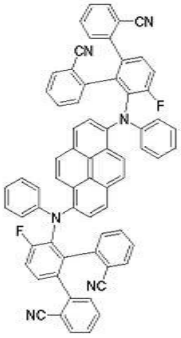
[0080]



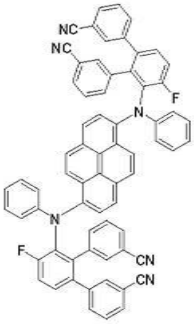
A-137



A-138

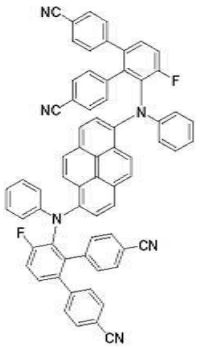


A-139

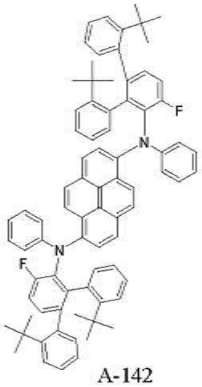


A-140

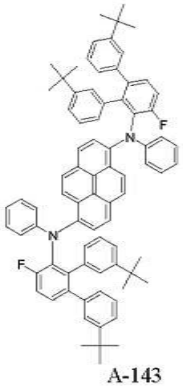
[0081]



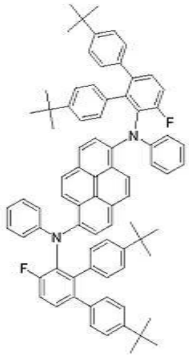
A-141



A-142

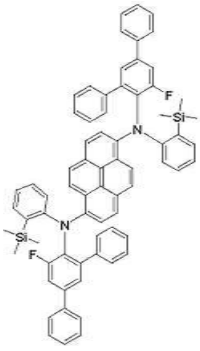


A-143

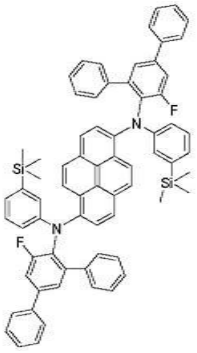


A-144

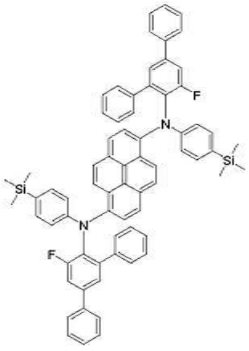
[0082]



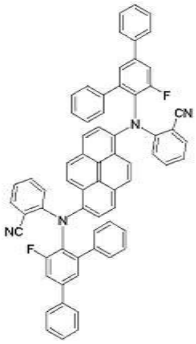
A-145



A-146

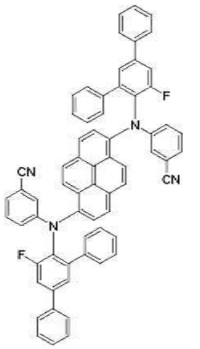


A-147

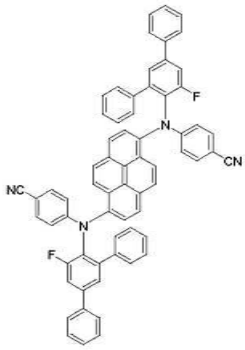


A-148

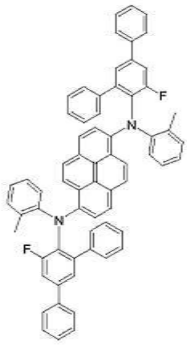
[0083]



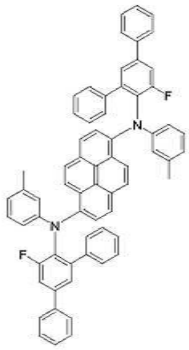
A-149



A-150

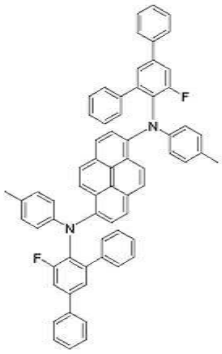


A-151

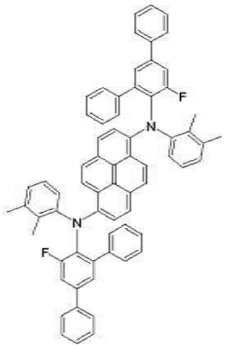


A-152

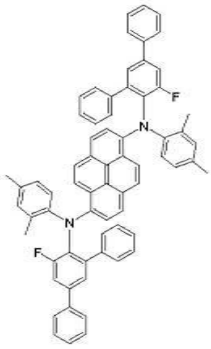
[0084]



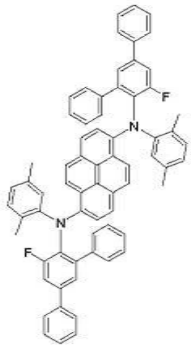
A-153



A-154

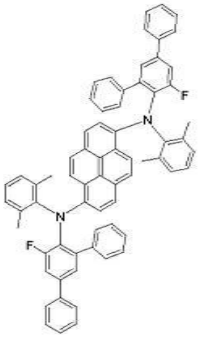


A-155

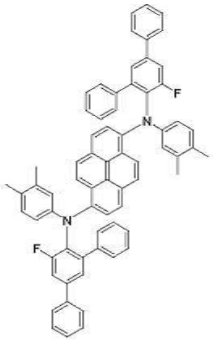


A-156

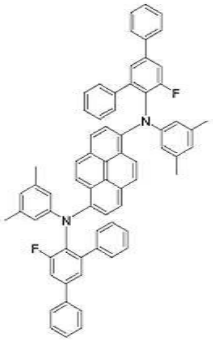
[0085]



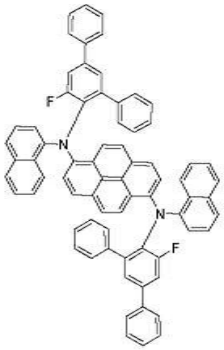
A-157



A-158

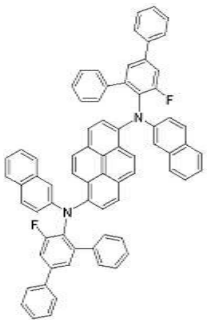


A-159

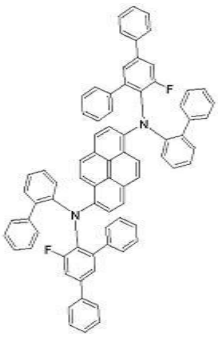


A-160

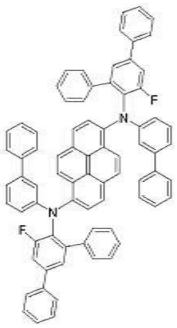
[0086]



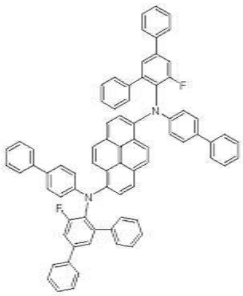
A-161



A-162

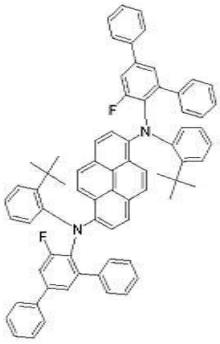


A-163

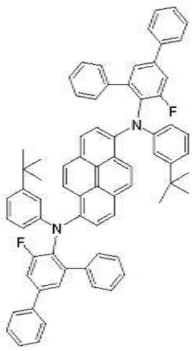


A-164

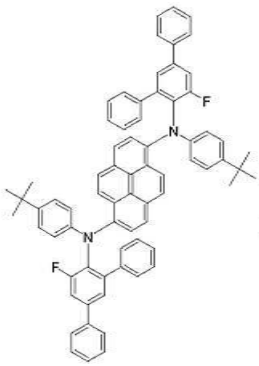
[0087]



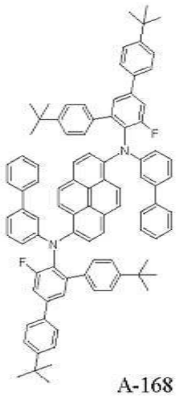
A-165



A-166

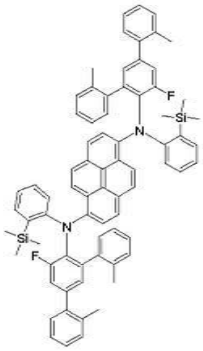


A-167

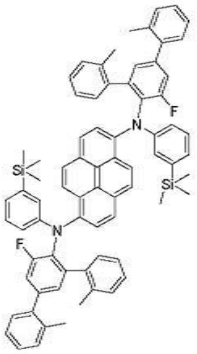


A-168

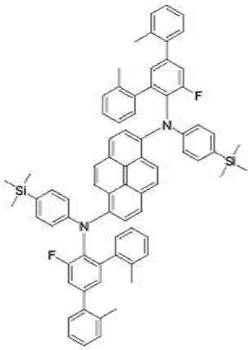
[0088]



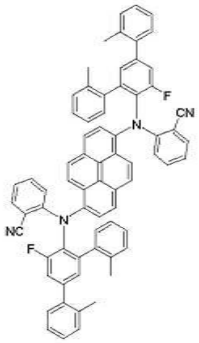
A-169



A-170

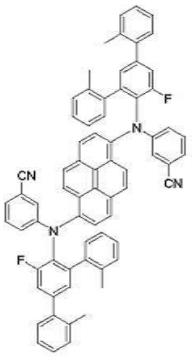


A-171

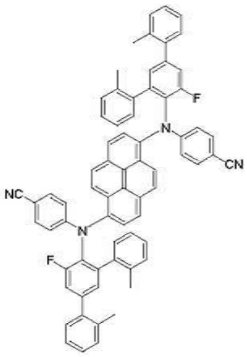


A-172

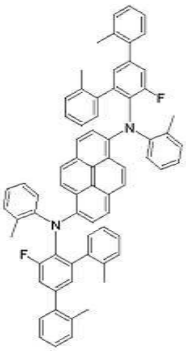
[0089]



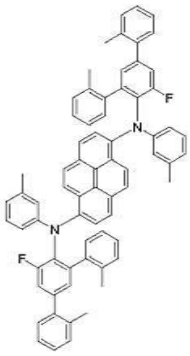
A-173



A-174

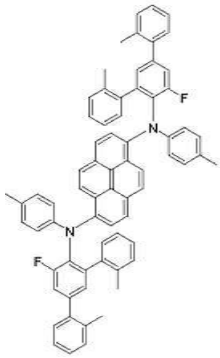


A-175

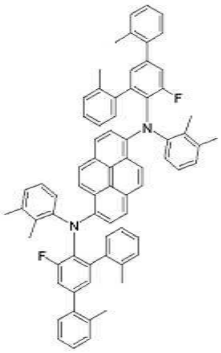


A-176

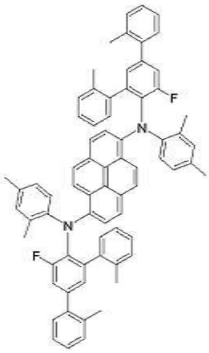
[0090]



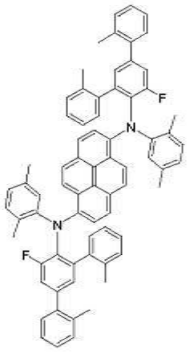
A-177



A-178

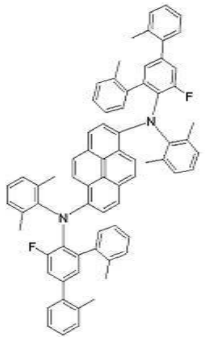


A-179

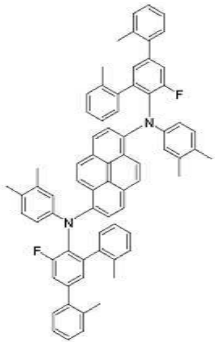


A-180

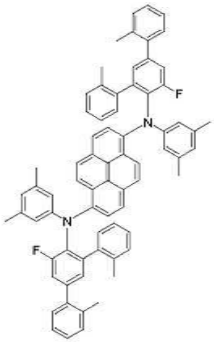
[0091]



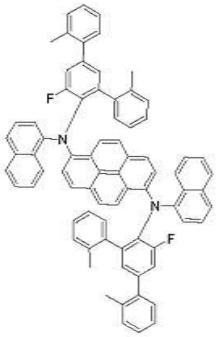
A-181



A-182

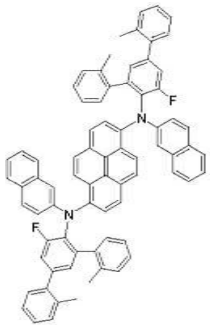


A-183

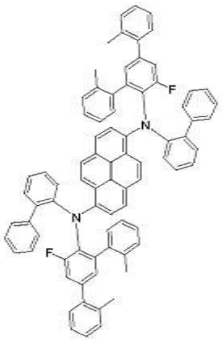


A-184

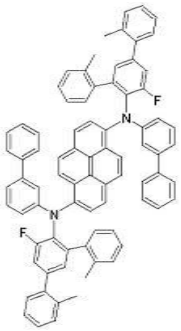
[0092]



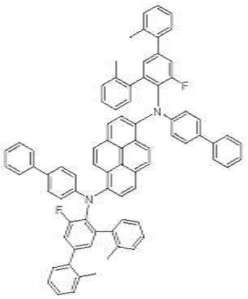
A-185



A-186

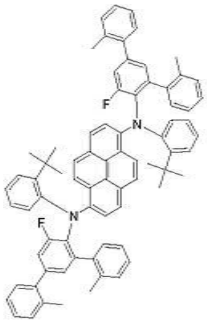


A-187

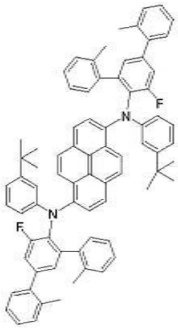


A-188

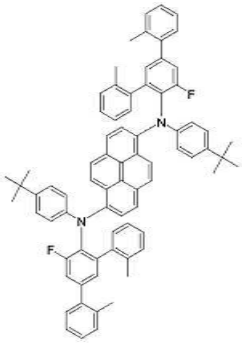
[0093]



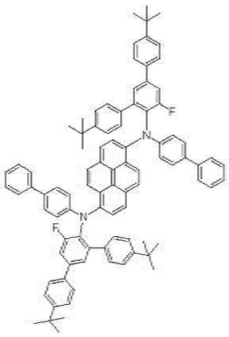
A-189



A-190

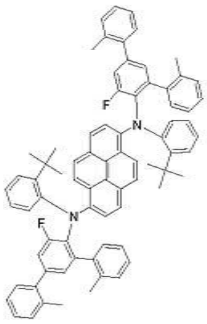


A-191

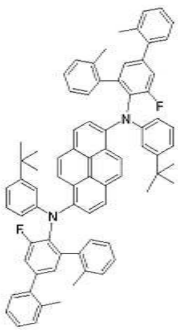


A-192

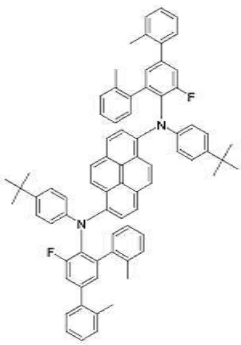
[0094]



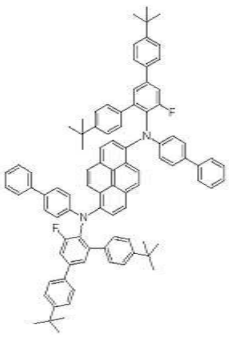
A-189



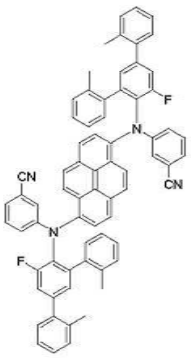
A-190



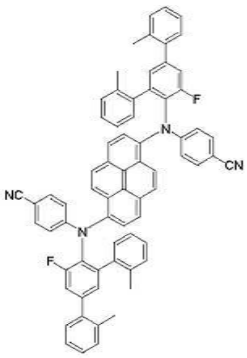
A-191



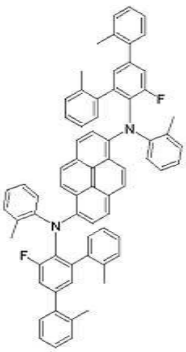
A-192



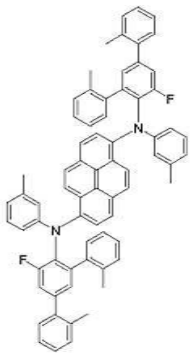
A-173



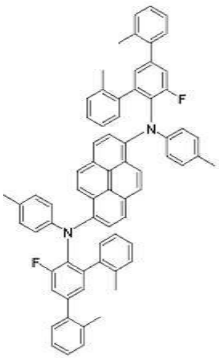
A-174



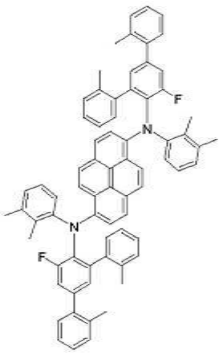
A-175



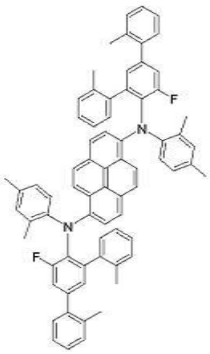
A-176



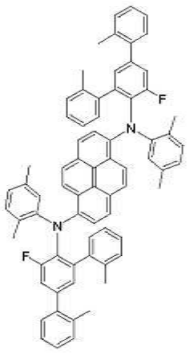
A-177



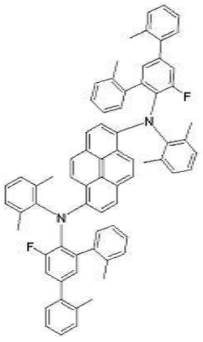
A-178



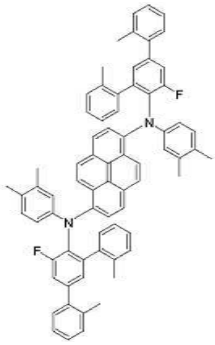
A-179



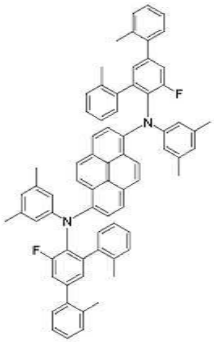
A-180



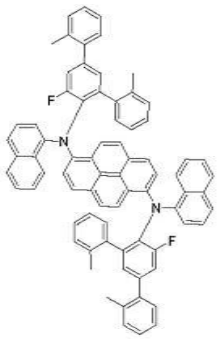
A-181



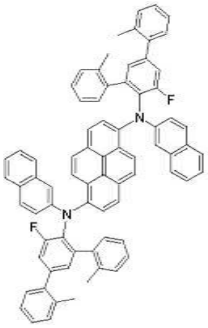
A-182



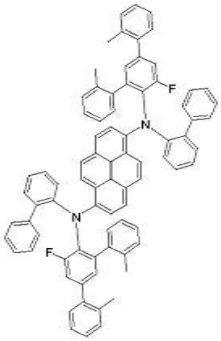
A-183



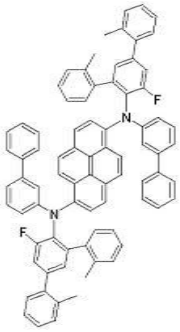
A-184



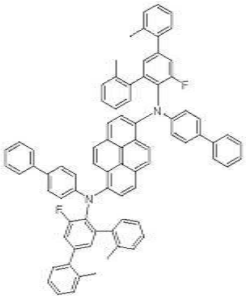
A-185



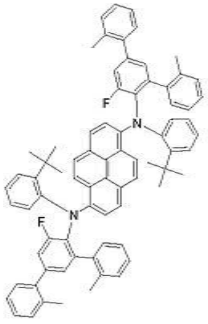
A-186



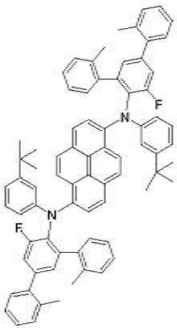
A-187



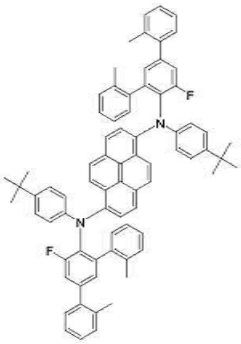
A-188



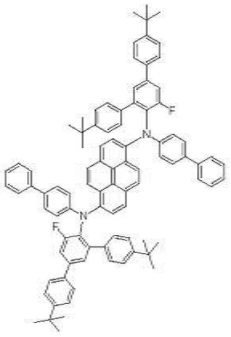
A-189



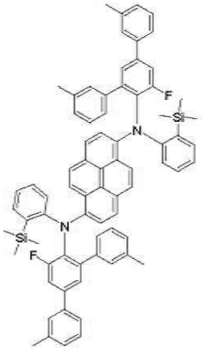
A-190



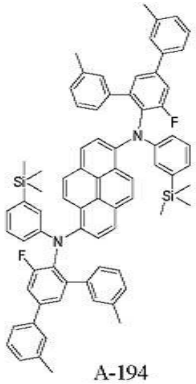
A-191



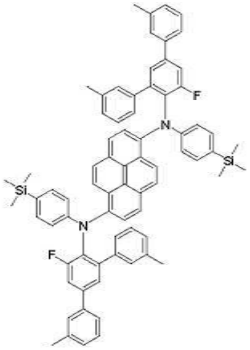
A-192



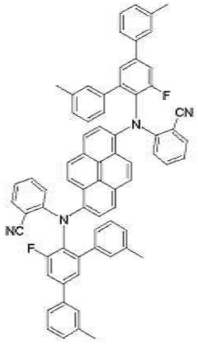
A-193



A-194



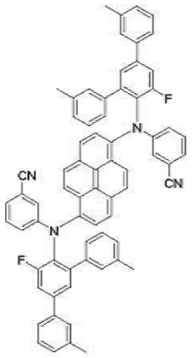
A-195



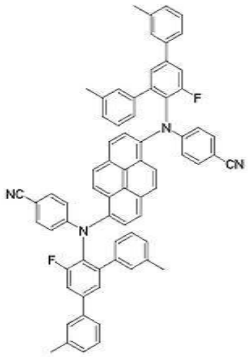
A-196

[0095]

