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Low et al.

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(54) **ORGANIC ELECTRONIC MATERIAL**

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(30) **Foreign Application Priority Data**

Mar. 9, 2015 (CN) 2015 1 0102569

(51) **Int. Cl.**

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C07C 13/567	(2006.01)
C07C 13/573	(2006.01)
C09K 11/06	(2006.01)
C07C 13/72	(2006.01)
C07D 213/06	(2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***H01L 51/0058*** (2013.01); ***C07C 13/567*** (2013.01); ***C07C 13/573*** (2013.01); ***C07C 13/72*** (2013.01); ***C07D 213/06*** (2013.01); ***C07D 213/16*** (2013.01); ***C09B 1/00*** (2013.01); ***C09K 11/06*** (2013.01); ***H01L 51/0052*** (2013.01); ***H01L 51/0056*** (2013.01); *C07C 2603/18* (2017.05); *C07C 2603/24* (2017.05); *C07C 2603/94* (2017.05); *C07C 2603/97* (2017.05); *C09K 2211/1007* (2013.01); *C09K 2211/1011* (2013.01); *H01L 51/5012* (2013.01); *Y02E 10/549* (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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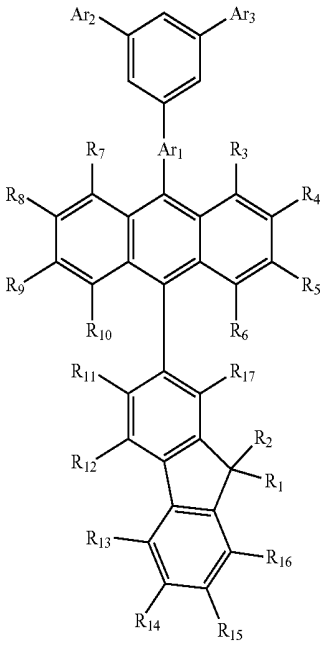
(74) *Attorney, Agent, or Firm* — Maschoff Brennan

(57) **ABSTRACT**

The present invention discloses an "organic electronic material", belonging to the organic light-emitting device (OLED) display materials field. The organic electronic material in the present invention has a structural formula (I), having good thermal stability, high luminous efficiency, high purity of light emission. The OLED made by this kind of organic light-emitting material has the advantages of excellent organic light-emitting efficiency, excellent color purity and long service life.

(I)



6 Claims, 5 Drawing Sheets

(51) **Int. Cl.**

C07D 213/16	(2006.01)
C09B 1/00	(2006.01)
H01L 51/50	(2006.01)

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KR	10-2009-0065201	A	6/2009
KR	10-2011-0081698	A	7/2011

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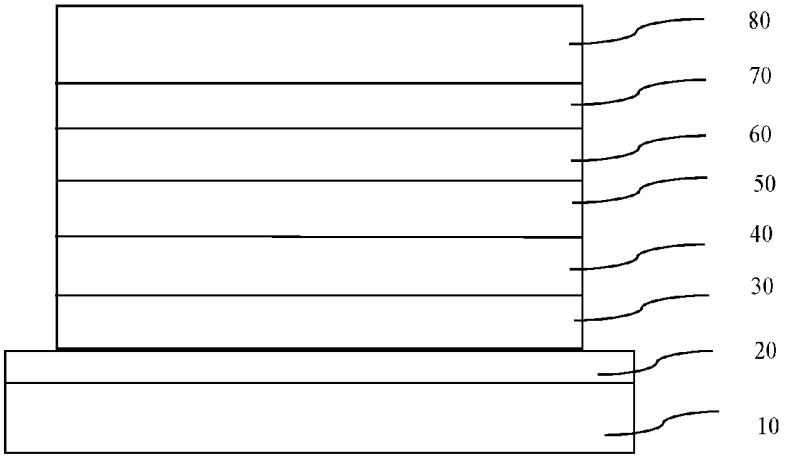


FIG. 1

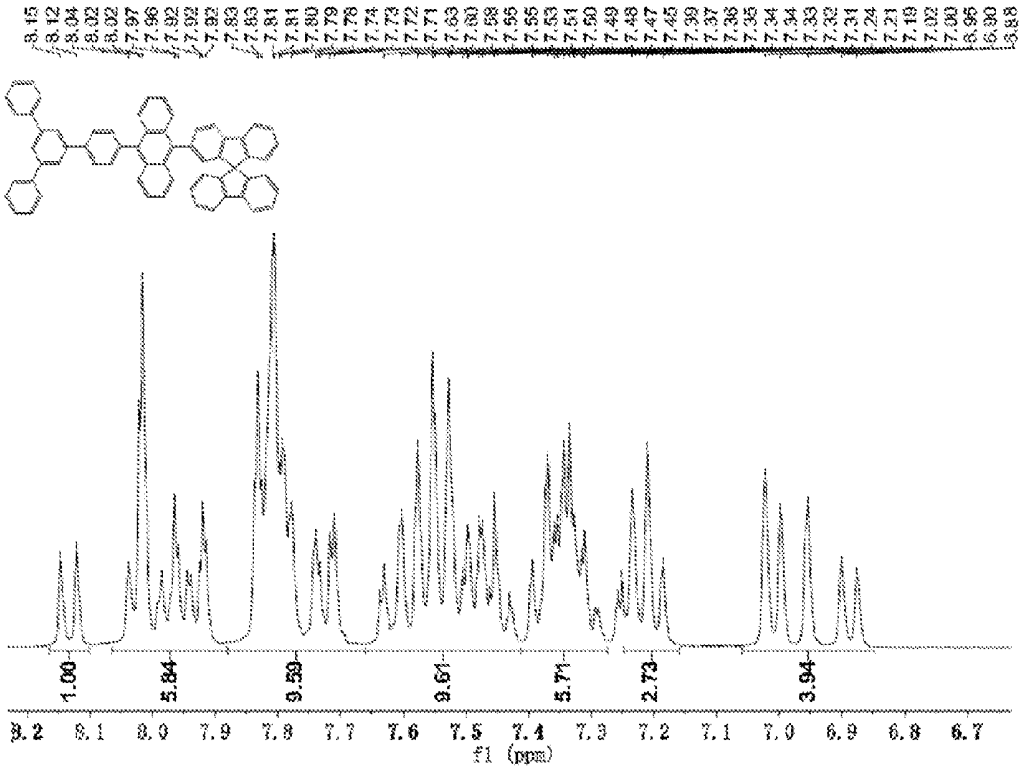


FIG. 2

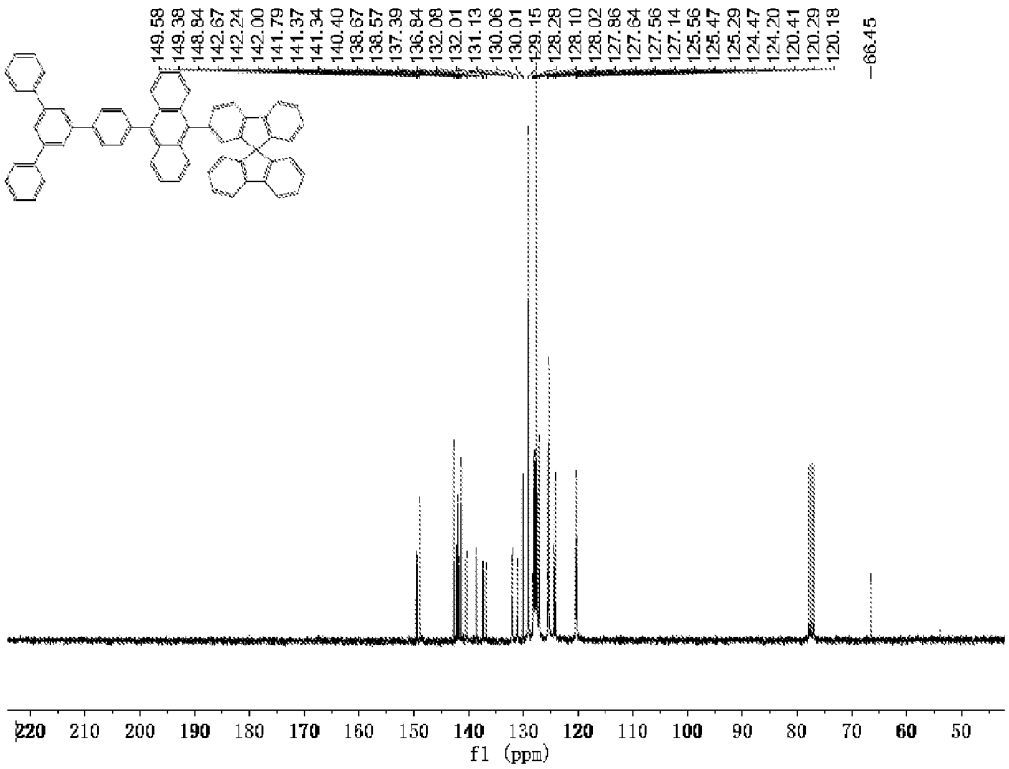

149.58
149.38
148.94
142.67
142.24
142.00
141.79
141.37
141.34
140.40
138.67
138.57
137.39
136.94
132.08
132.01
131.13
130.06
130.01
129.15
128.28
128.10
128.02
127.86
127.64
127.56
127.14
125.56
125.47
125.29
124.47
124.20
120.41
120.29
120.18
66.45
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
f1 (ppm)

FIG. 3

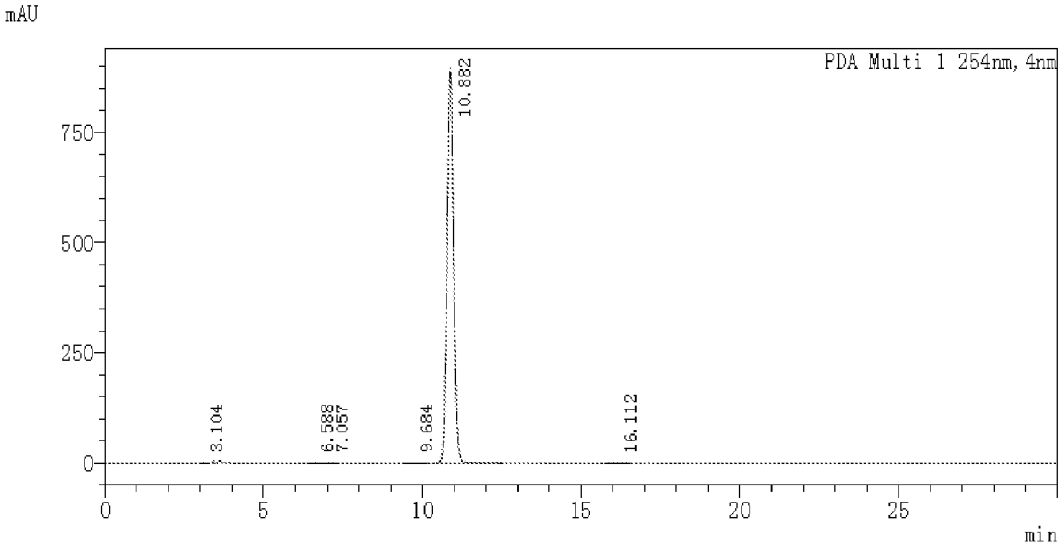

mAU
PDA Multi 1 254nm, 4nm
10.882
750
500
250
0
3.104
6.588
7.057
9.684
16.112
0
5
10
15
20
25
min

FIG. 4

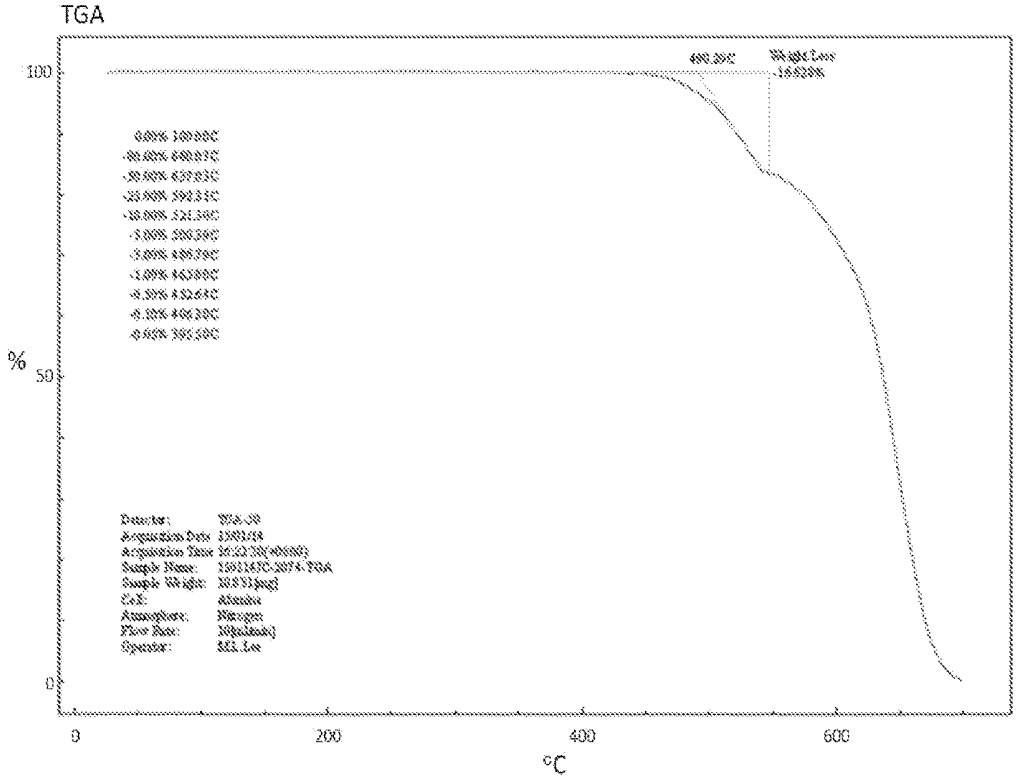

TGA
100
%
50
0
0
200
400
600
°C

FIG. 5

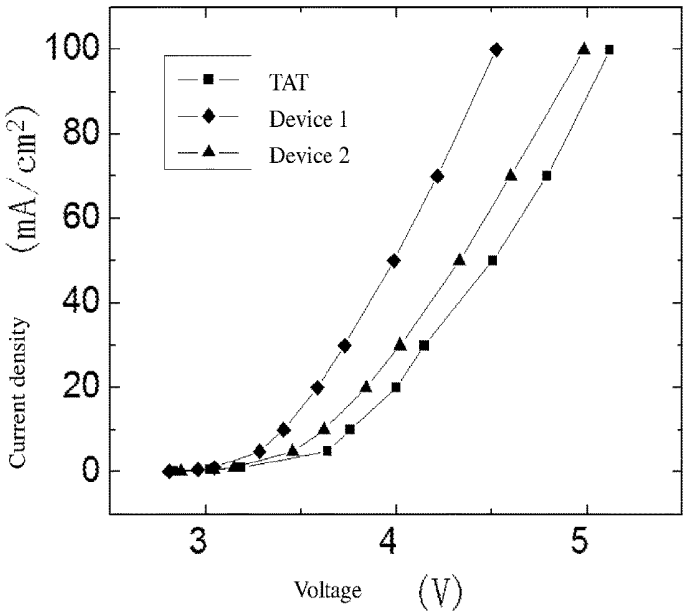

100
80
60
40
20
0
Current density (mA/cm²)
3
4
5
Voltage (V)
TAT
Device 1
Device 2

FIG. 6

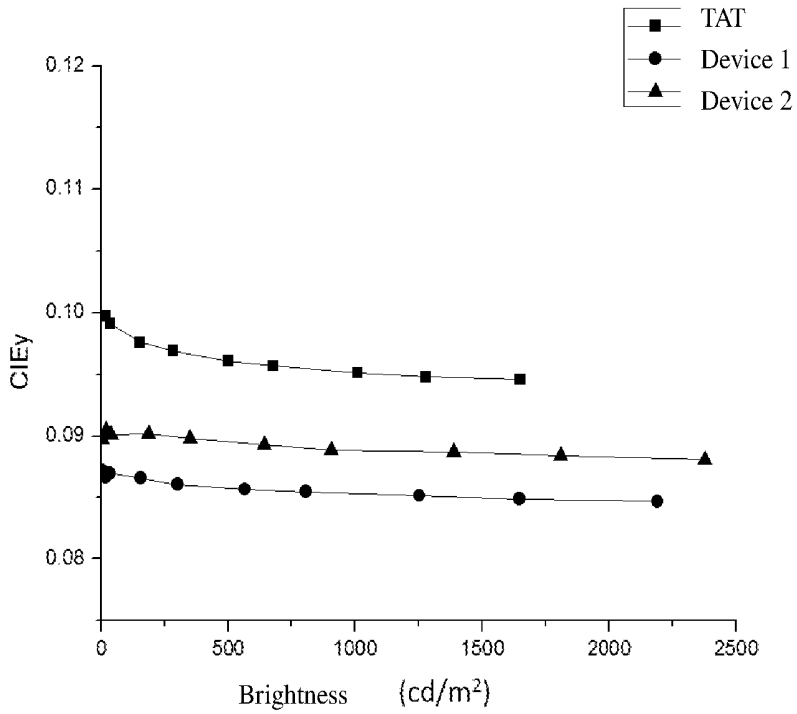

TAT
Device 1
Device 2
0.12
0.11
0.10
0.09
0.08
CIEy
0
500
1000
1500
2000
2500
Brightness (cd/m²)

FIG. 7

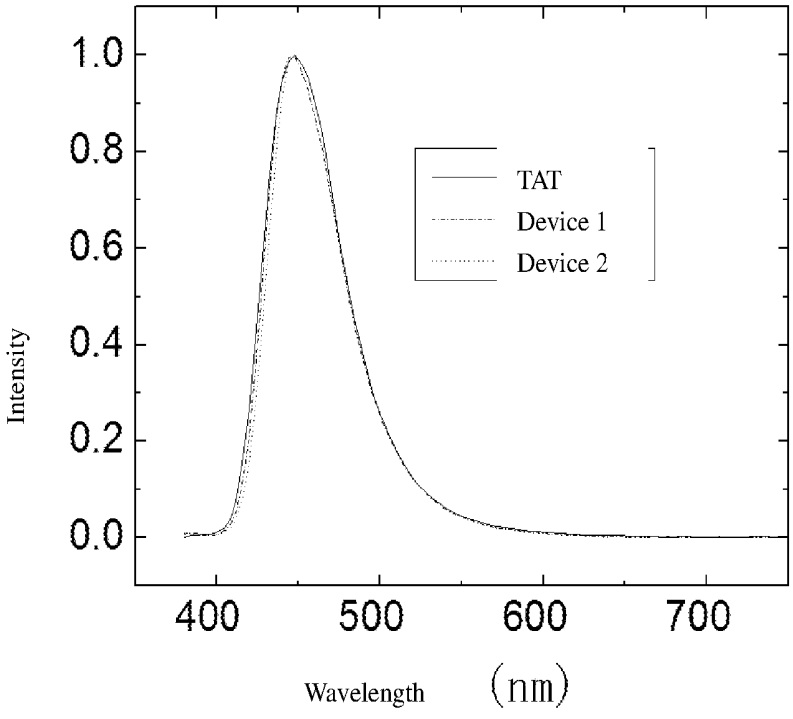

1.0
0.8
0.6
0.4
0.2
0.0
Intensity
TAT
Device 1
Device 2
400
500
600
700
Wavelength (nm)

FIG. 8

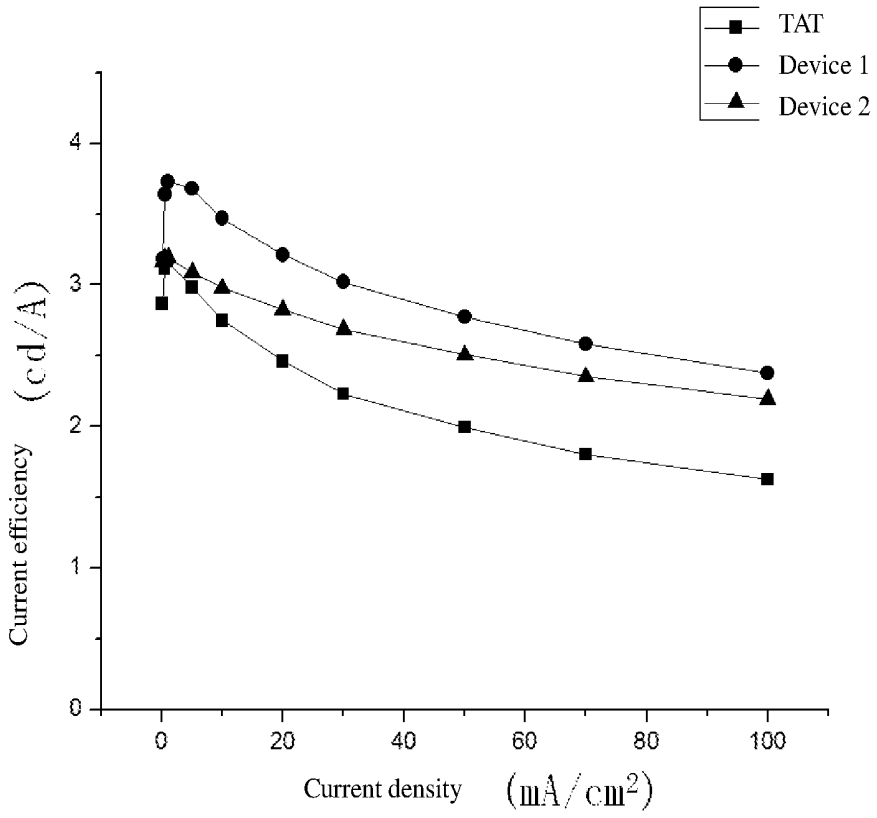

TAT
Device 1
Device 2
Current efficiency (cd/A)
Current density (mA/cm²)
0
1
2
3
4
0
20
40
60
80
100

FIG. 9

ORGANIC ELECTRONIC MATERIAL

TECHNICAL FIELD

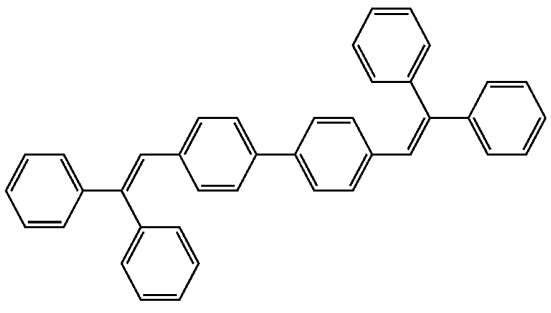
This invention relates to a new type of organic light-emitting material. By deposited into thin film through vacuum evaporation, it is used in organic light emitting diodes as a blue light-emitting material. It belongs to the Organic Light-emitting Device (OLED) display material field.

BACKGROUND ART

OLED, as a new type of display technology, has unique advantages such as self-illumination, wide viewing angle, low power consumption, high efficiency, thin, rich colors, fast response, extensive application temperature, low drive voltage, used to make flexible, bendable and transparent display panel and environmental friendliness, etc. Therefore, OLED technology can be applied to flat panel displays and new generation of lighting, or can be used as backlight of LCD.

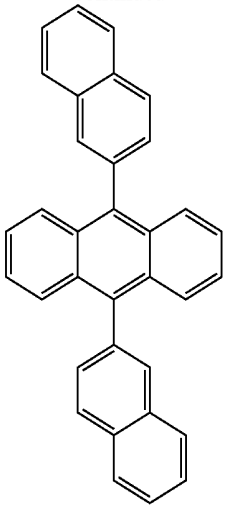
OLED is a device made through spin-coating or depositing a layer of organic material between two metal electrodes. A classic three-layer OLED comprises a hole transport layer, a light emitting layer and an electron transport layer. The holes generating from the anode through the hole transport layer and the electrons generating from the cathode through the electron transport layer combine to form excitons in the light emitting layer, emitting light. By changing the material of the light emitting layer, the OLED can emit red light, green light and blue light. Therefore, stable, efficient organic light-emitting materials with pure colors play an important role in the application and promotion of OLEDs. Meanwhile, it is also very urgent for the application and promotion of large area of panel display in OLEDs.

Among three primary colors (red, blue, green), the red and green light materials have made great development, which also meet the market demands of the panels. There are a series of commercially available materials for the blue light materials, and distyryl-biphenyl (DPVBi) compounds produced by Idemitsu are widely used in the early period. The devices made by this type of compound have high efficiency, but these materials often have poor stability, and even worse, this type of compound often emits sky blue light, and often y>0.15 of the CIE value. Therefore, its poor stability and impure color greatly restrict the application of this type of compounds in the full-color display devices. Another type of blue-light material is the Kodak ADN and tetra-butyl perylene, but their luminous efficiency is relatively poor, thus, it cannot be widely used.

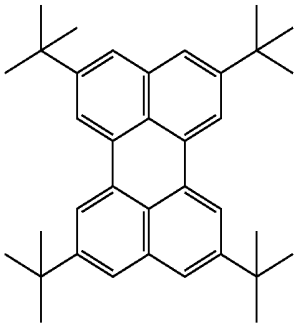


(DPVBi)

-continued



(ADN)

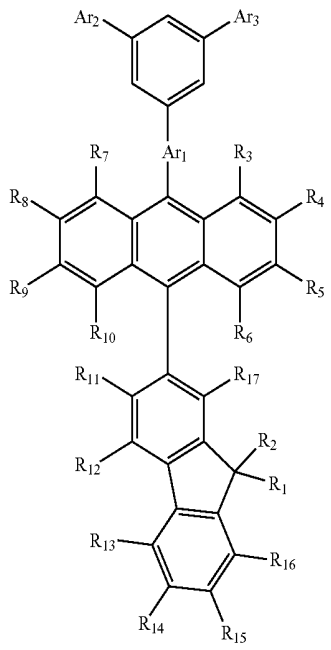


(Tetra-tert-butyl perylene)

SUMMARY OF THE INVENTION

In the present invention, a series of organic blue light-emitting materials with good thermal stability, high luminous efficiency, high purity of light-emitting are provided, to overcome the deficiencies of the above compounds. The OLEDs prepared thereof have the advantages of good electroluminescent efficiency, excellent color purity and long lifetime.

The said organic electronic material has the following structural formula (I):



(I)

Wherein R_1-R_{17} independently represent hydrogen, deuterium, halogen, cyano, nitro, C1-C8 alkyl, C1-C8 alkoxy, C6-C30 substituted or unsubstituted aryls, C3-C30 substituted or unsubstituted aryls containing one or more heteroatoms, C2-C8 substituted or unsubstituted alkenyl, C2-C8 substituted or unsubstituted alkynyl, wherein Ar_1-Ar_3 independently represent C6-C60 substituted or unsubstituted aryl, C3-C60 substituted or unsubstituted heteroaryl containing one or more heteroatoms, triaryl (C6-C30) amine.

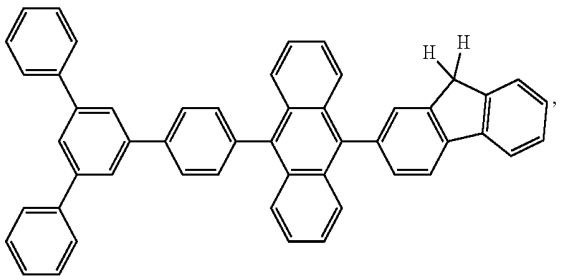
Preferably, wherein R_1-R_{17} independently represent hydrogen, halogen, cyano, nitro, C1-C8 alkyl, C1-C8 alkoxy, C2-C8 substituted or unsubstituted alkenyl, C2-C8 substituted or an unsubstituted alkynyl, C1-C4 alkyl substituted or unsubstituted phenyl, C1-C4 alkyl substituted or unsubstituted naphthyl, or combined C1-C4 alkyl substituted or unsubstituted fluorenyl; Ar_1-Ar_3 independently represent C1-C4 alkyl or C6-C30 aryl-substituted phenyl, C1-C4 alkyl or C6-C30 aryl-substituted naphthyl, phenyl, naphthyl, pyridyl, N—C6-C30 aryl or C1-C4 alkyl-substituted carbazolyl, dibenzothienyl, dibenzofuranyl, anthryl, phenanthryl, pyrenyl, perylenyl, fluoranthenyl, (9,9)-dialkyl) fluorenyl, (9,9-dialkyl substituted or unsubstituted aryl) fluorenyl, 9,9-spirofluorenyl.

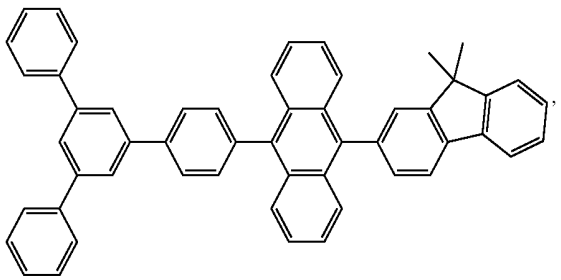
Preferably, wherein R_1-R_2 independently and preferably represent hydrogen, halogen, C1-C4 alkyl, C1-C4 alkyl substituted or unsubstituted phenyl, C1-C4 alkyl substituted or unsubstituted naphthyl, or combined C1-C4 alkyl-substituted or unsubstituted fluorenyl; wherein R_3-R_{17} may independently represent hydrogen, halogen, C1-C4 alkyl, C1-C4 alkyl substituted or unsubstituted phenyl, C1-C4 alkyl-substituted or unsubstituted naphthyl, preferably Ar_1-Ar_3 independently represent phenyl, tolyl, xylyl, t-butylphenyl, naphthyl, pyridyl, methyl naphthalene, biphenyl, diphenylphenyl, naphthylphenyl, diphenylbiphenyl, diarylamine phenyl, N-phenylcarbazolyl, (9,9-dialkyl) fluorenyl, (9,9-dialkyl substituted or unsubstituted phenyl) fluorenyl, 9,9-spirofluorenyl.

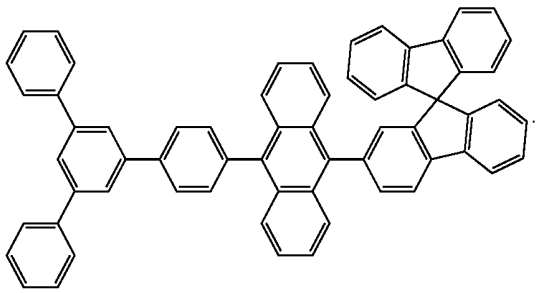
Preferably, wherein R_3-R_{17} preferably represents hydrogen, and R_1 and R_2 may independently represent hydrogen, methyl, ethyl, propyl, isopropyl, t-butyl, phenyl, biphenyl, naphthyl, or combined fluorenyl; Ar_1-Ar_3 may independently represent phenyl, pyridyl, tolyl, xylyl, naphthyl, methylnaphthalene, biphenyl, diphenylphenyl, naphthylphenyl, diphenylbiphenyl, (9,9-dialkyl) fluorenyl, (9,9-dimethyl-substituted or unsubstituted phenyl) fluorenyl, 9,9-spirofluorenyl.

Preferably, R_3-R_{17} represent hydrogen preferably; R_1, R_2 independently represent hydrogen, methyl or combined fluorenyl; Ar_1, Ar_2, Ar_3 independently represent phenyl and naphthyl.

Preferably,



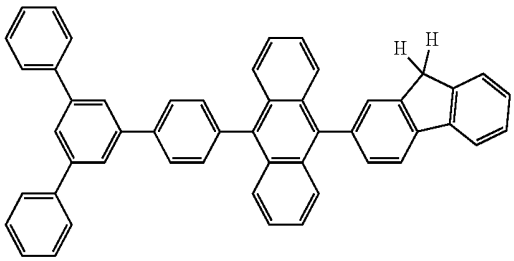




The applications of the above said organic electronic material in such fields as organic light-emitting devices, organic solar cells, organic thin-film transistors or organic photoreceptors.

