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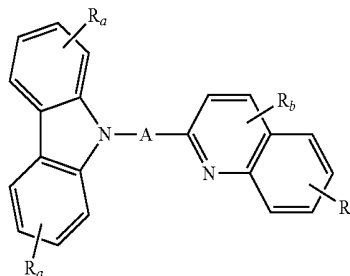
(19) **United States**(12) **Patent Application Publication**
CHEN et al.(10) **Pub. No.: US 2014/0191205 A1**(43) **Pub. Date: Jul. 10, 2014**(54) **BIPOLAR COMPOUND AND ORGANIC
ELECTROLUMINESCENT DEVICE
EMPLOYING THE SAME**(71) Applicant: **Industrial Technology Research
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City (TW)(21) Appl. No.: **13/935,170**(22) Filed: **Jul. 3, 2013**(30) **Foreign Application Priority Data**

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H01L 51/00 (2006.01)(52) **U.S. Cl.**
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USPC **257/40; 546/173; 546/167**(57) **ABSTRACT**

The present disclosure relates to a bipolar compound represented by the following formula (I); and an organic luminescent diode device containing the same.

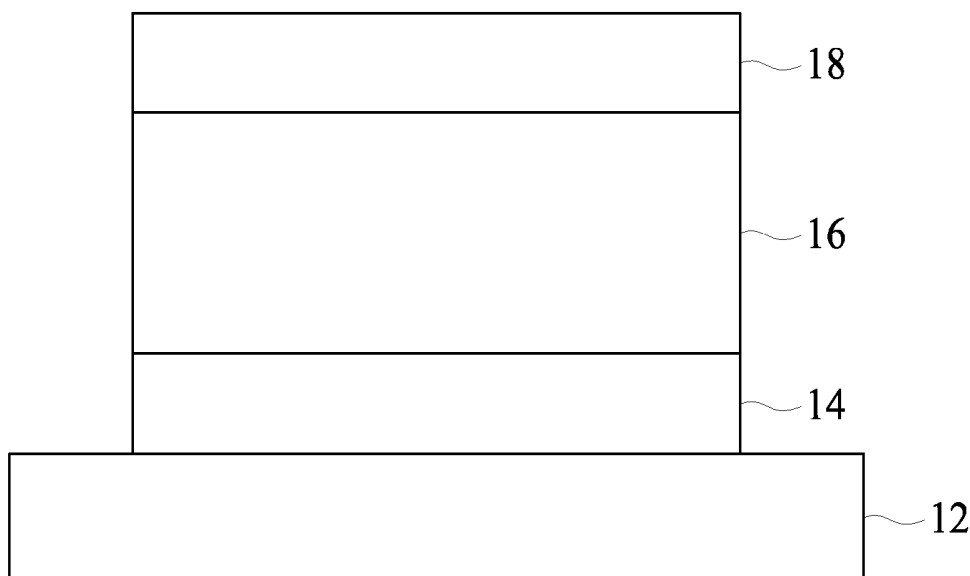
Formula (I)



wherein A represents a phenyl, a biphenyl, or a terphenyl group; and

R_a , R_b , and R_c are independently selected from a group consisting of a hydrogen, a halo, a cyano, a trifluoromethyl, an amino, a C_1 - C_{10} alkyl, a C_2 - C_{10} alkenyl, a C_2 - C_{10} alkynyl, a C_3 - C_{20} cycloalkyl, a C_3 - C_{20} cycloalkenyl, a C_1 - C_{20} heterocyclic alkyl, a C_1 - C_{20} heterocyclic alkenyl, an aryl, and a heteroaryl groups.

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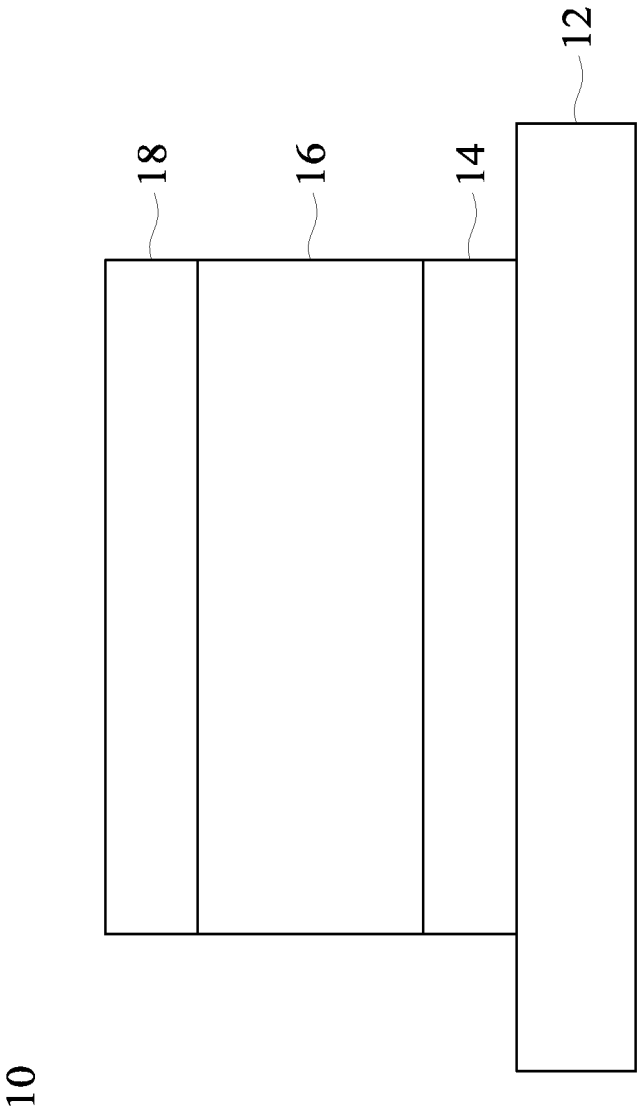


FIG.1

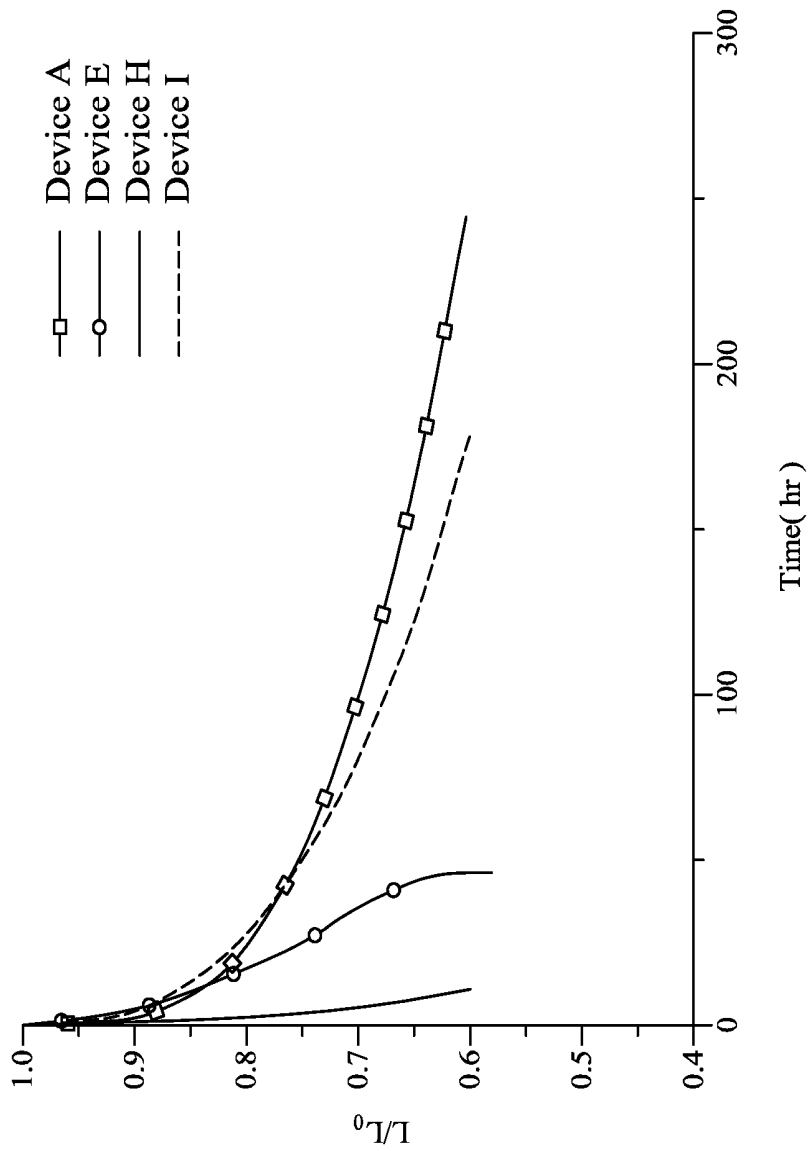


FIG.2

BIPOLAR COMPOUND AND ORGANIC ELECTROLUMINESCENT DEVICE EMPLOYING THE SAME

[0001] This application claims the benefit of Taiwan application Serial No. 102100572, filed Jan. 8, 2013, the disclosure of which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to a bipolar compound and an organic electroluminescent device employing the same.