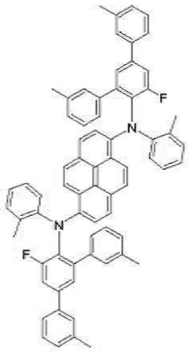
[0096]



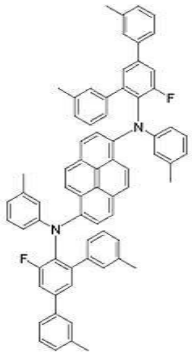
A-197



A-198

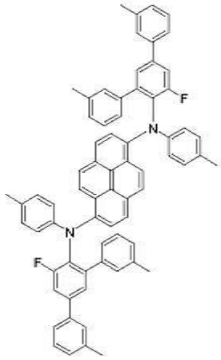


A-199

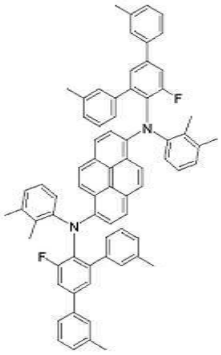


A-200

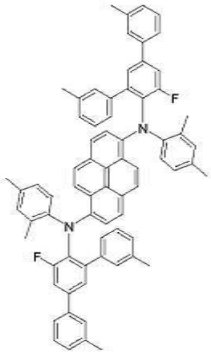
[0097]



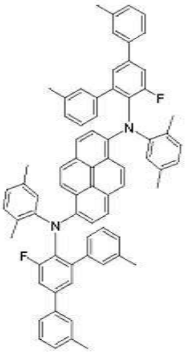
A-201



A-202

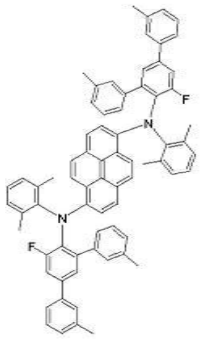


A-203

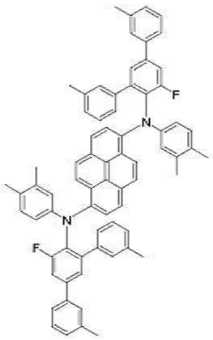


A-204

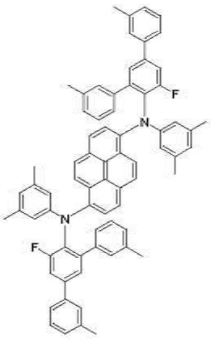
[0098]



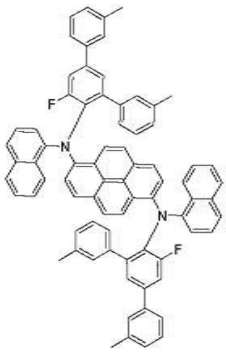
A-205



A-206

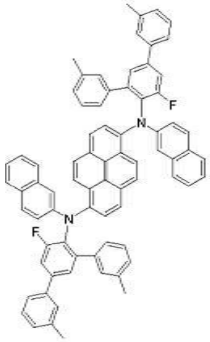


A-207

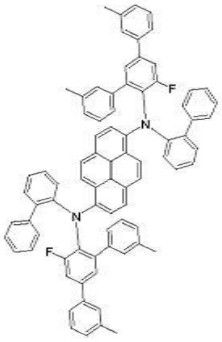


A-208

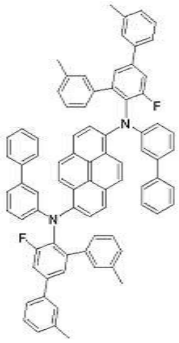
[0099]



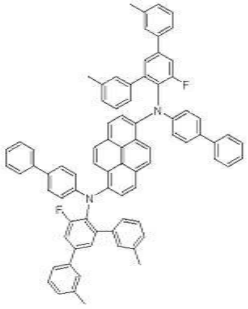
A-209



A-210

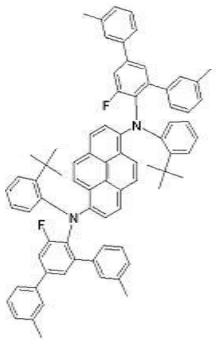


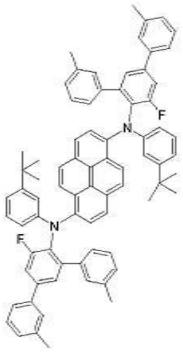
A-211

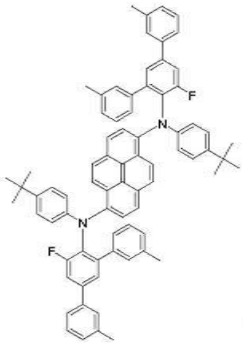


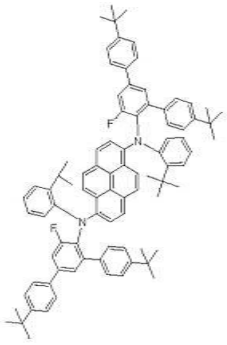
A-212

[0100]

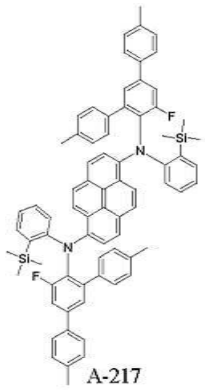

A-213

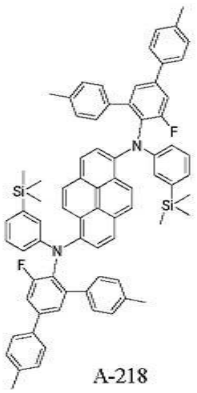

A-214

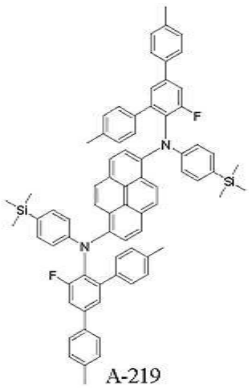

A-215

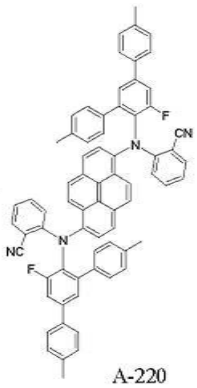

A-216

[0101]

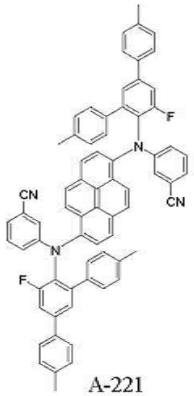

A-217

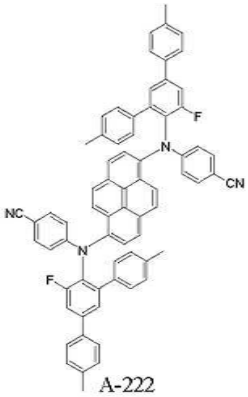

A-218

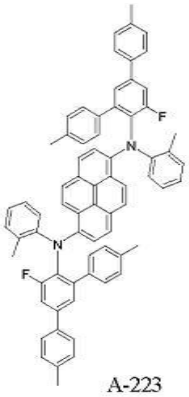

A-219

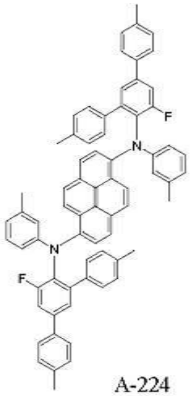

A-220

[0102]

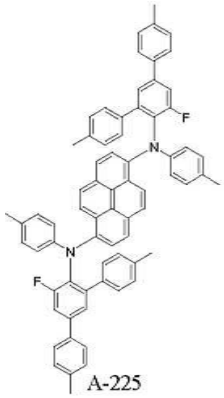

A-221

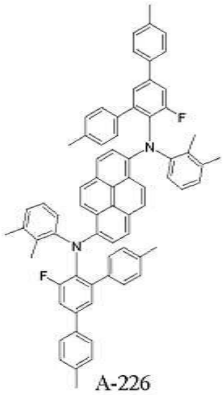

A-222

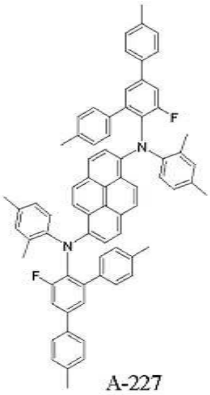

A-223

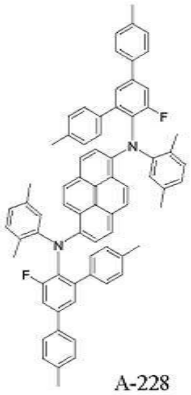

A-224

[0103]

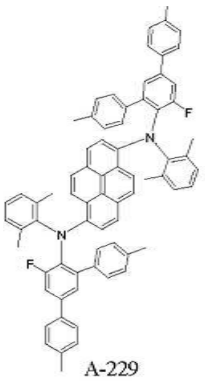

A-225

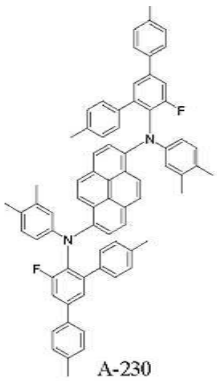

A-226

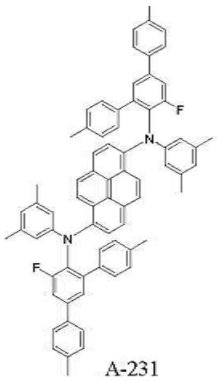

A-227

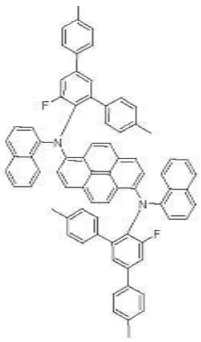

A-228

[0104]

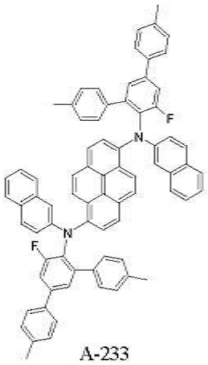

A-229

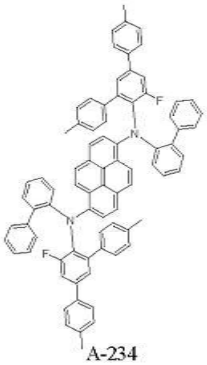

A-230

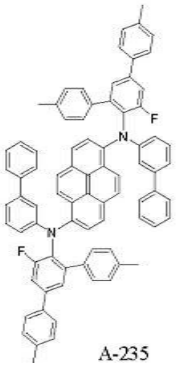

A-231

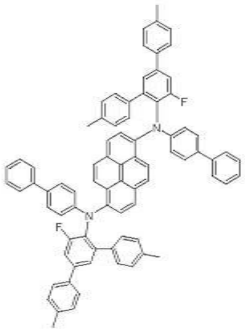

A-232

[0105]

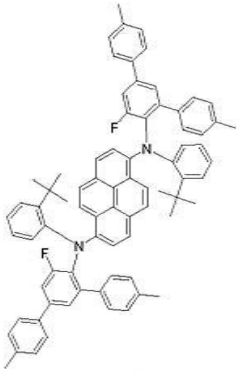

A-233

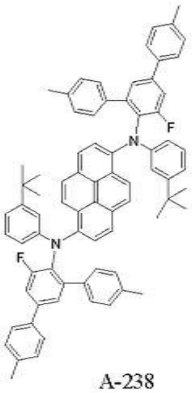

A-234

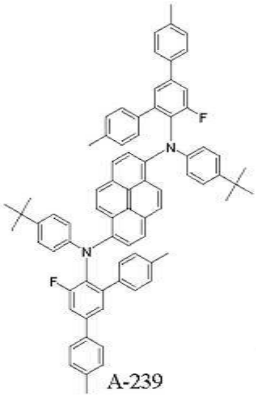

A-235

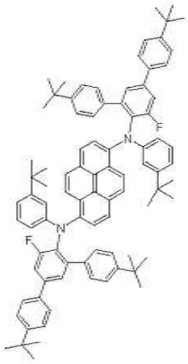

A-236

[0106]

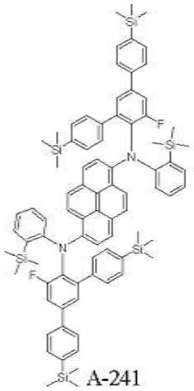

A-237

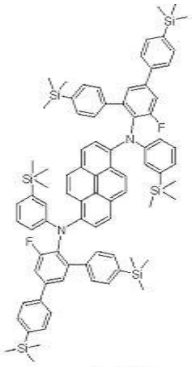

A-238

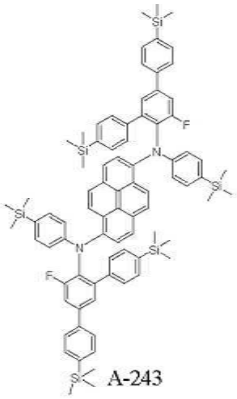

A-239

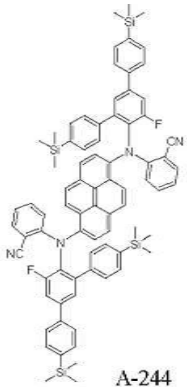

A-240

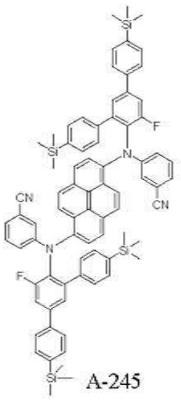
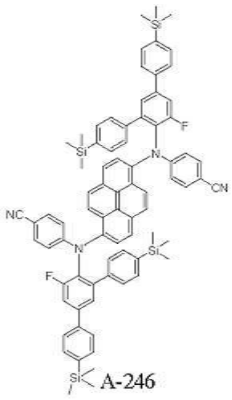
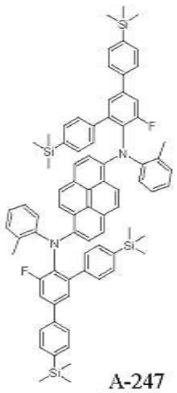
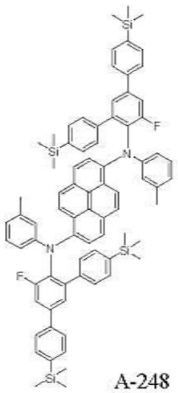
[0107]

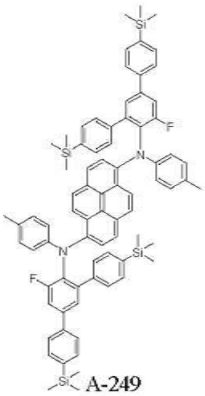
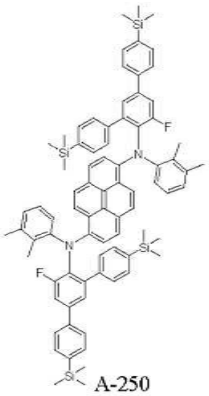
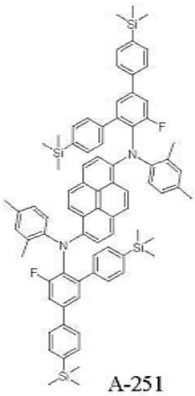
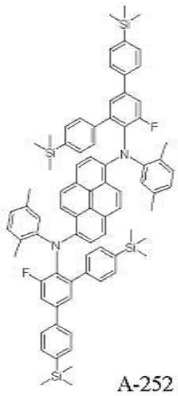

A-241

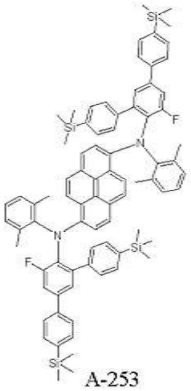
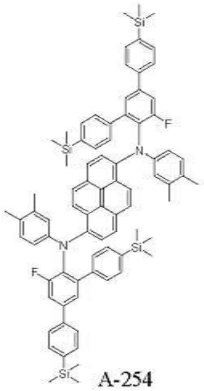
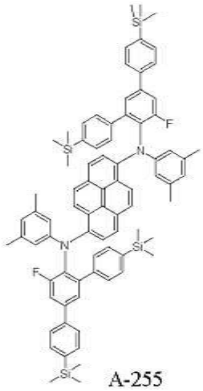
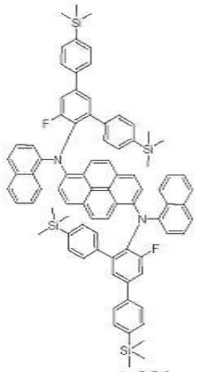

A-242

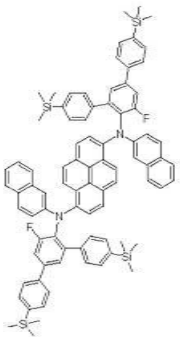
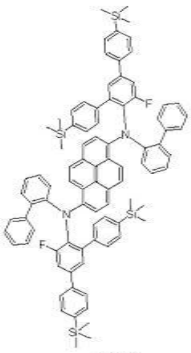
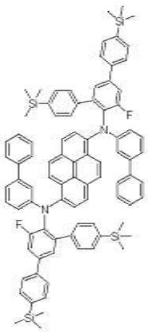
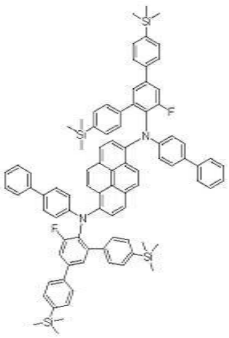

A-243


A-244

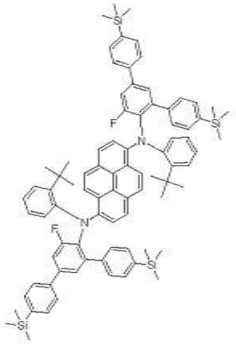
[0108]  A-245  A-246  A-247  A-248

[0109]  A-249  A-250  A-251  A-252

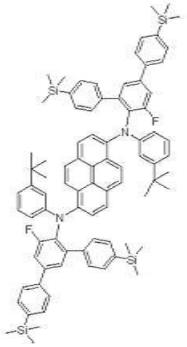
[0110]  A-253  A-254  A-255  A-256

[0111]  A-257  A-258  A-259  A-260

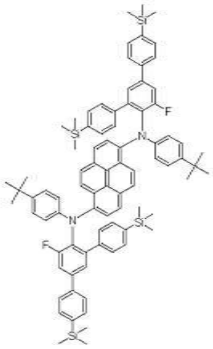
[0112]



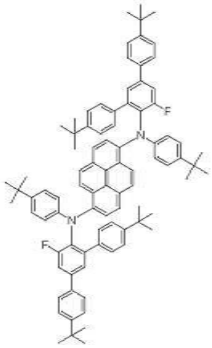
A-261



A-262

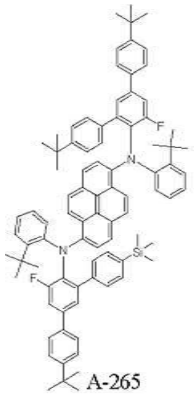


A-263

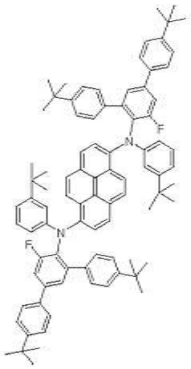


A-264

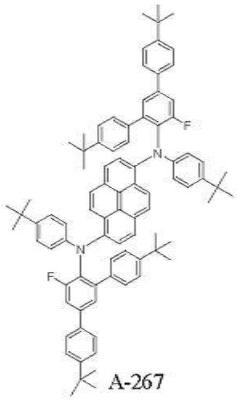
[0113]



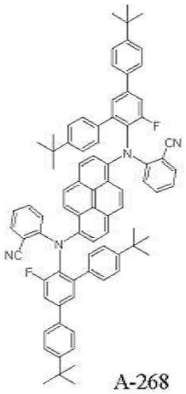
A-265



A-266

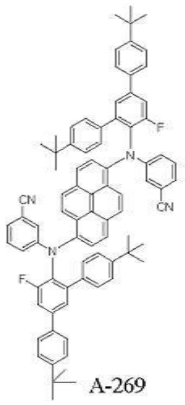


A-267

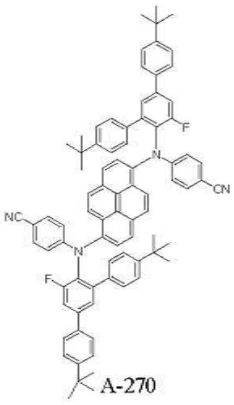


A-268

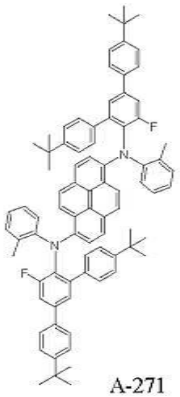
[0114]