As mentioned above, the specific embodiments in the invention are as follows, but not limited to the structures as below:

1



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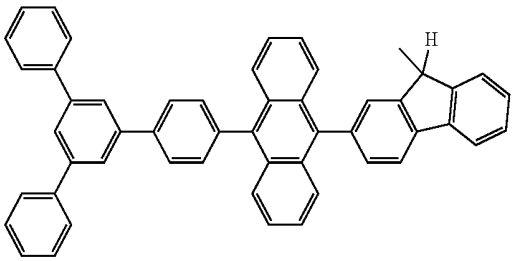

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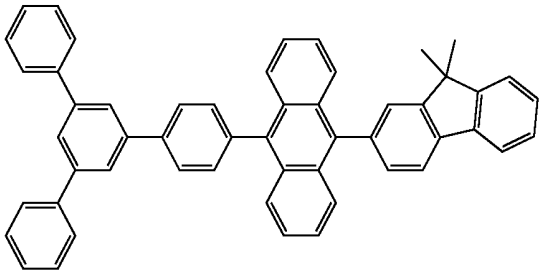

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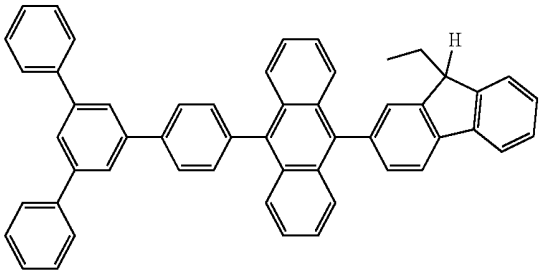

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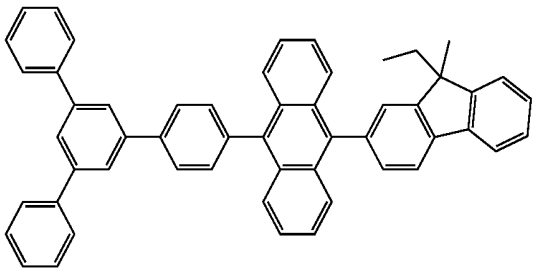

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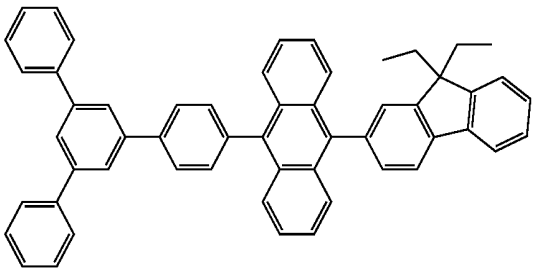

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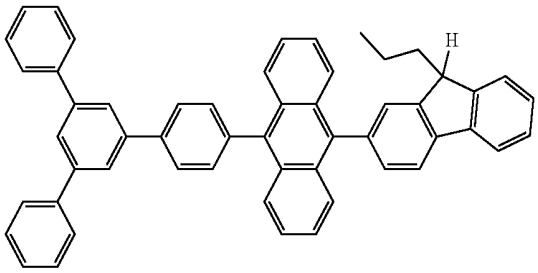

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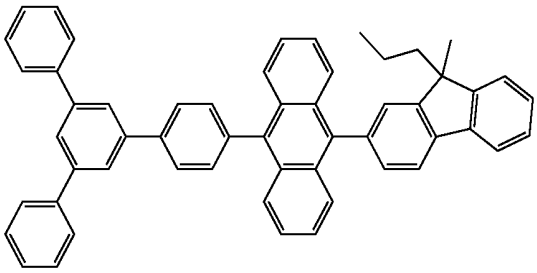

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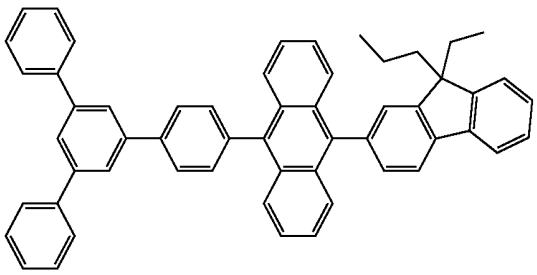

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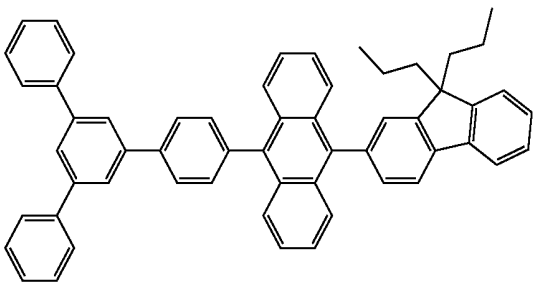

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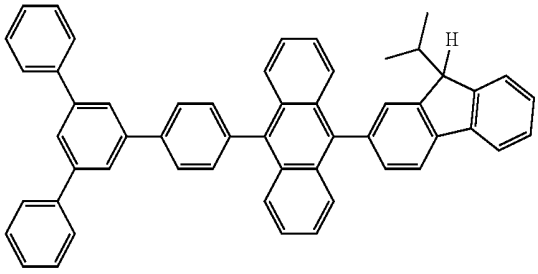

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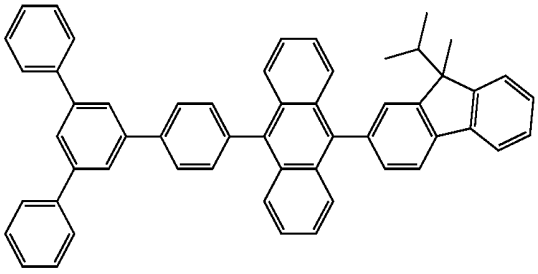

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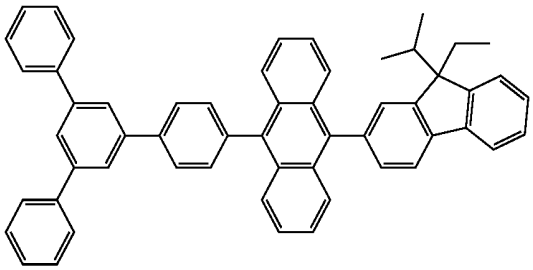

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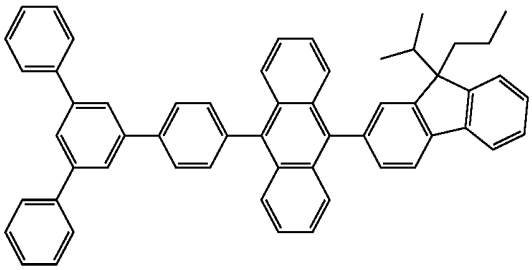

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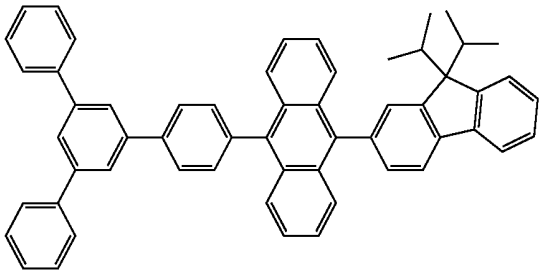

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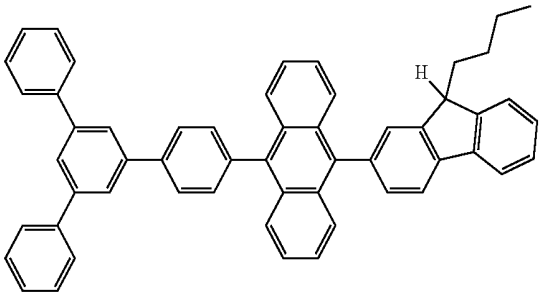

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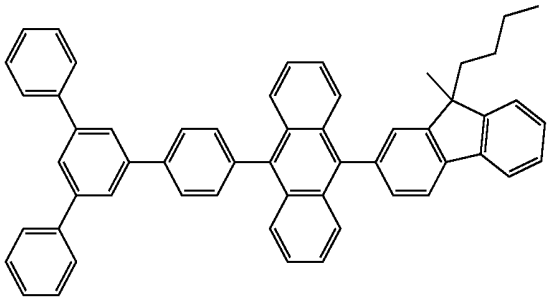

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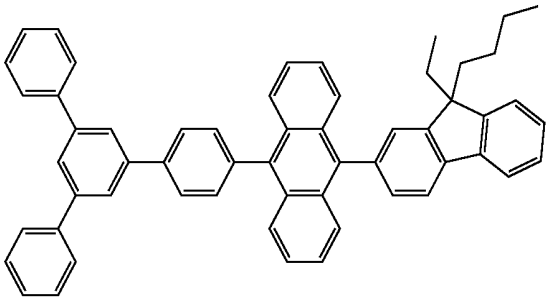

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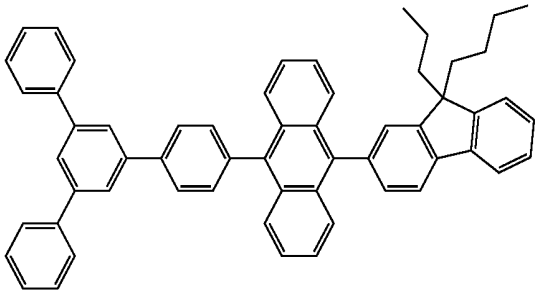

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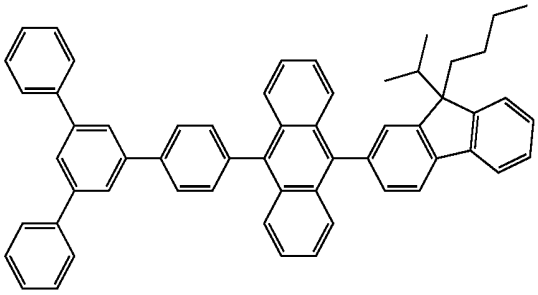

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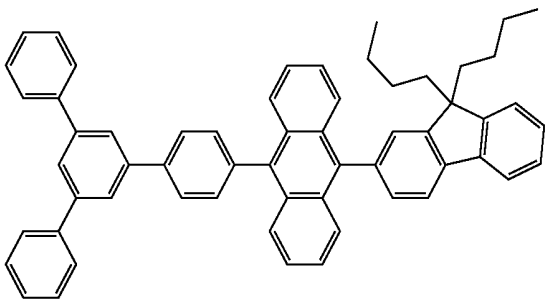

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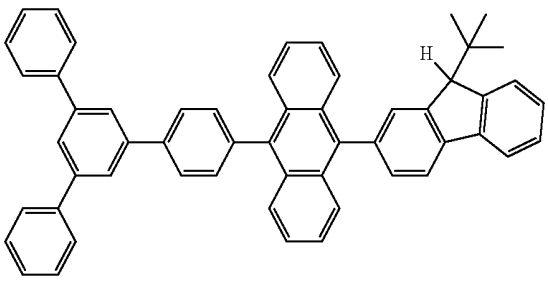

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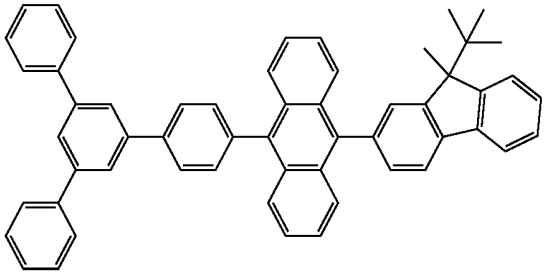

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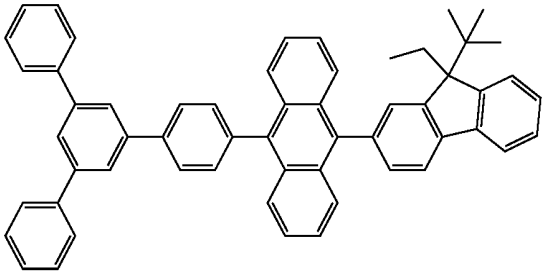

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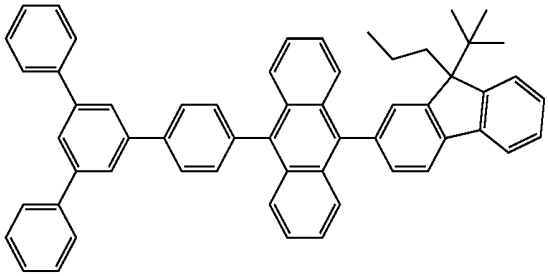

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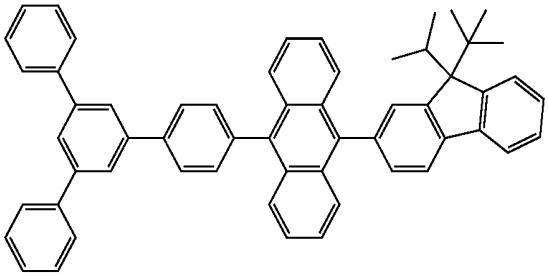

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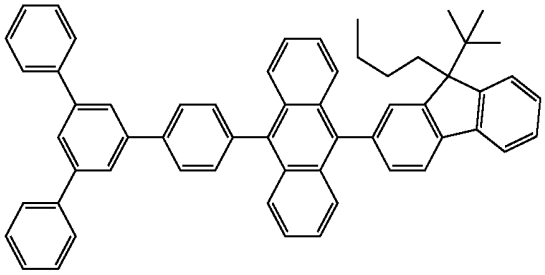

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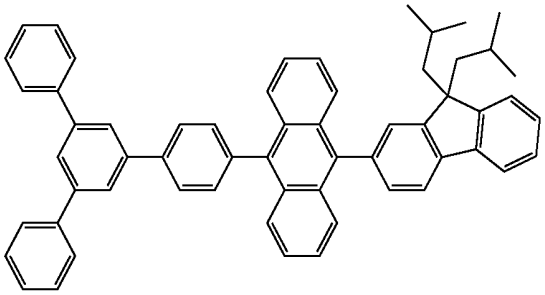

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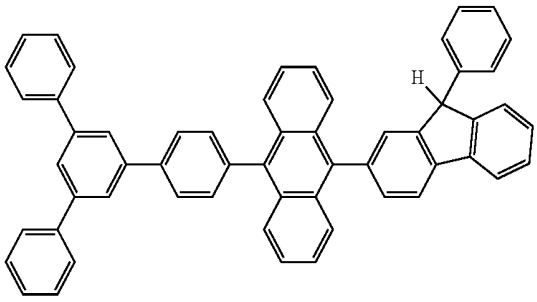

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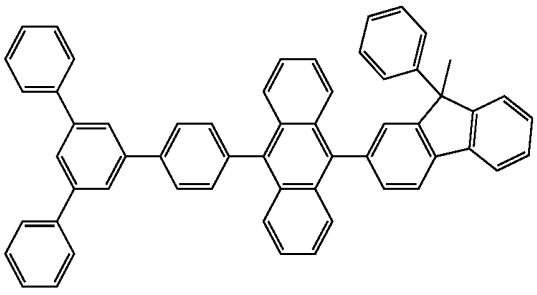

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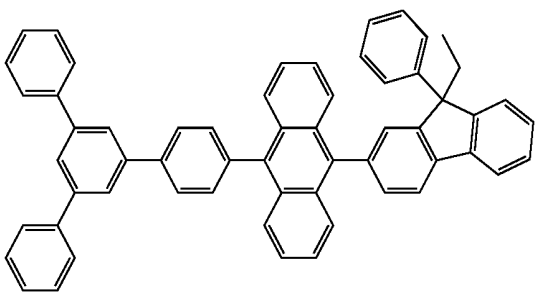

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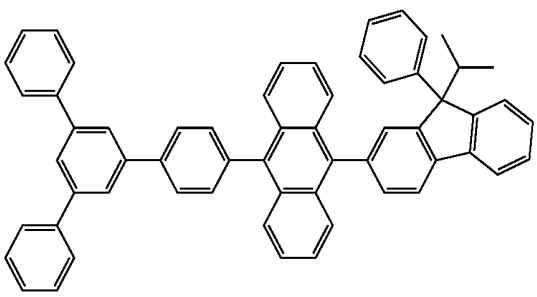

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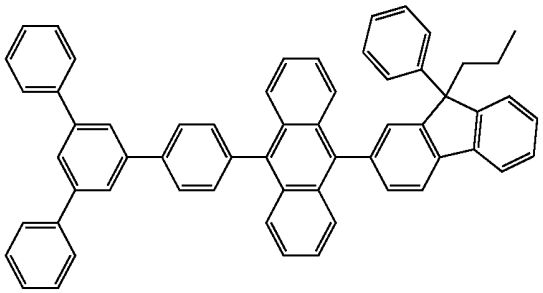

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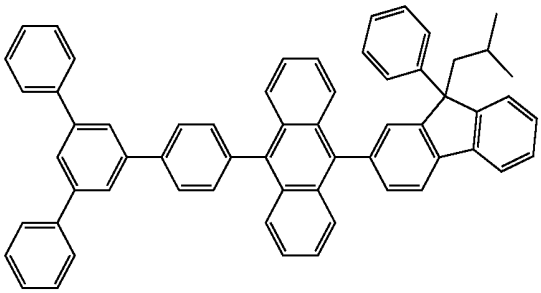

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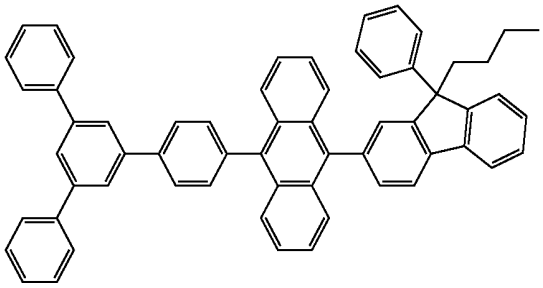

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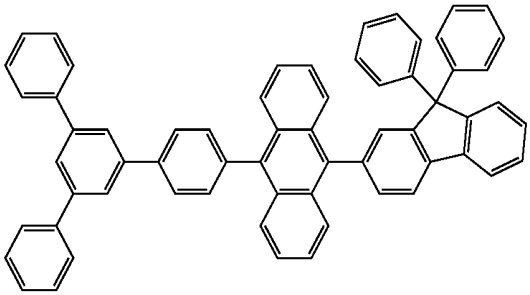

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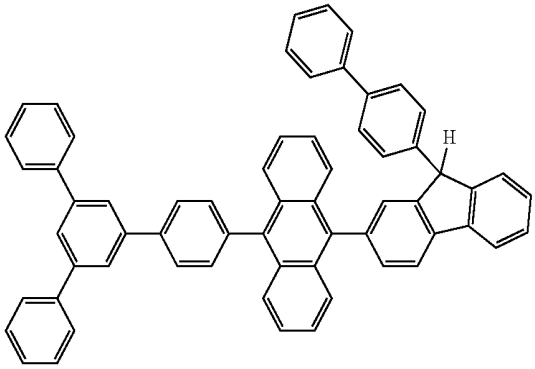

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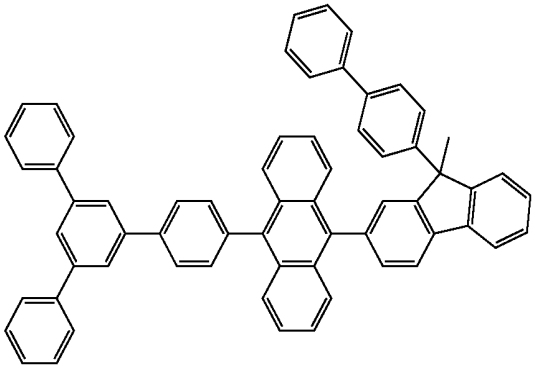

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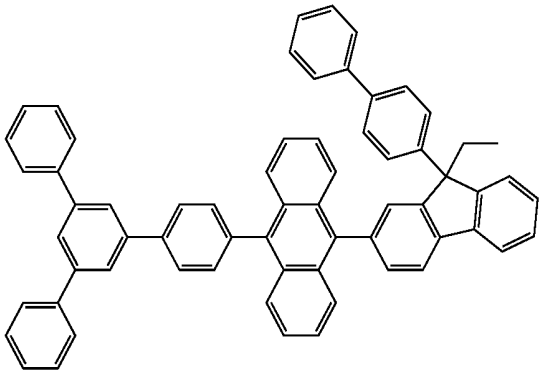

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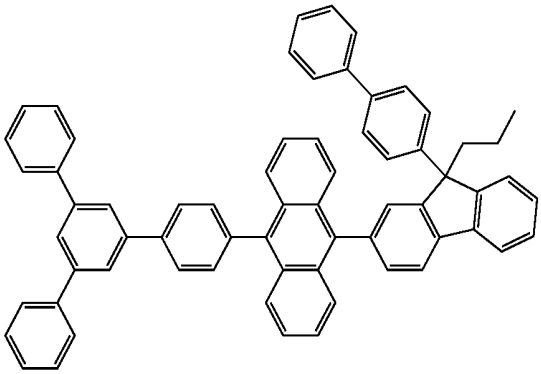

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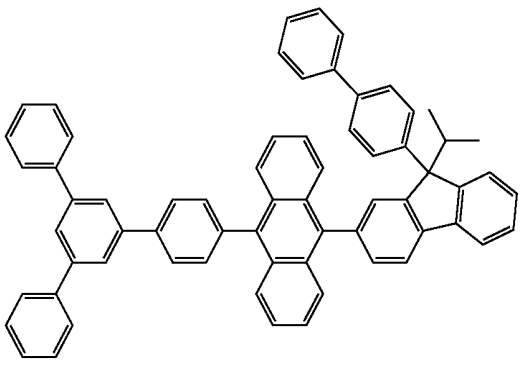

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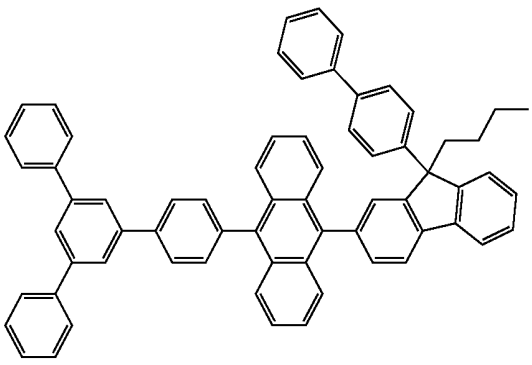

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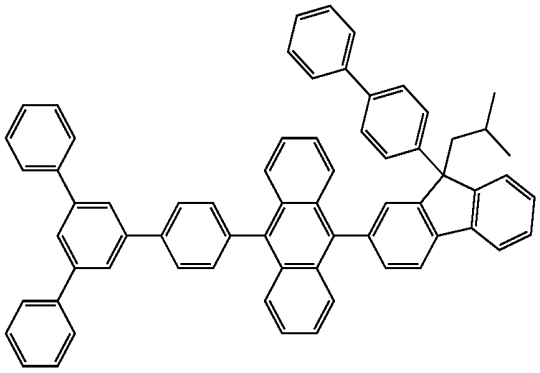

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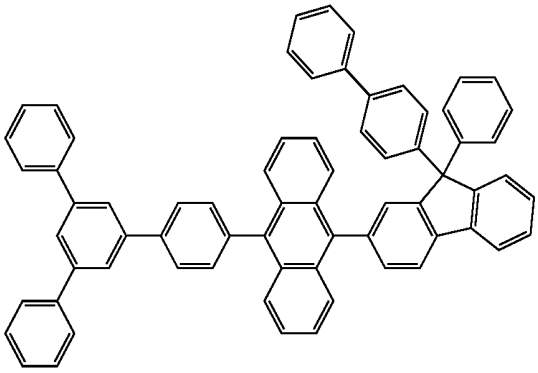

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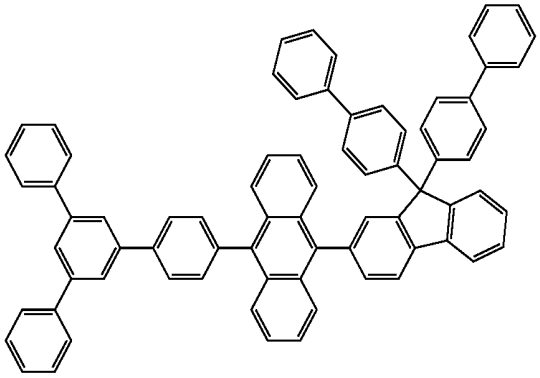

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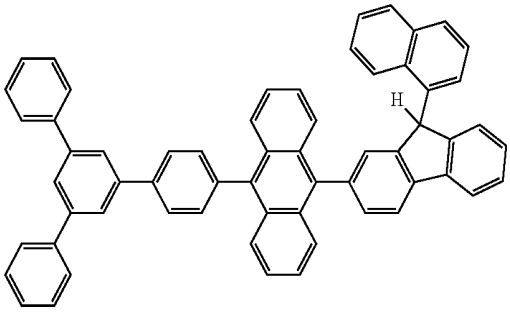

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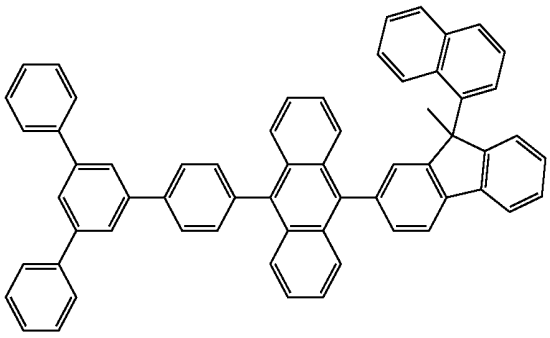

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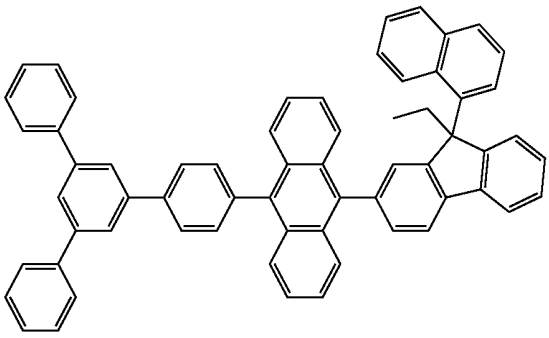

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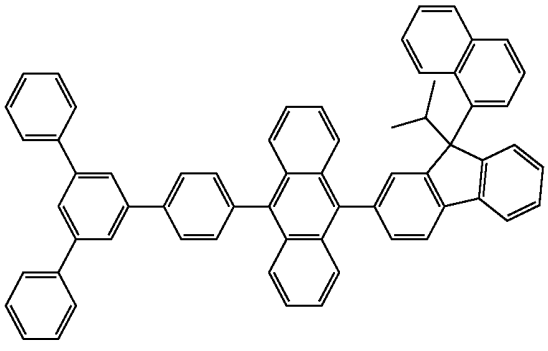

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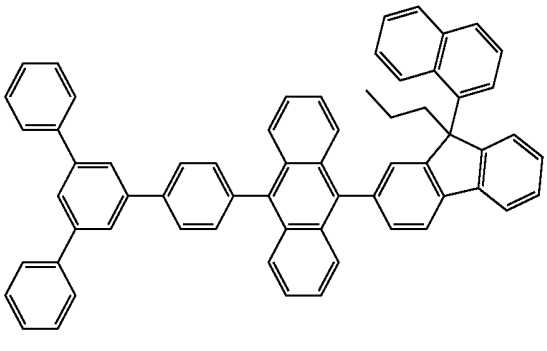

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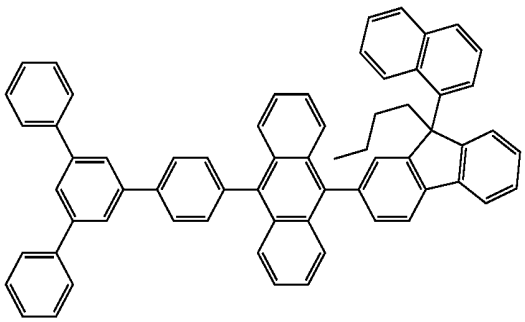

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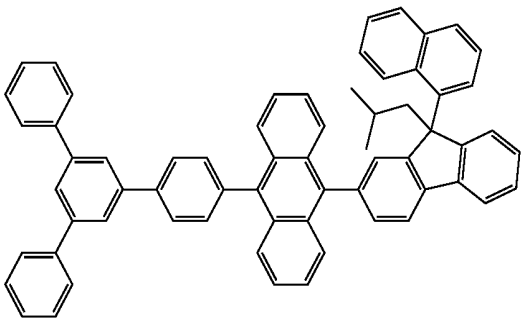

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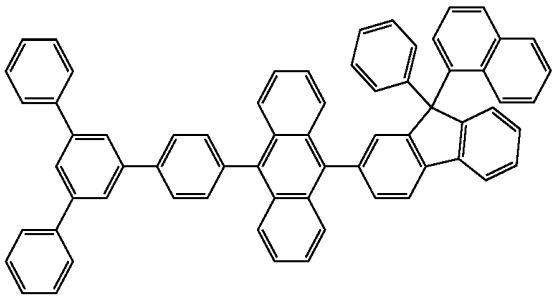

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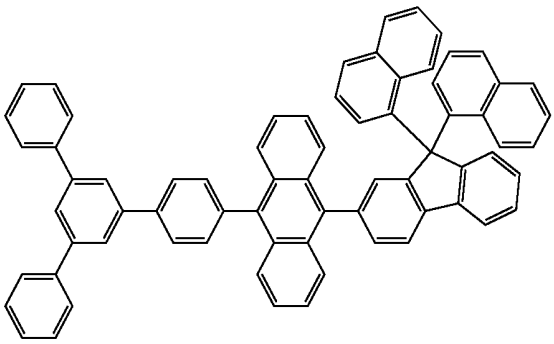

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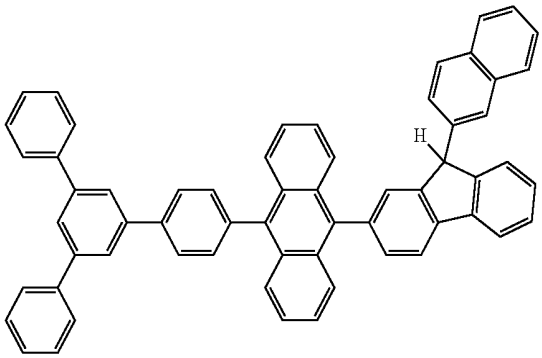

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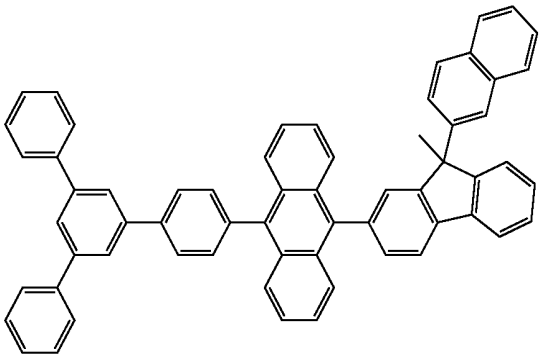

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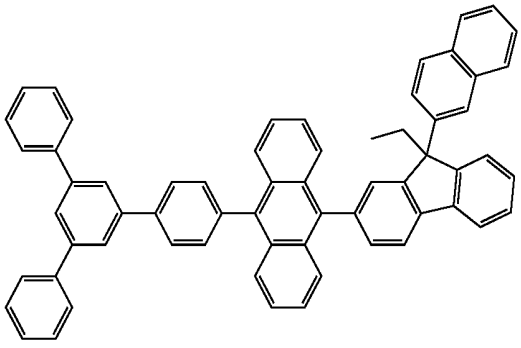

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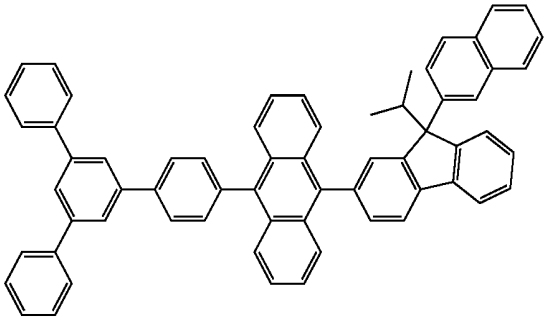

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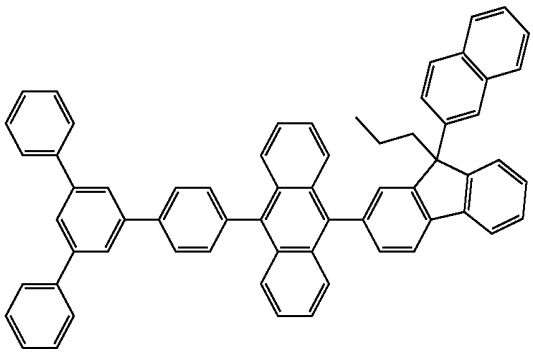

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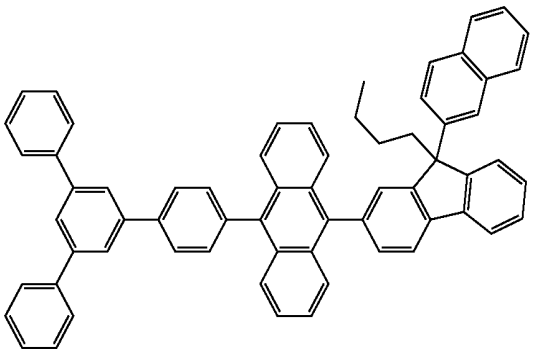