BACKGROUND

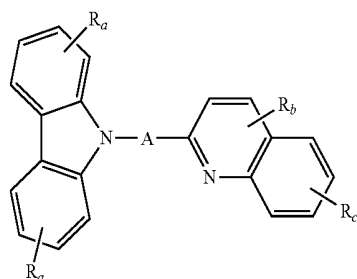
[0003] Organic electroluminescence is a self luminescent phenomenon, such a luminescent phenomenon occurs due to that organic compounds excited by electric energy generated from applying electric field and thus emits light. Recently, the development for organic electroluminescence has increased rapidly and thus the industries in this filed invest their money in production of organic luminescent diode aggressively. The principle for organic luminescent diode is similar to that for inorganic luminescent diode, which generally classifies into two classes, i.e. small molecular organic luminescent diode and macro molecular organic luminescent diode. Among them, the small molecular organic luminescent diode uses small molecular dye or pigment as a host material while macro molecular organic luminescent diode uses conjugate polymer as a host material.

[0004] The critical point to produce excellent organic luminescent diode is the material constituting diode, especial the emission material used in emission layer. A useful emission material should satisfy the following conditions: (1) it possesses fluorescence with high quantum efficiency and its fluorescence spectrum mainly distributes in visible region of from 400~700 nm; (2) it has excellent semi-conductance, high electric conductivity, is capable of transporting electron or hole, or both; (3) it is easily formed into film without occurring pin-hole in the film in several tens thickness; and (4) it possesses thermal stability.

[0005] In production of organic luminescent diode, the emission material is critical, especial host emission material. The host emission material should exhibit properties of quickly capturing carriers, energy transition, high glass transition temperature, high thermal stability, suitable singlet and triplet energy gap. Furthermore, in addition to the luminescent efficiency, another requirement for emission material is its life time. Thus there is still a room for developing host emission material in organic luminescent diode.

SUMMARY

[0006] The present disclosure provides a bipolar compound represented by the following formula (I):

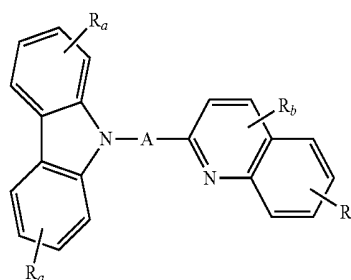


Formula (I)

[0007] wherein A represents a phenyl, biphenyl, or terphenyl group; and

[0008] R_a , R_b , and R_c are independently selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

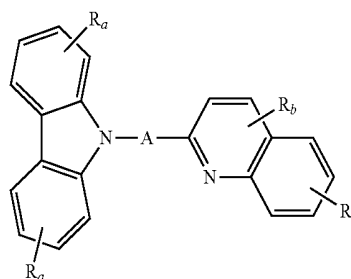
[0009] The present disclosure also provides an organic luminescent diode device comprising a pair of electrodes; and an electroluminescent element disposed between said pair of electrodes; wherein said electroluminescent element containing a compound having the following formula (I):



Formula (I)

[0010] wherein all symbols are defined the same as the above.

[0011] The present disclosure also provides an organic electroluminescent diode device comprising a pair of electrodes; and an electroluminescent element disposed between said pair of electrodes; wherein said electroluminescent element comprises an emission layer and said emission layer comprises a dopant material and a compound having the following formula (I) as a host material:



Formula (I)

[0012] wherein all symbols are defined the same as the above.

BRIEF DESCRIPTION OF DRAWINGS

[0013] The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings

[0014] FIG. 1 is a schematic diagram showing an organic luminescent diode device containing the present compound.

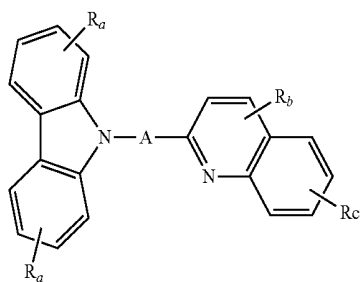
[0015] FIG. 2 is a graph showing the luminescent efficiency of devices A, E, H, I with time.

DETAILED DESCRIPTION

[0016] In the following detailed description, for purposes of explanation, numerous specific details are set forth in order

to provide a thorough understanding of the disclosed embodiments. It will be apparent, however, that one or more embodiments may be practiced without these specific details. In other instances, well-known structures and devices are schematically shown in order to simplify the drawing.

[0017] The present disclosure provides a bipolar compound represented by the following formula (I):



Formula (I)

[0018] wherein A represents phenyl, biphenyl, or terphenyl group; and R_a , R_b , and R_c are independently selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

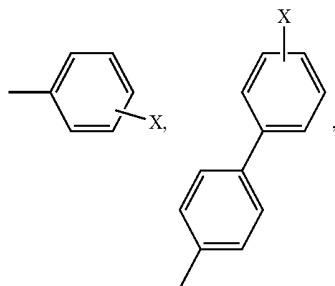
[0019] In one embodiment, the A is further substituted by at least one substituent selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl groups.

[0020] In one embodiment, the aryl is a phenyl group or a substituted phenyl group. The term "substituted phenyl group" means phenyl group which is substituted by substituent(s), such as halogen, alkyl, alkylphenyl, or heteroaryl group, and the like, but the substituents are not limited in the list.

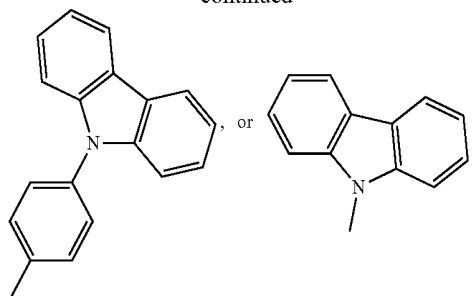
[0021] In one embodiment, the heteroaryl may be, but not limited to, carbazolyl group.

[0022] In one embodiment, the R_a and R_c are different by each other.

[0023] In one embodiment, the R_a and R_c are independently selected from the following groups:

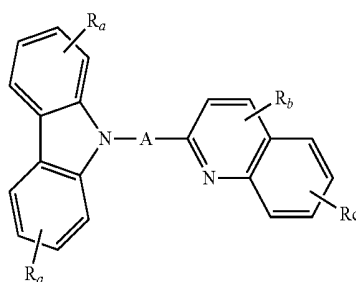


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[0024] wherein X represents hydrogen, halo, cyano, trifluoromethyl, amino, or C_1 - C_{10} alkyl group, but are not limited in the list.

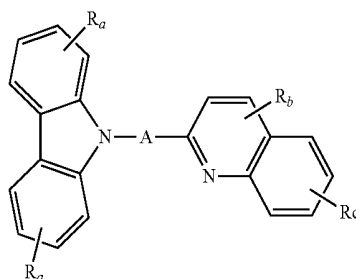
[0025] The present disclosure also provides an organic luminescent diode device comprising a pair of electrodes; and an organic luminescent unit positioned between said pair of electrodes; wherein said organic luminescent unit containing a compound having the following formula (I):



Formula (I)

[0026] wherein all symbols are defined the same as the above.

[0027] The present disclosure also provides an organic electroluminescent diode device comprising a pair of electrodes; and an organic luminescent unit positioned between said pair of electrodes; wherein said organic luminescent unit comprising a luminescent layer containing a dopant material and a compound having the following formula (I) as a host material:



Formula (I)

[0028] wherein all symbols are defined the same as the above.

