International Bureau

(43) International Publication Date

25 February 2016 (25.02.2016)





(10) International Publication Number WO 2016/026122 A1

- (51) International Patent Classification: C09K 11/06 (2006.01) H01L 51/50 (2006.01)
- C07D 209/82 (2006.01)
 (21) International Application Number:

PCT/CN2014/084915

(22) International Filing Date:

21 August 2014 (21.08.2014)

(25) Filing Language:

English

(26) Publication Language:

English

- (71) Applicants: DOW GLOBAL TECHNOLOGIES LLC [US/US]; 2040 Dow Center, Midland, Michigan 48674 (US). ROHM AND HAAS ELECTRONIC MATERI-ALS LLC [US/US]; 455 Forest Street, Marlborough, Massachusetts 01752 (US).
- (72) Inventors; and
- (71) Applicants (for SC only): ZHU, Minrong [CN/CN]; Room 1601, No. 36, Lane 2250, Dongjing Rd., PUDONG District, Shanghai 201208 (CN). FENG, Jichang [CN/CN]; Room 303, No. 78 Dongjing Rd., Pudong District, Shanghai 201207 (CN). FENG, Shaoguang [US/CN]; Lane 1, Weifang West Road, Building #2, 50C, Shanghai 200120 (CN). LIU, Chun [CN/US]; 2600 Abbott Road, Apt A6, Midland, Michigan 48642 (US). MCDOUGAL, Nolan T. [US/US]; 4806 Chenevert Street, Houston, Texas 77004 (US). DEVORE, David D. [US/US]; 4901 E Shaffer, Midland, Michigan 48642 (US). TREFONAS, Peter [US/US]; 40 Summer Hill Rd, Medway, Massachusetts 02053 (US). SPENCER, Liam P.

[CA/US]; 2602 Joshua Tree Lane, Manvel, Texas 77578 (US).

- (74) Agent: WU, FENG & ZHANG CO.; Room 305, Tower B, Beijing Aerospace CPMIEC Building, No. 30, Haidian South Road, Haidian District, Beijing 100080 (CN).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: BENZOCYCLOBUTENES DERIVED COMPOSITIONS, AND ELECTRONIC DEVICES CONTAINING THE SAME

$$(R_3)c$$
 R_{19}
 R_{19}
 R_{18}
 R_{19}
 R_{18}
 R_{18}
 R_{18}
 R_{18}
 R_{18}
 R_{18}
 R_{18}
 R_{18}
 R_{19}
 R_{19}
 R_{19}
 R_{19}
 R_{19}

(Structure A)

(57) Abstract: Disclosed is a composition comprising at least one compound selected from (Structure A), as described herein, and for films and electronic devices containing the same.

BENZOCYCLOBUTENES DERIVED COMPOSITIONS, AND ELECTRONIC DEVICES CONTAINING THE SAME

BACKGROUND

5

10

15

20

25

30

Organic light-emitting diodes (OLEDs) have attracted considerable interest for the potential applications, as the next generation flat-panel displays and solid-state lighting sources. OLEDs are double charge injection devices, which require the simultaneous supply of both holes and electrons to the emissive layer. To realize facile and balanced charge transport, most highly efficient OLEDs tend to have multilayer device configurations, a hole transport layer (HTL), an electron transport layer (ETL) and an emissive layer (EML), some also have a hole-injection and an electron injection layer. The charge injection/transport layers are used to inject and transport holes and electrons to the EML, where the charges recombine and form the excitons. There is continuous need to develop new charge transport materials to improve device performance and lifetime.

In the case of the HTL layer, the process by which the layer is deposited is critical for its end-use application. Methods for depositing the HTL layer in small display applications involve evaporation of a small organic compound with a fine metal mask to direct the deposition. Solution processes, such as spin-coating, inkjet printing and roll-to-roll fabrication, offer an attractive alternative approach, in terms of their low-cost and large-area manufacturability, which is more amenable to commercial interests. With these findings in mind, new compositions and processes are still needed to deposit HTLs, and which satisfy these challenges and which can be directly applied to large display applications.

Although some polymeric materials can be fabricated by a solution process, their batch-to-batch variations in solubility, molecular weight, and purity, can result in different processing properties and device performance. Since higher molecular precision of small-molecule materials can overcome the abovementioned discrepancies, the development of solution-processable, small-molecule materials, suitable for OLEDs, is highly desirable to realize this goal. One approach that appears promising is a solution process which involves the deposition of a small molecule followed by crosslinking or polymerization chemistry. There have been extensive efforts in this area along these lines; however these chemistries have their own shortcomings. In particular, the current technology can hardly produce an insoluble HTL film, with few to no reactive end groups, at desirable process conditions.

The benzocyclobutene (BCB) group is an example of a moiety that undergoes a thermally activated dimerization, typically at 200°C or above, in this case forming a

dibenzocyclooctadiene ring, which is formed by scission of one of the cyclobutene C-C bonds, followed by an irreversible cycloaddition. It is been documented in the open literature that the substitution of oxygen-based donors at the cyclobutene ring above has a dramatic effect on the ring-opening temperature of the BCB (Dobish, J.N.; Hamilton, S.K.; Harth, E. *Polymer Chemistry* **2012**, *3*, 857-860); this phenomenon has yet to be utilized for OLEDs applications.

Benzocyclobutene (BCB) chemistries and their use in OLEDs are described in the following: US20040004433, US20080315757, US20080309229, US20100133566, US20110095278, US20110065222, US20110198573, US20110042661, JP2010062120, US7893160, US20110089411, US20070181874, US20070096082, CN102329411, US20120003790, WO2012052704, WO2012175975, WO2013007966.

However, there remains a need for new compositions for improved hole-transporting materials, and for improved processing of the same. These needs have been met by the following invention.

SUMMARY OF INVENTION

5

10

15

20

25

The invention provides a composition comprising at least one compound selected from Structure A:

$$(R_3)c$$
 R_{19}
 R_{19}
 R_{13}
 R_{10}
 R_{10}
 R_{10}
 R_{11}
 R_{11}
 R_{12}
 R_{12}
 $(Structure A),$

wherein groups R_4 to R_{19} are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₁ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₁)a is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₂ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₂)b is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₃ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₃)c is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups (R₁)a, (R₂)b, (R₃)c or R₄ to R₁₉ is independently selected the benzocyclobutene structures of Structure B, Structure C, Structure D, or Structure E, as follows:

(Structure B), wherein Structure B is connected

to Structure A though -L-;

B)

5

10

15

20

25

wherein, for Structure B:

1b) one of R^a₁, R^a₂, R^a₃ or R^a₄ is –L-; and wherein –L– is selected from the following: –O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-alkylene-O-; -O-alkylene-O-alkylene-; -O-alkylene-O-alkylene-; -O-arylene-; -O-arylene-; -O-arylene-; -O-arylene-; or a covalent bond linking 'Structure B" to "Structure A"; and

2b) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

3b) R^a₅, R^a₆, R^a₇ or R^a₈ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

(Structure C), wherein Structure C is

connected to Structure A though -L-;

5

10

15

20

25

wherein, for Structure C:

