

US00997726B2

(12) **United States Patent**
Lin et al.

(10) **Patent No.:** **US 9,997,726 B2**
(45) **Date of Patent:** **Jun. 12, 2018**

(54) **DIBENZOTHIOPHENE-CONTAINING MATERIALS IN PHOSPHORESCENT LIGHT EMITTING DIODES**

(71) Applicant: **Universal Display Corporation**,
Ewing, NJ (US)

(72) Inventors: **Chun Lin**, Langhorne, PA (US); **Alexey Dyatkin**, Ambler, PA (US); **Zeinab Elshenawy**, Holland, PA (US); **Walter Yeager**, Yardley, PA (US)

(73) Assignee: **UNIVERSAL DISPLAY CORPORATION**, Ewing, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 286 days.

(21) Appl. No.: **14/802,051**

(22) Filed: **Jul. 17, 2015**

(65) **Prior Publication Data**

US 2016/0372685 A1 Dec. 22, 2016

Related U.S. Application Data

(62) Division of application No. 14/026,868, filed on Sep. 13, 2013, now Pat. No. 9,123,903, which is a division
(Continued)

(51) **Int. Cl.**
H01L 51/50 (2006.01)
H01L 51/00 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **H01L 51/0074** (2013.01); **C07D 209/86**
(2013.01); **C07D 235/18** (2013.01);
(Continued)

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,769,292 A 9/1988 Tang et al.
5,061,569 A 10/1991 VanSlyke et al.
(Continued)

FOREIGN PATENT DOCUMENTS

EP 0650955 5/1995
EP 1725079 11/2006
(Continued)

OTHER PUBLICATIONS

Xu, et al., "Facile syntehtsis of novel monodisperse linear 3,9-linked oligocarbazoles," Tetrahedron Letters 46 (2005) p. 6883-6886.

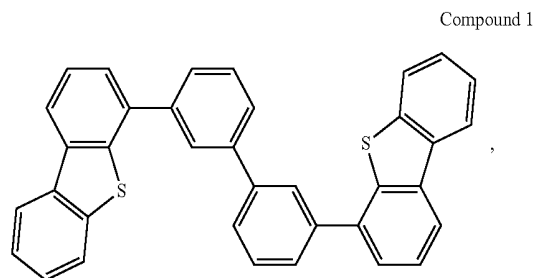
(Continued)

Primary Examiner — Gregory D Clark

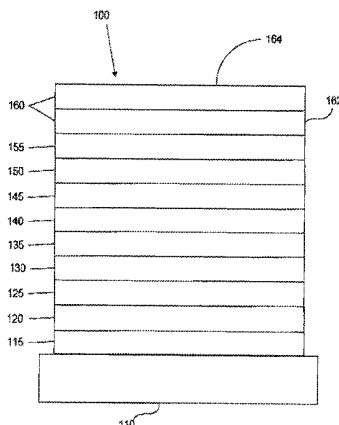
(74) *Attorney, Agent, or Firm* — Duane Morris LLC

(57) **ABSTRACT**

An organic light emitting device that includes an anode, a cathode, and an emissive layer that includes an organic compound selected from

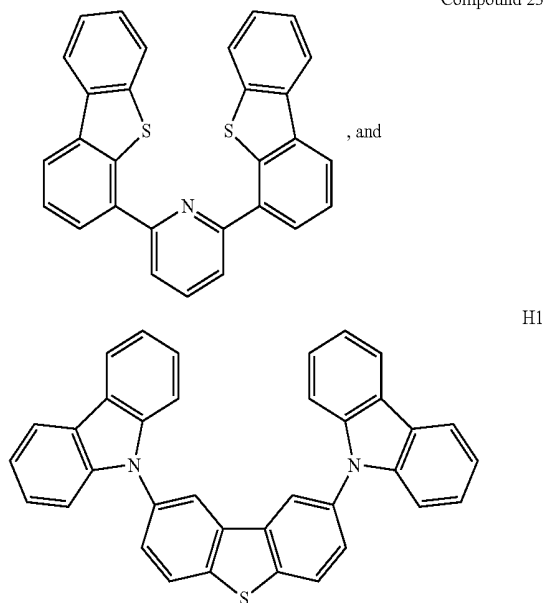


(Continued)



-continued

Compound 23



and at least one emissive dopant. The emissive dopant can be one of a variety of organometallic iridium complexes.

11 Claims, 14 Drawing Sheets

Related U.S. Application Data

of application No. 13/186,204, filed on Jul. 19, 2011, now Pat. No. 8,580,402, which is a division of application No. 12/208,907, filed on Sep. 11, 2008, now Pat. No. 8,007,927.

(60) Provisional application No. 61/017,480, filed on Dec. 28, 2007.

(51) Int. Cl.

C07D 209/86 (2006.01)
C07D 235/18 (2006.01)
C07D 235/20 (2006.01)
C07D 333/76 (2006.01)
C07D 405/14 (2006.01)
C07D 409/10 (2006.01)
C07D 409/14 (2006.01)
C07D 413/10 (2006.01)
C07D 471/04 (2006.01)
C07D 487/04 (2006.01)
C07F 5/02 (2006.01)
C07F 7/08 (2006.01)
C09K 11/02 (2006.01)
C09K 11/06 (2006.01)

(52) U.S. Cl.

CPC **C07D 235/20** (2013.01); **C07D 333/76** (2013.01); **C07D 405/14** (2013.01); **C07D 409/10** (2013.01); **C07D 409/14** (2013.01); **C07D 413/10** (2013.01); **C07D 471/04** (2013.01); **C07D 487/04** (2013.01); **C07F 5/027** (2013.01); **C07F 7/0814** (2013.01); **C09K 11/025** (2013.01); **C09K 11/06** (2013.01); **H01L 51/0067** (2013.01); **H01L**

51/0071 (2013.01); **H01L 51/0072** (2013.01); **H01L 51/0085** (2013.01); **C09K 2211/1007** (2013.01); **C09K 2211/1029** (2013.01); **C09K 2211/1044** (2013.01); **C09K 2211/185** (2013.01); **H01L 51/5016** (2013.01)

(56)

References Cited

U.S. PATENT DOCUMENTS

5,247,190	A	9/1993	Friend et al.
5,703,436	A	12/1997	Forrest et al.
5,707,745	A	1/1998	Forrest et al.
5,834,893	A	11/1998	Bulovic et al.
5,844,363	A	12/1998	Gu et al.
6,013,982	A	1/2000	Thompson et al.
6,087,196	A	7/2000	Sturm et al.
6,091,195	A	7/2000	Forrest et al.
6,097,147	A	8/2000	Baldo et al.
6,294,398	B1	9/2001	Kim et al.
6,303,238	B1	10/2001	Thompson et al.
6,337,102	B1	1/2002	Forrest et al.
6,468,819	B1	10/2002	Kim et al.
6,528,187	B1	3/2003	Okada
6,687,266	B1	2/2004	Ma et al.
6,835,469	B2	12/2004	Kwong et al.
6,921,915	B2	7/2005	Takiguchi et al.
7,087,321	B2	8/2006	Kwong et al.
7,090,928	B2	8/2006	Thompson et al.
7,154,114	B2	12/2006	Brooks et al.
7,250,226	B2	7/2007	Tokito et al.
7,279,704	B2	10/2007	Walters et al.
7,329,722	B2	2/2008	Vaitkeviciene et al.
7,332,232	B2	2/2008	Ma et al.
7,338,722	B2	3/2008	Thompson et al.
7,393,599	B2	7/2008	Thompson et al.
7,396,598	B2	7/2008	Takeuchi et al.
7,431,968	B1	10/2008	Shtein et al.
7,445,855	B2	11/2008	Mackenzie et al.
7,504,769	B2	3/2009	Rado et al.
7,534,505	B2	5/2009	Lin et al.
7,651,791	B2	1/2010	Nakano et al.
7,989,644	B2	8/2011	Tanabe et al.
8,007,927	B2	8/2011	Lin et al.
8,221,905	B2	7/2012	Lin et al.
8,367,850	B2	2/2013	Ma et al.
2002/0034656	A1	3/2002	Thompson et al.
2002/0134984	A1	9/2002	Igarashi
2002/0158242	A1	10/2002	Son et al.
2003/0138657	A1	7/2003	Li et al.
2003/0151042	A1	8/2003	Marks et al.
2003/0152802	A1	8/2003	Tsuboyama et al.
2003/0175553	A1	9/2003	Thompson et al.
2003/0230980	A1	12/2003	Forrest et al.
2004/0036077	A1	2/2004	Ise
2004/0137267	A1	7/2004	Igarashi et al.
2004/0137268	A1	7/2004	Igarashi et al.
2004/0174116	A1	9/2004	Lu et al.
2005/0003233	A1*	1/2005	Igarashi C07F 15/0033 428/690
2005/0025993	A1	2/2005	Thompson et al.
2005/0112407	A1	5/2005	Ogasawara et al.
2005/0238919	A1	10/2005	Ogasawara
2005/0244673	A1	11/2005	Satoh et al.
2005/0260441	A1	11/2005	Thompson et al.
2005/0260449	A1	11/2005	Walters et al.
2006/0008670	A1	1/2006	Lin et al.
2006/0202194	A1	9/2006	Jeong et al.
2006/0240279	A1	10/2006	Adamovich et al.
2006/0251923	A1	11/2006	Lin et al.
2006/0263635	A1	11/2006	Ise
2006/0280965	A1	12/2006	Kwong et al.
2007/0075631	A1	4/2007	Tung et al.
2007/0088167	A1*	4/2007	Lin C07F 15/0033 548/103
2007/0190359	A1	8/2007	Knowles et al.
2007/0224446	A1	9/2007	Nakano et al.
2007/0278938	A1	12/2007	Yabunouchi et al.

(56)

References Cited

U.S. PATENT DOCUMENTS

2008/0015355	A1	1/2008	Schafer et al.	
2008/0018221	A1	1/2008	Egen et al.	
2008/0106190	A1	5/2008	Yabunouchi et al.	
2008/0124572	A1	5/2008	Mizuki et al.	
2008/0220265	A1	9/2008	Kia et al.	
2008/0297033	A1	12/2008	Knowles et al.	
2009/0008605	A1	1/2009	Kawamura et al.	
2009/0009065	A1	1/2009	Nishimura et al.	
2009/0017330	A1	1/2009	Iwakuma et al.	
2009/0030202	A1	1/2009	Iwakuma et al.	
2009/0039776	A1	2/2009	Yamada et al.	
2009/0045730	A1	2/2009	Nishimura et al.	
2009/0045731	A1	2/2009	Nishimura et al.	
2009/0066226	A1 *	3/2009	Sugita	C07D 405/14 313/504
2009/0101870	A1	4/2009	Pakash et al.	
2009/0108737	A1	4/2009	Kwong et al.	
2009/0115316	A1	5/2009	Zheng et al.	
2009/0153034	A1	6/2009	Lin et al.	
2009/0165846	A1	7/2009	Johannes et al.	
2009/0167162	A1	7/2009	Lin et al.	
2009/0179554	A1	7/2009	Kuma et al.	
2011/0057559	A1	3/2011	Xia et al.	
2011/0084599	A1	4/2011	Brooks et al.	
2011/0278552	A1	11/2011	Numata	
2013/0020565	A1	1/2013	Numata	
2013/0175510	A1	7/2013	Ma et al.	

FOREIGN PATENT DOCUMENTS

EP	2034538	3/2009
JP	62283341	12/1987
JP	07-053950	2/1995
JP	200511610	1/2005
JP	2007123392	5/2007
JP	2007126403	5/2007
JP	2007254297	10/2007
JP	2008074939	4/2008
JP	2008078362	4/2008
WO	2001039234	5/2001
WO	2002002714	1/2002
WO	200215645	2/2002
WO	2003040257	5/2003
WO	2003060956	7/2003
WO	2004093207	10/2004
WO	2004107822	12/2004
WO	2005014551	2/2005
WO	2005019373	3/2005
WO	2005030900	4/2005
WO	2005089025	9/2005
WO	2005123873	12/2005
WO	2006009024	1/2006
WO	2006056418	6/2006
WO	2006072002	7/2006
WO	2006082742	8/2006
WO	2007/029798	9/2006
WO	2006098120	9/2006
WO	2006100298	9/2006
WO	2006103874	10/2006
WO	2006114966	11/2006
WO	2006/12880	12/2006
WO	2006132173	12/2006
WO	2007002683	1/2007
WO	2007004380	1/2007
WO	2007/069569	6/2007
WO	2007063754	6/2007
WO	2007063796	6/2007
WO	2007/077810	7/2007
WO	2007/238500	9/2007
WO	2008056746	5/2008
WO	2008101842	8/2008
WO	2008132085	11/2008
WO	2009000673	12/2008
WO	2009/008099	1/2009

WO	2009/008100	1/2009
WO	2009003898	1/2009
WO	2009008311	1/2009
WO	2009018009	2/2009
WO	2009/030981	3/2009
WO	2009050290	4/2009
WO	2009/060742	5/2009
WO	2009021126	5/2009
WO	2009062578	5/2009
WO	2009063833	5/2009
WO	2009066778	5/2009
WO	2009066779	5/2009
WO	2009086028	7/2009
WO	2009100991	8/2009

OTHER PUBLICATIONS

Tsai, et al., "3-(9-Carbazolyl)carbazoles and 3,6-Di(9-carbazolyl)carbazoles as effective host materials for efficient blue organic electrophosphorescence" *Adv. Mater.* 2007, 19, 862-866.

Adachi, Chihaya et al., "Organic Electroluminescent Device Having a Hole Conductor as an Emitting Layer," *Appl. Phys. Lett.*, 55(15): 1489-1491 (1989).

Adachi, Chihaya et al., "Nearly 100% Internal Phosphorescence Efficiency in an Organic Light Emitting Device," *J. Appl. Phys.*, 90(10): 5048-5051 (2001).

Adachi, Chihaya et al., "High-Efficiency Red Electrophosphorescence Devices," *Appl. Phys. Lett.*, 78(11):1622-1624 (2001).

Aonuma, Masaki et al., "Material Design of Hole Transport Materials Capable of Thick-Film Formation in Organic Light Emitting Diodes," *Appl. Phys. Lett.*, 90:183503-1-183503-3.

Baldo et al., Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices, *Nature*, vol. 395, 151-154, (1998).

Baldo et al., Very high-efficiency green organic light-emitting devices based on electrophosphorescence, *Appl. Phys. Lett.*, vol. 75, No. 3, 4-6 (1999).

Gao, Zhiqiang et al., "Bright-Blue Electroluminescence From a Silyl-Substituted ter-(phenylene-vinylene) derivative," *Appl. Phys. Lett.*, 74(6): 865-867 (1999).

Guo, Tzung-Fang et al., "Highly Efficient Electrophosphorescent Polymer Light-Emitting Devices," *Organic Electronics*, 115-20 (2000).

Hamada, Yuji et al., "High Luminance in Organic Electroluminescent Devices with Bis(10-hydroxybenzo[h]quinolinato)beryllium as an Emitter," *Chem. Lett.*, 905-906 (1993).

Holmes, R.J. et al., "Blue Organic Electrophosphorescence Using Exothermic Host-Guest Energy Transfer," *Appl. Phys. Lett.*, 82(15):2422-2424 (2003).

Hu, Nan-Xing et al., "Novel High Tg Hole-Transport Molecules Based on Indolo[3,2-b]carbazoles for Organic Light-Emitting Devices," *Synthetic Metals*, 111-112:421-424 (2000).

Huang, Jinsong et al., "Highly Efficient Red-Emission Polymer Phosphorescent Light-Emitting Diodes Based on Two Novel Tris(1-phenylisoquinolinato-C2,N)iridium(III) Derivates," *Adv. Mater.*, 19:739-743 (2007).

Huang, Wei-Sheng et al., "Highly Phosphorescent Bis-Cyclometalated Iridium Complexes Containing Benzoimidazole-Based Ligands," *Chem. Mater.*, 16(12):2480-2488 (2004).

Hung, L.S. et al., "Anode Modification in Organic Light-Emitting Diodes by Low-Frequency Plasma Polymerization of CHF₃," *Appl. Phys. Lett.*, 78(5):673-675 (2001).

Ikai, Masamichi and Tokito, Shizuo, "Highly Efficient Phosphorescence From Organic Light-Emitting Devices with an Exciton-Block Layer," *Appl. Phys. Lett.*, 79(2):156-158 (2001).

Ikeda, Hisao et al., "P-185 Low-Drive-Voltage OLEDs with a Buffer Layer Having Molybdenum Oxide," *SID Symposium Digest*, 37:923-926 (2006).

Inada, Hiroshi and Shirota, Yasuhiko, "1,3,5-Tris[4-(diphenylamino)phenyl]benzene and its Methylsubstituted Derivatives as a Novel Class of Amorphous Molecular Materials," *J. Mater. Chem.*, 3(3):319-320 (1993).

(56)

References Cited

OTHER PUBLICATIONS

- Kanno, Hiroshi et al., "Highly Efficient and Stable Red Phosphorescent Organic Light-Emitting Device Using bis[2-(2-benzothiazoyl)phenolato]zinc(II) as host material," *Appl. Phys. Lett.*, 90:123509-1-123509-3 (2007).
- Kido, Junji et al., 1,2,4-Triazole Derivative as an Electron Transport Layer in Organic Electroluminescent Devices, *Jpn. J. Appl. Phys.*, 32:L917-L920 (1993).
- Kuwabara, Yoshiyuki et al., "Thermally Stable Multilayered Organic Electroluminescent Devices Using Novel Starburst Molecules, 4,4',4"-Tri(N-carbazolyl)triphenylamine (TCTA) and 4,4',4"-Tris(3-methylphenylphenyl-amino)triphenylamine (m-MTDATA), as Hole-Transport Materials," *Adv. Mater.*, 6(9):677-679 (1994).
- Kwong, Raymond C. et al., "High Operational Stability of Electrophosphorescent Devices," *Appl. Phys. Lett.*, 81(1) 162-164 (2002).
- Lamansky, Sergey et al., "Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes," *Inorg. Chem.*, 40(7):1704-1711 (2001).
- Lee, Chang-Lyoul et al., "Polymer Phosphorescent Light-Emitting Devices Doped with Tris(2-phenylpyridine) Iridium as a Triplet Emitter," *Appl. Phys. Lett.*, 77(15):2280-2282 (2000).
- Lo, Shih-Chun et al., "Blue Phosphorescence from Iridium(III) Complexes at Room Temperature," *Chem. Mater.*, 18(21)5119-5129 (2006).
- Ma, Yuguang et al., "Triplet Luminescent Dinuclear-Gold(I) Complex-Based Light-Emitting Diodes with Low Turn-On voltage," *Appl. Phys. Lett.*, 74(10):1361-1363 (1999).
- Mi, Bao-Xiu et al., "Thermally Stable Hole-Transporting Material for Organic Light-Emitting Diode an Isoindole Derivative," *Chem. Mater.*, 15(16):3148-3151 (2003).
- Nishida, Jun-ichi et al., "Preparation, Characterization, and Electroluminescence Characteristics of α -Diimine-type Platinum(II) Complexes with Perfluorinated Phenyl Groups as Ligands," *Chem. Lett.*, 34(4): 592-593 (2005).
- Niu, Yu-Hua et al., "Highly Efficient Electrophosphorescent Devices with Saturated Red Emission from a Neutral Osmium Complex," *Chem. Mater.*, 17(13):3532-3536 (2005).
- Noda, Tetsuya and Shirota, Yasuhiko, "5,5'-Bis(dimesitylboryl)-2,2'-bithiophene and 5,5'-Bis(dimesitylboryl)-2,2',2"-terthiophene as a Novel Family of Electron-Transporting Amorphous Molecular Materials," *J. Am. Chem. Soc.*, 120 (37):9714-9715 (1998).
- Okumoto, Kenji et al., "Green Fluorescent Organic Light-Emitting Device with External Quantum Efficiency of Nearly 10%," *Appl. Phys. Lett.*, 89:063504-1-063504-3 (2006).
- Palilis, Leonidas C., "High Efficiency Molecular Organic Light-Emitting Diodes Based on Silole Derivatives and Their Exciplexes," *Organic Electronics*, 4:113-121 (2003).
- Paulose, Betty Marie Jennifer S. et al., "First Examples of Alkenyl Pyridines as Organic Ligands for Phosphorescent Iridium Complexes," *Adv. Mater.*, 16(22):2003-2007 (2004).
- Ranjan, Sudhir et al., "Realizing Green Phosphorescent Light-Emitting Materials from Rhenium(I) Pyrazolato Diimine Complexes," *Inorg. Chem.*, 42(4):1248-1255 (2003).
- Sakamoto, Youichi et al., "Synthesis, Characterization, and Electron-Transport Property of Perfluorinated Phenylene Dendrimers," *J. Am. Chem. Soc.*, 122(8):1832-1833 (2000).
- Salbeck, J. et al., "Low Molecular Organic Glasses for Blue Electroluminescence," *Synthetic Metals*, 91209-215 (1997).
- Shirota, Yasuhiko et al., "Starburst Molecules Based on p-Electron Systems as Materials for Organic Electroluminescent Devices," *Journal of Luminescence*, 72-74:985-991 (1997).
- Sotoyama, Wataru et al., "Efficient Organic Light-Emitting Diodes with Phosphorescent Platinum Complexes Containing N^CN^A-Coordinating Tridentate Ligand," *Appl. Phys. Lett.*, 86:153505-1-153505-3 (2005).
- Sun, Yiru and Forrest, Stephen R., "High-Efficiency White Organic Light Emitting Devices with Three Separate Phosphorescent Emission Layers," *Appl. Phys. Lett.*, 91:263503-1-263503-3 (2007).
- T. Östergård et al., "Langmuir-Blodgett Light-Emitting Diodes of Poly(3-Hexylthiophene) Electro-Optical Characteristics Related to Structure," *Synthetic Metals*, 87:171-177 (1997).
- Takizawa, Shin-ya et al., "Phosphorescent Iridium Complexes Based on 2-Phenylimidazo[1,2- α]pyridine Ligands Tuning of Emission Color toward the Blue Region and Application to Polymer Light-Emitting Devices," *Inorg. Chem.*, 46(10):4308-4319 (2007).
- Tang, C.W. and VanSlyke, S.A., "Organic Electroluminescent Diodes," *Appl. Phys. Lett.*, 51(12):913-915 (1987).
- Tung, Yung-Liang et al., "Organic Light-Emitting Diodes Based on Charge-Neutral Ru II Phosphorescent Emitters," *Adv. Mater.*, 17(8):1059-1064 (2005).
- Van Slyke, S. A. et al., "Organic Electroluminescent Devices with Improved Stability," *Appl. Phys. Lett.*, 69 (15):2160-2162 (1996).
- Wang, Y. et al., "Highly Efficient Electroluminescent Materials Based on Fluorinated Organometallic Iridium Compounds," *Appl. Phys. Lett.*, 79(4):449-451 (2001).
- Wong, Keith Man-Chung et al., A Novel Class of Phosphorescent Gold(III) Alkynyl-Based Organic Light-Emitting Devices with Tunable Colour, *Chem. Commun.*, 2906-2908 (2005).
- Wong, Wai-Yeung, "Multifunctional Iridium Complexes Based on Carbazole Modules as Highly Efficient Electrophosphors," *Angew. Chem. Int. Ed.*, 45:7800-7803 (2006).