[0029] In one embodiment, the dopant material in the luminescent layer may comprise a green emitting dopant material in an amount of from 0 to 10 wt. %. In the embodiment, the

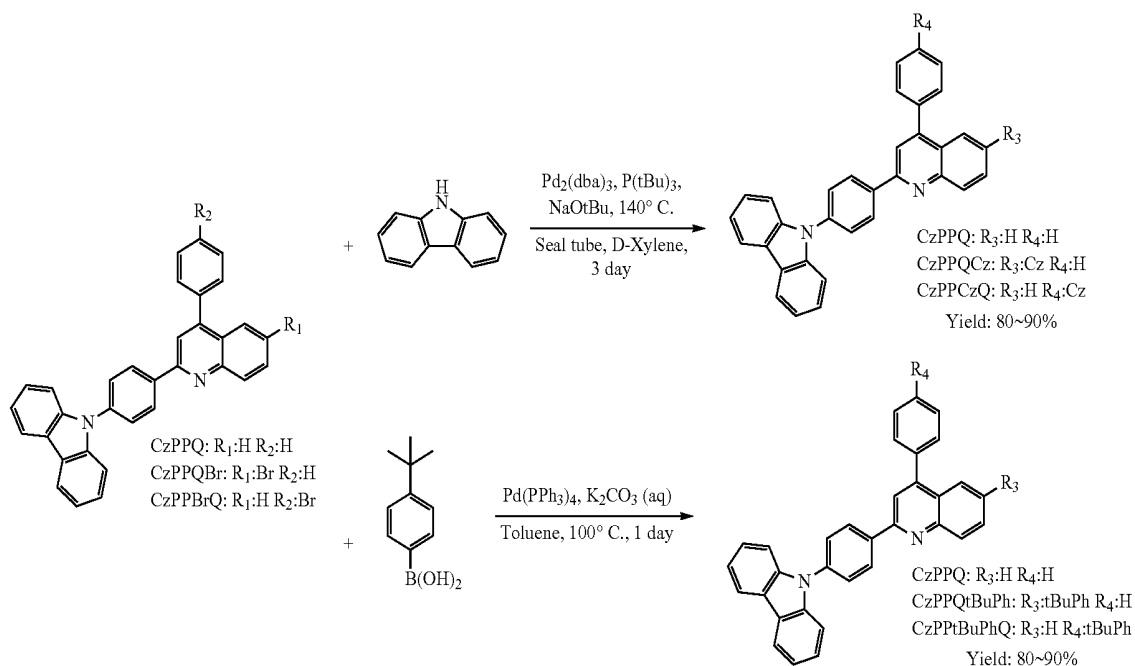
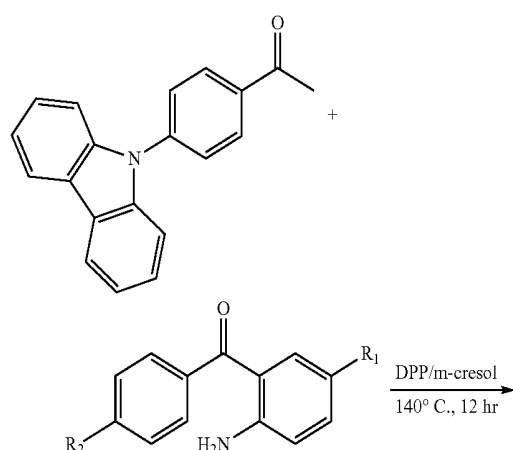
green emitting dopant material may be, but not limited to, tris(2-phenylpyridine)iridium (Ir(ppy)_3).

[0030] In one embodiment, the dopant material in the luminescent layer may comprise an orange emitting dopant material in an amount of from 0 to 10 wt. %. In the embodiment, the orange emitting dopant material may be, but not limited to, tris(2-phenylquinoline)iridium (Ir(pq)_3).

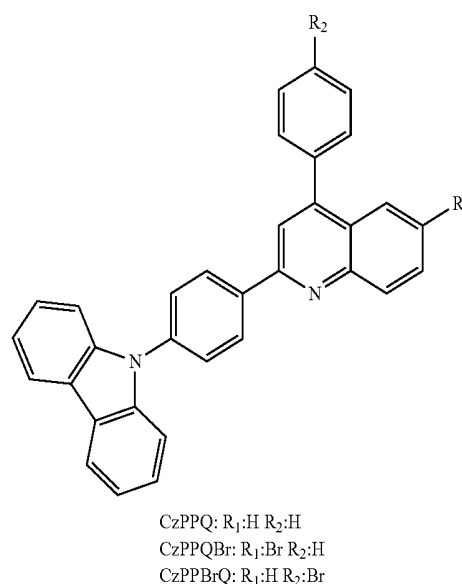
[0031] In one embodiment, the dopant material in the luminescent layer may comprise a red emitting dopant material in an amount of from 0 to 10 wt. %. In the embodiment, the red emitting dopant material may be, but not limited to, tris(2-phenyl-isoquinoline)iridium (Ir(piq)_3).

A. Synthesis of the Present Compound

[0032] The compound having a quinolyl and carbazolyl groups of the present disclosure is synthesized, e.g. through the following scheme.



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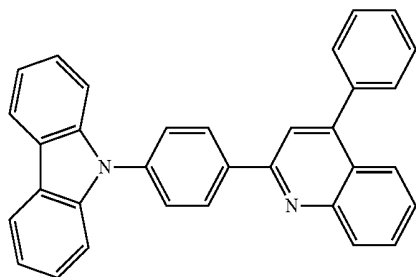


[0033] CzPPQ derivatives are produced by reacting 1-(4-(9H-carbazol-9-yl)phenyl)-ethanone and 2-aminobenzophenone in the presence of diphenyl phosphate and m-cresol at a temperature of 140°C . The other compounds having a quinolyl and a carbazolyl groups are produced by using appropriate starting materials.

Preparation Example 1

Preparation of 9-(4-(4-phenylquinolin-2-yl)phenyl)-9H-carbazole (CzPPQ)

[0034]



CzPPQ

[0035] 1-(4-(9H-carbazol-9-yl)phenyl)-ethanone (285 mg, 1.00 mmol), 2-aminobenzo-phenone (400 mg, 2.00 mmol), diphenyl phosphate (DPP) (751 mg, 3.00 mmol), and as-distilled m-cresol (1.0 mL) were added into a round-bottom flask and reacted under nitrogen atmosphere with heating to a temperature 140° C. for 12 hours. When the reaction completed, the resultant mixture was added with 10 wt. % triethylamine/methanol and then the precipitate was filtered out and purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 381 mg of 9-(4-(4-phenylquinolin-2-yl)phenyl)-9H-carbazole, yield=85.4%.

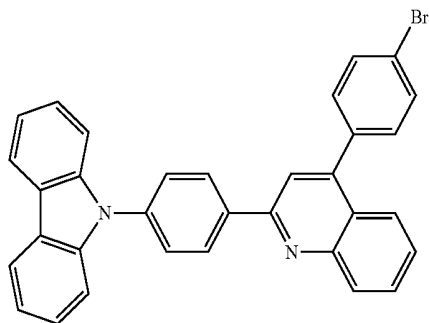
[0036] The NMR data of the product was as follows.

[0037] ¹H NMR (400 MHz, CDCl₃, δ): 7.31 (dd, 2H, J=7.6, 7.2 Hz), 7.44 (dd, 2H, J=8.0, 7.6 Hz), 7.50-7.62 (m, 8H), 7.73-7.80 (m, 3H), 7.91 (s, 1H), 7.95 (d, 1H, J=8.4 Hz), 8.16 (d, 2H, J=7.6 Hz), 8.30 (d, 1H, J=8.4 Hz), 8.43 (d, 2H, J=8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 109.8, 119.1, 120.1, 120.3, 123.5, 125.7, 125.8, 126.0, 126.5, 127.2, 128.5, 128.6, 129.0, 129.5, 129.7, 130.1, 138.2, 138.5, 138.7, 140.6, 148.8, 149.4, 155.9; HRMS (EI, m/z): [M⁺] calcd for C₃₃H₂₂N₂, 446.1783. found, 446.1779. Anal. calcd. for C₃₃H₂₂N₂: C, 88.76; H, 4.97; N, 6.27. found: C, 88.49; H, 4.87; N, 6.35.