- 1c) one of R^a₅, R^a₆, R^a₇ or R^a₈ is –L–; and wherein –L- is selected from the following: –O–; -alkylene-; -O-alkylene-; -O-alkylene-; -O-alkylene-o-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-alkylene-o-alkylene-o-alkylene-; -O-alkylene-o-arylene-; -O-arylene-o-alkylene-; -O-arylene-o-arylene-; or a covalent bond linking 'Structure C" to "Structure A";
- 2c) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 3c) R^a₁, R^a₂, R^a₃ and R^a₄ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

wherein Structure D is connected to Structure A though -L-;

wherein, for Structure D:

- 1di) for one $-L_1$ -, one of R^a_1 , R^a_2 , R^a_3 or R^a_4 of the benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ is selected from the following: -O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-O-; -O-alkylene-O-alkylene-O-; -O-alkylene-O-alkylene-O-alkylene-o-alkylene-; -O-alkylene-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-; or a covalent bond linking the 4 carbon ring to Ar;
- 1dii) for the other $-L_1$ -, one of R^a_1 , R^a_2 , R^a_3 or R^a_4 of the other benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ -

is selected from the following: –O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-alkylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-; or a covalent bond linking the 4 carbon ring to Ar;

- 2d) Ar is a substituted or unsubstituted C5-C60 arylene group;
- 3d) -L- is selected from the following: -O-; -alkylene-; -arylene-; -O-alkylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-; -O-alkylene-O-arylene-; -O-arylene-O-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-arylene-
- 4di) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 4dii) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 5di) R^a₅, R^a₆, R^a₇ or R^a₈ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 5dii) R^a₅, R^a₆, R^a₇ or R^a₈ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;

wherein

5

10

15

20

25

30

Structure E is connected to Structure A though –L-; wherein, for Structure E:

lei) for one $-L_1$ -, one of R^a_5 , R^a_6 , R^a_7 or R^a_8 of the benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ - is selected from the following: -O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-arylene-; -O-alkylene-arylene-O-; -O-alkylene-O- alkylene-O-; -O-arylene-O-; -O-arylene-O-alkylene-O-arylene-; -O-arylene-O-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; or a covalent bond linking the 6- carbon ring to Ar;

5

10

15

20

25

30

- leii) for the other –L₁-, one of R^a₅, R^a₆, R^a₇ or R^a₈ of the other benzocyclobutene moiety directly bonded to this –L₁-, is independently –L₁-; and wherein –L1is selected from the following: –O-; -alkylene-; –arylene-; -O-alkylene-; -Oarylene-; -O-alkylene-arylene-; -O-alkylene-O-; -O-alkylene-O- alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-Oalkylene-; -O-arylene-; or a covalent bond linking the 6- carbon ring to Ar;
 - 2e) Ar is a substituted or unsubstituted C5-C60 arylene group; and
- 3e) -L- is selected from the following: -O-; -alkylene-; -arylene-; -O-alkylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; or a covalent bond linking 'Structure E" to "Structure A";
- 4ei) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 4eii) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 5ei) R^a₁, R^a₂, R^a₃ and R^a₄ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl
- 5eii) R^a₁, R^a₂, R^a₃ and R^a₄ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl; and

wherein for Structure A, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A, one or more hydrogen atoms may be optionally substituted with deuterium.

5

10

15

20

DETAILED DESCRIPTION

Crosslinkable BCB-functionalized materials have been discovered, which mitigate these drawbacks in conventional OLEDs applications. In terms of hole mobility, it has been discovered that the use of different attachment points on the HTL core to introduce BCB chemistry that can be utilized to tune the polymeric architecture after crosslink, and hence influence the flexibility of the HTL core. This approach should also allow for more effective stacking of the molecular cores, with respect to each other, which will increase the mobility of the hole in the HTL film, and improve device lifetime and efficiency. With different substitutions, such as alkyl, alkoxy, phenoxy, etc., on the four-member ring of BCB compound, the inventive composition described herein can also satisfy the solution-process conditions, with desirable curing temperature and curing times.

It has also been discovered that the use of compositions containing BCB derivatives, as described herein, can used to form polymers. Also, the polymerization chemistry can occur at substantially lower temperatures, as compared to other chemical reactions of the art. With unsubstituted BCB derivatives, the ring opening temperatures has been noted to occur at temperatures ~250°C (Kirchhoff, R.A.; Bruza, K.J. *Progress in Polymer Science* **1993**, *18*, 85-185). In this invention, the substitution of an oxygen donor results in a significant reduction in the ring opening temperatures to values from 100 to 120°C, which has significant process advantages over previous art.

25

30

Also, it has been discovered that once a reactive *o*-quinodimethane moiety has been formed, Diels-Alder reactions can occur to generate new C-C bonds in either a 1- or 2-component approach. In the case of a 2-component approach, the addition of an external polydienophiles can allow for full consumption of the reactive *o*-quinodimethane moieties, which allows for fewer reactive end groups. Reactive end-groups can introduce impurities into the HTL films which can adversely affect device lifetime and efficiency. Also, Fréchet et al. discloses polystyrene with bis-(diarylamino)biphenyl and cross- linkable benzocyclobutene side groups use as hole-transport material, in solution-processed OLEDs (*Chem. Mater.* 2007, 19, 4827.). In contrast, it has been discovered the inventive

compositions are crosslinkable materials with high molecular precision and high purity that will significantly benefit device performances.

As discussed above, the invention provides a composition comprising at least one compound selected from Structure A, as described above:

$$(R_3)c$$
 R_{19}
 R_{19}
 R_{13}
 R_{10}
 R_{10}
 R_{10}
 R_{11}
 R_{11}
 R_{12}
 R_{12}
 $(Structure A).$

An inventive composition may comprise a combination of two or more embodiments as described herein.

As used herein $R_1 = R1$, $R_2 = R2$, $R_3 = R3$, and the like.

5

10

15

In one embodiment, Structure A is selected from Structure A-I as follows:

$$(R_3)c$$
 Ar_3
 R_4
 R_5
 R_{19}
 R_{18}
 $R_{2.1}$
 $R_{2.2}$
 $R_{2.3}$
 $R_{2.4}$
 $R_{1.1}$
 $R_{1.2}$
 $R_{1.3}$
 $R_{1.4}$
 $R_{1.5}$
 $R_{1.5}$
 $R_{1.7}$
 $R_{1.6}$
 $R_{1.6}$
 $R_{1.7}$
 $R_{1.6}$
 $R_{1.6}$
 $R_{1.7}$
 $R_{1.6}$
 $R_{1.6}$
 $R_{1.7}$
 $R_{1.6}$
 $R_{1.7}$
 $R_{1.8}$
 $R_{1.8}$

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} or R_{2-4} is (R_2) b; and

wherein R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} and R_{1-9} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} or R_{1-9} is $(R_1)a$; and

wherein R_{1-2} and R_{1-3} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, or a halogen; and

wherein groups R_4 to R_{19} are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₃ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

5

10

15

20

(R₃)c is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected from Structure B, Structure C, or Structure D, or Structure E; and

wherein for Structure A-I, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-I, one or more hydrogen atoms may be optionally substituted with deuterium.