* cited by examiner

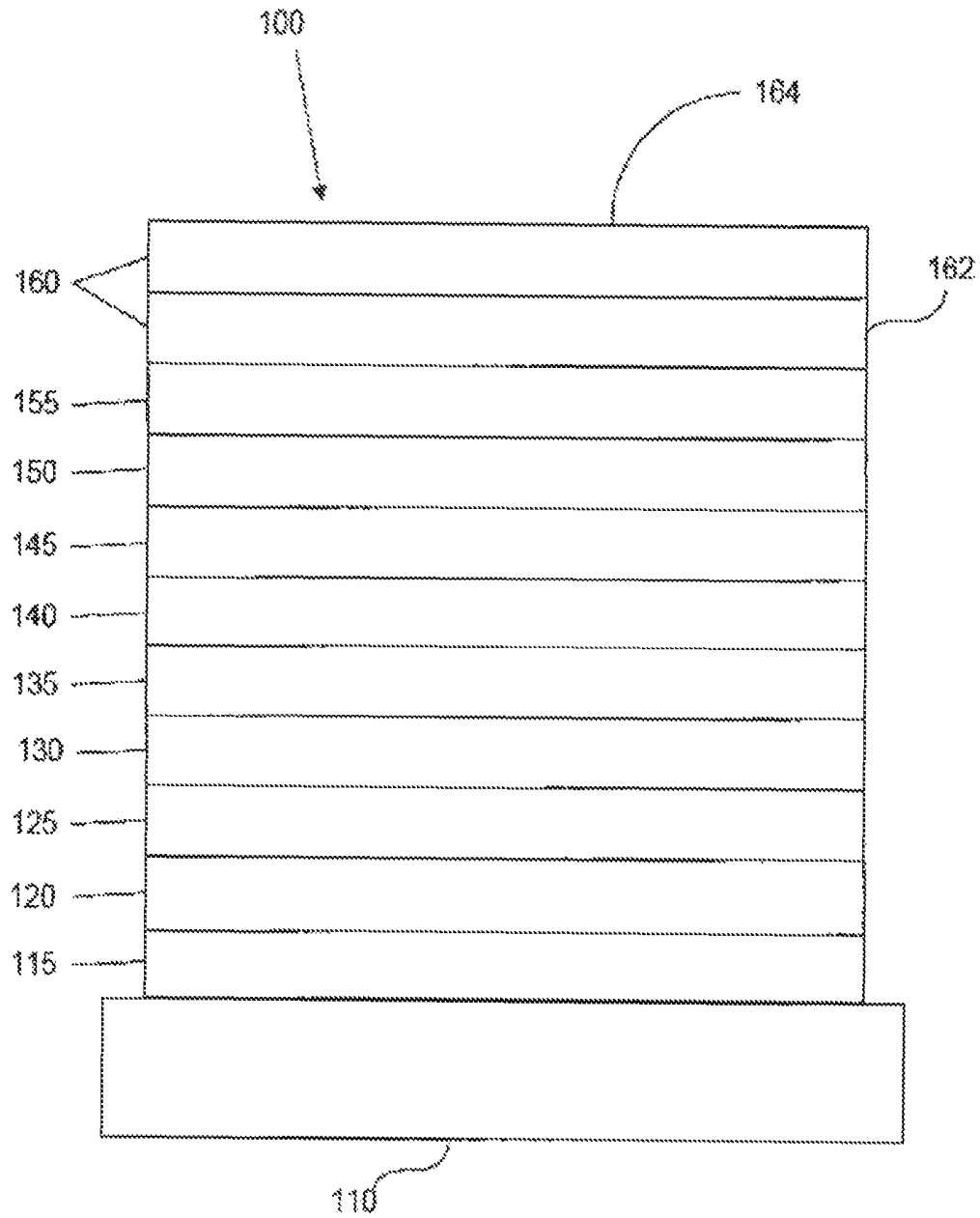


FIGURE 1

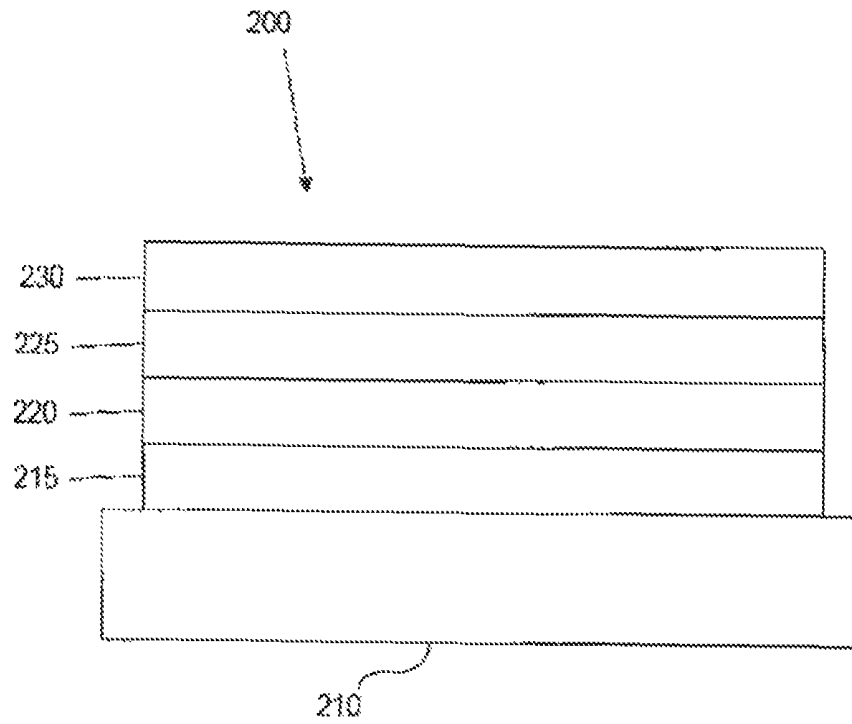


FIGURE 2

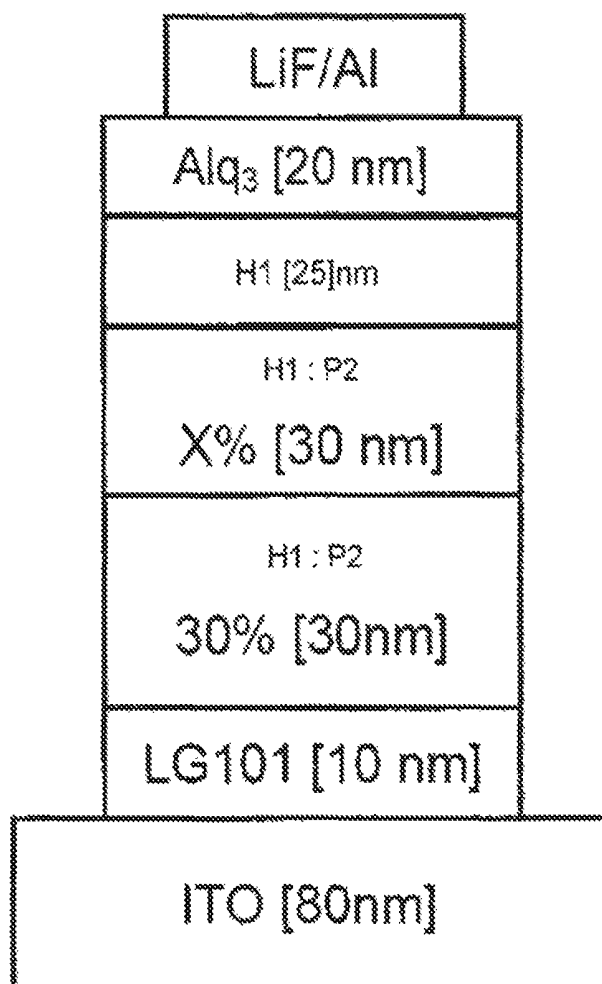


FIGURE 3

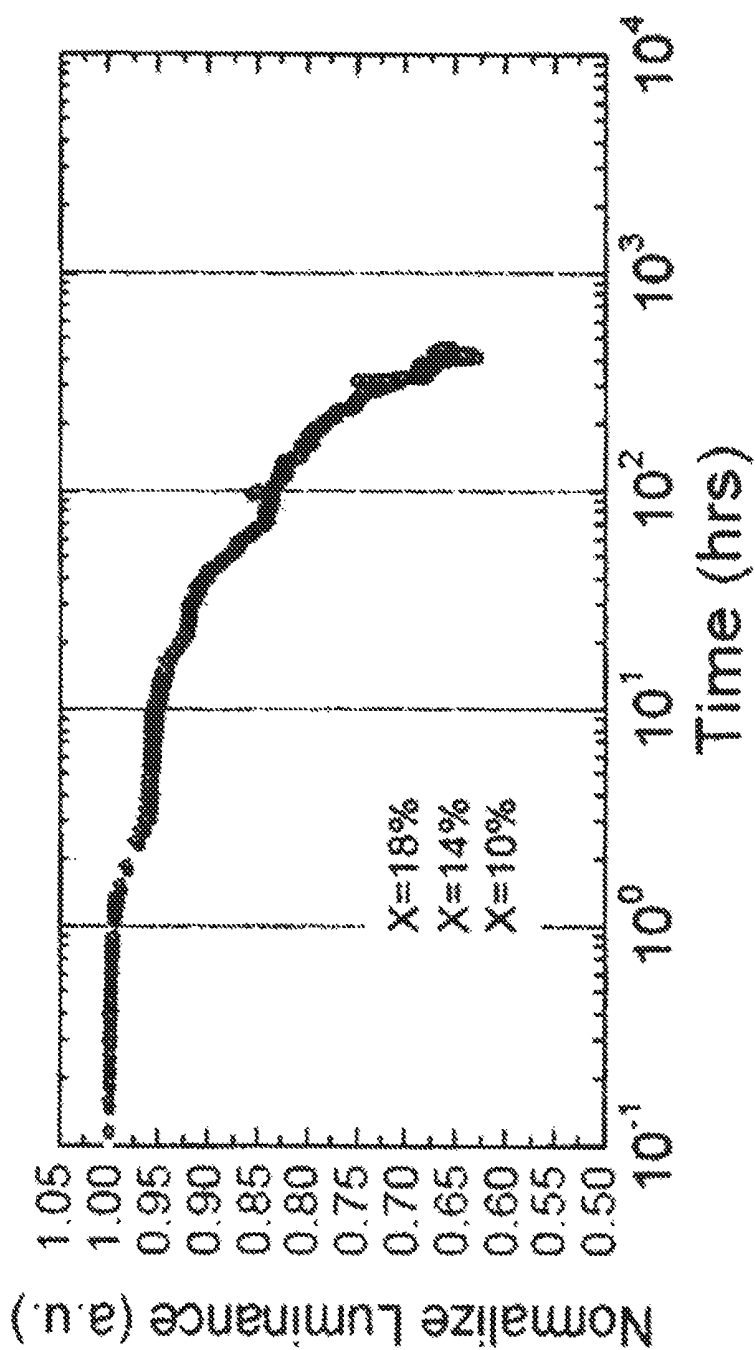


FIGURE 4

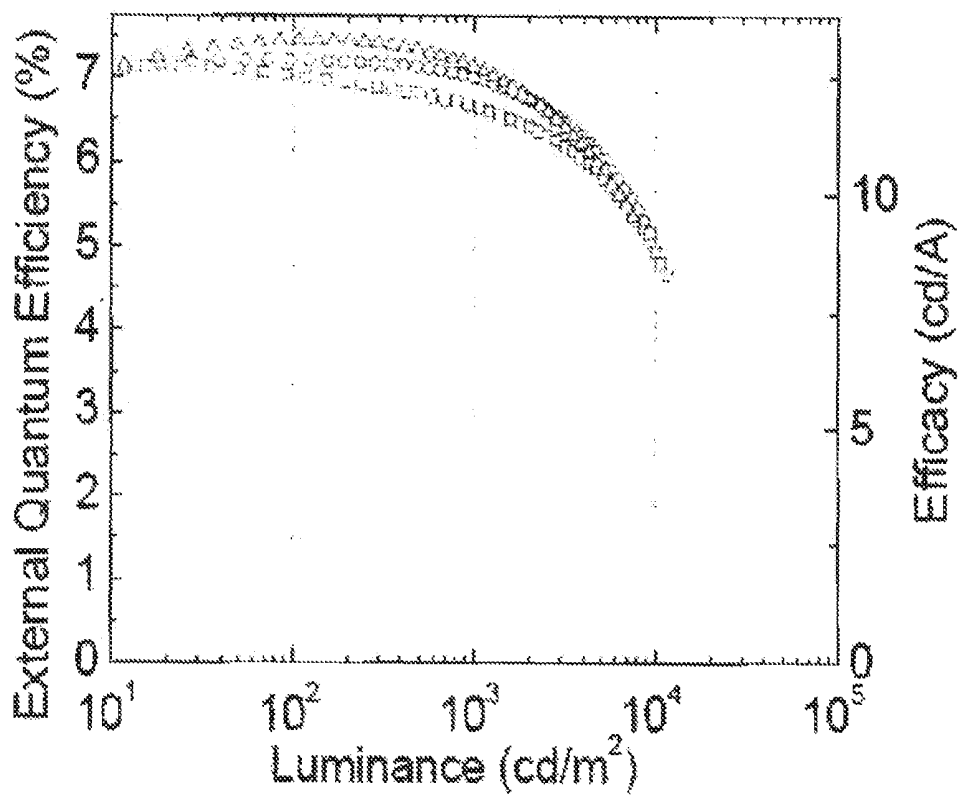


FIGURE 5

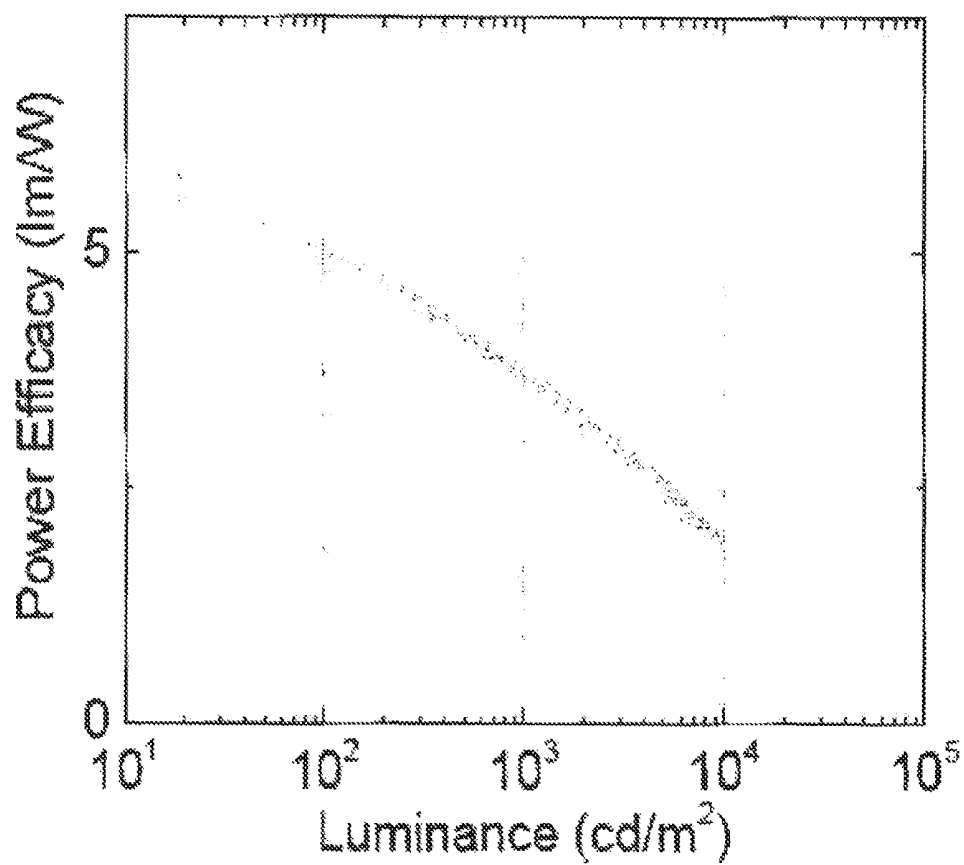


FIGURE 6

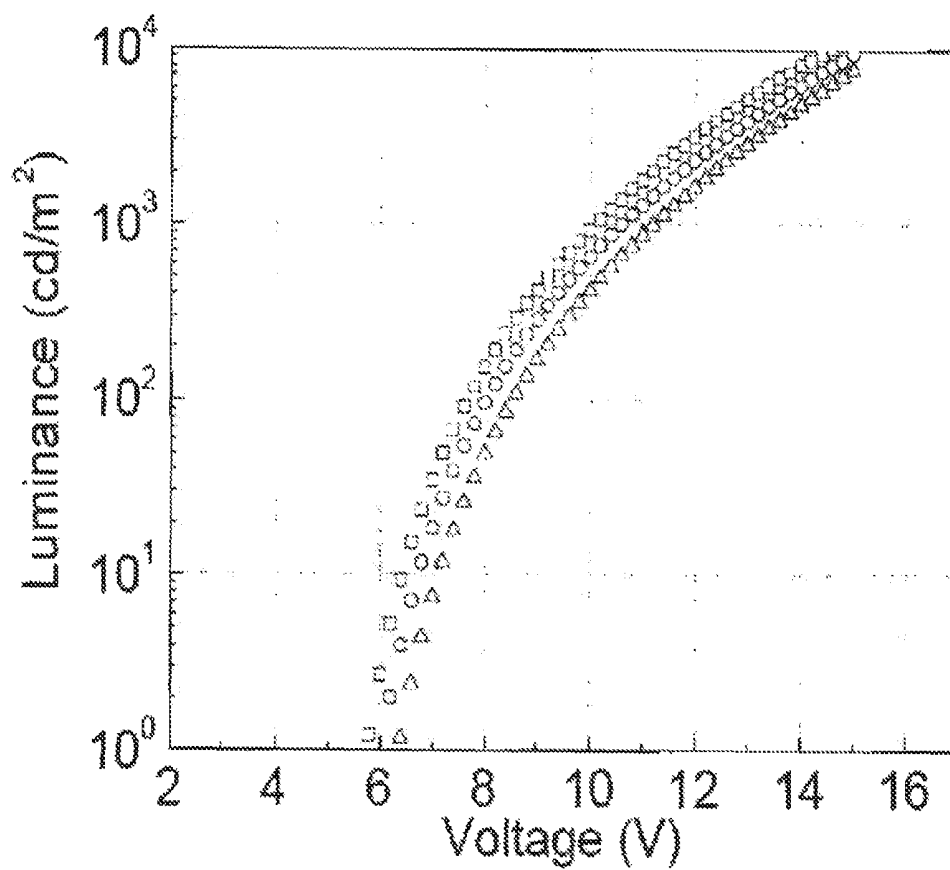


FIGURE 7

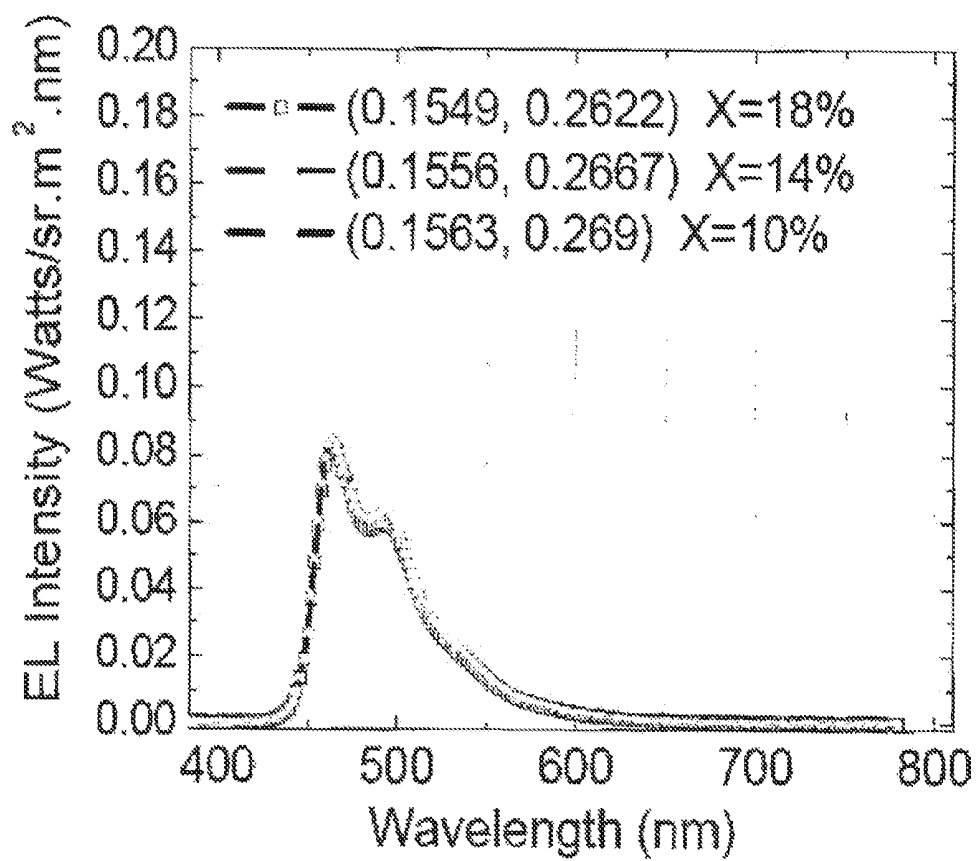


FIGURE 8

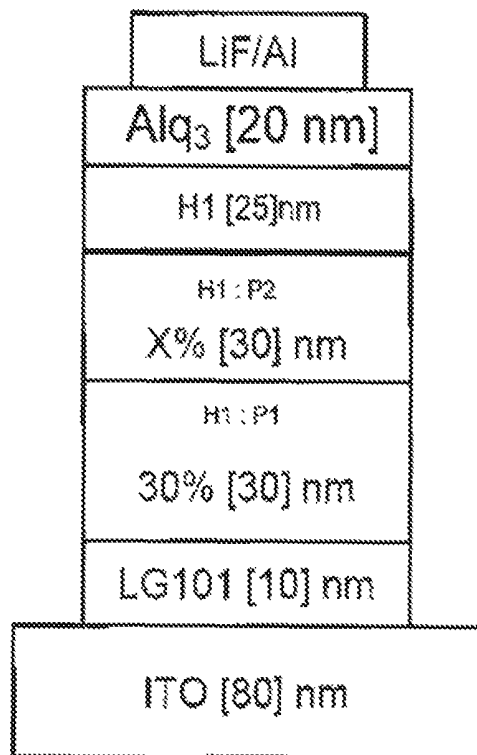


FIGURE 9

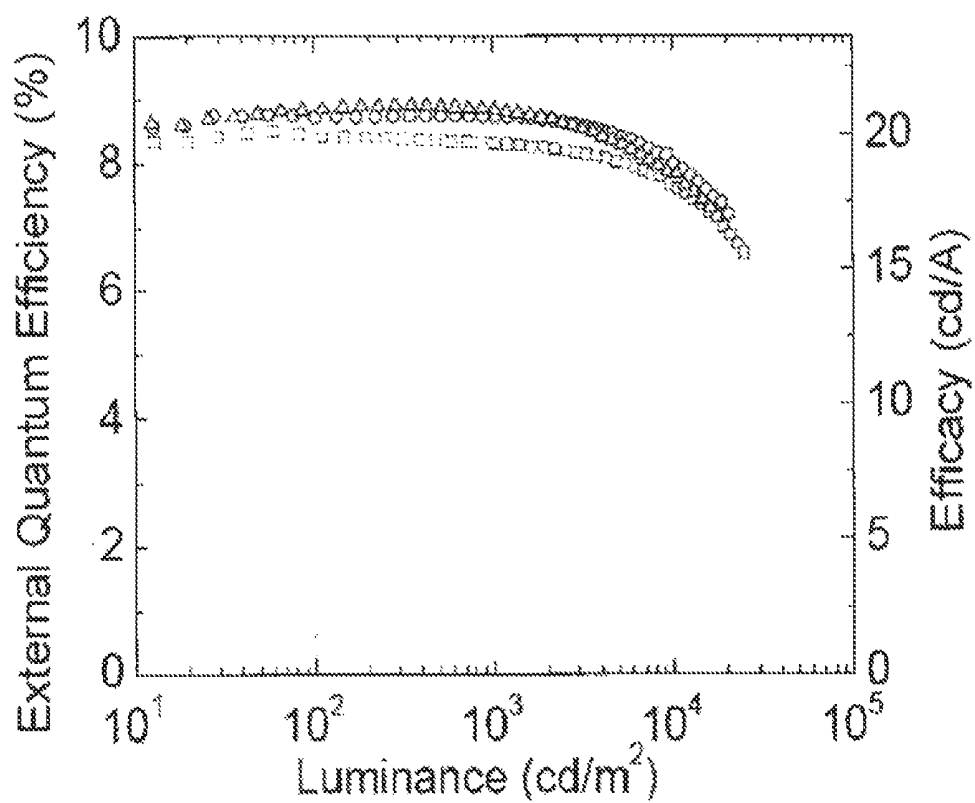


FIGURE 10

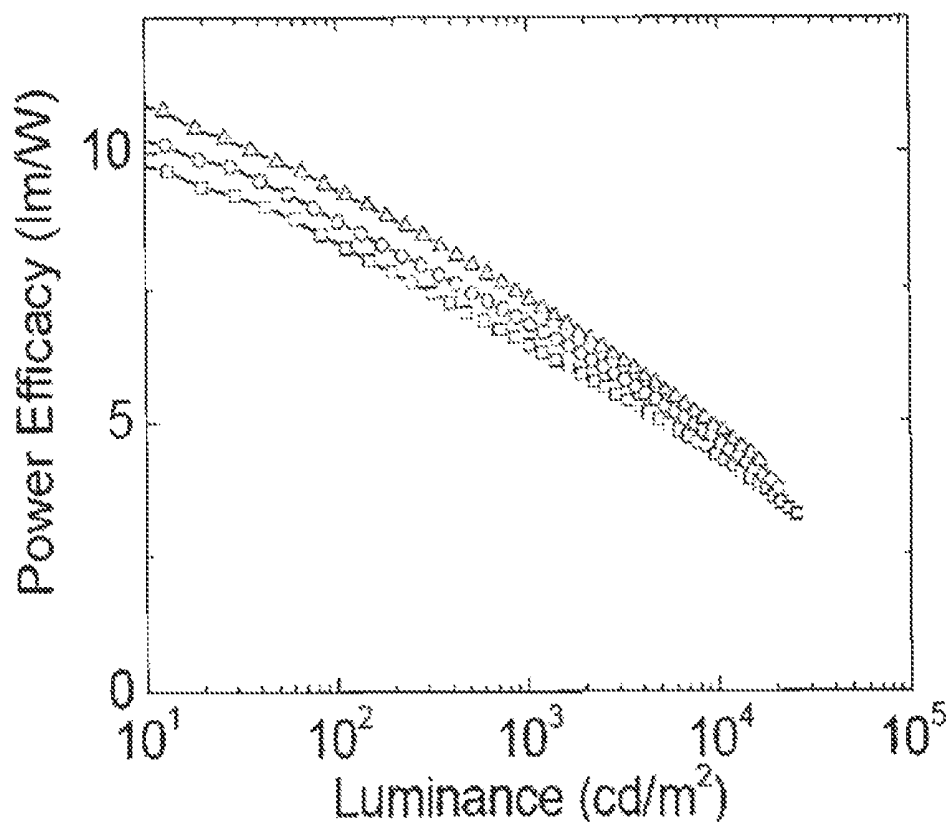


FIGURE 11

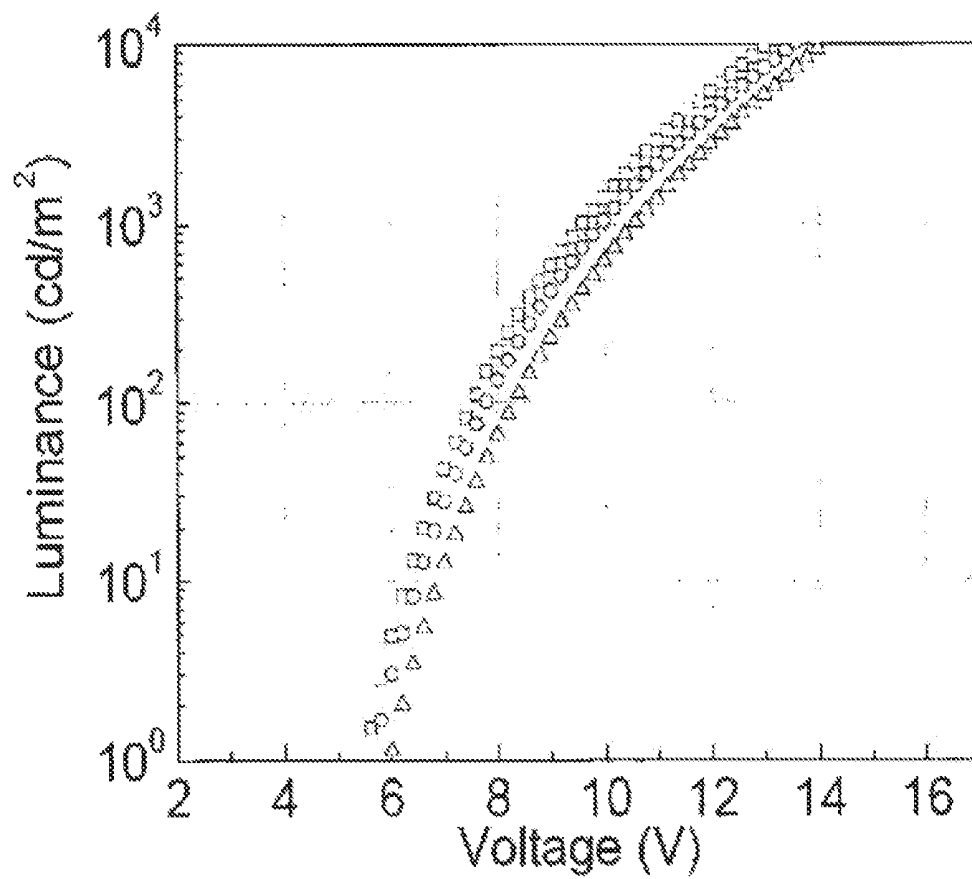


FIGURE 12

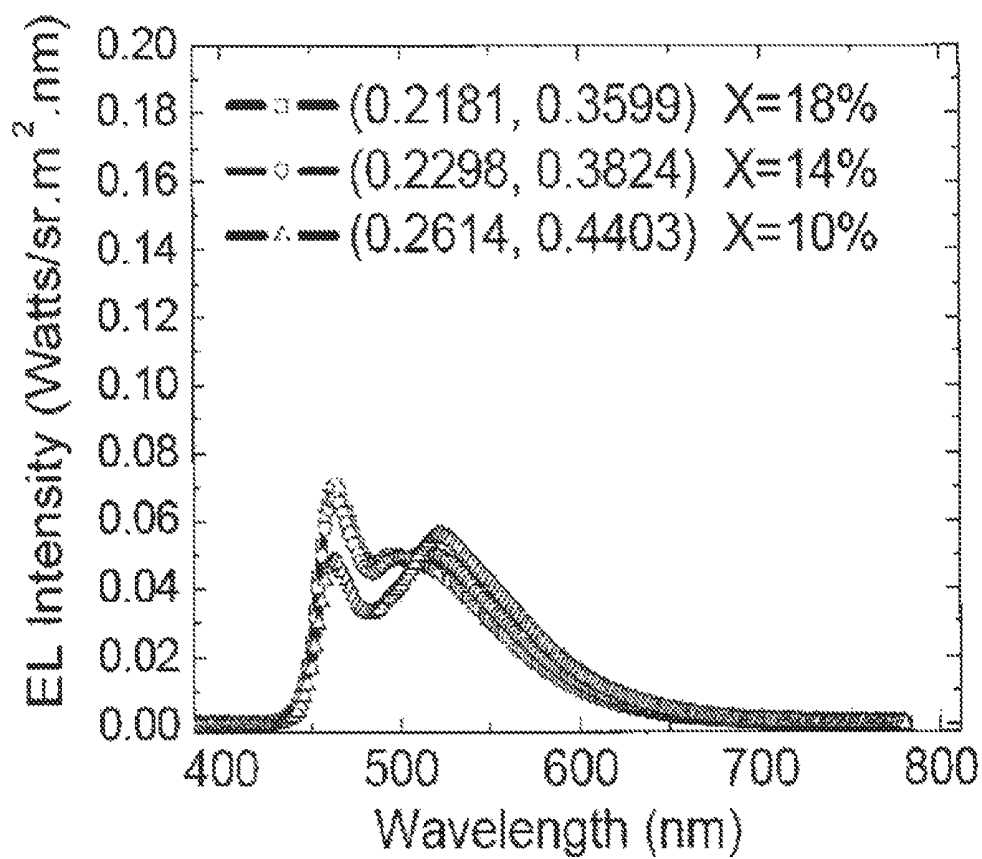


FIGURE 13

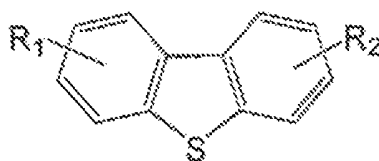


FIGURE 14

DIBENZOTHIOPHENE-CONTAINING MATERIALS IN PHOSPHORESCENT LIGHT EMITTING DIODES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 14/026,868, filed Sep. 13, 2013, which is a divisional of U.S. application Ser. No. 13/186,204, filed Jul. 19, 2011, which issued as U.S. Pat. No. 8,580,402 on Nov. 12, 2013, which is a divisional of U.S. application Ser. No. 12/208,907, filed Sep. 11, 2008, which issued as U.S. Pat. No. 8,007,927 on Aug. 30, 2011, which claims priority to U.S. Provisional Application Ser. No. 61/017,480, filed Dec. 28, 2007, the disclosures of which are herein expressly incorporated by reference in their entirety. This application is also related to International Application No. PCT/IB2007/004687, filed Dec. 28, 2007.

PARTIES TO A JOINT RESEARCH AGREEMENT

The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of the University of Michigan, Princeton University, The University of Southern California, and the Universal Display Corporation. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

FIELD OF THE INVENTION

The present invention is directed to organic light emitting devices (OLEDs). More specifically, the present invention relates to phosphorescent light emitting materials and devices that may have improved device lifetime.

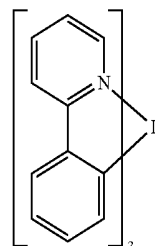
BACKGROUND

Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as “saturated” colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)₃, which has the structure of Formula I:



In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

As used herein, the term “organic” includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. “Small molecule” refers to any organic material that is not a polymer, and “small molecules” may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the “small molecule” class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a “small molecule,” and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

As used herein, “top” means furthest away from the substrate, while “bottom” means closest to the substrate. Where a first layer is described as “disposed over” a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is “in contact with” the second layer. For example, a cathode may be described as “disposed over” an anode, even though there are various organic layers in between.

As used herein, “solution processible” means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

A ligand may be referred to as “photoactive” when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as “ancillary” when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

As used herein, and as would be generally understood by one skilled in the art, a first “Highest Occupied Molecular Orbital” (HOMO) or “Lowest Unoccupied Molecular Orbital” (LUMO) energy level is “greater than” or “higher than” a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since

3

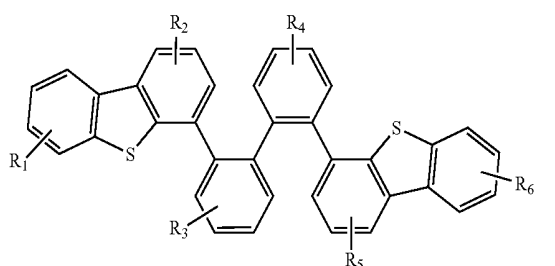
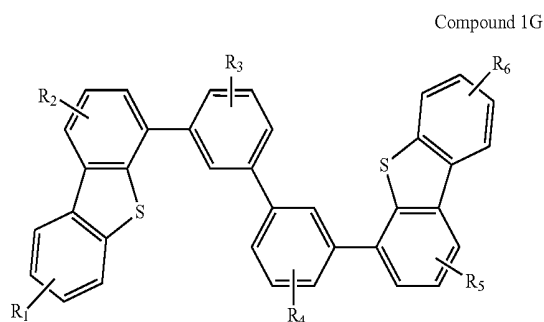
ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having a smaller absolute value (an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A “higher” HOMO or LUMO energy level appears closer to the top of such a diagram than a “lower” HOMO or LUMO energy level.

As used herein, and as would be generally understood by one skilled in the art, a first work function is “greater than” or “higher than” a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a “higher” work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a “higher” work function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

SUMMARY OF THE INVENTION

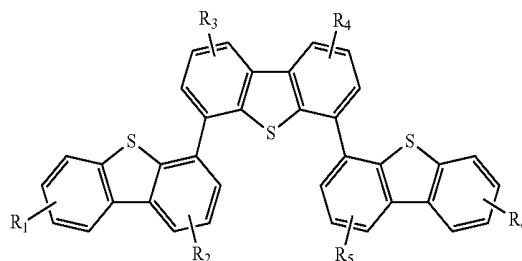
A new type of materials is provided. The new class of materials has a dibenzothiophene-containing compound selected from the group consisting of:



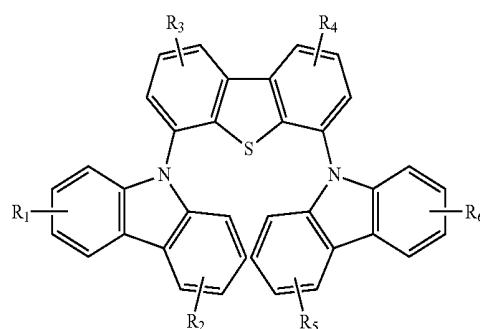
4

-continued

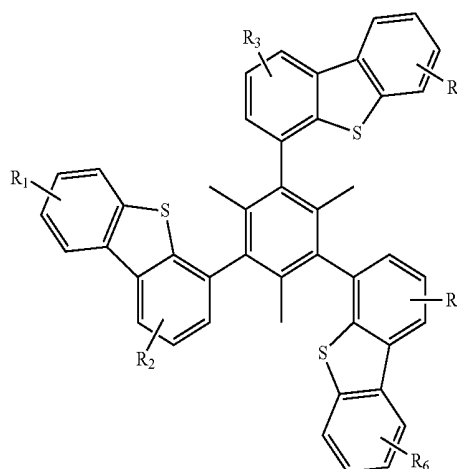
Compound 3G



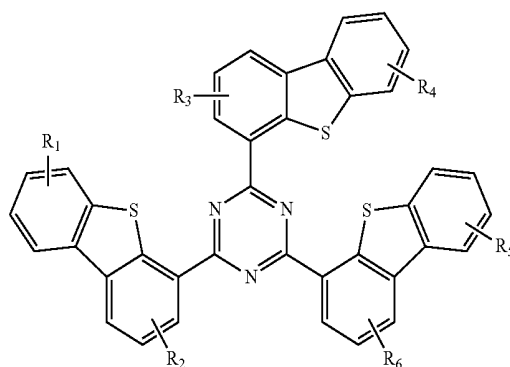
Compound 4G



Compound 5G



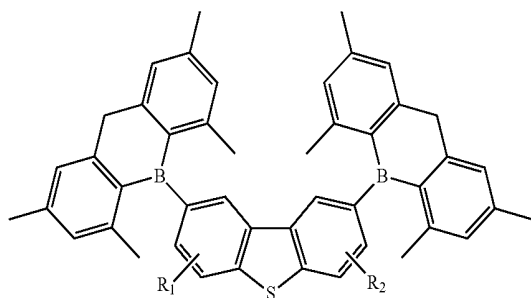
Compound 6G



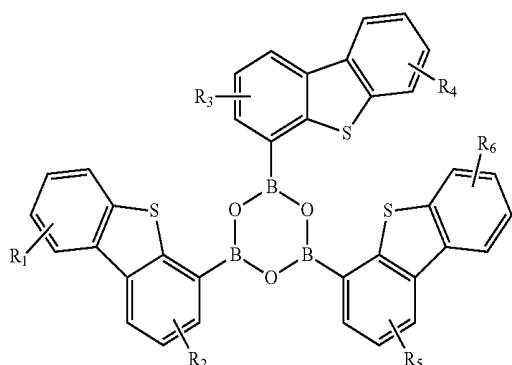
5

-continued

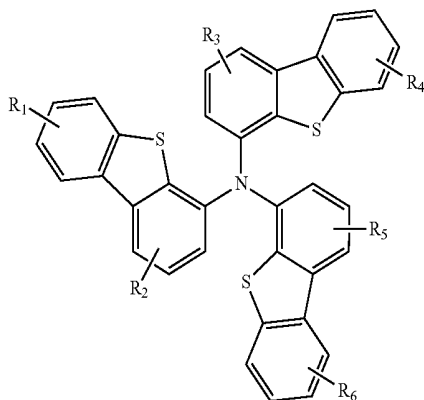
Compound 7G



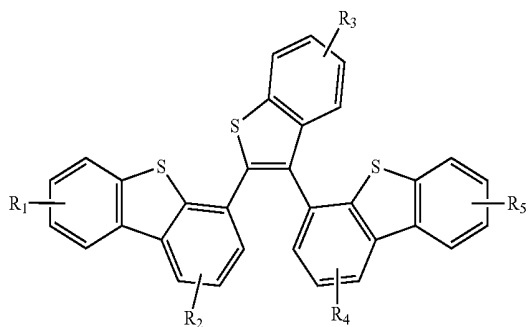
Compound 8G



Compound 9G



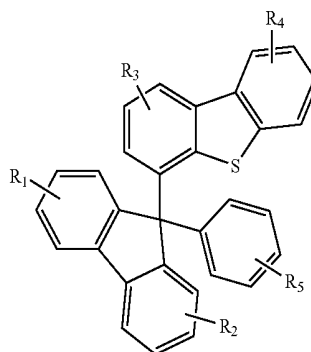
Compound 10G



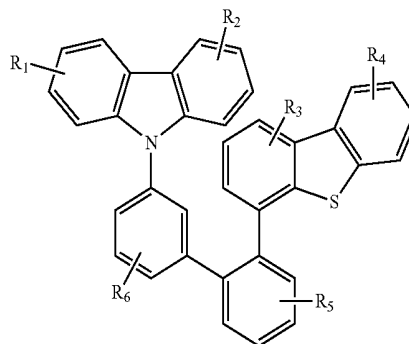
6

-continued

Compound 11G



Compound 12G

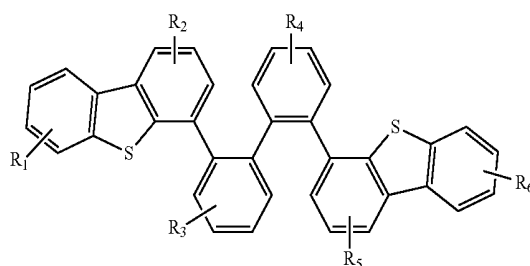


where each of R_1 through R_6 are independently selected from the group consisting of any aryl and alkyl substituents and H, and where each of R_1 through R_6 may represent multiple substitutions. In one aspect, all of R_1 through R_6 are H.