Preparation Example 2

Preparation of 9-(4-(4-(4-bromophenyl)quinolin-2-yl)phenyl)-9H-carbazole (CzPPBrQ)

[0038]



CzPPBrQ

[0039] 1-(4-(9H-carbazol-9-yl)phenyl)ethanone (285 mg, 1.00 mmol), (2-aminophenyl) (4-bromophenyl)-methanone (553 mg, 2.00 mmol), diphenyl phosphate (DPP) (751 mg, 3.00 mmol), and as-distilled m-cresol (1.0 mL) were added into a round-bottom flask and reacted under nitrogen atmo-

sphere with heating to a temperature 140° C. for 12 hours. When the reaction completed, the resultant mixture was added with 10 wt. % triethylamine/methanol and then the precipitate was filtered out and purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 426 mg of 9-(4-(4-(4-bromo-phenyl)quinolin-2-yl)phenyl)-9H-carbazole, yield=81.2%.

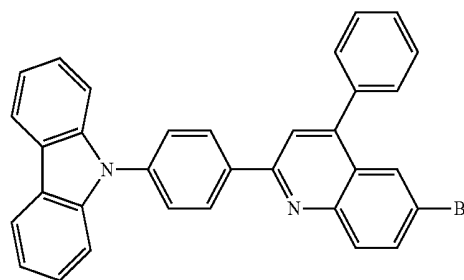
[0040] The NMR data of the product was as follows.

[0041] ¹H NMR (400 MHz, CDCl₃, δ): 7.30 (dd, 2H, J=7.2, 7.2 Hz), 7.40-7.52 (m, 7H), 7.69-7.80 (m, 7H), 7.86-7.88 (m, 2H), 8.14 (d, 2H, J=7.2 Hz), 8.27 (d, 1H, J=8.8 Hz), 8.41 (d, 2H, J=8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 109.8, 119.0, 120.1, 120.4, 122.9, 123.6, 125.3, 125.5, 126.0, 126.8, 127.3, 129.1, 129.9, 130.3, 131.2, 131.9, 137.2, 138.4, 138.9, 140.7, 148.2, 148.9, 156.0; HRMS (EI, m/z): [M⁺] calcd for C₃₃H₂₁BrN₂, 524.0888. found, 524.0893.

Preparation Example 3

Preparation of 9-(4-(6-bromo-4-phenylquinolin-2-yl)-phenyl)-9H-carbazole (CzPPQBr)

[0042]



CzPPQBr

[0043] 1-(4-(9H-carbazol-9-yl)phenyl)ethanone (285 mg, 1.00 mmol), (2-amino-5-bromo-phenyl)(phenyl)methanone (553 mg, 2.00 mmol), diphenyl phosphate (DPP) (751 mg, 3.00 mmol), and as-distilled m-cresol (1.0 mL) were added into a round-bottom flask and reacted under nitrogen atmosphere with heating to a temperature 140° C. for 12 hours. When the reaction completed, the resultant mixture was added with 10 wt. % triethylamine/methanol and then the precipitate was filtered out and purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 437 mg of 9-(4-(6-bromo-4-phenylquinolin-2-yl)phenyl)-9H-carbazole, yield=83.2%.

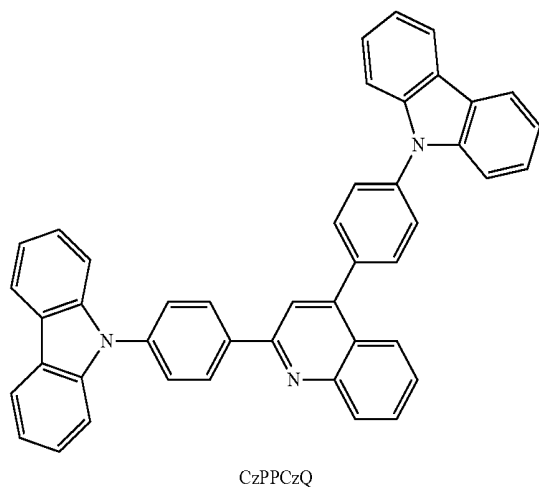
[0044] The NMR data of the product was as follows.

[0045] ¹H NMR (400 MHz, CDCl₃, δ): 7.30 (ddd, 2H, J=8.0, 7.6, 1.0 Hz), 7.42 (ddd, 2H, J=8.0, 6.8, 1.2 Hz), 7.48-7.50 (m, 2H), 7.55-7.60 (m, 5H), 7.73 (d, 2H, J=8.4 Hz), 7.82 (dd, 1H, J=9.0, 6.2 Hz), 7.91 (s, 1H), 8.07 (d, 1H, J=3.0 Hz), 8.13-8.16 (m, 3H), 8.41 (d, 2H, J=8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 109.7, 109.8, 119.9, 120.2, 120.4, 120.7, 123.6, 126.4, 127.1, 127.3, 127.9, 128.8, 128.9, 129.1, 129.4, 131.8, 133.3, 137.6, 138.0, 139.1, 140.6, 148.8, 156.2; HRMS (EI, m/z): [M⁺] calcd for C₃₃H₂₁BrN₂, 524.0888. found, 524.0897.

Preparation Example 4

Preparation of (9,9'-(quinolin-2,4-diyl)-bis-(4,1-phenylene))-bis(9H-carbazole) (CzPPCzQ)

[0046]



[0047] 9-(4-(4-(4-Bromo-phenyl)quinolin-2-yl)phenyl)-9H-carbazole (525 mg, 1.00 mmol), carbazole (200 mg, 1.2 mmol), Pd(dba)₂ (33 mg, 0.060 mmol), tri-tert-butylphosphine (96 mg, 0.048 mmol), sodium tert-butoxide (432 mg, 4.50 mmol) and solvent o-xylene (3.00 mL) were added into a high pressure tube, and reacted and heated at a temperature of 150° C. for 48 hours. When the reaction completed, the resultant mixture was filtered through Celite to remove metal salts and washed with methylene chloride several times. The filtrates were collected and concentrated. The resultant product was purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 528 mg of (9,9'-(quinolin-2,4-diyl)-bis-(4,1-phenylene))-bis(9H-carbazole), yield=86.3%.

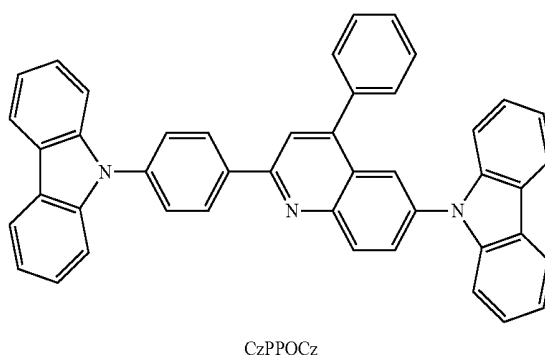
[0048] The NMR data of the product was as follows.

[0049] ¹H NMR (400 MHz, CDCl₃, δ): 7.28-7.33 (m, 4H), 7.39-7.46 (m, 7H), 7.51 (dd, 4H, J=8.0, 8.0 Hz), 7.61 (d, 2H, J=7.2 Hz), 7.78 (d, 2H, J=8.4 Hz), 7.96 (d, 1H, J=8.8 Hz), 8.00 (s, 1H), 8.11-8.18 (m, 5H), 8.47-8.51 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 109.5, 109.8, 120.0, 120.2, 120.3, 120.3, 120.4, 123.1, 123.5, 123.6, 126.0, 126.1, 126.6, 127.2, 128.9, 129.2, 129.3, 131.7, 135.8, 137.5, 139.2, 140.6, 140.7, 156.2; HRMS (EI, m/z): [M⁺] calcd for C₄₅H₂₉N₃, 611.2361. found, 611.2365. Anal. calcd. for C₄₅H₂₉N₃: C, 88.35; H, 4.78; N, 6.87. found: C, 88.15; H, 4.74; N, 7.02.