In one embodiment, Structure A is selected from Structure A-II as follows:

$$R_{3.5}$$
 $R_{3.4}$
 $R_{3.2}$
 $R_{3.5}$
 $R_{3.4}$
 $R_{3.3}$
 $R_{3.4}$
 R_{4}
 R_{5}
 R_{19}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 R_{2}
 $R_{3.5}$
 R_{4}
 R_{5}
 R_{5}
 R_{6}
 R_{2}
 R_{2}
 R_{11}
 R_{12}
 R_{12}
 R_{11}
 R_{12}
 R_{12}
 R_{12}
 R_{12}
 R_{12}
 R_{12}
 R_{13}
 R_{14}
 R_{15}
 R

(Structure A-II),

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} is $(R_2)b$; and

wherein R₃₋₁, R₃₋₂, R₃₋₃, R₃₋₄ and R₃₋₅ are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R₃₋₁, R₃₋₂, R₃₋₃, R₃₋₄ or R₃₋₅ is (R₃)c; and

wherein groups R_4 to R_{19} are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₁ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₁)a is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected from Structure B, Structure C, or Structure D, or Structure E; and

wherein for Structure A-II, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-II, one or more hydrogen atoms may be optionally substituted with deuterium.

In one embodiment, Structure A is selected from Structure A-III as follows:

5

10

15

20

(Structure A-III),

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} is (R_2) b; and

wherein R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} and R_{1-9} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} or R_{1-9} is $(R_1)a$; and

wherein R_{1-2} and R_{1-3} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, or a halogen; and

wherein R₃₋₁, R₃₋₂, R₃₋₃, R₃₋₄ and R₃₋₅ are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R₃₋₁, R₃₋₂, R₃₋₃, R₃₋₄ or R₃₋₅ is (R₃)c; and

wherein groups R₄ to R₁₉ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; with the proviso that at least one of groups (R₁)a, (R₂)b, (R₃)c or R₄ to R₁₉ is independently selected from Structure B, Structure C, or Structure D, or Structure E; and with the proviso that at least one of groups (R₁)a, (R₂)b, (R₃)c or R₄ to R₁₉ is independently selected from Structure B, Structure C, or Structure D, or Structure E; and wherein for Structure A-III, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-III, one or more hydrogen atoms may be optionally substituted with deuterium.

5

10

15

20

In one embodiment, at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected from Structure B. In a further embodiment, for Structure B, -L- is selected from the following: -O-, -alkylene, -O-alkylene-, -O-phenylene-, -O-alkylene-phenylene-, or a covalent bond linking 'Structure B" to "Structure A".

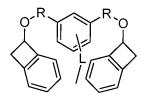
In one embodiment, Structure B is selected from the following structures (i) or (ii):

In one embodiment, at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected from Structure C. In a further embodiment, for Structure C, -L-is selected from the following: -O-, -alkylene, -O-alkylene-, -O-phenylene-, -O-alkylene-phenylene, or a covalent bond linking "Structure C" to "Structure A".

In one embodiment, Structure C is selected from the following structures (iii) or (iv):

\ (iv), wherein R_1 is hydrogen, a hydrocarbon or a substituted hydrocarbon; and R_2 is hydrogen, a hydrocarbon or a substituted hydrocarbon.

In one embodiment, Structure D is selected from the following structure (v):



(v), wherein each R is independently hydrogen, a hydrocarbon or a

5 substituted hydrocarbon

In one embodiment, for Structure A, R6-R11, R13-R17 and R23-R25 are each hydrogen.

In one embodiment, for Structure A, R4, R5 and R26 are each hydrogen.

In one embodiment, Structure A is selected from the following structures (a) through

10 (r):

In one embodiment, Structure A has a molecular weight from 500g/mole to 5000 g/mole.

In one embodiment, Structure A has a triplet energy from 2.30 eV to 3.20 eV.

The invention also provides a film comprising at least one Layer A formed from an inventive composition.

An inventive film may comprise a combination of two or more embodiments described herein.

5

10

15

20

25

The invention also provides an article comprising at least one component formed from an inventive composition.

In one embodiment, the article is an electroluminescent device.

The invention also provides an article comprising at least one component formed from an inventive film.

In one embodiment, the article is an electroluminescent device.

The invention also provides an electroluminescent device comprising at least one component formed from an inventive composition.

An inventive article may comprise a combination of two or more embodiments described herein.

An inventive device may comprise a combination of two or more embodiments described herein.

In one embodiment, the inventive composition comprises at least one deuterium atom.

In one embodiment, the compound of Structure A has a purity greater than 99 percent.

In one embodiment, the composition comprises at least two compounds selected from Structure A.

In one embodiment, the composition comprises from 50 to 90 weight percent of at least one compound selected from Structure A, based on the weight of the composition. In a further embodiment, the composition comprises from 70 to 90 weight percent, further from

90 to 99 weight percent of at least one compound selected from Structure A, based on the weight of the composition.

In one embodiment, the composition further comprises an organometal compound, and further a metal quinolate. In a further embodiment, the metal quinolate is a lithium quinolate with or without substituents.

In one embodiment, the organometal compound comprises lithium. In a further embodiment, the organometal is lithium quinolate with or without substituents. In one embodiment, the weight ratio of the at least one compound (Formula 1 or Formula 2) to the organometal compound is from 9/1 to 1/1, further from 4/1 to 1/1, further from 3/2 to 1/1.

DEFINITIONS

5

10

15

20

25

30

The term "hydrocarbon," as used herein, refers to a chemical group containing only hydrogen and carbon atoms.

The term "substituted hydrocarbon," as used herein, refers to a hydrocarbon in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom. Heteroatoms include, but are not limited to, O, N, P and S. Substituents include, but are not limited to, OR', NR'_2 , PR'_2 , $P(=O)R'_2$, SiR'_3 ; where each R' is a C_1 - C_{20} hydrocarbyl group.

The term "aryl," *as* described herein, refers to an organic radical derived from aromatic hydrocarbon by deleting one hydrogen atom therefrom. An aryl group may be a monocyclic and/or fused ring system, each ring of which suitably contains from 4 to 7, preferably from 5 or 6 atoms. Structures wherein two or more aryl groups are combined through single bond(s) are also included. Specific examples include, but are not limited to, phenyl, naphthyl, biphenyl, anthryl, indenyl, fluorenyl, benzofluorenyl, phenanthryl, triphenylenyl, pyrenyl, perylenyl, chrysenyl, naphtacenyl, fluoranthenyl and the like, but are not restricted thereto. The naphthyl may be 1-naphthyl or 2-naphthyl, the anthryl may be 1-anthryl, 2-anthryl or 9-anthryl, and the fluorenyl may be any one of 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl.

The term "substituted aryl," as used herein, refers to an aryl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom. Heteroatoms include, but are not limited to, O, N, P and S. Substituents include, but are not limited to, OR', NR'₂, PR'₂, P(=O)R'₂, SiR'₃; where each R' is a C_{30} - C_{100} hydrocarbyl group.