An organic light emitting device is also provided. The device has an anode, a cathode, an and an organic layer disposed between the anode and the cathode. The organic layer further comprises a material containing a compound from the group consisting of Compound 1G through 12G, as described above, with or without substituents. Preferably the organic layer is an emissive layer having a host and an emissive dopant, and the compound is the host. The compound may also preferably be used as a material in an enhancement layer.

New materials are provided. The materials have a dibenzothienophene-containing and/or dibenzofuran-containing compound selected from the group consisting of:

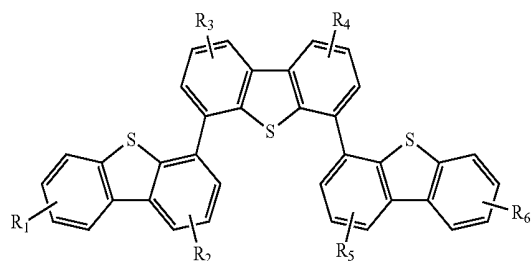
Compound 2G



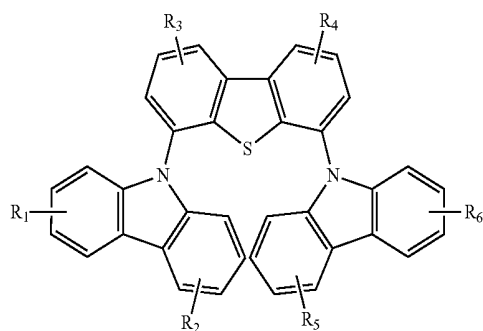
7

-continued

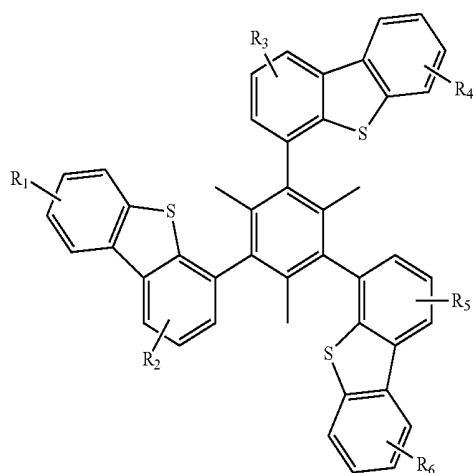
Compound 3G



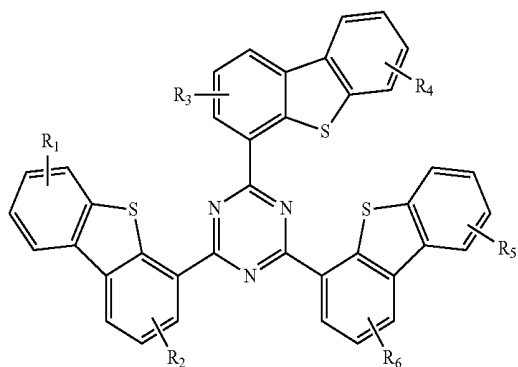
Compound 4G



Compound 5G



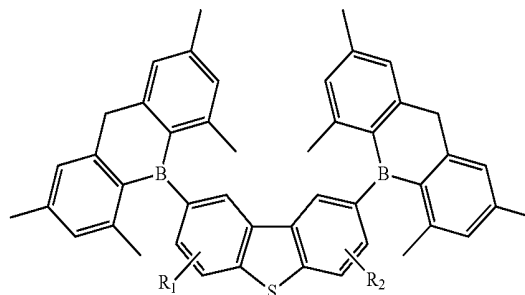
Compound 6G



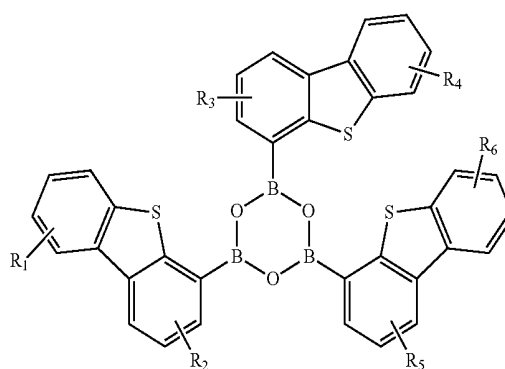
8

-continued

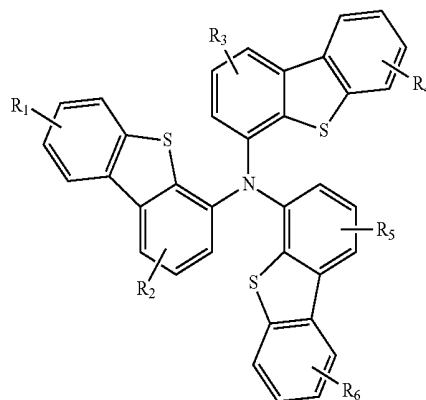
Compound 7G



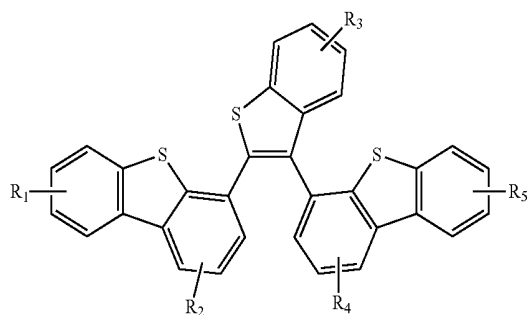
Compound 8G



Compound 9G

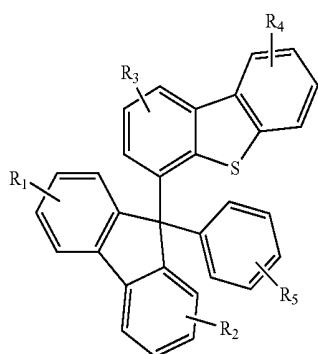


Compound 10G



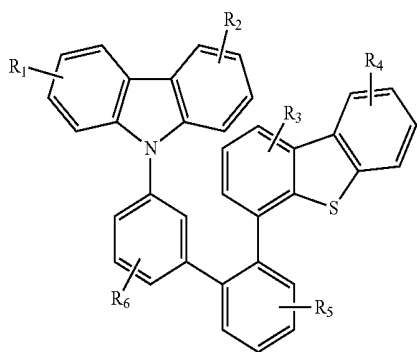
9

-continued

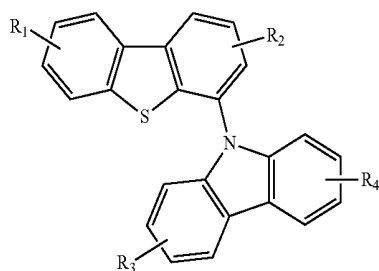


Compound 11G

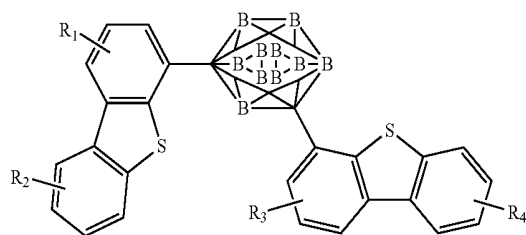
Compound 12G



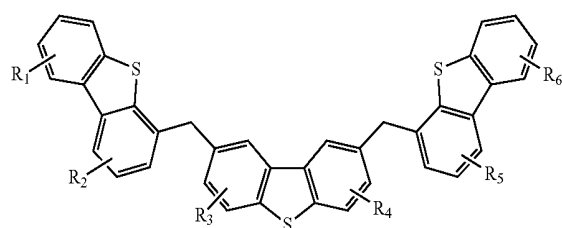
Compound 13G



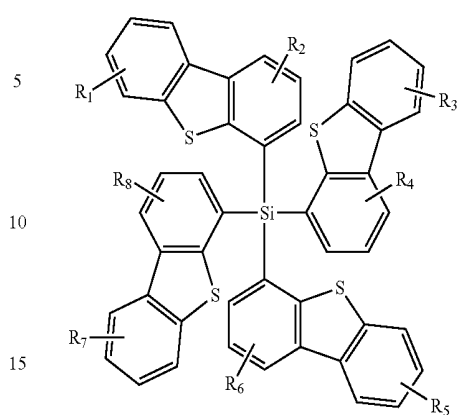
Compound 14G



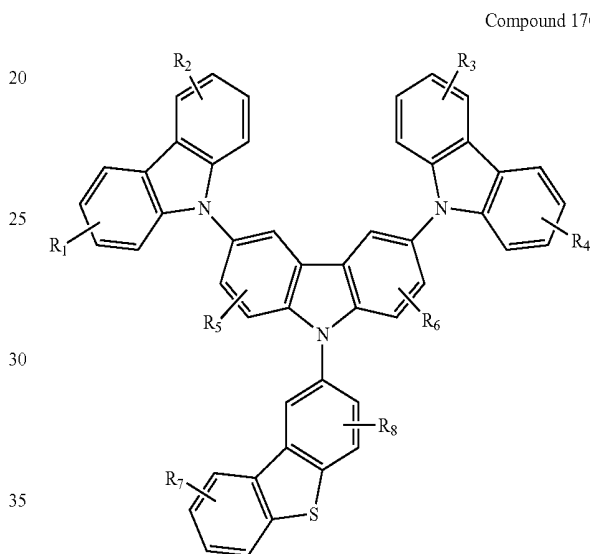
Compound 15G

**10**

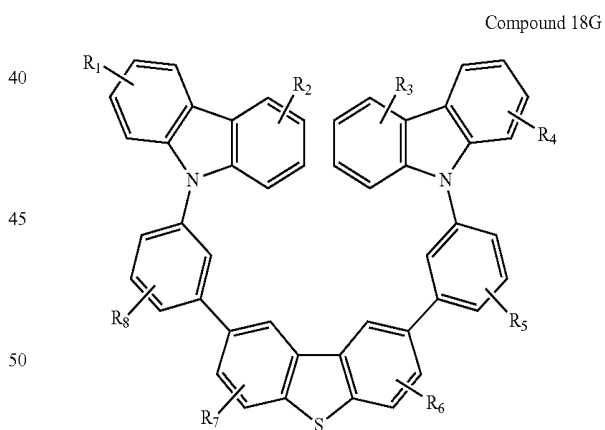
-continued



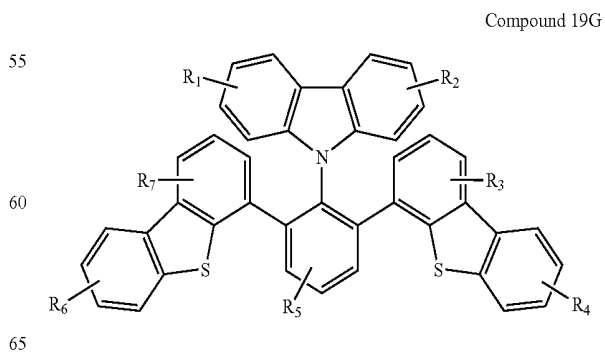
Compound 16G



Compound 17G



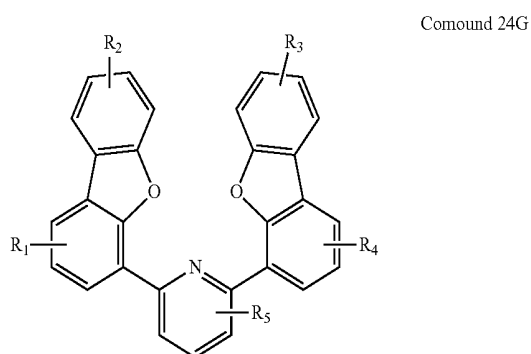
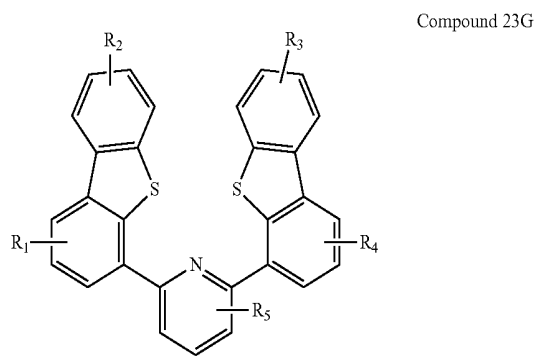
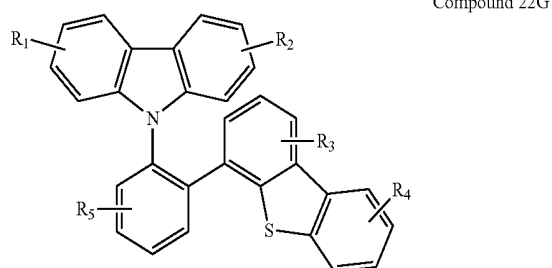
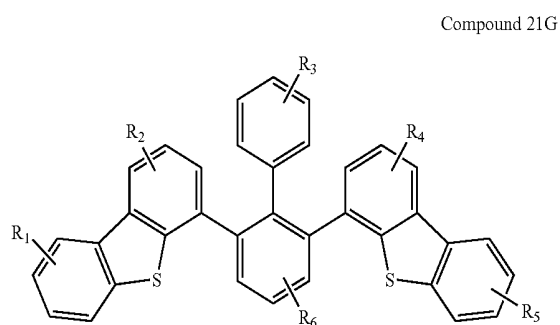
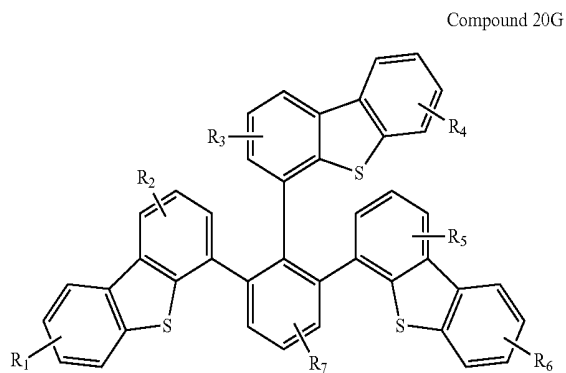
Compound 18G



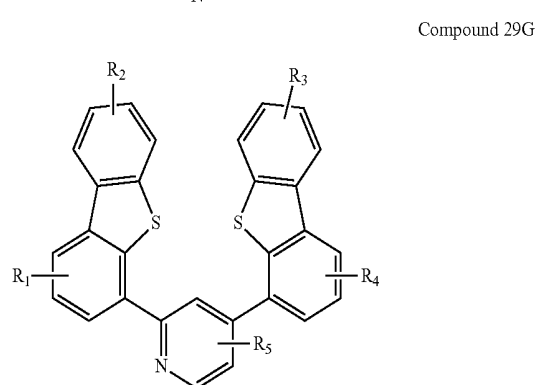
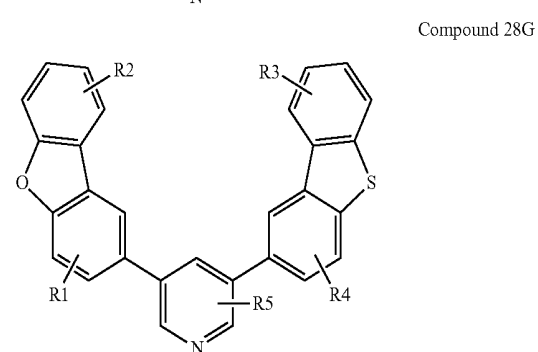
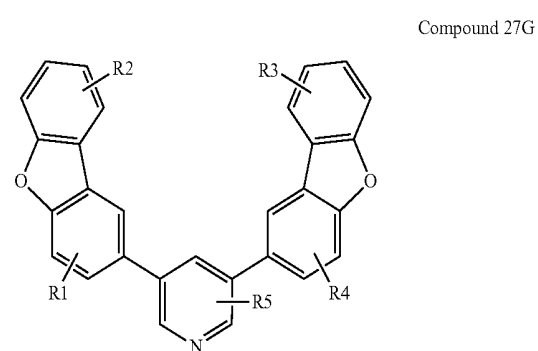
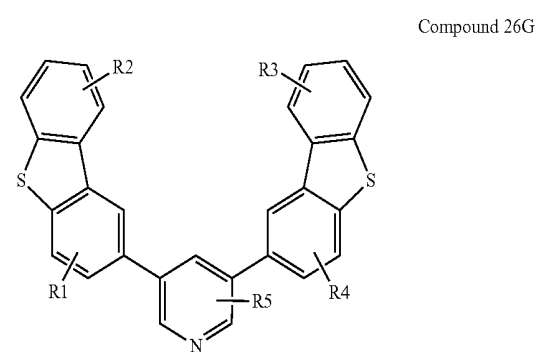
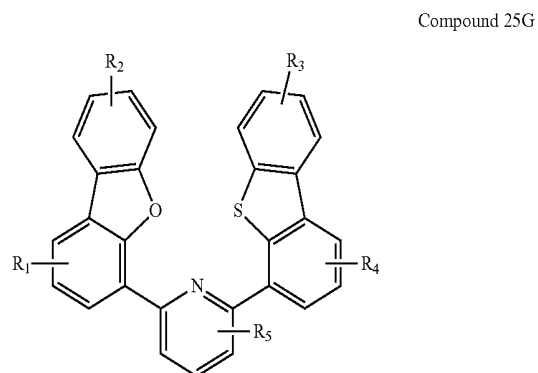
Compound 19G

11

-continued

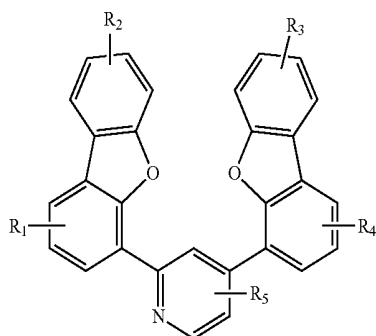
**12**

-continued

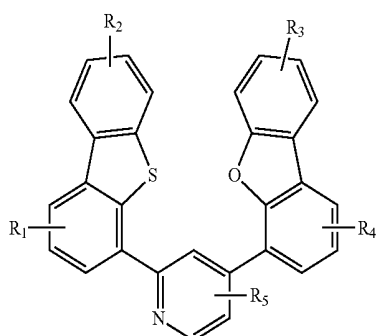


13

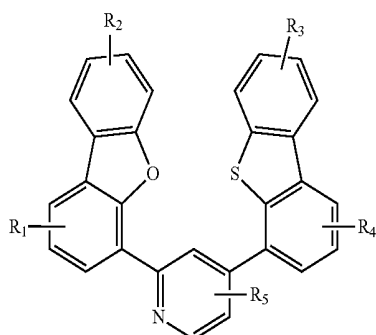
-continued



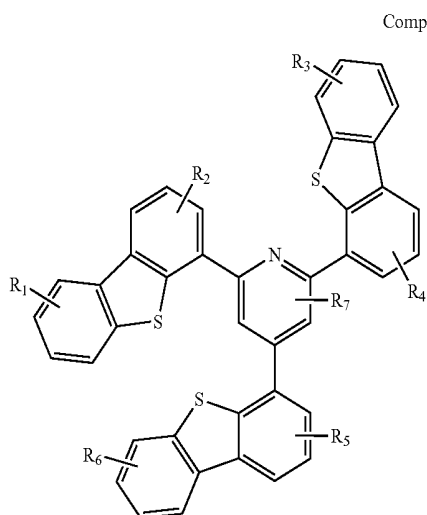
Compound 30G



Compound 31G



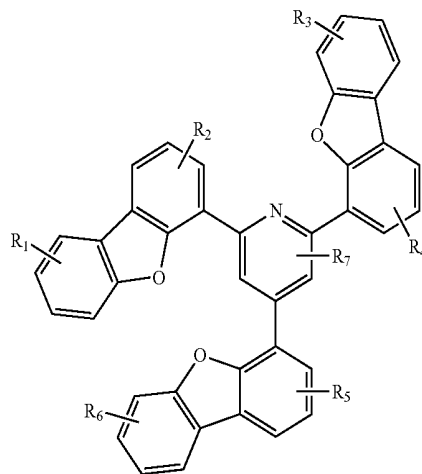
Compound 32G



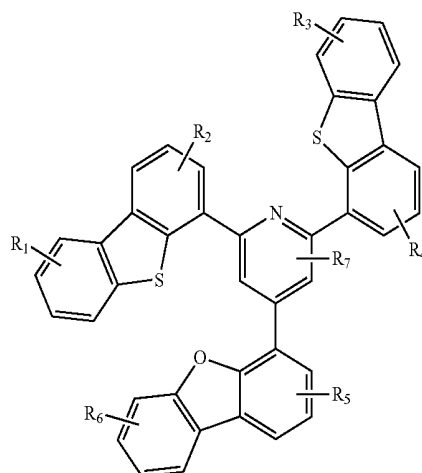
Compound 33G

14

-continued



Compound 34G



Compound 35G

40 where each of R_1 through R_8 are independently selected from the group consisting of any aryl and alkyl substituents and H, and where each of R_1 through R_8 may represent multiple substitutions. In one aspect, all of R_1 through R_8 are H.

45 An organic light emitting device is also provided. The device has an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer further comprises a material containing a compound from the group consisting of Compound 2G through 35G, as described above, with or without substituents. Preferably the organic layer is an emissive layer having a host and an emissive dopant, and the compound is the host. The compound may also preferably be used as a material in an enhancement layer.

55 A consumer product is also provided. The product contains a device that has an anode, a cathode, and an organic layer disposed between the anode and the cathode, where the organic layer further comprises a material containing a compound from the group consisting of Compounds 2G through 35G, as described above, with or without substituents.

BRIEF DESCRIPTION OF THE DRAWINGS

65 FIG. 1 shows an organic light emitting device.
FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

FIG. 3 shows an organic light emitting device including compounds disclosed herein.

FIG. 4 shows a plot of normalized luminescence versus time for the device of FIG. 3.

FIG. 5 shows a plot of external quantum efficiency versus luminance for the device of FIG. 3.

FIG. 6 shows a plot of power efficacy versus luminance for the device of FIG. 3.

FIG. 7 shows a plot of luminance versus voltage for the device of FIG. 3.

FIG. 8 shows a plot of EL intensity versus wavelength for the device of FIG. 3.

FIG. 9 shows an organic light emitting device including compounds disclosed herein.

FIG. 10 shows a plot of external quantum efficiency versus luminance for the device of FIG. 9.

FIG. 11 shows a plot of power efficacy versus luminance for the device of FIG. 9.

FIG. 12 shows a plot of luminance versus voltage for the device of FIG. 9.

FIG. 13 shows a plot of EL intensity versus wavelength for the device of FIG. 9.

FIG. 14 shows a dibenzothiophene-containing compound.

DETAILED DESCRIPTION

Generally, an OLED comprises at least one organic layer disposed between and electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an "exciton," which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," *Nature*, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," *Appl. Phys. Lett.*, vol. 75, No. 3, 4-6 (1999) ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

FIG. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120 (HIL), a hole transport layer 125 (HTL), an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these

various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F .sub.4-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. An "enhancement layer" occupies the same position in a device as a blocking layer described above, and may have blocking functionality or other functionality that improves device performance.

FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole

transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al., which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active

matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C. to 30 degrees C., and more preferably at room temperature (20-25 degrees C.).

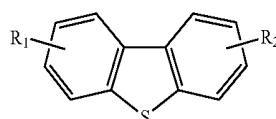
The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

The terms halo, halogen, alkyl, cycloalkyl, alkenyl, alkynyl, arylkyl, heterocyclic group, aryl, aromatic group, and heteroaryl are known to the art, and are defined in U.S. Pat. No. 7,279,704 at cols. 31-32, which are incorporated herein by reference.

Dibenzo[b,d]thiophene (also referred to herein as "dibenzothiophene")-containing materials are provided, which can be used in the PHOLED devices fabricated by both vapor deposition or solution processing, giving long lifetime stable devices with low voltage. The materials may be used as a stable host in PHOLED devices, or in other layers, such as an enhancement layer.

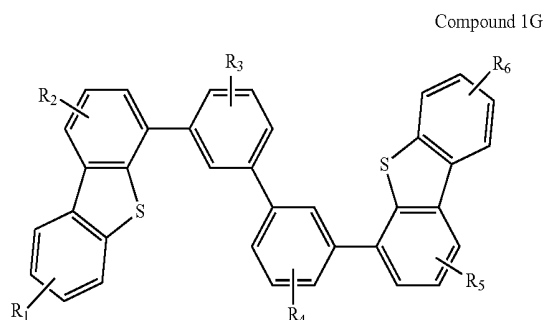
Compounds are provided comprising dibenzothiophene and/or dibenzofuran. Dibenzothiophenes and dibenzofurans may be used as hole and/or electron transporting organic conductors, they usually exhibit more reversible electrochemical reduction in solution than some common organic groups, such as biphenyl. The triplet energies of dibenzothiophenes and dibenzofurans are relatively high. Therefore, a compound containing dibenzothiophene and/or dibenzofuran may be advantageously used as a host or a material for an enhancement layer in PHOLED devices. For example, the triplet energy of dibenzothiophene is high enough for use in a blue or green PHOLED device. Dibenzothiophene and/or dibenzofuran-containing compounds may provide improved device stability while maintaining good device efficiency.

Dibenzothiophene-containing materials may have the following general structure:



Each of R_1 and R_2 may be independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl, and hydrogen, and where R_1 and R_2 may represent multiple substitutions.

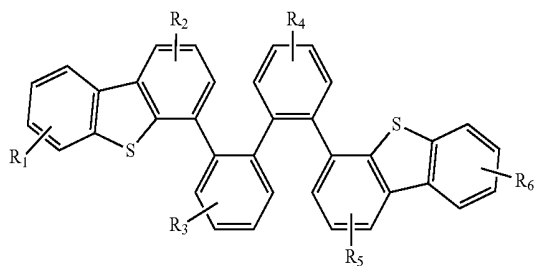
Particular dibenzothiophene compounds are provided, which may be advantageously used in OLEDs, having the following structures:



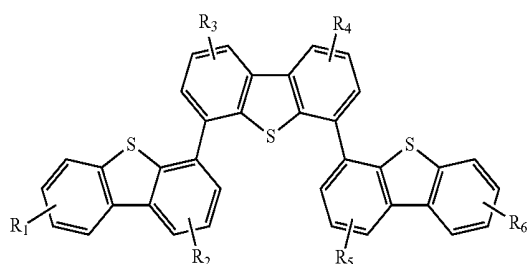
19

-continued

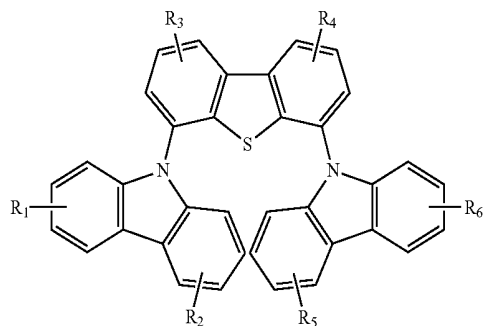
Compound 2G



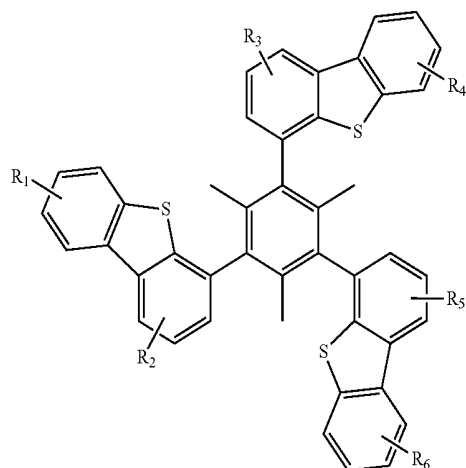
Compound 3G



Compound 4G

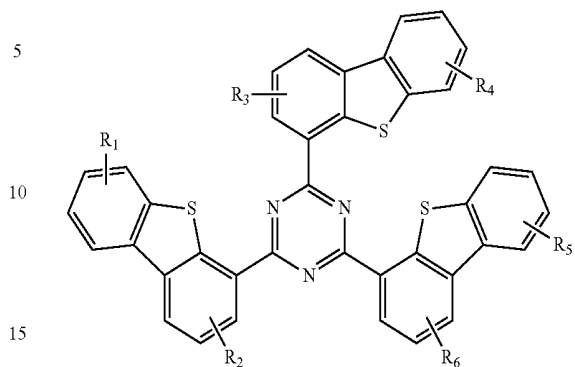


Compound 5G

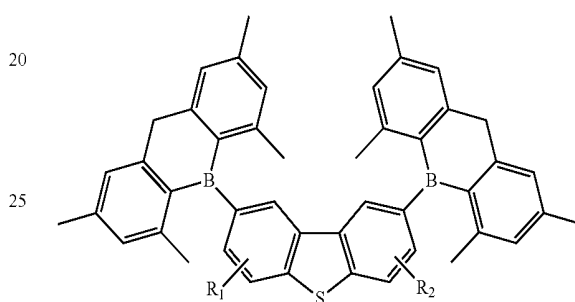
**20**

-continued

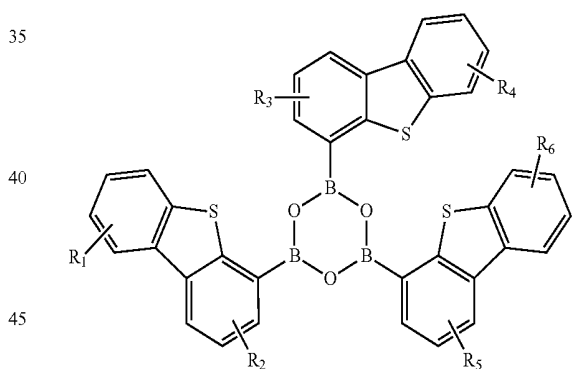
Compound 6G



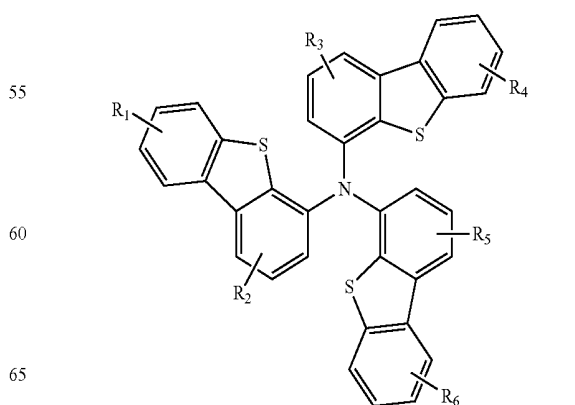
Compound 7G



Compound 8G



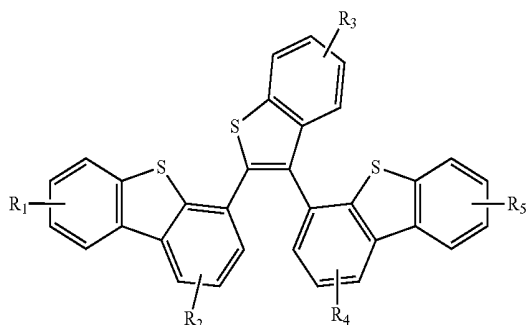
Compound 9G



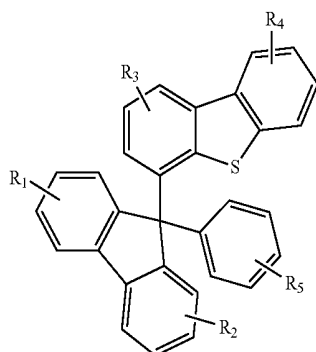
21

-continued

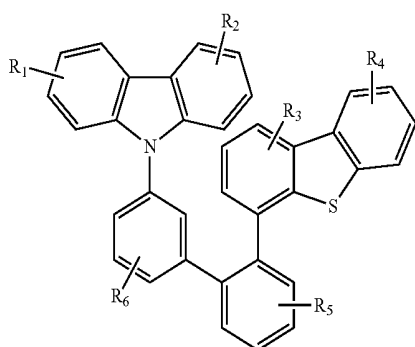
Compound 10G



Compound 11G



Compound 12G



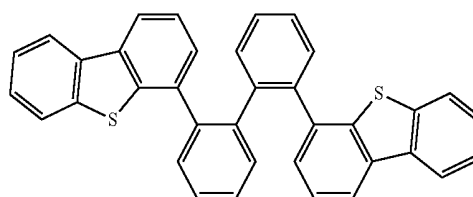
Each of R_1 through R_6 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl, and hydrogen, and where each of R_1 through R_6 may represent multiple substitutions.