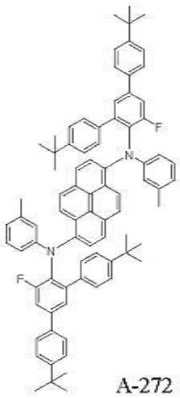
A-269



A-270

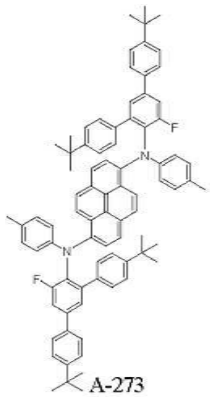


A-271

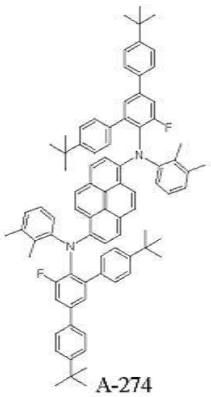


A-272

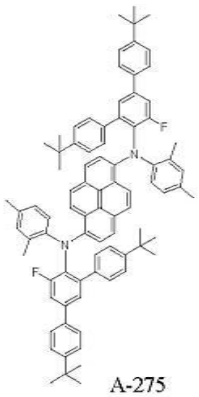
[0115]



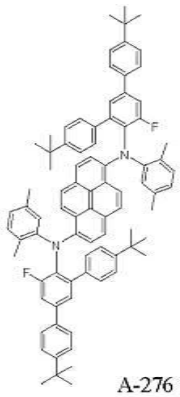
A-273



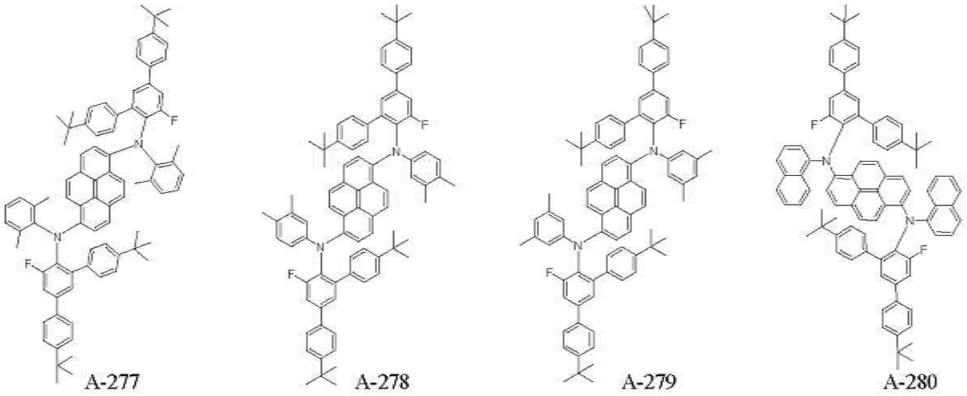
A-274

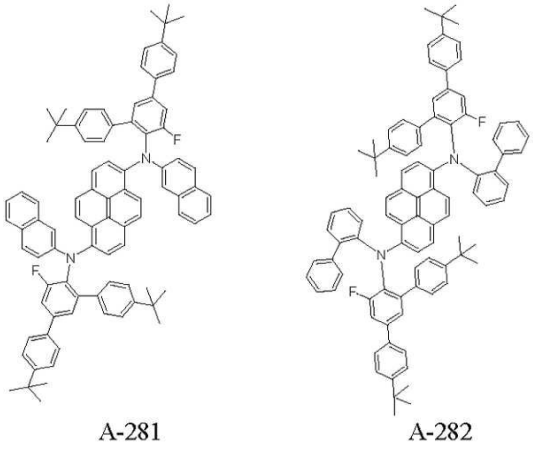


A-275



A-276

[0116] 

[0117] 

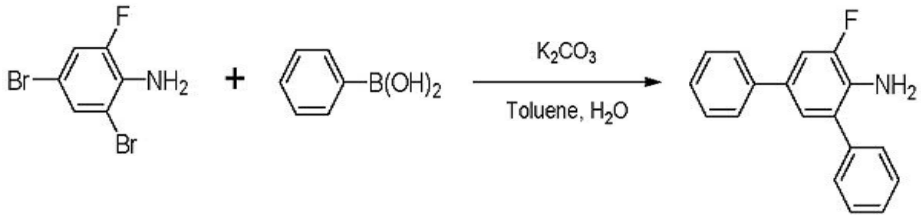
[0118] 이하에서는, 본 발명의 제 1 실시예에 따른 유기전계발광소자용 청색 형광 물질 중, 상기 화학식3에서 A-97로 표시된 물질인 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine을 예로 들어, 본 발명의 청색 형광물질의 합성예를 설명한다.

[0119] 합성예

[0120] (1) 2,4-diphenyl-6-fluoroaniline의 합성

[0121] 2,4-diphenyl-6-fluoroaniline은 아래와 같은 반응식1에 의해 합성된다.

[0122] 반응식1

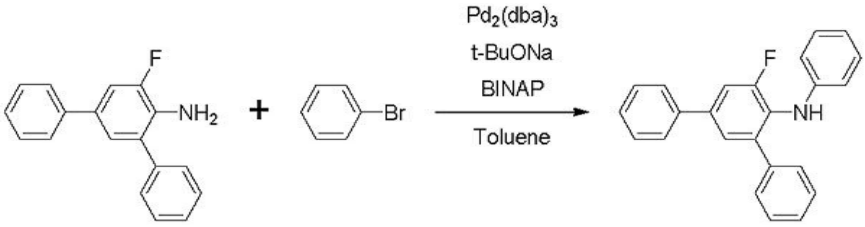
[0123] 

[0124] 구체적으로, 2구 둥근 바닥 플라스크에, 10mmol의 2,4-dibromo-6-fluoroaniline, 24mmol의 benzeneboronic acid, 1 mmol의 tetrakis(triphenylphosphine) palladium(0)과 12g의 Potassium carbonate를, 30mL의 Toluene, 10mL의 H_2O에 녹인 후 , 100 ℃의 bath에서 24시간 교반시킨 후 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한다. 이후 감압 증류하여 실리카겔 여과(silica gel column) 후 용매를 감압 증류하고 Dichloromethane과 petroleum ether 를 사용하여 재결정 한다. 이후 여과(filtering)하여 2,4-Diphenyl-6-fluoroaniline 결정 2.1g을 얻었다.

[0125] (2) 2,4-diphenyl-6-fluoro-N-phenylbenzenamine의 제조

[0126] 2,4-diphenyl-6-fluoro-N-phenylbenzenamine은 아래와 같은 반응식2에 의해 얻어진다.

[0127] 반응식2

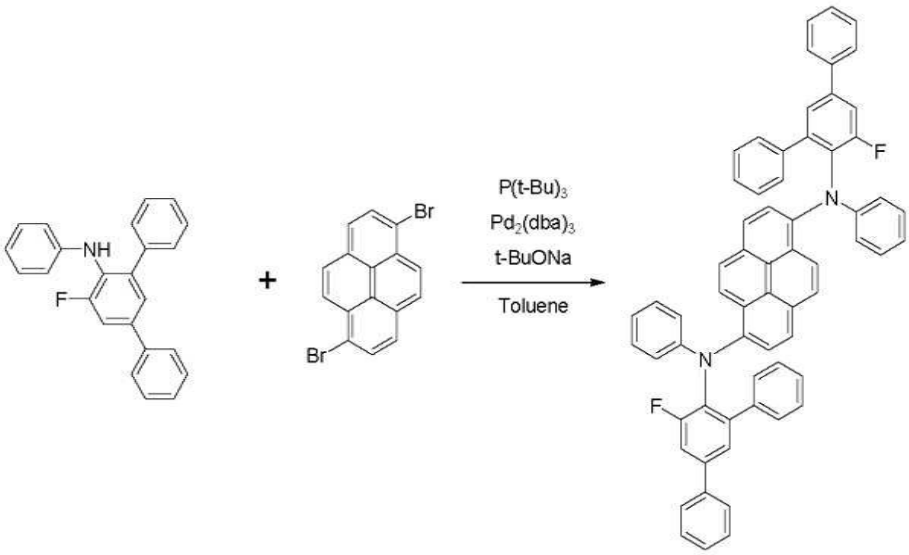
[0128] 

[0129] 이구 둥근 바닥 플라스크에 12mmol의 2,4-diphenyl-6-fluoroaniline, 10mmol의 bromobenzene, 0.15mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.3mmol의 (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene과 14mmol의 Sodium tert-butoxide를, 30mL의 Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔 여과 후 용매를 감압 증류하였다. 이후 Dichloromethane과 petroleum ether를 사용하여 재결정하고 여과하여 2,4-diphenyl-6-fluoro-N-phenylbenzenamine 결정 2.5g을 얻었다.

[0130] (3)N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine의 제조

[0131] 상기 화학식 3에서 A-97로 표시된 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine은 아래와 같은 반응식3에 의해 얻어진다.

[0132] 반응식3

[0133] 

[0134] 이구 둥근 바닥 플라스크에 6mmol의 2,4-diphenyl-6-fluoro-N-phenylbenzenamine, 5mmol의 1,6-dibromopyrene, 0.075mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.15mmol의 tri-tert-butylphosphine과 7mmol의 Sodium tert-butoxide를, 15mL의 Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압하고 실리카겔 여과 후 용매를 감압 증류하였다. 이후 Dichloromethane과 acetone를 사용하여 재결정을 하고 여과한 후, 열정제를 실시하여 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine을 얻었다.

[0135] 이하, 상기한 본 발명의 실시예1에 따른 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 실험예1 내지 실험예5와, 종래의 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 비교예1을 통해, 본 발명에 의한 청색 형광 물질 및 이를 이용한 유기전계발광소자의 성능을 비교 설명한다.

[0136] 실험예1

[0137] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식3에서 A-97로 표시된 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine을 도펀트로 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å , Al 약 1000Å의 두께로 순차 적층하였다.

[0138] 10mA/cm^{2}에서 606cd/m^2(4.36V)를 나타내었으며 이때 CIE x = 0.136, y = 0.142를 나타내었다.

[0139]

[0140] 실험예2

[0141] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 650Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식3에서 A-147로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0142] 10mA/cm^{2}에서 618cd/m^2(4.45V)를 나타내었으며 이때 CIE x = 0.135, y = 0.133를 나타내었다.

[0143] 실험예3

[0144] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식3에서 A-164로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0145] 10mA/cm^{2}에서 683cd/m^2(4.46V)를 나타내었으며 이때 CIE x = 0.131, y = 0.157를 나타내었다.

[0146] 실험예4

[0147] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 패터닝한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식3에서 A-171로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å , Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0148] 10mA/cm^{2}에서 583cd/m^2(4.49V)를 나타내었으며 이때 CIE x = 0.137, y = 0.136를 나타내었다.

[0149] 실험예5

[0150] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 패터닝한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 하고 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식3에서 A-257로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0151] 10mA/cm2에서 641cd/m2(4.54V)를 나타내었으며 이때 CIE x = 0.137, y = 0.176를 나타내었다.

[0152] 비교예1

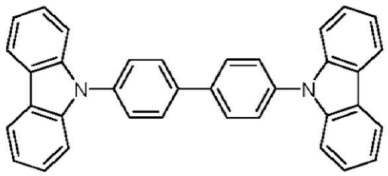
[0153] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 패터닝한 후 세정하였다. 상기 기

판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 유기물을 ITO위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식1-3으로 표시된 BD-a를 도펀트로 약 1% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

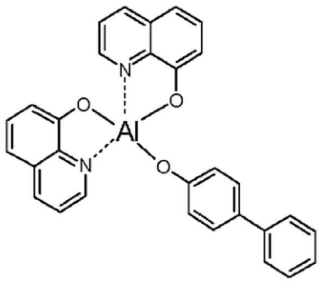
[0154] 10mA/cm^2에서 526 cd/m^2(6.7 V)를 나타내었으며 이때 CIE x = 0.136, y = 0.188를 나타내었다.

[0155] 여기서, 상기 CuPC와 상기 DPVBi 각각은 상기 화학식1-1 및 상기 화학식1-2로 표시되며, 상기 NPD는 하기 화학식4-1로 표시되고, 상기 Alq_3는 하기 화학식4-2로 표시된다.

[0156] 화학식4-1

[0157] 

[0158] 화학식4-2

[0159] 

[0160] 상술한 실험예1 내지 실험예5와 비교예1의 비교결과를 아래 표1에 나타내었다. 여기서 전압의 단위는 V, 전류의 단위는 mA/cm^2, 휘도의 단위는 cd/m^2이다.

[0161] 표1

[0162]

	전압	전류	휘도	CIE(X)	CIE(Y)
실험예1	4.36	10	606	0.136	0.142
실험예2	4.45	10	618	0.135	0.133
실험예3	4.46	10	683	0.131	0.157
실험예4	4.49	10	583	0.137	0.136
실험예5	4.54	10	641	0.137	0.176
비교예	6.7	10	526	0.136	0.188

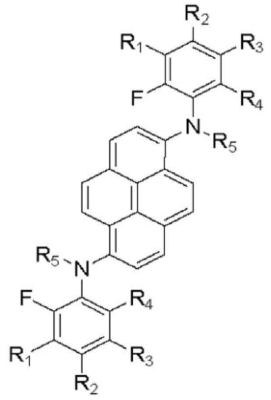
[0163] 표1을 통해 알 수 있는 바와 같이, 실험예1 내지 실험예5에서는 발광효율 및 색순도가 향상되었다. 특히, 비교예에 비해 저전압구동이 가능함을 알 수 있다.

[0164] -제 2 실시예-

[0165] 본 발명의 제 1 실시예에 따른 청색 형광 물질은 6-플루오로페닐아민 유도체가 1,6-파이렌에 치환된 구조에서 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 및 질소 중 적어도 하나는 중수소(D)로 치환된 방향족 그룹에서 선택되는 물질로 치환되고, 플루오로페닐아민 부분의 2,3,4,5 위치 탄소 중 적어도 두개는 수소, 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되며, 질소에는 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되는 물질로 치환되어, 색순도와 발광효율 및

발광수명이 향상되는 것이 특징이며, 하기 화학식5로 표시된다.

[0166] 화학식5



[0167]

[0168] 여기서, R1, R2, R3, R4, R5 중 적어도 하나는 중수소로 치환된 방향족 그룹에서 선택되고, R1, R2, R3, R4 중 적어도 두개는 수소, 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택되며, R5는 치환 또는 비치환된 방향족 그룹 또는 이형고리(heterocycle) 그룹에서 선택된다.

[0169] 보다 구체적으로 상기 화학식2에서 R1, R2, R3, R4, R5 각각은 페닐(phenyl), 바이페닐(biphenyl), 나프틸(naphthyl), 페난스렌(phenanthrene), 터페닐(terphenyl), 플루오레닐(fluorenyl) 등 방향족 그룹과 이들의 치환체 등으로부터 선택될 수 있다. 또한, 상기 화학식2에서 R1, R2, R3, R4, R5 각각은 퓨란(furan), 티오펜(thiophene), 피롤(pyrrole), 피리딘(pyridine), 피리미딘(pyrimidine) 등 이형고리 그룹으로부터 선택될 수 있다.

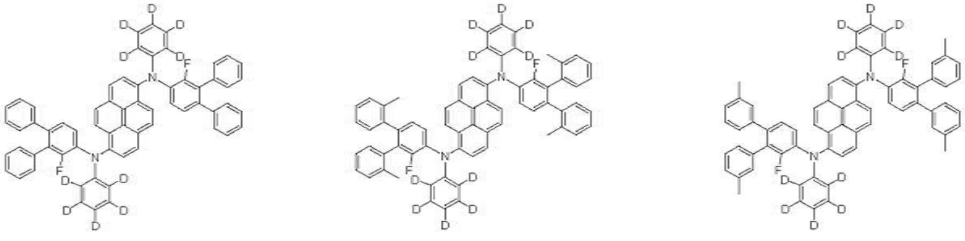
[0170] 또한, 상기 중수소로 치환된 방향족 그룹은 중수소로 치환된 페닐(deuterium substituted phenyl)일 수 있다.

[0171] 방향족 그룹의 치환체는 메틸(methyl), 에틸(ethyl), 프로필(propyl), 이소프로필(i-propyl), 터셔리부틸(tert-butyl) 등과 같은 C1~C6 의 알킬(alkyl) 그룹, 시아노(cyano) 그룹, 실릴(silyl) 그룹, 플루오린(fluorine)에서 선택될 수 있다.

[0172] 제 2 실시예에서는 파이렌(pyrene) 중심부에 수소, 치환 또는 비치환된 방향족 그룹, 이형고리 그룹이 적어도 두 개가 포함된 6-플루오로페닐아민기로 치환하고, 아민기에 치환 또는 비치환된 방향족 그룹, 이형고리 그룹으로 치환하며, 중수소로 치환된 방향족 그룹을 적어도 한 개 치환하여 발광효율 및 색순도가 높고 수명이 향상된 것을 특징으로 하는 청색 형광물질을 제공한다.

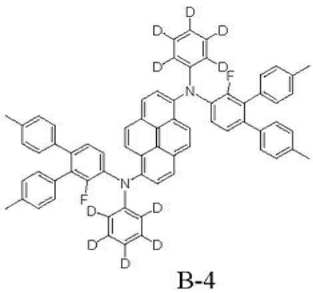
[0173] 결과적으로, 상기 화학식5는 하기 화학식6에 표시된 다수의 물질 중 어느 하나이다. 설명의 편의를 위해, 각 물질에 B-1 내지 B-170의 번호를 부여하였다.

[0174] 화학식6

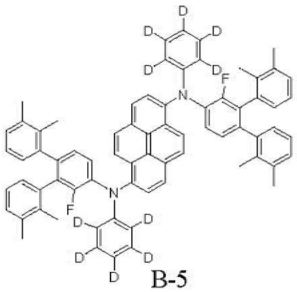


[0175] B-1 B-2 B-3

[0176]

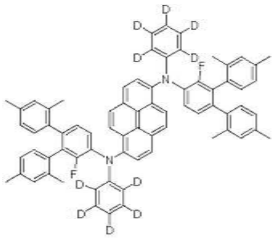


B-4

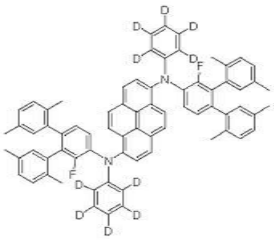


B-5

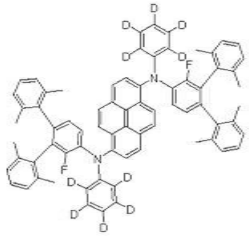
[0177]



B-6

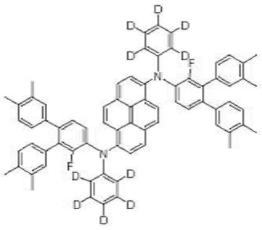


B-7

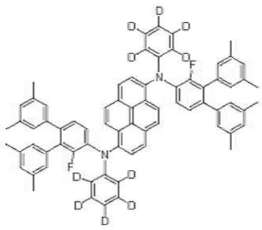


B-8

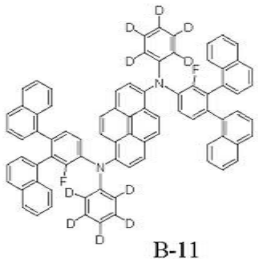
[0178]



B-9

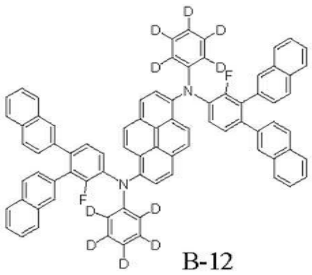


B-10

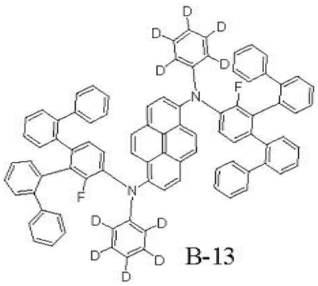


B-11

[0179]

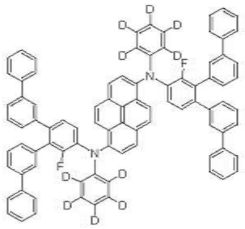


B-12

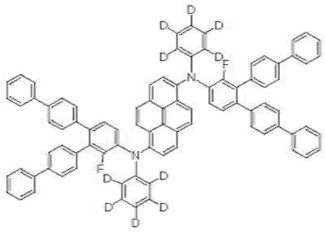


B-13

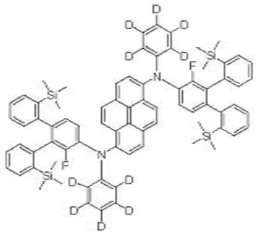
[0180]