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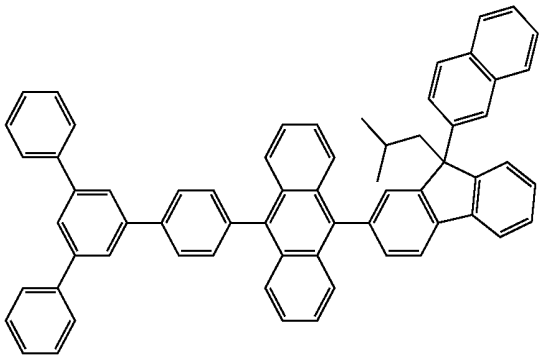

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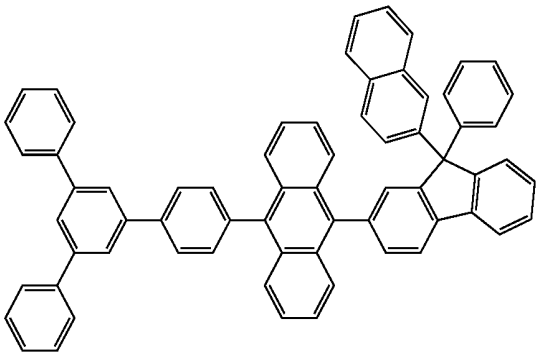

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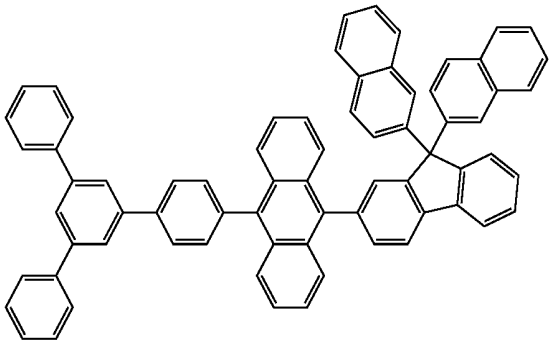

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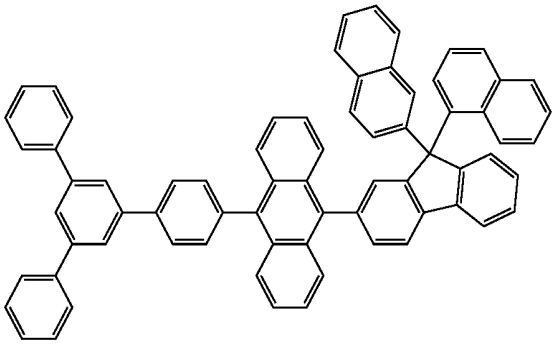

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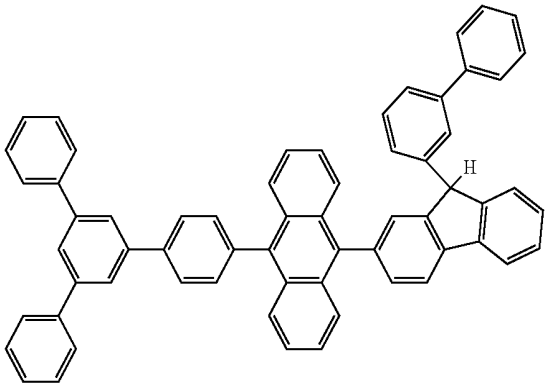

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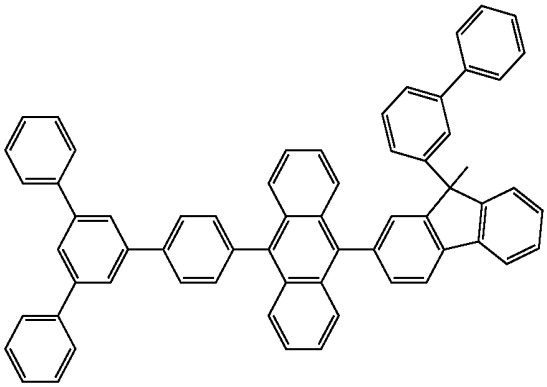

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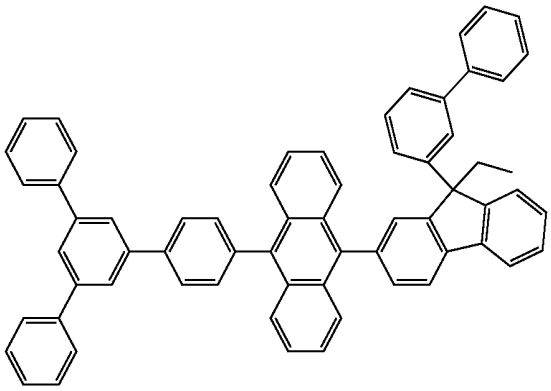

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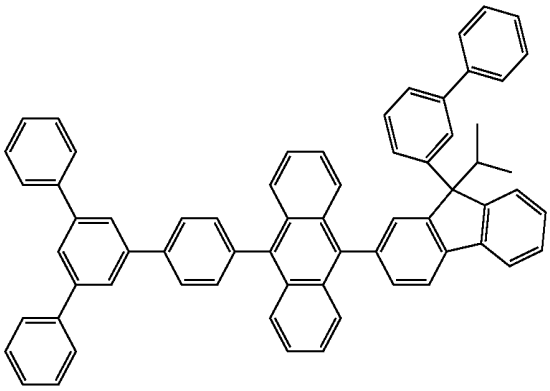

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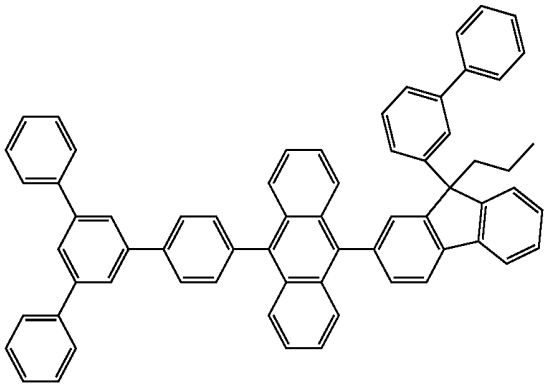

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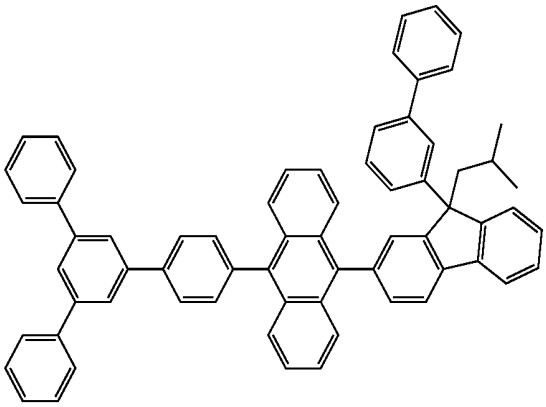

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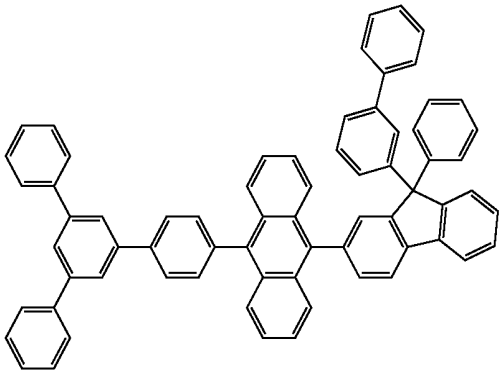

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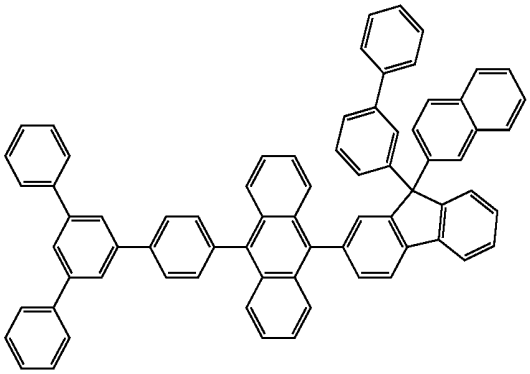

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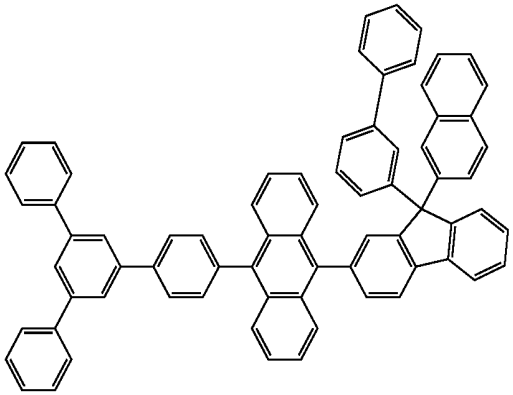

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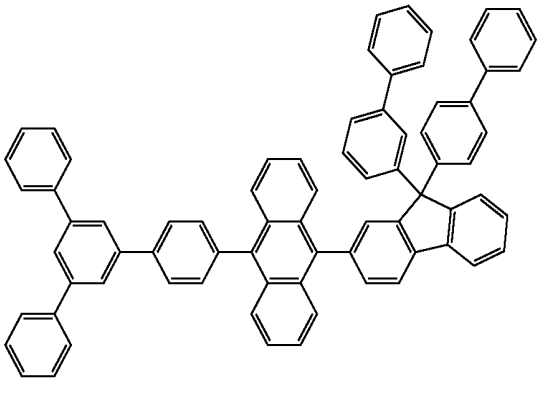

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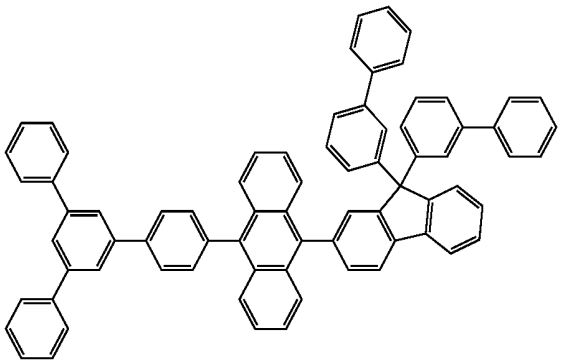

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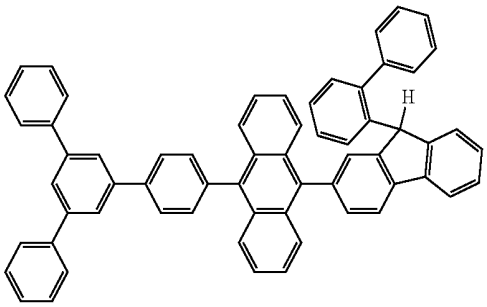

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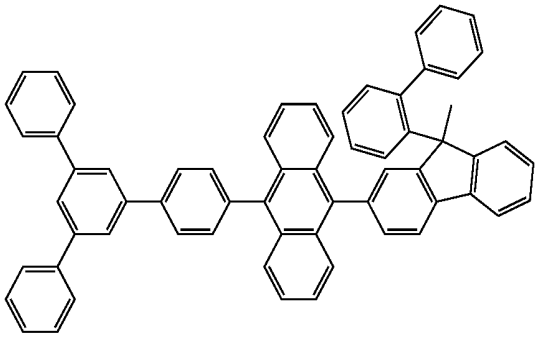

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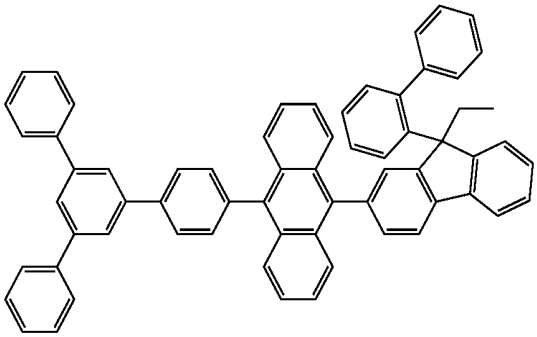

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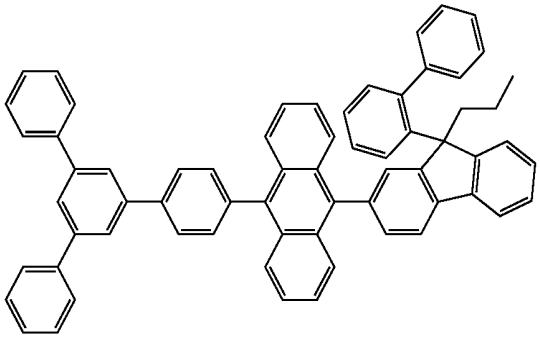

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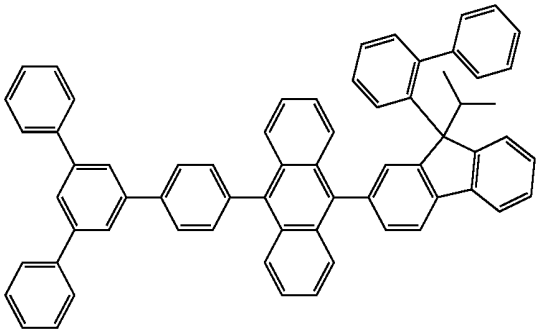

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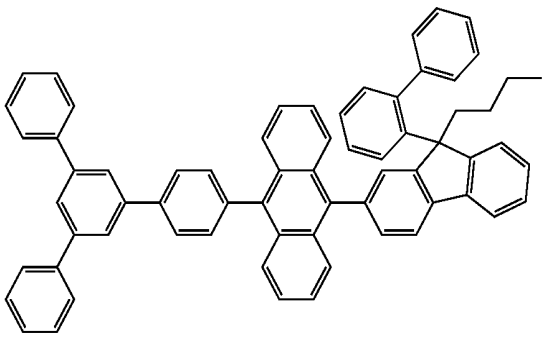

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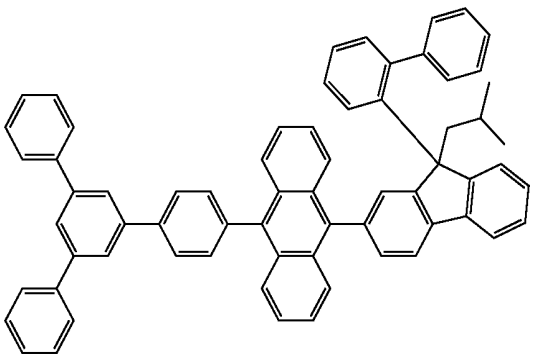

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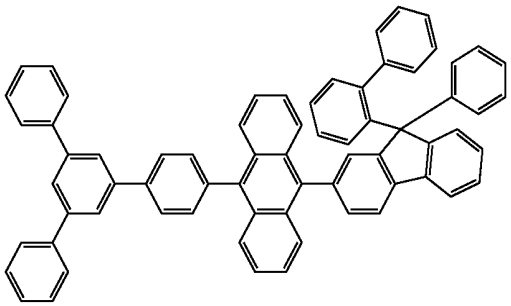

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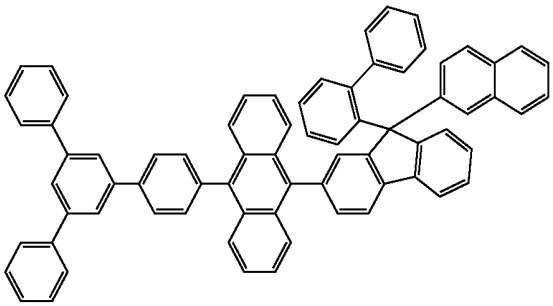

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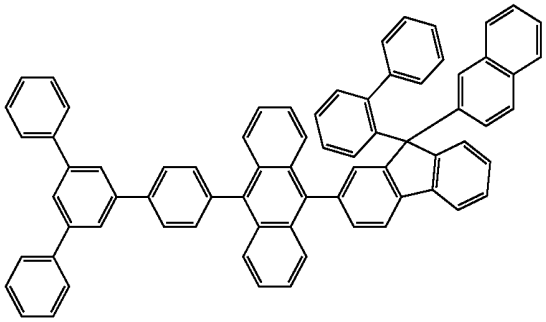

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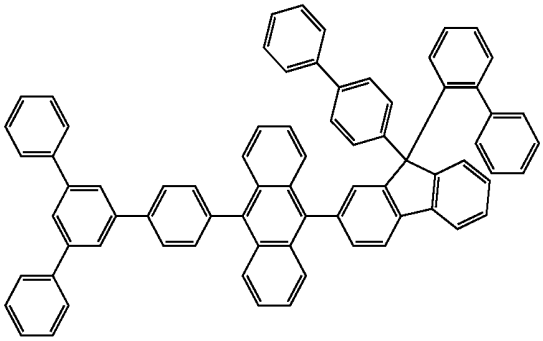

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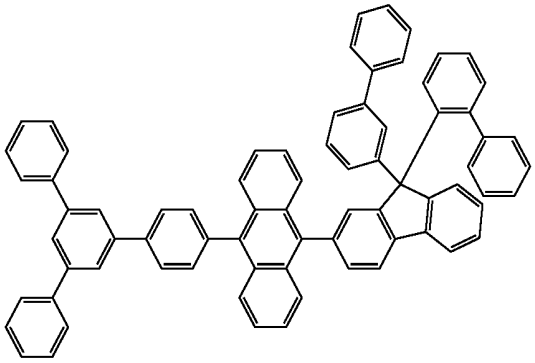

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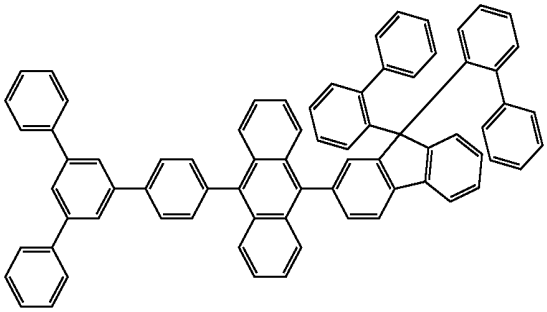

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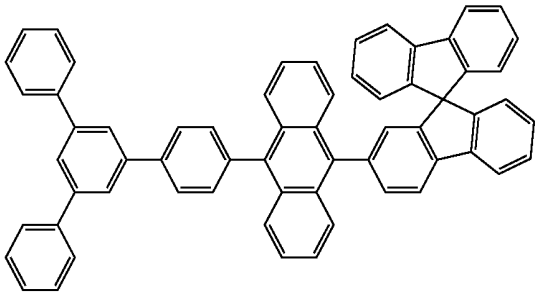

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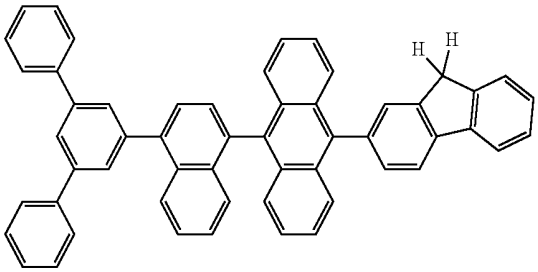

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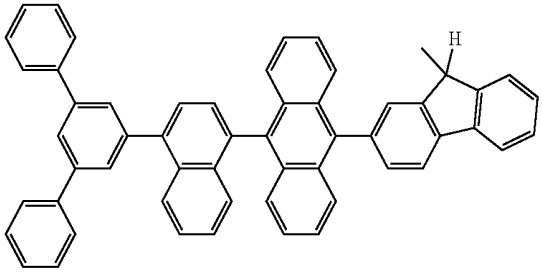

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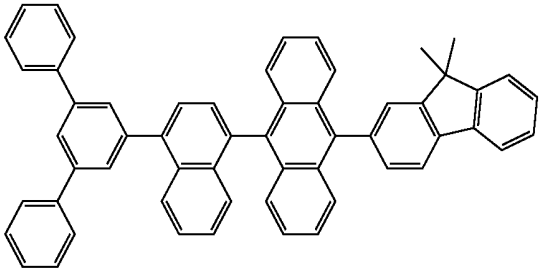

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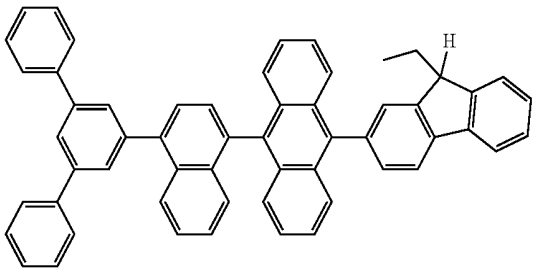

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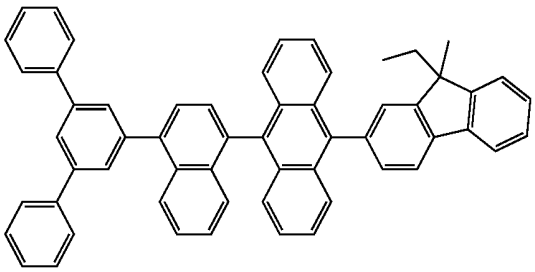

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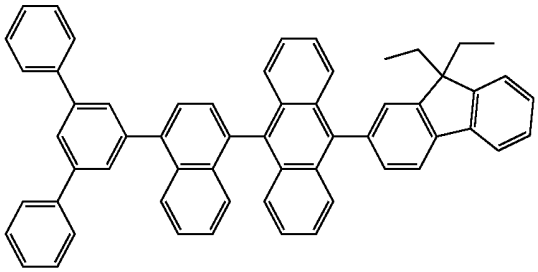

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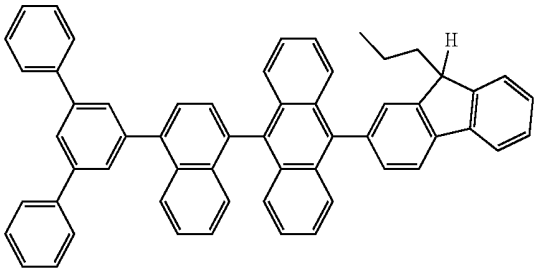

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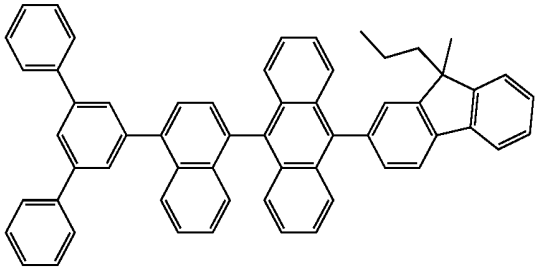

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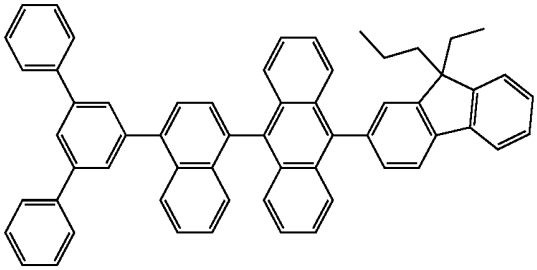

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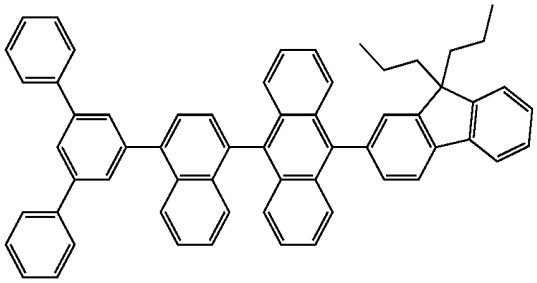

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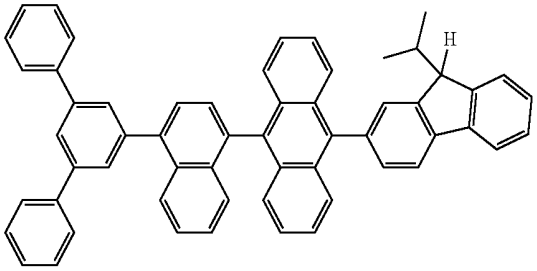

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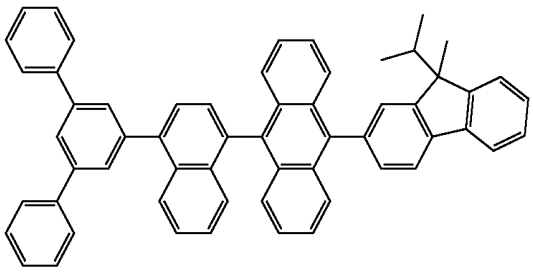

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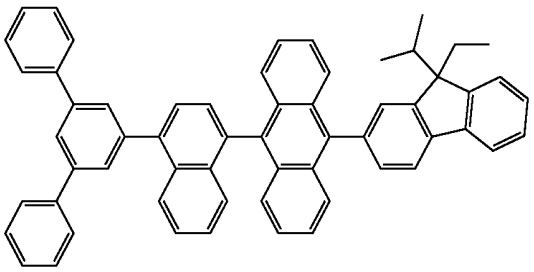

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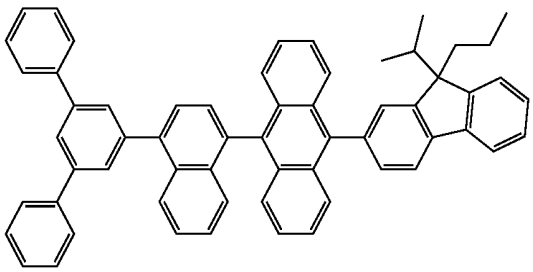

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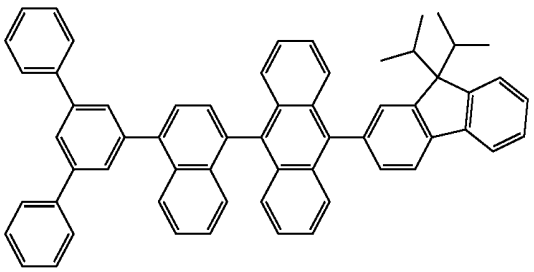

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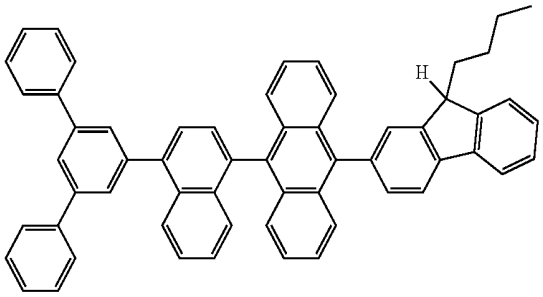

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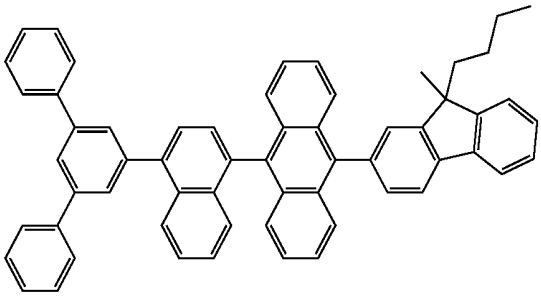

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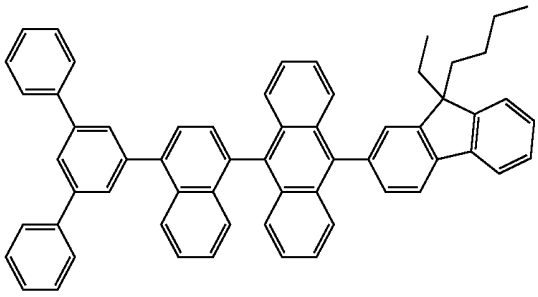

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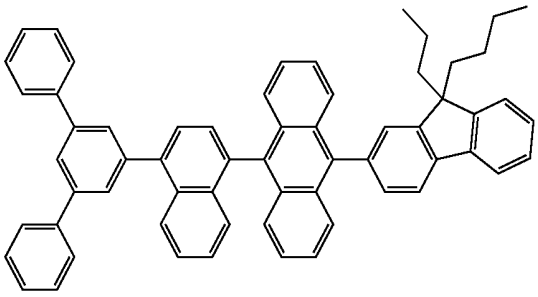

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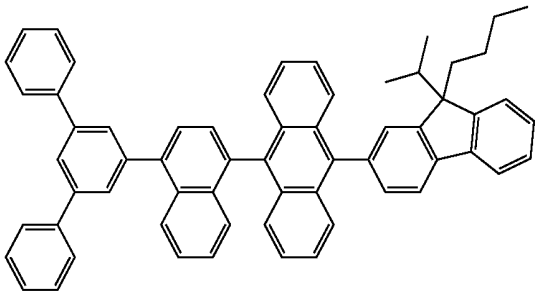

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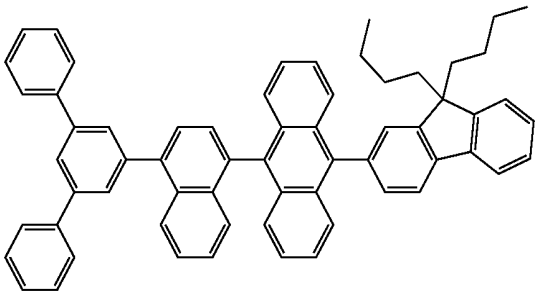

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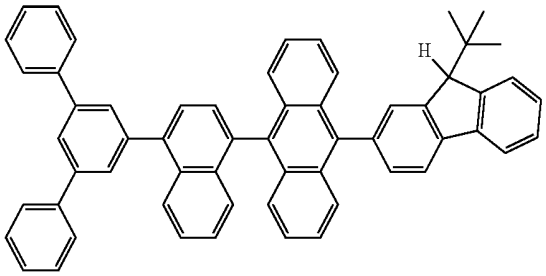

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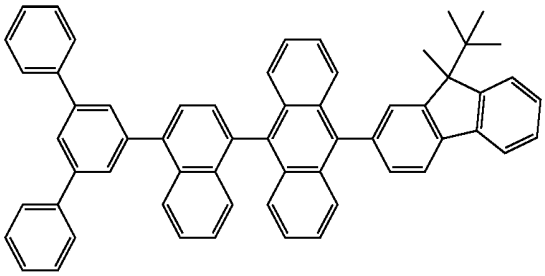

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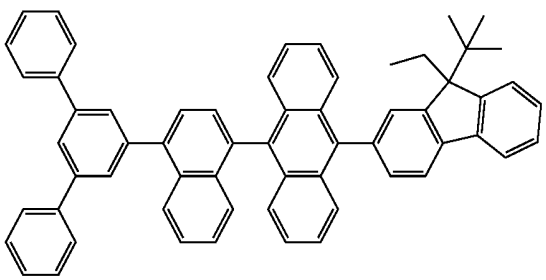

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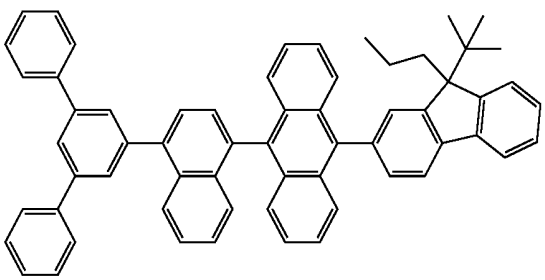

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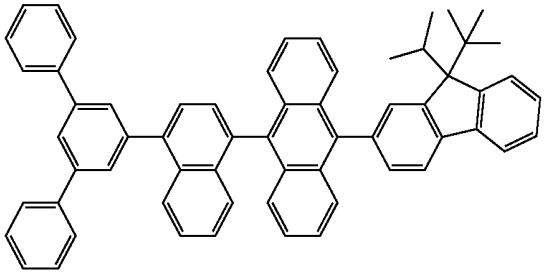

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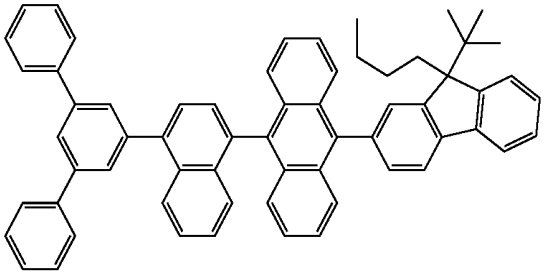

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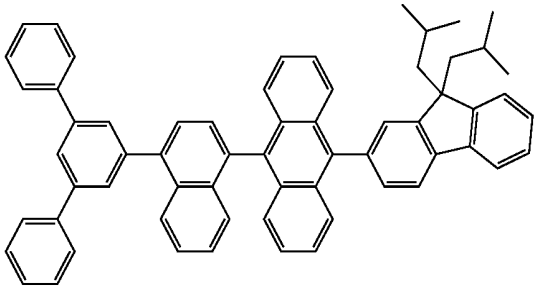

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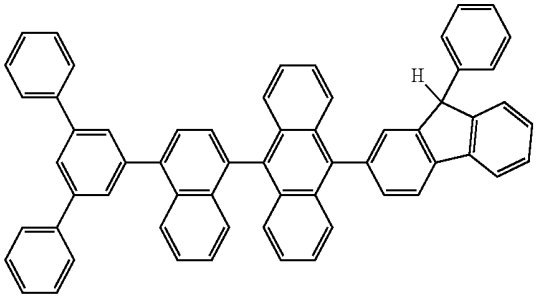