The term "heteroaryl," as described herein, refers to an aryl group, in which at least one carbon atom or CH group or CH₂ is substituted with a heteroatom (for example, B, N, O, S, P(=O), Si and P) or a chemical group containing at least one heteroatom. The heteroaryl may be a 5- or 6-membered monocyclic heteroaryl or a polycyclic heteroaryl which is fused with one or more benzene ring(s), and may be partially saturated. The structures having one or more heteroaryl group(s) bonded through a single bond are also included. The heteroaryl groups may include divalent aryl groups of which the heteroatoms are oxidized or quarternized to form N-oxides, quaternary salts, or the like. Specific examples include, but are not limited to, monocyclic heteroaryl groups, such as furyl, thiophenyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiazolyl, isothiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, triazinyl, tetrazinyl, triazolyl, tetrazolyl, furazanyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl; polycyclic heteroaryl groups, such as benzofuranyl, fluoreno[4, 3b]benzofuranyl, benzothiophenyl, fluoreno[4, 3-b]benzothiophenyl, isobenzofuranyl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzisoxazolyl, benzoxazolyl, isoindolyl, indolyl, indazolyl, benzothia- diazolyl, quinolyl, isoquinolyl, cinnolinyl, quinazolinyl, quinoxalinyl, carbazolyl, phenanthridinyl and benzodioxolyl; and corresponding N-oxides (for example, pyridyl N-oxide, quinolyl N-oxide) and quaternary salts thereof.

5

10

15

20

25

30

The term "substituted heteroaryl," as used herein, refers to a heteroaryl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom. Heteroatoms include, but are not limited to, O, N, P and S. Substituents include, but are not limited to, OR', NR'_2 , PR'_2 , $P(=O)R'_2$, SiR'_3 ; where each R' is a C_1 - C_{20} hydrocarbyl group.

The term "polymer," as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into and/or within the polymer structure), and the term interpolymer as defined hereinafter.

The term "interpolymer," as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers (employed to refer to polymers prepared from two different types of monomers), and polymers prepared from more than two different types of monomers.

EXPERIMENTAL

Reagents and Test Methods

All solvents and reagents were obtained from commercial vendors, and were used in the highest available purities, and/or when necessary, recrystallized before use. Dry solvents were obtained from in-house purification/dispensing system (hexane, toluene, and tetrahydrofuran), or purchased from Sigma-Aldrich. All experiments involving "water sensitive compounds" were conducted in "oven dried" glassware, under nitrogen atmosphere, or in a glovebox. Reactions were monitored by analytical, thin-layer chromatography (TLC) on precoated aluminum plates (VWR 60 F254), and visualized by UV light and/or potassium permanganate staining. Flash chromatography was performed on an ISCO COMBIFLASH system with GRACERESOLV cartridges.

Modeling

5

10

15

20

25

30

All computations utilized the Gaussian09 program¹. The calculations were performed with the hybrid density functional theory (DFT) method, B3LYP,² and the 6-31G* (5d) basis set.³ The singlet state calculations used the closed shell approximation, and the triplet state calculations used the open shell approximation. All values are quoted in electronvolts (eV). The HOMO and LUMO values were determined from the orbital energies of the optimized geometry of the singlet ground state. The triplet energies were determined as the difference between the total energy of the optimized triplet state and the optimized singlet state.

- 1. Gaussian 09, Revision A.02, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, N.; Vreven, T.; Montgomery, Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.;
 - 2. (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.*

J.V.; Cioslowski, J.; Fox, D.J., Gaussian, Inc., Wallingford CT, 2009.

Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz,

1989, 157, 200.

3. (a) Ditchfield, R.; Hehre, W.J.; Pople, J.A. J. Chem. Phys. 1971, 54, 724. (b) Hehre, W.J.; Ditchfield, R.; Pople, J.A. J. Chem. Phys. 1972, 56, 2257. (c) Gordon, M.S. Chem. Phys. Lett. 1980, 76, 163.

5 NMR:

15

20

25

30

The 1H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. Chemical shifts were reported versus tetramethylsilane (TMS) in CDCl₃. LC/MS:

Sample was dissolved in THF at around 1mg/mL. 1 uL solution was injected for

10 LC/MS analysis.

Instrument: Agilent 1220 HPLC/ G6224A TOF mass spectrometer

Column: Agilent eclipse-C18 4.6*50mm, 1.7um

Column oven temperature: 30 Deg C

Solvent: A:THF; B: 0.1%FA in water/ACN 95/5 Gradient: 0-6 min 40-80% A, hold for 9 min

Flow: 0.3 mL/min

UV detector: Diode Array 254 nm

MS condition:

Capillary Voltage: 3900 kV (Neg), 3500 kV (Pos)

Mode: Neg and Pos Scan: 100-2000 amu

Rate: 1s/scan

Desolvation temperature: 300 deg C

HPLC:

Approximately 1 mg of the samples weighed then was diluted with 1 mL tetrahydrofuran. The sample solution was at last filtrated through a 0.45 µm syringe filter and 5 µl of the filtrate was injected to HPLC system.

Parameter	Paramete	Parameter Value					
Injection volume	5 μL						
Instrument	Agilent 1200 HPLC						
Column	Agilent Zo	Agilent Zorbax C8 4.6*250mm, 5 um					
Temperature	40°C						
Detector	DAD=330 nm, ref=470 nm						
Mobile Phase	Eluent A:	Eluent A: Water(0.1% FA); Eluent B: THF					
Time	A%	В%	Flow Rate (mL/min)				
0.0	42	58	1				
40	35	65	1				
47	34	66	1				
48	10	90	1				

I) Materials and Synthesis

Materials used in this study are shown in Tables 1A and 1B.

Table 1A: Materials

Material name	Chemical structure	Supplier	Note
Bromobenzene	Br	SCRC	A.R.
4-bromobenzaldehyde	CHO Br	SCRC	A.R.
9 <i>H</i> -carbazole	H	SCRC	A.R.
N-([1,1'-biphenyl]-4-yl)-9,9- dimethyl-9H-fluoren-2- amine	00"06	SCRC	A.R.
Titanium tetrachloride	TiCl ₄	SCRC	A.R.
Tris(dibenzylideneacetone)di palladium(0)	Pd(OAc) ₂	Shanghai Darui Fine Chemicals	A.R.
Tetrakis(triphenylphosphine) palladium	Pd(PPh ₃) ₄	Shanghai Darui Fine Chemicals	A.R.
[1,1'- Bis(diphenylphosphino)ferro cene]palladium(II) chloride	Pd(dppf)Cl ₂	Shanghai Darui Fine Chemicals	A.R.
2-(Dicyclohexylphosphino)- 2',4',6'-triisopropylbiphenyl (X-Phos)		Shang hai Demo Medical Tech Co. Ltd.	A.R.

A.R. = Analytical Reagent

Table 1B: Materials

Material name	Chemical structure	Supplier	Note
4,4,4',4',5,5,5',5'-octamethyl- 2,2'-bi(1,3,2-dioxaborolane)	D B-B O	SCRC	A.R.
N-Bromosuccinimide	NBS	SCRC	A.R.
Cuprous Iodide		SCRC	A.R.
Sodium hydride (NaH)		TCI	A.R.
Sodium borohydride (NaBH ₄)		SCRC	A.R.
Potassium carbonate		SCRC	A.R.
Potassium <i>tert</i> -butoxide (<i>t</i> BuOK)		TCI	A.R.
Potassium Acetate (KOAc)		SCRC	A.R.
dichloro(methoxy)methane		SCRC	A.R.
Dimethylformamide		SCRC	A.R.
1,4-dioxane		SCRC	A.R.
Dichloromethane		SCRC	A.R.
Tetrahydrogenfuran		SCRC	A.R.
Toluene		SCRC	A.R.