B-14

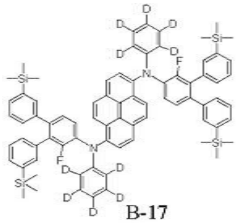


B-15

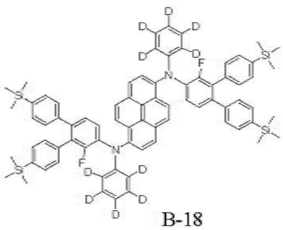


B-16

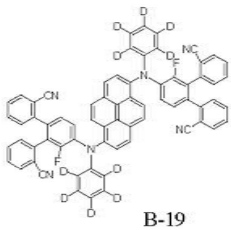
[0181]



B-17

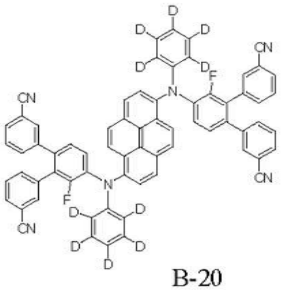


B-18

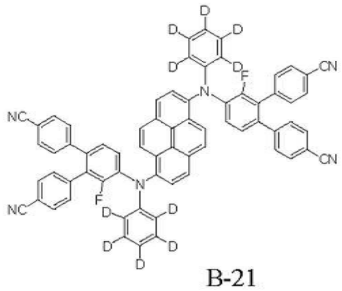


B-19

[0182]

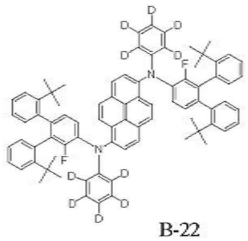


B-20

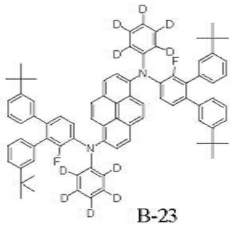


B-21

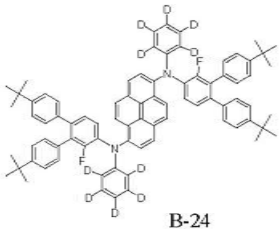
[0183]



B-22

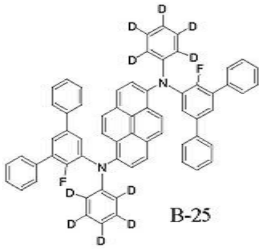


B-23

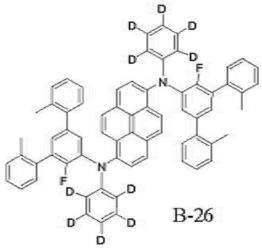


B-24

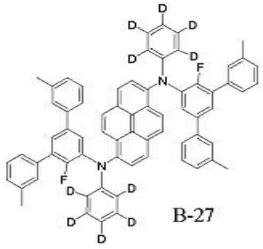
[0184]



B-25

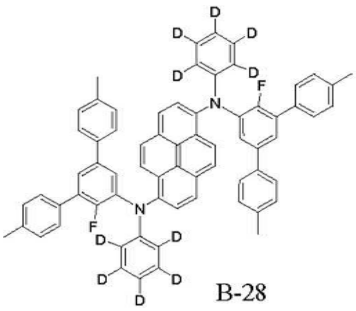


B-26

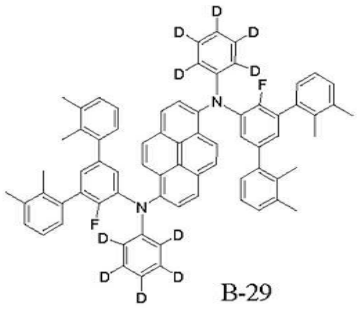


B-27

[0185]

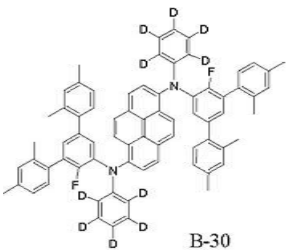


B-28

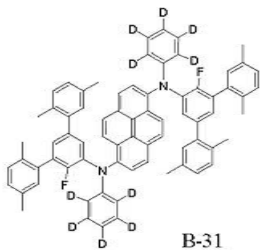


B-29

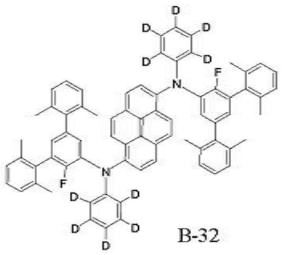
[0186]



B-30

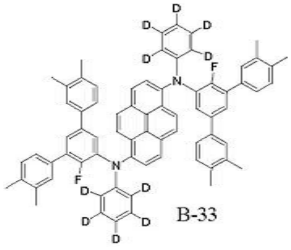


B-31

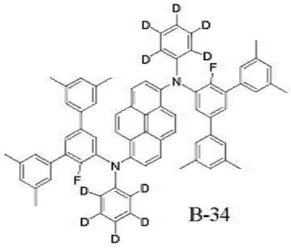


B-32

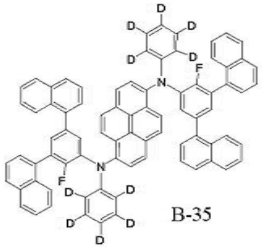
[0187]



B-33

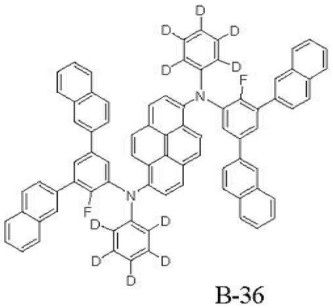


B-34

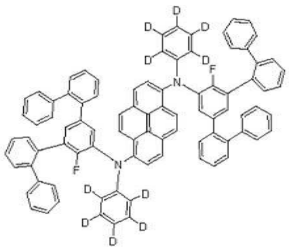


B-35

[0188]

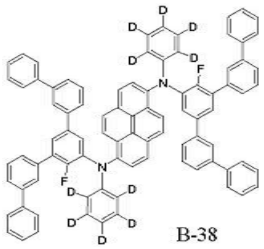


B-36

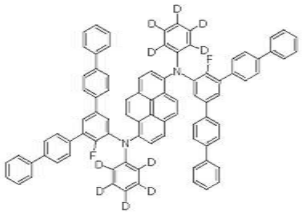


B-37

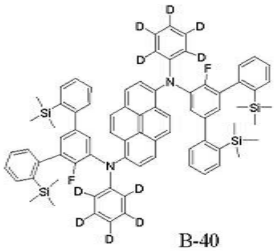
[0189]



B-38

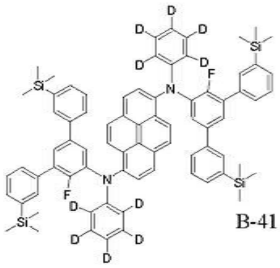


B-39

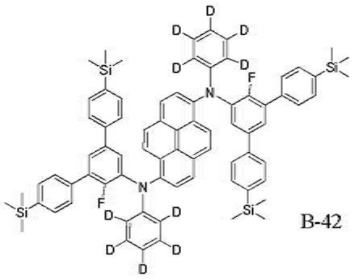


B-40

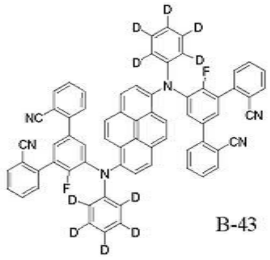
[0190]



B-41

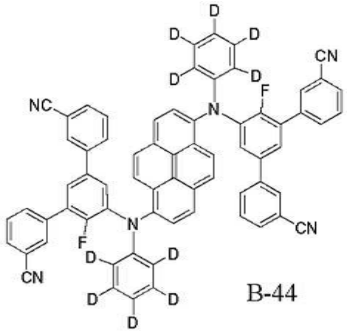


B-42

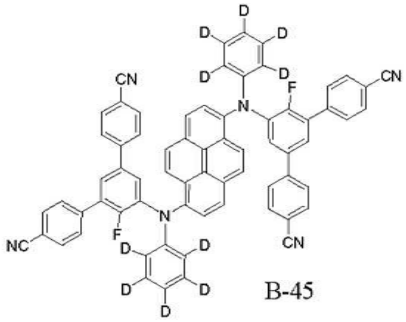


B-43

[0191]

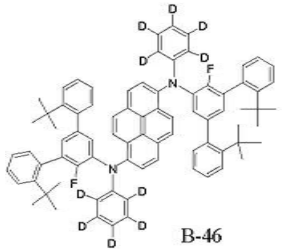


B-44

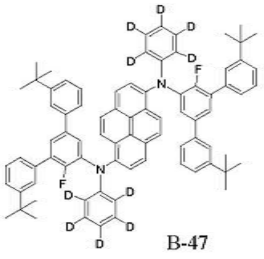


B-45

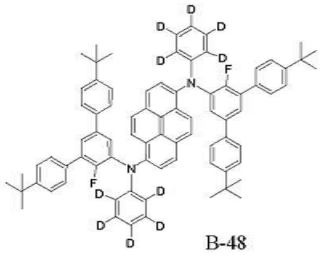
[0192]



B-46

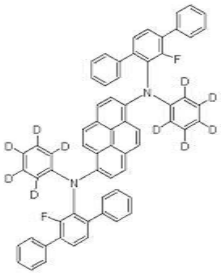


B-47

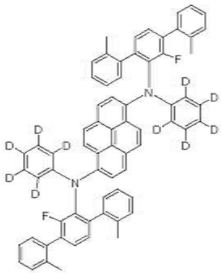


B-48

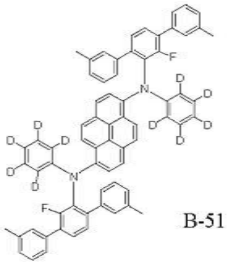
[0193]



B-49

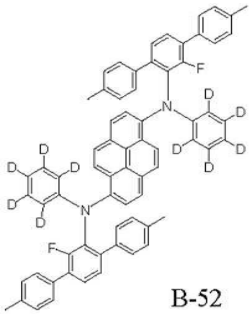


B-50

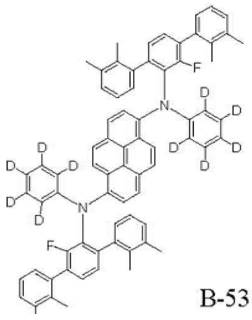


B-51

[0194]

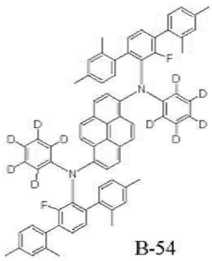


B-52

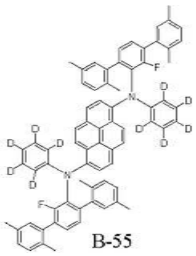


B-53

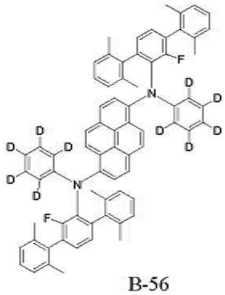
[0195]



B-54

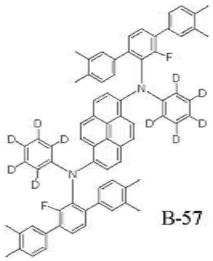


B-55

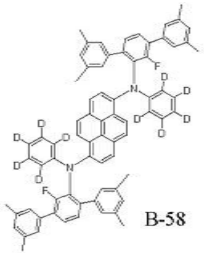


B-56

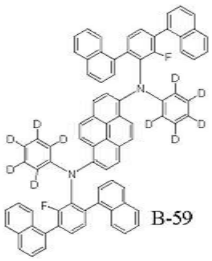
[0196]



B-57

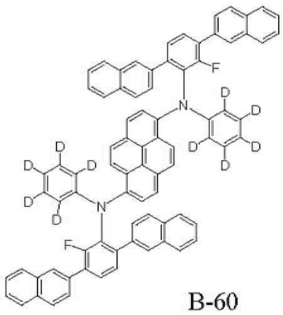


B-58

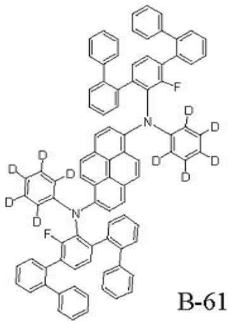


B-59

[0197]

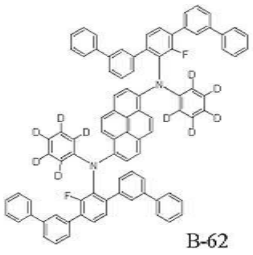


B-60

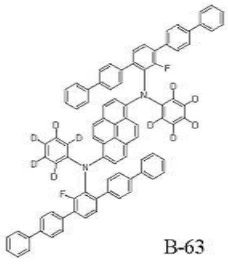


B-61

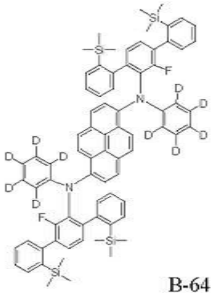
[0198]



B-62

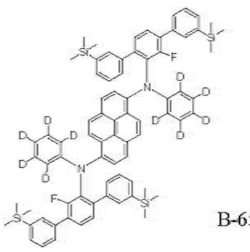


B-63

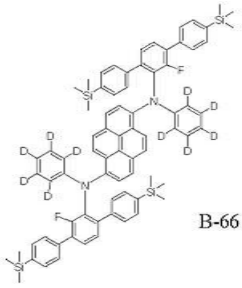


B-64

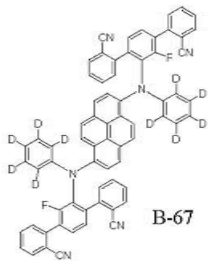
[0199]



B-65

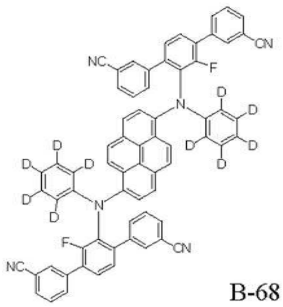


B-66

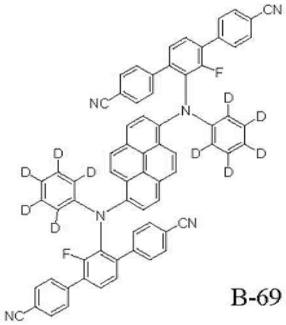


B-67

[0200]

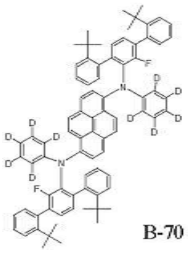


B-68

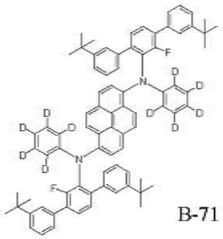


B-69

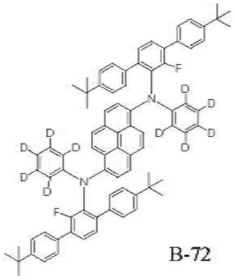
[0201]



B-70

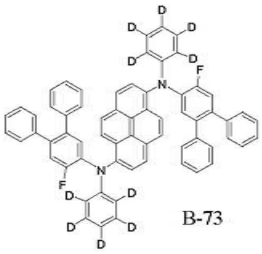


B-71

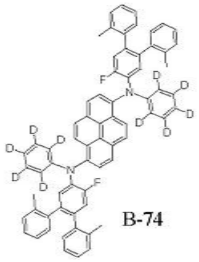


B-72

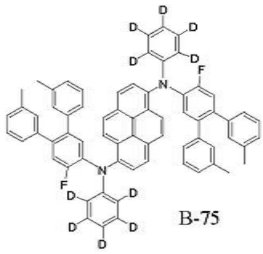
[0202]



B-73

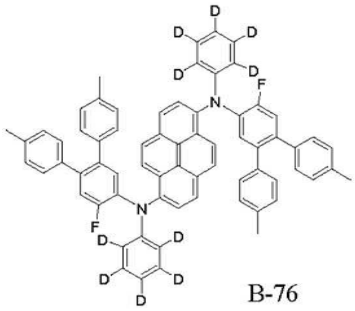


B-74

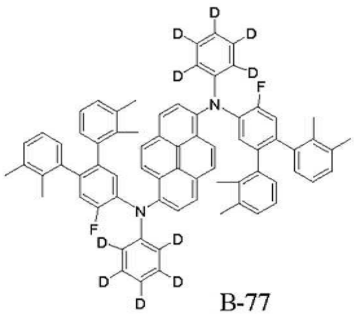


B-75

[0203]

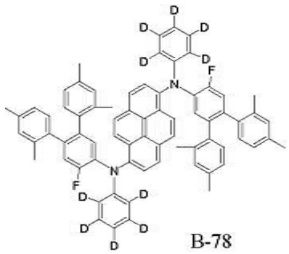


B-76

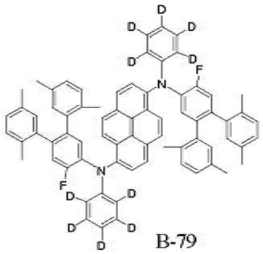


B-77

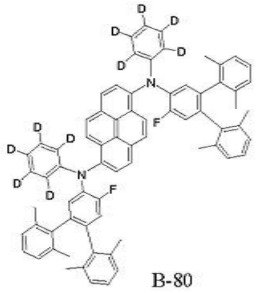
[0204]



B-78

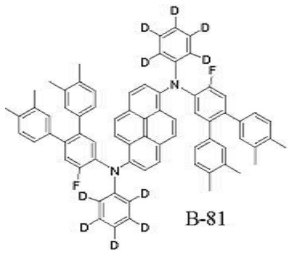


B-79

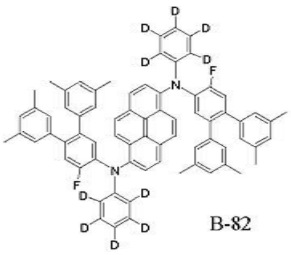


B-80

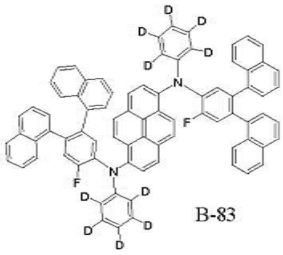
[0205]



B-81

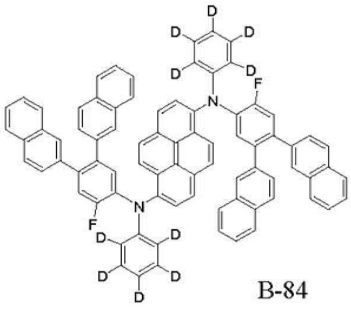


B-82

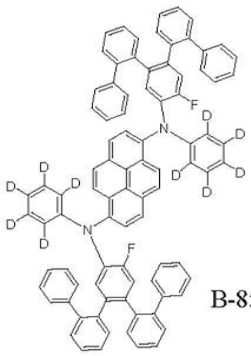


B-83

[0206]

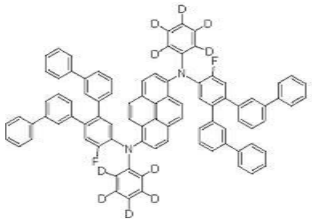


B-84

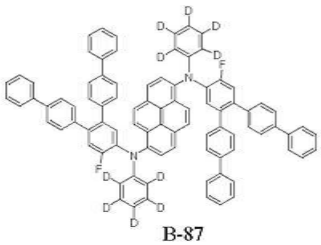


B-85

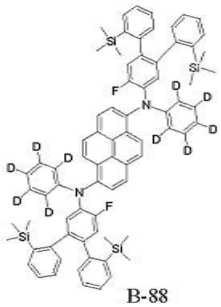
[0207]



B-86

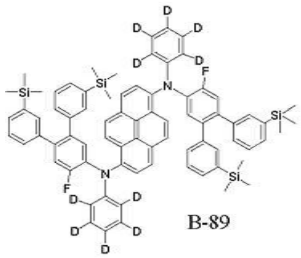


B-87

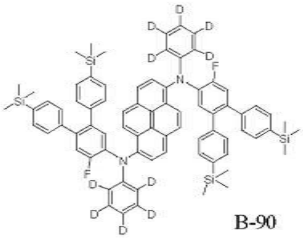


B-88

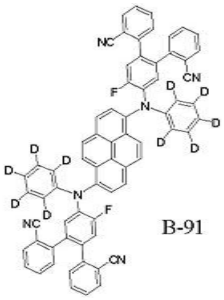
[0208]



B-89

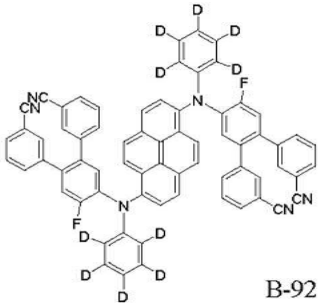


B-90

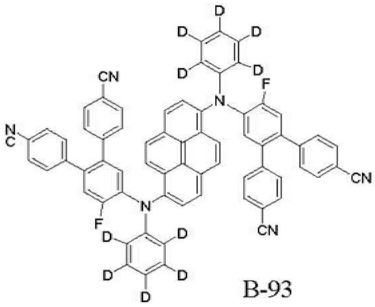


B-91

[0209]