Additionally, particular dibenzothiophene-containing compounds, which may be advantageously used in OLEDs, are provided:

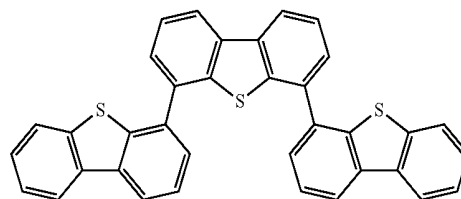
22

-continued

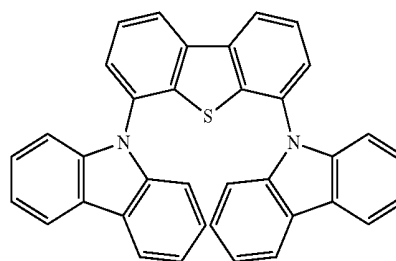
Compound 2



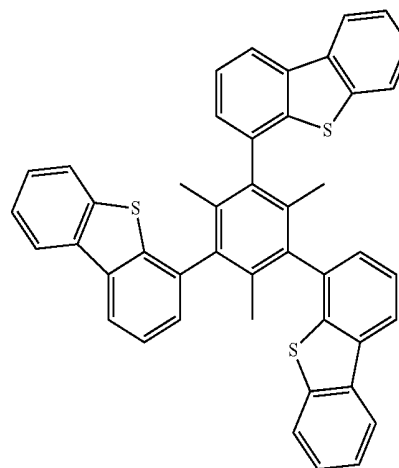
Compound 3



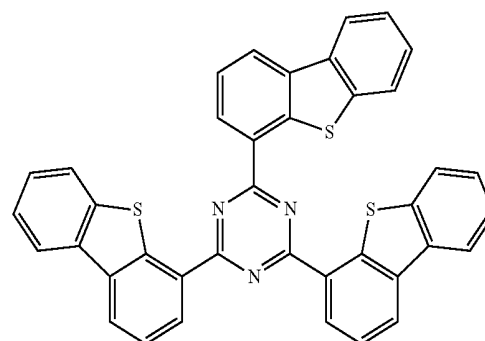
Compound 4



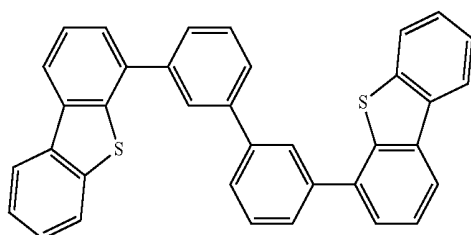
Compound 5



Compound 6

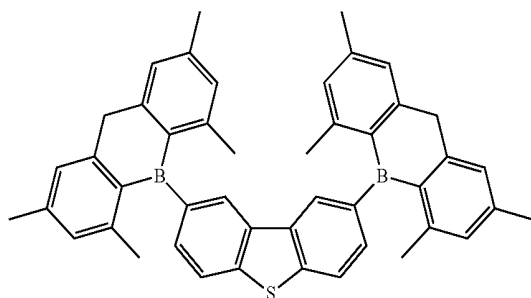


Compound 1



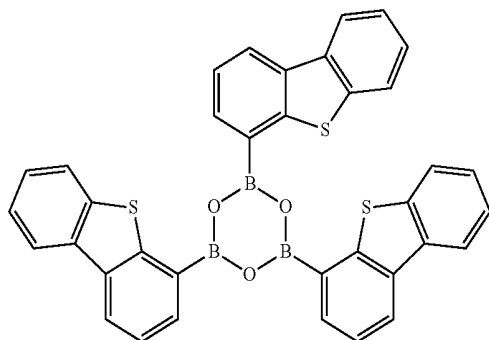
23

-continued

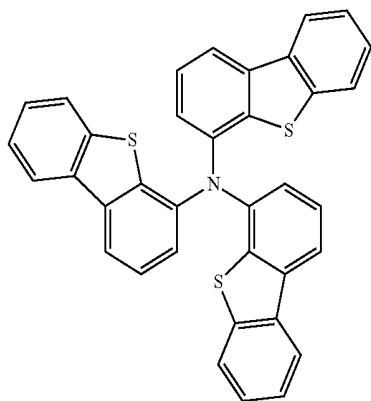


Compound 7

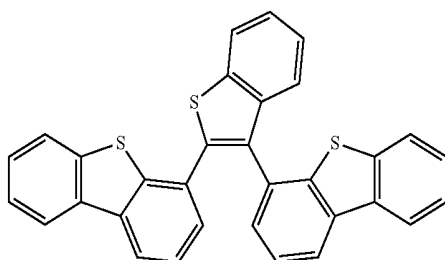
Compound 8



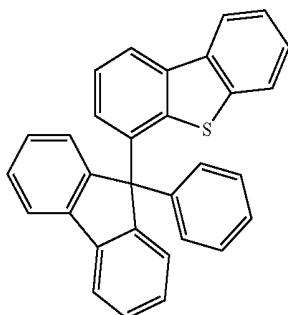
Compound 9



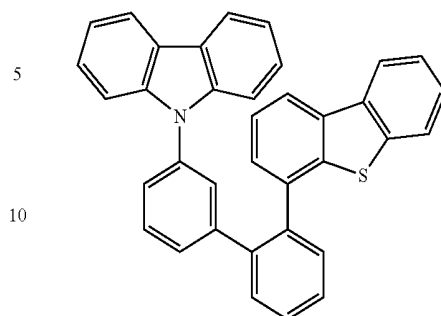
Compound 10



Compound 11

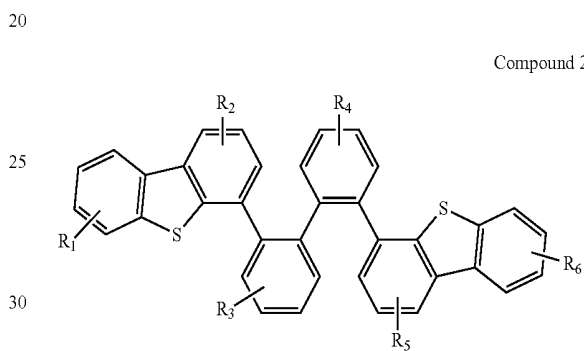
**24**

-continued

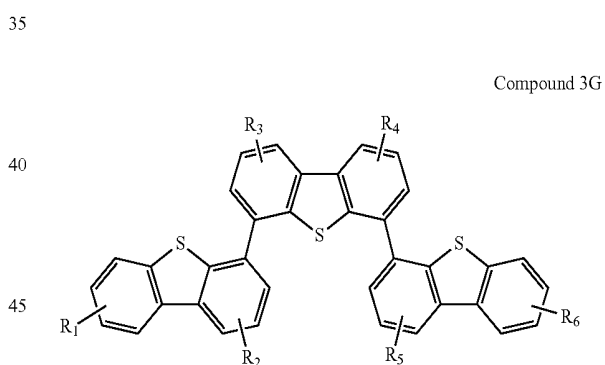


Compound 12

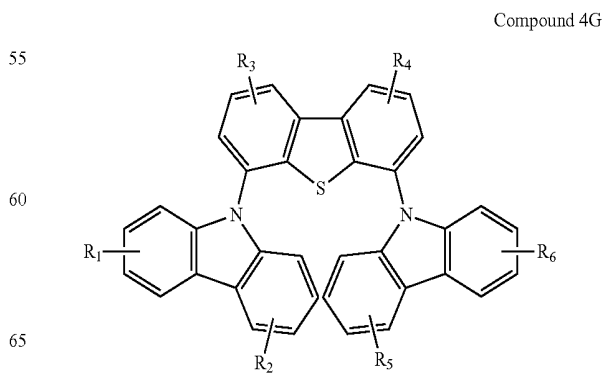
Dibenzothiophene-containing and/or dibenzofuran-containing compounds are provided, which may be advantageously used in OLEDs, having the following structures:



Compound 2G



Compound 3G

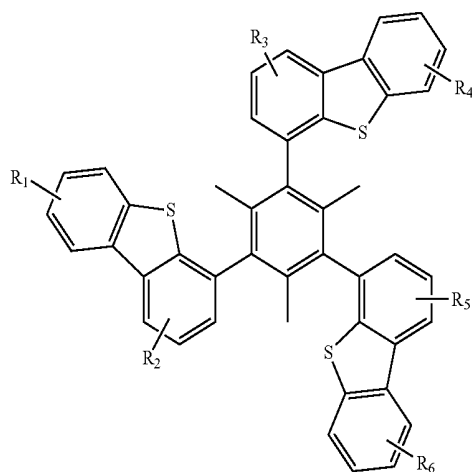


Compound 4G

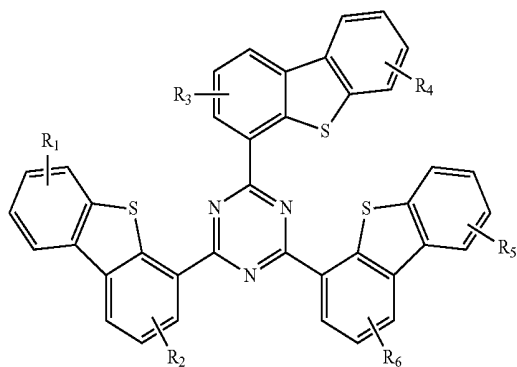
25

-continued

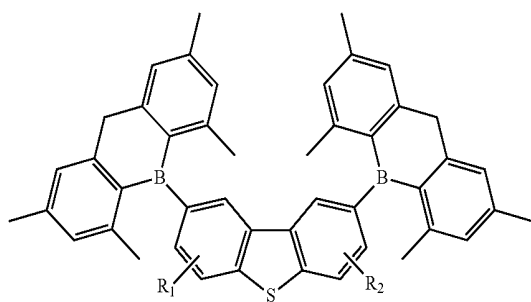
Compound 5G



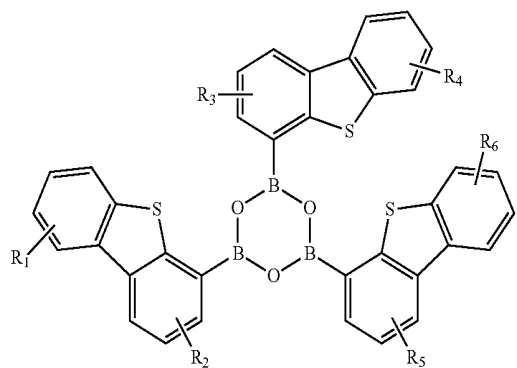
Compound 6G



Compound 7G

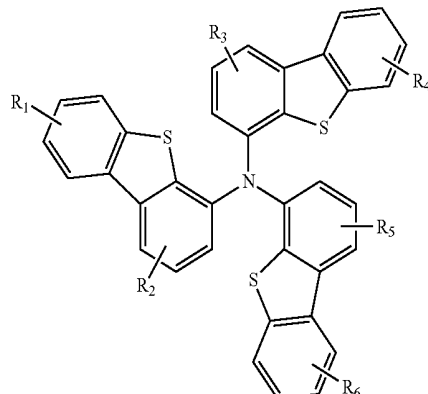


Compound 8G

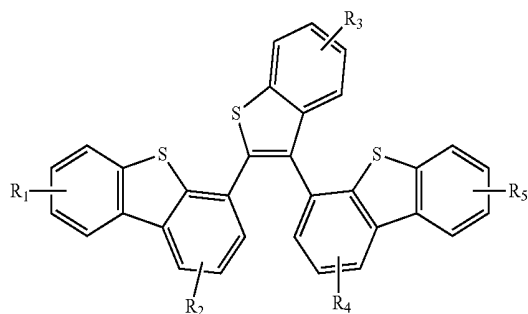
**26**

-continued

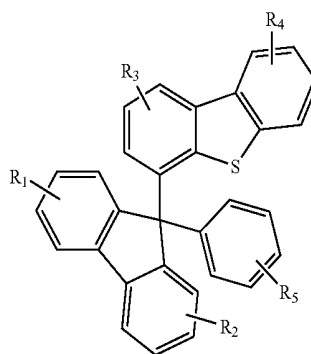
Compound 9G



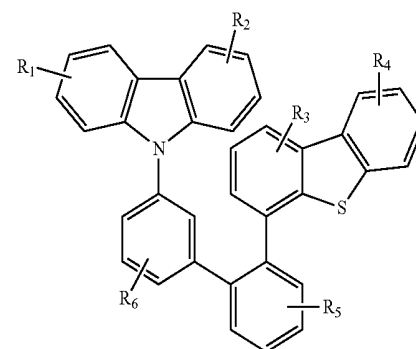
Compound 10G



Compound 11G

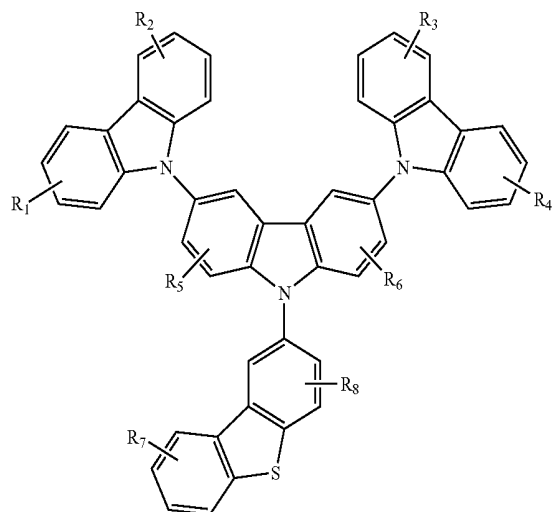
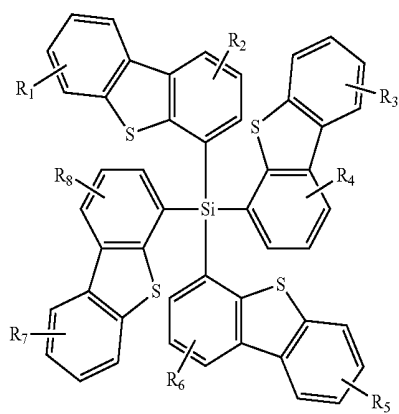
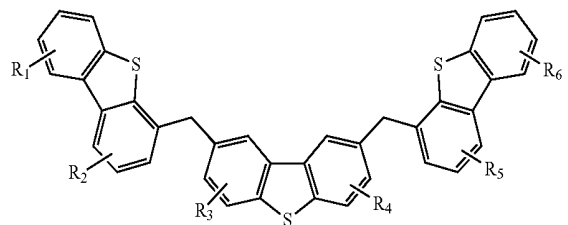
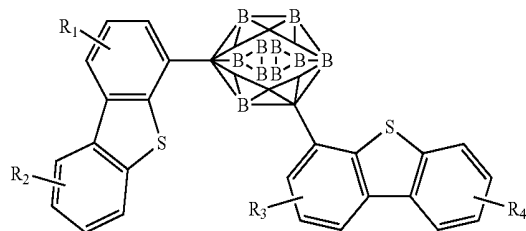
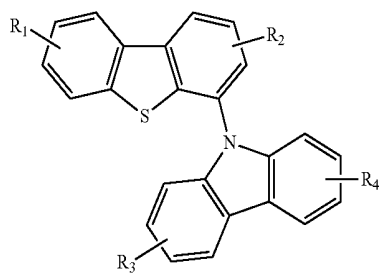


Compound 12G

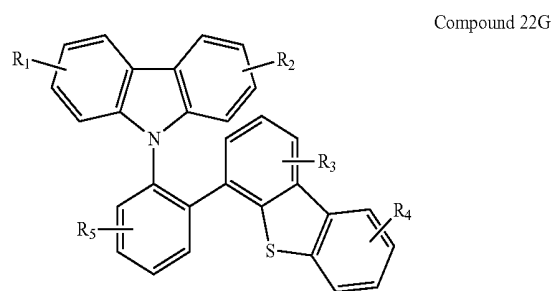
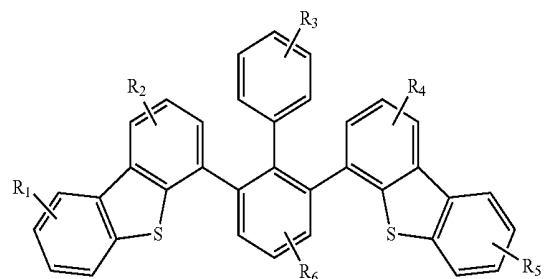
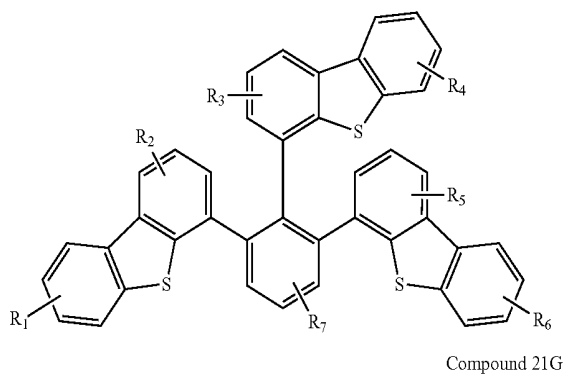
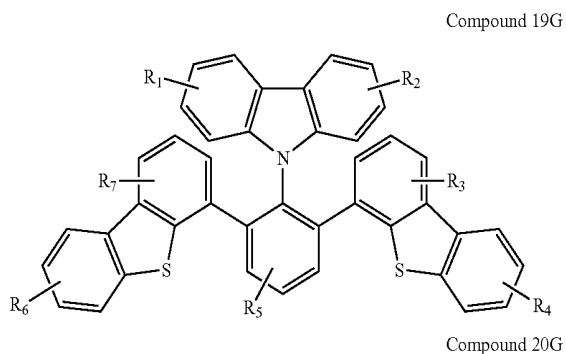
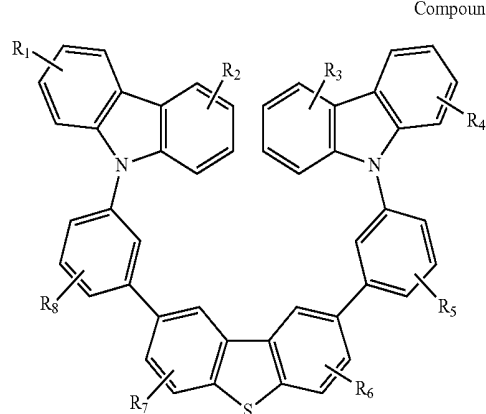


27

-continued

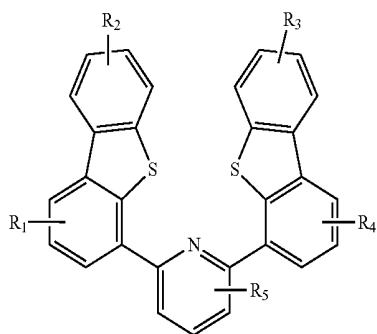
**28**

-continued



29

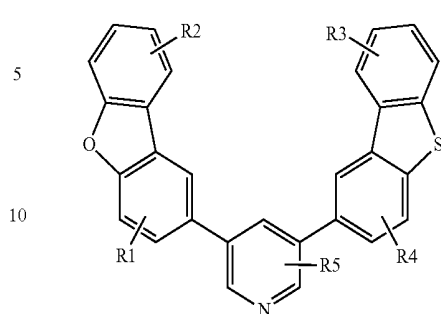
-continued



Compound 23G

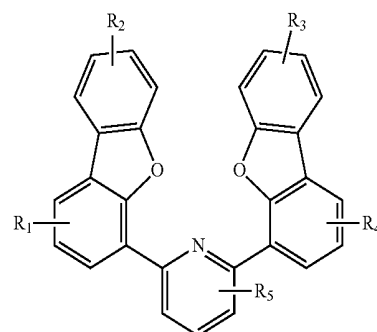
30

-continued

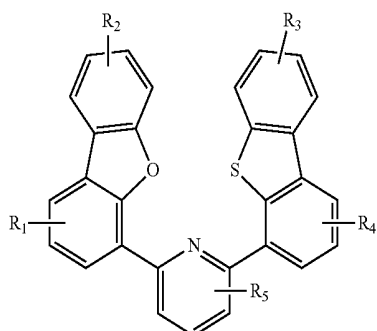


Compound 28G

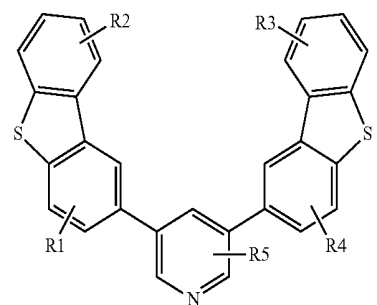
Compound 24G



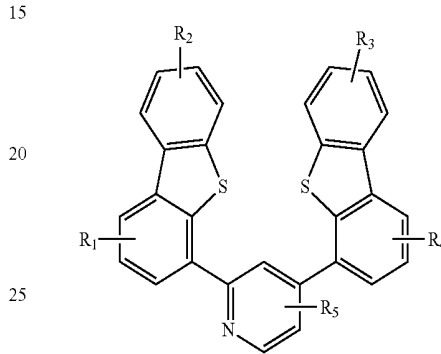
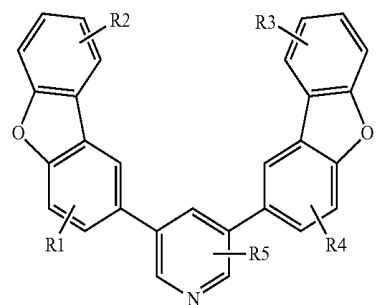
Compound 25G



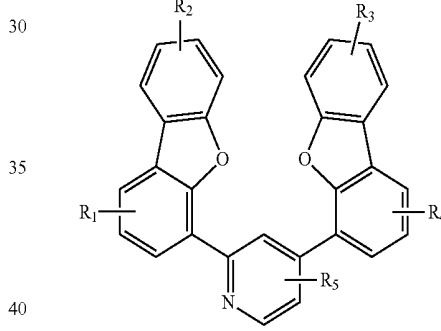
Compound 26G



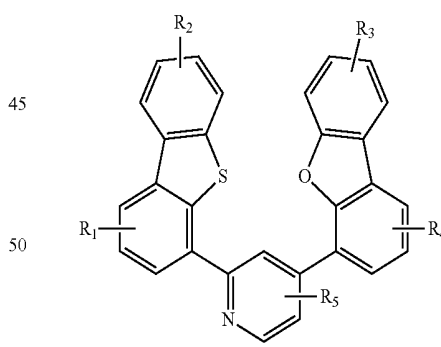
Compound 27G



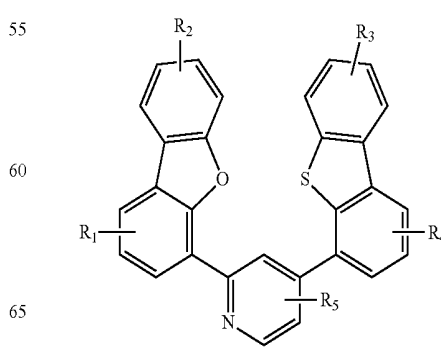
Compound 29G



Compound 30G



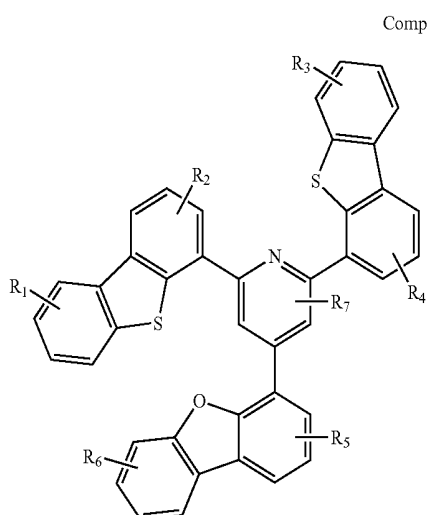
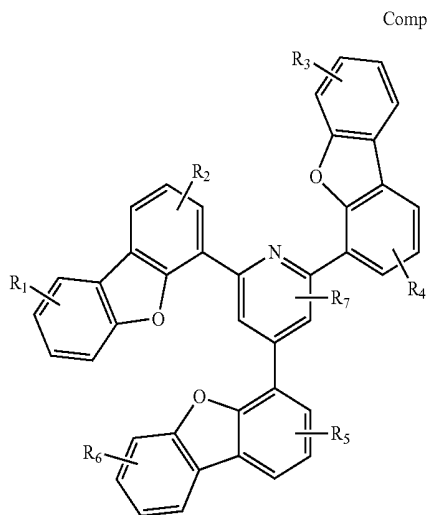
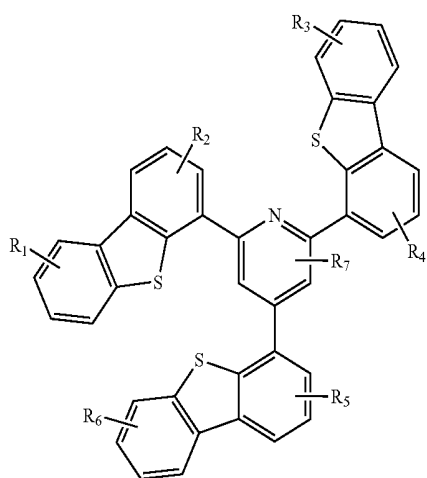
Compound 31G



Compound 32G

31

-continued

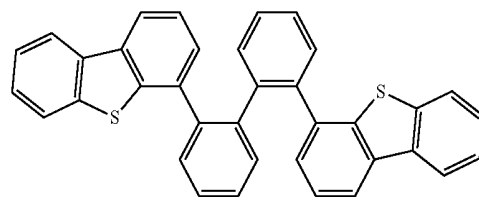


Each of R_1 through R_8 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl, and hydrogen, and where each of R_1 through R_8 may represent multiple substitutions.

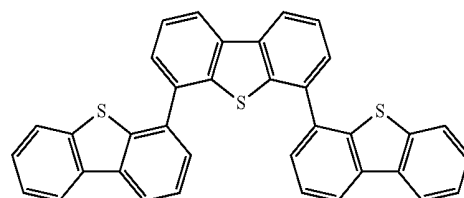
Additionally, dibenzothiophene-containing and/or dibenzofuran-containing compounds are provided, which may be advantageously used in OLEDs, are provided:

32

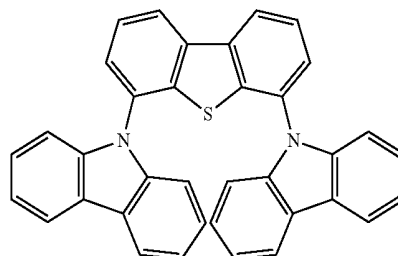
Compound 2



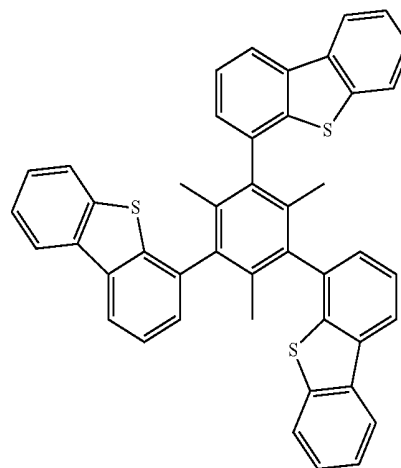
Compound 3



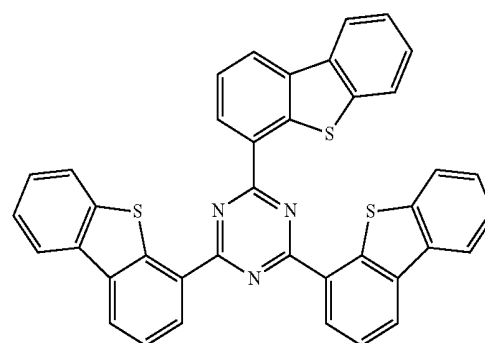
Compound 4



Compound 5



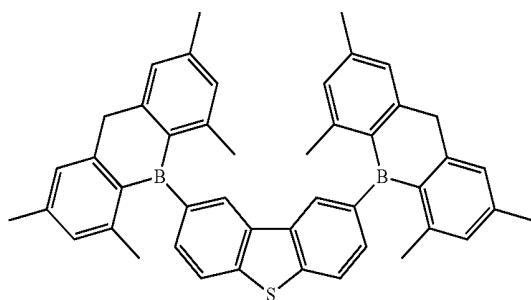
Compound 6



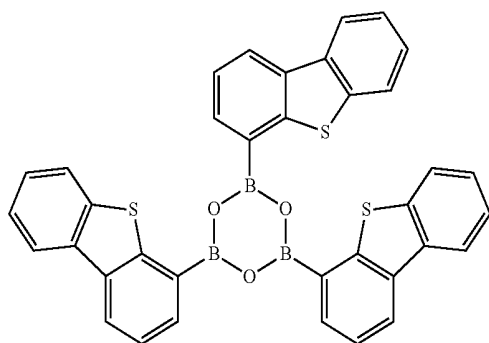
33

-continued

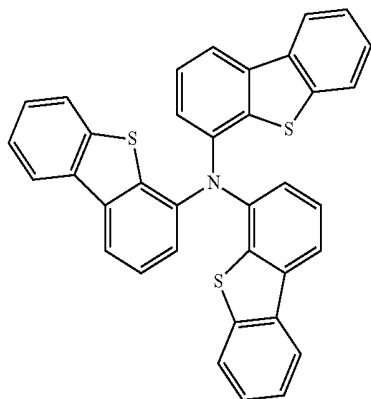
Compound 7



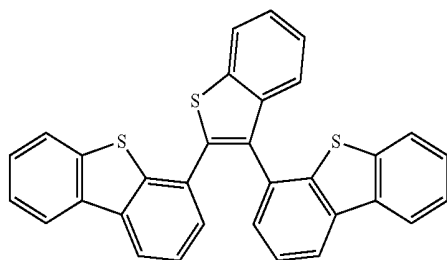
Compound 8



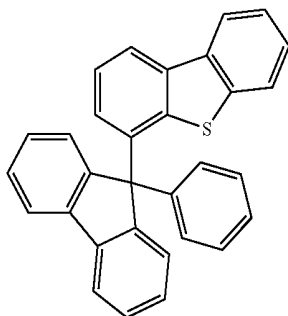
Compound 9



Compound 10



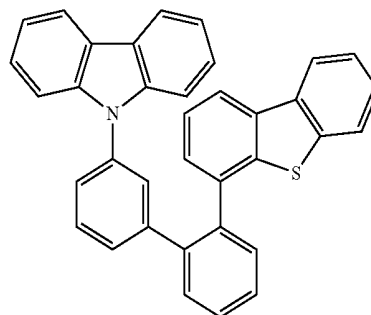
Compound 11



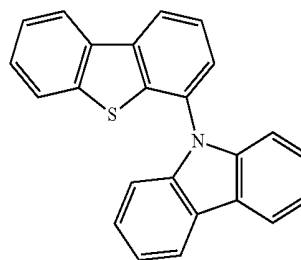
34

-continued

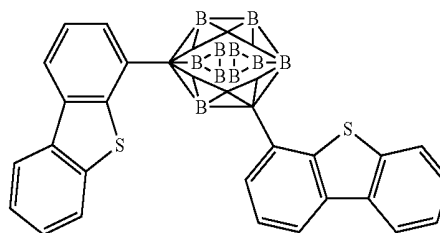
Compound 12



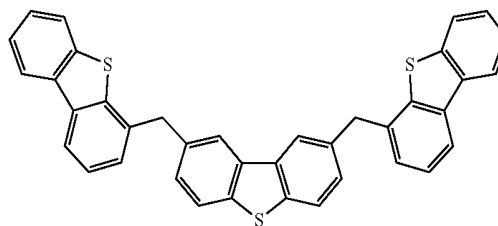
Compound 13



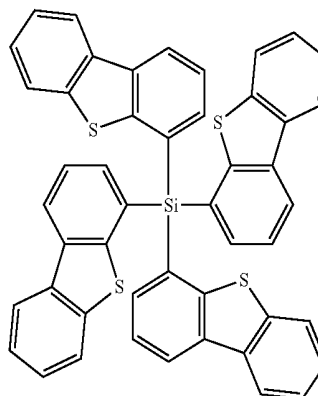
Compound 14



Compound 15



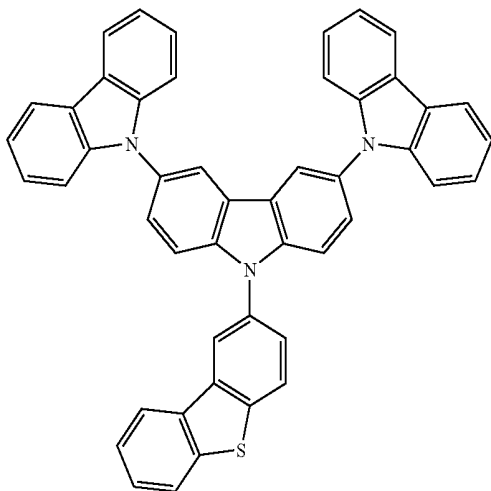
Compound 16



35

-continued

Compound 17



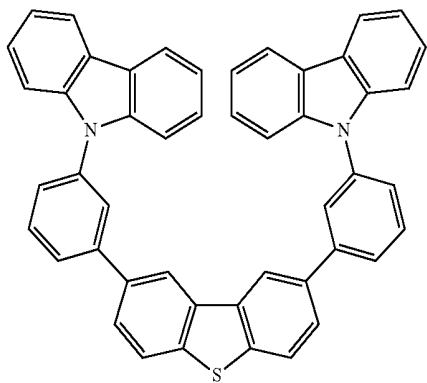
5

10

15

20

Compound 18

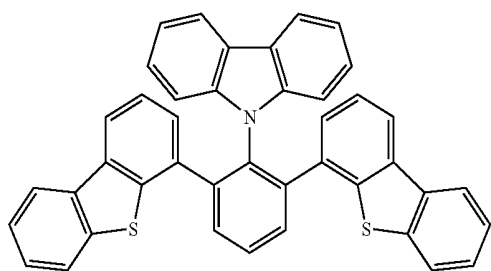


25

30

35

Compound 19

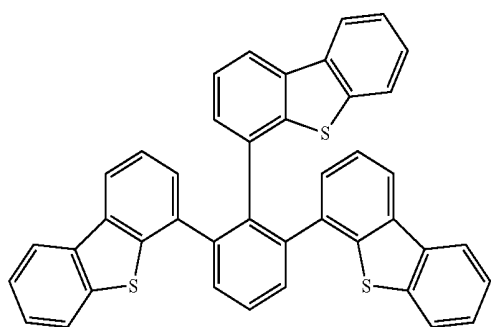


40

45

50

Compound 20



55

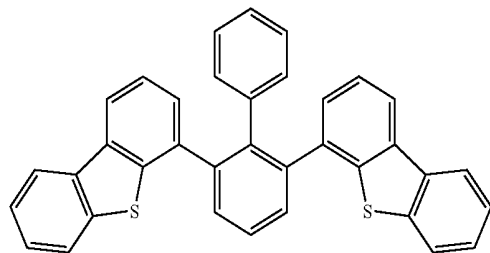
60

65

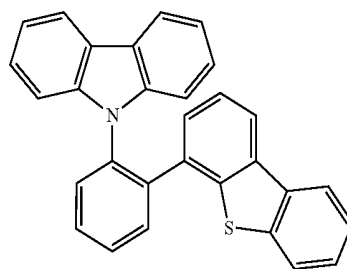
36

-continued

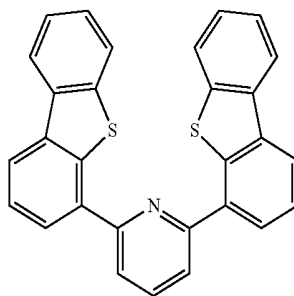
Compound 21



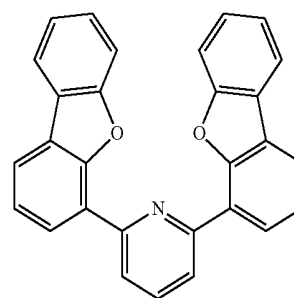
Compound 22



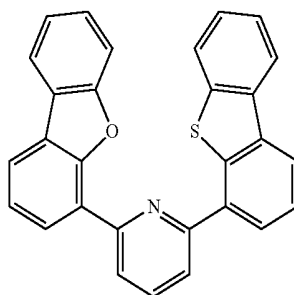
Compound 23



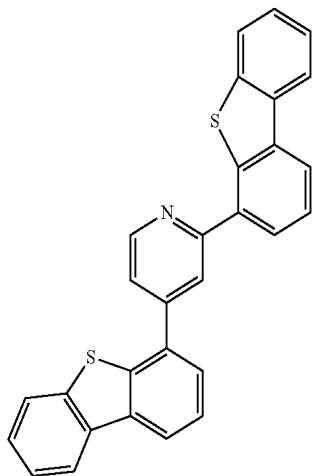
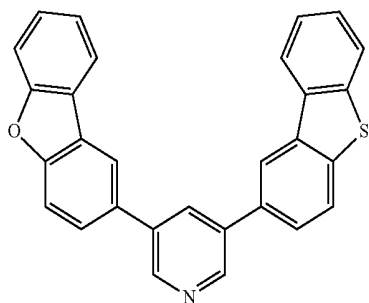
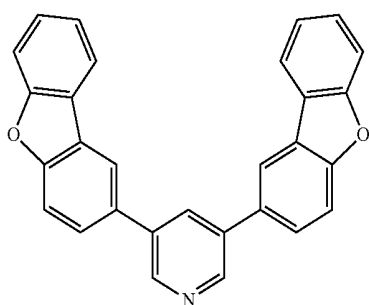
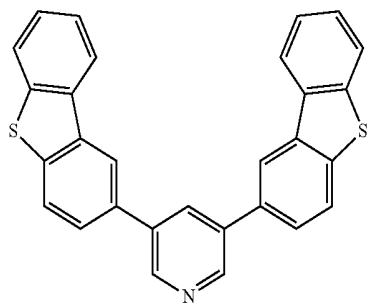
Compound 24



Compound 25



37
-continued



Compound 26

5

10

15

Compound 27

20

25

30

Compound 28

35

40

45

Compound 29

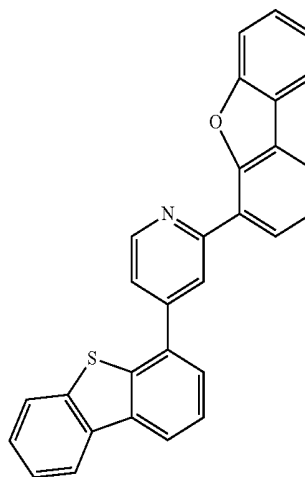
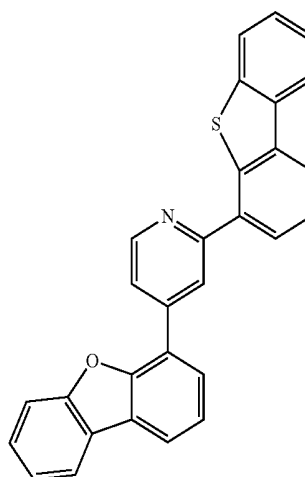
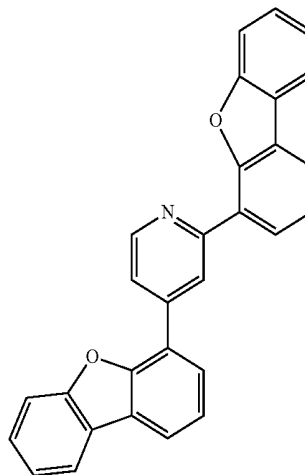
50

55

60

65

38
-continued



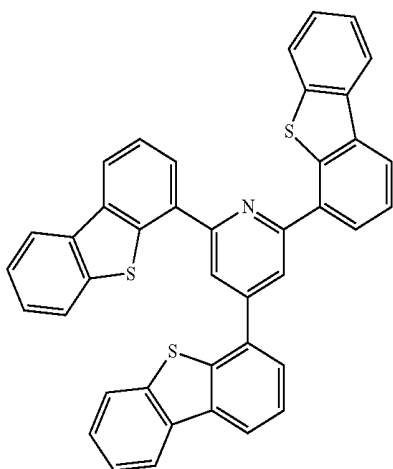
Compound 30

Compound 31

Compound 32

39

-continued



Compound 33

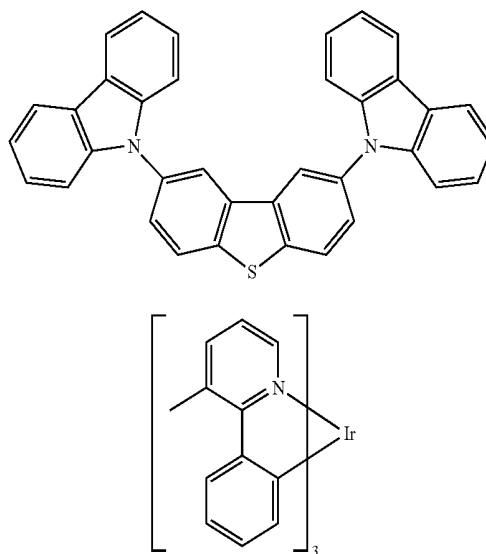
40

5

10

15

20



H1

P1

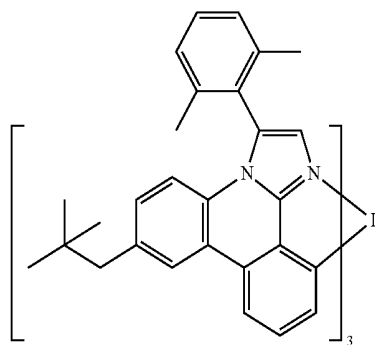
P2

Compound 34

25

30

35



40

45

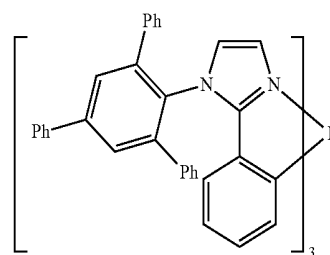
Compound 35

50

55

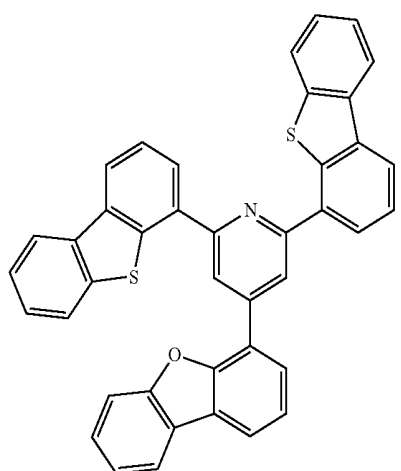
60

65



P3

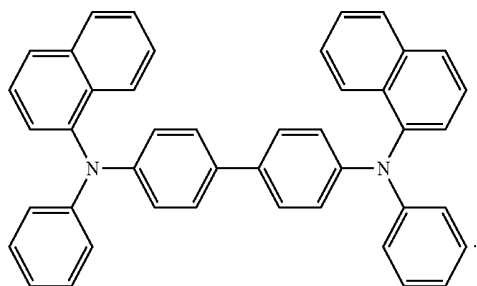
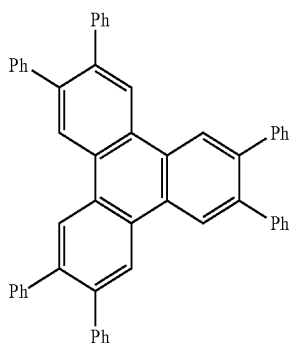
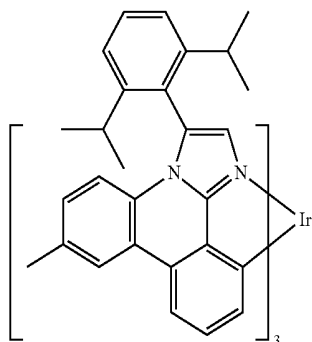
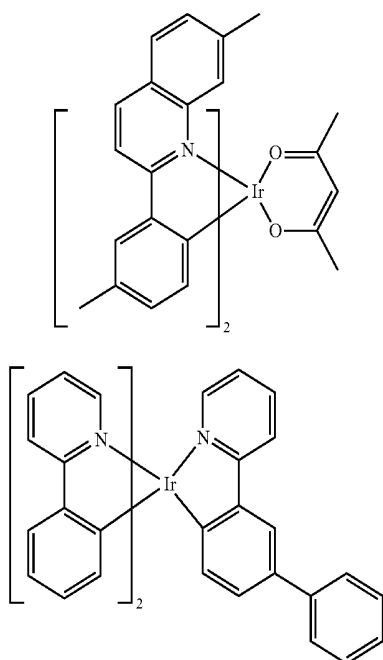
P4



As used herein, the following compounds have the following structures:

41

-continued



42

P5 Particular host-dopant combinations for the emissive layer of an OLED are also provided which may lead to devices having particularly good properties. Specifically, devices having an emissive layer using H1 as the host and P1, P2, or P7 as an emissive dopant are demonstrated to have particularly good properties. Such devices may be particularly favorable when the emissive layer includes two organic layers, a first organic layer including H1 doped with P1, and a second organic layer including H1 doped with P2, as illustrated in FIG. 3.

P6 Similarly, devices having an emissive layer using Compound 1 as the host and P3, P4 and/or P5 as dopants may lead to devices having particularly good properties. Specifically, devices having an emissive layer using Compound 1 as the host and P3 as an emissive dopant, and/or an emissive layer with multiple dopants using Compound 1 as the host and P4 and P5 as dopants, where P5 is the primary emissive dopant in the layer. Such devices may be particularly favorable when the emissive layer includes two organic layers, a first organic layer including Compound 1 doped with P3, and a second organic layer including Compound 1 doped with P4 and P5, as illustrated in FIG. 9.

P7 Devices having an emissive layer using Compound 23 as the host and P1 as the dopant may also lead to devices having particularly good properties.

30 Additionally, a consumer product comprising a device having an anode, a cathode, and an organic layer, disposed between the anode and the cathode. The organic layer further comprises a material containing a compound selected from the group consisting of Compound 2G-35G where R₁ through R₈ are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl and hydrogen, and where each of R₁ through R₈ may represent multiple substitutions.

HPT 40 The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

NPD 55 In addition to and/or in combination with the materials disclosed herein, many hole injection materials, hole transporting materials, host materials, dopant materials, exciton/hole blocking layer materials, electron transporting and electron injecting materials may be used in an OLED. Non-limiting examples of the materials that may be used in an OLED in combination with materials disclosed herein are listed in Table 1 below. Table 1 lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.

TABLE 1

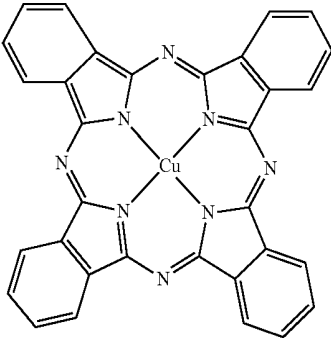
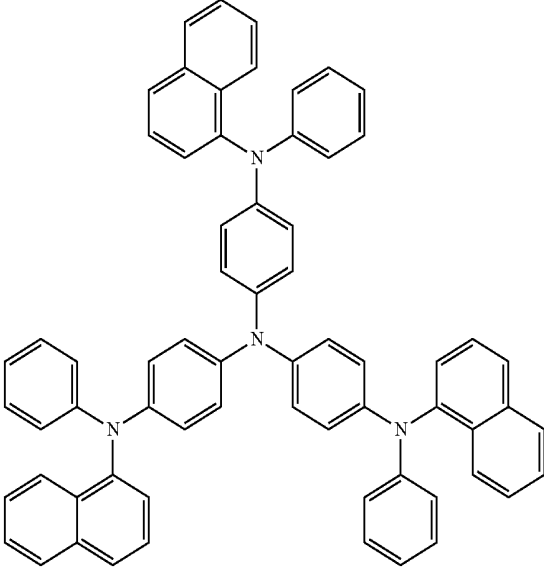
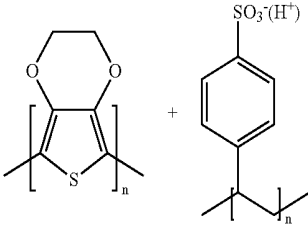
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Hole injection materials		
Phthalocyanine and porphyrin compounds		Appl. Phys. Lett. 69, 2160 (1996)
Starburst triaryl amines		J. Lumin. 72-74, 985 (1997)
CF _x Fluorocarbon polymer	$-[-CH_xF_y-]_n-$	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT: PSS, polyaniline, polythiophene)		Synth. Met. 87, 171 (1997)

TABLE 1-continued

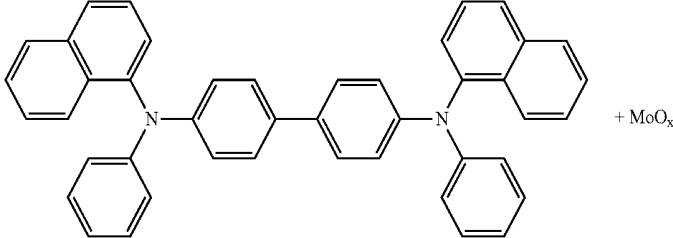
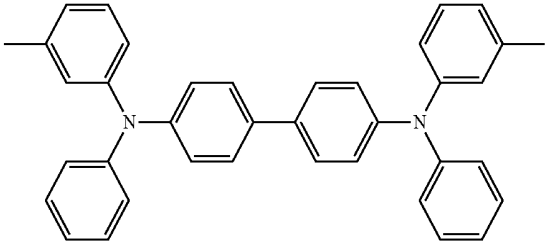
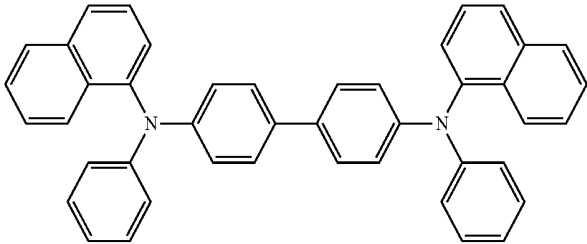
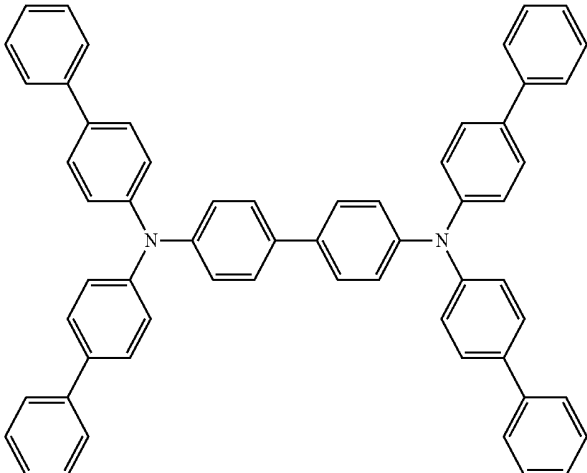
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Aryla- mines com- plexed with metal oxides such as mo- lyb- denum and tung- sten oxides	 <chem>c1ccc(cc1)N(c2ccccc2)c3cc4ccccc4cc3c5ccccc5N(c6ccccc6)c7cc8ccccc8cc7</chem> + MoO _x	SID Symposium Digest, 37, 923 (2006)
Hole transporting materials		
Tri- aryla- mines (e.g., TPD, α- NPD)	 <chem>Cc1ccc(cc1)N(c2ccccc2)c3cc4ccccc4cc3c5ccccc5N(c6ccccc6)c7cc8ccccc8cc7</chem>	Appl. Phys. Lett. 51, 913 (1987)
	 <chem>c1ccc(cc1)N(c2cc3ccccc3cc2)c4cc5ccccc5cc4c6ccccc6N(c7ccccc7)c8cc9ccccc9cc8</chem>	US5061569
	 <chem>c1ccc(cc1)N(c2ccc(cc2)-c3ccccc3)c4cc5ccccc5cc4c6ccccc6N(c7ccc(cc7)-c8ccccc8)c9cc10ccccc10cc9</chem>	EP650955

TABLE 1-continued

MA-
TE-
RIAL

EXAMPLES OF MATERIAL

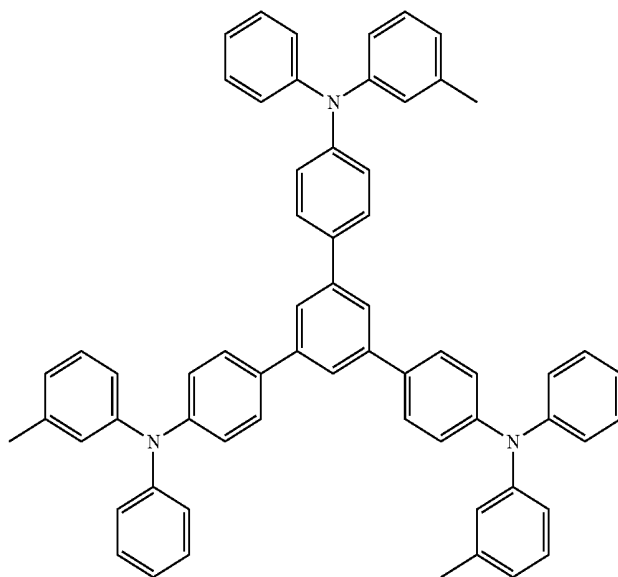
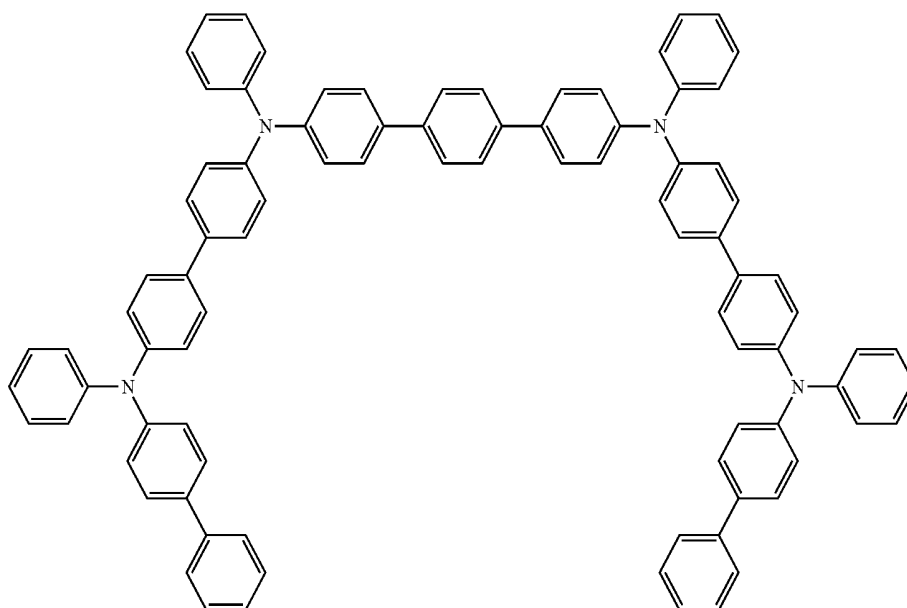
PUBLI-
CATIONSJ. Mater.
Chem. 3, 319
(1993)Appl. Phys.
Lett. 90,
183503 (2007)

TABLE 1-continued

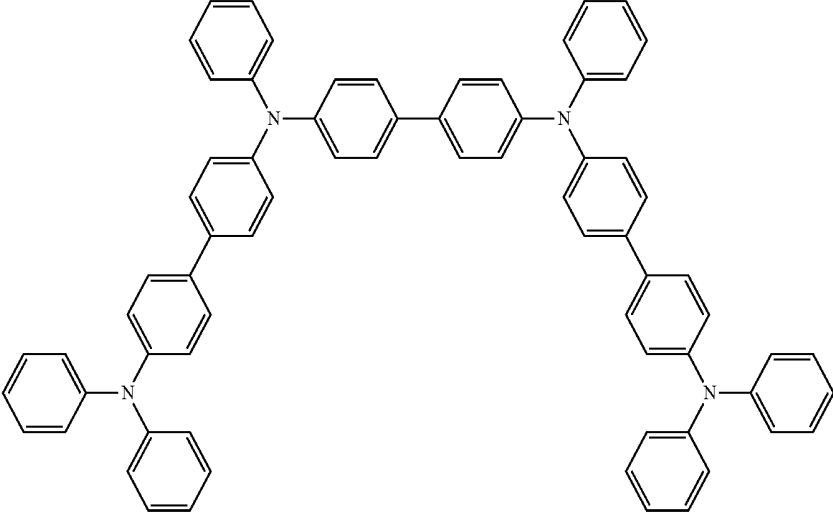
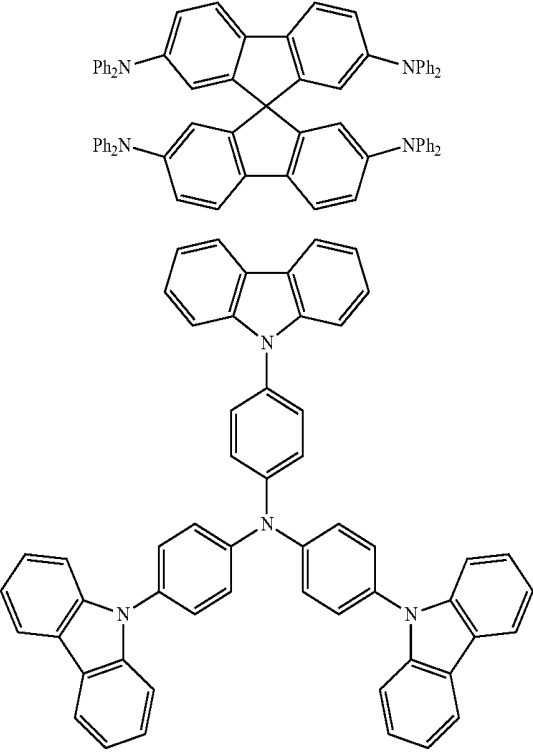
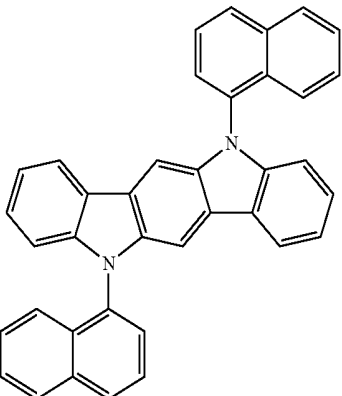
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Tri- aryl- amine on spiro- fluor- ene core		Appl. Phys. Lett. 90, 183503 (2007)
Aryl- amine carb- azole com- pounds		Synth. Met. 91, 209 (1997)
In- dolo- carb- azoles		Synth. Met. 111, 421 (2000)

TABLE 1-continued

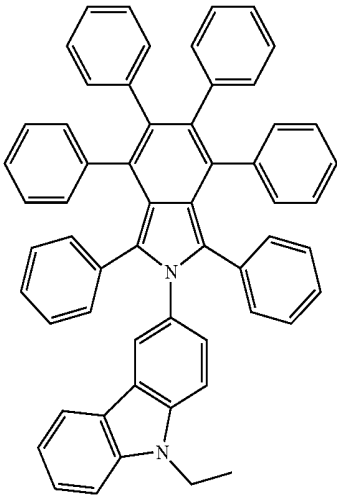
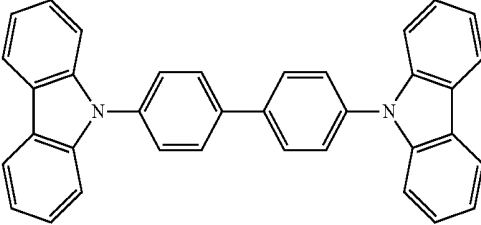
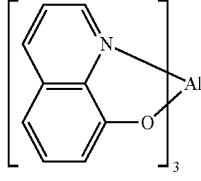
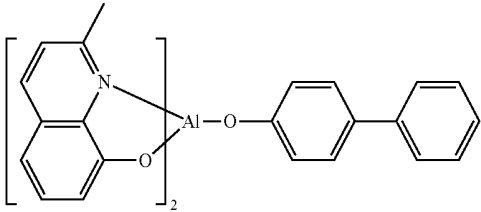
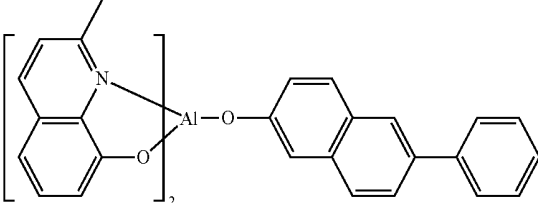
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Iso- indole com- pounds		Chem. Mater. 15, 3148 (2003)
Phosphorescent OLED host materials		
Red hosts		
Aryl- carb- azoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hy- droxy- quino- lates (e.g., Alq ₃ , BALq)		Nature 395, 151 (1998)
		US20060202194
		WO2005014551

TABLE 1-continued

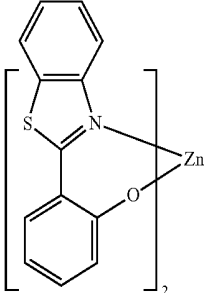
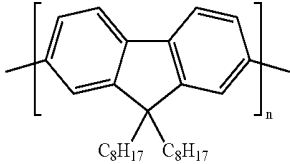
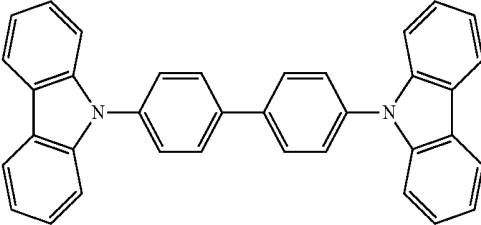
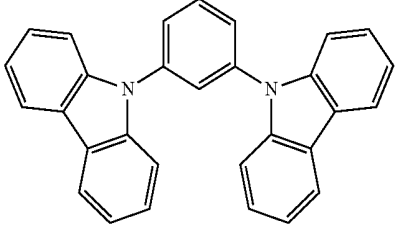
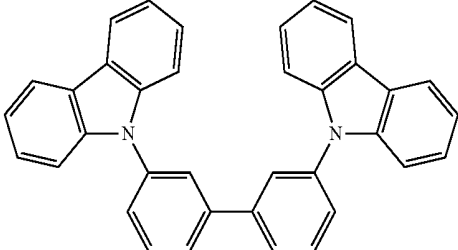
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Metal phen- oxy- benzo- thia- zole com- pounds		Appl. Phys. Lett. 90, 123509 (2007)
Con- ju- gated oligo- mers and poly- mers (e.g., poly- fluor- ene)		Org. Electron. 1, 15 (2000)
Green hosts		
Aryl- carba- zoles		Appl. Phys. Lett. 78, 1622 (2001)
		US2003175553
		WO2001039234

TABLE 1-continued

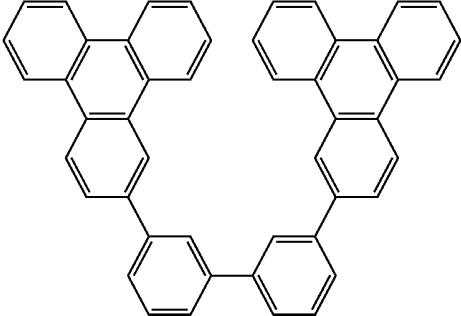
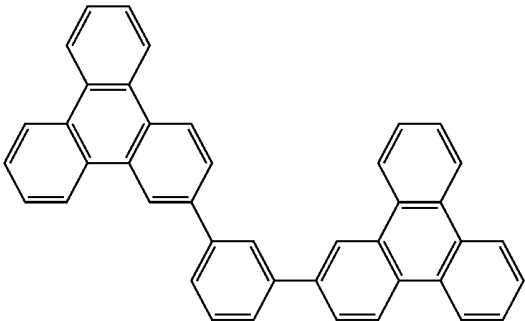
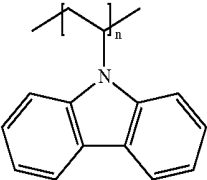
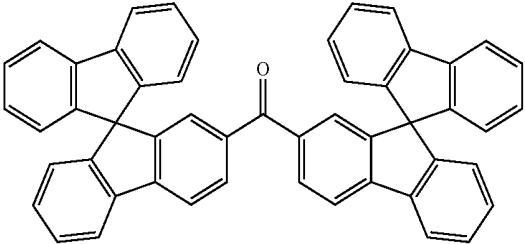
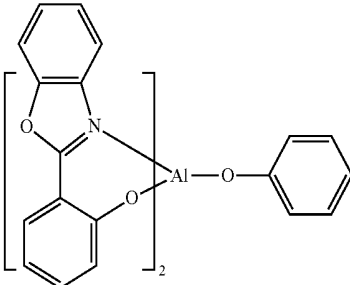
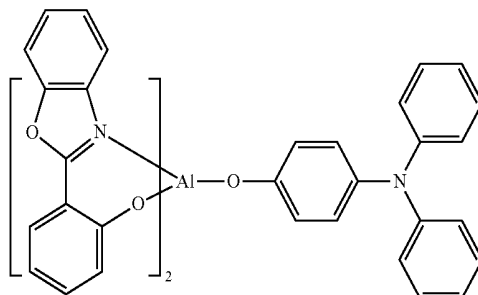
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Aryl- tri- phen- ylene com- pounds		US20060280965
		US20060280965
Poly- mers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spiro- fluor- ene com- pounds		WO2004093207
Metal phen- oxy- benzo- oxa- zole com- pounds		WO05089025