A.R. = Analytical Reagent

Syntheses

Synthesis of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (1)

Scheme 1

5

10

15

20

25

N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2-amine (40.0 g, 110 mmol), bromobenzene (23.4 g, 150 mmol), Pd(OAc)₂ (616 mg, 2.75 mmol), X-Phos (1.57 g, 3.3 mmol), tBuOK (24.6 g, 220 mmol) were added into a 250 mL, three-necked round-bottom flask, equipped with a reflux condenser. After addition of 250 mL dry toluene, under N₂ atmosphere, the suspension was heated to 90°C, and stirred overnight under a flow of N₂. After cooling to room temperature, water was added, and the organic layer was separated. The solvent was evaporated under vacuum, and the residue was used for the next step without further purification (yield: 95%). MS (ESI): 437.02 [M+H]⁺.

Synthesis of N-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine (2)

Scheme 2

To a solution of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (1) (35.0 g, 80 mmol) in 150 mL DMF, N-bromosuccinimide (NBS) (16.02 g, 90 mmol), in 100 mL DMF, was added dropwise in 30 minutes. After addition, the mixture was stirred at room temperature for 12 hours, and then poured into water to precipitate. The solid was filtered, and recrystallized from dichloromethane and ethanol to give white solid (yield: 92%). MS (ESI): 516.12 [M+H]⁺.

Synthesis of 7-([1,1'-biphenyl]-4-yl(4-bromophenyl)amino)-9,9-dimethyl-9H-fluorene-2-carbaldehyde (3)

Scheme 3

5

10

15

20

To a solution of triarylamine (25.8 g, 50 mmol) in 100 mL CH₂Cl₂ at 0 °C, TiCl₄ (54.6 mL, 500 mmol), diluted with 100 mL CH₂Cl₂, were added in 30 minutes. The mixture was stirred for an additional 30 minutes at 0 °C. Then, CH₃OCHCl₂ (27.0 mL, 300 mmol), in 200 mL of CH₂Cl₂, was added dropwise in 30 minutes. The dark-green solution was stirred for another one hour at 0°C. After completion, water, with crushed ice, was slowly added to quench the reaction. The organic layer was separated, and washed consecutively with saturated sodium bicarbonate solution, brine, and dried over anhydrous sodium sulphate. After filtration, the solvent was removed under vacuum, and the residue was purified through column chromatography to give crude product (yield: 55%). MS (ESI): 544.12 [M+H]⁺.

Synthesis of 4-(9H-carbazol-9-yl)benzaldehyde (4)

Scheme 4

A mixture of 9*H*-carbazole (9.53 g, 57 mmol), 4-bromobenzaldehyde (21.1 g, 114 mmol), Copper(I) iodide (1.80 g, 9.4 mmol), K₂CO₃ (11.8 g, 86 mmol), in 60 mL dry DMF, was heated to 140°C, under nitrogen atmosphere for 12 hours. After cooling to room temperature, the inorganic solid was filtered, and the residue was poured into ice water to precipitate the product. The so-formed solid was collected, and washed by water, ethanol several times, then crystallized from CH₂Cl₂ and ethanol, to give light-yellow solid (yield: 95%). MS (ESI): 272.10 [M+H]⁺.

Synthesis of 4-(3-bromo-9H-carbazol-9-yl)benzaldehyde (5)

25 Scheme 5

To a solution of 4-(9*H*-carbazol-9-yl)benzaldehyde (26.6 g, 98 mmol) in 100 mL DMF, NBS (17.4 g, 98 mmol), in 100 mL DMF, was added dropwise in 30 minutes. After addition, the mixture was stirred at room temperature for 12 hours. The solution was poured into ice water to precipitate the product. After filtration, the solid was collected, and washed

21

by water, ethanol several times, then dried under vacuum, and used for the next step without further purification (yield: 96%). MS (ESI): 350.01 [M+H]⁺.

Synthesis of 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)benzaldehyde (6)

Scheme 6

5

10

15

20

25

A mixture of 3-bromo-9-(4-formylphenyl)-9*H*-carbazole (10.51 g, 30 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (9.14 g, 36 mmol, 253), Pd(dppf)₂Cl₂ (571 mg, 0.75 mmol), CH₃COOK (4.41 g, 45 mmol), and 60 mL of dry dioxane, was heated at 85°C, under nitrogen atmosphere for 12 hours. After cooling to room temperature, the solvent was removed under vacuum, and then water was added. The mixture was extracted with CH₂Cl₂. The organic layer was collected, and dried over anhydrous sodium sulphate. After filtration, the filtrate was evaporated to remove solvent, and the residue was purified through column chromatography on silica gel, to give white solid (yield: 84%). MS (ESI): 398.16 [M+H]⁺.

Synthesis of 7-([1,1'-biphenyl]-4-yl(4-(9-(4-formylphenyl)-9H-carbazol-3-yl)phenyl)amino)-9,9-dimethyl-9H-fluorene-2-carbaldehyde (7)

Scheme 7

A mixture of **6** (0.7 g, 1.76 mmol), **3** (0.8 g, 1.47 mmol), Pd(PPh₃)₄ (76 mg, 0.064 mmol), 2M K₂CO₃ (0.8 g, 6 mmol, 3 mL H₂O), 3 mL ethanol and 3 mL of toluene, was heated at 90°C, under nitrogen atmosphere for 12 hours. After cooling to room temperature, the solvent was removed under vacuum, and the residue was dissolved with CH₂Cl₂. The organic layer was washed with water, and then dried over anhydrous sodium sulphate. After

filtration, the filtrate was evaporated to remove solvent, and the residue was purified through column chromatography on silica gel, to give white solid (yield: 85%). MS (ESI): 735.29 [M+H]⁺.

5 Synthesis of (7-([1,1'-biphenyl]-4-yl(4-(9-(4-(hydroxymethyl)phenyl)-9H-carbazol-3-yl)phenyl)amino)-9,9-dimethyl-9H-fluoren-3-yl)methanol (8)

Scheme 8

To a solution of **7** (734 mg, 1 mmol) in 10 mL THF and 10 mL ethanol at 40°C,

NaBH₄ (302 mg, 8 mmol), was added under nitrogen atmosphere. The solution was allowed to stir at room temperature for 2 hours. Then, aqueous hydrochloric acid solution was added, until pH 5, and the mixture was kept stirring for 30 minutes. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The product was then dried under vacuum, and used for the next step without further purification. MS (ESI): 739.32

[M+H]⁺.

Synthesis of N-([1,1'-biphenyl]-4-yl)-6-((bicyclo[4.2.0]octa-1,3,5-trien-7-yloxy)methyl)-N-(4-(9-(4-((bicyclo[4.2.0]octa-1,3,5-trien-7-yloxy)methyl)phenyl)-9H-carbazol-3-yl)phenyl)-9,9-dimethyl-9H-fluoren-2-amine $(\mathbf{9})$

20

Scheme 9

To a solution of **8** (3.69 g, 5 mmol, 738) in 50 mL dry DMF was added NaH (432 mg, 18 mmol, 24), then the mixture was stirred at room temperature for one hour. Then BCB-Br (2.75 g, 15 mmol, 183) was added to above solution via syringe. The mixture was heated to 60°C for 24 hours. After quenched with water, the mixture was poured into water to remove DMF. The residue was filtrated, and the resulting solid was dissolved with dichloromethane, which was then washed with water. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The product was then obtained by column chromatography on silica gel with PE:EA (5:1) as the eluent. MS (ESI): 943.42 [M+H]⁺.