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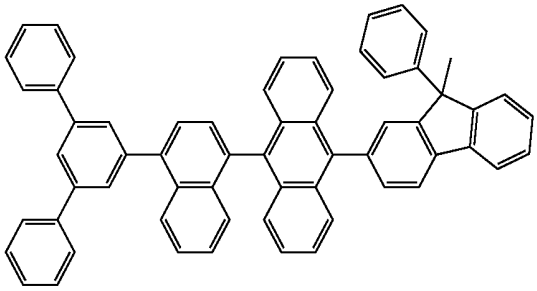

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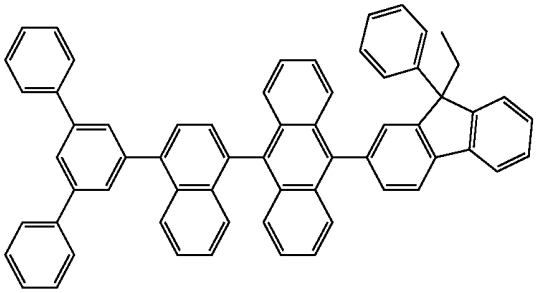

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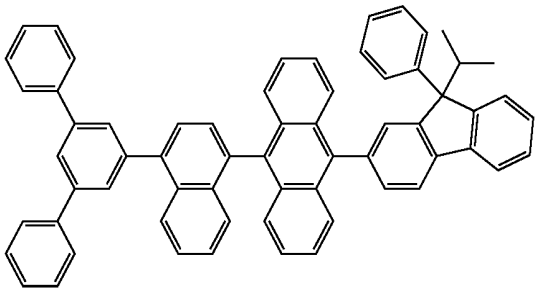

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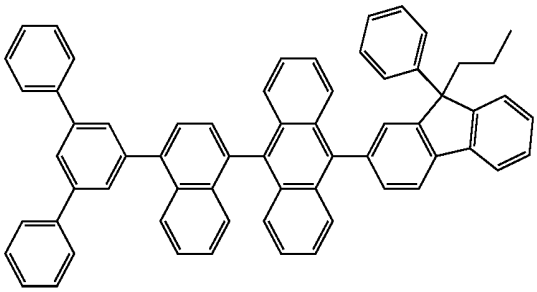

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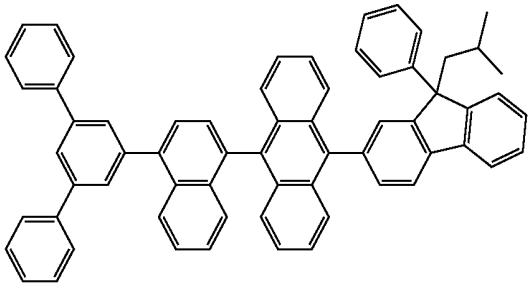

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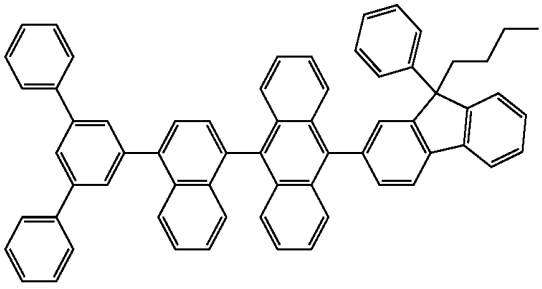

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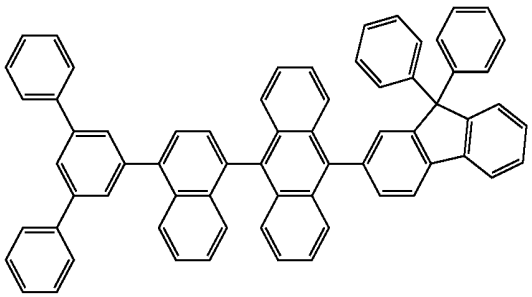

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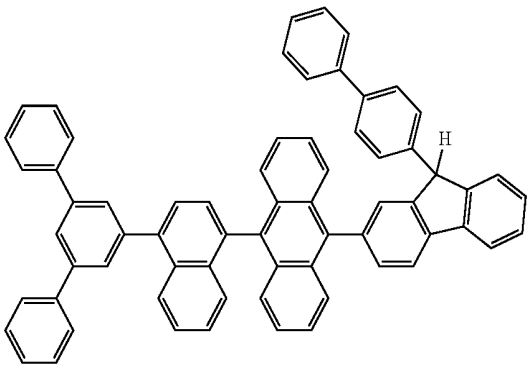

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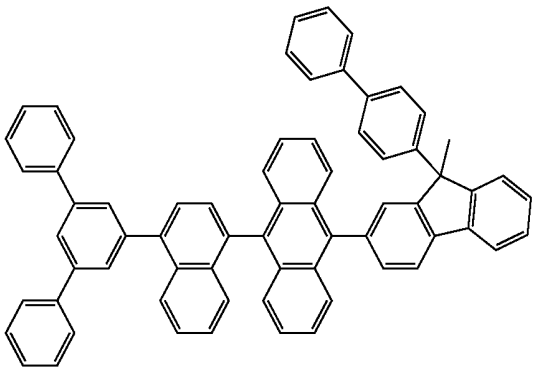

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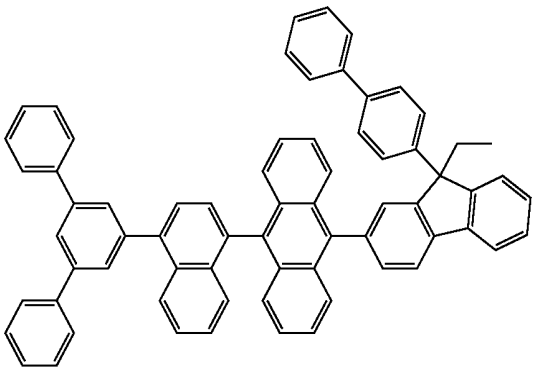

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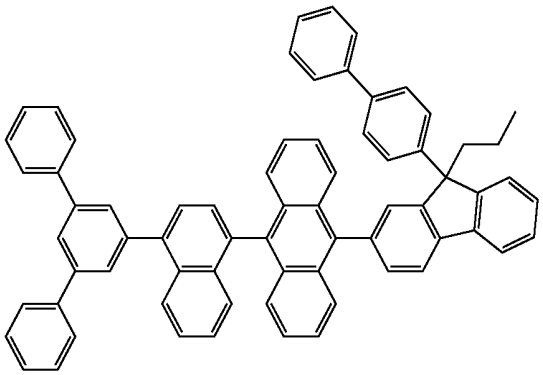

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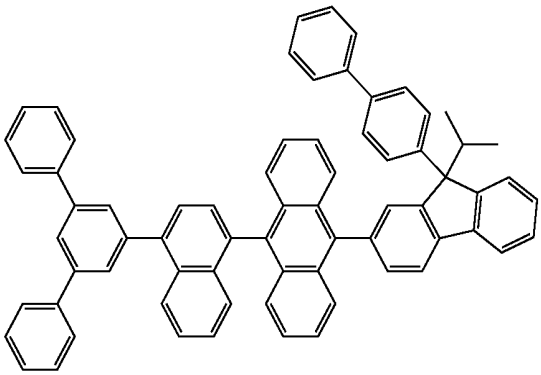

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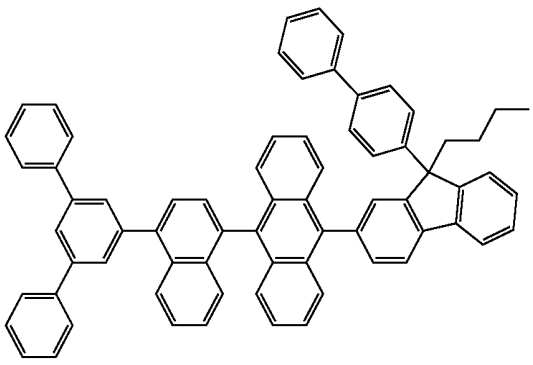

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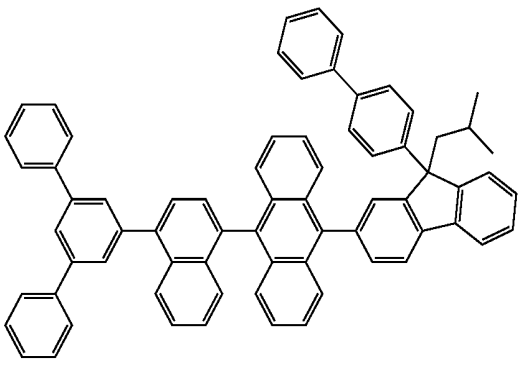

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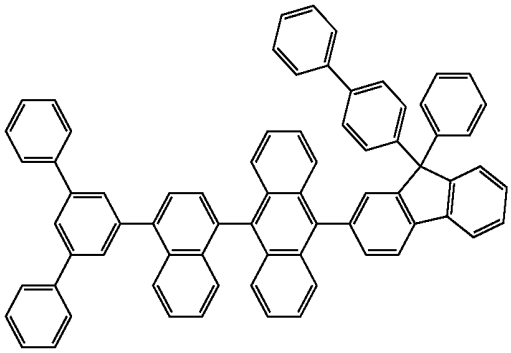

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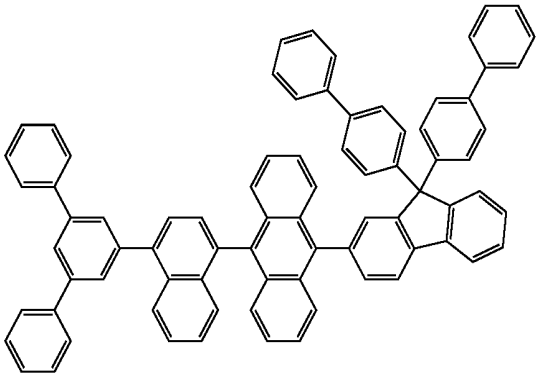

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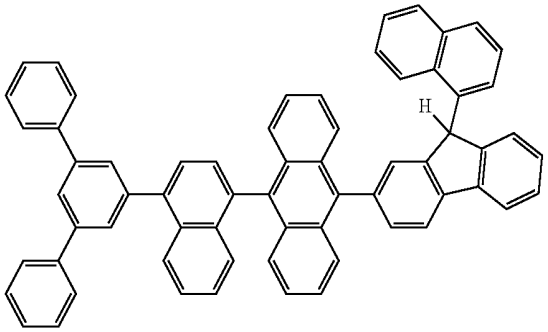

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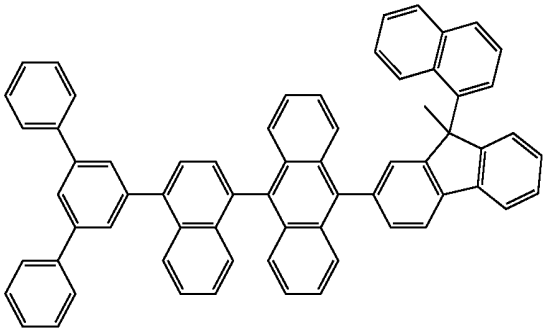

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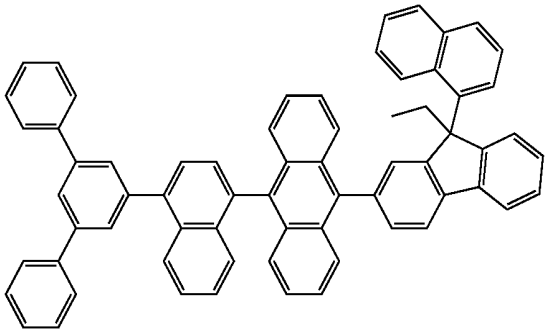

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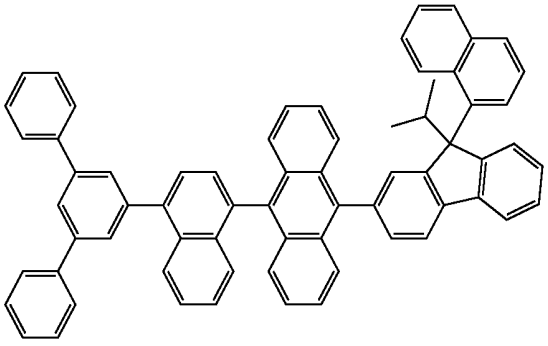

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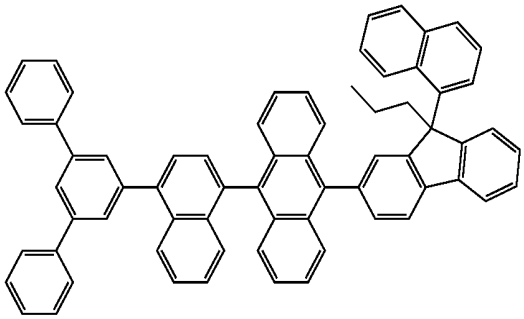

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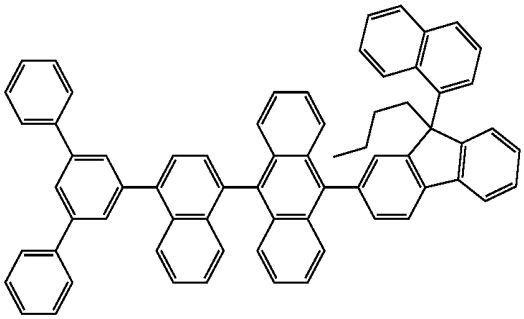

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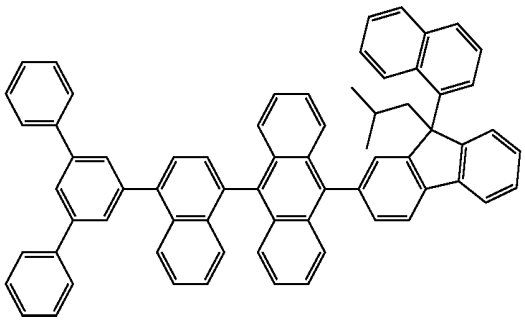

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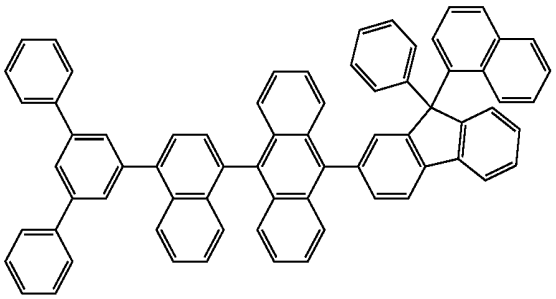

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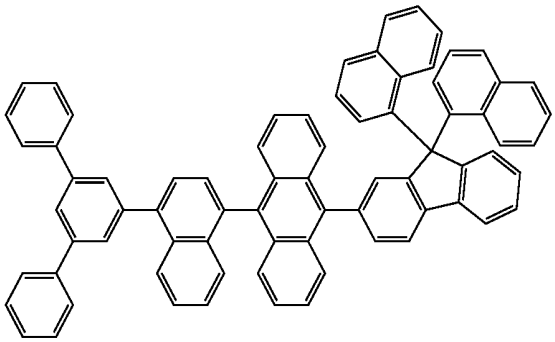

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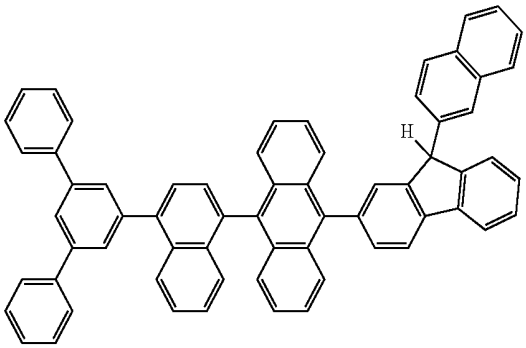

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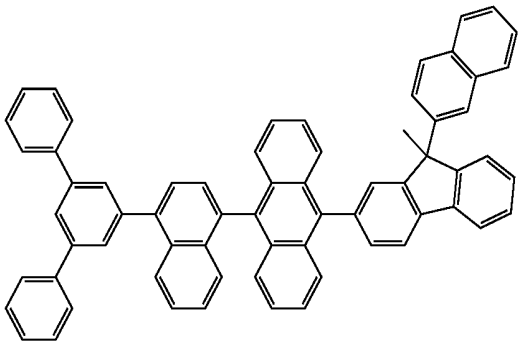

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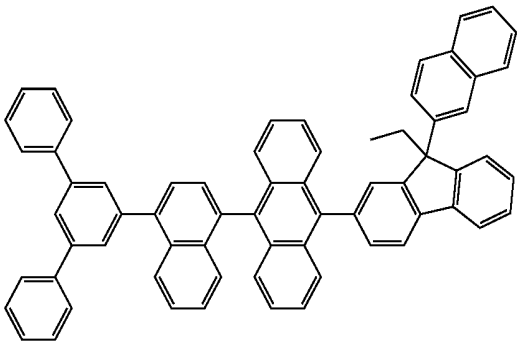

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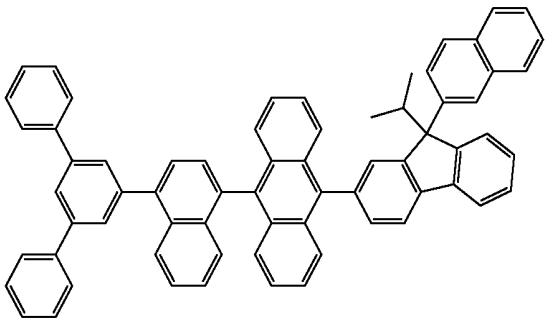

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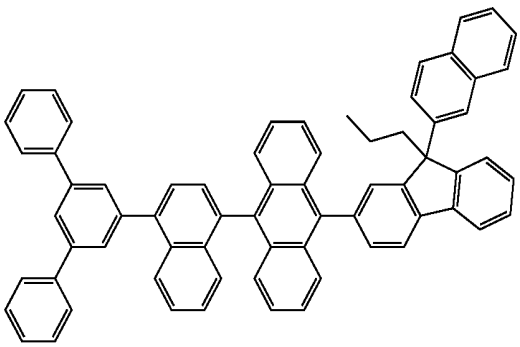

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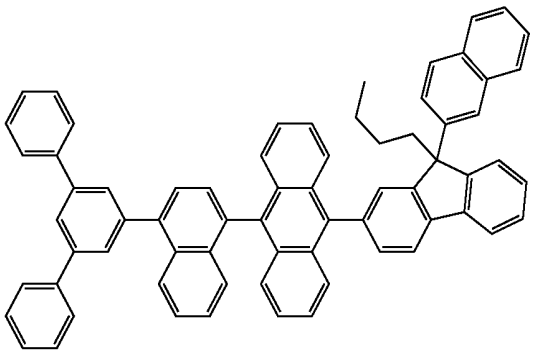

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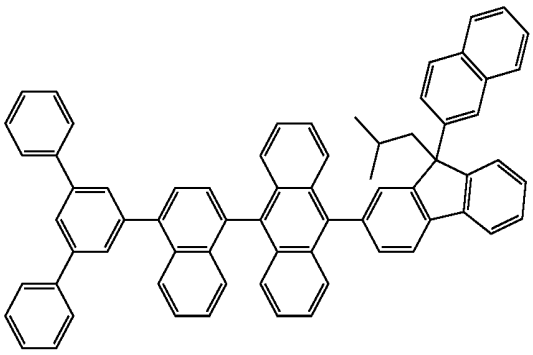

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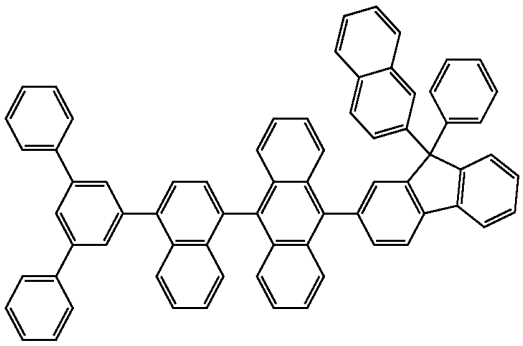

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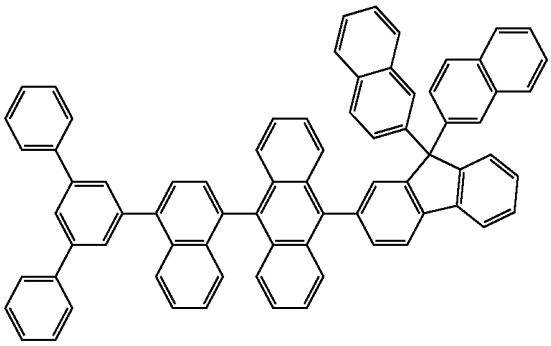

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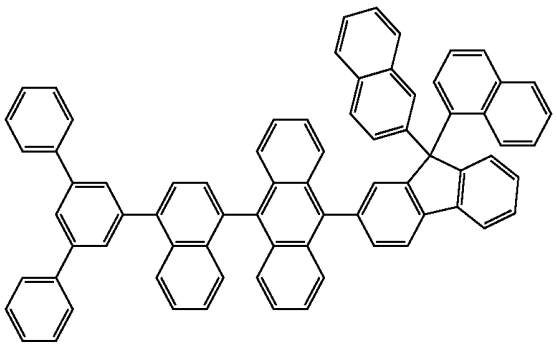

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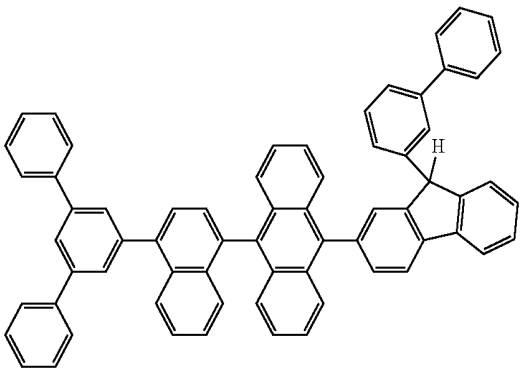

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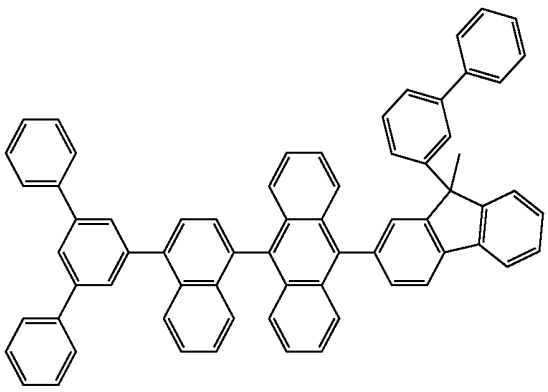

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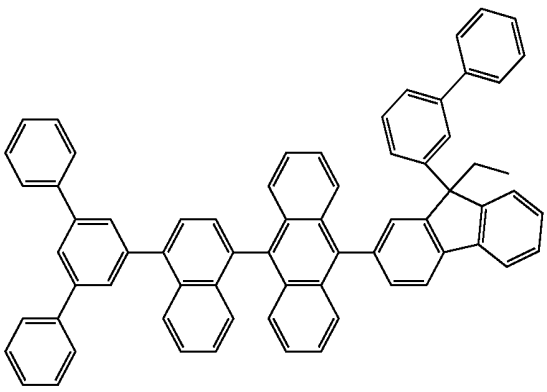

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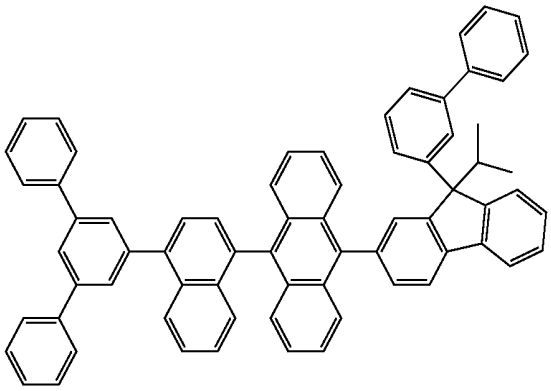

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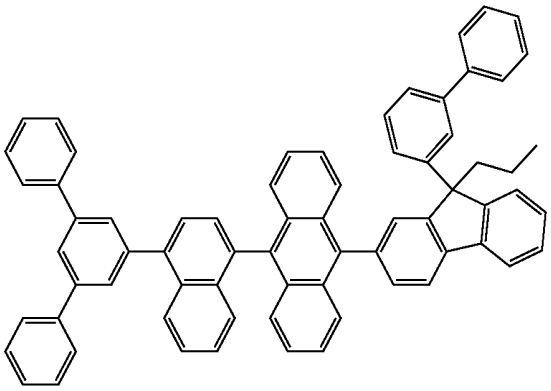

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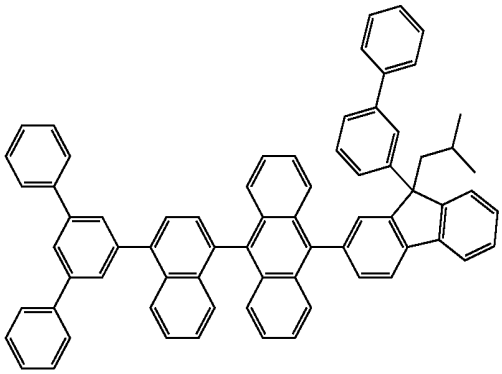

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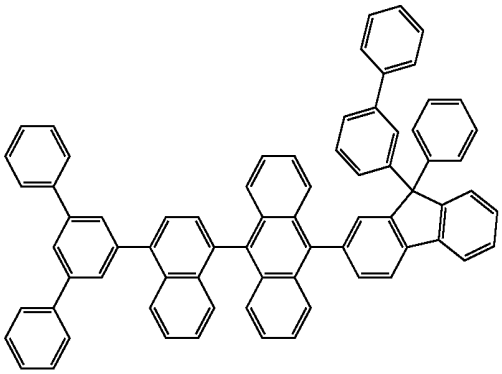

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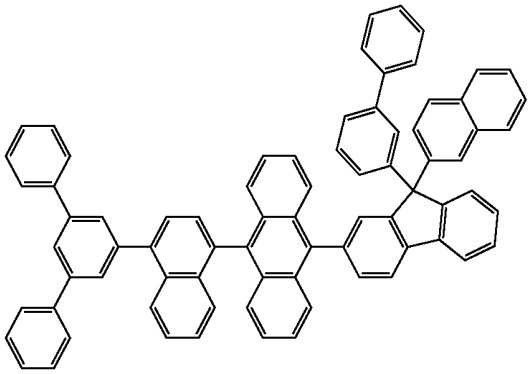

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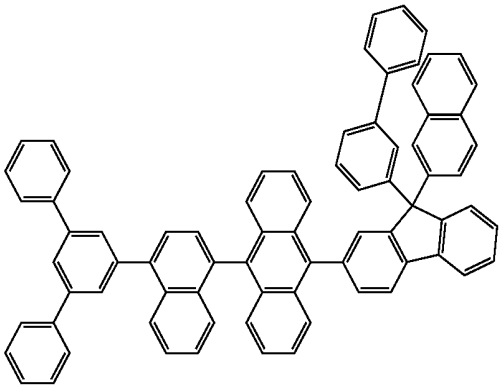

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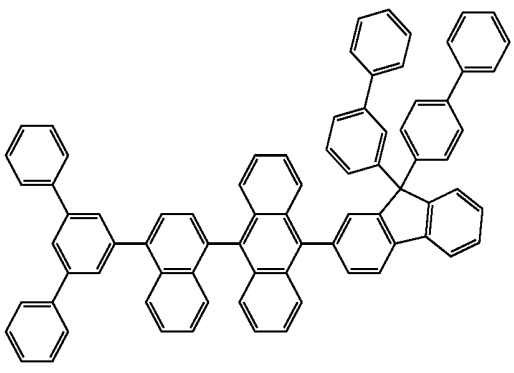

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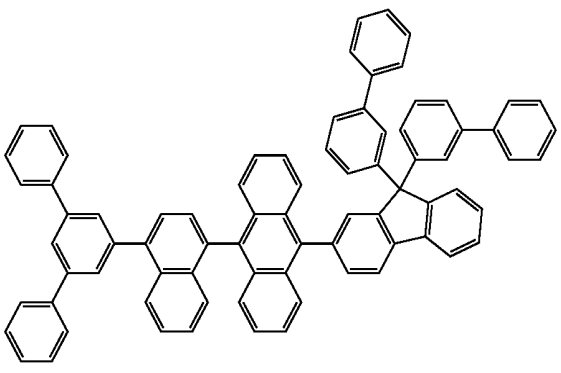

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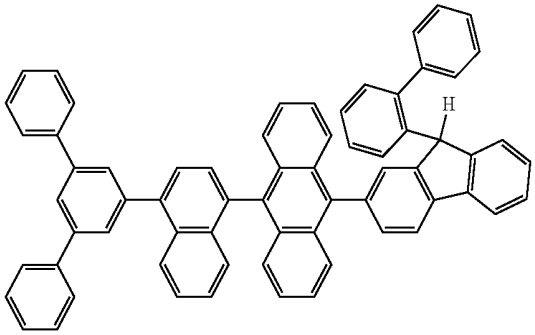

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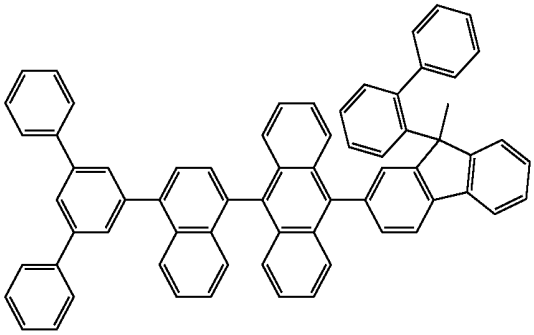

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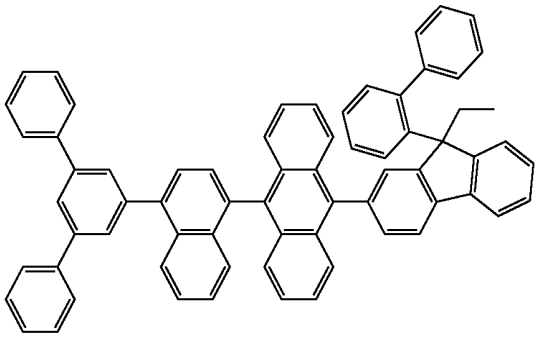

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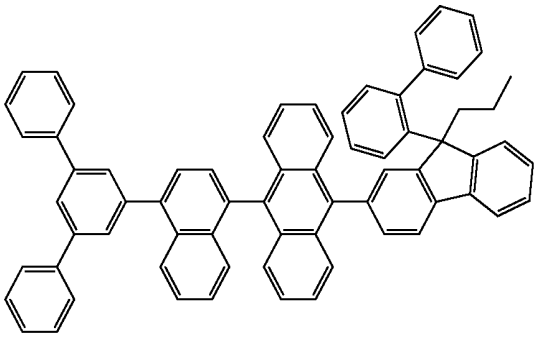

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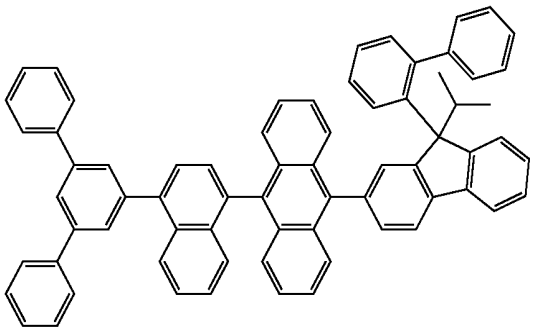

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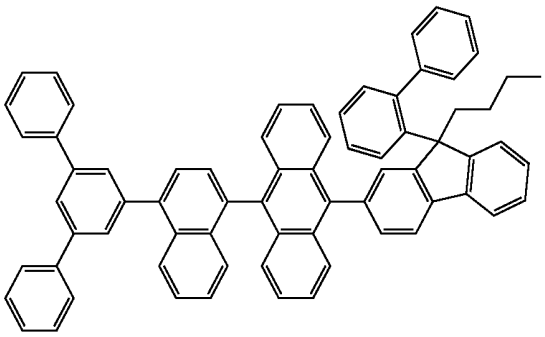