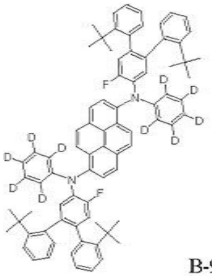


B-92

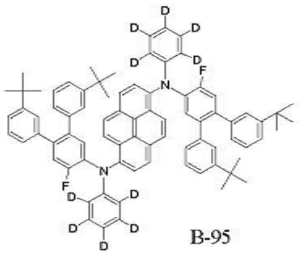


B-93

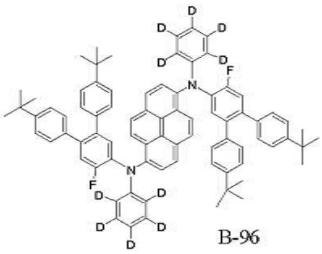
[0210]



B-94

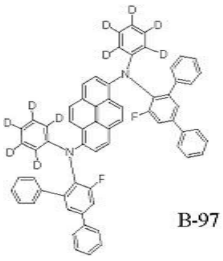


B-95

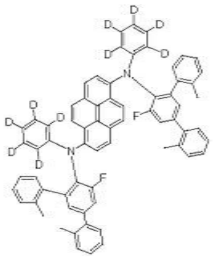


B-96

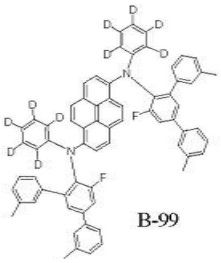
[0211]



B-97

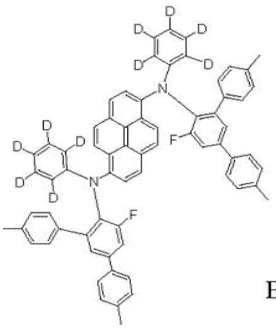


B-98

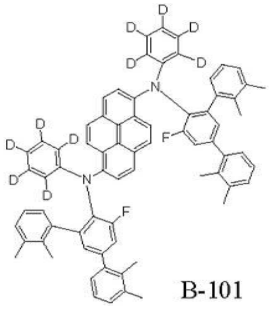


B-99

[0212]

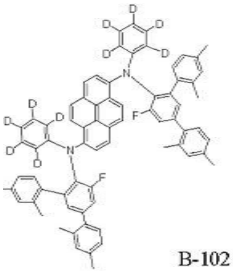


B-100

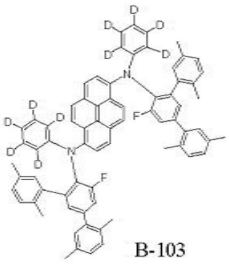


B-101

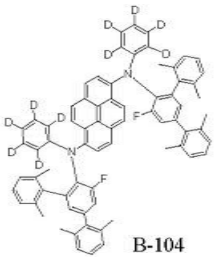
[0213]



B-102

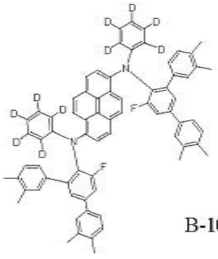


B-103

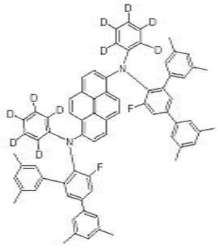


B-104

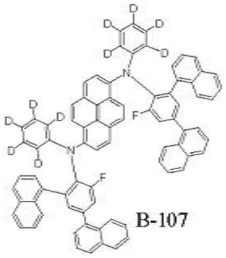
[0214]



B-105

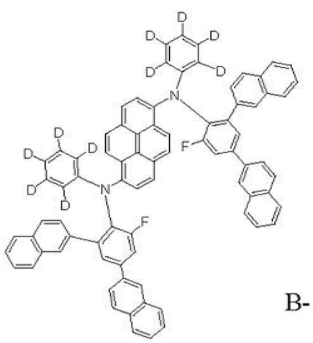


B-106

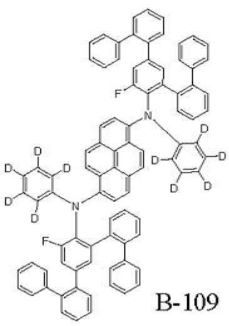


B-107

[0215]

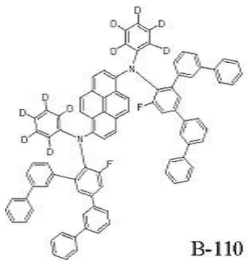


B-108

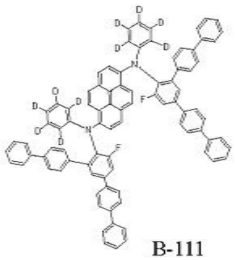


B-109

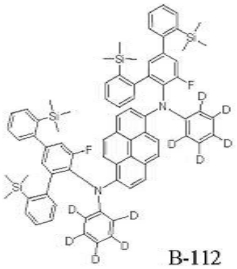
[0216]



B-110

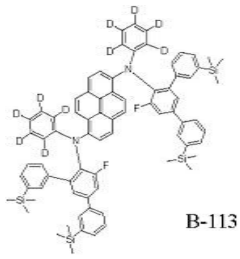


B-111

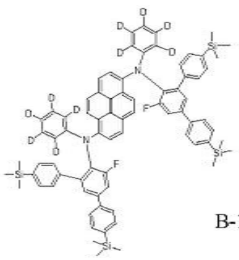


B-112

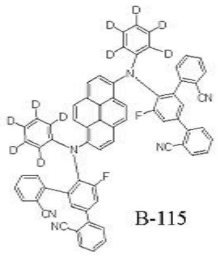
[0217]



B-113

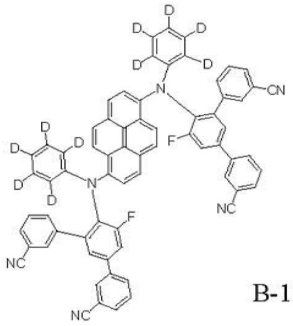


B-114

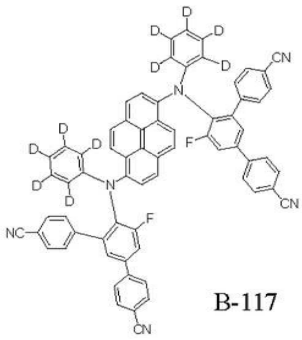


B-115

[0218]

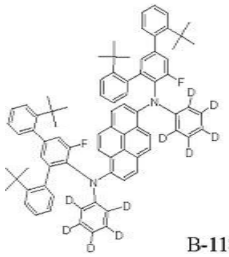


B-116

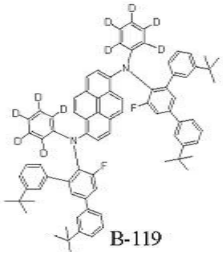


B-117

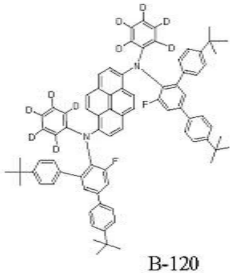
[0219]



B-118

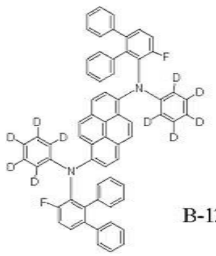


B-119

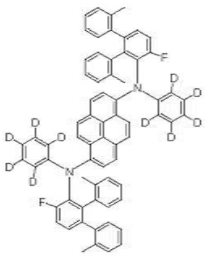


B-120

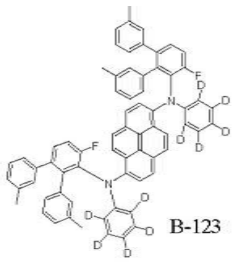
[0220]



B-121

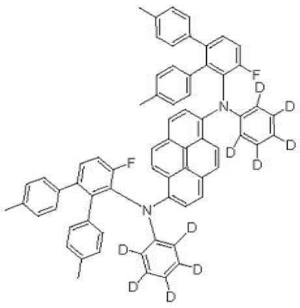


B-122

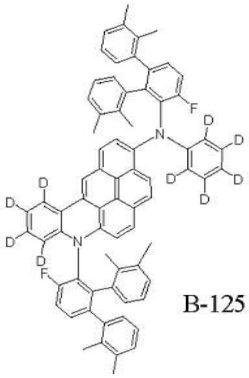


B-123

[0221]

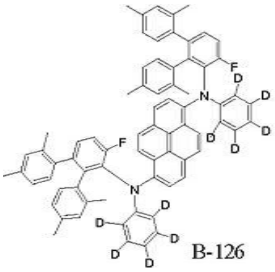


B-124

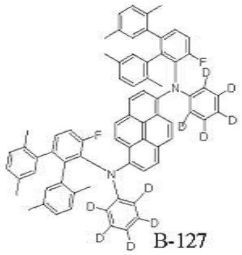


B-125

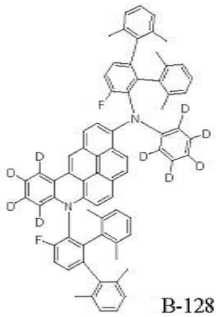
[0222]



B-126

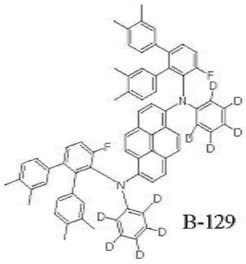


B-127

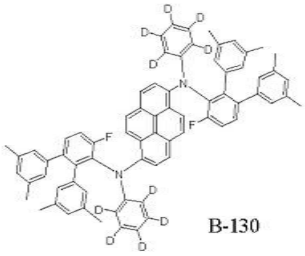


B-128

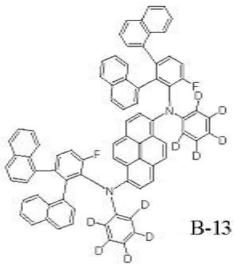
[0223]



B-129

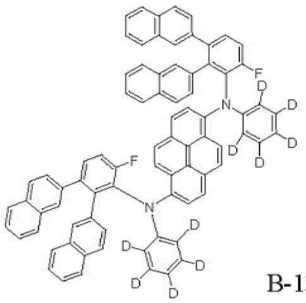


B-130

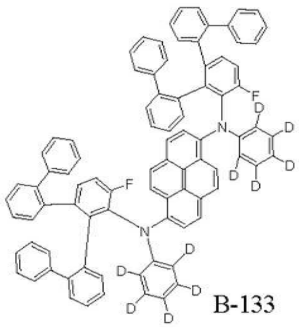


B-131

[0224]

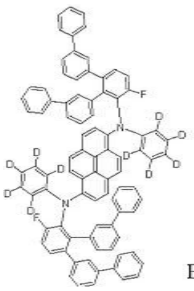


B-132

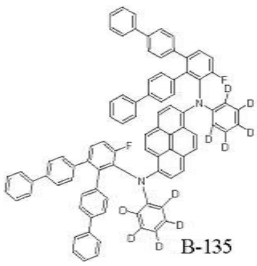


B-133

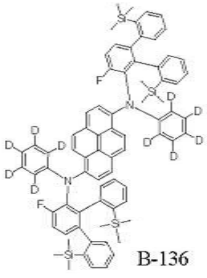
[0225]



B-134

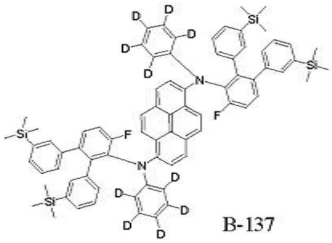


B-135

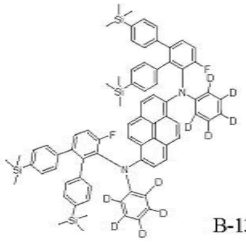


B-136

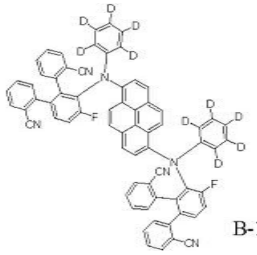
[0226]



B-137

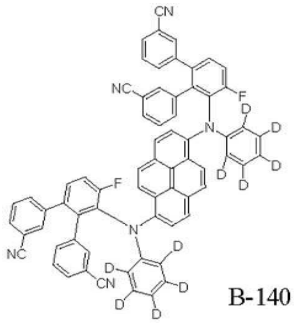


B-138

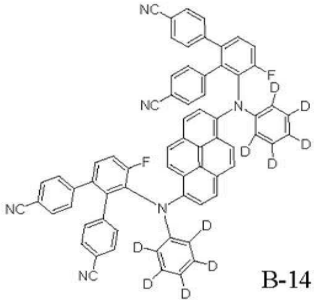


B-139

[0227]

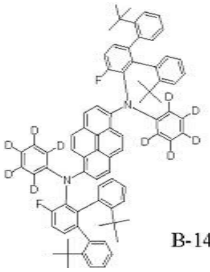


B-140

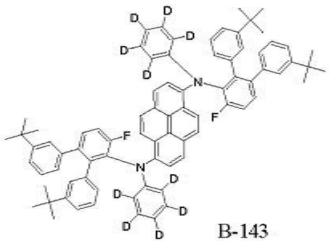


B-141

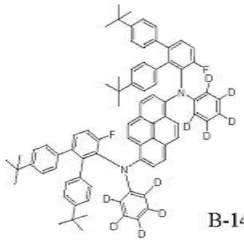
[0228]



B-142

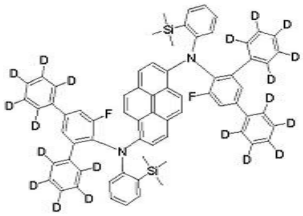


B-143

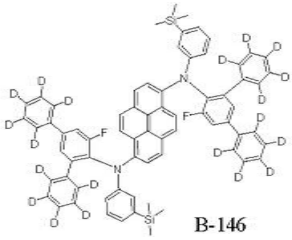


B-144

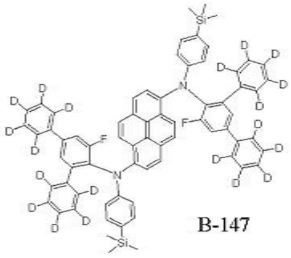
[0229]



B-145

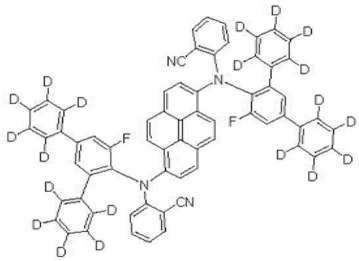


B-146

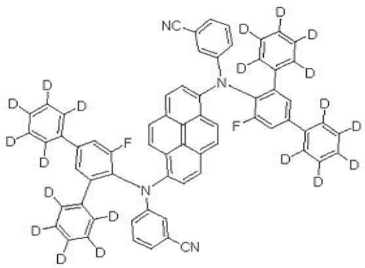


B-147

[0230]

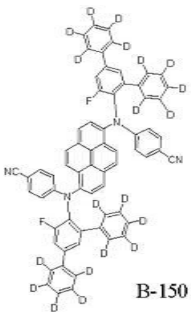


B-148

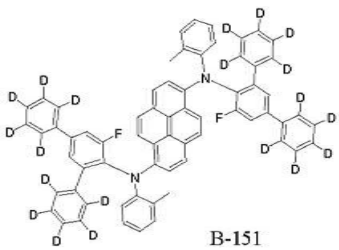


B-149

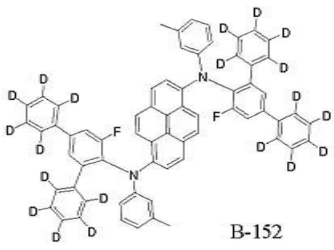
[0231]



B-150

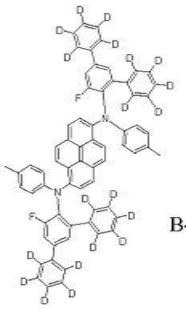


B-151

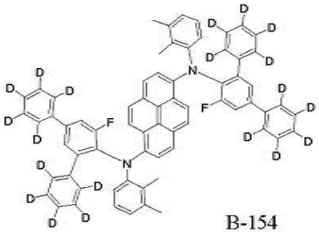


B-152

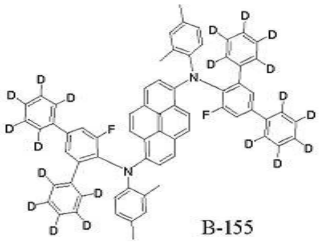
[0232]



B-153

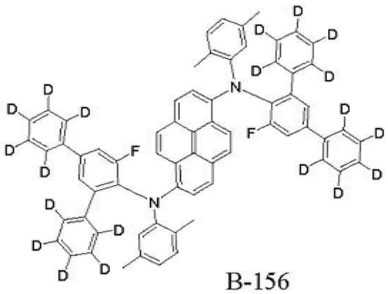


B-154

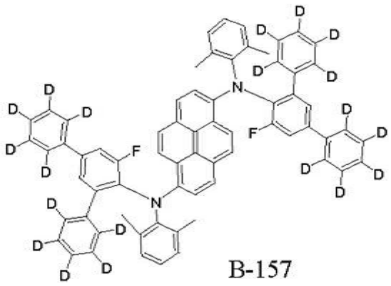


B-155

[0233]

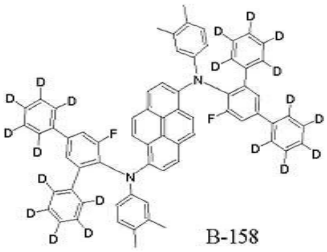


B-156

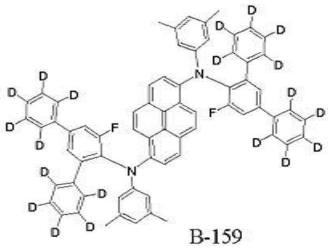


B-157

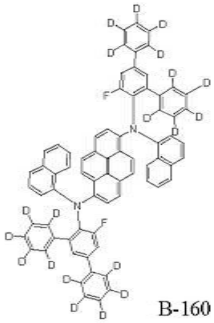
[0234]



B-158

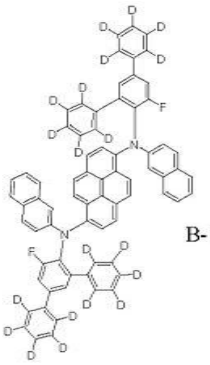


B-159

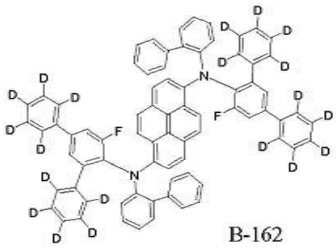


B-160

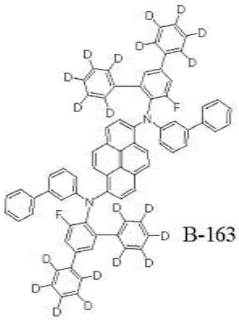
[0235]



B-161

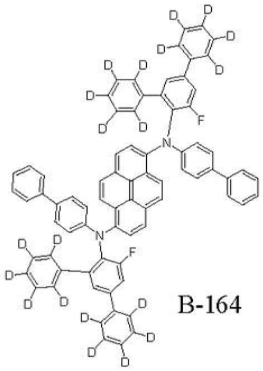


B-162

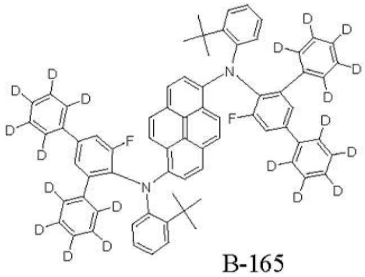


B-163

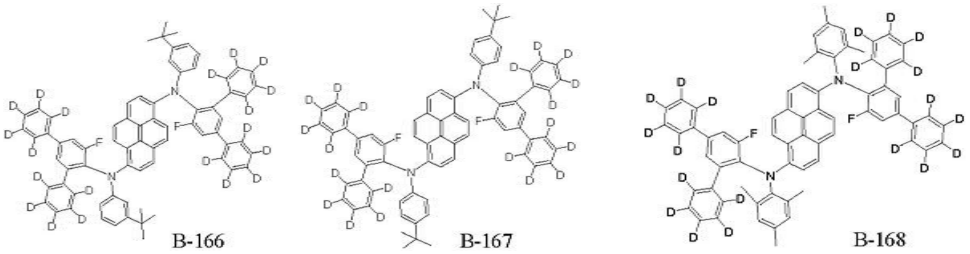
[0236]

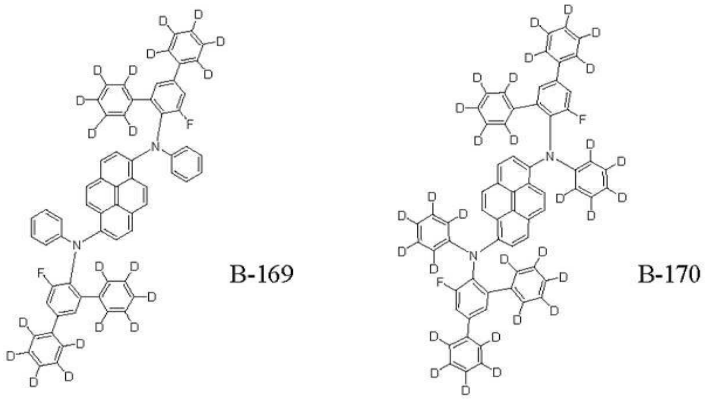


B-164



B-165

[0237] 

[0238] 

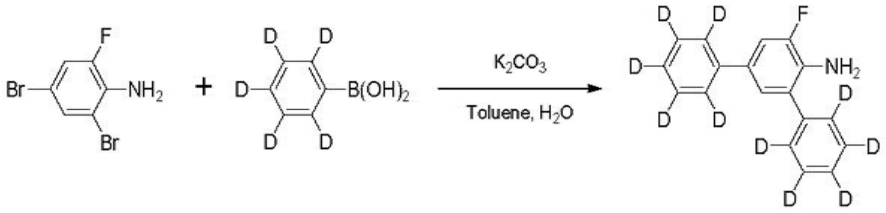
[0239] 이하에서는, 본 발명의 제 2 실시예에 따른 유기전계발광소자용 청색 형광 물질 중, 상기 화학식6에서 B-169로 표시된 물질인 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine을 예로 들어, 본 발명의 청색 형광물질의 합성예를 설명한다.