10

5

Synthesis of 3-bromo-9-(4-bromophenyl)-9H-carbazole (10)

Scheme 10

To a solution of *9* (*4-bromophenyl*)-9*H-carbazole* (32.2 g, 100 mmol) in 150 mL DMF, *N*-bromosuccinimide (NBS) (17.8 g, 100 mmol) in 100 mL DMF, was added dropwise in 30 minutes. After addition, the mixture was stirred at room temperature for 12 hours, and then poured into water to precipitate the product. The solid was filtrated, and recrystallized from dichloromethane and ethanol, to give white solid (yield: 92%). MS (ESI): 402.09 [M+H]⁺.

20

25

15

Synthesis of 9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde (11)

Scheme 11

To a solution of **10** (8.02 g, 20 mmol) in THF (500m L), *n*-BuLi (24 mL of a 2.5 M solution in hexanes, 60 mmol) was added at a rate to keep the internal temperature at -78°C. The mixture was stirred at -78°C for one hour, and 10 mL DMF, with 10mL THF, was added dropwise. After the addition, the reaction mixture was stirred at -45°C for 30 minutes, and at 0°C for an additional 30 minutes. Saturated aqueous NH4Cl (400 mL) was added. The layers were separated, and the aqueous layer was washed with a solution of ether:CH₂Cl₂ (2 x

100m L, 9:1). The combined organic layers were washed with H₂O, saturated aqueous NaCl, dried over anhydrous MgSO4, and concentrated under reduced pressure. The residual was further purified through column chromatography to give crude product (yield: 65%). MS (ESI): 300.09 [M+H]⁺.

5

10

Synthesis of 6-bromo-9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde (12)

Scheme 12

To a solution of **11** (0.898 g, 3 mmol, 1.00 equiv) in DCM (20m L), NBS (0.587mg, 3.3 mmol) was added. After stirred for 4 hours, the precipitate formed was filtered, and washed with ethanol to afford the product (yield: 84%). MS (ESI): 378.01 [M+H]⁺.

Synthesis of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine (13)

15

20

Scheme 13

A mixture of **2** (15.48 g, 30 mmol), 4,4,4',4',5,5,5',5'-octamethyl -2,2'-bi(1,3,2-dioxaborolane) (9.14 g, 36 mmol), Pd(dppf)₂Cl₂ (571 mg, 0.75 mmol), CH₃COOK (4.41 g, 45 mmol), and 60 mL of dry dioxane, was heated at 85°C, under nitrogen atmosphere for 12 hours. After cooling to room temperature, the solvent was removed under vacuum, and then water was added. The mixture was extracted with CH₂Cl₂. The organic layer was collected, and dried over anhydrous sodium sulphate. After filtration, the filtrate was evaporated to remove solvent, and the residue was purified through column chromatography on silica gel to give white solid (yield: 84%). MS (ESI): 564.30[M+H]+.

25

 $Synthesis\ of\ 6-(4-([1,1'-biphenyl]-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amino) phenyl)-9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde\ \textbf{(14)}$

Scheme 14

A mixture of **12** (0.756g, 2mmol), 13 (1.24g, 2.2mmol), Pd(OAc)₂ (12.8mg, 0.06mmol) and X-Phos (28.6mg, 0.06mmol), was added into 20mL of a "1:1:2 mixture of aq. 2.0M Na₂CO3:ethanol: toluene." The reaction mixture was stirred overnight, under an nitrogen atmosphere at 90°C, and then poured into EtOAc. The organics were washed with water and brine, and then dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was purified through column chromatography on silica gel, to give yellow solid (yield: 64%). MS (ESI): 735.29 [M+H]+.

10

5

Synthesis of (4-(3-(4-([1,1'-biphenyl]-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-6-(hydroxymethyl)-9H-carbazol-9-yl)phenyl)methanol (15)

Scheme 15

15

20

25

To a solution of **14** (734 mg, 1 mmol) in 10 mL THF and 10 mL ethanol, at 40°C, NaBH₄ (302 mg, 8 mmol) was added under nitrogen atmosphere. The solution was allowed to stir at room temperature for 2 hours. Then, aqueous hydrochloric acid solution was added until pH 5, and the mixture was kept stirring for 30 minutes. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The product was then dried under vacuum, and used for the next step, without further purification. MS (ESI): 739.32 [M+H]⁺.

Synthesis of N-([1,1'-biphenyl]-4-yl)-N-(4-(6-((bicyclo[4.2.0]octa-1(6),2,4-trien-7-yloxy)methyl)-9-(4-((bicyclo[4.2.0]octa-1(6),2,4-trien-7-yloxy)methyl)phenyl)-9H-carbazol-3-yl)phenyl)-9,9-dimethyl-9H-fluoren-2-amine (16)

Scheme 16

5

10

15

To a solution of **15** (3.69 g, 5 mmol, 738) in 50 mL dry DMF, was added NaH (432 mg, 18 mmol), then the mixture was stirred at room temperature for one hour. And BCB-Br (2.75 g, 15 mmol) was added to above solution via syringe. The mixture was heated to 60°C for 24 hours. After being quenched with water, the mixture was poured into water to remove DMF. The residue was filtrated, and the resulting solid was dissolved with dichloromethane, which was then washed with water. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The product was then obtained by column chromatography on silica gel with PE:EA (5:1) as the eluent. MS (ESI): 943.42 [M+H]⁺.

The inventive compositions can be used to form hole-transporting materials for use in electroluminescent devices.

CLAIMS

1. A composition comprising at least one compound selected from Structure A:

$$(R_3)c$$
 R_{19}
 R

wherein groups R₄ to R₁₉ are each, independently, selected from hydrogen, a

5 hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

 Ar_1 is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₁)a is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₂ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

 (R_2) b is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₃ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₃)c is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected the benzocyclobutene structures of Structure B, Structure C, Structure D, or Structure E, as follows:

10

15

20

B)

(Structure B), wherein Structure B is connected

to Structure A though –L-;

5

10

15

20

25

30

wherein, for Structure B:

1b) one of R^a₁, R^a₂, R^a₃ or R^a₄ is –L-; and wherein –L- is selected from the following: –O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-alkylene-O-; -O-alkylene-; -O-alkylene-; -O-alkylene-; -O-arylene-; -O-arylene-; -O-arylene-; or a covalent bond linking 'Structure B" to "Structure A"; and

- 2b) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and
- 3b) R^a₅, R^a₆, R^a₇ or R^a₈ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

 R^{a}_{7} R^{a}_{6} R^{a}_{5} R^{a}_{1} R^{a}_{2} R^{a}_{3}

(Structure C), wherein Structure C is

connected to Structure A though -L-;

wherein, for Structure C:

- 1c) one of R^a₅, R^a₆, R^a₇ or R^a₈ is –L–; and wherein –L- is selected from the following: –O–; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-o-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; or a covalent bond linking 'Structure C" to "Structure A";
- 2c) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 3c) R^a₁, R^a₂, R^a₃ and R^a₄ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

wherein Structure D is connected to Structure A though –L-; wherein, for Structure D:

5

10

15

20

25

- 1di) for one $-L_1$ -, one of R^a_1 , R^a_2 , R^a_3 or R^a_4 of the benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ is selected from the following: -O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-O-; -O-alkylene-O- alkylene-O-; -O-alkylene-O-alkylene-O-alkylene-O-alkylene-; -O-alkylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-; or a covalent bond linking the 4 carbon ring to Ar;
- ldii) for the other $-L_1$ -, one of R^a_1 , R^a_2 , R^a_3 or R^a_4 of the other benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ is selected from the following: -O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-alkylene-O-alkylene-O-arylene-; -O-arylene-O-arylene-O-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-alkylene-arylene-O-; or a covalent bond linking the 4 carbon ring to Ar;
 - 2d) Ar is a substituted or unsubstituted C5-C60 arylene group;
- 3d) -L- is selected from the following: -O-; -alkylene-; -arylene-; -O-alkylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-; -O-alkylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-; -O-arylene-O-arylene-; -O-arylene-
- 4di) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;

4dii) the remaining R^a₁, R^a₂, R^a₃ and R^a₄ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;

- 5di) R^a₅, R^a₆, R^a₇ or R^a₈ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 5dii) R^a₅, R^a₆, R^a₇ or R^a₈ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;

wherein

5

10

15

20

25

Structure E is connected to Structure A though -L-; wherein, for Structure E:

- lei) for one $-L_1$ -, one of R^a_5 , R^a_6 , R^a_7 or R^a_8 of the benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ is selected from the following: -O-; -alkylene-; -O-alkylene-; -O-arylene-; -O-arylene-; -O-alkylene-arylene-O-; -O-alkylene-O- alkylene-O-; -O-arylene-O-; -O-alkylene-O-alkylene-O-arylene-O-arylene-; -O-arylene-O-arylene-; -O-arylene-
- leii) for the other $-L_1$ -, one of R^a_{5} , R^a_{6} , R^a_{7} or R^a_{8} of the other benzocyclobutene moiety directly bonded to this $-L_1$ -, is independently $-L_1$ -; and wherein $-L_1$ is selected from the following: -O-; -alkylene-; -arylene-; -O-alkylene-; -O-arylene-; -O-alkylene-arylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-arylene-
 - 2e) Ar is a substituted or unsubstituted C5-C60 arylene group; and

3e) -L- is selected from the following: -O-; -alkylene-; -arylene-; -O-alkylene-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-alkylene-O-; -O-arylene-O-; -O-arylene-O-alkylene-; -O-arylene-O-arylene-; -O-arylene-O-; -O-arylene-O-arylene-; -O-arylene-O-arylene-; or a covalent bond linking 'Structure E" to "Structure A";

5

10

15

20

- 4ei) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 4eii) the remaining R^a₅, R^a₆, R^a₇ or R^a₈ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl;
- 5ei) R^a₁, R^a₂, R^a₃ and R^a₄ of one benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl
- 5eii) R^a₁, R^a₂, R^a₃ and R^a₄ of the other benzocyclobutene moiety are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, or a hydroxyl; and

wherein for Structure A, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A, one or more hydrogen atoms may be optionally substituted with deuterium.

2. The composition of claim 1, wherein Structure A is selected from Structure A-I as follows:

$$(R_3)c$$

$$Ar_3$$

$$R_4$$

$$R_5$$

$$R_{19}$$

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} or R_{2-4} is (R_2) b; and

wherein R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} and R_{1-9} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} or R_{1-9} is $(R_1)a$; and

wherein R_{1-2} and R_{1-3} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, or a halogen; and

wherein groups R_4 to R_{19} are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

 Ar_3 is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

(R₃)c is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups $(R_1)a$, $(R_2)b$, $(R_3)c$ or R_4 to R_{19} is independently selected from Structure B, Structure C, or Structure D, or Structure E; and

wherein for Structure A-I, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-I, one or more hydrogen atoms may be optionally substituted with deuterium.

3. The composition of claim 1, wherein Structure A is selected from Structure A-II as follows:

$$R_{3.5}$$
 $R_{3.4}$
 $R_{3.2}$
 $R_{3.3}$
 R_{4}
 R_{4}
 R_{5}
 R_{18}
 $R_{2.1}$
 $R_{2.3}$
 $R_{2.4}$
 R_{11}
 R_{12}
 R_{13}
 R_{14}
 R_{15}
 R_{15}
 R_{17}
 R_{10}
 R_{10}
 R_{11}
 R_{12}
 R_{12}
 R_{13}
 R_{14}
 R_{15}
 R_{15}
 R_{15}
 R_{17}
 R_{19}
 R_{11}
 R_{12}
 R_{13}
 R_{14}
 R_{15}
 R_{15}

25

5

10

15

20

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} is (R_2) b; and

wherein R_{3-1} , R_{3-2} , R_{3-3} , R_{3-4} and R_{3-5} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{3-1} , R_{3-2} , R_{3-3} , R_{3-4} or R_{3-5} is $(R_3)c$; and

5

10

15

wherein groups R₄ to R₁₉ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

Ar₁ is selected from a substituted aryl, an unsubstituted aryl, a substituted heteroaryl, or an unsubstituted heteroaryl;

 (R_1) a is selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and

with the proviso that at least one of groups (R₁)a, (R₂)b, (R₃)c or R₄ to R₁₉ is independently selected from Structure B, Structure C, or Structure D, or Structure E; and wherein for Structure A-II, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-II, one or more hydrogen atoms may be optionally substituted with deuterium.

4. The composition of any one of the previous claims, wherein Structure A is selected from Structure A-III as follows:

$$R_{3.5}$$
 $R_{3.4}$
 $R_{3.3}$
 $R_{3.4}$
 R_{4}
 R_{5}
 R_{18}
 R_{18}

wherein R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{2-1} , R_{2-2} , R_{2-3} and R_{2-4} is (R_2) b; and

wherein R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} and R_{1-9} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{1-1} , R_{1-4} , R_{1-5} , R_{1-6} , R_{1-7} , R_{1-8} or R_{1-9} is (R_1) a; and

5

10

15

20

25

wherein R_{1-2} and R_{1-3} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, or a halogen; and

wherein R_{3-1} , R_{3-2} , R_{3-3} , R_{3-4} and R_{3-5} are each independently selected from the following: hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl; and wherein one of R_{3-1} , R_{3-2} , R_{3-3} , R_{3-4} or R_{3-5} is $(R_3)c$; and

wherein groups R₄ to R₁₉ are each, independently, selected from hydrogen, a hydrocarbon, a substituted hydrocarbon, a halogen, a cyano, a nitro, an alkoxy, or a hydroxyl;

with the proviso that at least one of groups (R₁)a, (R₂)b, (R₃)c or R₄ to R₁₉ is independently selected from Structure B, Structure C, or Structure D, or Structure E; and wherein for Structure A-III, two or more R groups may optionally form one or more ring structures; and

wherein for Structure A-III, one or more hydrogen atoms may be optionally substituted with deuterium.