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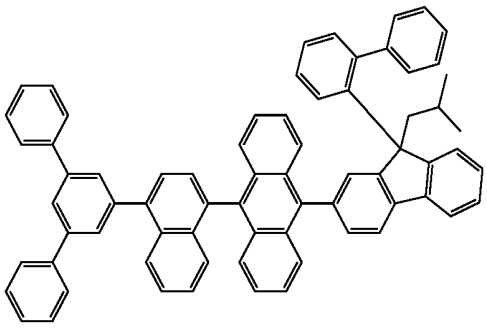

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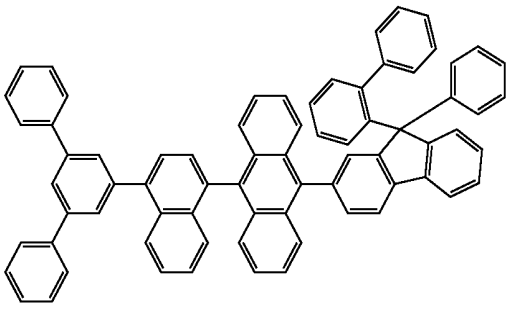

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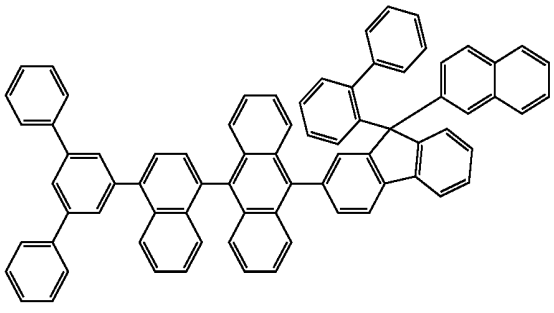

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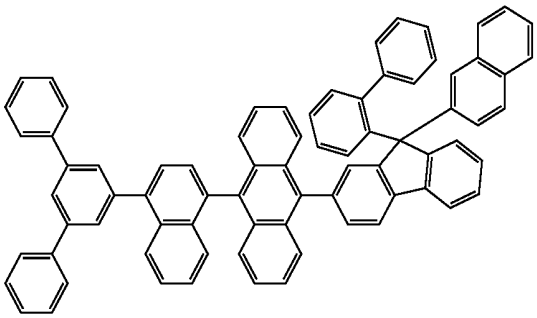

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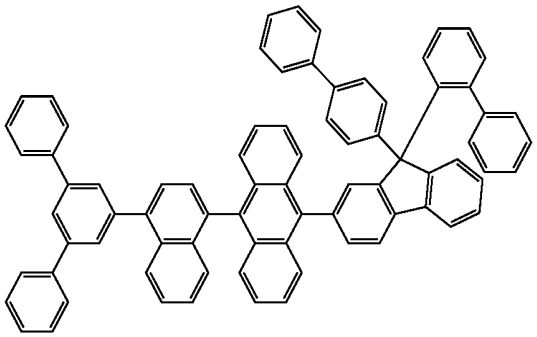

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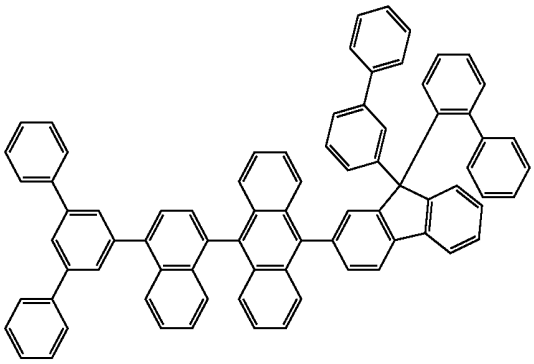

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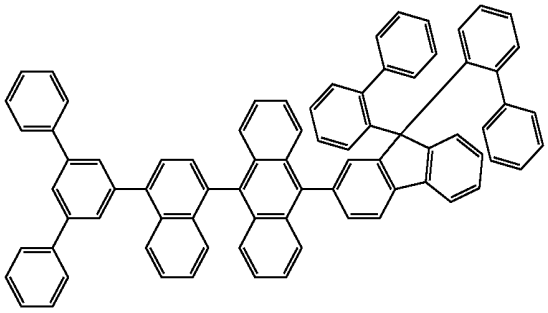

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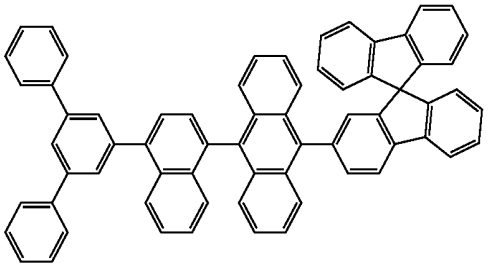

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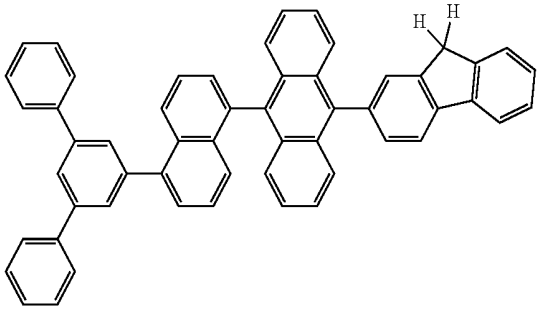

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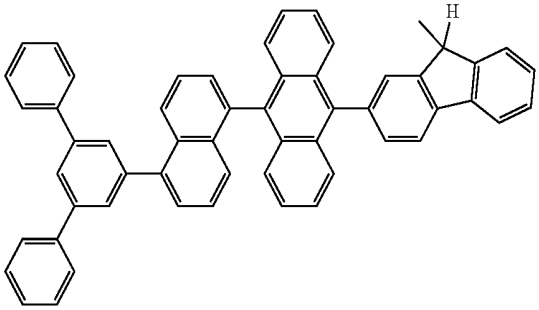

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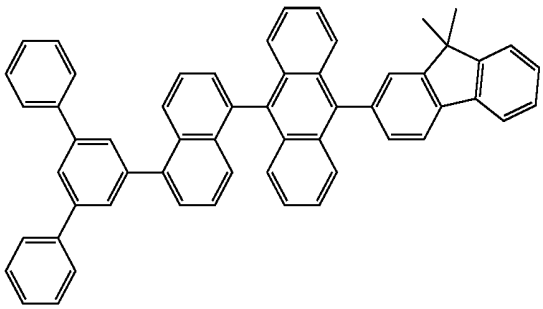

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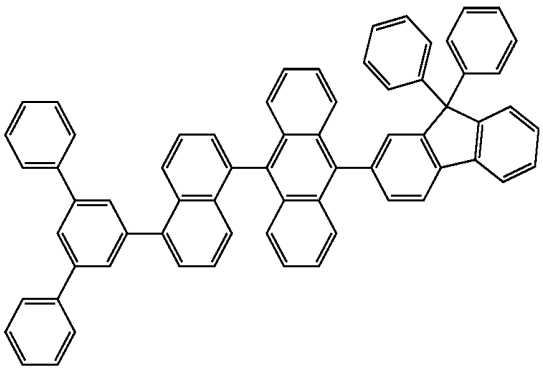

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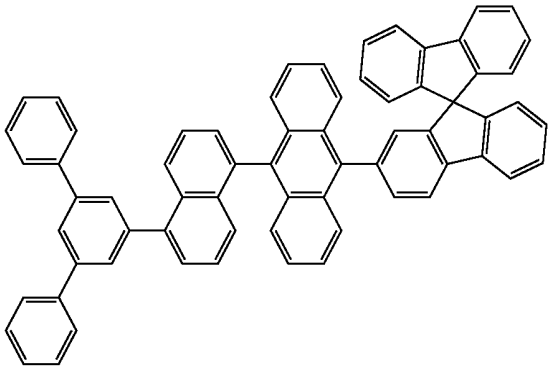

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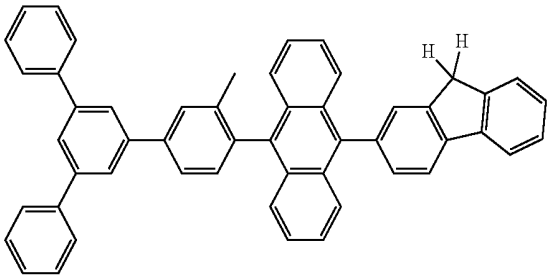

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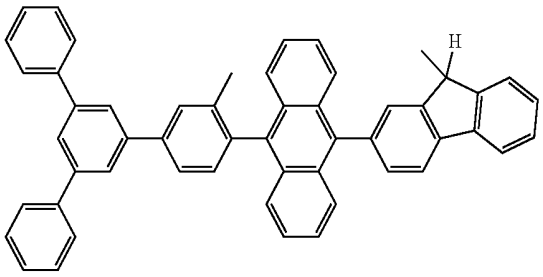

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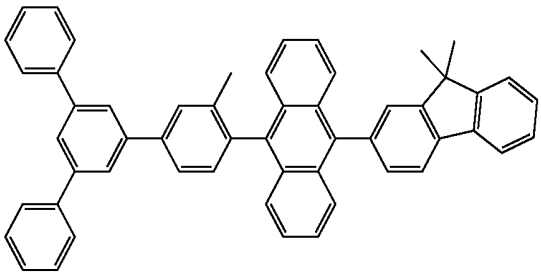

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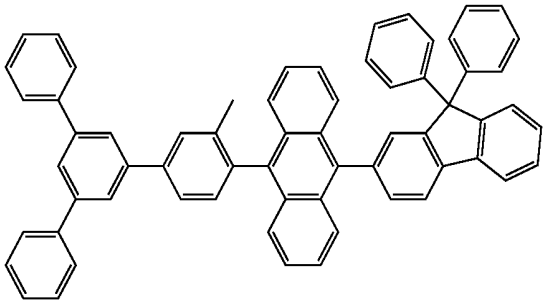

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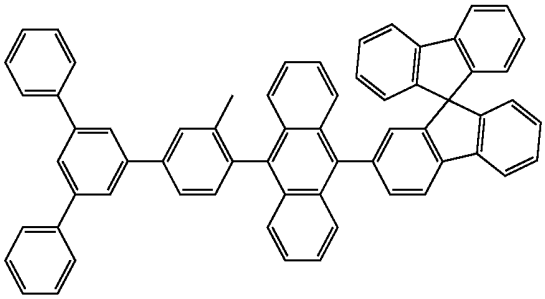

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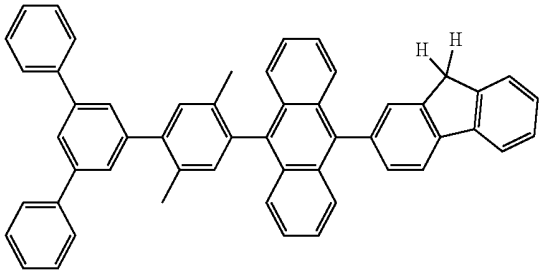

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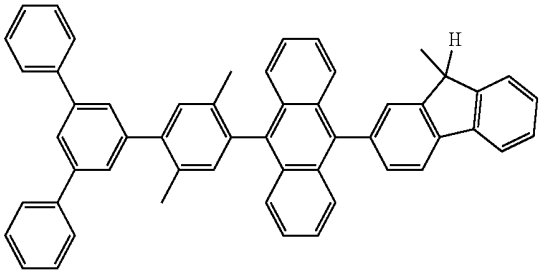

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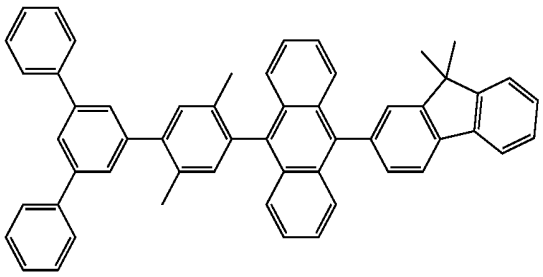

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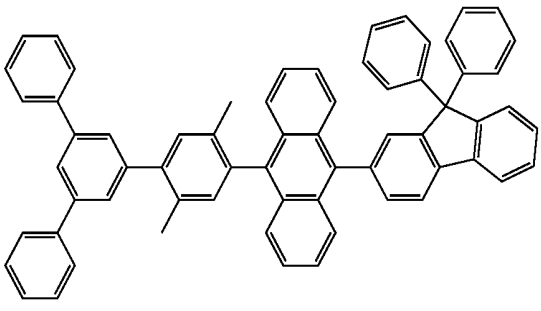

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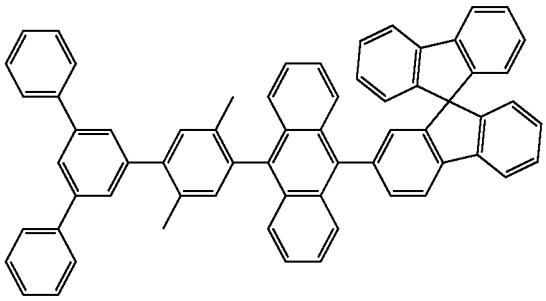

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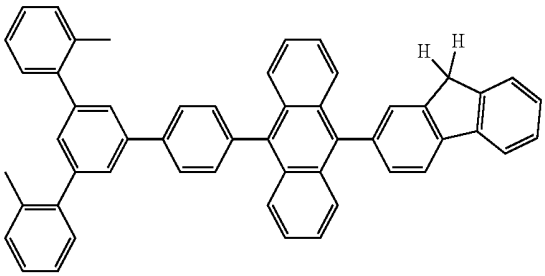

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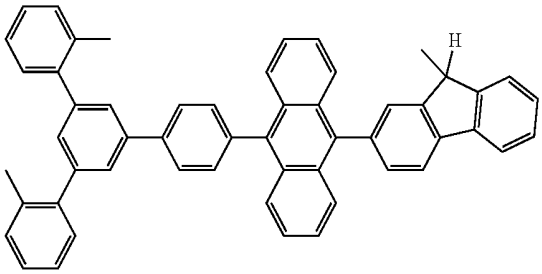

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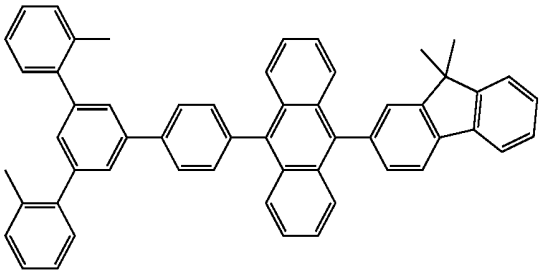

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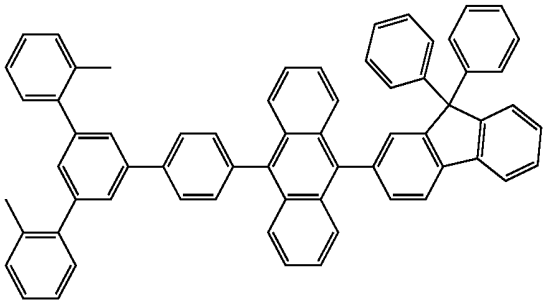

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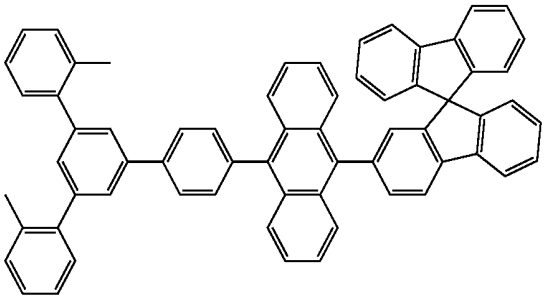

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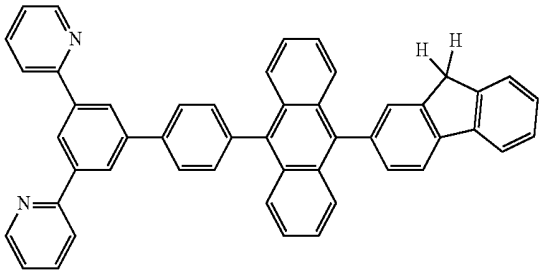

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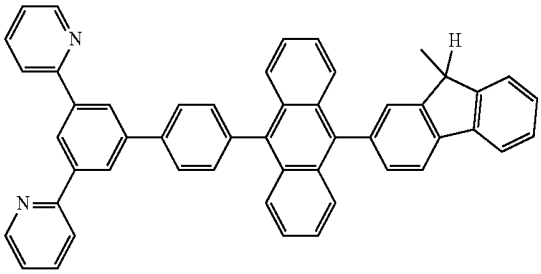

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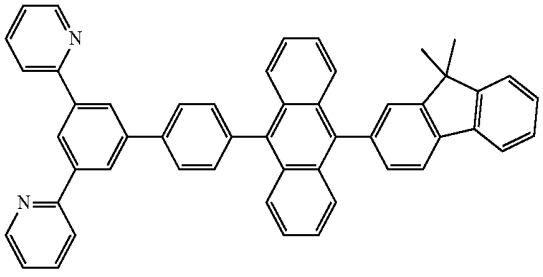

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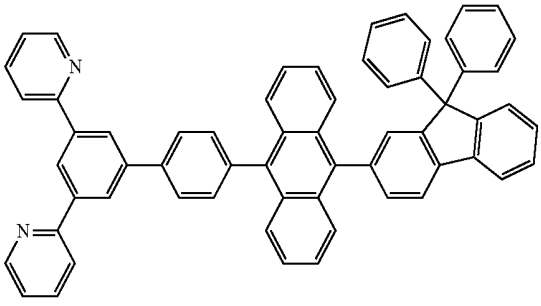

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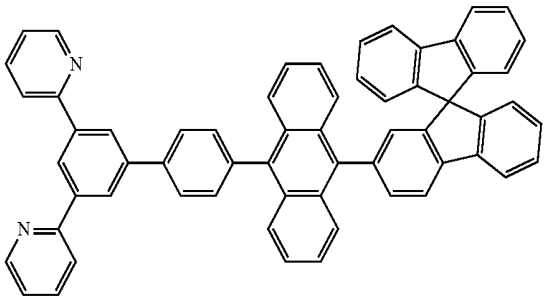

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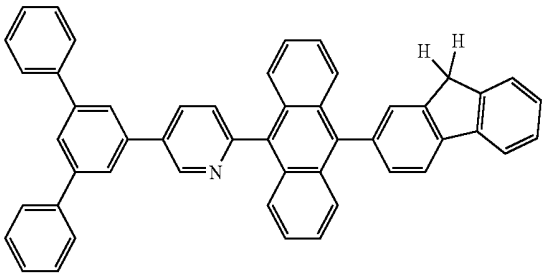

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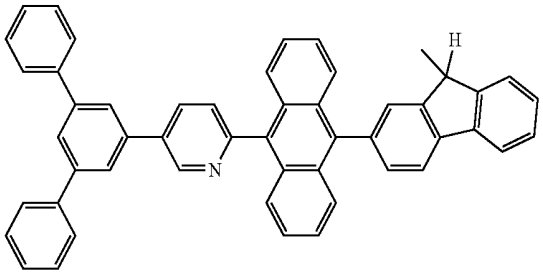

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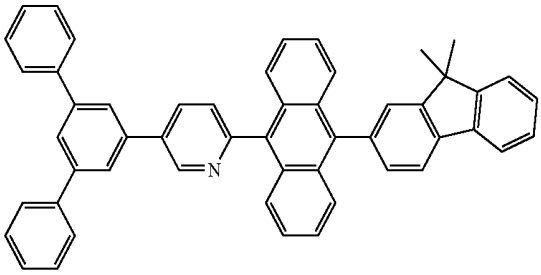

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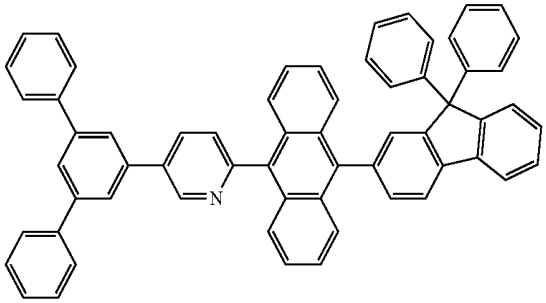

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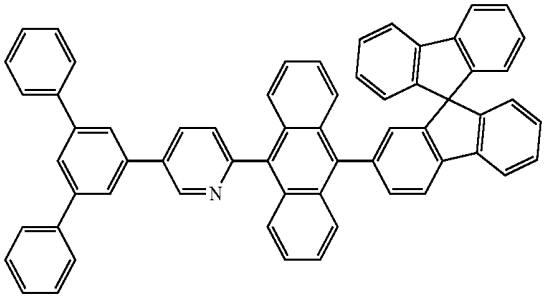

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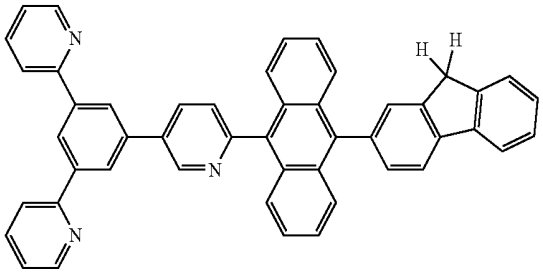

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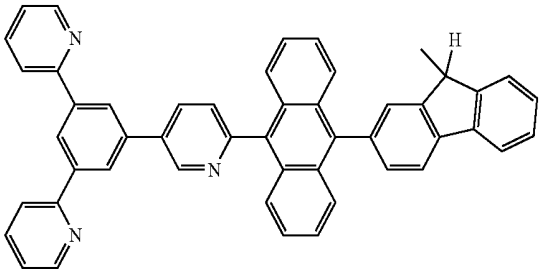

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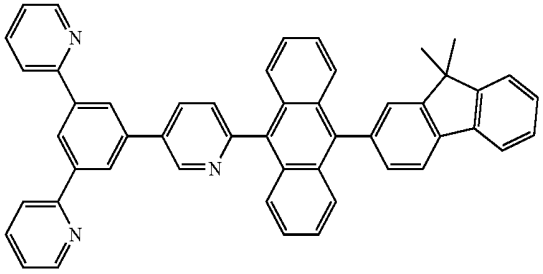

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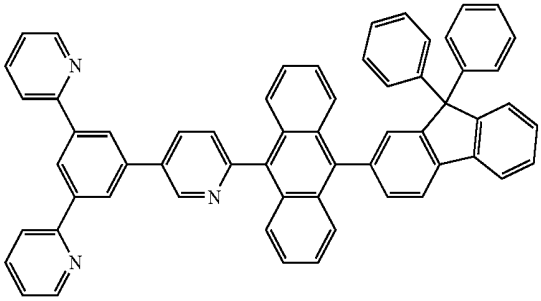

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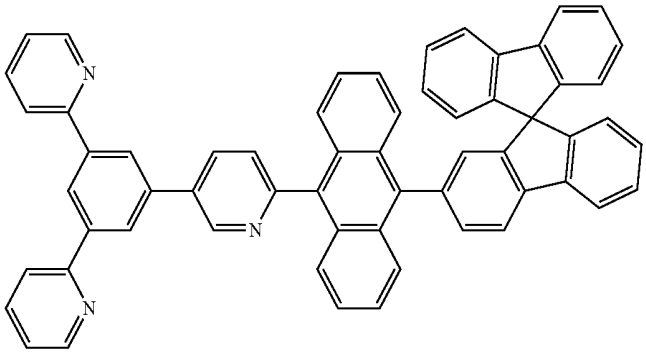

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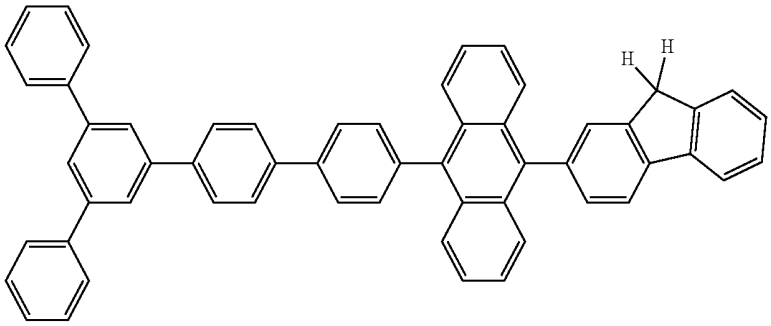

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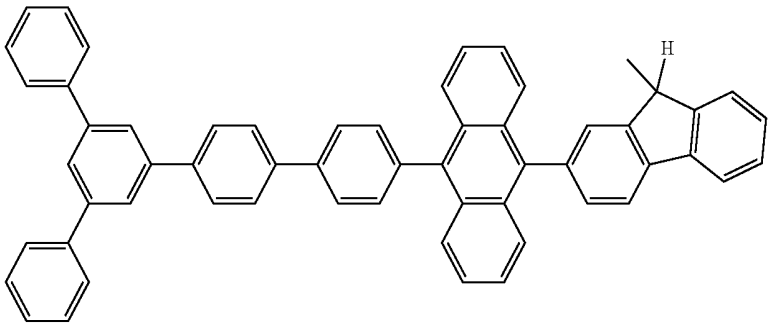

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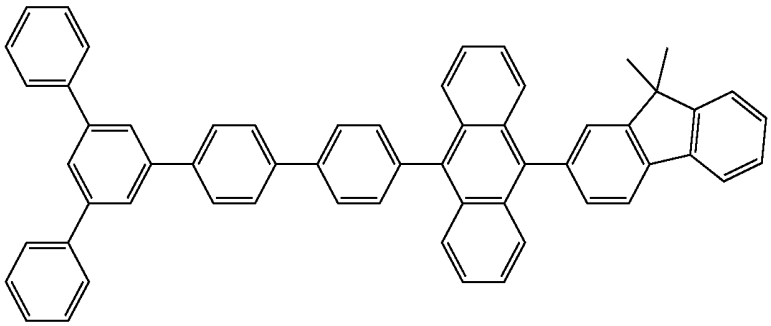

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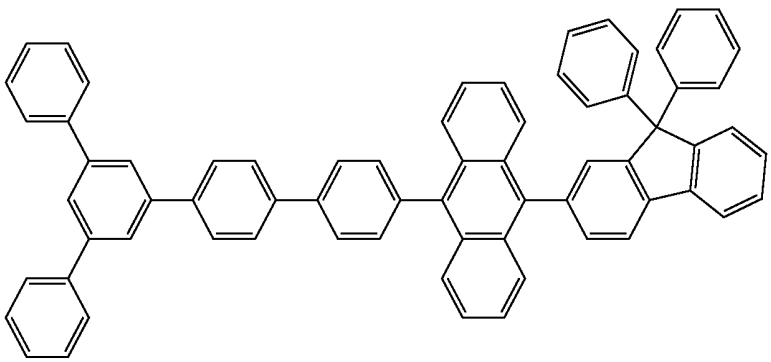

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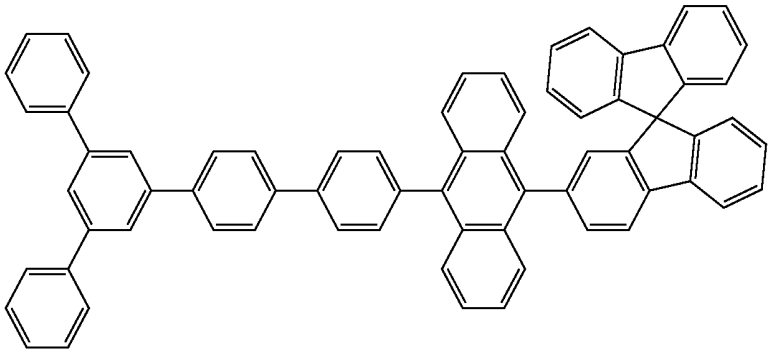

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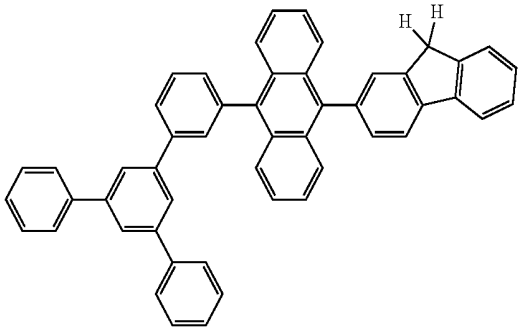

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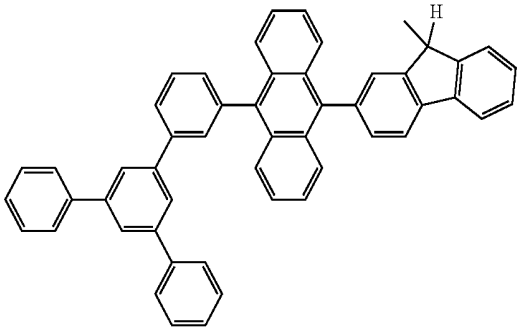

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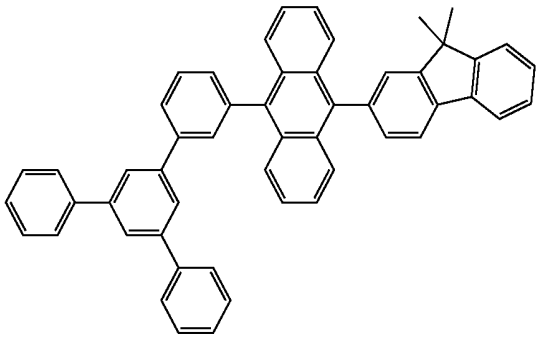

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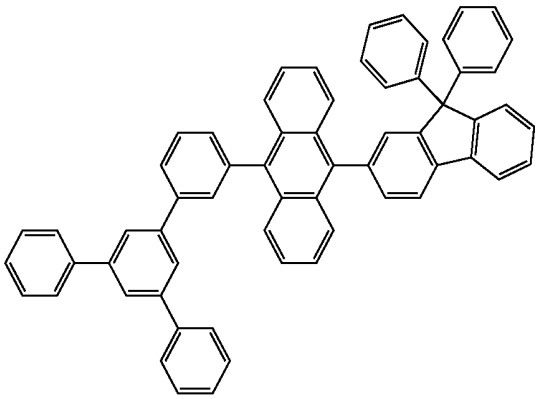

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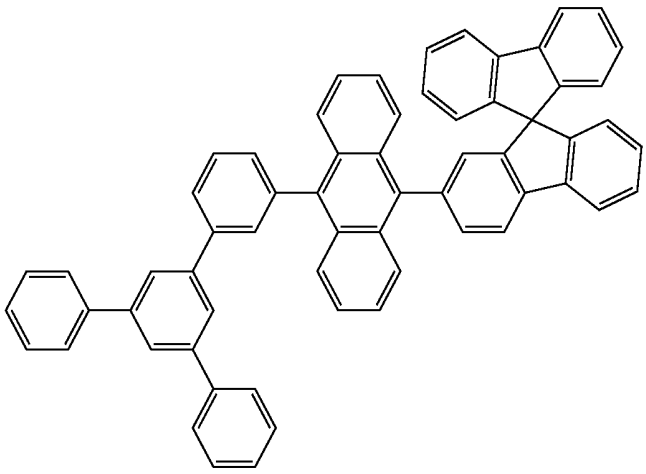


The organic electronic material provide in the present invention can be used to make OLED, which comprises an anode, a cathode, and a layer or multiple layers of organic layers. The said organic layer includes at least one layer of said organic electronic material with the structural formula I.

The said multiple organic layers are hole injection layer, hole transport layer, light emitting layer, hole blocking layer and electron transport layer, respectively, and in particular, not all organic layers are necessary according to the demands.

The said hole transport layer, electron transport layer and light emitting layer contain the said organic material with the structural formula 1.

The materials of the hole transport layer and hole injection layer in the present invention should have good hole transport performance, which can effectively transport the holes from the anode to the organic light emitting layer. The materials used can include small molecule and polymer organic materials, including but not limited to tri-aromatic amine compounds, benzidine compounds, thiazole compounds, oxazole compounds, imidazole compounds, fluorene compound, phthalocyanine compounds, hexanitrile hexaazatriphenylene, 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoanthraquinodimethane dimethyl-p-benzoquinone (F4-TCNQ), polyvinyl carbazole, polythiophene, polyethylene, polyethylene sulfonic acid.

The organic light emitting layer in the present invention contains, in addition to the compounds with the structural formula (I), the following but not limited to the following compounds: naphthalene compounds, pyrene compounds, fluorene compounds, phenanthrene compounds, chrysene compounds, fluoranthene compounds, anthracene compounds, dibenzanthracene compounds, perylene compound, bi-aryl vinyl compounds, triphenylamine vinyl compounds, amine compounds, benzimidazole compounds, furan compounds and organic metal chelate compounds.

The organic electron transport material of the organic electronic devices in the present invention should have good electron-transport performance, which can efficiently transfer electrons from the cathode to the light emitting layer. These materials can select the following compounds, but not limited to oxa oxazole, thiazoles, triazole compounds, tridiazoxide compounds, tri-aza benzene compounds, quinoxaline compounds, dinitrogen anthracene compounds, silicon-containing heterocyclic compounds, quinoline compounds, phenanthroline compounds, metal chelates, fluoro-substituted benzene compounds.