Preparation Example 5

Preparation of 9-(4-(6-(9H-carbazol-9-yl)-4-phenylquinolin-2-yl)phenyl)-9H-carbazole (CzPPQCz)

[0050]



[0051] 9-(4-(6-Bromo-4-phenylquinolin-2-yl)phenyl)-9H-carbazole (525 mg, 1.00 mmol), carbazole (200 mg, 1.2 mmol), Pd(dba)₂ (33 mg, 0.060 mmol), tri-tert-butylphosphine (96 mg, 0.048 mmol), sodium tert-butoxide (432 mg, 4.50 mmol) and solvent o-xylene (3.00 mL) were added into a high pressure tube, and reacted and heated at a temperature of 150° C. for 48 hours. When the reaction completed, the resultant mixture was filtered through Celite to remove metal salts and washed with methylene chloride several times. The filtrates were collected and concentrated. The resultant product was purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 524 mg of 9-(4-(6-(9H-carbazol-9-yl)-4-phenylquinolin-2-yl)phenyl)-9H-carbazole, yield=85.7%.

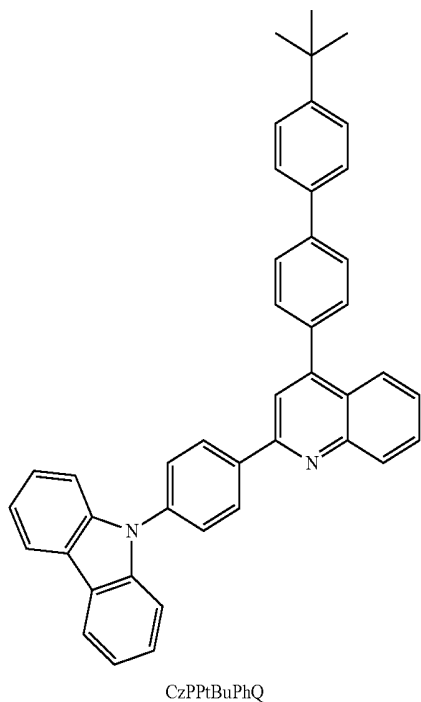
[0052] The NMR data of the product was as follows.

[0053] ¹H NMR (400 MHz, CDCl₃, δ): 7.30-7.37 (m, 4H), 7.43-7.54 (m, 6H), 7.58-7.64 (m, 3H), 7.76-7.87 (m, 7H), 8.03 (s, 1H), 8.10 (d, 1H, J=8.4 Hz), 8.16-8.21 (m, 4H), 8.35 (d, 2H, J=8.8 Hz), 8.48 (d, 2H, J=8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 109.7, 109.8, 119.3, 120.1, 120.3, 120.4, 120.5, 123.5, 123.6, 125.5, 125.7, 126.0, 126.1, 126.8, 127.1, 127.3, 129.1, 139.9, 130.0, 131.1, 137.2, 138.1, 138.5, 138.9, 14.07, 148.5, 149.0, 156.0; HRMS (EI, m/z): [M⁺] calcd for C₄₅H₂₉N₃, 611.2361. found, 611.2367. Anal. calcd. for C₄₅H₂₉N₃: C, 88.35; H, 4.78; N, 6.87. found: C, 88.25; H, 4.96; N, 6.54.

Preparation Example 6

Preparation of 9-(4-(4-(4-(tert-butyl)-[1,1'-biphenyl]-4-yl)-quinolin-2-yl)phenyl)-9H-carbazol (Cz-PPtBuPhQ)

[0054]



[0055] 1-(4-(9H-carbazol-9-yl)phenyl)ethanone (285 mg, 1.00 mmol), 4-tert-butylphenyl-boronic (0.36 g, 2.00 mmol) and potassium carbonate (3.32 g, 24.00 mmol) were added into a single-neck flask. Into the flask was added with water (12 ml) and toluene (36 ml) and heated to a temperature of 60° C. to allow the solid dissolve completely. Then the flask was purged with nitrogen several times and quickly added with Pd(PPh₃)₄ (0.06 g, 0.05 mmol), purged with nitrogen several times again and the content in the flask was reacted at a temperature of 100° C. for 24 hours. When the reaction completed, the resultant mixture was extracted with ethyl acetate and water. The organic layer was dried with magnesium sulfate and then added with silica gel along with concentration. Finally, the resultant product was purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 501 mg of 9-(4-(4-(4-(tert-butyl)-[1,1'-biphenyl]-4-yl)-quinolin-2-yl)phenyl)-9H-carbazol, yield=86.7%.

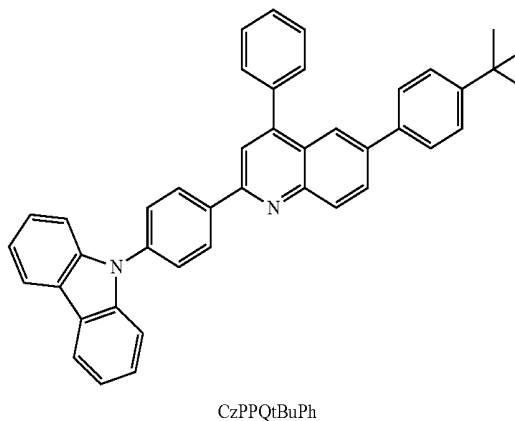
[0056] The NMR data of the product was as follows.

[0057] ¹H NMR (400 MHz, CDCl₃, δ): 1.40 (s, 9H), 7.30 (dd, 2H, J=7.2, 7.6 Hz), 7.41-7.44 (m, 2H), 7.49-7.56 (m, 5H), 7.64-7.68 (m, 3H), 7.73-7.80 (m, 5H), 7.95 (s, 1H), 8.03 (d, 1H, J=8.4 Hz), 8.15 (d, 1H, J=7.6 Hz), 8.29 (d, 1H, J=8.4 Hz), 8.43 (d, 1H, J=8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 31.4, 34.6, 109.8, 119.2, 120.1, 120.3, 123.5, 125.8, 125.9, 126.0, 126.1, 126.6, 126.8, 127.2, 127.3, 129.1, 129.8, 130.0, 130.2, 136.9, 137.5, 138.7, 138.8, 140.7, 141.3, 148.9, 149.2, 150.8, 156.0; HRMS (EI, m/z): [M⁺] calcd for C₃₃H₂₁BrN₂, 578.2722. found, 578.2714.

Preparation Example 7

Preparation of 9-(4-(6-(4-(tert-butyl)phenyl)-4-phenyl-quinolin-2-yl)phenyl)-9H-carbazol (CzPPQt-BuPh)

[0058]



[0059] 1-(4-(9H-carbazol-9-yl)phenyl)ethanone (285 mg, 1.00 mmol), 4-tert-butylphenyl-boronic (0.36 g, 2.00 mmol) and potassium carbonate (3.32 g, 24.00 mmol) were added into a single-neck flask. Into the flask was added with water (12 ml) and toluene (36 ml) and heated to a temperature of 60° C. to allow the solid dissolve completely. Then the flask was purged with nitrogen several times and quickly added with Pd(PPh₃)₄ (0.06 g, 0.05 mmol), purged with nitrogen several times again and the content in the flask was reacted at a temperature of 100° C. for 24 hours. When the reaction completed, the resultant mixture was extracted with ethyl acetate and water. The organic layer was dried with magnesium sulfate and then added with silica gel along with concentration. Finally, the resultant product was purified by column chromatography using hexane/ethyl acetate in volume ratio of 10:1 to obtain 501 mg of 9-(4-(6-(4-(tert-butyl)phenyl)-4-phenyl-quinolin-2-yl)phenyl)-9H-carbazol, yield=86.7%.

[0060] The NMR data of the product was as follows.

[0061] ¹H NMR (400 MHz, CDCl₃, δ): 1.35 (s, 9H), 7.30 (dd, 2H, J=7.6, 7.2 Hz), 7.40-7.65 (m, 13H), 7.43 (d, 2H, J=7.6), 7.91 (s, 1H), 8.02 (d, 1H, J=8.8 Hz), 8.11 (s, 1H), 8.15 (d, 2H, J=7.6 Hz), 8.31 (d, 2H, J=8.4 Hz), 8.43 (d, 1H, J=7.6 Hz); ¹³C NMR (100 MHz, CDCl₃, δ): 31.3, 34.6, 109.9, 119.6, 120.1, 120.3, 123.2, 123.5, 125.8, 126.0, 126.1, 127.1, 127.3, 128.6, 128.7, 128.9, 129.4, 129.6, 130.5, 137.7, 138.4, 138.7, 139.2, 140.7, 148.2, 149.6, 150.8, 155.7; HRMS (EI, m/z): [M⁺] calcd for C₃₃H₂₁BrN₂, 578.2722. found, 578.2730.