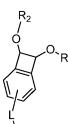
- 5. The composition of any one of the previous claims, wherein, for Structure B, -L- is selected from the following: -O-, -alkylene, -O-alkylene-, -O-phenylene-, -O-alkylene-phenylene-, or a covalent bond linking 'Structure B" to "Structure A".
- 6. The composition of any one of the previous claims, wherein, for Structure C, -L- is selected from the following: -O-, -alkylene, -O-alkylene-, -O-phenylene-, -O-alkylene-phenylene, or a covalent bond linking "Structure C" to "Structure A".
- 7. The composition of any one of the previous claims, wherein Structure B is selected from the following structures (i) or (ii):

8. The composition of any one of the previous claims, wherein Structure C is selected from the following structures (iii) or (iv):

5

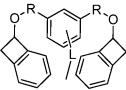
20

(iii), wherein R is hydrogen, a hydrocarbon or a substituted hydrocarbon;



\ (iv), wherein R_1 is hydrogen, a hydrocarbon or a substituted hydrocarbon; and R_2 is hydrogen, a hydrocarbon or a substituted hydrocarbon.

10 9. The composition of any one of the previous claims, wherein Structure D is selected from the following structure (v):



(v), wherein each R is independently hydrogen, a hydrocarbon or a substituted hydrocarbon

- 15 10. The composition of any one of the previous claims, wherein, for Structure A, R6-R11, R13-R17 and R23-R25 are each hydrogen.
 - 11. The composition of any one of the previous claims, wherein, for Structure A, R4, R5 and R26 are each hydrogen.

12. The composition of any one of the previous claims, wherein Structure A is selected from the following structures (a) through (r):

5 13. The composition of any one of the previous claims, wherein the Structure A has a molecular weight from 500 g/mole to 5000 g/mole.

10

- 14. The composition of any one of the previous claims, wherein Structure A has a triplet energy from 2.30 eV to 3.20 eV.
- 15. A film comprising at least one Layer A formed from the composition of any one of the previous claims.
- 16. An electroluminescent device comprising at least one component formed from the composition of any one of claims 1-14.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/084915

A. CLASSIFICATION OF SUBJECT MATTER

 $C09K\ 11/06(2006.01)i;\ C07D\ 209/82(2006.01)i;\ H01L\ 51/50(2006.01)i$

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K11; C07D209; H01L51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI,EPODOC,CNTXT,CNKI,REGISTRY(STN),CAPLUS(STN);benzocyclobutene?,BCB,carbazol+,organic light emitting diode?,OLED?,hole transport,biphenyl,arylamine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Е	WO 2015030469 A1 (DUK SAN NEOLUX CO., LTD.) 05 March 2015 (2015-03-05) abstract, description, paragraphs [17]-[21] and [112], compound 1-22	1, 3, 5-6, 11, 13-16
X	US 2012037894 A1 (MITSUBISHI CHEMICAL CORPORATION) 16 February 2012 (2012-02-16) description, paragraphs [0022]-[0027], [0056]-[0063], [0075] and [0097]	1-16
A	US 2012003790 A1 (PLEXTRONICS, INC.) 05 January 2012 (2012-01-05) description, paragraphs [0069]-[0070] and [0130]-[0131]	1-16
A	US 2011198573 A1 (MITSUBISHI CHEMICAL CORPORATION) 18 August 2011 (2011-08-18) description, paragraphs [0017]-[0018] and [0164]-[0166]	1-16
A	US 2011042661 A1 (MITSUBISHI CHEMICAL CORPORATION) 24 February 2011 (2011-02-24) description, paragraphs [0017]-[0027]	1-16

	Further documents are listed in the continuation of Box C.	1	See patent family annex.		
神	Special categories of cited documents:				
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L"			document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is		
"O"			combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family		
Date	Date of the actual completion of the international search		Date of mailing of the international search report		
16 April 2015		22 May 2015			
Name	Name and mailing address of the ISA/CN		Authorized officer		
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN) 6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China			HAN,Tao		
Facsi	Facsimile No. (86-10)62019451		Telephone No. (86-10)61648369		

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/084915

C. DOCUMENTS CONSIDERED TO BE RELEVANT							
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.					
Α	MA Biwu, et al. "New Thermally Cross-Linkable Polymer and Its Application as a Hole-Transporting Layer for Solution Processed Multilayer Organic Light Emitting Diodes" <i>Chem. Mater.</i> , Vol. Vol.19, No. No.19, 25 August 2007 (2007-08-25), 4827-4832	1-16					

INTERNATIONAL SEARCH REPORT Information on patent family members

International application No.

PCT/CN2014/084915

Patent document cited in search report			Publication date (day/month/year)	Pate	ent family member	(s)	Publication date (day/month/year)
WO	2015030469	A1	05 March 2015		None		
US	2012037894	A1	16 February 2012	EP	2333862	A1	15 June 2011
				CN	102349172	Α	08 February 2012
				TW	201041436	A	16 November 2010
				JP	2015005529	Α	08 January 2015
				EP	2333862	A 4	09 May 2012
				WO	2010104184	A 1	16 September 2010
				KR	20110134399	Α	14 December 2011
				EP	2333862	B1	17 September 2014
US	2012003790	A1	05 January 2012	EP	2588526	A2	08 May 2013
			•	CN	102959009	Α	06 March 2013
				US	8535974	B2	17 September 2013
				US	8815639	В2	26 August 2014
				CN	102959008	A	06 March 2013
				US	2012001127	A 1	05 January 2012
				WO	2012003482	A2	05 January 2012
				KR	20130043169	Α	29 April 2013
				KR	20130040229	Α	23 April 2013
				JP	2013536570	Α	19 September 2013
				JP	2013537682	Α	03 October 2013
				WO	2012003482	A3	26 April 2012
				WO	2012003485	A2	05 January 2012
				WO	2012003485	A3	10 May 2012
				EP	2588527	A2	08 May 2013
				US	2013344648	A 1	26 December 2013
US	2011198573	A1	18 August 2011	WO	2010018813	A1	18 February 2010
O.S	2011170373	7	10 744 545 2011	CN	102105511	В	02 January 2013
				CN	102105511	A	22 June 2011
				JP	4935952	B2	23 May 2012
				US	8610112	B2	17 December 2013
				TW	I447143	В	01 August 2014
				EP	2314639	A4	07 August 2013
				JР	2010065213	A	25 March 2010
				EP	2314639	A1	27 April 2011
				KR	20110039444	A	18 April 2011
				JP	2012015539	A	19 January 2012
				TW	201012849	A	01 April 2010
				JP	5491796	В2	14 May 2014
US	2011042661	A1	24 February 2011	US	2014051827	A1	20 February 2014
03	2011042001	AI	24 restuary 2011	KR	101323557	B1	29 October 2013
				TW	200942564	A	16 October 2009
				US	8653508	B2	18 February 2014
				JP	2009287000	A	10 December 2009
				EP	2270069	A1	05 January 2011
				CN	101945925	A	12 January 2011
				JP	5564801	B2	06 August 2014
				EP	2270069	Б2 А4	27 June 2012
				WO	2009102027	A4 A1	27 June 2012 20 August 2009
				KR	20100111718	A	15 October 2010
					ZAZ I UNZI I I Z I ()		1.3 CAUDUL 2010

Form PCT/ISA/210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT Information on patent family members

International application No.

PCT/CN2014/084915

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)