One electron injection layer can be added to the organic electronic device of the present invention as required. The electron injection layer may effectively inject the electrons from the cathode into the organic layer, mainly selected from alkali metals or alkali metal compounds, or selected from alkaline earth metals or alkaline earth metal compounds, including but not limited to the following: lithium, lithium fluoride, lithium oxide, lithium nitride, 8-hydroxyquinoline lithium, cesium, cesium carbonate, 8-hydroxyquinoline cesium, calcium, calcium fluoride, calcium oxide, magnesium, magnesium fluoride, magnesium carbonate, magnesium oxide.

Experimental results show that, the organic electronic material with structural formula (I) has a good thermal stability, high light-emitting efficiency, high purity of light-emitting. The OLEDs made from this organic light-emitting material will have advantages of good light-emitting efficiency, excellent color purity and long lifetime.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a structural charge of the device, of which, **10** denotes a glass substrate, **20** denotes an anode, **30** denotes hole injection layer, **40** denotes hole transport layer, **50** denotes light emitting layer, **60** denotes electron transport layer, **70** denotes electron injection layer, **80** denotes cathode.

FIG. **2** is the ^{1}H NMR diagram of compound 89.

FIG. **3** is the ^{13}C NMR diagram of compound 89.

FIG. **5** is the TGA map of compound 89.

FIG. **6** shows the voltage-current density curves of Embodiments 4 and 5 and Comparative Example 1.

FIG. **7** shows the brightness –CIEy plot of Embodiments 4 and 5 and Comparative Example 1.

FIG. **8** shows the light-emitting spectra of Embodiments 4 and 5 and Comparative Example 1.

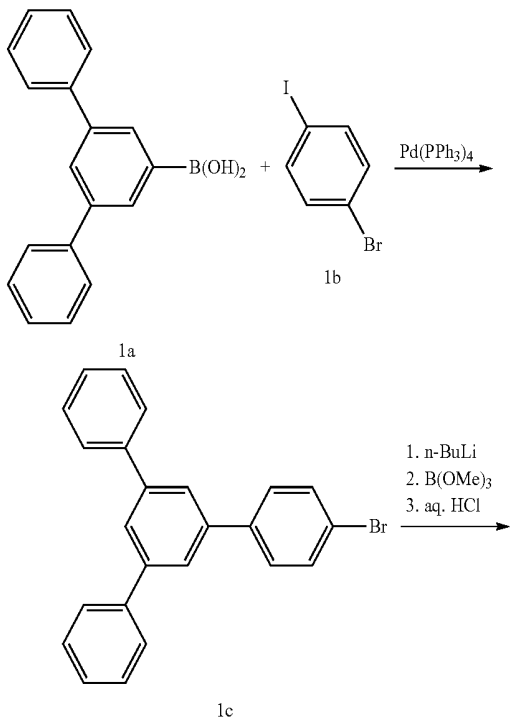
FIG. **9** shows the current density-current efficiency curves of Embodiments 4 and 5 and Comparative Example 1.

DETAILED DESCRIPTIONS OF THE PREFERRED EMBODIMENTS

In the following, the present invention is described in details by combining the following examples.

(The compounds 1a, 1b, 1e, 1h, 3a, 89a are common materials available in the markets)

Embodiment 1



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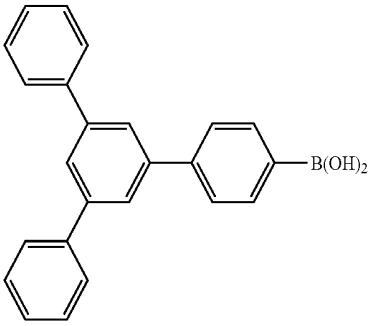
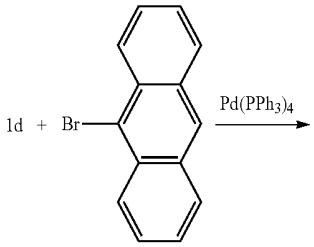


1d



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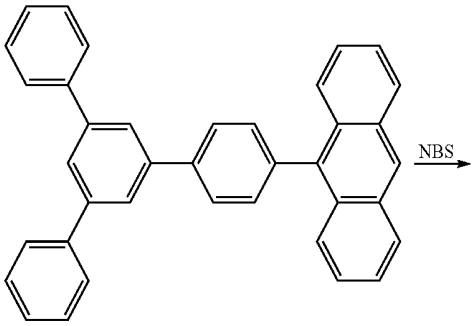

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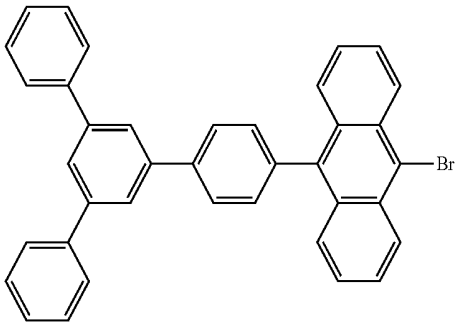
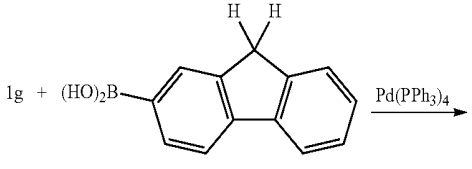


1g



1h

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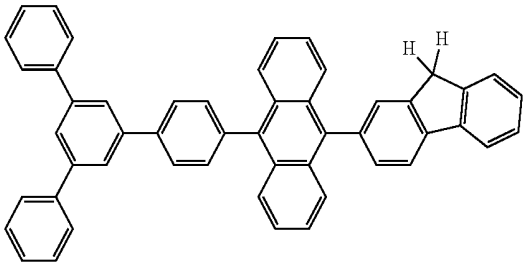


1

Synthesis of Intermediate 1c

Add 1a (240.00 g, 0.88 mol), 1b (496.32 g, 1.76 mol), $Pd(PPh_3)_4$ (20.35 g, 17.60 mmol), potassium carbonate (302.52 g, 2.20 mol), toluene (2400 mL), pure water (1200 mL) to a reaction flask. Start to heat after extracting air for three times, and when the reaction solution temperature reaches 95-105V, maintain it for 8-12 h; take samples for TLC and HPLC, to completely react. Stop heating and cool down to 20-30° C., perform suction filtration to separate the organic layer from filtrate. Extract the aqueous layer with ethyl acetate, combine the organic layer, then wash with water, dry by anhydrous magnesium sulfate, and perform suction filtration, to get the filtrate. Concentrate the filtrate to get a dark yellow solid crude product. The crude product is recrystallized from petroleum ether to get an off-white solid product, with a yield of 90% and a purity of 95%.

Synthesis of Intermediate 1d

Add 1c (302 g, 0.78 mol), $B(OEt)_3$ (142 g, 0.97 mol), n-BuLi/THF (1.6 M, 600 mL), and anhydrous THF (3000 mL) at appropriate ratio to a reaction flask. After extracting with nitrogen for three times, cool down until the reaction solution temperature is −75~−65° C., slowly add n-BuLi/THF solution dropwise and control the temperature at −75~−65° C.; after dripping, continue to maintain this temperature for reaction 0.5-1 h. Then add appropriate amount of $B(OEt)_3$ dropwise, to control the reaction solution temperature at −75~−65° C., after dripping, continue to maintain this temperature for reaction 0.5-1 h. Then transfer the solution to room temperature for naturally heating reaction 4-6 h, then add 2M dilute hydrochloric acid to adjust the PH value to 2-3, after stirring about 1 h, stop the reaction. Add ethyl acetate to extract the solution, and the aqueous layer is extracted by EA. The organic layers are combined and dried over anhydrous magnesium sulfate, then suction filtration is conducted. The filtrate is concentrated to get an off-white solid product, with a purity of 95% and a yield of 62.5%.

Synthesis of Intermediate 1f

Add 1d (150 g, 0.43 mol), 1e (500 g, 0.86 mol), $Pd(PPh_3)_4$ (5.0 g, 0.44 mmol), potassium carbonate (130 g, 0.92 mol), toluene (1000 mL), pure water (500 mL) to a reaction flask. Start to heat after extracting nitrogen for three times, and when the reaction solution temperature reaches 95-105° C., maintain it for 8-12 h; take samples for TLC and HPLC, to completely react. Stop heating and cool down to 20-30° C., perform suction filtration to separate the organic layer from filtrate. Extract the aqueous layer with ethyl acetate, combine the organic layers, dry by anhydrous magnesium sulfate, and perform suction filtration. The filtrate is concentrated to get dark yellow solid crude product, with a purity of 80% and a yield of 78.1%.

Synthesis of Intermediate 1g

Add 1f (210 g, 0.42 mol), NBS (135 g, 0.71 mol), DMF (5 L) to a reaction flask. Start to heat after extracting nitrogen for three times, and when the reaction solution temperature reaches 60-65° C., maintain it for 6-8 h; take samples for TLC and HPLC, to completely react. Stop heating and cool down to 20-30° C., then pour the reaction solution to ice-water to separate dark yellow solid, and then perform suction filtration to get yellow solid and bake to obtain 1 g of crude product. Add the crude product to DCM/MeOH until the solution becomes slightly turbid, continue to stir for about 30 min, to separate out a large amount of solid, then perform suction filtration to get pale yellow solid product, with a yield of approximate 54.05% and a purity of 98.5%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J=8.8 Hz, 2H), 7.99-7.90 (m, 4H), 7.87 (t, J=1.6 Hz, 1H), 7.78 (dd, J=9.3, 2.3 Hz, 6H), 7.61 (ddd, J=8.8, 6.5, 1.1 Hz, 2H), 7.56-7.48 (m, 6H), 7.46-7.38 (m, 4H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 142.67 (s), 142.03 (s), 141.26 (s), 140.69 (s), 137.83 (s), 137.52 (s), 131.87 (s), 131.24 (s), 130.44 (s), 129.09 (s), 128.80 (s), 128.38-127.40 (m), 127.18 (s), 126.05-125.21 (m), 123.08 (s), 77.74 (s), 77.31 (s), 76.89 (s), 30.10 (s).

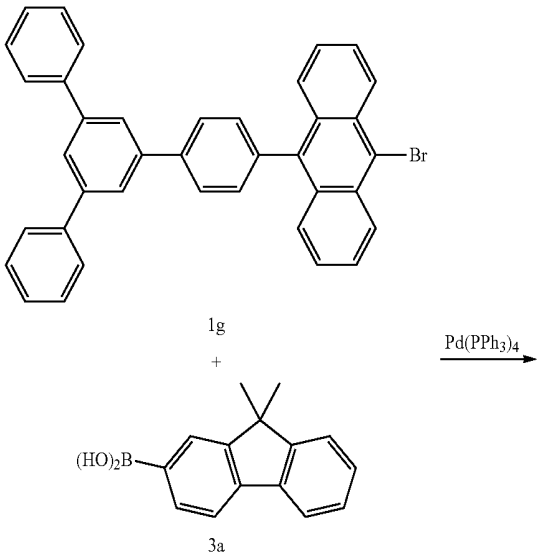
Synthesis of Compound 1

Add 1 g (9.5 g, 16.92 mmol), 1h (6.41 g, 30.51 mmol), $Pd(PPh_3)_4$ (1.5 g, 1.3 mmol), potassium carbonate (5.84 g, 42.3 mmol), toluene (150 mL) and pure water (75 mL) to a 500 ml three-necked flask. After extracting nitrogen for three times, reaction occurs at 105° C. The time of reaction stop is around 12 h, which is detected by liquid phase. The reaction solution is earth yellow of catalyst at the beginning, slowly turning into a yellow solution. After reaction stops, the upper layer is bright and light yellow, and the lower layer is water. After reaction stops, filter the solution, wash the filter residues with ethyl acetate until no product in the residue, then collect the filtrate, spin-dry, to separate out a large amount of off white solid. Collect the filter residue to dry, to get the target product, with purity of 98%; after vacuum sublimation, gray-white solid powder with purity of 99.5% is obtained.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.10-8.21 (d, 2H), 7.96-7.98 (dd, 3H), 7.87-7.89 (m, 2H), 7.81-7.86 (m, 4H), 7.78-7.81 (d, 4H), 7.62-7.65 (m, 2H), 7.59 (s, 1H), 7.51-7.57 (m, 5H), 7.45-7.48 (m, 2H), 7.36-7.43 (m, 7H), 3.88 (s, 2H).

Embodiment 2

Synthesis of Compound 3



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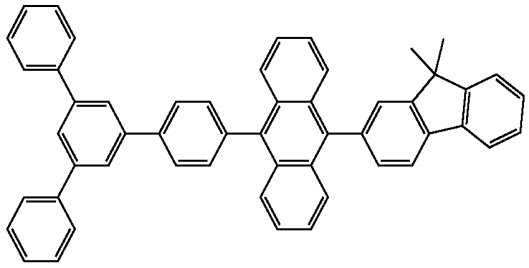


3

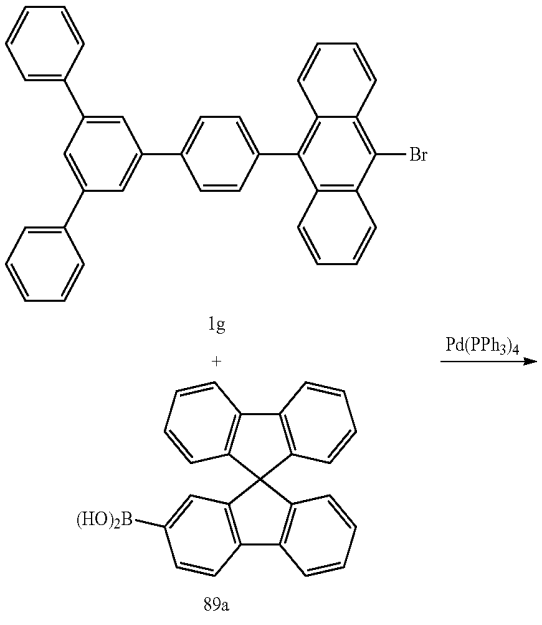
Add 1 g (9.5 g, 16.92 mmol), 3a (7.25 g, 30.46 mmol), $Pd(PPh_3)_4$ (1.5 g, 1.3 mmol), potassium carbonate (5.84 g, 42.3 mmol), toluene (150 mL) and pure water (75 mL) to a 500 ml three-necked flask. After extracting nitrogen for three times, reaction occurs at 105° C. The time of reaction stop is around 12 h, which is detected by liquid phase.

The reaction solution is earth yellow of catalyst at the beginning, slowly turning into a yellow solution. After reaction stops, the upper layer is bright and light yellow, and the lower layer is water. After reaction stops, filter the solution, wash the filter residues with ethyl acetate until no product in the residue, then collect the filtrate, spin-dry, to separate out a large amount of off white solid. Collect the filter residue to dry, to get the target product, with purity of 98%; after vacuum sublimation, gray-white solid powder with purity of 99.7% is obtained.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.1-8.2 (d, 2H), 7.96-7.99 (dd, 3H), 7.88-7.89 (m, 2H), 7.81-7.86 (m, 4H), 7.78-7.81 (d, 4H), 7.61-7.65 (m, 2H), 7.59 (s, 1H), 7.51-7.56 (m, 5H), 7.46-7.48 (m, 2H), 7.35-7.43 (m, 7H), 1.61 (s, 6H).

Embodiment 3

Synthesis of Compound 89



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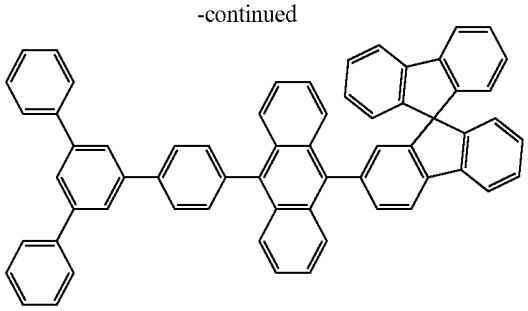


89

Add 1 g (10.0 g, 17.8 mmol), 89a (7.1 g, 19.6 mmol), $Pd(PPh_3)_4$ (432.2 mg, 0.35 mmol), K2CO3 (6.14 g, 44.5 mmol), toluene (300 mL) and water (150 mL) successively to a reaction tank. After deoxygenization of the device and introduction of nitrogen, heat to 100° C. for reaction overnight, apply to the plates at a ratio of DCM:PE=1:5. The product gives out intensive blue light under UV light at 365 nm wavelength, with the Rf value at about 0.2. Perform suction filtration with the reaction solution, wash the filter cake with ethyl acetate (100 mL) twice and separate. Extract the aqueous layer with ethyl acetate (100 mL) once, combine the organic layers, then wash the organic layer once with water (200 mL). spin dry to remove the solvent. The crude product is recrystallized from 120 ml DCM/MeOH, then suction filtration is performed to get 13.1 g yellow solid powder, with a purity of 98.7% and a yield of 92.2% yield. After vacuum sublimation, a slight yellow solid powder with purity of 99.7% is obtained. m/z=797.

As shown from FIG. **2** and FIG. **3**, the hydrogen spectra and carbon spectra of compound 89 are completely consistent with the structures. From the high performance liquid chromatogram of compound 89 in FIG. **4**, the product made by the synthesis method in the invention has high purity. According to the thermal gravametric analysis of compound 89 in FIG. **5**, the decomposition temperature of this type of compound is higher than 400 degrees centigrade, indicating that it has very high thermal stability.

Embodiment 4

Preparation of OLED1

Prepare OLED by the Organic Electronic Material in the Present Invention

Firstly, the ITO transparent conductive glass substrate **10** (with anode **20** above) is washed with detergent solution and deionized water, ethanol, acetone, deionized water in sequence, then treated with oxygen plasma for 30 seconds.

Then, perform vacuum evaporation of 10 nm HAT-CN_6 in ITO, which is used as the hole injection layer **30**.

Then, perform vacuum evaporation of NPB, to form 30 nm thick of hole transport layer **40**.

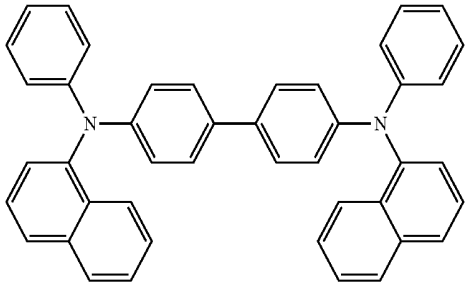
Then, perform vacuum evaporation of 30 nm thick of compound 3 in hole transport layer, which is used as light emitting layer **50**.

And then, perform vacuum evaporation of 15 nm thick of TPBi in light emitting layer, which is used as electron transport layer **60**.

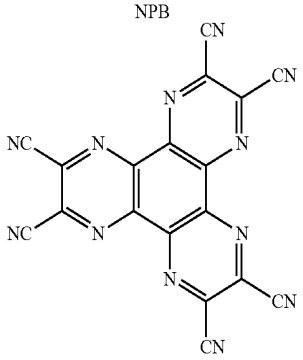
Finally, perform vacuum evaporation of 15 nm BPhen:Li as electron injection layer **70**, and vacuum evaporation of 150 nm Al as the device cathode **80**.

The voltage of the device made in 20 mA/cm2 of operating current density is 3.58 V, the current efficiency is 3.21 cd/A. The CIEy at the luminance of 1000 cd/m2 is 0.0853. It emits blue light.

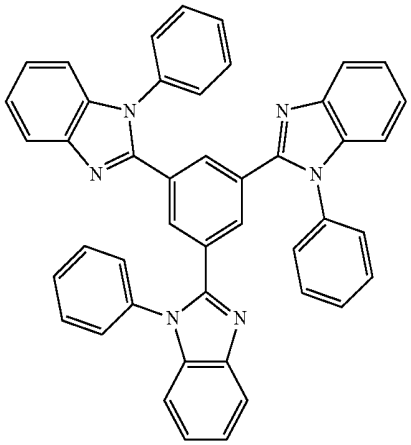
The Said Structural Formula of the Device



NPB



HAT—CN_6



TPBi

Embodiment 5

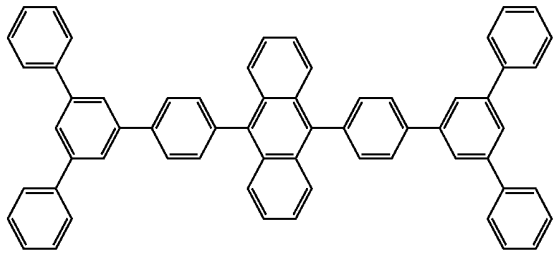
Preparation of OLED2

Procedures are the same as Embodiment 4. OLED is made using compound 89 instead of compound 3 The voltage of the device made in 20 mA/cm2 of operating current density is 3.84 V, the current efficiency is 2.83 cd/A. The CIEy at the luminance of 1000 cd/m2 is 0.0888. It emits blue light.

Comparative Example 1

The procedures are the same as Embodiment 4. OLED is made using the following compound TAT instead of compound 3, for comparison.

TAT Structural Formula



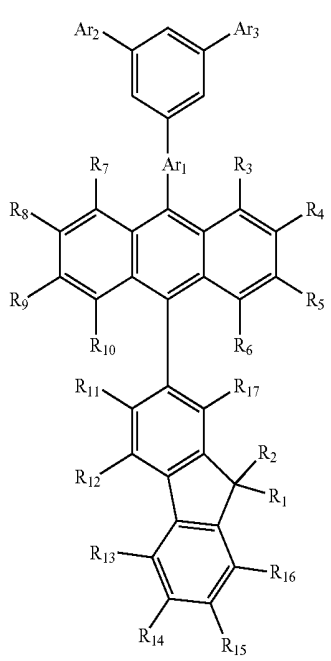
TAT

The voltage of the device made in 20 mA/cm2 of operating current density is 4.00 V, the current efficiency is 2.46 cd/A. The CIEy at the luminance of 1000 cd/m2 is 0.0952. It emits blue light.

The embodiments 4 and 5 are the specific applications of the material in the present invention. The blue light-emitting, efficiency and luminance of the devices are higher than those in the comparison example. Therefore, as stated above, the material in the present invention has high stability, and the OLED made in the invention has high efficiency and light purity.

The invention claimed is:

1. An organic electronic material comprising the following structural formula (I):



(I)

Wherein

R_1-R_{17} independently represent hydrogen, halogen, cyano, nitro, C_1-C_8 alkyl, C_1-C_8 alkoxy, C_2-C_8 substituted or unsubstituted alkenyl, C_2-C_8 substituted or an unsubstituted alkynyl, C_1-C_4 alkyl substituted or unsubstituted phenyl, C_1-C_4 alkyl substituted or unsubstituted naphthyl, or combined C_1-C_4 alkyl substituted or unsubstituted fluorenyl; and

Ar_1-Ar_3 independently represent C_1-C_4 alkyl substituted phenyl, phenyl, pyridyl.

2. The organic electronic material according to claim **1**, wherein

R_1-R_2 independently and preferably represent hydrogen, halogen, C_1-C_4 alkyl, C_1-C_4 alkyl substituted or unsubstituted phenyl, C_1-C_4 alkyl substituted or unsubstituted naphthyl, or combined C_1-C_4 alkyl-substituted or unsubstituted fluorenyl; and

R_3-R_{17} may independently represent hydrogen, halogen, C_1-C_4 alkyl, C_1-C_4 alkyl substituted or unsubstituted phenyl, C_1-C_4 alkyl-substituted or unsubstituted naphthyl, preferably Ar_1-Ar_3 independently represent phenyl, tolyl, xylyl, t-butylphenyl.

3. The organic electronic material according to claim **2**, wherein

R_3-R_{17} preferably represents hydrogen, and

R_1 and R_2 may independently represent hydrogen, methyl, ethyl, propyl, isopropyl, t-butyl, phenyl, biphenyl, naphthyl, or combined fluorenyl; Ar_1-Ar_3 may independently represent phenyl, pyridyl, tolyl, xylyl.

4. The organic electronic material according to claim **3**, wherein

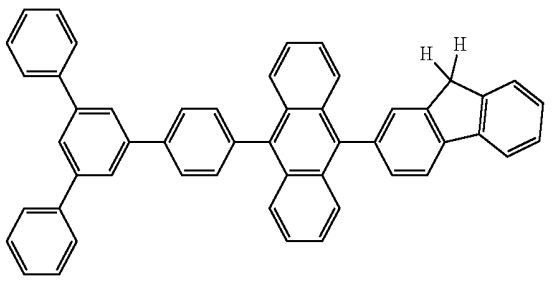
R_3-R_{17} represent hydrogen preferably;

R_1, R_2 independently represent hydrogen, methyl or combined fluorenyl; and

Ar_1, Ar_2, Ar_3 independently represent phenyl.

5. The organic electronic material according to claim **1**, wherein its structure is as follows:

1



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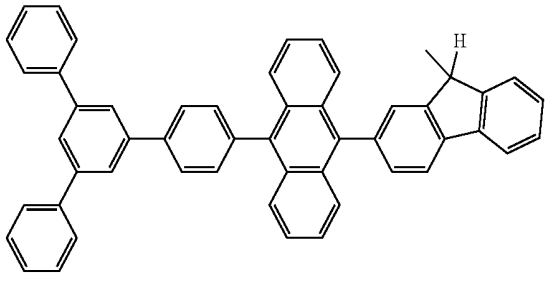

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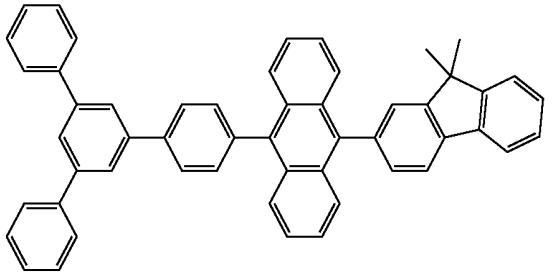

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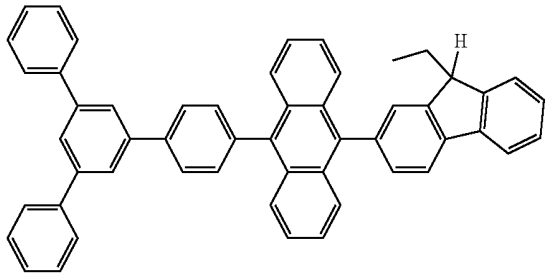

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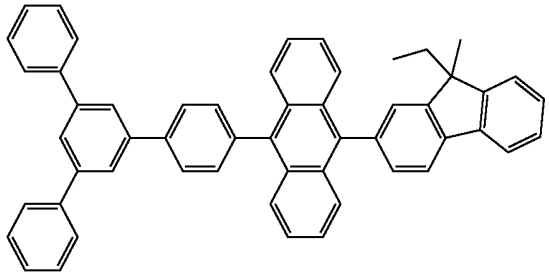

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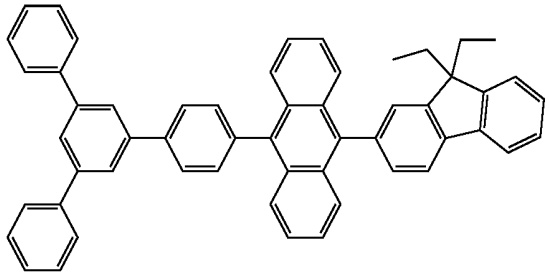

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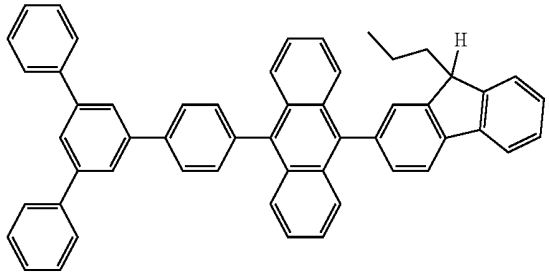

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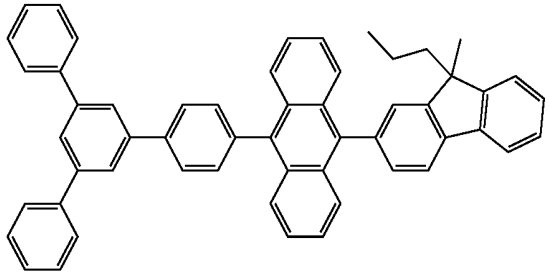

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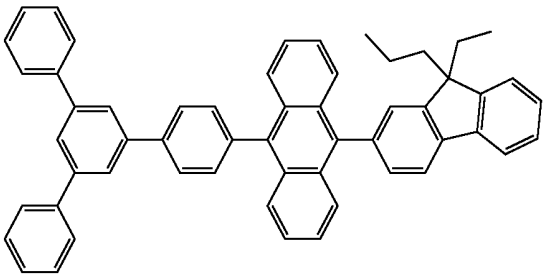

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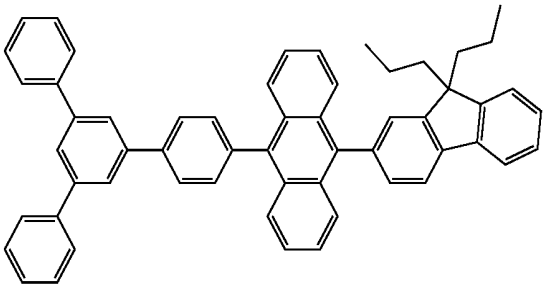

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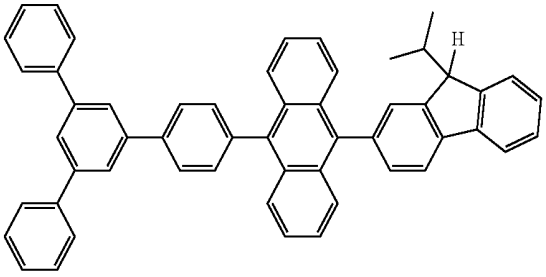

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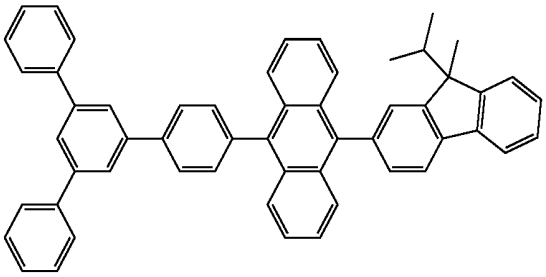

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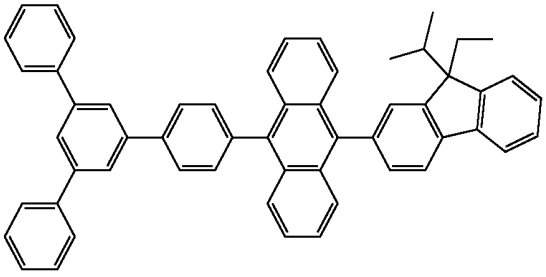

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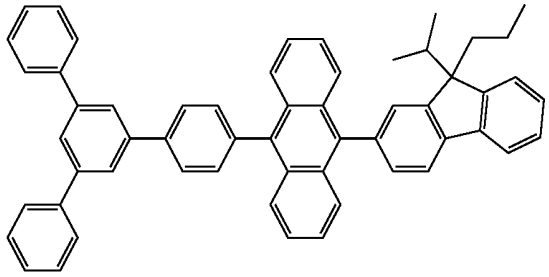

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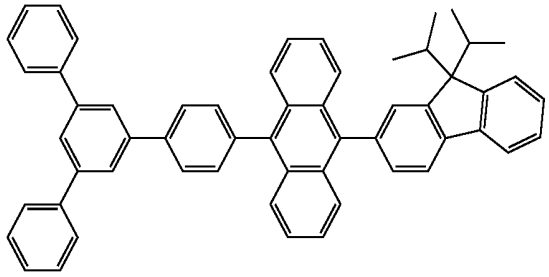

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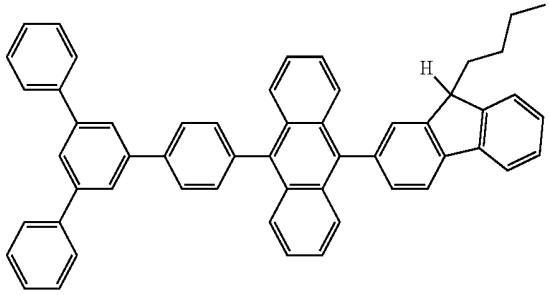

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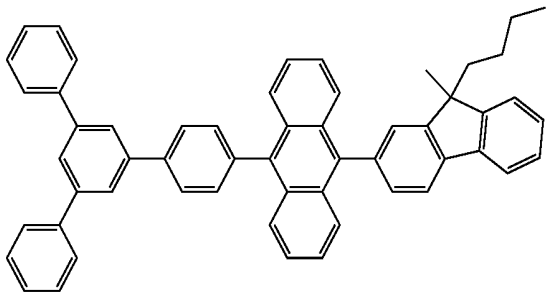