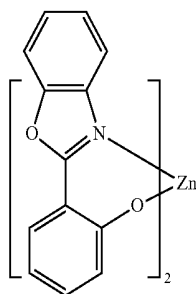
TABLE 1-continued

MA-
TE-
RIAL

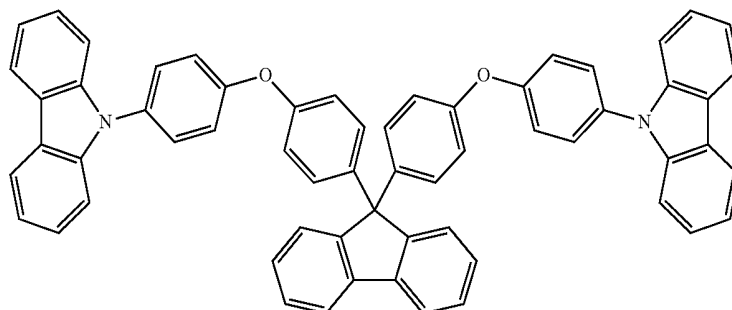
EXAMPLES OF MATERIAL

PUBLI-
CATIONS

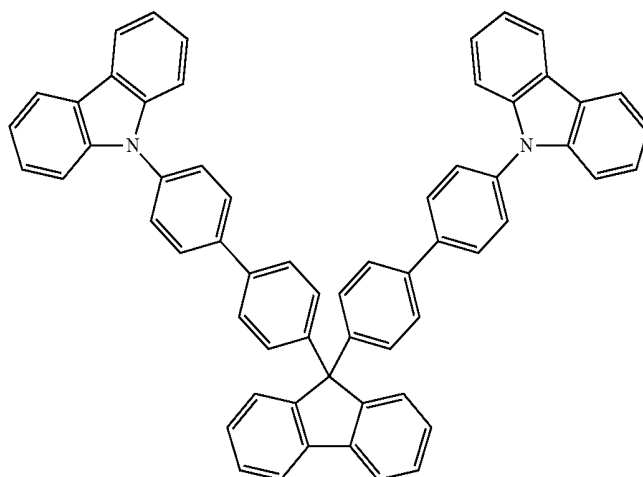
WO06132173



JP200511610

Spiro-
fluor-
ene-
carb-
azole
com-
pounds

JP2007254297



JP2007254297

TABLE 1-continued

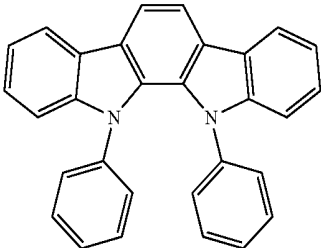
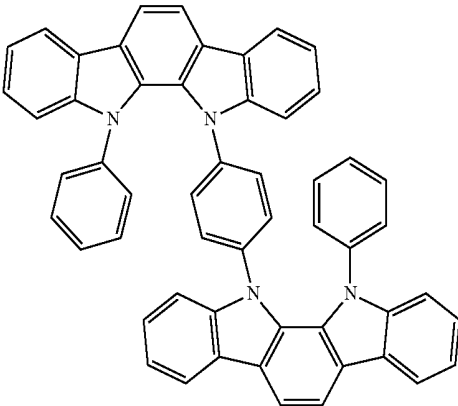
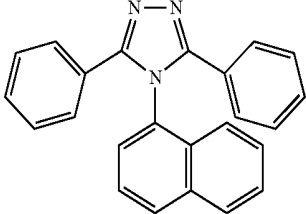
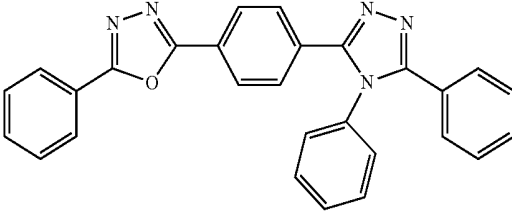
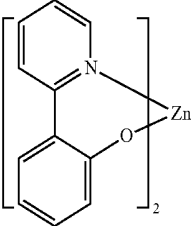
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
In- dolo- caba- zoles		WO07063796
		WO07063754
5- mem- ber ring elec- tron defi- cient he- tero- cycles (e.g., tri- azole, oxa- dia- zole)		J. Appl. Phys. 90, 5048 (2001)
		WO04107822
Metal phen- oxy- pyri- dine com- pounds		WO05030900

TABLE 1-continued

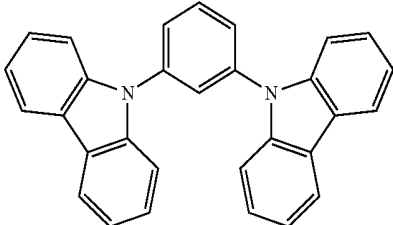
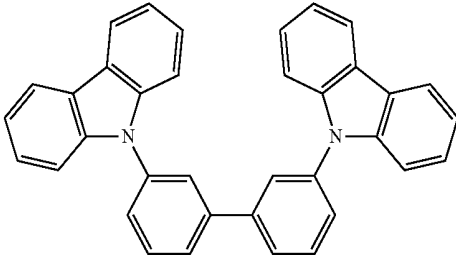
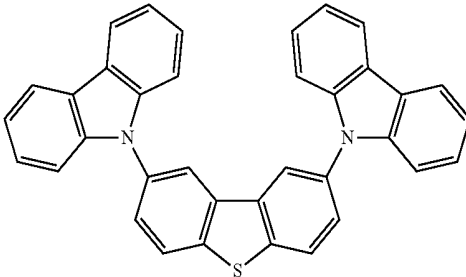
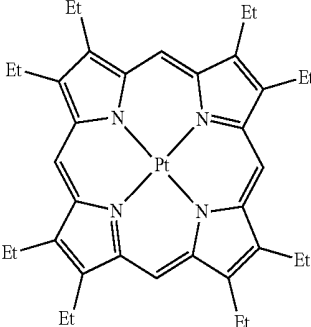
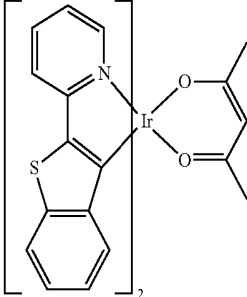
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Aryl- carb- azoles		Appl. Phys. Lett. 82, 2422 (2003)
		US20070190359
Di- benzo- thio- phene- carb- azole com- pounds		WO2006114966
Phosphorescent dopants		
Red dopants		
Heavy metal por- phy- rins (e.g., Pt- OEP)		Nature 395, 151 (1998)
Iri- dium (III) or- gano- metal- lic com- plexes		Appl. Phys. Lett. 78, 1622 (2001)

TABLE 1-continued

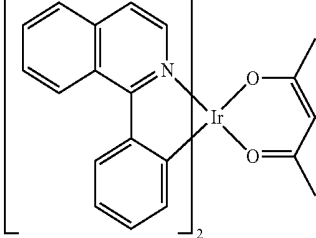
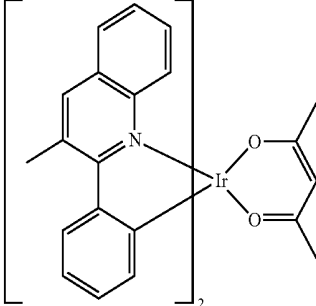
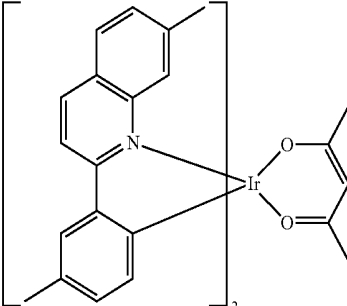
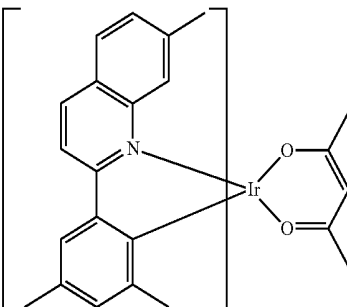
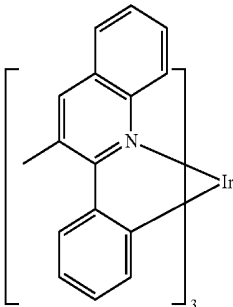
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
		US06835469
		US06835469
		US20060202194
		US20060202194
		US07087321

TABLE 1-continued

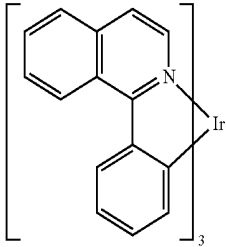
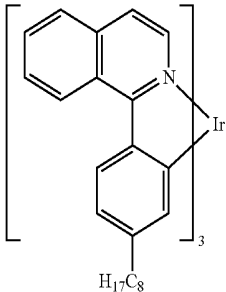
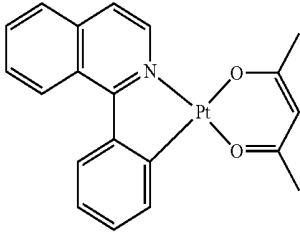
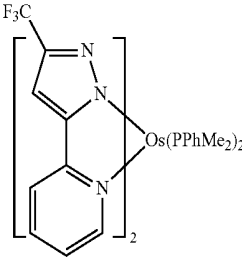
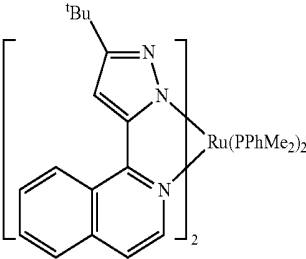
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
		US07087321
		Adv. Mater. 19, 739 (2007)
Plat- inum (II) or- gano- metal- lic com- plexes		WO2003040257
Osmi- num (III) com- plexes		Chem. Mater. 17, 3532 (2005)
Ruth- enium (II) com- plexes		Adv. Mater. 17, 1059 (2005)
Green dopants		

TABLE 1-continued

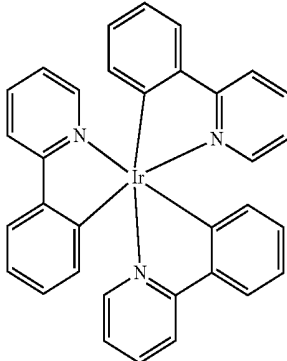
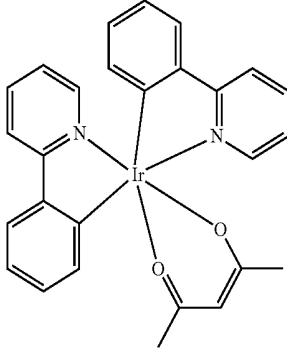
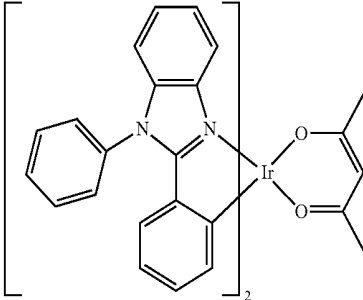
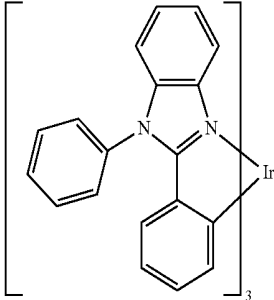
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Iri- dium (III) or- gano- metal- lic com- plexes	 <p data-bbox="671 804 804 824">and its derivatives</p>	Inorg. Chem. 40, 1704 (2001)
		US2002034656
		US06687266
		Chem. Mater. 16, 2480 (2004)

TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Pt(II) or- gano- metal- lic com- plexes		US2007190359
		US 2006008670 JP2007123392
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800
		Appl. Phys. Lett. 86, 153505 (2005)

TABLE 1-continued

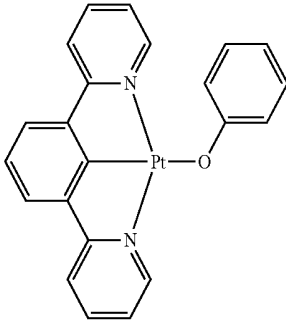
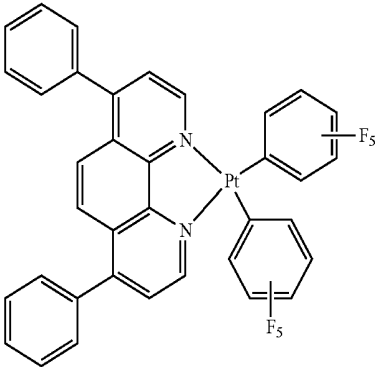
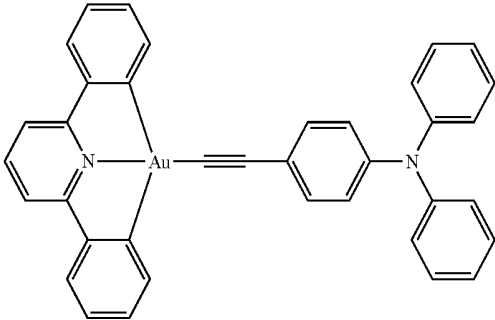
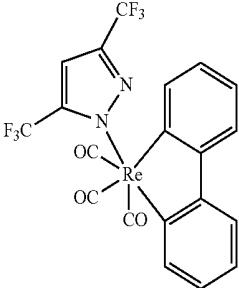
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
		Appl. Phys. Lett. 86, 153505 (2005)
		Chem. Lett. 34, 592 (2005)
Gold com- plexes		Chem. Commun. 2906 (2005)
Rhe- nium (III) com- plexes		Inorg. Chem. 42, 1248 (2003)
Blue dopants		

TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Iri- dium (III) or- gano- metal- lic com- plexes		WO2002002714
		WO2006009024
		US2006251923
		WO2006056418, US2005260441
		US2007190359
		US2002134984

TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
		Angew. Chem. Int. Ed. 47, 1 (2008)
		Chem. Mater. 18, 5119 (2006)
		Inorg. Chem. 46, 4308 (2007)
		WO05123873
		WO05123873

TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
		WO07004380
		WO06082742
Os- mium (II) com- plexes		US2005260449
		Organo- metallics 23, 3745 (2004)
Gold com- plexes		Appl. Phys. Lett. 74, 1361 (1999)

TABLE 1-continued

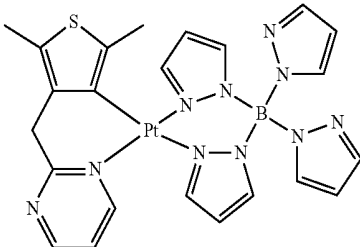
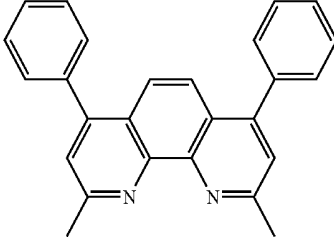
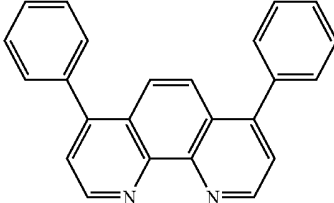
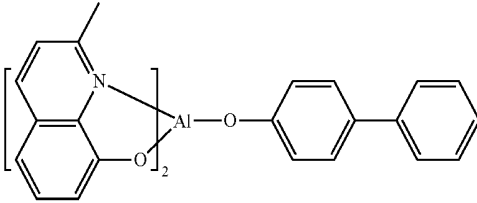
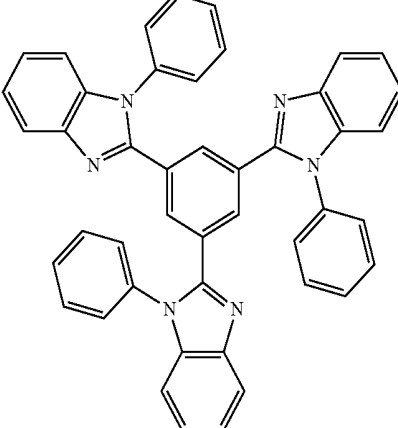
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Plati- num (II) com- plexes		WO06098120, WO06103874
Exciton/hole blocking layer materials		
Bath- ocu- prine com- pounds (e.g., BCP, B- Phen)		Appl. Phys. Lett. 75, 4 (1999)
		Appl. Phys. Lett. 79, 449 (2001)
Metal 8-hy- droxy- quin- olates (e.g., BAlq)		Appl. Phys. Lett. 81, 162 (2002)
5- mem- ber ring elec- tron defi- cient hetero- cycles such as tri- azole, oxadi- azole, imida- zole, benzo- imida- zole		Appl. Phys. Lett. 81, 162 (2002)

TABLE 1-continued

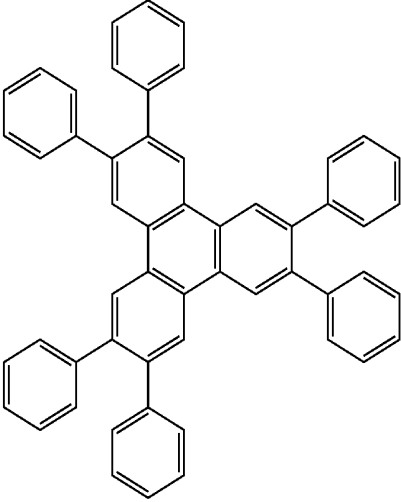
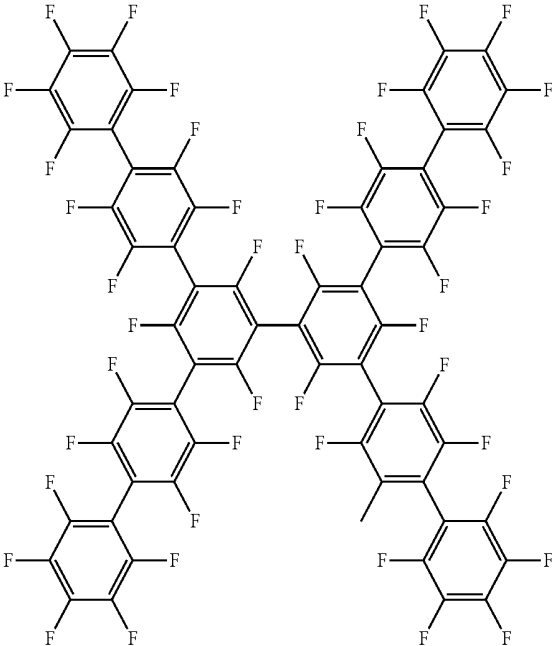
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Tri- phen- ylene com- pounds		US20050025993
Fluor- inated aro- matic com- pounds		Appl. Phys. Lett. 79, 156 (2001)
Electron transporting materials		

TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
An- thra- cene- benzo- imida- zole com- pounds		WO03060956
An- thra- cene- benzo- thia- zole com- pounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hy- droxy- quin- olates (e.g., Alq ₃)		Appl. Phys. Lett. 51, 913 (1987)
Metal hy- droxy- beno- quino- lates		Chem. Lett. 5, 905 (1993)
Batho- cu- prine com- pounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)

TABLE 1-continued

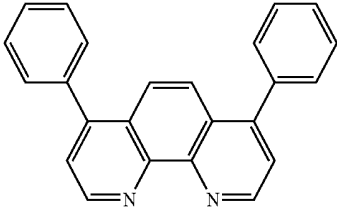
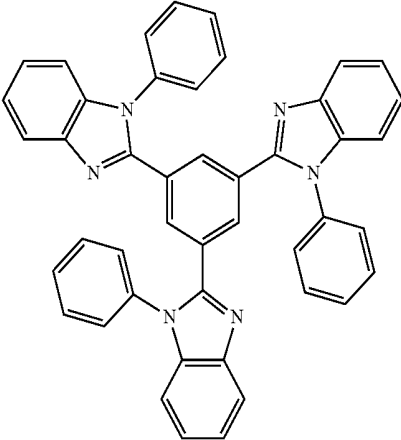
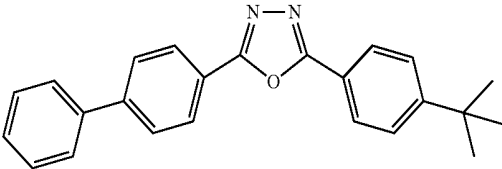
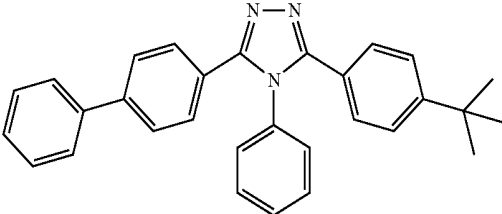
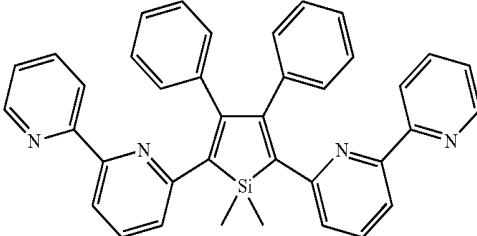
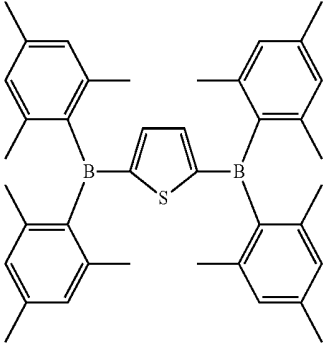
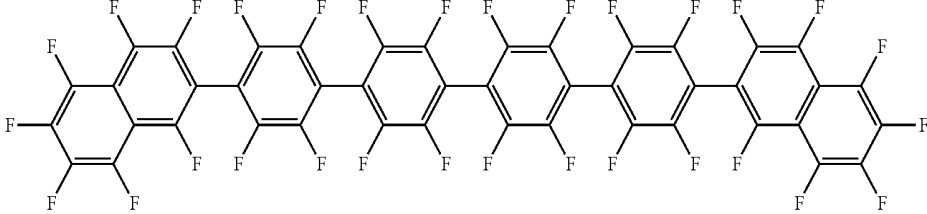
MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
5- mem- ber ring elec- tron defi- cient hetero- cycles (e.g., tria- zole, oxadi- azole, imida- zole, benzo- imida- zole)		Appl. Phys. Lett. 79, 449 (2001)
		Appl. Phys. Lett. 74, 865 (1999)
		Appl. Phys. Lett. 55, 1489 (1989)
Silole com- pounds		Jpn. J. Apply. Phys. 32, L917 (1993)
		Org. Electron. 4, 113 (2003)

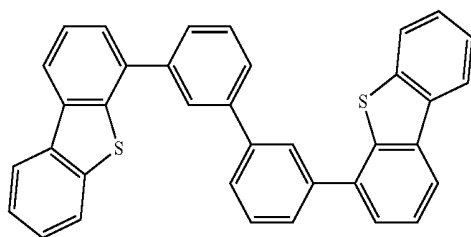
TABLE 1-continued

MA- TE- RIAL	EXAMPLES OF MATERIAL	PUBLI- CATIONS
Aryl- borane com- pounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aro- matic com- pounds		J. Am. Chem. Soc. 122, 1832 (2000)

EXPERIMENTAL

Compound Examples

Some of the dibenzothiophene-containing compounds were synthesized, as follows:



Compound 1

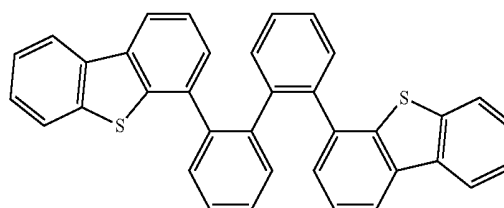
Step 1. 3,3'-dihydroxybiphenyl (9.3 g, 50 mmol) was dissolved in 100 mL of CH₂Cl₂, followed by the addition of pyridine (15.8 g, 200 mmol). To this solution at -15° C., Tf₂O (42.3 g, 150 mmol) was added dropwise. The mixture was continued to stir at room temperature for 5 h. The organic phase was separated and washed with brine once. The crude product was further purified by a silica column. 3,3'-ditriflatebiphenyl was obtained as pale white solid (21.3 g).

Step 2. To a 500 mL round flask was added 3,3'-ditriflatebiphenyl (2.7 g, 6 mmol), 4-dibenzothiopheneboronic acid (4.1 g, 18 mmol), Pd₂(dba)₃ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.3 g, 0.8 mmol), potassium phosphate tribasic (5.1 g, 24 mmol), and 150 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 2.6 g.

30

Compound 2

35

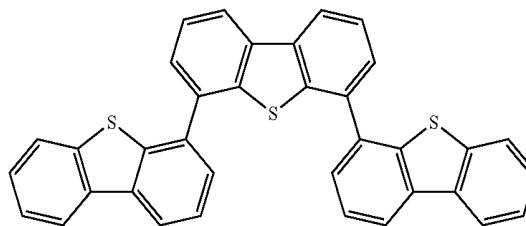


40

45

To a 500 mL round flask was added 2,2'-ditriflatebiphenyl (2.7 g, 6 mmol), 4-dibenzothiopheneboronic acid (4.1 g, 18 mmol), Pd₂(dba)₃ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.3 g, 0.8 mmol), potassium phosphate tribasic (5.1 g, 24 mmol), and 150 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 2.5 g.

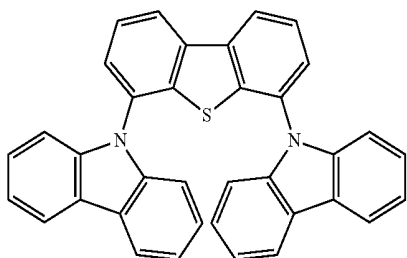
Compound 3



To a 500 mL round flask was added 4,6-diiododibenzothiophene (4.2 g, 9.6 mmol), 4-dibenzothiopheneboronic acid (5.3 g, 23.1 mmol), Pd₂(dba)₃ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.3 g, 0.8 mmol), potassium phosphate tribasic (7.4 g, 35 mmol), and 150 mL of toluene. The reaction was heated to reflux and

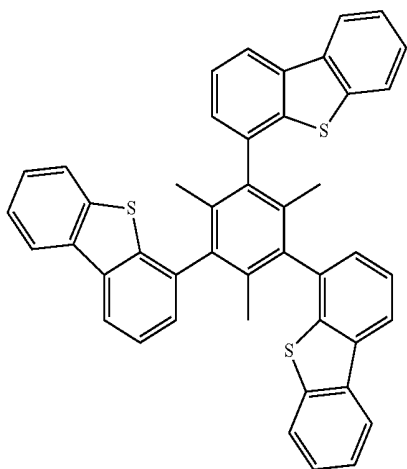
89

stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 2.4 g.



Compound 4

To a 500 mL round flask was added 4,6-diiododibenzothiophene (3.9 g, 8.9 mmol), carbazole (3.3 g, 19.6 mmol), $\text{Pd}_2(\text{dba})_3$ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.3 g, 0.8 mmol), sodium t-butoxide (5.8 g, 60 mmol), and 200 mL of xylene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 2.2 g.



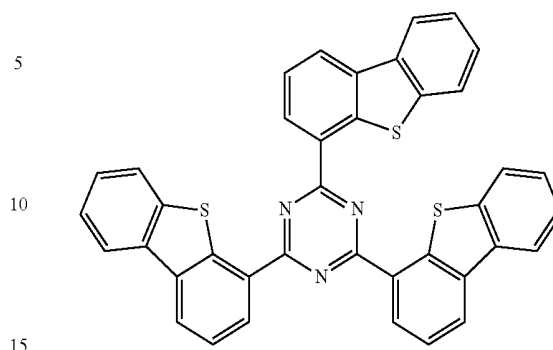
Compound 5

Step 1. 2,6-Dibromo-1,3,5-trimethylbenzene (8.34 g, 30 mmol) was dissolved in 50 ml of CHCl_3 and suspended with 1.0 g of iron powder in 200 ml round-bottom flask. Bromine (2.00 ml, 31 mmol) was added dropwise at room temperature and reaction mixture was heated to reflux for 3 hours, cooled down to room temperature and stirred overnight. Solution was decanted, washed with NaOH 10% aq., filtered and evaporated. The solid residue was crystallized from chloroform, providing 7.00 g of yellow solid (2,4,6-tribromo-1,3,5-trimethylbenzene).

Step 2. The 1 L round-bottom flask equipped with magnetic stirrer and reflux condenser was charged with 2,4,6-tribromo-1,3,5-trimethylbenzene (3.4 g, 9.5 mmol), 4-dibenzothiopheneboronic acid (8.7 g, 38 mmol), $\text{Pd}_2(\text{OAc})_2$ (0.16 g, 0.7 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.46 g, 1.1 mmol), potassium phosphate tribasic (53 g, 250 mmol), 1.2 ml of water and 700 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 5.2 g.

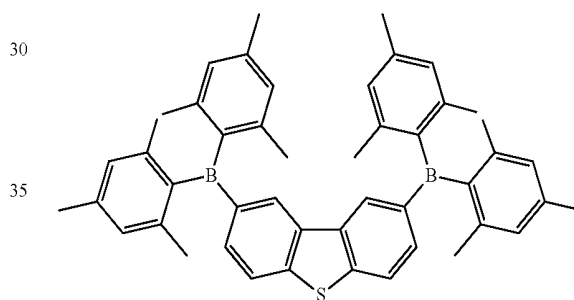
90

Compound 6



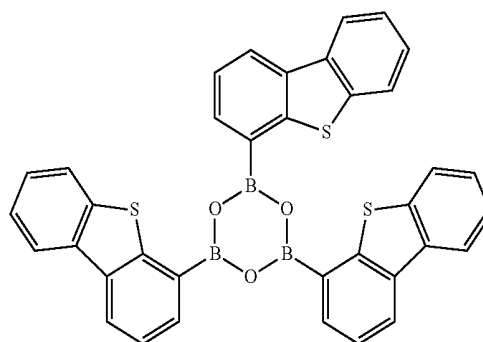
To a 500 mL round flask was added cyanuric chloride (1.5 g, 8.0 mmol), 4-dibenzothiopheneboronic acid (6.8 g, 30 mmol), $\text{Pd}_2(\text{dba})_3$ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.3 g, 0.8 mmol), potassium phosphate tribasic (8.5 g, 40 mmol), and 250 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was filtered. The product was further purified by recrystallization from EtOAc. Yield was 3.0 g.

Compound 7



2,8-Dibromobenzothiophene (2.5 g, 7.3 mmol) in 150 mL of THF was treated with n-BuLi (1.6 M in hexane, 10 mL, 16 mmol) at -78°C . for 1 h. Dimesitylboron fluoride (5.0 g, 16.8 mmol) in 40 mL of ether was added dropwise. After the mixture was stirred for another 1 h, the mixture was slowly warmed up to room temperature and continued to stir overnight. The product was purified by a silica gel column. Yield was 2.8 g.

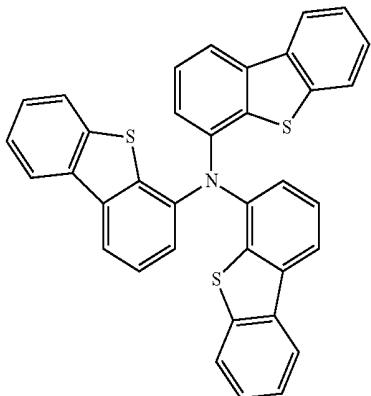
Compound 8



4-Dibenzothiopheneboronic acid (5.0 g) was suspended in 300 mL of xylene and performed the Dean-Stark extraction

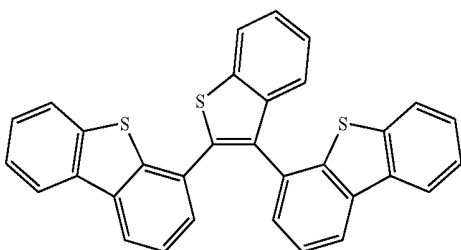
91

for 5 h. After cooling down, the solid was collected, washed with EtOAc and hexane, and sublimed at 320° C. twice. Yield was 3.6 g.



Compound 9

To a 500 mL round flask lithium amide (0.2 g, 10 mmol), 4-iododibenzothiophene (9.9 g, 32 mmol), Pd₂(dba)₃ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.4 g, 0.8 mmol), sodium t-butoxide (2.9 g, 30 mmol), and 200 mL of toluene were added. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 4.0 g.

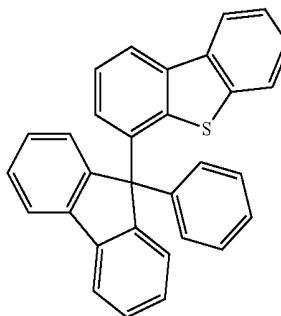


Compound 10

The 500 mL round flask was charged with 2,3-dibromobenzo[b]thiophene (5.0 g, 17.1 mmol), 4-dibenzothiopheneboronic acid (10.0 g, 43.8 mmol), Pd₂(PPh₃)₄ (0.8 g, 0.7 mmol), potassium carbonate (14.2 g, 103 mmol) in 30 ml water followed by 200 ml of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, separation of aqueous phase and evaporation the mixture was purified by a silica gel column (hexane/ethyl acetate 4/1 mixture), providing target compound as solidified colorless oil (4.6 g).