B. Energy Level and Thermal Stability of the Compounds Having Quinolyl and Carbazolyl Groups

[0062] The comparison of energy level and thermal stability of the compounds produced from Preparation Examples 1 to 7 with commonly used host material 4,4'-N,N-dicarbazole-biphenyl (CBP) was shown in Table 1. From Table 1, it is shown that CzPPCzQ and CzPPQCz exhibited better glass transition temperature and decomposition temperature.

TABLE 1

Energy level and thermal stability of the compounds having quinolyl and carbazolyl groups						
Compound	T _g (° C.)	T _d (° C.)	HOMO (eV)	LUMO (eV)	E _g (eV)	E _T (eV)
CzPPQ	89	345	5.77	2.45	3.32	2.50
CzPPCzQ	145	419	5.79	2.50	3.29	2.77
CzPPQCz	146	421	5.83	2.71	3.12	2.38
CzPPtBuPhQ	N/A	N/A	5.83	2.58	3.25	2.39
CzPPQtBuPh	N/A	N/A	5.79	2.60	3.19	2.39
CBP	62	373	5.91	2.51	3.40	2.56

Note:

T_g = glass transition temperature, T_d = decomposition temperature, N/A = non available

C. Structure of Organic Luminescent Diode Device

[0063] FIG. 1 is a schematic drawing showing an organic luminescent diode device containing the present compound according to an embodiment of the present disclosure. The organic luminescent diode device **10** comprises a substrate **12**, a bottom electrode **14**, an electroluminescent element **16**, and a top electrode **18**. The electroluminescent element **16** further comprises an emission layer containing the bipolar compound having quinolyl and carbazolyl groups of the present disclosure. The bipolar compound having quinolyl and carbazolyl groups could function as either a host emission material or a dopant. In the case, the bipolar compound serves as a host emission material in the host emission layer.

[0064] Moreover, the organic luminescent diode device **10** may optionally comprises a hole barrier layer, an exciton

barrier layer, an electron barrier layer, and an electron injecting layer. Such layers are easily determined by those skilled in the art depending on the desired design.

[0065] Using the bipolar compound having quinolyl and carbazolyl groups in green, orange, and red organic luminescent diode and their luminescent effect are described as follows.

Test Example 1

Green Organic Luminescent Diode

[0066] The tested green organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0067] NPB(20)/TCTA(10)/7% Ir(ppy)₃:CzPPQanalogue (30)/BCP(10)/Alq(40)/LiF(1)

[0068] In the doped green organic luminescent diode, the substrate was made from ITO (indium tin oxide), the electrode to be tested was LiF/Al, the hole transport layer contained TCTA (4,4,4-tri(N-carbazolyl)triphenylamine) and NPB (N,N'-Bis-(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine); and the electron transport layer contained BAlq (Bis (2-methyl-8-quinolinolato-N1,O8)-(1,1'-Biphenyl-4-olato)-aluminum). In this Test Example, the bipolar compound having quinolyl and carbazolyl groups of the present disclosure was used as host material in the emission layer, and CBP (4,4'-Bis(9H-carbazol-9-yl)biphenyl) was used as a control. Dopant was added into various emission materials in the emission layer. In the green organic luminescent diode, the dopant was 7% Ir(ppy)₃ (tris(2-phenylpyridine)iridium (III)) and their luminescent efficiency are presented in Table 2.

TABLE 2

Luminescent efficiency of the present compound in green organic luminescent diode								
Device	V _d [V]	η _{ext} [%]	L [cd/m ² , V]	η _c [cd/A, V]	η _p [lm/W, V]	λ _{em} [nm]	CIE, 8 V (x, y)	
CzPPQ	2.7	13.1, 4.0	100914, 15.0	50.0, 4.0	51.0, 3.0	516	(0.28, 0.65)	
CzPPCzQ	3.0	16.0, 4.5	104983, 17.5	61.9, 4.5	51.5, 3.5	516	(0.28, 0.65)	
CzPPQCz	2.9	1.6, 3.0	14923, 15.0	6.0, 3.0	6.3, 3.0	518	(0.30, 0.63)	
CzPPtBuPhQ	2.2	15.0, 2.5	77416, 16.0	58.5, 2.5	73.6, 2.5	514	(0.29, 0.64)	
CzPPQtBuPh	3.2	0.24, 3.5	3055, 16.5	0.9, 3.5	0.9, 3.5	522	(0.31, 0.61)	
CBP	2.7	13.1, 4.0	100914, 15.0	50.0, 4.0	51.0, 3.0	516	(0.28, 0.65)	

Note:

V_d: driving voltage; η_{ext}: external quantum efficiency; L: maximal lightness; η_c: current efficiency; η_p: energy efficiency; λ_{em}: emission wavelength

Test Example 2

Orange Organic Luminescent Diode

[0069] The tested orange organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0070] NPB(20)/TCTA(10)/4% Ir(pq)₃:CzPPQ analogue (30)/BCP(15)/Alq(50)/LiF(1)

[0071] The configuration and material used in each layers in the doped orange organic luminescent diode were similar to those in the Test Example 1 except that the dopant was 4% Ir(pq)₃ (tris(2-phenylquinoline)iridium (III)) and their luminescent efficiency are presented in Table 3.

TABLE 3

Luminescent efficiency of the present compound in orange organic luminescent diode							
Device	V_d [V]	η_{ext} [% V]	L [cd/m ² , V]	η_c [cd/A, V]	η_p [lm/W, V]	λ_{em} [nm]	CIE, 8 V (x, y)
CzPPQ	3.0	25.6, 3.5	129885, 14.5	75.8, 3.5	68.1, 3.5	580	(0.55, 0.45)
CzPPCzQ	3.0	21.6, 3.5	144746, 16.5	59.4, 3.5	53.4, 3.5	586	(0.56, 0.44)
CzPPQCz	2.7	17.2, 4.0	120274, 17.0	51.2, 4.0	50.1, 3.0	582	(0.55, 0.45)
CzPPtBuPhQ	2.5	17.3, 3.0	84045, 15.0	47.4, 3.5	49.7, 3.5	584	(0.56, 0.44)
CzPPQtBuPh	2.6	15.1, 3.0	69878, 16.5	42.3, 3.0	44.3, 3.0	584	(0.56, 0.44)
GH-PhCz	2.8	25.8, 3.0	118075, 17.0	68.4, 3.0	71.7, 3.0	588	(0.57, 0.43)

Note:

V_d : driving voltage; η_{ext} : external quantum efficiency; L: maximal lightness; η_c : current efficiency; η_p : energy efficiency; λ_{em} : emission wavelength

Test Example 3

Red Organic Luminescent Diode

[0072] The tested red organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0073] NPB(20)/TCTA(10)/7% Ir(piq)₃:CzPPQ analogue(30)/BCP(15)/Alq(50)/LiF(1)

[0074] The configuration and material used in each layers in the doped red organic luminescent diode were similar to those in the Test Example 1 except that the dopant was 7% Ir(piq)₃ (tris(2-phenyl-isoquinoline)iridium(III)) and their luminescent efficiency are presented in Table 4.