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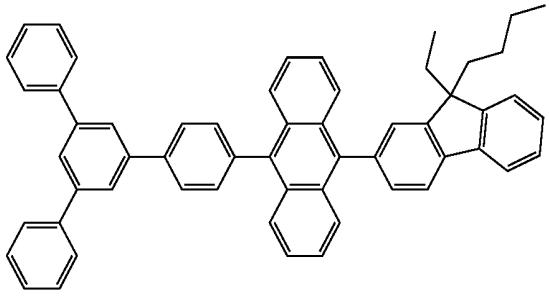

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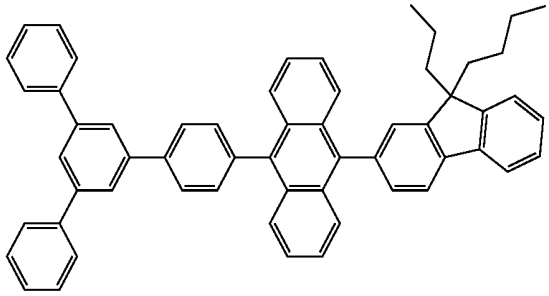

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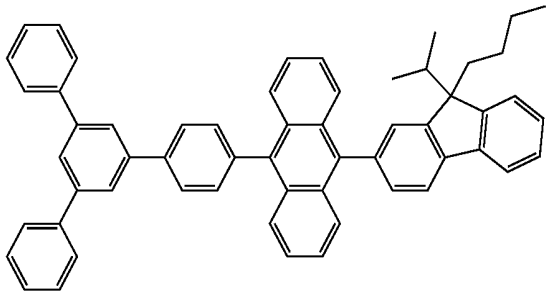

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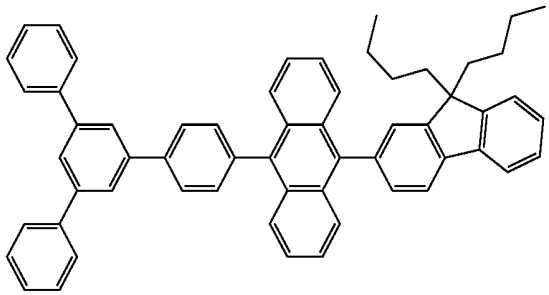

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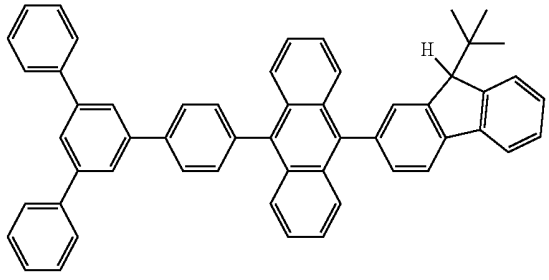

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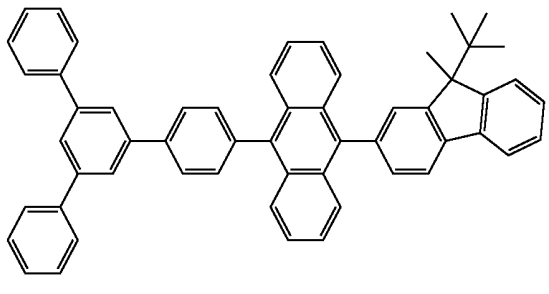

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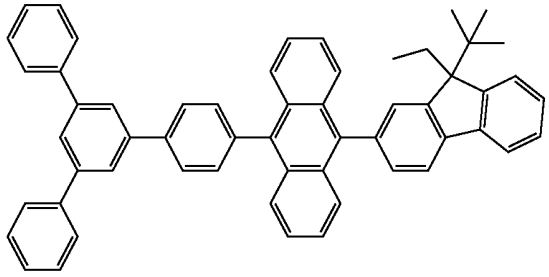

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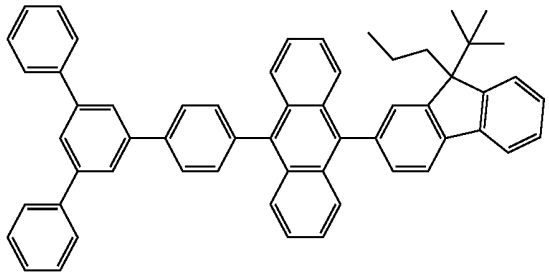

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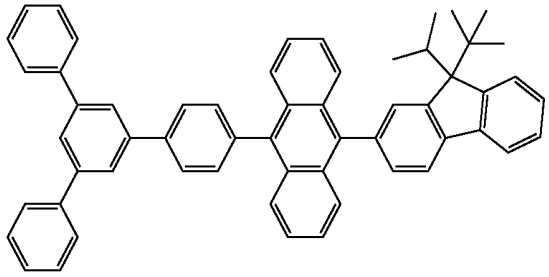

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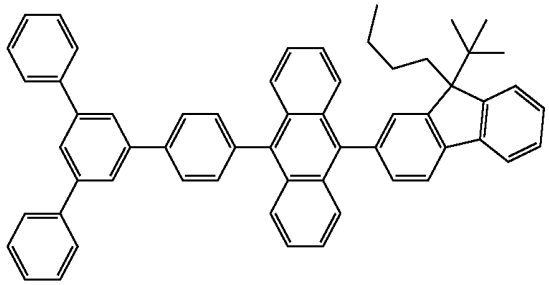

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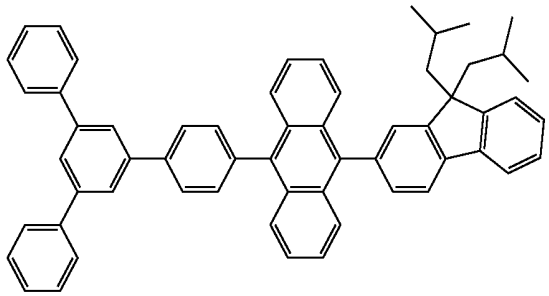

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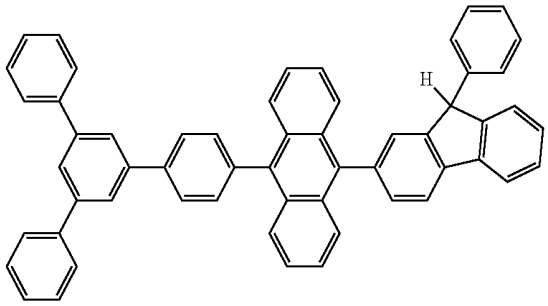

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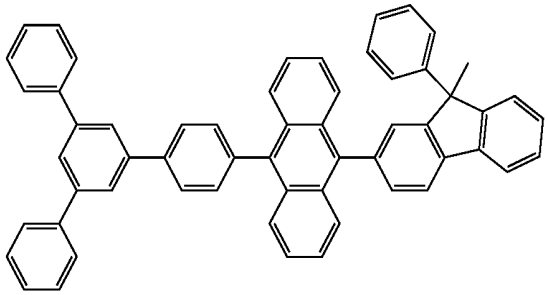

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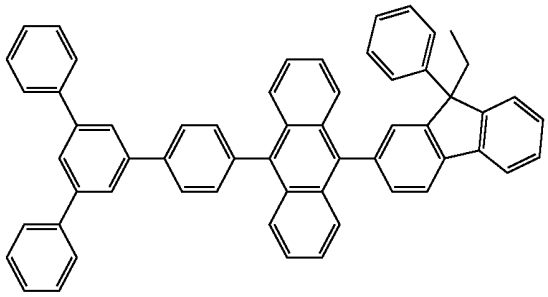

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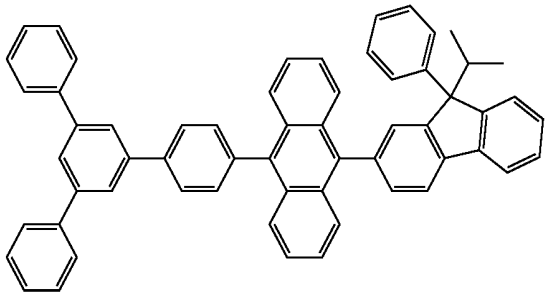

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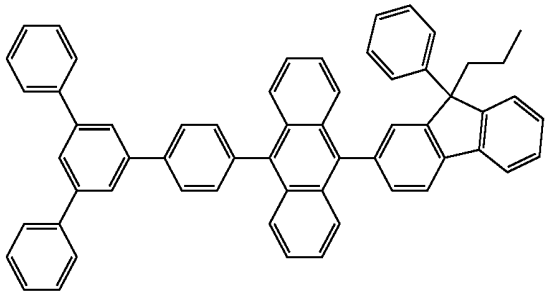

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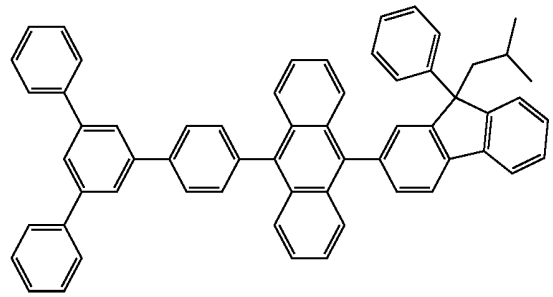

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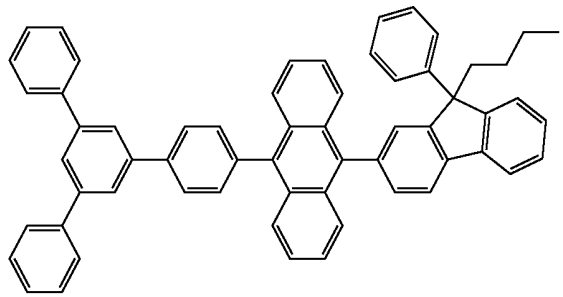

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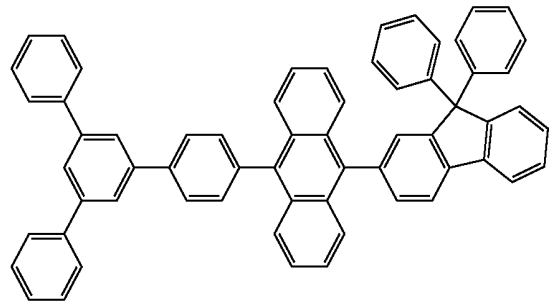

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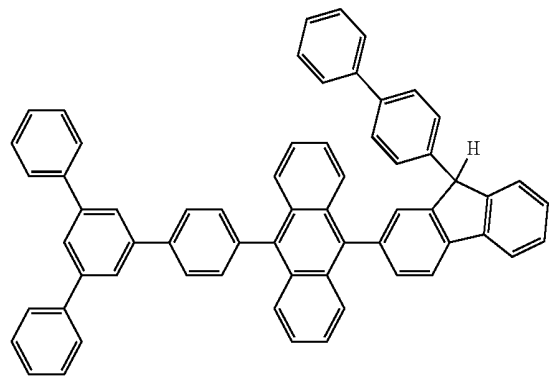

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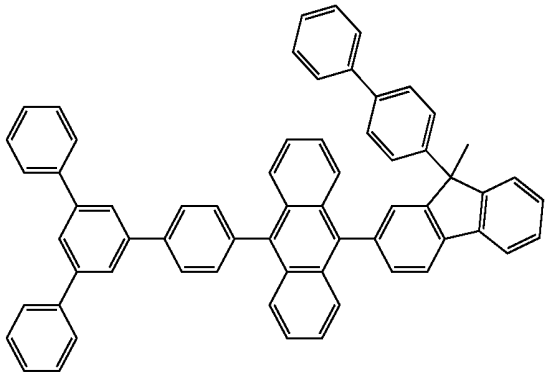

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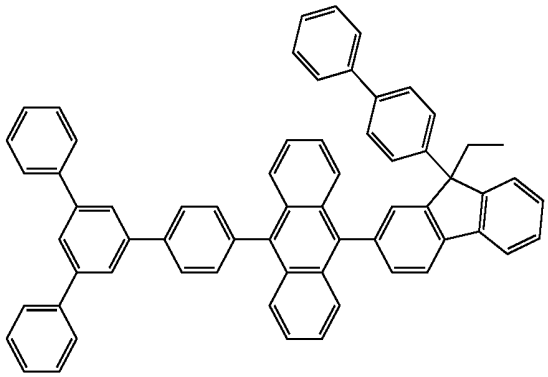

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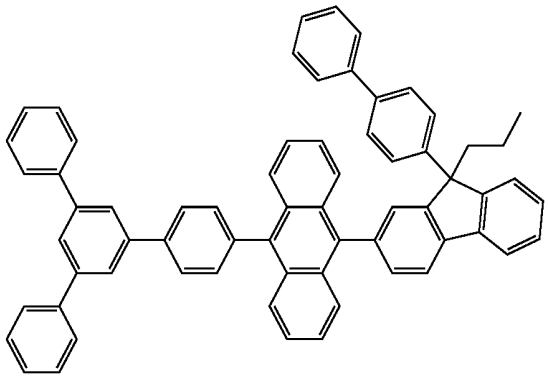

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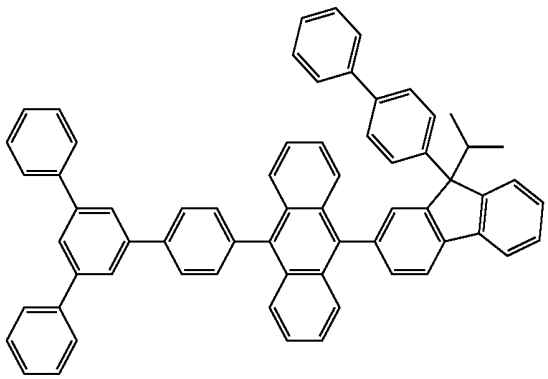

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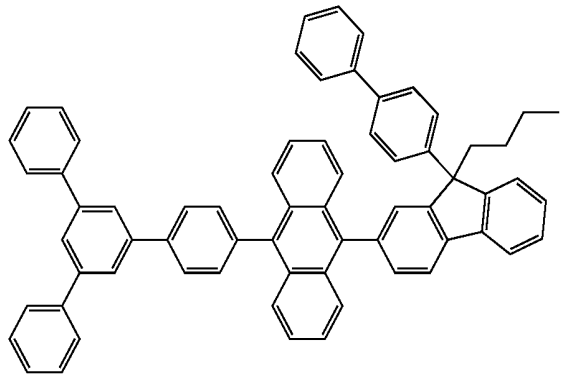

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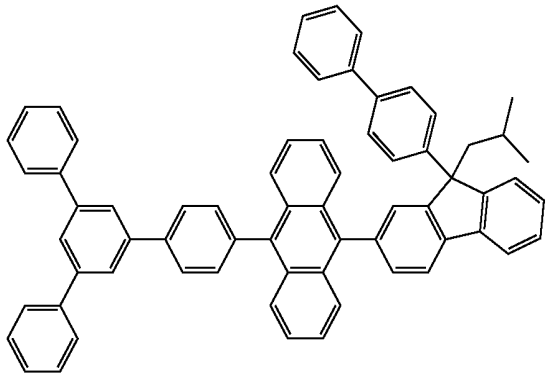

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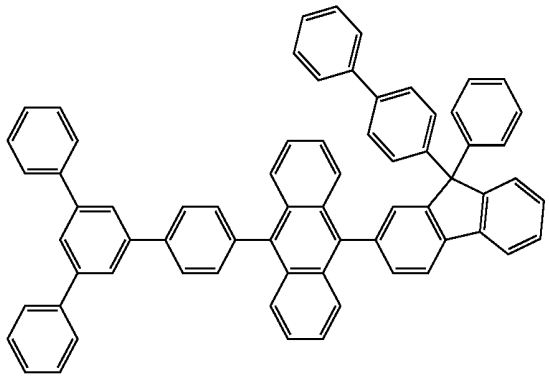

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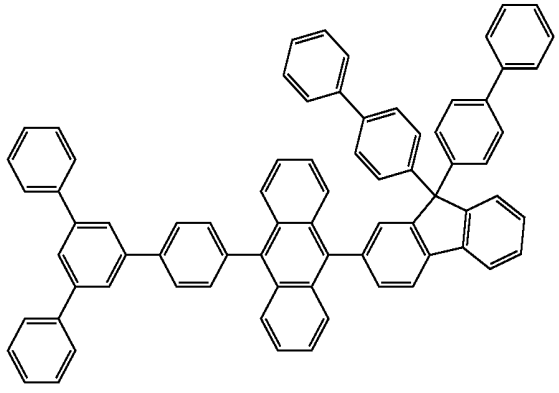

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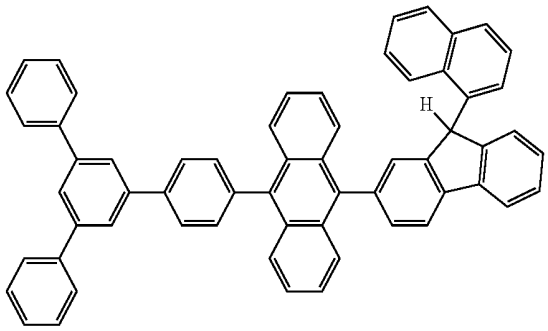

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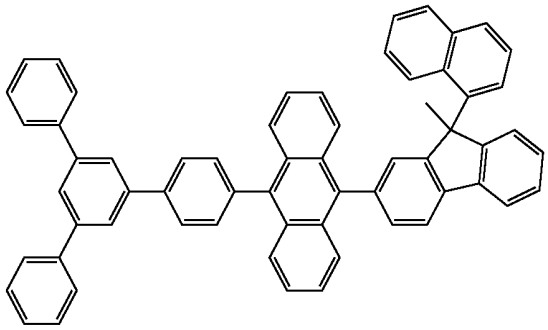

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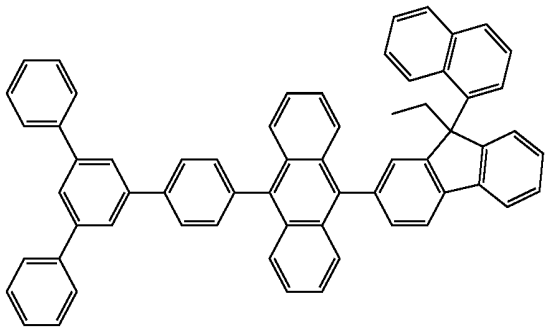

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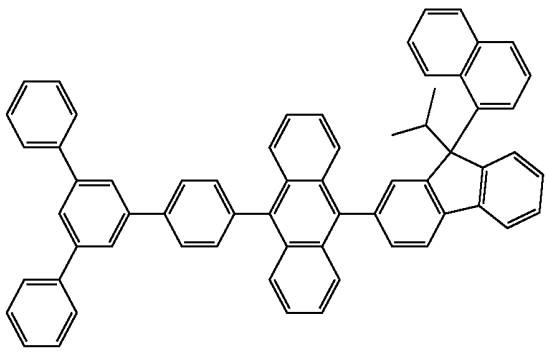

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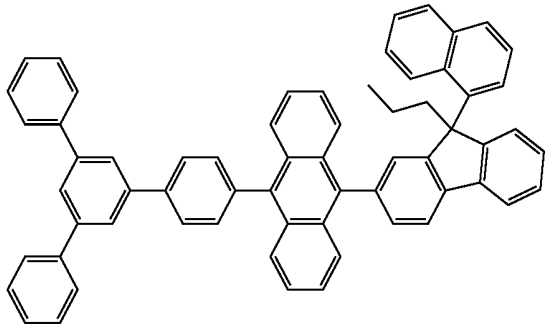

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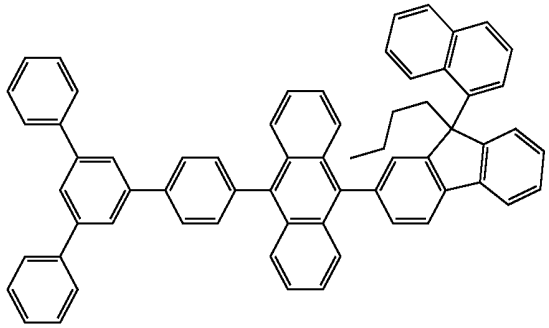

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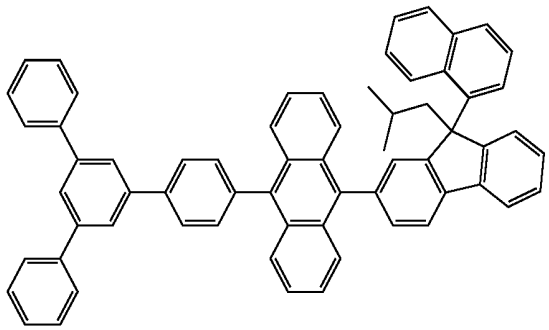

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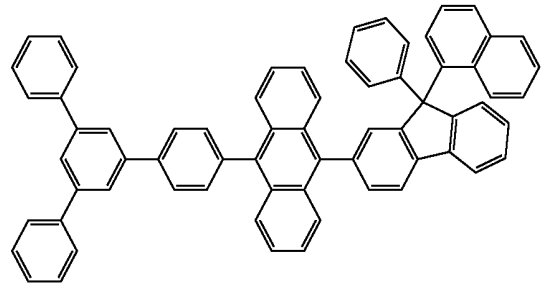

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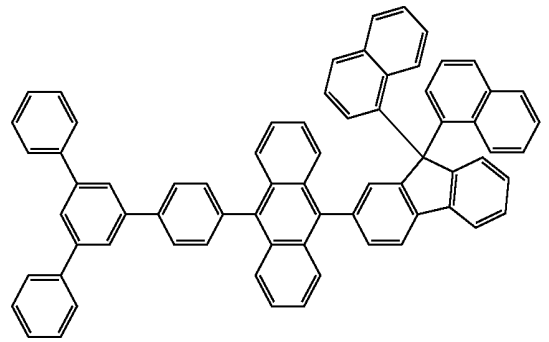

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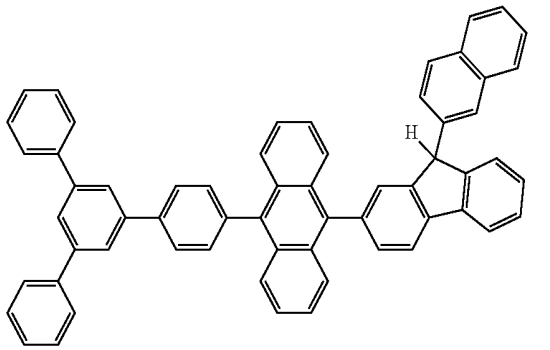

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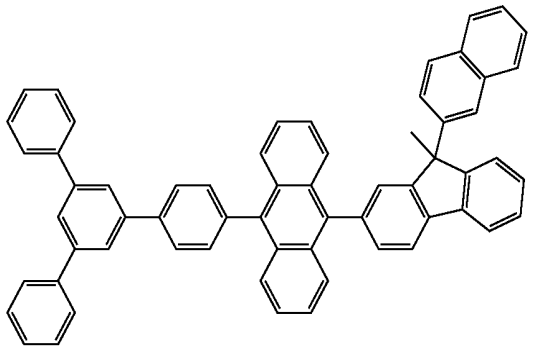

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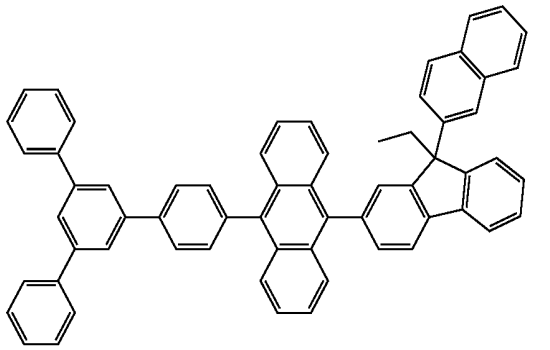

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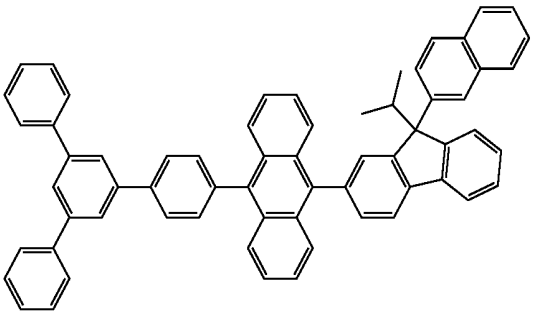

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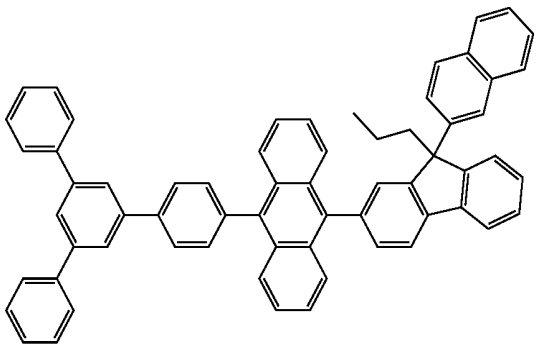

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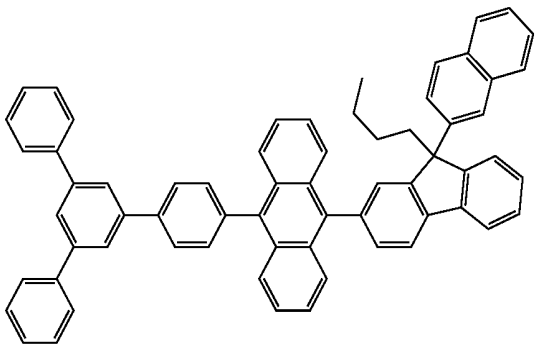

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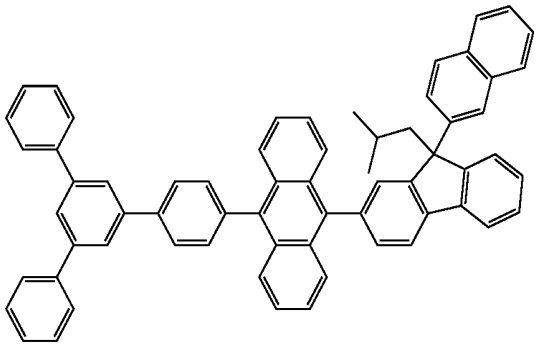

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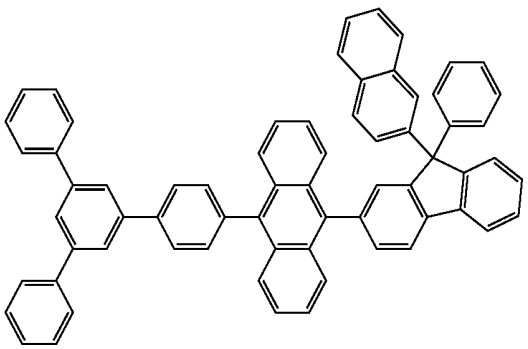

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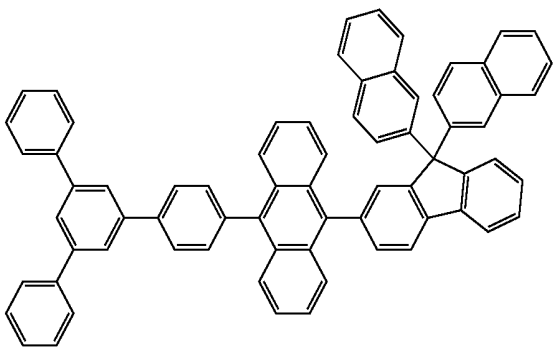

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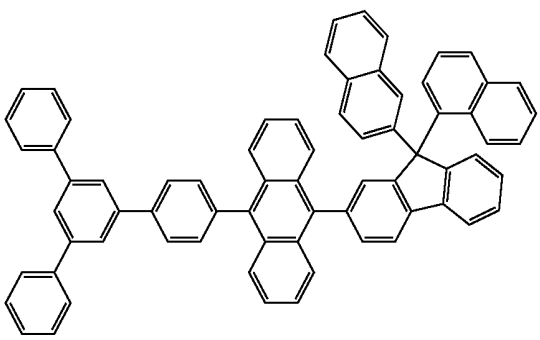

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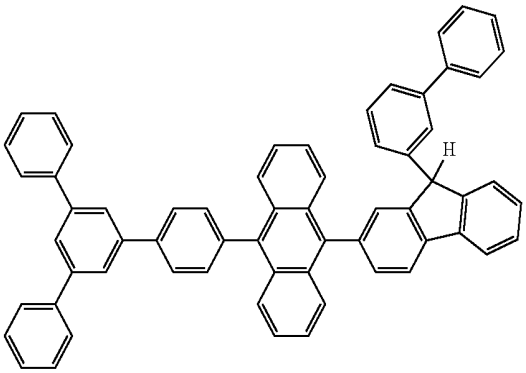

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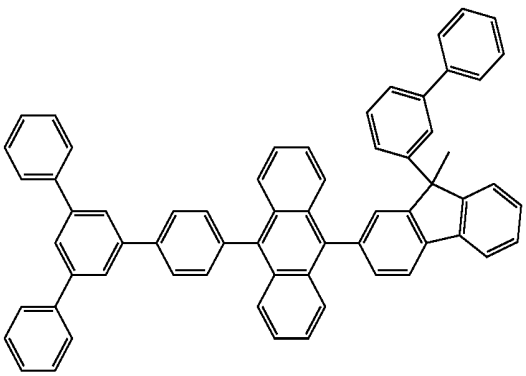

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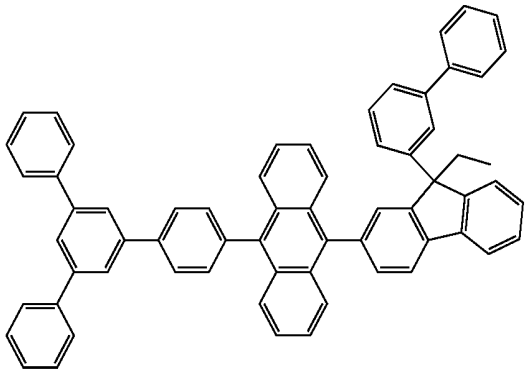

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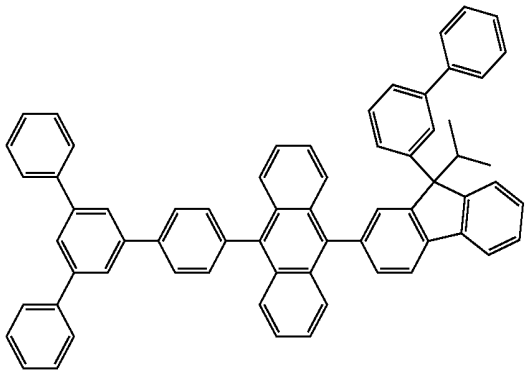

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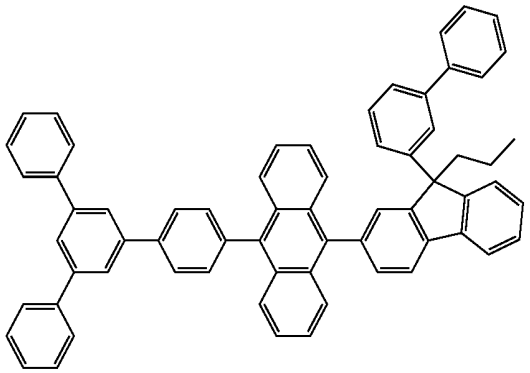

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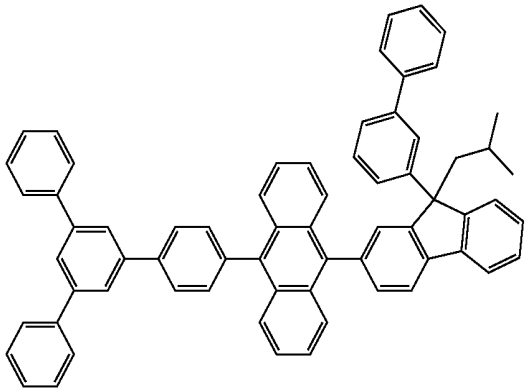

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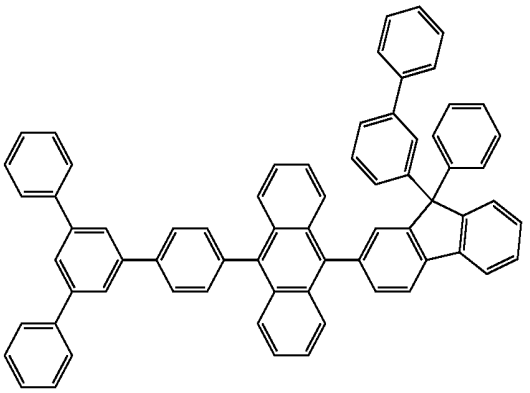