[0240] 합성예

[0241] (1) 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoroaniline의 합성

[0242] 상기 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoroaniline은 아래 반응식4에 의해 얻어진다.

[0243] 반응식4

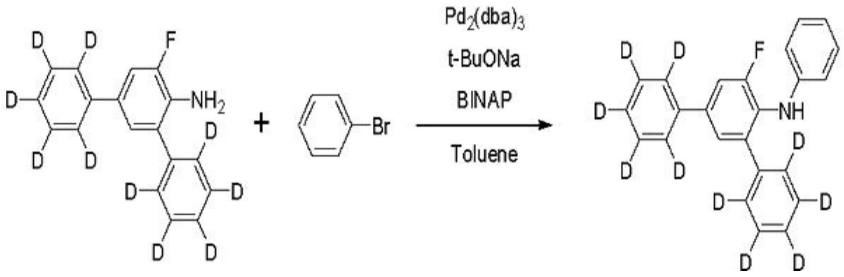
[0244] 

[0245] 구체적으로, 이구 둥근 바닥 플라스크에 10mmol의 2,4-dibromo-6-fluoroaniline, 24mmol의 2,3,4,5,6-pentadeuteriumbenzeneboronic acid, 1mmol의 tetrakis(triphenylphosphine) palladium(0)과 12g의 Potassium carbonate를, 30mL의 Toluene, 10mL의 H_2O에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류한다. 이후 Dichloromethane과 petroleum ether를 사용하여 재결정을 하고 여과하여 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoroaniline 결정 2.2g을 얻었다.

[0246] (2) 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoro-N-phenylbenzenamine의 제조

[0247] 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoro-N-phenylbenzenamine 는 하기 반응식5에 의해 얻어진다.

[0248] 반응식5



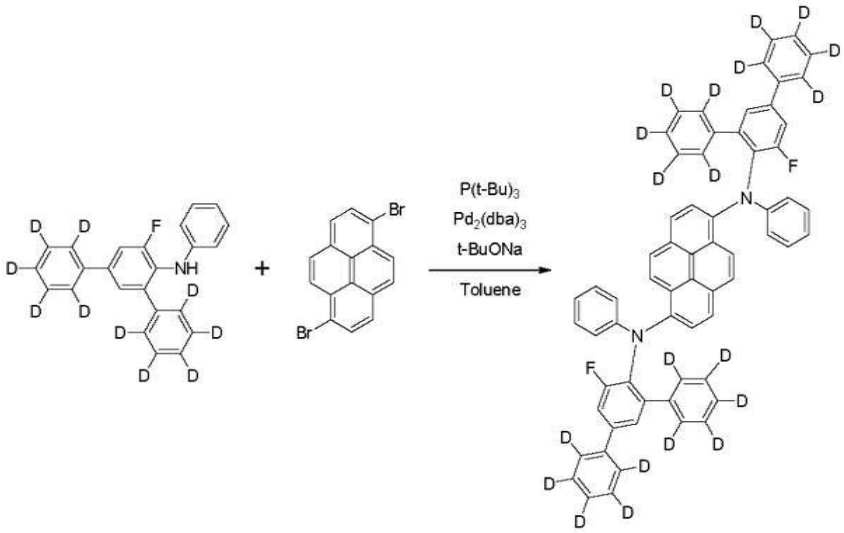
[0249]

[0250] 구체적으로, 이구 둥근 바닥 플라스크에 12mmol의 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoroaniline, 10mmol의 bromobenzene, 015mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.3mmol의 (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene과 14mmol의 Sodium tert-butoxide를, 30mL의 Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료가 되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류하였다. 이후, Dichloromethane과 petroleum ether를 사용하여 재결정을 하고 여과하여 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoro-N-phenylbenzenamine 결정 2.6g을 얻었다.

[0251] (3) N^1,N^6-bis(2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine의 제조

[0252] 상기 화학식6에서 B-169로 표시된 물질인 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine은 아래 반응식6에 의해 얻어진다.

[0253] 반응식6



[0254]

[0255] 구체적으로, 이구 둥근 바닥 플라스크에 6mmol의 2,4-di(2,3,4,5,6-pentadeuterium)phenyl-6-fluoro-N-phenylbenzenamine, 5mmol의 1,6-dibromopyrene, 0.075mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.15mmol의 tri-tert-butylphosphine과 7mmol의 Sodium tert-butoxide를, 15mL의 Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류하였다. 이후, Dichloromethane과 acetone를 사용하여 재결정을 하고 여과한 후, 열정제를 실시하여 상기 N^1,N^6-bis(2,4-diphenyl-6-fluorophenyl)-N^1,N^6-diphenylpyrene-1,6-diamine를 얻었다.

[0256] 이하, 상기한 본 발명의 제 2 실시예에 따른 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 실험예6 내지 실험예9와, 종래의 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 비교예2를 통해, 본 발명에 의한 청색 형광 물질 및 이를 이용한 유기전계발광소자의 성능을 비교 설명한다.

[0257] 실험예6

[0258] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식6에서 B-97로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0259] $10mA/cm^2$에서 $614cd/m^2$(4.73V)를 나타내었으며 이때 CIE x = 0.139, y = 0.130를 나타내었다.

[0260] 실험예7

[0261] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 650Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식6에서 B-114로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0262] $10mA/cm^2$에서 $628cd/m^2$(4.61V)를 나타내었으며 이때 CIE x = 0.140, y = 0.131를 나타내었다.

[0263] 실험예8

[0264] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식6에서 B-147로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0265] $10mA/cm^2$에서 $659cd/m^2$(4.42V)를 나타내었으며 이때 CIE x = 0.139, y = 0.143를 나타내었다.

[0266] 실험예9

[0267] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식6에서 B-169로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0268] $10mA/cm^2$에서 $602cd/m^2$(4.65V)를 나타내었으며 이때 CIE x = 0.132, y = 0.136를 나타내었다.

[0269] 비교예2

[0270] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 패터닝한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 $1X10^{-6}$torr가 되도록 한 후 유기물을 ITO위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식1-3으로 표시된 BD-a를 도펀트로 약 1% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0271] $10mA/cm^2$에서 526 cd/m^2(6.7 V)를 나타내었으며 이때 CIE x = 0.136, y = 0.188를 나타내었다.

[0272] 여기서, 상기 CuPC와 상기 DPVBi 각각은 상기 화학식1-1 및 상기 화학식1-2로 표시되며, 상기 NPD는 상기 화학식4-1로 표시되고, 상기 Alq_3는 상기 화학식4-2로 표시된다.

[0273] 상술한 실험예6 내지 실험예9와 비교예2의 비교결과를 아래 표2에 나타내었다. 여기서 전압의 단위는 V, 전류의 단위는 mA/cm^2, 휘도의 단위는 cd/m^2이다.

[0274] 표2

[0275]

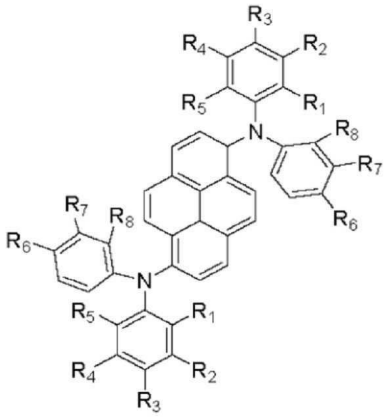
	전압	전류	휘도	CIE(X)	CIE(Y)
실험예6	4.73	10	614	0.139	0.130
실험예7	4.61	10	628	0.140	0.131
실험예8	4.42	10	659	0.139	0.143
실험예9	4.65	10	602	0.132	0.136
비교예2	6.7	10	526	0.136	0.188

[0276] 표2를 통해 알 수 있는 바와 같이, 실험예1 내지 실험예5에서는 발광효율 및 색순도가 향상되었다. 특히, 비교예에 비해 저전압구동이 가능함을 알 수 있다.

[0277] -제 3 실시예-

[0278] 본 발명의 제 3 실시예에 따른 청색 형광 물질은 페닐아민 유도체가 1,6-파이렌에 치환된 구조에서, 질소의 제 1 페닐기에는 플로린, 시아닌, 트리플로로메틸기 중 적어도 어느 하나가 치환되고, 제 2 페닐기에는 적어도 두 개의 아릴기가 치환되어 색순도와 발광효율 및 발광수명이 향상되는 것이 특징이며, 하기 화학식7로 표시된다.

[0279] 화학식7

[0280] 

[0281] 여기서, R1, R2, R3, R4, R5 각각은 수소, C1~C6까지의 알킬기, C6 이상의 치환 또는 비치환된 아릴기 중에서 선택되어질 수 있으며 적어도 두 개는 C6이상의 치환 또는 비치환된 아릴기에서 선택되고, R6, R7, R8 각각은 수소, C1~C6까지의 알킬기, C6이상의 치환 또는 비치환된 아릴기, 플로린, 시아닌, 트리플로로메틸기 중에서 선택되어질 수 있고 적어도 하나는 플로린, 시아닌, 트리플롤로메틸기에서 선택된다.

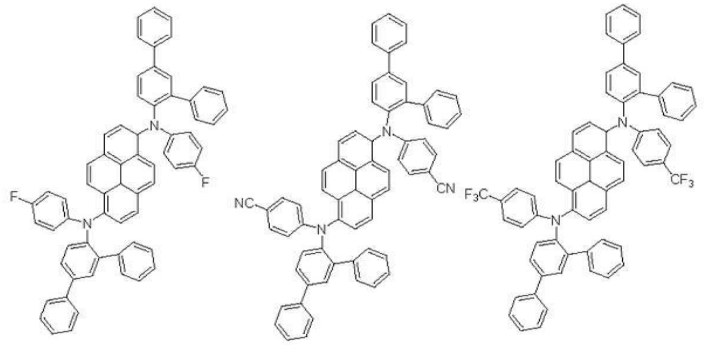
[0282] C1 내지 C6의 알킬기는 메틸, 에틸, n-프로필, i-프로필, n-부틸, i-부틸 및 t-부틸 중 어느 하나일 수 있다.

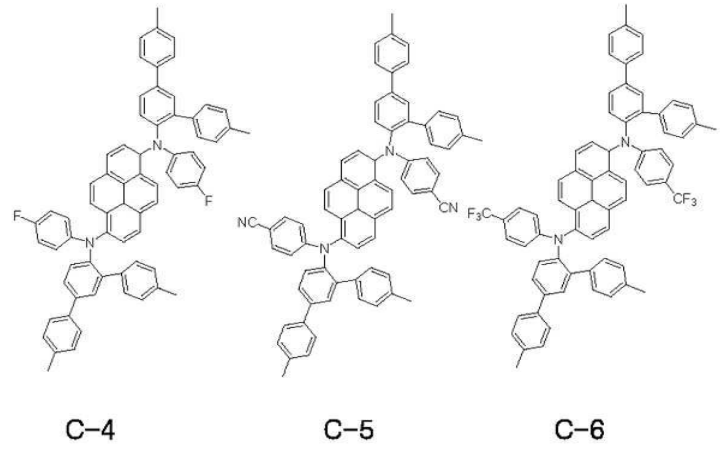
[0283] 또한, C6 이상의 치환 또는 비치환된 아릴기는 페닐, o-톨루일, m-톨루일, p-톨루일, o-자일릴, m-자일릴 ,p-자일릴 1-나프틸, 2-나프틸, 트리메틸실릴페닐 중 어느 하나일 수 있다. 예를 들어, C6 이상의 치환된 아릴기는 중수소로 치환된 페닐기일 수 있다.

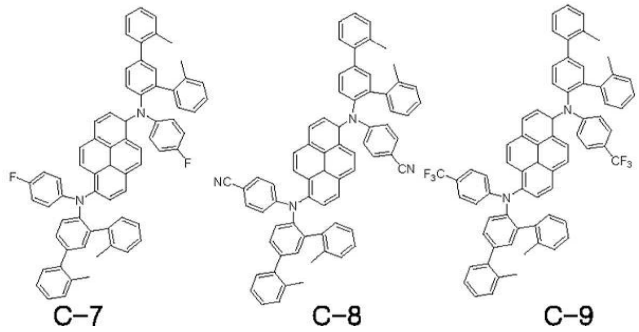
[0284] 제 3 실시예에서는 페닐아민 유도체가 1,6-파이렌에 치환된 구조에서, 질소의 제 1 페닐기에는 플로린, 시아닌, 트리플로로메틸기 중 적어도 어느 하나가 치환되고, 제 2 페닐기에는 적어도 두개의 아릴기가 치환되어 색순도와 발광효율 및 발광수명이 향상되는 것이 특징으로 하는 청색 형광물질을 제공한다.

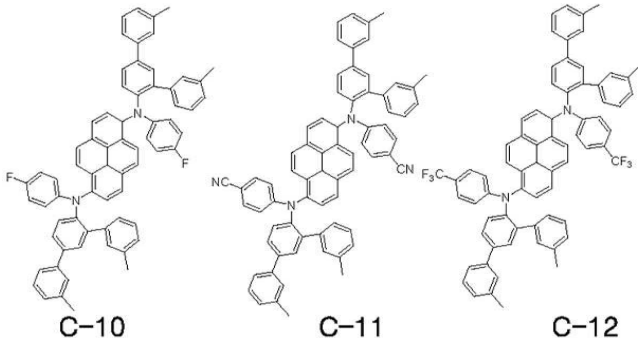
[0285] 결과적으로, 상기 화학식7은 하기 화학식8에 표시된 다수의 물질 중 어느 하나이다. 설명의 편의를 위해, 각 물질에 C1 내지 C152의 번호를 부여하였다.

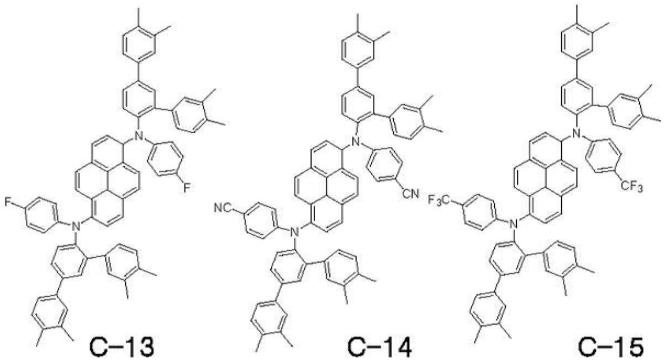
[0286] 화학식8

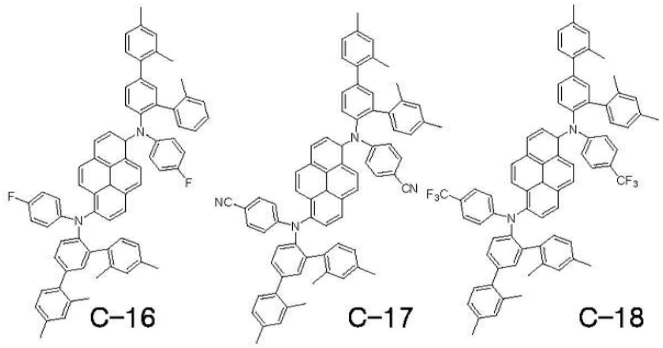
[0287] 

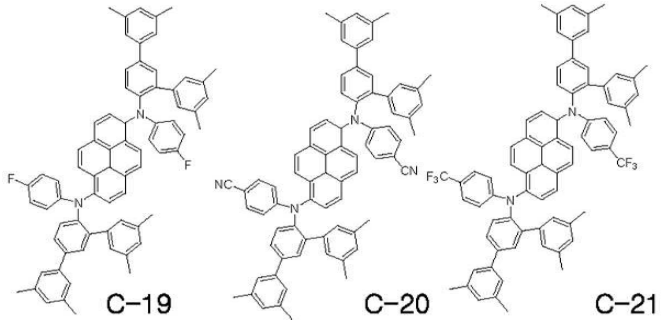
[0288] 

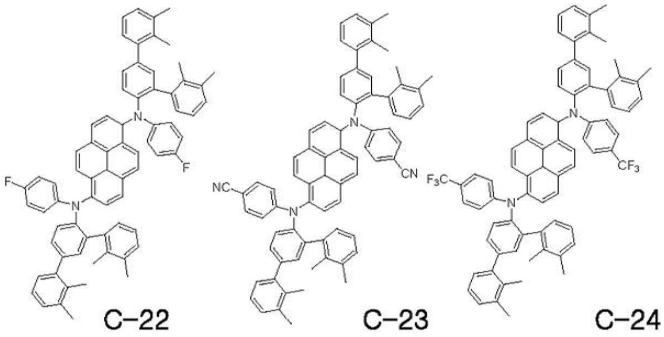
[0289] 

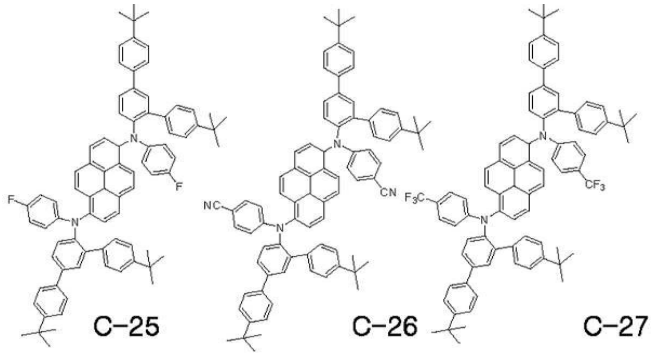
[0290] 

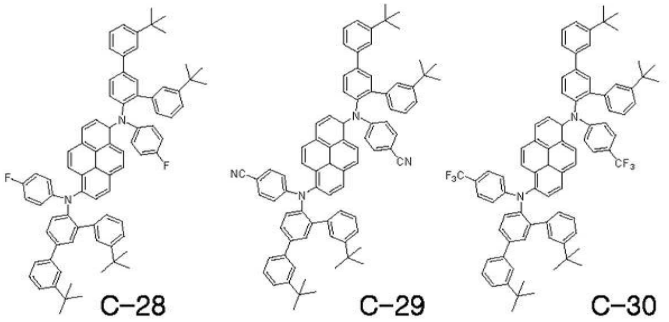
[0291] 

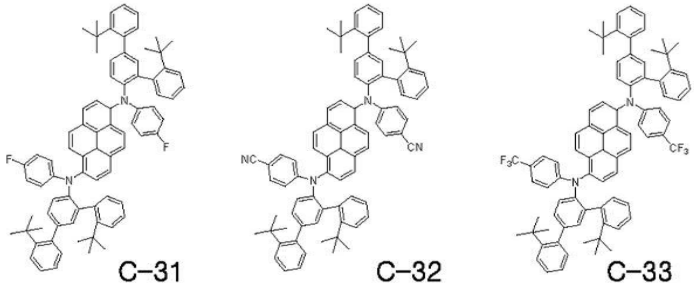
[0292] 

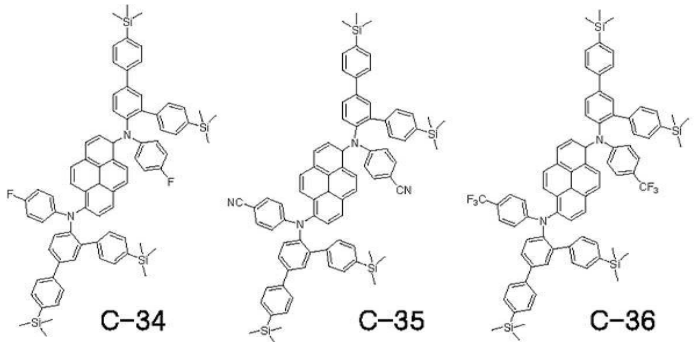
[0293] 

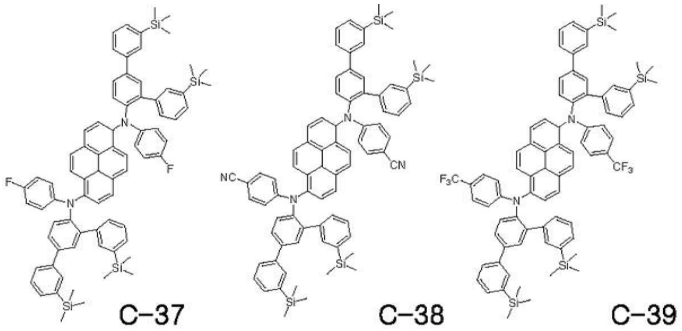
[0294] 