TABLE 4

Luminescent efficiency of the present compound in red organic luminescent diode							
Device	V_d [V]	η_{ext} [% V]	L [cd/m ² , V]	η_c [cd/A, V]	η_p [lm/W, V]	λ_{em} [nm]	CIE, 8 V (x, y)
CzPPQ	2.9	19.3, 4.0	61485, 14.5	24.8, 4.0	24.4, 3.0	620	(0.67, 0.33)
CzPPCzQ	3.0	21.5, 4.5	68384, 16.5	27.5, 4.5	24.1, 3.5	620	(0.67, 0.33)
CzPPQCz	2.2	17.5, 2.5	48967, 14.5	24.8, 2.5	31.3, 2.5	618	(0.66, 0.34)
CzPPtBuPhQ	2.6	15.0, 3.0	38130, 14.5	20.3, 3.0	21.3, 3.0	618	(0.66, 0.34)
CzPPQtBuPh	2.9	19.3, 4.0	61485, 14.5	24.8, 4.0	24.4, 3.0	620	(0.67, 0.33)
CBP	3.1	18.2, 5.0	56041, 15.0	24.6, 5.0	21.5, 3.5	620	(0.66, 0.34)

Note:

V_d : driving voltage; η_{ext} : external quantum efficiency; L: maximal lightness; η_c : current efficiency; η_p : energy efficiency; λ_{em} : emission wavelength

Test Example 4

Green Organic Luminescent Diode Adding with Hole Injection Material NPNPB

[0075] The tested green organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0076] NPNPB(60)/NPB(10)/TCTA(10)/7% Ir(ppy)₃:Cz-PPQ analogue(30)/BAIq(30)/LiF(1)

[0077] The configuration and material used in each layers in the doped green organic luminescent diode were similar to those in the Test Example 1 except that it further included hole injection material NPNPB and their luminescent efficiency are presented in Tables 5-1 and 5-2.

TABLE 5-1

Luminescent efficiency of the present compound in green organic luminescent diode							
Device	L, 10 V [cd/m ²]	η_{ext} [% 10 V]	η_c , 10 V [cd/A]	λ_{em} , 8 V [nm]	FWHM [nm]	CIE, 8 V (x, y)	T75 @ 500 nits (h)
CzPPQ	13614	6.70	25.05	514	54	(0.25, 0.66)	46
CzPPCzQ	8297	11.56	44.73	516	60	(0.27, 0.65)	1035
CzPPQCz	82	1.37	5.21	522	72	(0.32, 0.61)	4
CzPPtBuPhQ	36890	3.87	14.58	514	56	(0.26, 0.66)	214

TABLE 5-1-continued

Luminescent efficiency of the present compound in green organic luminescent diode							
Device	L, 10 V [cd/m ²]	η_{ext} [%], 10 V]	η_c , 10 V [cd/A]	λ_{em} , 8 V [nm]	FWHM [nm]	CIE, 8 V (x, y)	T75 @ 500 nits (h)
CzPPQtBuPh	929	0.14	0.54	516	62	(0.29, 0.63)	6
CBP	7819	13.9	50.4	510	54	(0.24, 0.62)	2331

Note:

FWHM: full width at half maximum; T₇₅ @ 500 nits (h): time required when the brightness is reduced 25% relative to initial brightness at 500 nit

TABLE 5-2

Luminescent efficiency of the present compound in green organic luminescent diode					
Device	V, 500 nits	Current Density [mA/cm ² , 500 nits]	η_{ext} [%, 500 nits]	η_c [cd/A, 500 nits]	η_p [lm/W, 500 nits]
CzPPQ	5.7	1.451	9.27	34.64	19.17
CzPPCzQ	6.2	0.820	15.79	61.09	31.23
CzPPQCz	12.1	10.922	1.21	4.58	1.19
CzPPtBuPhQ	3.7	1.273	10.64	40.07	34.31
CzPPQtBuPh	7.8	84.53	0.16	0.59	0.23
CBP	6.9	1.213	11.35	41.08	18.53

Note:

 η_{ext} : external quantum efficiency; η_c : current efficiency; η_p : energy efficiency

TABLE 6-2

Luminescent efficiency of the present compound in orange organic luminescent diode					
Device	V, 500 nits	Current Density [mA/cm ² , 500 nits]	η_{ext} [%, 500 nits]	η_c [cd/A, 500 nits]	η_p [lm/W, 500 nits]
CzPPQ	6.5	2.050	8.05	24.31	11.81
CzPPCzQ	6.9	1.026	16.24	48.53	22.16
CzPPQCz	6.2	2.467	6.72	20.04	10.13
CzPPtBuPhQ	6.2	4.078	4.03	12.15	6.23
CzPPQtBuPh	6.5	8.069	2.082	6.17	2.97
CBP	6.7	1.156	14.14	43.14	20.32

Note:

 η_{ext} : external quantum efficiency; η_c : current efficiency; η_p : energy efficiency

Test Example 5

Orange Organic Luminescent Diode Adding with Hole Injection Material NPNPB

[0078] The tested orange organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0079] NPNPB(60)/NPB(10)/TCTA(10)/4% Ir(pq)₃:Cz-PPQ analogue(30)/BAIq(30)/LiF(1)

[0080] The configuration and material used in each layers in the doped orange organic luminescent diode were similar to those in the Test Example 2 except that it further included hole injection material NPNPB and their luminescent efficiency are presented in Tables 6-1 and 6-2.

TABLE 6-1

Luminescent efficiency of the present compound in orange organic luminescent diode							
Device	L, 10 V [cd/m ²]	η_{ext} [%], 10 V]	η_c , 10 V [cd/A]	λ_{em} , 8 V [nm]	FWHM [nm]	CIE, 8 V (x, y)	T75 @ 500 nits (h)
CzPPQ	5379	13.18	39.78	580	64	(0.54, 0.46)	6095
CzPPCzQ	4517	17.58	52.53	582	66	(0.55, 0.45)	6106
CzPPQCz	8463	8.30	24.78	582	66	(0.54, 0.45)	289
CzPPtBuPhQ	5293	8.91	26.86	580	64	(0.54, 0.46)	5861
CzPPQtBuPh	6403	6.28	18.63	580	64	(0.55, 0.45)	635
CBP	7082	12.2	37.1	580	62	(0.54, 0.46)	2415

Note:

FWHM: full width at half maximum; T₇₅ @ 500 nits (h): time required when the brightness is reduced 25% relative to initial brightness at 500 nit

Test Example 6

Red Organic Luminescent Diode Adding with Hole Injection Material NPNPB

[0081] The tested red organic luminescent diode has the following structure in which the number in the parentheses means the thickness in nm.

[0082] NPNPB(60)/NPB(10)/TCTA(10)/4% Ir(piq)₃:Cz-PPQ analogue(30)/BAIq(30)/LiF(1)

[0083] The configuration and material used in each layers in the doped red organic luminescent diode were similar to those in the Test Example 3 except that it further included hole injection material NPNPB and their luminescent efficiency are presented in Tables 7-1 and 7-2.

TABLE 7-1

Luminescent efficiency of the present compound in red organic luminescent diode							
Device	L, 10 V [cd/m ²]	η_{ext} [%], 10 V]	η_c , 10 V [cd/A]	λ_{em} , 8 V [nm]	FWHM [nm]	CIE, 8 V (x, y)	T ₇₅ @ 500 nits (h)
CzPPQ	3155	12.99	18.39	616	52	(0.66, 0.34)	771
CzPPCzQ	5865	12.76	17.55	618	50	(0.66, 0.33)	486
CzPPQCz	1425	10.11	13.04	618	54	(0.66, 0.33)	246
CzPPtBuPhQ	1262	11.00	15.36	616	50	(0.66, 0.34)	1009
CzPPQtBuPh	1425	8.40	11.19	618	52	(0.66, 0.34)	185
CBP	1027	1.6	0.9	620	52	(0.62, 0.33)	97

Note:

FWHM: full width at half maximum; T₇₅ @ 500 nits (h): time required when the brightness is reduced 25% relative to initial brightness at 500 nit

TABLE 7-2

Luminescent efficiency of the present compound in red organic luminescent diode					
Device	V, 500 nits	Current Density [mA/cm ² , 500 nits]	η_{ext} [%], 500 nits]	η_c [cd/A, 500 nits]	η_p [lm/W, 500 nits]
CzPPQ	7.5	2.260	15.64	22.15	9.23
CzPPCzQ	6.7	8.746	4.12	5.58	2.58
CzPPQCz	8.5	3.522	11.00	14.20	5.27
CzPPtBuPhQ	7.3	2.767	12.96	18.09	7.77
CzPPQtBuPh	8.6	3.930	9.4	12.52	4.53
CBP	13.3	8.396	4.69	5.97	1.41

Note:

 η_{ext} : external quantum efficiency; η_c : current efficiency; η_p : energy efficiency

D. Determination of Life Time for Luminescent Diode Device Containing the Present Compound

[0084] Luminescent diode devices A, E, H, and I were determined their life time wherein each devices has the following structure in which the number in the parentheses means the thickness in nm. In these devices, Devices A and I are the present device using the present compound as the emission material and Devices E and H are control group using conventional BCP as the emission material.