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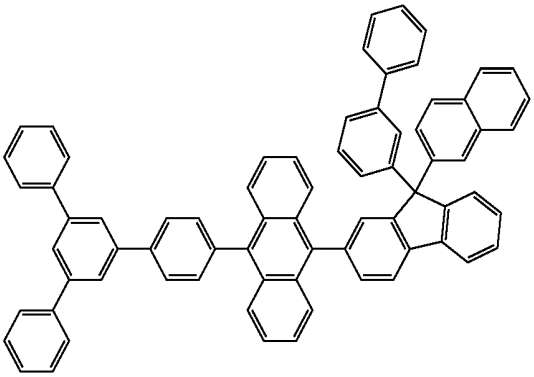

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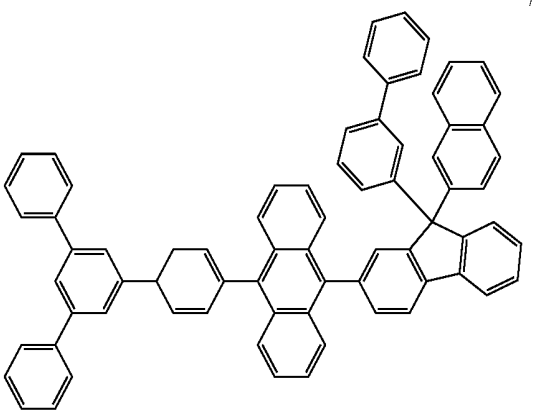

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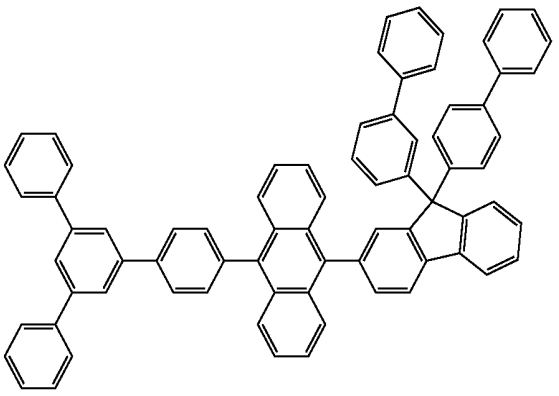

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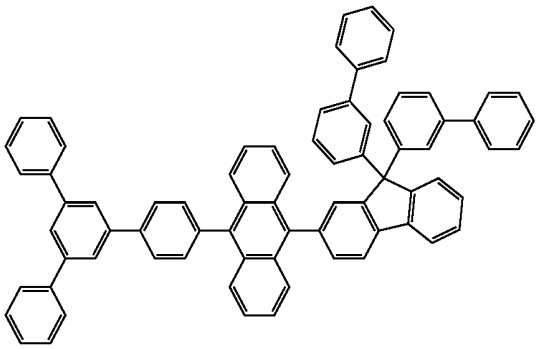

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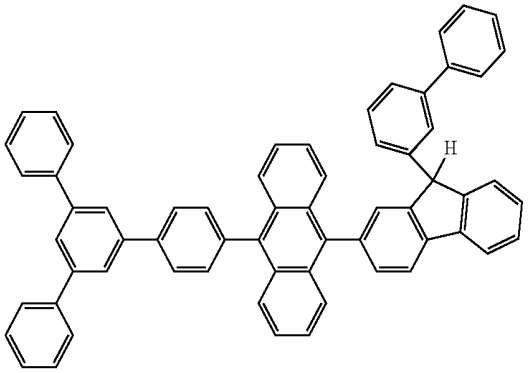

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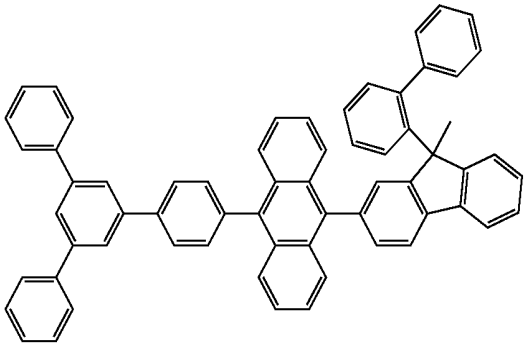

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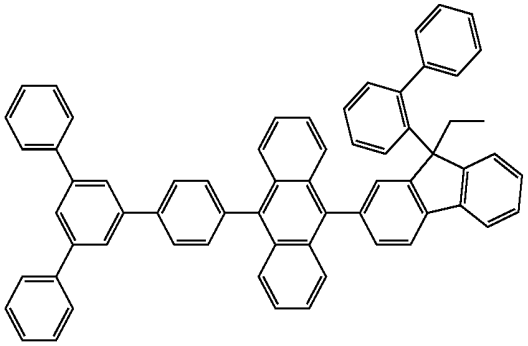

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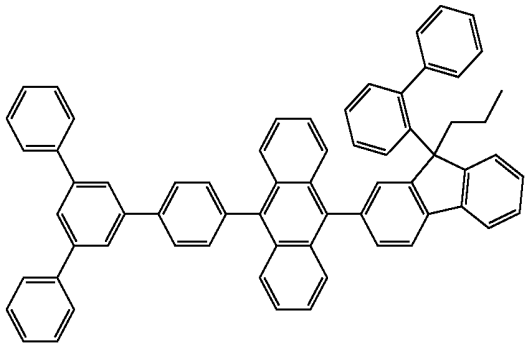

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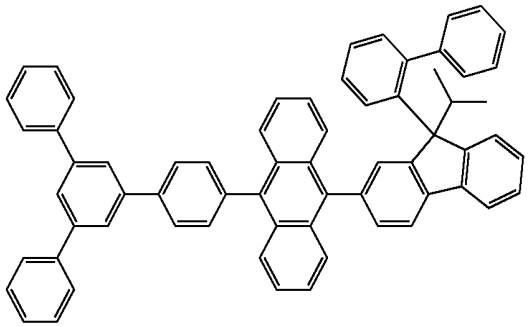

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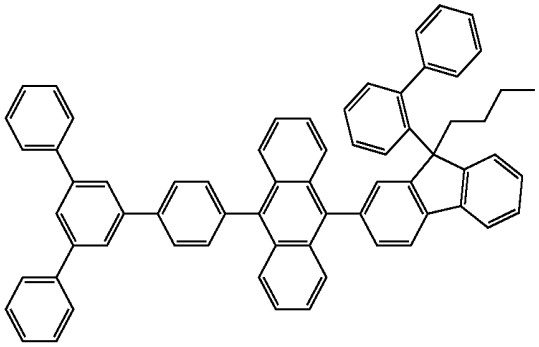

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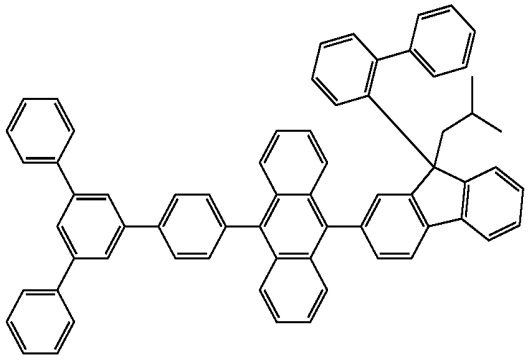

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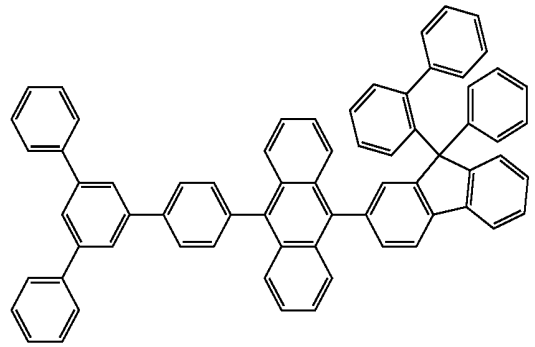

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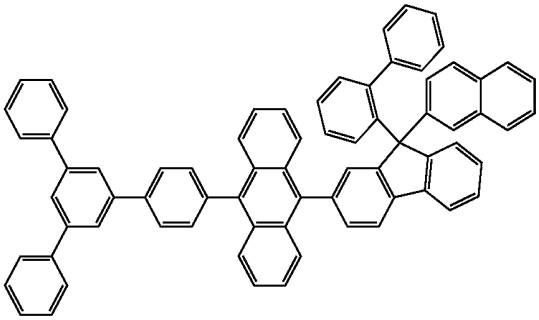

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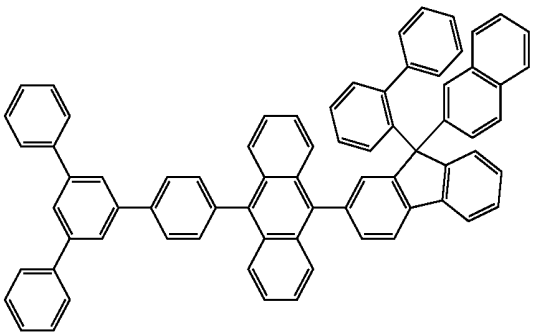

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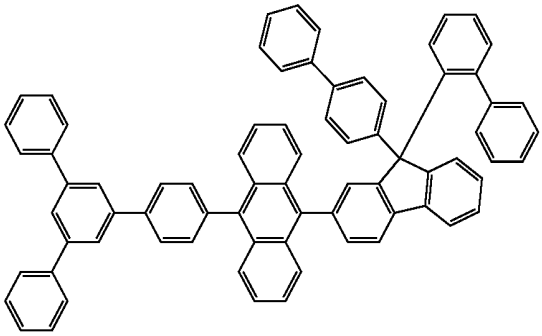

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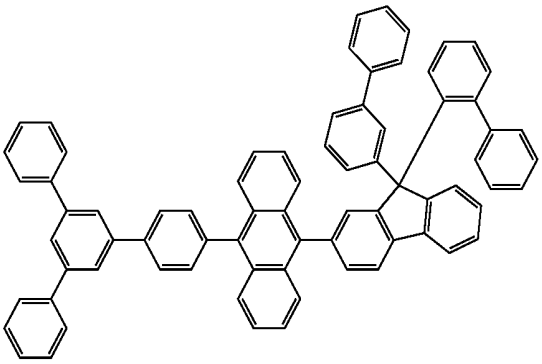

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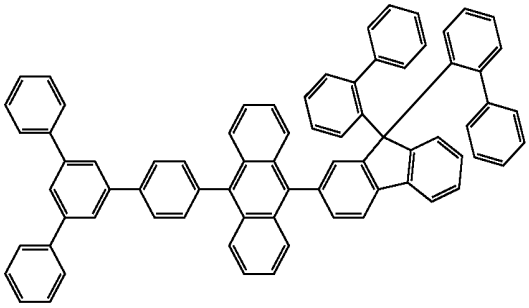

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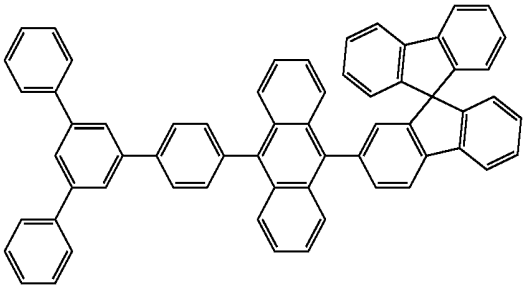

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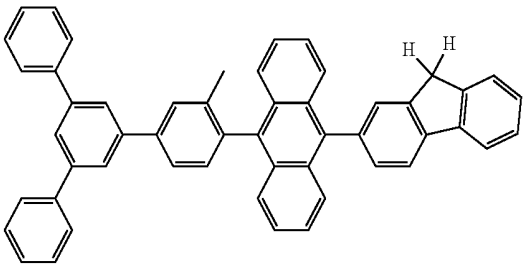

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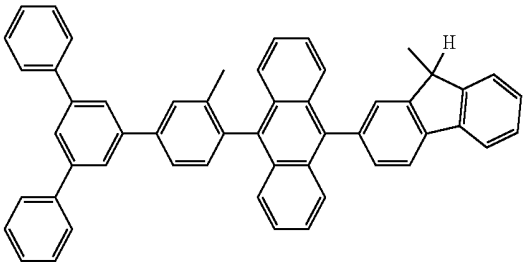

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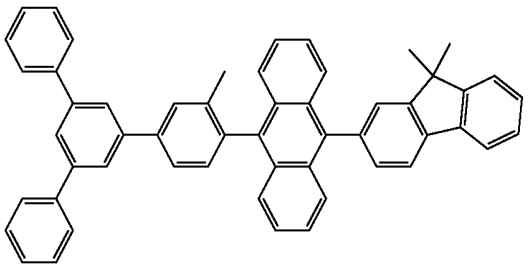

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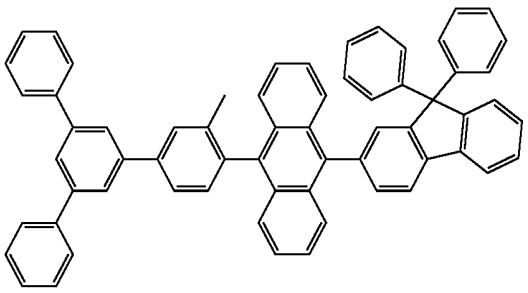

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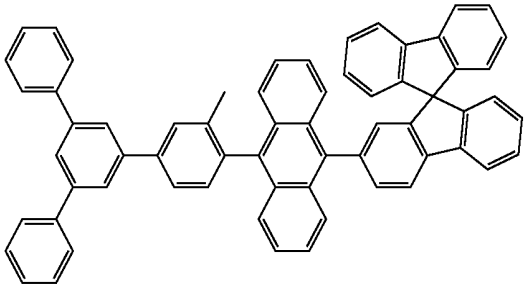

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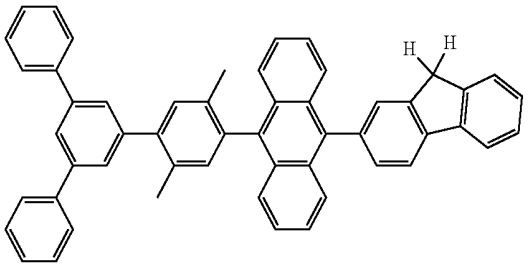

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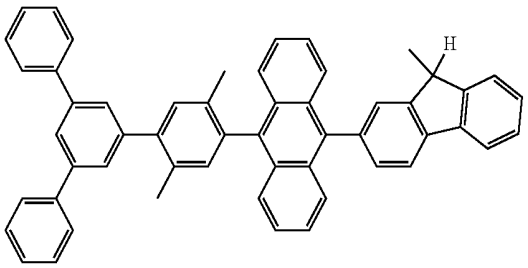

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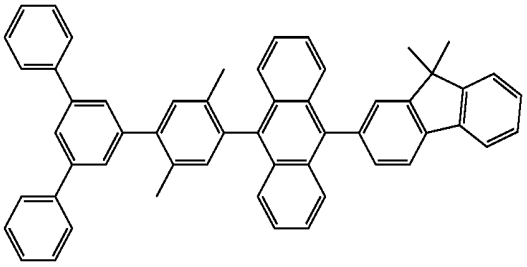

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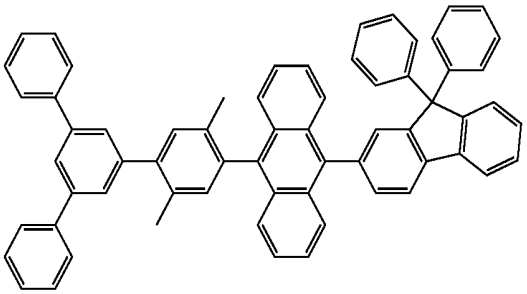

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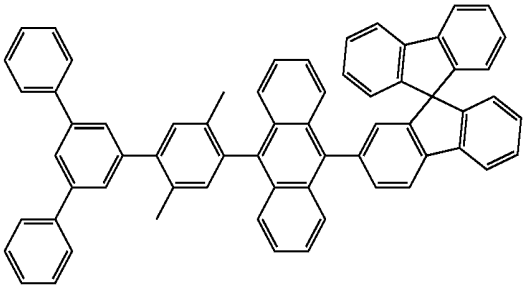

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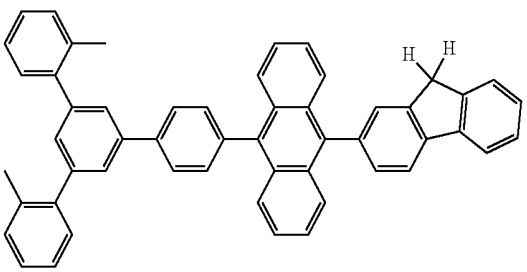

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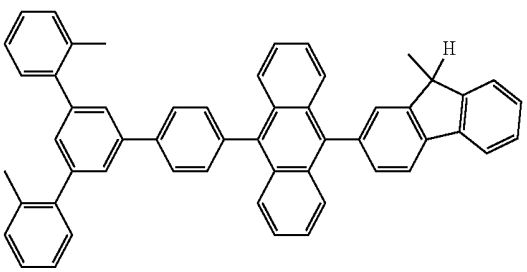

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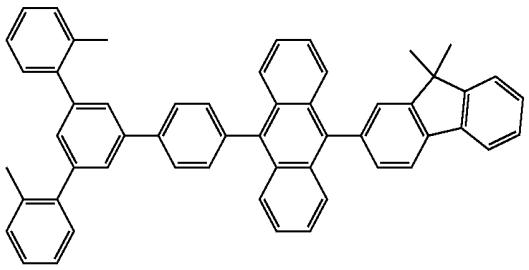

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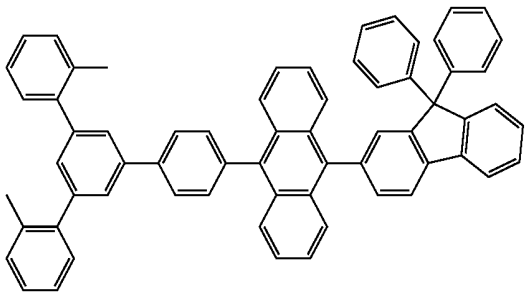

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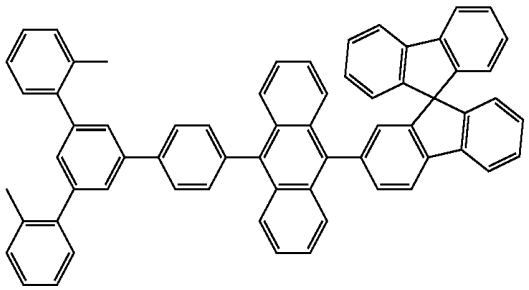

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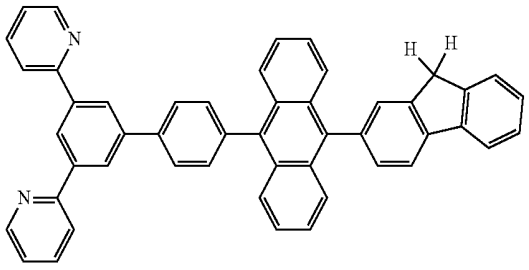

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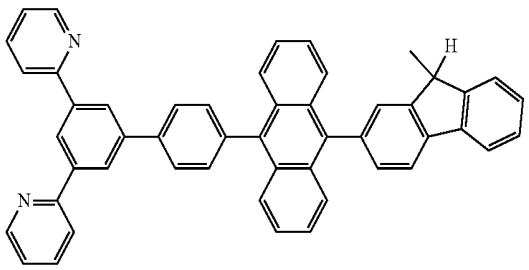

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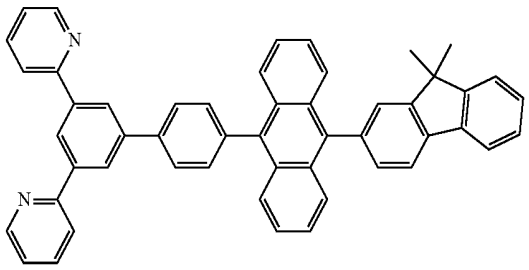

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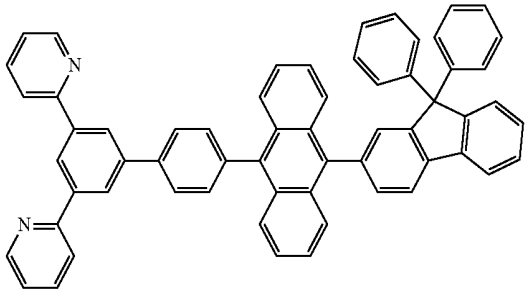

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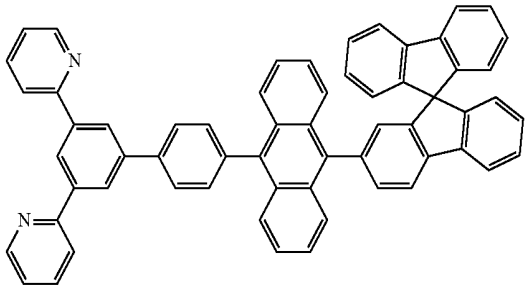

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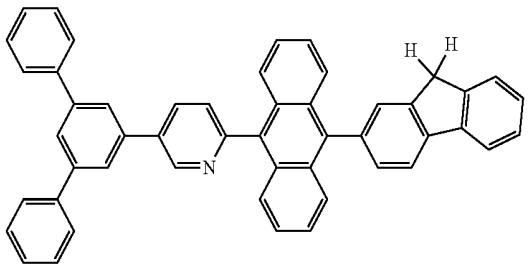

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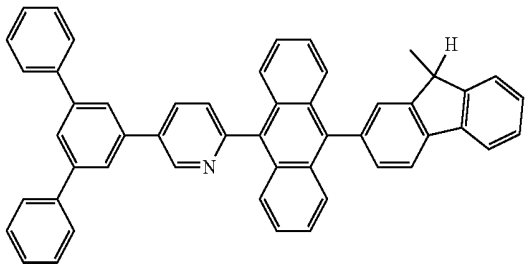

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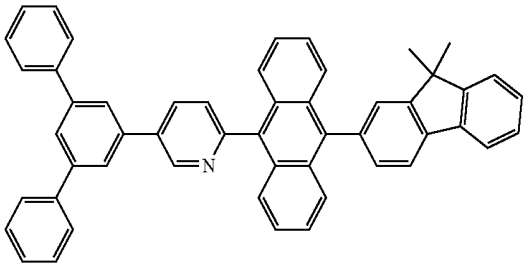

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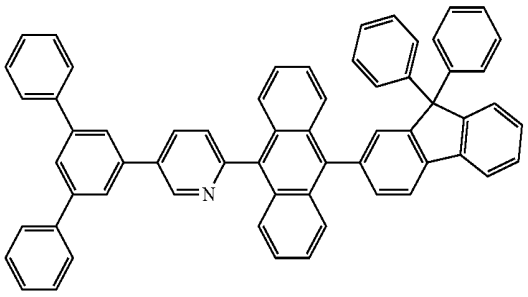

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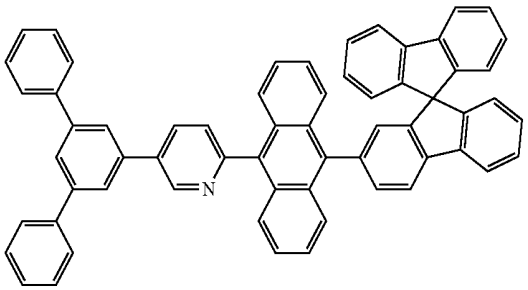

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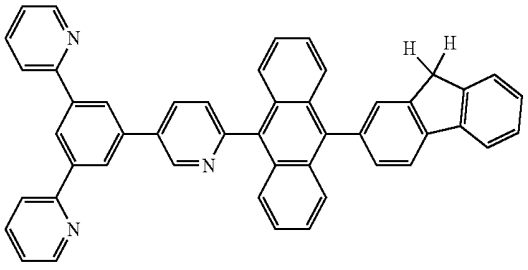

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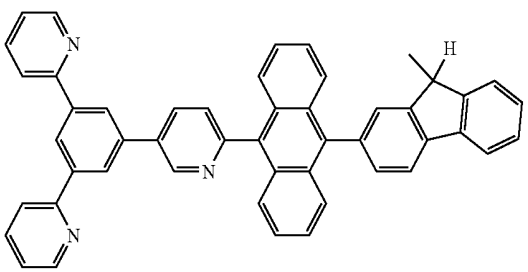

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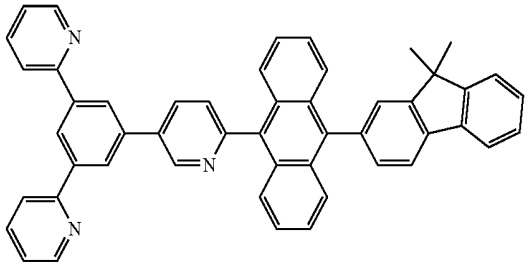

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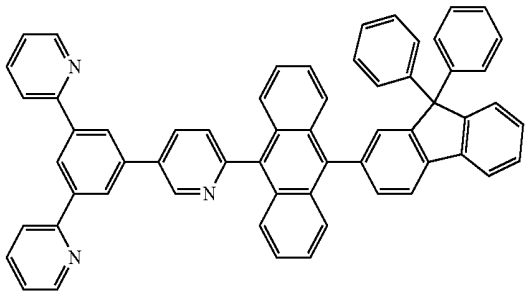

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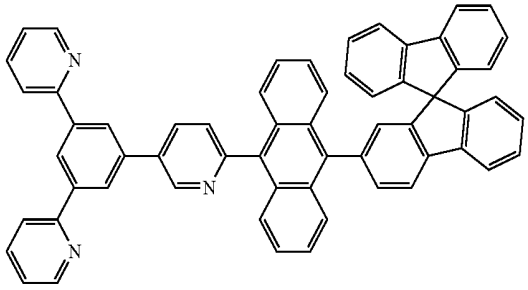

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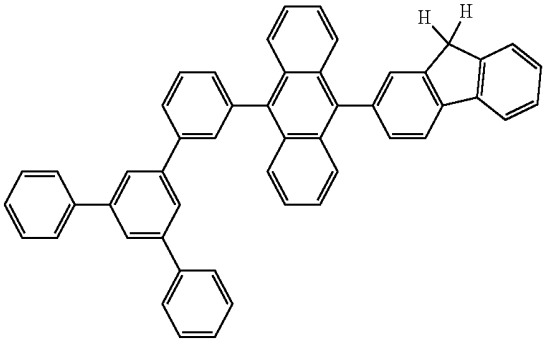

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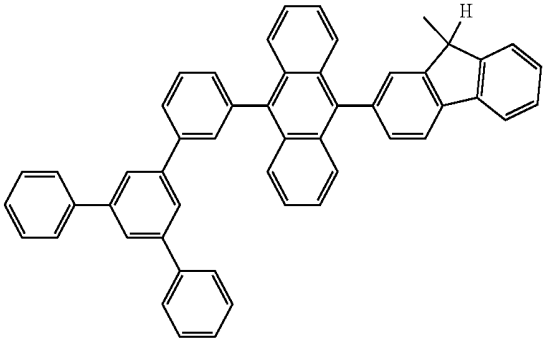

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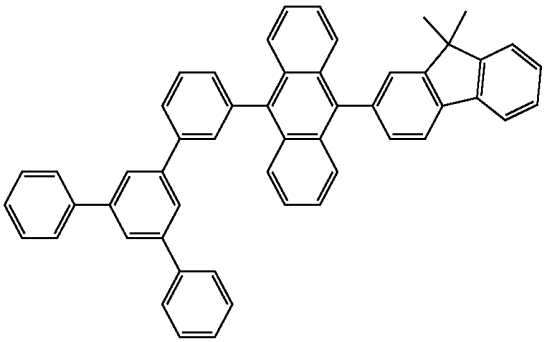

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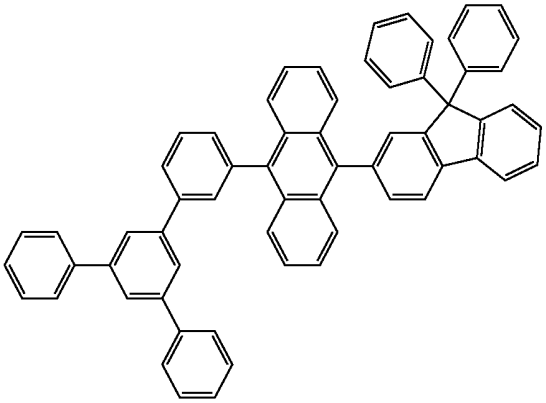

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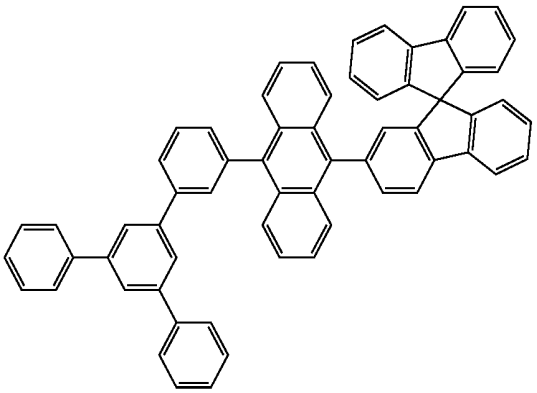
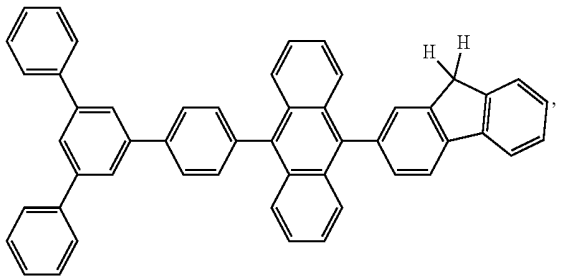


6. The organic electronic material according to claim 5, wherein its structure is as follows:

1



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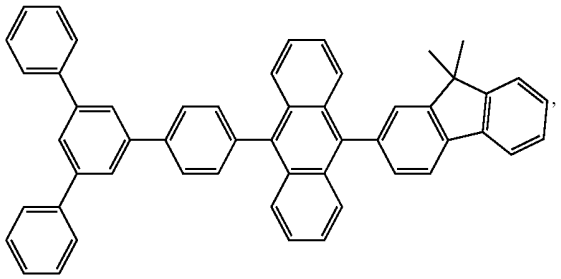

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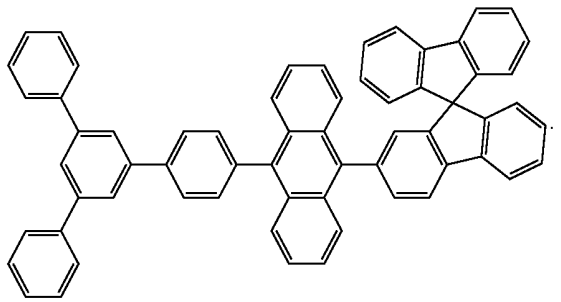

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专利名称(译)	有机电子材料		
公开(公告)号	US10347843	公开(公告)日	2019-07-09
申请号	US15/557097	申请日	2015-09-01
[标]申请(专利权)人(译)	广东阿格蕾雅光电材料有限公司 北京阿格蕾雅科技发展有限公司		
申请(专利权)人(译)	广东树兰光电子材料有限公司. 北京树兰科技发展有限公司.		
当前申请(专利权)人(译)	广东树兰光电子材料有限公司. 北京树兰科技发展有限公司.		
[标]发明人	LOW KAM HUNG LI ZHE CHEN JINXIN CAI LIFEI		
发明人	LOW, KAM-HUNG LI, ZHE CHEN, JINXIN CAI, LIFEI		
IPC分类号	H01L51/00 C07D213/16 C07C13/72 C09K11/06 C09B1/00 C07D213/06 C07C13/567 C07C13/573 H01L51/50		
CPC分类号	H01L51/0058 C07C13/573 C07C13/72 C07D213/06 C07D213/16 C09B1/00 C09K11/06 H01L51/0052 H01L51/0056 C07C13/567 Y02E10/549 C07C2603/18 C07C2603/24 C07C2603/94 C07C2603/97 C09K2211/1007 C09K2211/1011 H01L51/5012		
优先权	201510102569.3 2015-03-09 CN		
其他公开文献	US20180047909A1		
外部链接	Espacenet		

摘要(译)

本发明公开了一种“有机电子材料”，属于有机发光器件（OLED）显示材料领域。本发明的有机电子材料具有结构式（I），具有良好的热稳定性，高发光效率，高发光纯度。由这种有机发光材料制成的OLED具有有机发光效率优异，色纯度高，使用寿命长的优点。