92

Compound 11



5

10

15

20

25

30

35

40

45

50

55

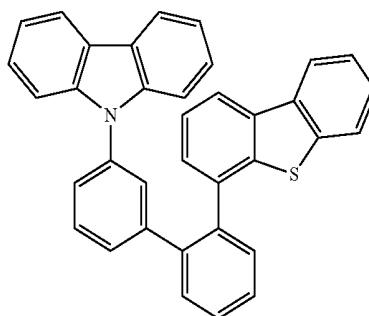
60

65

Step 1. Dibenzothiophene (9.21 g, 50 mmol) was dissolved in 100 ml of dry THF and solution was cooled to -50° C. n-BuLi (1.6 molar solution in hexanes, 40 ml, 64 mmol) was added dropwise. The reaction mixture was warmed to room temperature, stirred for 4 hours and cooled to -30° C. Dibenzofluorenone (9.0 g, 50 mmol) in 70 ml THF was added dropwise, reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with ethyl acetate (75 ml), washed with brine 3 times, dried over MgSO₄, filtered and evaporated. The solid residue was purified by column chromatography on silica (hexane/ethyl acetate 7/3) providing 12.0 g of 9-(dibenzo[b,d]thiophen-4-yl)-9H-fluoren-9-ol as white solid.

Step 2. 9-(Dibenzo[b,d]thiophen-4-yl)-9H-fluoren-9-ol (product from the Step 1, 3.64 g, 10 mmol) were dissolved in 100 ml of dry toluene. Twenty drops of 10% solution of P₂O₅ in CH₃SO₃H were added at room temperature, and reaction mixture was stirred for 5 hours. The solution was decanted from solid residue, filtered through silica plug and evaporated. The solid residue was subjected to column chromatography (silica, hexane/ethyl acetate 4/1) providing 4.0 g of white solid.

Compound 12



Step 1. The 200 ml round-bottom flask equipped with reflux condenser and magnetic stirrer was charged with carbazole (14.75 g, 88 mmol), 3-iodobromobenzene (25.0 g, 88 mmol), Pd₂(dba)₃ (0.8 g, 0.85 mmol) and dppf (1,1'-bis(diphenylphosphino)ferrocene, 0.98 g, 1.8 mmol), sodium t-butoxide (25 g, 265 mmol) and 100 ml of dry xylene. Reaction mixture was refluxed under N₂ atmosphere for 48 hours, cooled down to room temperature and evaporated. The solid residue was subjected to column chromatography on silica (eluent-hexane/ethyl acetate 9/1) providing 11.7 g of 9-(3-bromophenyl)-9H-carbazole as white solid.

Step 2. 9-(3-Bromophenyl)-9H-carbazole (11.7 g, 36 mmol), Bis(pinacolato)diboron (13.85 g, 54 mmol), potas-

93

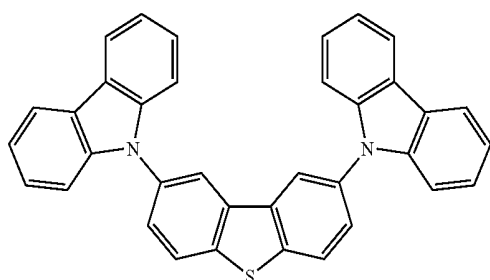
sium acetate (7.00 g, 71 mmol), 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (0.6 g) were dissolved in 100 ml of dry dioxane and refluxed under N₂ atmosphere overnight. Then reaction mixture was cooled down to room temperature, diluted with ethyl acetate, washed with brine, dried over magnesium sulfate, and evaporated. The solid residue was subjected to column chromatography on silica (eluent hexane/ethyl acetate 5/1), providing 8.00 g of 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole as yellow solid. Analytically pure material may be prepared by crystallization from hexane, otherwise product was used without additional purification.

Step 3. 2-Bromoanisole (5.61 g, 30 mmol) and 4-dibenzothiopheneboronic acid (6.84 g, 30 mmol), Pd₂(PPh₃)₄ (1.00 g, 0.8 mmol) were dissolved in 100 ml of toluene. Saturated solution of sodium carbonate (12.5 g in water) was added, and reaction mixture was heated to reflux under N₂ atmosphere overnight. Then reaction mixture was cooled down to room temperature, separated organic phase and evaporated toluene. The solid residue was subjected to column chromatography on silica (eluent-hexane/ethyl acetate 4/1) providing 4-(2-methoxyphenyl)dibenzo[b,d]thiophene as 6.6 g of colorless solidified oil.

Step 4. 4-(2-Methoxyphenyl)dibenzo[b,d]thiophene (6.6 g, 23 mmol) and pyridinium hydrochloride (27 g, 230 mmol) were mixed together, placed in the 100 ml round bottom flask and heated to reflux for 45 min. Reaction mixture was cooled to 60° C., diluted with 100 ml water and extracted with ethyl acetate. The organic phase was separated, dried over magnesium sulfate, filtered and evaporated. The residue was subjected to column chromatography on silica (eluent hexane/ethyl acetate 5/1), providing 4.00 g of 2-(dibenzo[b,d]thiophen-4-yl)phenol as clear solidified oil.

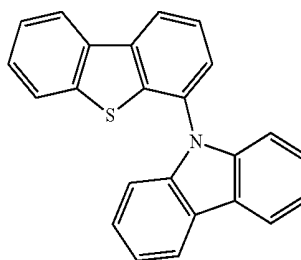
Step 5. 2-(Dibenzo[b,d]thiophen-4-yl)phenol (3.9 g, 14 mmol) was dissolved in 80 ml of dry dichloromethane, containing 5 ml of dry pyridine, and solution was cooled in the ice bath. The triflic anhydride (5 ml, 28 mmol) was added dropwise, the reaction mixture was stirred overnight at room temperature, washed with water and evaporated. The residue was purified by column chromatography on silica (eluent hexane/ethyl acetate 9/1), providing 4.2 g of clear colorless solidified oil.

Step 6. The 200 ml round bottom flask with reflux condenser and magnetic stirrer was charged with triflate from Step 5 (4.1 g, 10 mmol) and boronic ester from Step 2 (3.7 g, 10 mmol) followed by tribasic potassium phosphate (6.36 g, 30 mmol), palladium acetate (0.67 g, 0.3 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.8 g, 0.6 mmol), 200 ml of toluene and 6 ml of water. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column with eluent hexane/ethyl acetate 4/1, providing 2.8 g of target compound as white solid.



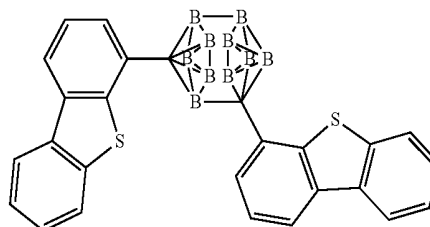
94

To a 500 mL round flask carbazole (3.7 g, 22 mmol), 2,8-dibromobenzothiophene (3.4 g, 10 mmol), Pd(OAc)₂ (0.1 g, 0.5 mmol), tri-*t*-butylphosphine (1 M in toluene, 1.5 mL, 1.5 mmol), sodium *t*-butoxide (6.3 g, 66 mmol), and 200 mL of xylene were added. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 4.7 g.



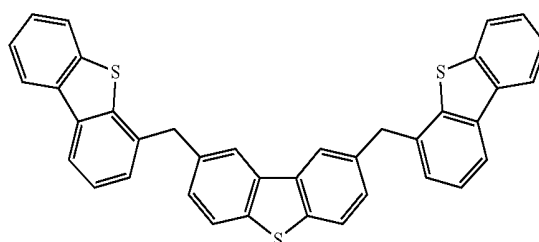
Compound 13

To a 500 mL round flask 4-iododibenzothiophene (6.2 g, 20 mmol), carbazole (4.0 g, 24 mmol), Pd₂(dba)₃ (0.9 g, 1.0 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (1.6 g, 4.0 mmol), sodium *t*-butoxide (5.8 g, 60 mmol), and 200 mL of xylene were added. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 2.4 g.



Compound 14

m-Carborane (5.0 g, 35 mmol) in 200 mL of dry DME was treated with *n*-BuLi (1.6 M in hexane, 48 mL, 76 mmol) at 0° C. for 30 min under nitrogen. After the mixture was warm up to room temperature, CuCl (9.5 g, 96 mmol) was added. The mixture continued to stir for 1 h, and 30 mL of dry pyridine, 4-iododibenzothiophene (22.6 g, 73 mmol) were added. The resulting mixture was refluxed for 60 h. After cooling, the mixture was purified by a silica gel column. Yield was 1.8 g.



Compound 15

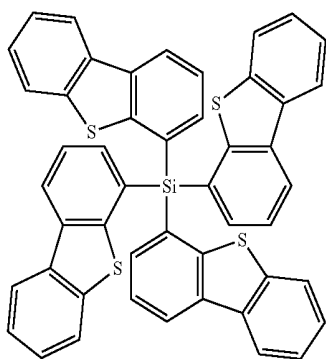
Step 1. Dibenzothiophene (27 g, 147 mmol) in 400 mL of THF was treated slowly with *n*-BuLi (1.6 M in hexane 100

95

mL, 160 mmol) at -50°C . The resulting mixture was slowly warmed up to room temperature and continued to stir for 5 h. The solution was cooled back to -78°C ., DMF (61 mL) in 100 mL of THF was added slowly. The mixture continued to stir for another 2 h at this temperature and then warmed up to room temperature. The product was extracted with EtOAc and further purified by a silica gel column. Yield of 4-dibenzothiophenealdehyde was 21 g.

Step 2. To a 300 mL of THF solution of 2,8-dibromodibenzothiophene (3.4 g, 10 mmol) at -78°C . was added slowly by n-BuLi (1.6 M in hexane, 13.8 mL, 22 mmol). After stirred for 1 h at this temperature, the mixture was treated slowly with a 100 mL of THF solution of 4-dibenzothiophenealdehyde (4.2 g, 20 mmol). The solution was then allowed to warm up to room temperature. The product was extracted with EtOAc and further purified by a silica gel column. Yield of dicarbinol intermediate was 4.2 g.

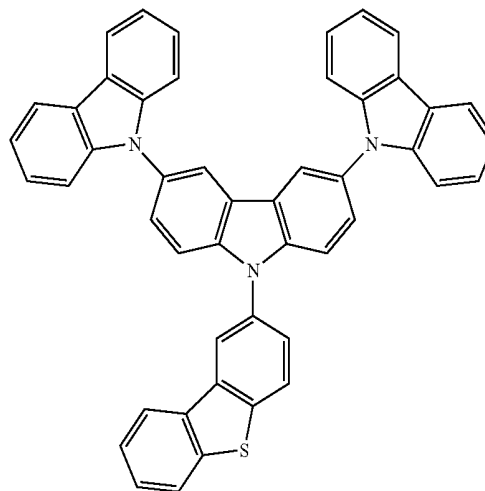
Step 3. To a 50 mL of CH_2Cl_2 solution of above dicarbinol intermediate (4.5 g, 7.4 mmol) and CF_3COOH (60 mL) was added portionwise of solid powder of sodium borohydride (2.8 g, 74 mmol). The mixture was stirred under nitrogen overnight. The solvents was removed by rotovap, and the solid was washed with water then with NaHCO_3 solution. The crude product was further purified by a silica gel column. Yield of final product was 2.4 g.



Dibenzothiophene (14 g, 76 mmol) in 200 mL of THF was treated slowly with n-BuLi (1.6 M in hexane, 50 mL, 80 mmol) at -50°C . The resulting mixture was slowly warmed up to room temperature and continued to stir for 5 h. The solution was cooled back to -78°C ., SiCl_4 (2.0 g, 12 mmol) was added slowly. The mixture continued to stir for another 2 h at this temperature and 12 h at room temperature. The product was extracted with EtOAc and further purified by a silica gel column. Yield was 3.5 g.

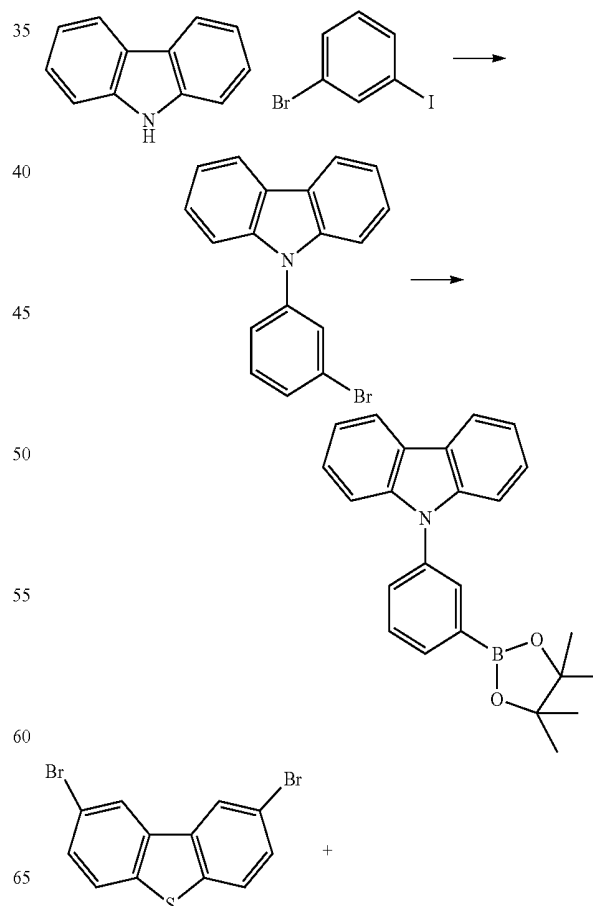
96

Compound 17



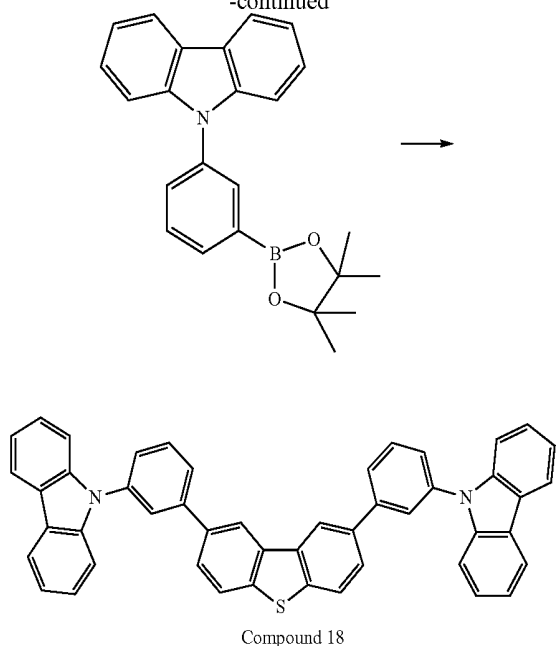
To a 500 mL round flask 3,6-di(9-carbazolyl)carbazole (3.0 g, 6 mmol, prepared similarly as described above for 3-(9-carbazolyl)carbazole), 2-bromobenzothiophene (2.1 g, 7.8 mmol), CuI (0.4 g, 2.0 mmol), trans-1,2-Diaminocyclohexane (0.4 g, 3.6 mmol), potassium phosphate tribasic (3.2 g, 15 mmol), and 250 mL of toluene were added. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the mixture was purified by a silica gel column. Yield was 3.1 g.

Compound 16



97

-continued

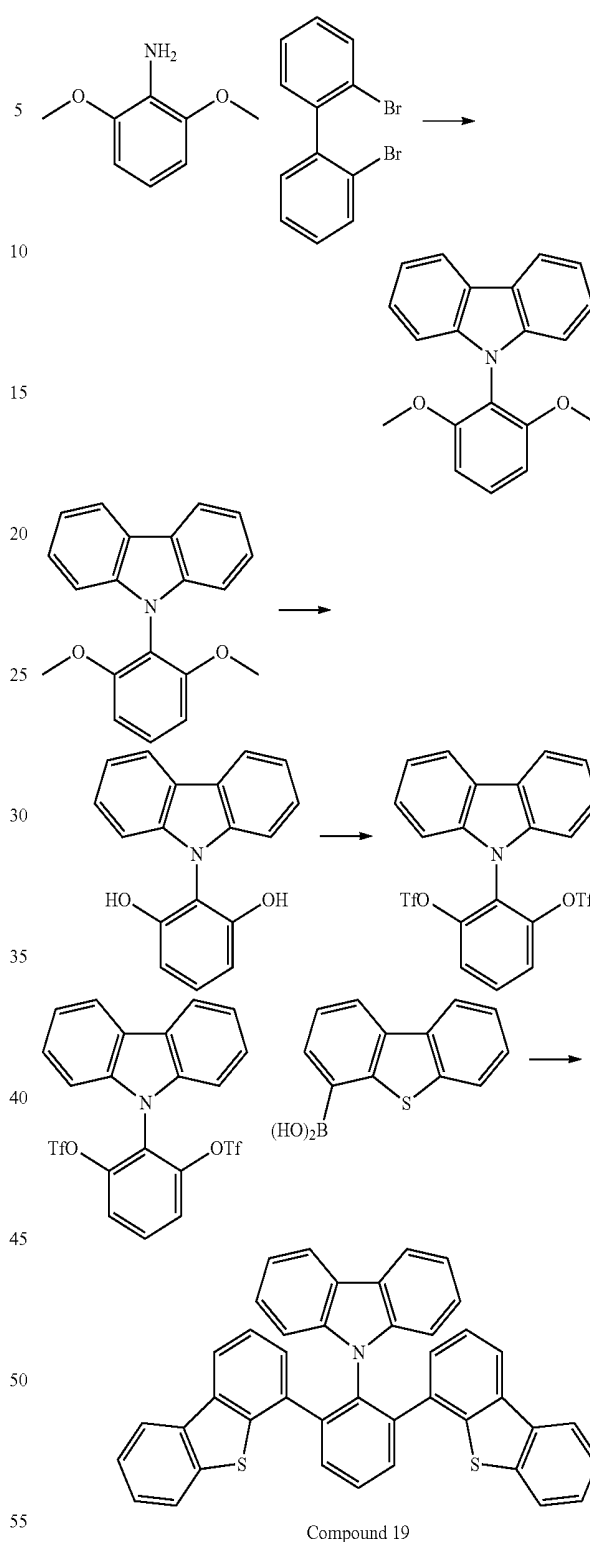


The 300 mL round bottom flask, equipped with magnetic stirrer and refluxed condenser, was charged with carbazole (7.1 g, 42.5 mmol), 3-iodobromobenzene (25.00 g, 88 mmol), $\text{Pd}_2(\text{dba})_3$ (800 mg, 1 mol %), dppf (1',1'-bis(diphenylphosphino)ferrocene) (975 mg, 2 mol %), sodium t-butoxide (6.3 g) and m-xylene (100 ml). The reaction mixture was heated to reflux and stirred under nitrogen atmosphere for 48 hours. Then reaction was cooled down to room temperature, filtered through silica plug and evaporated. The residue was subjected to column chromatography on silica gel, eluent gradient mixture hexane-hexane/ethyl acetate mixture 9:1, providing 7.00 g of 9-(3-bromo-phenyl)-9H-carbazole as white solid, structure was confirmed by NMR and GCMS spectroscopy.

7.00 g of 9-(3-bromo-phenyl)-9H-carbazole (21.7 mmol), bis-pinacolatodiborane (8.3 g, 32.7 mmol), potassium acetate (4.30 g) and (1',1'-bis(diphenylphosphino)-ferrocene) dichloropalladium (II) (500 mg) were dissolved in 100 ml of dioxane and refluxed under nitrogen for 24 hours. After evaporation the residue was subjected to column chromatography on silica gel (eluent hexane/ethyl acetate 9/1 mixture), providing pure 9-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-9H-carbazole as white solid (11.8 g).

The 300 mL round bottom flask, equipped with magnetic stirrer and refluxed condenser, was charged with 2,8-dibromo-dibenzothiophene (3.42 g, 10 mmol), 9-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-9H-carbazole (11.7 g, 30 mmol), palladium (II) acetate (64 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (234 mg), potassium phosphate tribasic anhydrous (53.0 g), 700 ml of toluene and 2 ml of water. The reaction mixture was heated to reflux and stirred under nitrogen atmosphere for 24 hours. Then reaction was cooled down to room temperature, filtered through silica plug and evaporated. The residue was washed with hexane, ethanol, water, ethanol and hexane, then was crystallized from toluene. Sublimation (255° C. at 10^{-5} mm Hg) provided pure material (white solid, 2.0 g, structure confirmed by NMR).

98



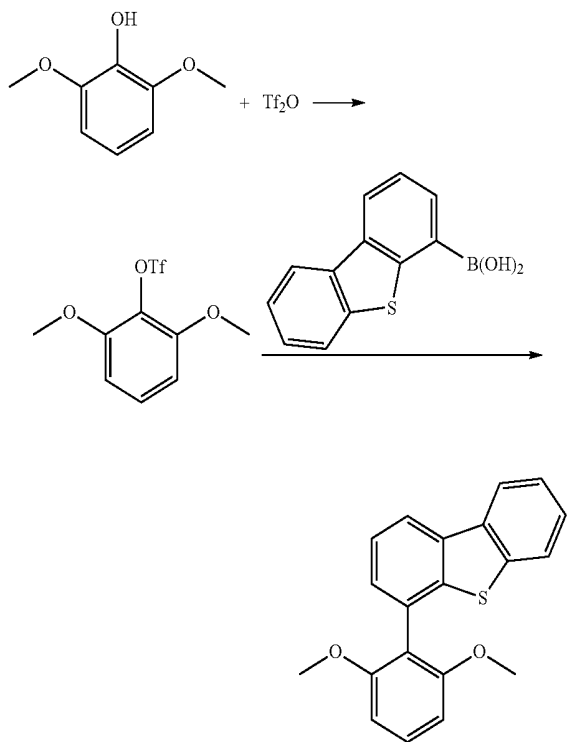
2,6-Dimethoxyaniline (5.5 g, 0.036 mol), 2,2'-dibromobiphenyl (13.45 g, 0.043 mol), sodium tert-butoxide (8.58 g, 0.089 mol) and $\text{Pd}_2(\text{dba})_3$ (1.15 g, 13 mmol) were charged into a 500 mL 3-neck flask with 300 mL of anhydrous toluene. This flask was evacuated and back filled with N_2 (this procedure was repeated a total of 3 times). Lastly, (9.6 mL, 96 mmol) $\text{P}(\text{t-Bu})_3$ 1.0 M in toluene was syringed into the reaction vessel through a septum. The reaction mixture was heated at reflux for 18 h. Heating was then discontinued. The reaction mixture was diluted with 200 mL of water. The

99

toluene layer was separated. The aqueous was extracted 1×200 mL toluene. The toluene extracts were combined, were dried over magnesium sulfate then were filtered and concentrated under vacuum. Silica gel chromatography of the crude product. Solvent system used was 20-35% methylene chloride/hexanes.

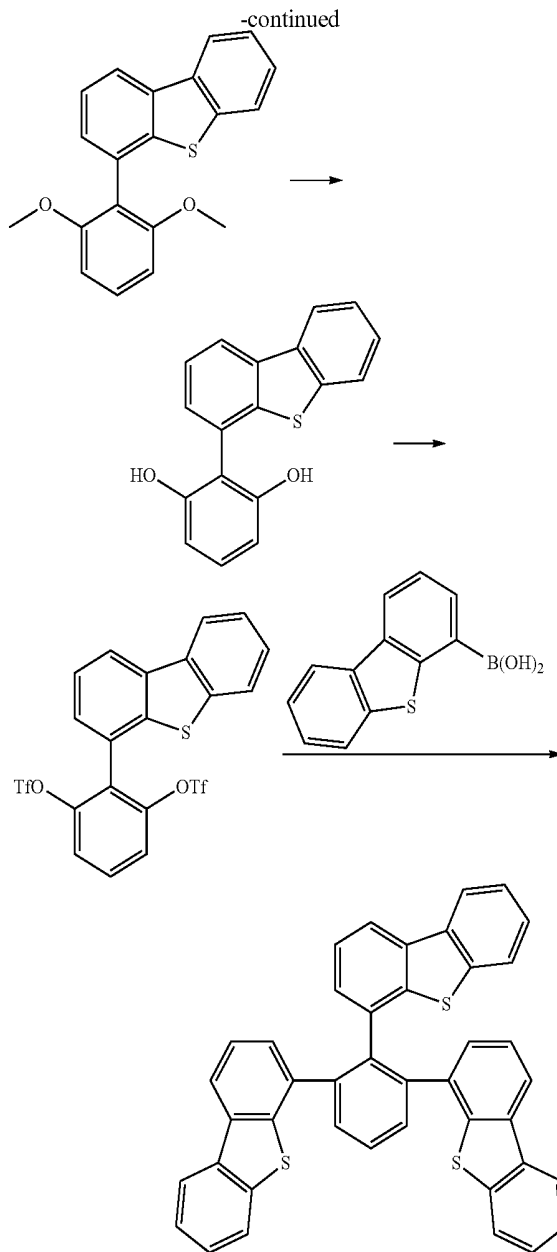
9-(2,6-Dimethoxyphenyl)-9H-carbazole (10.00 g) and pyridinium hydrochloride (50.0 g) were placed in the 250 ml round-bottom flask, equipped with magnetic stirrer and immersed in the pre-heated oil bath (230° C., 45 min). The reaction mixture was cooled down to room temperature, diluted with 400 ml water and extracted with ethyl acetate (3×150 ml). Organic fractions were combined, dried over sodium sulfate anhydrous, filtered and evaporated, providing 5.5 g of pure 2-carbazol-9-yl-benzene-1,3-diol. 2-Carbazol-9-yl-benzene-1,3-diol (5.5 g, 20 mmol) and pyridine (6.0 ml) were dissolved in 50 ml DCM (anhydrous) and cooled in the ice bath. Solution of triflic anhydride (6.0 ml) in 20 ml DCM was added dropwise upon intensive stirring, reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was washed with water, dried over sodium sulfate, filtered and evaporated, providing crude triflate. Pure material (white solid, 6.0 g) was obtained by column chromatography on silica gel (eluent hexane/ethyl acetate 1/1 mixture).

Bis-triflate (3.13 g, 5.8 mmol), 4-dibenzothiopheneboronic acid (3.30 g, 14.5 mmol), Pd₂(dba)₃ (212 mg, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (190 mg, 4 mol %), potassium phosphate tribasic monohydrate (8.00 g), 100 ml of toluene and 1 ml of water were refluxed in the round-bottom flask under nitrogen atmosphere for 24 hours, filtered hot through silica plug and evaporated. The residue was washed with hexane, ethanol, water, ethanol and hexane, then crystallized from toluene, providing pure material (4.1 g).



100

-continued



Compound 20

2,6-Dimethoxyphenol (15.4 g, 0.1 mol) and 15 ml of pyridine were dissolved in 150 ml DCM and solution was cooled in the ice bath. Triflic anhydride was added dropwise upon vigorous stirring, reaction mixture was allowed to warm up to room temperature, washed with water and evaporated. Kugelrohr distillation (200° C., 2 mm Hg) provided 25 g of solidified clear oil.

2,6-Dimethoxytriflate (8.58 g, 30 mmol), 4-dibenzothiopheneboronic acid (6.84 g, 30 mmol), potassium phosphate tribasic monohydrate (20.7 g), palladium (II) acetate (672 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (700 mg) and 150 ml of toluene and 3 ml of water were heated to reflux and stirred under nitrogen atmosphere for 24 hours. Hot reaction mixture was filtered through silica plug and evaporated, the residue was subjected to column chromatography on silica (eluent hexane/ethyl acetate 4/1 mixture), providing 4-(2,6-dimethoxyphenyl)-dibenzothiophene (9.00 g, prism crystals from ethyl acetate).

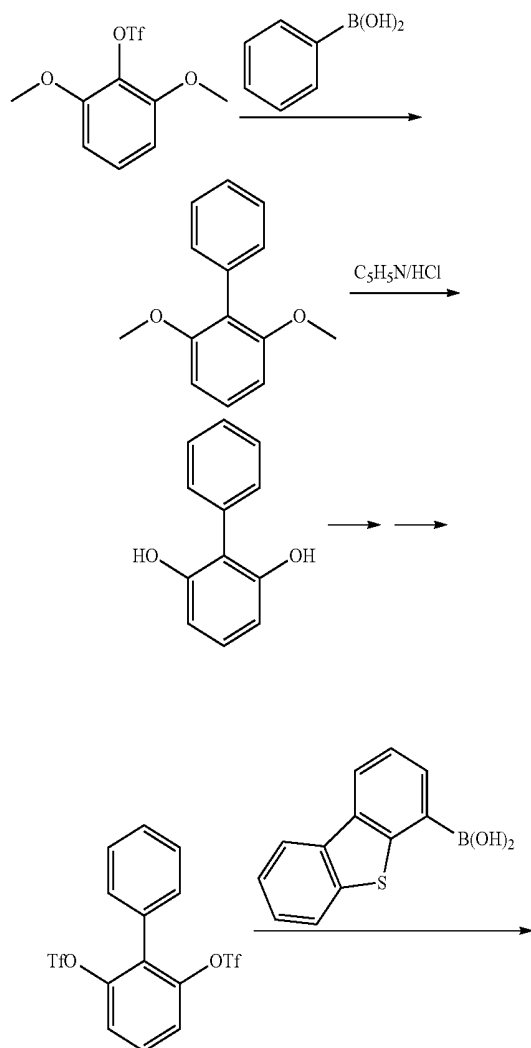
4-(2,6-Dimethoxyphenyl)-dibenzothiophene (9.00 g) and pyridinium hydrochloride (20 g) were placed in the 100 mL

101

round-bottom flask, equipped with a magnetic stirrer. The flask was immersed in the pre-heated oil bath (220° C., 1 hour), cooled down to room temperature and dissolved in 200 ml of water. The solution was extracted with ethyl acetate (4×50 mL), organic fractions were combined, dried over sodium sulfate, filtered and evaporated, providing 2-(dibenzo[b,d]thiophen-4-yl)benzene-1,3-diol (7.2 g, white solid).

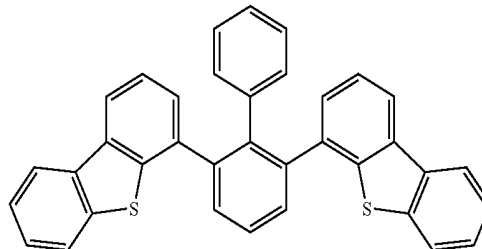
2-(Dibenzo[b,d]thiophen-4-yl)benzene-1,3-diol (7.2 g) was dissolved in 150 mL of dry DCM, containing 15 mL of pyridine. Solution was cooled in the ice bath, then triflic anhydride (18 mL in 25 mL of DCM) was added dropwise. Reaction was allowed to warm up to room temperature and washed with 10% sodium bicarbonate solution in water. DCM was evaporated, and the residue was subjected to column chromatography, providing 14.5 g of bis-triflate.

Triflate (5.56 g, 10 mmol), 4-dibenzothiopheneboronic acid (5.35 g, 25 mmol), palladium (II) acetate (44 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (161 mg) and potassium phosphate tribasic trihydrate (7.00 g) were suspended in 100 ml of toluene and refluxed under nitrogen atmosphere for 24 hours. Hot reaction mixture was filtered and evaporated, the residue was crystallized from toluene twice. Sublimation (245° C., 10⁻⁵ mm Hg) provided 5.0 g of target compound.



102

-continued



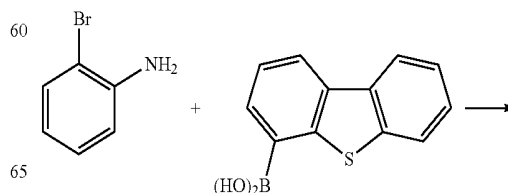
Compound 21

The 300 ml round-bottom flask equipped with reflux condenser and magnetic stirrer was charged with 2,6-dimethoxytriflate (10.00 g, 35 mmol), phenyl boronic acid (4.25 g, 35 mmol), potassium phosphate tribasic monohydrate (24.1 g), palladium (II) acetate (156 mg, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (573 mg, 4 mol %), toluene (100 ml) and water (2 ml). The reaction mixture was refluxed overnight, filtered through silica plug and evaporated. The residue was subjected to column chromatography on silica gel (eluent hexane/ethyl acetate 4/1 mixture), providing dimethoxybiphenyl as white solid (5.00 g).

2,6-Dimethoxybiphenyl (5.00 g) and 15 g of pyridinium hydrochloride were placed in the round-bottom flask and immersed in the oil bath (210° C., 1.5 hours). Then the reaction was cooled down to room temperature, diluted with 200 ml of water and extracted with ethyl acetate (4×50 ml). Organic fractions were combined, dried over sodium sulfate and evaporated. The residue was subjected to column chromatography on silica gel (eluent hexane/ethyl acetate 1/1 mixture), providing 3.3 of biphenyl-2,6-diol as yellow solid.