[0085] Device A: ITO/NPB(20 nm)/TCTA(10 nm)/Cz-PPQ: Ir(piq)₃(4 wt %)(30 nm)/BCP(15 nm)/Alq₃(50 nm)/LiF(1 nm)/Al(100 nm)

[0086] Device E: ITO/NPB(20 nm)/TCTA(10 nm)/CBP: Ir(piq)₃(4 wt %)(30 nm)/BCP(15 nm)/Alq₃(50 nm)/LiF(1 nm)/Al(100 nm)

[0087] Device H: ITO/NPB(20 nm)/TCTA(10 nm)/CBP: Ir(pq)₃(4 wt %)(30 nm)/BCP(15 nm)/Alq₃(50 nm)/LiF(1 nm)/Al(100 nm)

[0088] Device I: ITO/NPB(20 nm)/TCTA(10 nm)/CzPPQ: Ir(pq)₃(4 wt %)(30 nm)/BCP(15 nm)/Alq₃(50 nm)/LiF(1 nm)/Al(100 nm)

[0089] The decadence of luminescent efficiency with time for Device A, E, H, and I are shown in FIG. 2. From FIG. 2, it is known that the Device A and Device I using CzPPQ as emission material exhibit slower decadence than Device E and H using CBP as emission material.

[0090] Moreover, Device A, E, H, and I were determined their life time when the brightness was reduced 40% (T₆₀)

with an electroluminescence of 500 candela per square meter (cd/m²). The results are shown in Table 8. From Table 8, it shown that the life time for Device A and Device I was 8991 and 19111 hours, respectively, which were far higher than the control Device E and H.

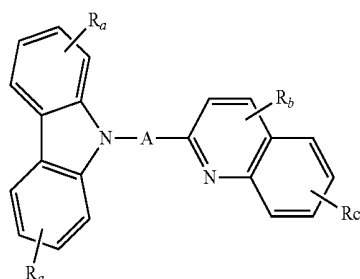
TABLE 8

Life time for luminescent diode devices		
Device	Emission material	T ₆₀ @ 500 cd/m ² (hr)
A	CzPPQ: Ir(piq) ₃ (4 wt %)	8991
E	CBP: Ir(piq) ₃ (4 wt %)	1672
H	CBP: Ir(pq) ₃ (4 wt %)	1110
I	CzPPQ: Ir(pq) ₃ (4 wt %)	19111

[0091] From the above, it is evident that the bipolar compound having quinolyl and carbazolyl groups of the present disclosure enhances the hole transport efficiency when using as emission material. While the present compound is used as host material in emission layer, it enhances the luminescent efficiency and electric property, and prolongs the life time of the OLED. Therefore, the bipolar compound of the present disclosure is potentially used as a substitute for current host material and can be used for producing OLED device having excellent luminescent efficiency.

[0092] While the disclosure has been described in detail, modifications within the spirit and scope of the disclosure will be readily apparent to those of skill in the art. In addition, it should be understood that aspects of the disclosure and portions of various embodiments and various features recited herein and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with one or more other embodiments, as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the disclosure.

1. A bipolar compound represented by the following formula (I):



Formula (I)

wherein A represents phenyl, biphenyl, or terphenyl group; and

R_a , R_b , and R_c are independently selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

2. The bipolar compound according to claim 1, wherein said A is further substituted by at least one substituent selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

3. The bipolar compound according to claim 1, wherein said aryl is phenyl group or substituted phenyl group.

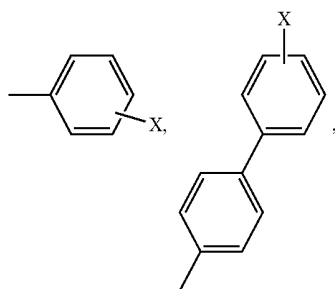
4. The bipolar compound according to claim 2, wherein said aryl is phenyl group or substituted phenyl group.

5. The bipolar compound according to claim 1, wherein said heteroaryl is carbazolyl group.

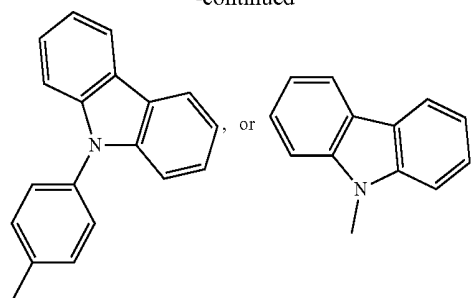
6. The bipolar compound according to claim 2, wherein said heteroaryl is carbazolyl group.

7. The bipolar compound according to claim 1, wherein said R_a and R_c are different by each other.

8. The bipolar compound according to claim 1, wherein said R_a and R_c are independently selected from the following groups:

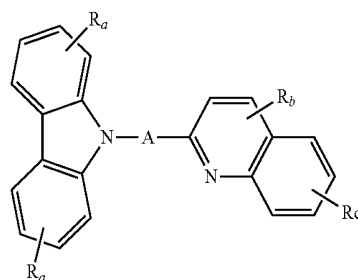


-continued



wherein X represents hydrogen, halo, cyano, trifluoromethyl, amino, or C_1 - C_{10} alkyl group.

9. An organic luminescent diode device comprising: a pair of electrodes; and an electroluminescent element, disposed between said pair of electrodes; wherein said electroluminescent element comprises a compound having the following formula (I):

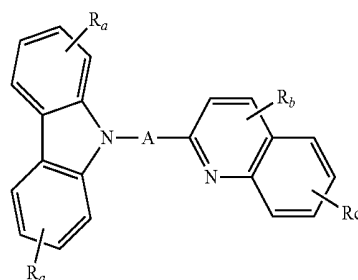


Formula (I)

wherein A represents phenyl, biphenyl, or terphenyl group; R_a , R_b , and R_c are independently selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

10. An organic electroluminescent diode device comprising:

a pair of electrodes; and an electroluminescent element disposed between said pair of electrodes; wherein said electroluminescent element comprises an emission layer and said emission layer comprises a dopant material and a compound having the following formula (I) as a host material:



Formula (I)

wherein A represents phenyl, biphenyl, or terphenyl group; R_a , R_b , and R_c are independently selected from a group consisting of hydrogen, halo, cyano, trifluoromethyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_3 - C_{20} cycloalkyl, C_3 - C_{20} cycloalkenyl, C_1 - C_{20} heterocyclic alkyl, C_1 - C_{20} heterocyclic alkenyl, aryl, and heteroaryl group.

11. The organic electroluminescent diode device according to claim 8, wherein said dopant material comprises a green emitting dopant material in an amount of from 0 to 10 wt. %.

12. The organic electroluminescent diode device according to claim 9, wherein said green emitting dopant material is tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$).

13. The organic electroluminescent diode device according to claim 8, wherein said dopant material comprises an orange emitting dopant material in an amount of from 0 to 10 wt. %.

14. The organic electroluminescent diode device according to claim 11, wherein said orange emitting dopant material is tris(2-phenylquinoline)iridium ($\text{Ir}(\text{pq})_3$).

15. The organic electroluminescent diode device according to claim 8, wherein said dopant material comprises a red emitting dopant material in an amount of from 0 to 10 wt. %.

16. The organic electroluminescent diode device according to claim 13, wherein said red emitting dopant material is tris(2-phenyl-isoquinoline)iridium ($\text{Ir}(\text{piq})_3$).

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专利名称(译)	双极化合物和使用其的有机电致发光器件		
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外部链接	Espacenet USPTO		

摘要(译)

本公开涉及由下式 (I) 表示的双极化合物;以及包含该装置的有机发光二极管装置。其中A代表苯基, 联苯基或三联苯基;和 Ra, Rb和Rc独立地选自氢, 卤素, 氰基, 三氟甲基, 氨基, C1-C10烷基, C2-C10烯基, C2-C10炔基, C3- C20环烷基, C3-C20环烯基, C1-C20杂环烷基, C1-C20杂环烯基, 芳基和杂芳基。