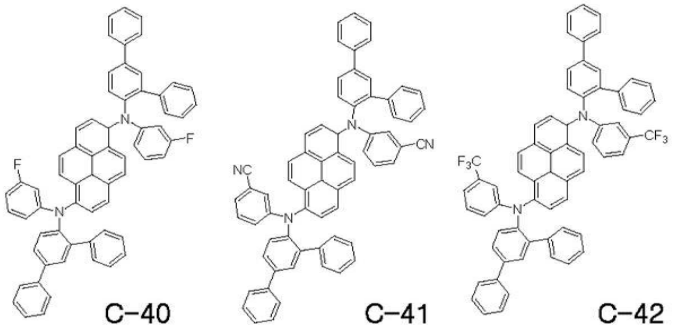
[0295] 

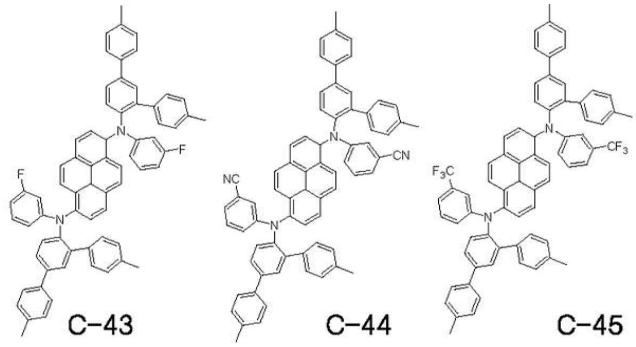
[0296] 

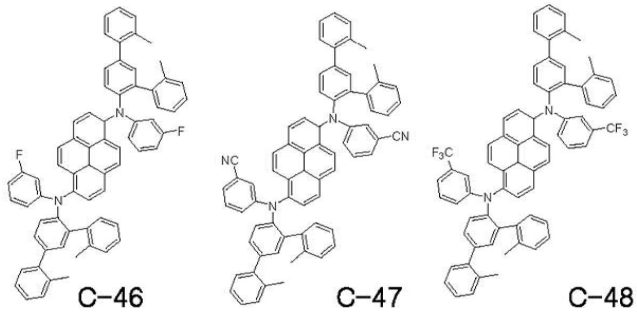
[0297] 

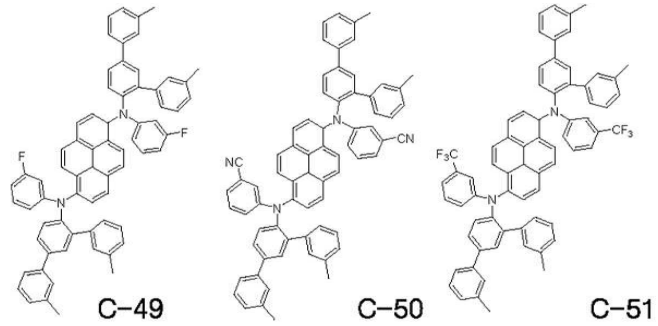
[0298] 

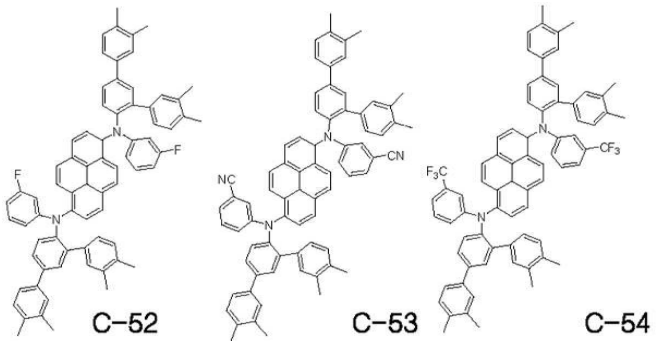
[0299] 

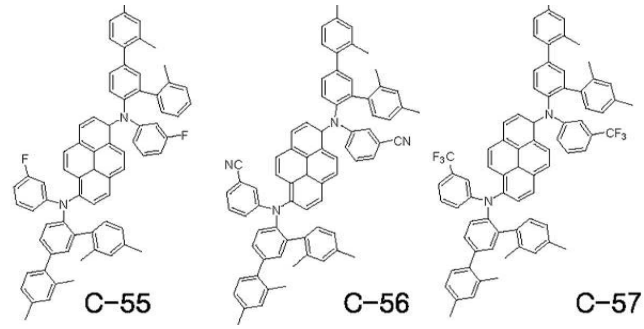
[0300] 

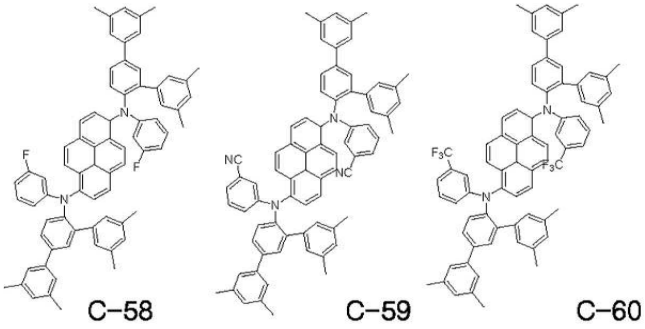
[0301] 

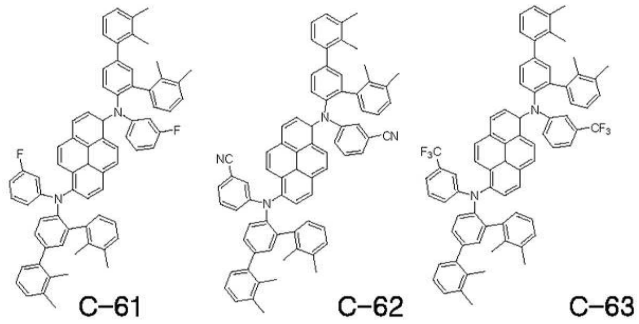
[0302] 

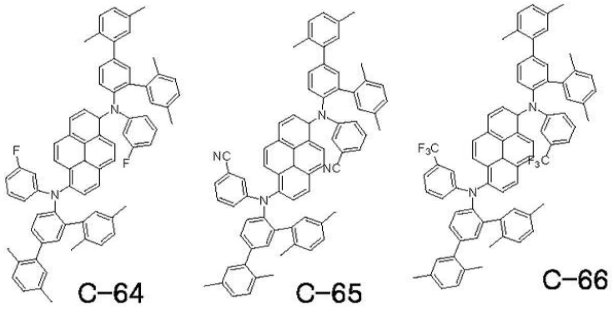
[0303] 

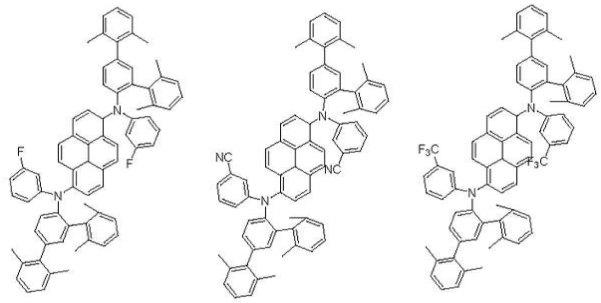
[0304] 

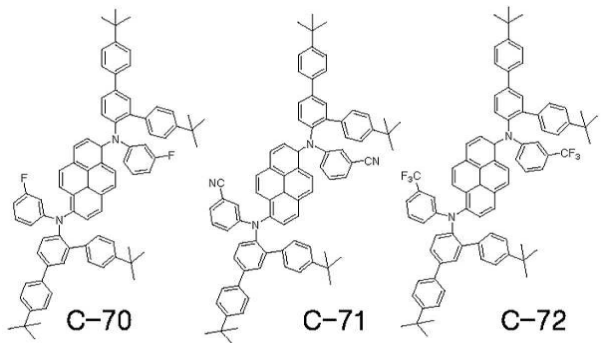
[0305] 

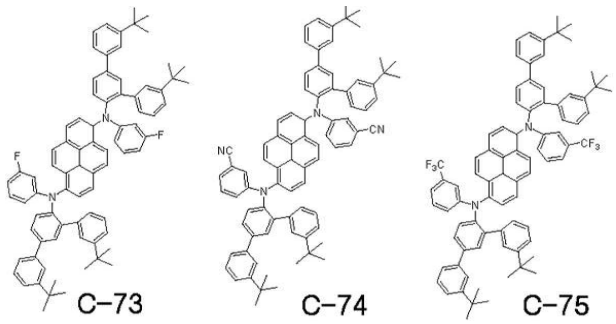
[0306] 

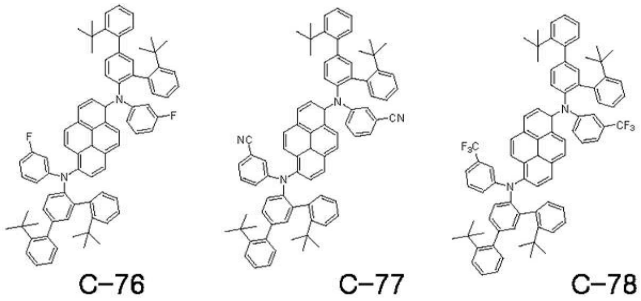
[0307] 

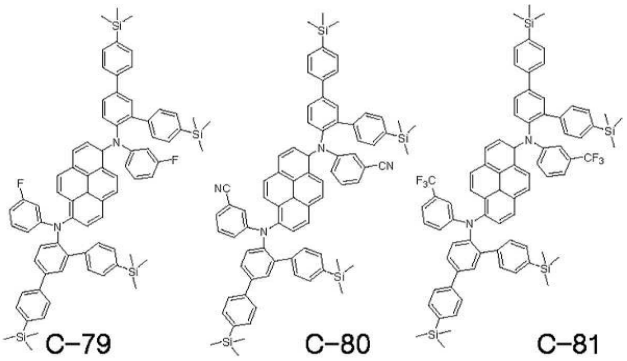
[0308] 

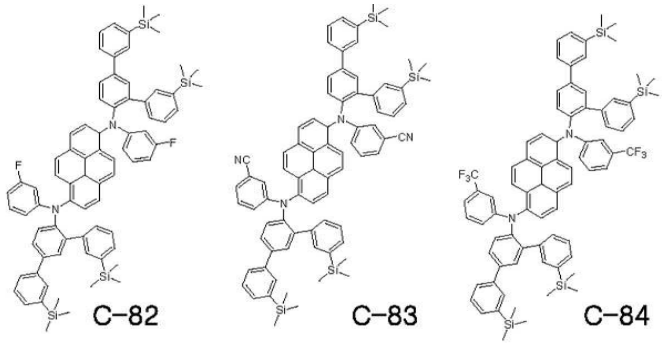
[0309] 

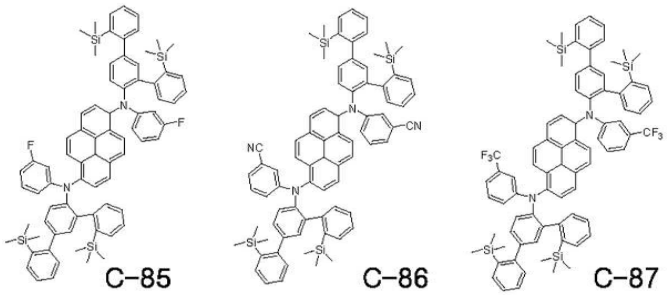
[0310] 

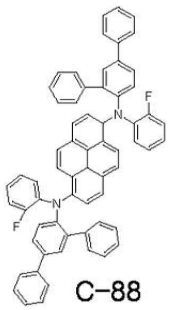
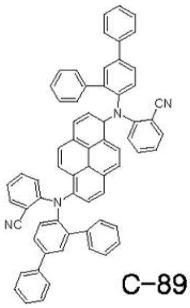
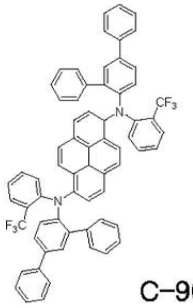
[0311] 

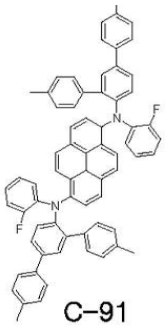
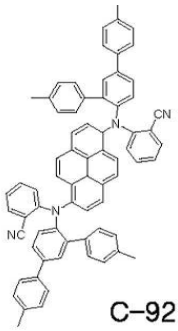
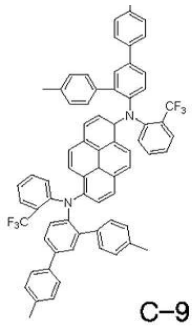
[0312] 

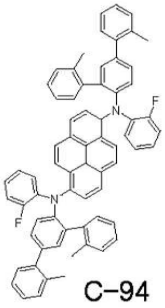
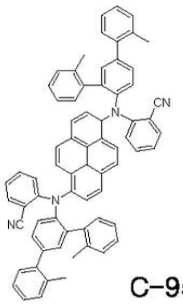
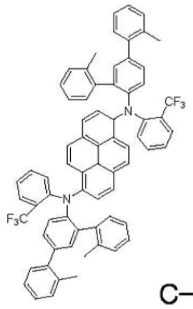
[0313] 

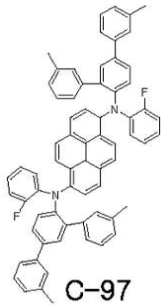
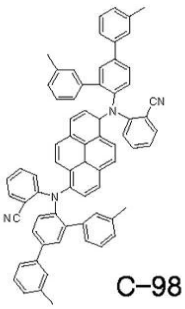
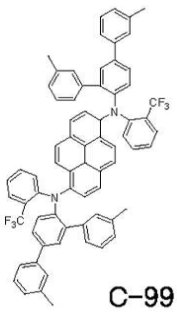
[0314] 

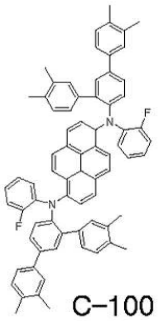
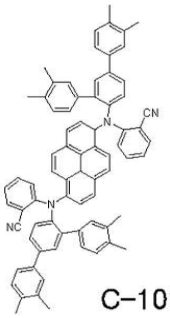
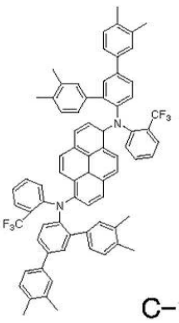
[0315] 

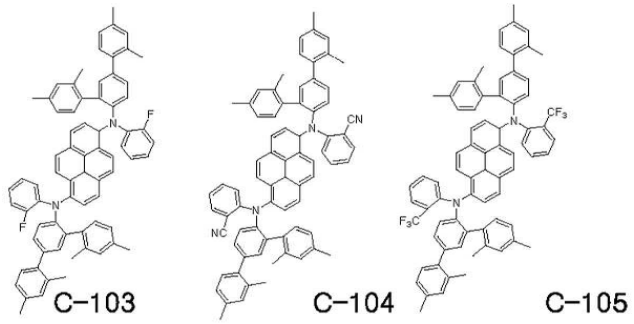
[0316]  C-88  C-89  C-90

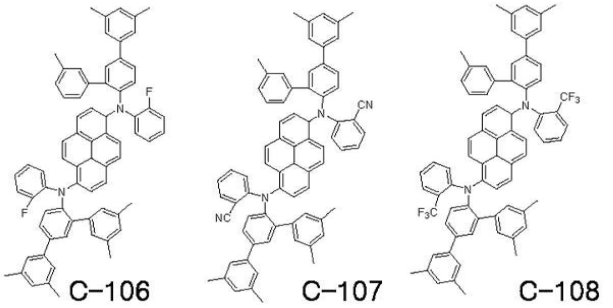
[0317]  C-91  C-92  C-93

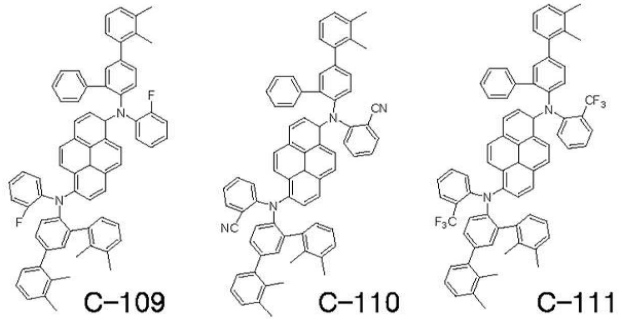
[0318]  C-94  C-95  C-96

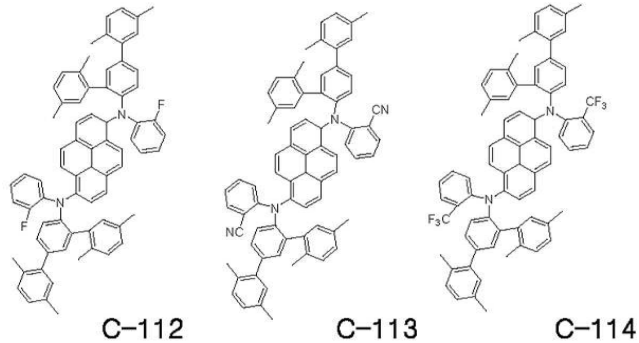
[0319]  C-97  C-98  C-99

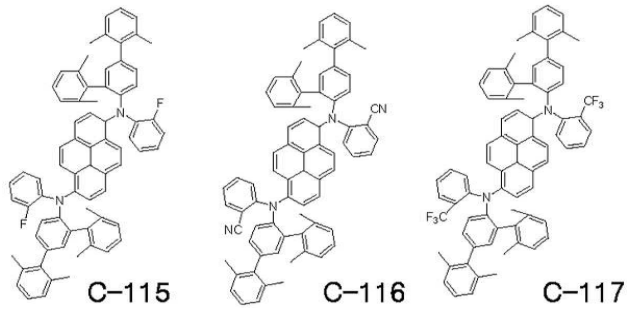
[0320]  C-100  C-101  C-102

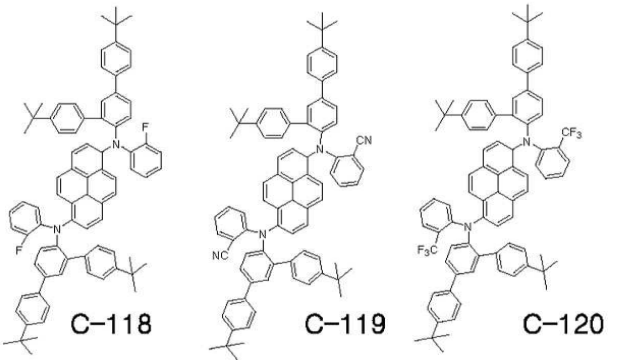
[0321] 

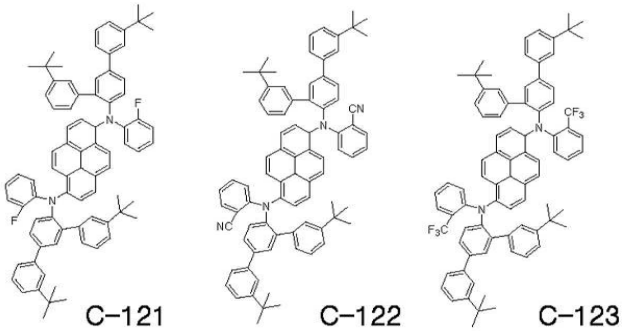
[0322] 

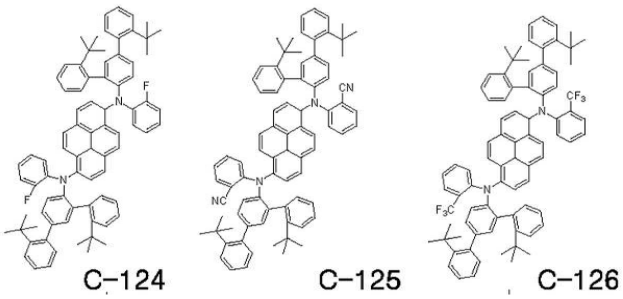
[0323] 

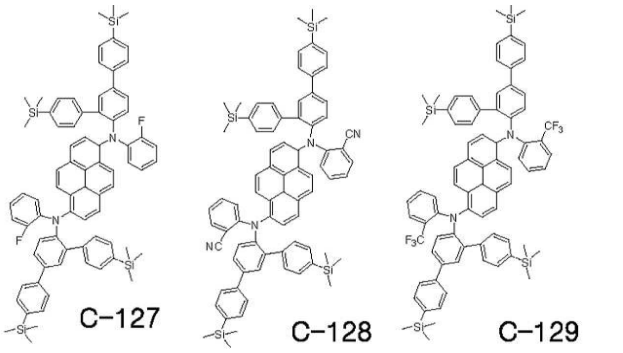
[0324] 

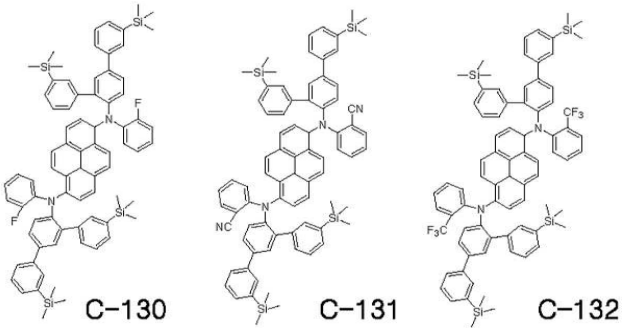
[0325] 