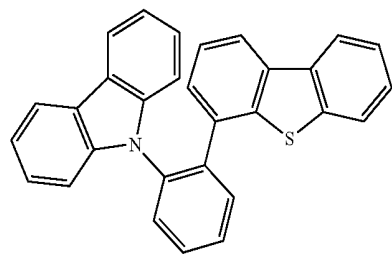
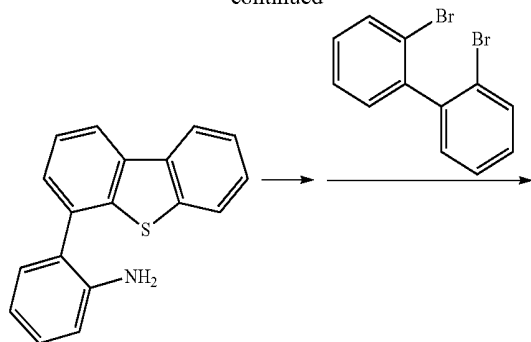
Biphenyl-2,6-diol (7.2 g, 39 mmol) was dissolved in DCM (100 ml) and pyridine (10 ml). The solution was cooled in the ice bath, and triflic anhydride (27.3 g) was added dropwise upon vigorous stirring. The reaction mixture was allowed to warm up to room temperature, was washed with water, dried and evaporated. The residue was subjected to column chromatography on silica gel (eluent hexane/ethyl acetate 4/1 mixture), providing 8.00 g of pure triflate.

The triflate (7.4 g, 16.4 mmol), 4-dibenzothiophene boronic acid (11.2 g, 49 mmol), potassium phosphate tribasic monohydrate (22.7 g), palladium (II) acetate (70 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (270 mg) and 100 ml of toluene were refluxed overnight under nitrogen atmosphere. The hot solution was filtered through silica plug and evaporated. The residue was crystallized hexane/ethyl acetate, providing target product as white solid (5.01 g). The material was additionally purified by sublimation (220° C., 10⁻⁵ mm Hg).



103

-continued

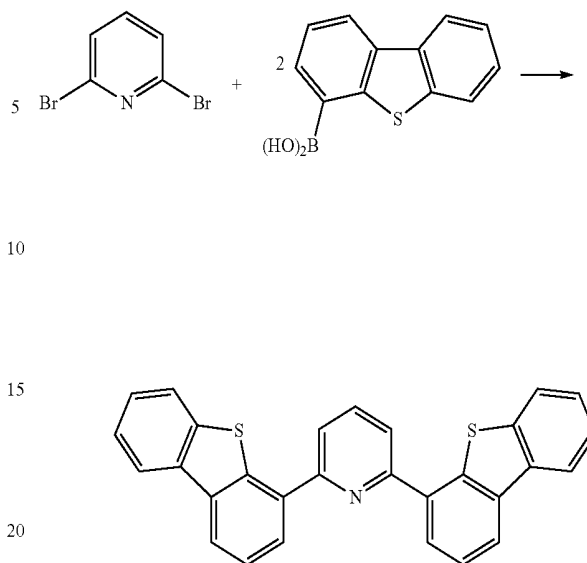


Compound 22

The 300 ml round-bottom flask equipped with reflux condenser and magnetic stirrer was charged with 2-bromoaniline (8.00 g, 46.5 mmol), 4-dibenzothiopheneboronic acid (10.5 g, 46.5 mmol), potassium carbonate (20 g, saturated solution in water), tetrakis(triphenylphosphine)palladium (0) (500 mg) and 100 ml of toluene. The reaction mixture was refluxed overnight under nitrogen atmosphere, filtered through silica plug and evaporated. Product was purified by column chromatography on silica gel, eluent hexane/ethyl acetate 4/1 mixture, providing 2-(dibenzo[b,d]thiophen-4-yl)aniline (10.1 g) as yellow oil.

2-(Dibenzo[b,d]thiophen-4-yl)aniline (10.1 g, 36.4 mmol), 2,2'-dibromobiphenyl (12.0 g, 38.5 mmol), sodium tert-butoxide (7.00 g, 72.9 mmol), and $\text{Pd}_2(\text{dba})_3$ (330 mg) were charged into a 500 mL 3-neck flask with 300 mL of anhydrous toluene. This flask was evacuated and back filled with N_2 (this procedure was repeated a total of 3 times). Lastly, (5 mL, 96 mmol) $\text{P}(\text{t-Bu})_3$ 1.0 M in toluene was syringed into the reaction vessel through a septum. The reaction mixture was heated at reflux for 18 h. Heating was then discontinued. The reaction mixture was diluted with 200 mL of water. The toluene layer was separated. The aqueous was extracted 1x200 mL toluene. The toluene extracts were combined, were dried over magnesium sulfate then were filtered and concentrated under vacuum. Crude material was washed with hexane and crystallized from toluene-DCM. The material was additionally purified by sublimation (190° C., 10^{-5} mm Hg), providing 6.23 g of pure crystalline material.

104



Compound 23

The 300 mL round-bottom flask equipped with magnetic stirrer and reflux condenser was charged with 2,6-dibromopyridine (2.20 g, 9.2 mmol), 4-dibenzothiopheneboronic acid (4.62 g, 20 mmol), $\text{Pd}_2(\text{dba})_3$ (180 mg), S-phos (220 mg), potassium triphosphate (6.00 g) and 100 mL of anhydrous toluene. The flask was filled with nitrogen, and solution was stirred under reflux overnight. Then hot reaction mixture was filtered through silica plug, silica was washed with hot toluene. Organic fractions were combined and evaporated. The residue was subjected to column chromatography on silica gel (eluent hexane/ethyl acetate 4/1 mixture), providing target compound as white solid (3.01 g). Material was additionally purified by sublimation (225° C. at 10^{-5} mm Hg) and used for device fabrication.

Device Examples

All example devices were fabricated by high vacuum ($<10^{-7}$ Torr) thermal evaporation. The anode electrode is ~800 Å, 1200 Å or 2000 Å of indium tin oxide (ITO), or 800 Å Sapphire/IZO. The cathode consists of 10 Å of LiF followed by 1000 Å of Al. All devices are encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package.

The organic stack of Device Examples 1-8 consisted of sequentially, from the ITO surface (1200 Å), 100 Å of P1 as the hole injection layer (HIL), 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α -NPD) as the hole transporting layer (HTL), 300 Å of the invention compound doped with 10 or 15 wt % of an Ir phosphorescent compound as the emissive layer (EML), 50 Å or 100 Å of HPT or the invention compound as the ETL2 and 400 or 450 Å of tris-8-hydroxyquinoline aluminum (Alq_3) as the ETL1.

Comparative Example 1 was fabricated similarly to the Device Examples except that CBP was used as the host.

The materials for the Emissive Layer, and the materials and thicknesses for ETL 2 and ETL1, of Device Examples 1-8 are provided in Table 2. The devices were tested, and the results measured are provided in Table 3. Compound is abbreviated using the term Cmpd.

TABLE 2

Device Example	Host	Dopant wt %	ETL2 (Å)	ETL1 (Å)	ITO thickness (Å)
Comparative 1	CBP	P1 10%	HPT (50)	Alq ₃ (450)	1200
1	Cmpd 1	P1 10%	Cmpd 1 (100)	Alq ₃ (400)	1200
2	Cmpd 1	P6 10%	Cmpd 1 (100)	Alq ₃ (400)	1200
3	Cmpd 1	P1 10%	HPT (50)	Alq ₃ (450)	1200
4	Cmpd 1	P6 10%	HPT (50)	Alq ₃ (450)	1200
5	Cmpd 2	P1 9%	HPT (50)	Alq ₃ (400)	800
6	Cmpd 3	P1 9%	HPT (50)	Alq ₃ (400)	800
7	Cmpd 4	P1 9%	HPT (50)	Alq ₃ (400)	1200
8	Cmpd 5	P1 9%	HPT (50)	Alq ₃ (400)	1200

TABLE 3

Device Example	CIE		Emission		At L = 1000 cd/m ²				At J = 40 mA/cm ²	
					V	LE	EQE	PE	L ₀	LT _{80%}
	X	Y	(nm)	(nm)	(V)	(cd/A)	(%)	(lm/W)	(cd/m ²)	(hr)
Comparative 1	0.346	0.613	522	75	6.2	57.0	16	28.9	13,304	105
1	0.337	0.619	523	73	7.4	48.2	13	20.5	13,611	325
2	0.328	0.620	520	73	7.4	36.8	10	15.6	12,284	340
3	0.338	0.618	524	73	6.3	60.3	17	30.1	13,683	300
4	0.328	0.621	520	73	6.4	52	14.4	25.5	14,014	187
5	0.336	0.623	524	72	5.9	53.8	15	28.7	16389	18
6	0.349	0.614	528	73	6.1	45.5	12	23.2	15672	28
7	0.355	0.609	528	74	6.8	39.6	11	18.3	13403	98
8	0.353	0.613	528	72	6.3	49.5	14	24.7	15442	5.5

From Device Examples 1-8, it can be seen that the Invention Compounds as hosts in green phosphorescent OLEDs give high device efficiency (LE>35 cd/A at 1000 cd/m²), indicating dibenzothiophene as a chromophore has triplet energy high enough for efficient green electrophosphorescence. Most notably is the high stability of the device incorporating Compounds 1 as the host. Device Example 3 and Comparative Example 1 are only different in the host. Device Example 3 uses Compound 1 as the host whereas Comparative Example 1 uses the commonly used host CBP. The lifetime, T_{80%} (defined as the time required for the initial luminance, L₀, to decay to 80% of its value, at a constant current density of 40 mA/cm² at room temperature) are 300 hours and 105 hours respectively, with Device Example 3 having a slightly higher L₀. This translates to almost a 3 fold improvement in the device stability. The invention compounds may function well as the enhancement layer (ETL2). Device Example 1 and Device Example 3 both have Compound 1 as the host, but Compound 1 and 2,3,6,7,10,11-hexaphenyltriphenylene (HPT) as the enhancement layer respectively. They have T_{0.8} of 325 and 300 hours respectively with similar L₀ (~13600 cd/m²), indicating the good performance of the invention compound as the enhancement layer.

The data suggest that arylbenzothiophenes, particularly biphenyl substituted dibenzothiophenes, are excellent hosts and enhancement layer for phosphorescent OLEDs, provid-

ing at least the same efficiency and multiple times of improvement in stability compared to the commonly used CBP as the host.

A number of devices were fabricated having two different doped emissive layers, where the devices do not include a hole transport layer using a material such as NPD. Table 4 shows the structures for these devices. Table 5 shows measured experimental results for these devices. In general, the devices had an ITO anode, a hole injection layer of LG101™ (purchased from LG Chemical, Korea), and an emissive layer having a first organic layer and a second organic layer with an interface in between. Some of the devices had an enhancement layer (ETL2). All of the devices had an electron transport layer (ETL1) of LG201, available from the same source as LG101. Devices 9-16 have first and second organic layers with the same non-emissive materials, and different phosphorescent materials, where the first organic layer additionally includes a lower energy emissive material. All of devices 9-16 include emissive layers having a first and second organic layer with an interface in between. In all of these devices, the concentration of phosphorescent material is higher in the first (closer to anode) organic layer. The materials and thicknesses for Device Examples 9-16 are provided in Table 4. The devices were tested, and the results measured are provided in Table 5. Compound is abbreviated using the term Cmpd. All percentages are wt % unless otherwise noted.

TABLE 4

Device	Anode	HIL	EML1	EML2	ETL2	ETL1
9	ITO [1200 Å]	LG101 [100 Å]	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (18%) [250 Å]	none	LG201 [300 Å]

TABLE 4-continued

Device	Anode	HIL	EML1	EML2	ETL2	ETL1
10	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (12%) [250 Å]	none	LG201 [300 Å]
11	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (24%) [250 Å]	none	LG201 [300 Å]
12	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (24%) [250 Å]	Cmpd 1 [50 Å]	LG201 [300 Å]
13	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (18%) [250 Å]	Cmpd 1 [50 Å]	LG201 [300 Å]
14	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [300 Å]	Cmpd 1: P3 (12%) [250 Å]	Cmpd 1 [50 Å]	LG201 [300 Å]
15	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [200 Å]	Cmpd 1: P3 (18%) [250 Å]	Cmpd 1 [50 Å]	LG201 [300 Å]
16	ITO	LG101	Cmpd 1: P4 (30%); P5 (0.5%) [200 Å]	Cmpd 1: P3 (18%) [250 Å]	Cmpd 1 [50 Å]	LG201 [300 Å]

TABLE 5

Device	At 1,000 cd/m ²							
	V	LE	EQE	PE	At 10 mA/cm ²		At L ₀ = 1,000 cd/m ²	
	(V)	(cd/A)	(%)	(lm/W)	CIE x	CIE y	LT _{70%} (hr)	LT _{60%} (hr)
9	6.1	23.7	10.9	12.3	0.467	0.457	Not measured	Not measured
10	6.2	31.7	15.1	16.1	0.500	0.445	35,500	100,000
11	6.2	14.9	6.9	7.5	0.467	0.457	Not measured	Not measured
12	6.1	29.5	13.5	15.2	0.456	0.460	78,000	140,000
13	6.3	32.4	15.3	16.1	0.437	0.451	90,000	230,000
14	7.0	33.2	16.3	15.0	0.505	0.439	88,000	180,000
15	6.4	29.0	13.9	14.3	0.472	0.449	Not measured	Not measured
16	6.2	29.4	14.2	14.9	0.467	0.448	Not measured	Not measured

From Device Examples 9, 10 and 11, it can be seen that the efficiency of the device decreased with increasing concentration of P3, and the device CIE red-shifted with decreasing P3 concentration. Device Examples 9-11 differ only in the concentration of the emissive compound P3 (i.e., devices contain varying concentrations of P3) as all of Device Examples 9-11 contained Inventive Compound 1 as the host, and were without a blocking layer between the EML and the LG201.

From Device Examples 12, 13, and 14, it can be seen that the efficiency of the device decreased with increasing concentration of P3, the device CIE red-shifted with decreasing P3 concentration, and device operating voltage increased with decreasing concentration of P3. Devices 12-14 differ only in the concentration of the emissive compounds P3, as all of devices 12-14 contained the inventive Compound 1 as the host and the blocking layer situated between the EML and ETL. Notably, Compound 1 is an efficient electron transport and blocking layer material, because the efficiency of each of Devices 12, 13, and 14 was shown to exceed that of Devices 9, 10, and 11. Also, the electron stability of

Compound 1 was found to be significant, because Devices 12-14 demonstrated an LT_{60%} stability that exceeded 100,000 hrs from 1,000 cd/m² initial luminance.

From Device Examples 15 and 16, it can be seen that the devices show variation in device characteristics (e.g., CIE, efficiency) when the injection layer LG101 thickness is varied (e.g., 200 Å versus 100 Å).

The organic stack of Device Examples 17-20 consisted of sequentially, from the ITO surface, 100 Å of P1 as the hole injection layer (HIL), 300 Å of NPD as the hole transport layer (HTL), 300 Å of the invention compound doped with 10 wt % or 15 wt % of P1, an Ir phosphorescent compound, as the emissive layer (EML), 50 Å or 100 Å of HPT or the invention compound as enhancement layer (ETL2), an electron transport layer (ETL1) of Alq₃ having a thickness identified in Table 5, and a LiF/Al cathode. In particular, the BL and ETL have a sum total of 500 Å. Thus, the general device structure for the devices of Table 5 was: ITO(1200 Å)/P1 (100 Å)/NPD(300 Å)/Host: P1 x % (300 Å)/ETL2 (50 Å or 100 Å)/Alq₃ (400 Å or 450 Å)/LiF(10 Å)/Al(1000 Å).

TABLE 6

Device example	Host Cmpd.	Dopant x %	ETL2 (Å)	ETL1 (Å)	At 1000 cd/m ²				At 40 mA/cm ²			
					CIE		V	L.E.	EQE	PE	L ₀	LT _{80%}
					X	Y	(V)	(cd/A)	(%)	(lm/W)	(cd/m ²)	(hr)
17	23	P1 10%	23 (100 Å)	Alq ₃ (400 Å)	0.355	0.605	7.1	42.2	11.7	18.66	13,580	160
18	23	P1 15%	23 (100 Å)	Alq ₃ (450 Å)	0.353	0.609	6.8	42.1	11.6	19.44	14,521	155
19	23	P1 1%	HPT (50 Å)	Alq ₃ (450 Å)	0.355	0.607	6.8	46.9	13	21.66	14,728	94

TABLE 6-continued

Device	Host	Dopant	ETL2	ETL1	CIE		At 1000 cd/m ²				At 40 mA/cm ²	
					X	Y	V	L.E.	EQE	PE	L ₀	LT _{80%}
example	Cmpd.	x %	(Å)	(Å)	X	Y	(V)	(cd/A)	(%)	(lm/W)	(cd/m ²)	(hr)
20	23	P1 15%	HPT (50 Å)	Alq ₃ (400 Å)	0.352	0.611	6.6	44.9	12.3	21.36	15,070	63

The data in Table 6 describes the performance of Devices Examples 17-20. The voltage, luminous efficiency, external quantum efficiency and power efficiency data were measured at 1000 cd/m² (display level brightness). The lifetime was measured at accelerated conditions: 40 ma/cm² DC. The initial device luminance (L₀) at life-test conditions (40 mA/cm²) is also shown in Table 5. Compound 23 was used as a host for the green phosphorescent emitter P1. Two different dopant concentrations (10% or 15%) and two different ETL1 layers (Alq₃ of 400 Å or 450 Å) were varied in the devices and tested experimentally. The data show no significant difference in the device performance due to dopant concentration variation. However, there was a difference in the device performance due to variation in the ETL1 layer. In devices having HPT as the ETL 1 layer, the device efficiency was slightly higher due to stronger BL properties of HPT. However, the lifetime of the devices with Compound 23 as the ETL1 was longer. The data suggests that Compound 23 can be used as an efficient host for green phosphorescent emitter and as a ETL1 in the device. The stability of devices having Compound 23 as the ETL1 layer in the devices is higher than the stability of devices having a similar overall structure except with HPT as the ETL 1 layer.

The organic stack of Device Examples 21-24 consisted of sequentially, from the anode surface, 100 Å of P1 or LG101 as the hole injection layer (HIL), 300 Å of NPD as the hole transport layer (HTL) or no HTL, 300 Å of the invention compound doped with 9 wt %, 15 wt % or 20 wt % of P2 or P7 Ir phosphorescent compounds as the emissive layer (EML), 50 Å, 150 Å or 250 Å of H1 as the enhancement layer (ETL2), and 200 Å, 300 Å or 400 Å of Alq₃ as the electron transport layer (ETL1). The materials and thicknesses of Device Examples 21-24 are provided in Table 7. The devices were tested, and the corresponding results measured are provided in Table 8.

TABLE 7

Device	Anode	HIL	HTL	EML	ETL2	ETL1
21	ITO	LG101	none	H1: P2 15%	H1	Alq ₃
	[800 Å]	[100 Å]		[600 Å]	[250 Å]	[200 Å]
22	ITO	LG101	NPD	H1: P2 9	H1	Alq ₃
	[2000 Å]	[100 Å]	[300 Å]	[300 Å]	[50 Å]	[400 Å]
23	ITO	P1	NPD	H1: P7 9%	H1	Alq ₃
	[800 Å]	[100 Å]	[300 Å]	[300 Å]	[50 Å]	[400 Å]
24	Sapphire/	LG101	none	H1: P7 20%	H1	Alq ₃
	IZO	[100 Å]		[300 Å]	[150 Å]	[300 Å]
	[800 Å]					

TABLE 8

Device	At 1,000 cd/m ²				At 10 mA/cm ²		LT _{80%}
	V	LE	EQE	PE	CIE x	CIE y	
(V)	(cd/A)	(%)	(lm/W)				(hr)
21	12.9	10.0	5.3	2.4	0.160	0.285	352
22	7.6	10.9	6.6	4.5	0.155	0.234	77
23	9.0	12.1	6.0	4.2	0.162	0.317	151
24	7.1	8.9	5.5	4.0	0.145	0.232	205

From Devices 21, 22, 23, and 24 it can be seen that the devices demonstrate differences between device structures having an emissive layer containing H1 and an emissive compound P2 or P7. Device Example 21 did not have an HTL, and used a thick EML to enhance device operational stability. The measured CIE coordinates of Device Example 21 were not blue saturated, so the structures of Device Examples 22, 23, and 24 used a 30 nm EML. Device Example 22 also incorporated a 200 nm ITO layer to saturate the device blue CIE. Device Example 23 was a standard blue PHOLED that was not optimized for operational stability. Device Example 24 was a blue PHOLED using the same emissive compound P7 as used in Device Example 23. However, Device Example 24 had several features that enabled longevity such as no NPD, sapphire heat sink substrate, a thick blocking layer, and high emitter concentration. Hence, the LT_{80%} of Device Example 24 exceeded the LT_{80%} of Device Example 23, and Device Example 24 had improved blue CIE compared to Device Example 23.

FIG. 3 shows an organic light emitting device having only a layer with a high hole conductivity between an emissive layer and the anode, an enhancement layer of the same material used as a non-emissive host in the emissive layer, and an emissive layer having first and second organic layers with different concentrations of phosphorescent material and non-emissive materials, where the concentration of phosphorescent material in the second organic layer is variable. The device of FIG. 3 includes a 10 nm thick hole injection layer of LG101, a 30 nm thick first organic emissive layer of H1 doped with 30 wt % P2, a 30 nm thick second organic emissive layer of H1 doped with X wt % P2, a 25 nm thick enhancement layer of H1, a 20 nm thick electron transport layer of Alq₃, and a LiF/Al cathode. X varies from 10 wt % to 18 wt % in the devices fabricated, with devices at X=10, 14 and 18 wt % as indicated in the legends for FIG. 4.

FIG. 4 shows a plot of normalized luminescence versus time for the device of FIG. 3.

FIG. 5 shows a plot of external quantum efficiency versus luminance for the device of FIG. 3.

FIG. 6 shows a plot of power efficacy versus luminance for the device of FIG. 3.

FIG. 7 shows a plot of luminance versus voltage for the device of FIG. 3.

111

FIG. 8 shows a plot of EL intensity versus wavelength for the device of FIG. 3.

FIG. 9 shows an organic light emitting device having only a layer with a high hole conductivity between an emissive layer and the anode, an enhancement layer of the same material used as a non-emissive host in the emissive layer, and an emissive layer having first and second organic layers with different phosphorescent materials in the first and second organic layers, where the concentration of phosphorescent material in the second organic emissive layer is variable. The device of FIG. 9 includes a 10 nm thick hole injection layer of LG101, a 30 nm thick first organic emissive layer of H1 doped with 30 wt % P1, a 30 nm thick second organic emissive layer of H1 doped with X wt % P2, a 25 nm thick enhancement layer of H1, a 20 nm thick electron transport layer of Alq₃, and a LiF/Al cathode. X varies from 10 wt % to 18 wt % in the devices fabricated, with devices at X=10, 14 and 18 wt % as indicated in the legends for FIG. 4. The device of FIG. 9 is very similar to that of FIG. 3, with the difference being that the device of FIG. 9 uses different emissive phosphorescent material in the first and second organic emissive layers, while the device of FIG. 3 uses the same phosphorescent material in both layers. The concentrations of the phosphorescent materials are the same in the device of FIG. 3 compared to the device of FIG. 9.

FIG. 10 shows a plot of external quantum efficiency versus luminance for the device of FIG. 9.

FIG. 11 shows a plot of power efficacy versus luminance for the device of FIG. 9.

FIG. 12 shows a plot of luminance versus voltage for the device of FIG. 9.

FIG. 13 shows a plot of EL intensity versus wavelength for the device of FIG. 9.

The device of FIG. 9 may be compared to the device of FIG. 3. In terms of device architecture, the devices are similar except in the emissive layer, where the device of FIG. 9 has an emissive layer doped with phosphorescent emitter P1 and another emissive layer doped phosphorescent emitter P2, whereas the device of FIG. 3 has only phosphorescent emitter P2. Both devices have a step in dopant concentration, and similar concentrations even in the layers where the actual dopant is different. Several points can be understood from comparing these two device architectures. First, the device of FIG. 9 exhibits a broad emission spectra that is a combination of emission from both P1 and P2. As a result, it can be inferred that the device of FIG. 3 is emitting from both the layer doped with 30% P2 and the layer doped with a lesser concentration of P2. Comparing FIG. 5 to FIG. 10, it can be seen that the device of FIG. 9 has better charge balance than the device of FIG. 3, as evidenced by a relatively flat external quantum efficiency over three orders of magnitude for the device of FIG. 9 as compared to two orders of magnitude for the device of FIG. 3.

It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. The present invention as claimed may therefore includes variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.

112

The invention claimed is:

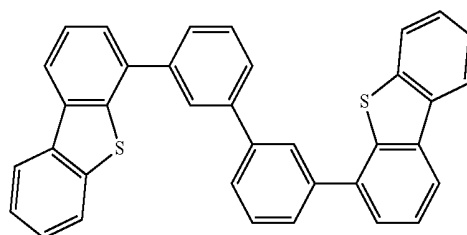
1. An organic light emitting device, comprising:

an anode;

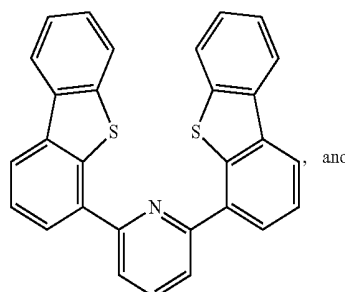
a cathode;

an emissive layer, the emissive layer comprising an organic compound selected from the group consisting of:

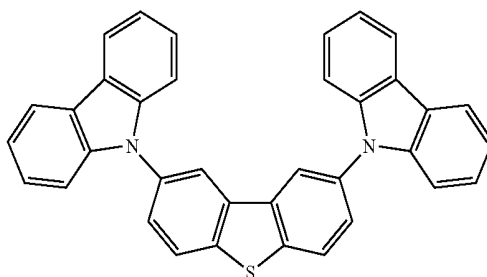
Compound 1



Compound 23

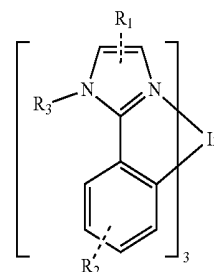


H1



and at least one emissive dopant;

wherein, when the organic compound is compound H1, the at least one emissive dopant comprises



wherein each R₁ is independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, heteroaryl and hydrogen;

wherein R₃ is selected from the group consisting of arylalkyl, aryl, and heteroaryl;

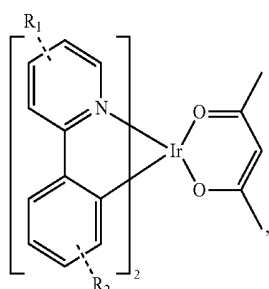
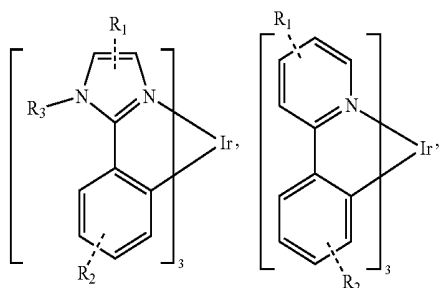
wherein the R₂ adjacent to the bond to the imidazole is a hydrogen fused to R₃ and R₃ is optionally further substituted; and

113

wherein the remaining R_2 substituents are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, heteroaryl and hydrogen.

2. The device of claim 1, wherein the organic compound is Compound 1, and Compound 1 is a host material.

3. The device of claim 1, wherein the organic compound is Compound 1, and the at least one emissive dopant comprises

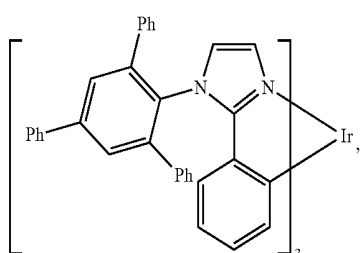


or combinations thereof,

wherein R_1 , R_2 , and R_3 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, heteroaryl and hydrogen, and

wherein R_1 , R_2 , and R_3 are optionally fused and further substituted.

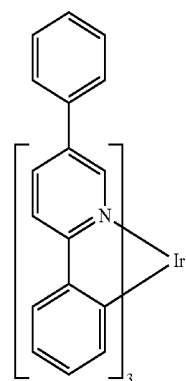
4. The device of claim 1, wherein the organic compound is Compound 1, and the at least one emissive dopant comprises a dopant selected from the group consisting of



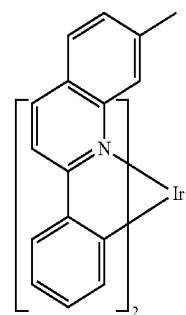
114

-continued

P4



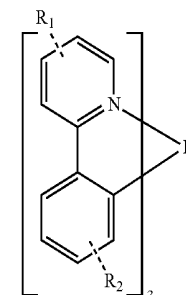
P5



and combinations thereof.

5. The device of claim 1, wherein the organic compound is Compound 23, and Compound 23 is a host material.

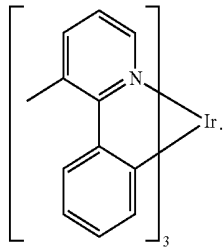
6. The device of claim 1, wherein the organic compound is Compound 23, and the at least one emissive dopant comprises



wherein R_1 and R_2 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, heteroaryl and hydrogen, and wherein R_1 and R_2 are optionally fused and further substituted.

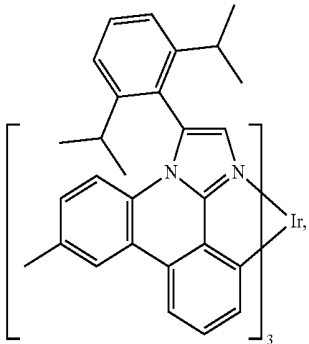
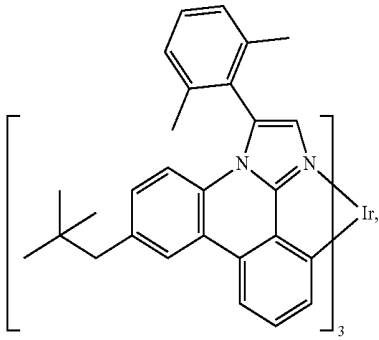
7. The device of claim 1, wherein the organic compound is Compound 23, and the at least one emissive dopant comprises

115



8. The device of claim 1, wherein organic compound is H1, and H1 is a host material.

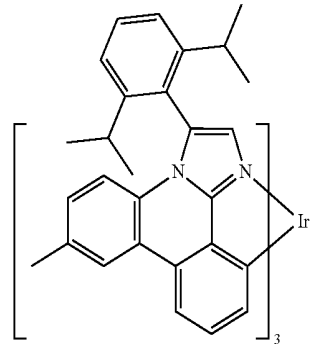
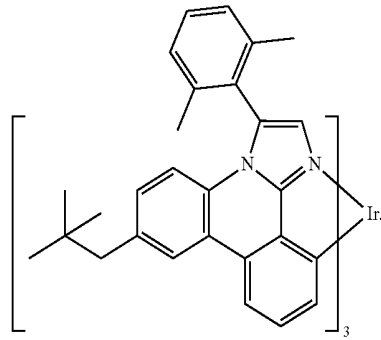
9. The device of claim 1, wherein the organic compound is H1, and the at least one emissive dopant comprises a dopant selected from the group consisting of



and combinations thereof.

116

10. The device of claim 1, wherein the organic compound is H1, and the at least one emissive dopant comprises



11. The device of claim 1, wherein the organic compound is H1, and the at least one emissive dopant comprises

* * * * *

专利名称(译)	磷光发光二极管中含二苯并噻吩的材料		
公开(公告)号	US9997726	公开(公告)日	2018-06-12
申请号	US14/802051	申请日	2015-07-17
[标]申请(专利权)人(译)	环球展览公司		
申请(专利权)人(译)	通用显示器公司		
当前申请(专利权)人(译)	通用显示器公司		
[标]发明人	LIN CHUN DYATKIN ALEXEY ELSHENAWY ZEINAB YEAGER WALTER		
发明人	LIN, CHUN DYATKIN, ALEXEY ELSHENAWY, ZEINAB YEAGER, WALTER		
IPC分类号	H01L51/50 C07D235/18 C07D235/20 C07D333/76 C07D405/14 C07D209/86 H01L51/00 C07D409/10 C07D409/14 C07D413/10 C07D471/04 C07D487/04 C07F5/02 C07F7/08 C09K11/02 C09K11/06		
CPC分类号	H01L51/0074 C07D235/18 C07D235/20 C07D333/76 C07D405/14 C07D409/10 C07D409/14 C07D413/10 C07D471/04 C07D487/04 C07F5/027 C07F7/0814 C09K11/025 C09K11/06 H01L51/0067 H01L51/0071 H01L51/0072 H01L51/0085 C07D209/86 H01L51/5016 C09K2211/1007 C09K2211/1029 C09K2211/1044 C09K2211/185		
审查员(译)	CLARK , GREGORYð		
优先权	61/017480 2007-12-28 US		
其他公开文献	US20160372685A1		
外部链接	Espacenet USPTO		

摘要(译)

一种有机发光器件，包括阳极，阴极和发光层，所述发光层包括选自的有机化合物 和至少一种发光掺杂剂。发光掺杂剂可以是各种有机金属铱络合物中的一种。