[0326] 

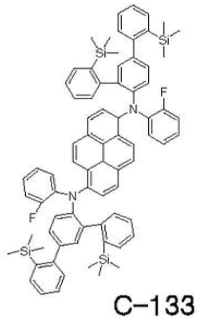
[0327] 

[0328] 

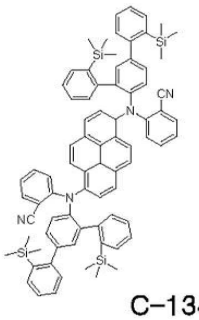
[0329] 

[0330] 

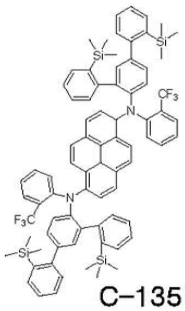
[0331]



C-133

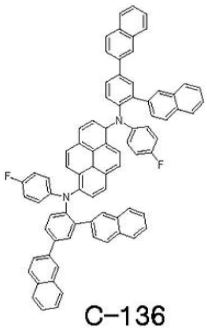


C-134

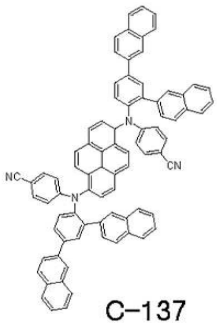


C-135

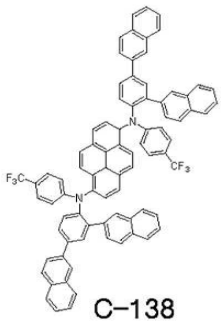
[0332]



C-136

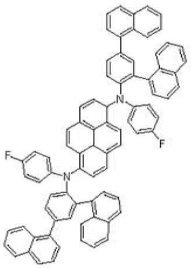


C-137

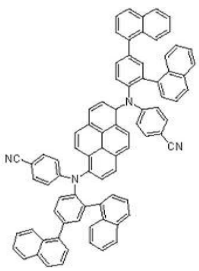


C-138

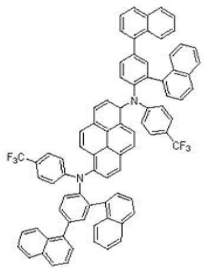
[0333]



C-139

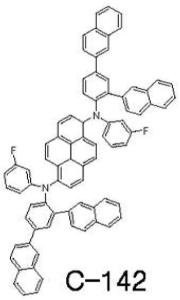


C-140

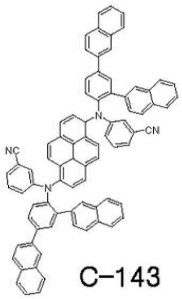


C-141

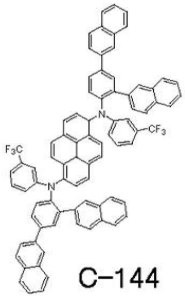
[0334]



C-142

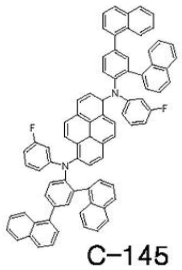


C-143

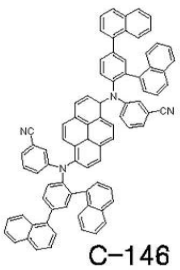


C-144

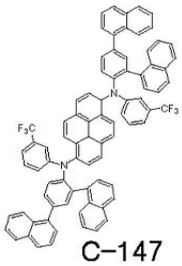
[0335]



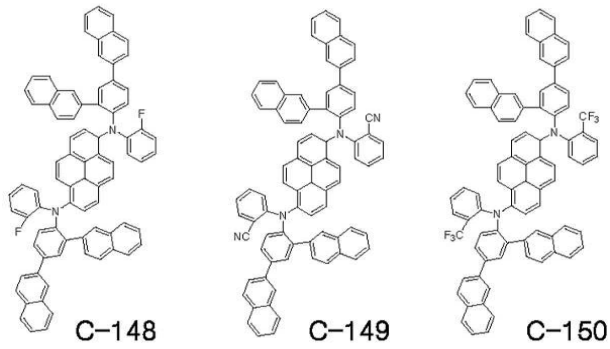
C-145

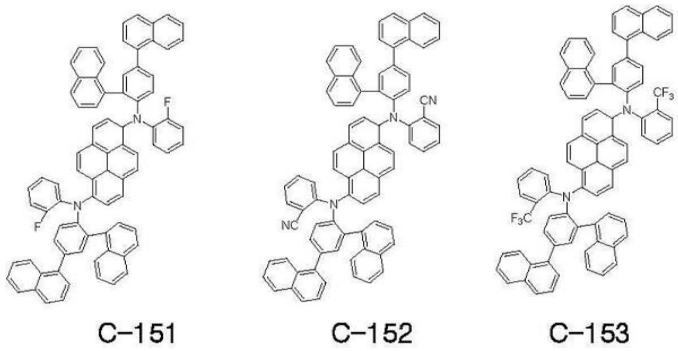


C-146



C-147

[0336] 

[0337] 

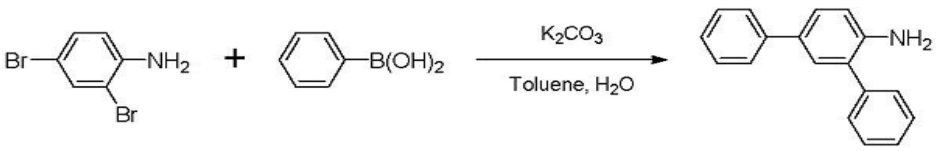
[0338] 이하에서는, 본 발명의 제 3 실시예에 따른 유기전계발광소자용 청색 형광 물질 중, 상기 화학식8에서 C-88로 표기된 물질인 N^1,N^6-bis(2,4-diphenylphenyl)-N^1,N^6-bis(2-fluorophenyl)pyrene-1,6-diamine을 예로 들어, 본 발명의 청색 형광물질의 합성예를 설명한다.

[0339] 합성예

[0340] (1) 2,4-diphenylaniline의 합성

[0341] 상기 2,4-diphenylaniline은 아래 반응식7에 의해 얻어진다.

[0342] 반응식7

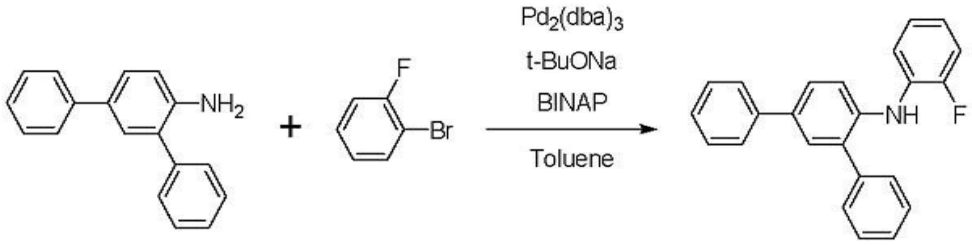
[0343] 

[0344] 구체적으로, 이구 둥근 바닥 플라스크에 10mmol의 2,4-dibromoaniline, 24mmol의 benzeneboronic acid, 1mmol의 tetrakis(triphenylphosphine) palladium(0)과 12g의 Potassium carbonate를, 30mL의 Toluene, 10mL의 H_2O에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류하였다. 이후, Dichloromethane과 petroleum ether를 사용하여 재결정을 하고 여과하여 2,4-Diphenylaniline 결정 2.0g을 얻었다.

[0345] (2) 2,4-diphenyl-N-2-fluorophenylaniline의 제조

[0346] 2,4-diphenyl-N-2-fluorophenylaniline은 하기 반응식8에 의해 얻어진다.

[0347] 반응식8



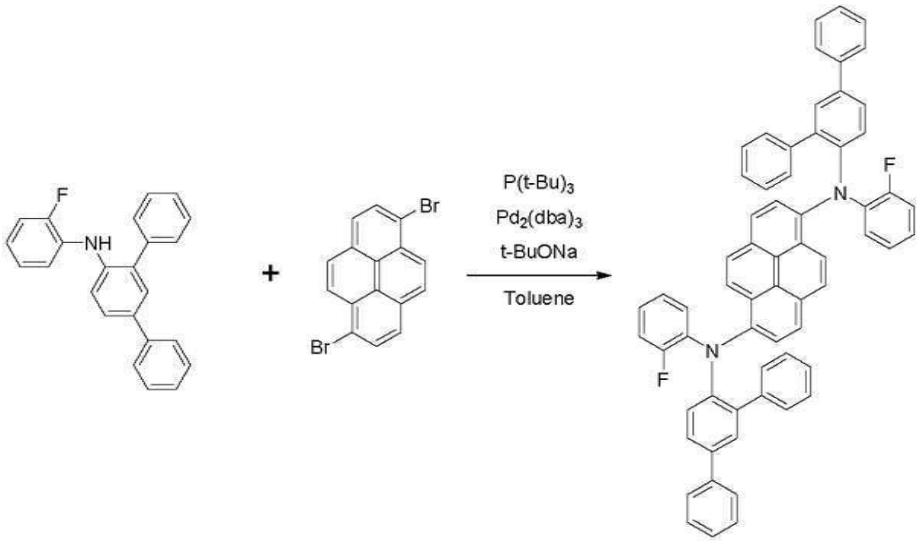
[0348]

[0349] 구체적으로, 이구 둥근 바닥 플라스크에 12mmol의 2,4-diphenylaniline, 10mmol의 1-bromo2-fluorobenzene, 0.15mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.3mmol의 (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene과 14mmol의 Sodium tert-butoxide를, 30mL Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류하였다. 이후, Dichloromethane과 petroleum ether를 사용하여 재결정을 하고 여과하여 2,4-diphenyl-N-2-fluorophenylaniline 결정 2.1g을 얻었다.

[0350] (3) N^1,N^6-bis(2,4-diphenylphenyl)-N^1,N^6-bis(2-fluorophenyl)pyrene-1,6-diamine의 제조

[0351] 상기 화학식8에서 C-88로 표시된 물질인 N^1,N^6-bis(2,4-diphenylphenyl)-N^1,N^6-bis(2-fluorophenyl)pyrene-1,6-diamine은 아래 반응식9에 의해 얻어진다.

[0352] 반응식9



[0353]

[0354] 구체적으로, 이구 둥근 바닥 플라스크에 6mmol의 2,4-diphenyl-N-2-fluorophenylaniline, 5mmol의 1,6-dibromopyrene, 0.075mmol의 Tris(dibenzylideneacetone) dipalladium(0), 0.15mmol의 tri-tert-butylphosphine과 7mmol의 Sodium tert-butoxide를, 15mL의 Toluene에 녹인 후 , 100 ℃의 bath에서 24시간 교반시켰다. 반응이 종료되면 Toluene을 제거 한 후 Dichloromethane과 물을 사용하여 추출한 후 감압 증류하고 실리카겔여과 후 용매를 감압 증류하였다. 이후, Dichloromethane과 acetone을 사용하여 재결정을 하고 여과한 후, 열정제를 실시하여 상기 N^1,N^6-bis(2,4-diphenylphenyl)-N^1,N^6-bis(2-fluorophenyl)pyrene-1,6-diamine을 얻었다.

[0355] 이하, 상기한 본 발명의 제 3 실시예에 따른 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 실험예10 내지 실험예11과, 종래의 청색 형광 물질을 이용하여 유기전계발광소자를 제작하는 비교예3을 통해, 본 발명에 의한 청색 형광물질 및 이를 이용한 유기전계발광소자의 성능을 비교 설명한다.

[0356] 실험예10

[0357] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 200Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식8에서 C-35로 표시된 물질을 도펀트로 약 3% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0358] 10mA/cm^{2}에서 723cd/m^2(4.30V)를 나타내었으며 이때 CIE x = 0.132, y = 0.152를 나타내었다.

[0359] 실험예11

[0360] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 patterning한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 상기 ITO층 위에 CuPC 약 650Å, NPD 약 400Å, 호스트 물질인 DPVBi에 상기 화학식8에서 C-88로 표시된 물질을 도펀트로 약 5% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약1000Å의 두께로 순차 적층하였다.

[0361] 10mA/cm^{2}에서 733cd/m^2(4.26V)를 나타내었으며 이때 CIE x = 0.135, y = 0.157를 나타내었다.

[0362] 비교예3

[0363] 기판 상에 인듐-틴-옥사이드(ITO)층의 발광 면적이 3mm X 3mm 크기가 되도록 패터닝한 후 세정하였다. 상기 기판을 진공 챔버에 장착한 후 공정압력이 1X10^{-6}torr가 되도록 한 후 유기물을 ITO위에 CuPC 약 200Å, NPD 약 400Å, 호스트물질인 DPVBi에 상기 화학식1-3으로 표시된 BD-a를 도펀트로 약 1% 첨가하여 약 200Å, Alq_3 약 350Å, LiF 약 5Å, Al 약 1000Å의 두께로 순차 적층하였다.

[0364] 10mA/cm^{2}에서 526 cd/m^2(6.7 V)를 나타내었으며 이때 CIE x = 0.136, y = 0.188를 나타내었다.

[0365] 상술한 실험예10 내지 실험예11과 비교예3의 비교결과를 아래 표3에 나타내었다. 여기서 전압의 단위는 V, 전류의 단위는 mA/cm^2, 휘도의 단위는 cd/m^{2}이다.

[0366] 표3

[0367]

	전압	전류	휘도	CIE(X)	CIE(Y)
실험예10	4.30	10	723	0.132	0.152
실험예11	4.26	10	733	0.135	0.157
비교예3	6.7	10	526	0.136	0.188

[0368] 표3를 통해 알 수 있는 바와 같이, 실험예10 내지 실험예11에서는 발광효율 및 색순도가 향상되었다. 특히, 비교예에 비해 저전압구동이 가능함을 알 수 있다.

[0369] 상기한 청색 형광 물질을 포함하여 이루어지는 유기전계발광소자의 유기발광다이오드에 대한 일 실시예를 도 2에 도시하였다.

[0370] 도시한 바와 같이, 유기전계발광소자는 제 1 기판(110), 상기 제 1 기판(110)과 마주보는 제 2 기판(미도시)과, 상기 제 1 기판(110)에 형성되어 있는 유기발광다이오드(E)를 포함한다.

[0371] 상기 유기발광다이오드(E)는 양극 역할을 하는 제 1 전극(120), 음극 역할을 하는 제 2 전극(130) 및 상기 제 1 및 제 2 전극(120, 130) 사이에 형성되는 유기발광층(140)으로 이루어진다. 도면에서는 제 1 전극(120)이 상기 제 1 기판(110)에 근접하여 위치하는 것을 보이고 있으나, 이와 달리 상기 제 2 전극(130)이 상기 제 1 기판

(110)에 근접하여 위치할 수 있다.

[0372] 상기 제 1 전극(120)은 일함수 값이 비교적 높은 물질, 예를 들어, 인듐-틴-옥사이드(ITO)로 이루어지며, 상기 제 2 전극(130)은 일함수 값이 비교적 낮은 물질, 예를 들어, 알루미늄(Al) 또는 알루미늄 합금(AlNd)로 이루어진다. 또한, 상기 유기발광층(140)은 적색, 녹색, 청색은 유기발광패턴으로 이루어진다.

[0373] 도면에는 나타내지 않았지만, 상기 유기발광층(140)은 발광효율을 극대화하기 위해, 다중층 구조 즉, 제 1 전극(120) 하면으로부터 순차적으로 정공수송층(hole transporting layer; HTL), 정공주입층(hole injection layer; HIL), 발광물질층(emitting material layer; EML), 전자주입층(electron injection layer; EIL) 및 전자수송층(electron transporting layer; ETL)으로 형성될 수도 있다.

[0374] 여기서, 상기 발광물질층 중 청색 발광 패턴은 전자 및 정공을 전달할 수 있는 물질인 호스트에 상기 화학식2, 화학식5 및 화학식7로 표시되는 물질 중 어느 하나를 도펀트로 첨가하여 이루어진다. 여기서 도펀트는 청색 형광 물질 전체 대비 약 0.1 중량% 내지 약 20 중량%로 첨가된다. 이때, 상기 호스트는 상기 화학식 1-2로 표시된 DPVBi일 수 있다.

[0375] 상기에서는 본 발명의 바람직한 실시예를 참조하여 설명하였지만, 해당 기술분야의 숙련된 당업자는 하기의 특허청구범위에 기재된 본 발명의 기술적 사상 및 영역으로부터 벗어나지 않는 범위 내에서 본 발명을 다양하게 수정 및 변경시킬 수 있음을 이해할 수 있을 것이다.

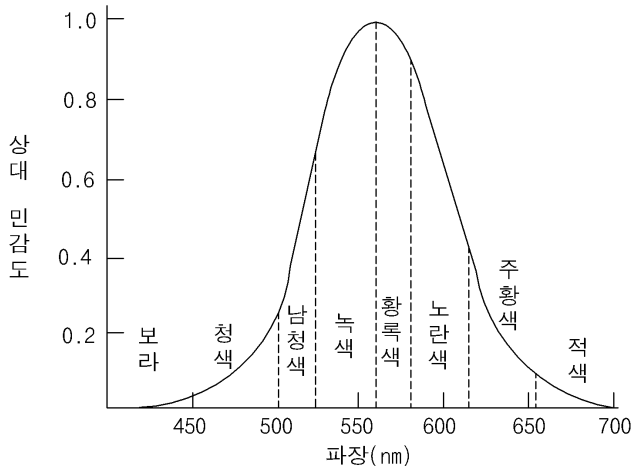
도면의 간단한 설명

[0376] 도 1은 유기전계발광소자의 색순도와 시감도(상대 민감도)의 관계를 보여주는 그래프이다.

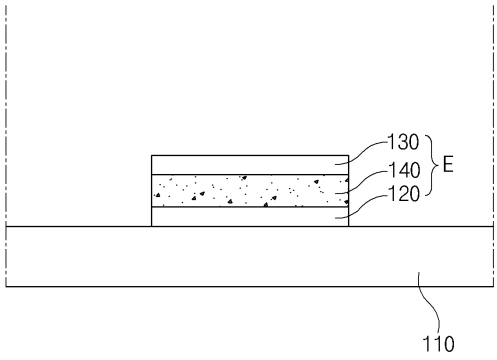
[0377] 도 2는 본 발명의 실시예에 따른 유기발광소자의 유기발광다이오드에 대한 개략적인 단면도이다.

도면

도면1

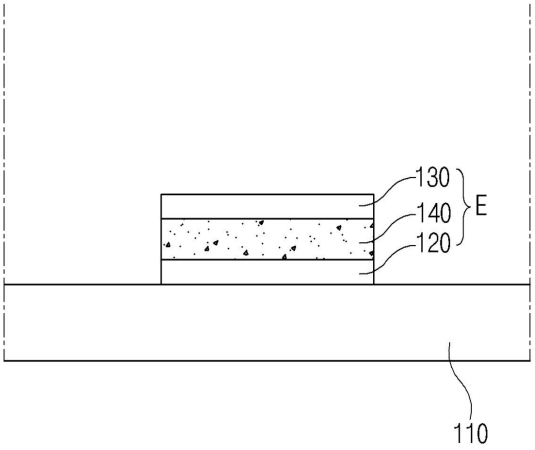


도면2



专利名称(译)	标题：蓝色磷光体和使用其的有机电致发光器件		
公开(公告)号	KR101359701B1	公开(公告)日	2014-02-11
申请号	KR1020080123423	申请日	2008-12-05
[标]申请(专利权)人(译)	乐金显示有限公司		
申请(专利权)人(译)	LG显示器有限公司		
当前申请(专利权)人(译)	LG显示器有限公司		
[标]发明人	LEE SEUNG JAE 이승재 SONG IN BUM 송인범 KIM JUNG KEUN 김종근 KIM DO HAN 김도한 PARK CHUN GUN 박춘건 OH HYOUNG YUN 오형윤 BIN JONG KWAN 빈종관 LEE KYUNG HOON 이경훈 JEONG HYUN CHEOL 정현철 YOO DONG HEE 유동희 CHO NAM SUNG 조남성 PARK JONG HYUN 박종현 YOO IN SUN 유인선 PARK TAE HAN 박태한 CHA SOON WOOK 차순욱		
发明人	이승재 송인범 김종근 김도한 박춘건 오형윤 빈종관 이경훈 정현철 유동희 조남성 박종현		

	유인선 박태한 차순욱
IPC分类号	C09K11/06 C09K
CPC分类号	C07C255/58 C09K2211/1011 C07C2103/50 H01L51/5012 C07C211/61 H05B33/14 H01L51/006 Y10S428/917 H01L51/0054 C09K2211/1014 H01L51/0058 C09K11/06 C07C2603/50
其他公开文献	KR1020100064815A
外部链接	Espacenet

摘要(译)

蓝色荧光化合物包括能够传输电子或空穴的主体材料;和由下式1表示的掺杂剂材料：其中R1，R2，R3和R4中的至少两个选自取代或未取代的芳族基团或取代或未取代的杂环基团，并且R5是选自取代或未取代的芳族基团或取代或未取代的杂环基团。