US007252894B2

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

(10) **Patent No.: US 7,252,894 B2**
(45) **Date of Patent: Aug. 7, 2007**

(54) **ANTHRACENE COMPOUND FOR ORGANIC ELECTROLUMINESCENT DEVICE**

(75) Inventors: **Chen-Ping Yu**, Longtan Township, Taoyuan County (TW); **Chung-Wen Ko**, Sijhih (TW)

(73) Assignee: **AU Optronics Corp.**, Hsinchu (TW)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 247 days.

(21) Appl. No.: **10/946,895**

(22) Filed: **Sep. 22, 2004**

(65) **Prior Publication Data**

US 2005/0260442 A1 Nov. 24, 2005

(30) **Foreign Application Priority Data**

May 24, 2004 (TW) .... 93114612 A

(51) **Int. Cl.**
H01L 51/50 (2006.01)
C09C 211/00 (2006.01)
C09K 11/06 (2006.01)

(52) **U.S. Cl.** **428/690**; 428/917; 313/504; 313/506; 564/427; 564/428; 564/433; 564/434

(58) **Field of Classification Search** 428/690, 428/917; 313/504, 506; 564/427, 428, 433, 564/434
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,759,444 A	6/1998	Enokida et al.	252/301.16
5,925,472 A *	7/1999	Hu et al.	428/690
6,465,115 B2	10/2002	Shi et al.	428/690
2005/0249972 A1 *	11/2005	Hatwar et al.	428/690

FOREIGN PATENT DOCUMENTS

JP	2003267973 A *	9/2003
JP	2004-091334	3/2004
JP	2004-095850	3/2004
JP	2004091334 A *	3/2004
JP	2004095850 A *	3/2004

OTHER PUBLICATIONS

Bull. Soc. Chim. Belg., 66, p. 413-437, (1957).*

Compt. rend. (1950), 230, p. 664-5 (with HCAPLUS database English abstract printout attached).*

Annali di Chimica Applicata (1947), 2(12), p. 739-89 (with HCAPLUS database English abstract printout attached).*

Comptes Rendus des Sciences de l'Academie des Sciences, Series C: Sciences Chimiques (1970), 271(20), p. 1258-1261 (with HCAPLUS database English abstract printout attached).*

Taiwan Office Action, no date listed.

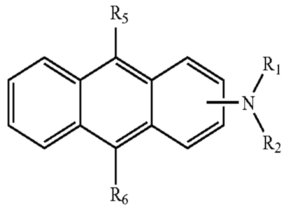
* cited by examiner

Primary Examiner—Dawn L. Garrett
(74) *Attorney, Agent, or Firm*—Thomas, Kayden, Horstemeyer & Risley

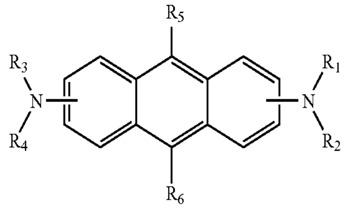
(57) **ABSTRACT**

An anthracene compound for an organic electroluminescent device, having formula (I) or (II)

(I)



(II)



wherein R_1, R_2, R_3, R_4, R_5, and R_6 are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is C_{1-10} alkyl, C_{1-10} alkoxy, or halogen.

10 Claims, 1 Drawing Sheet

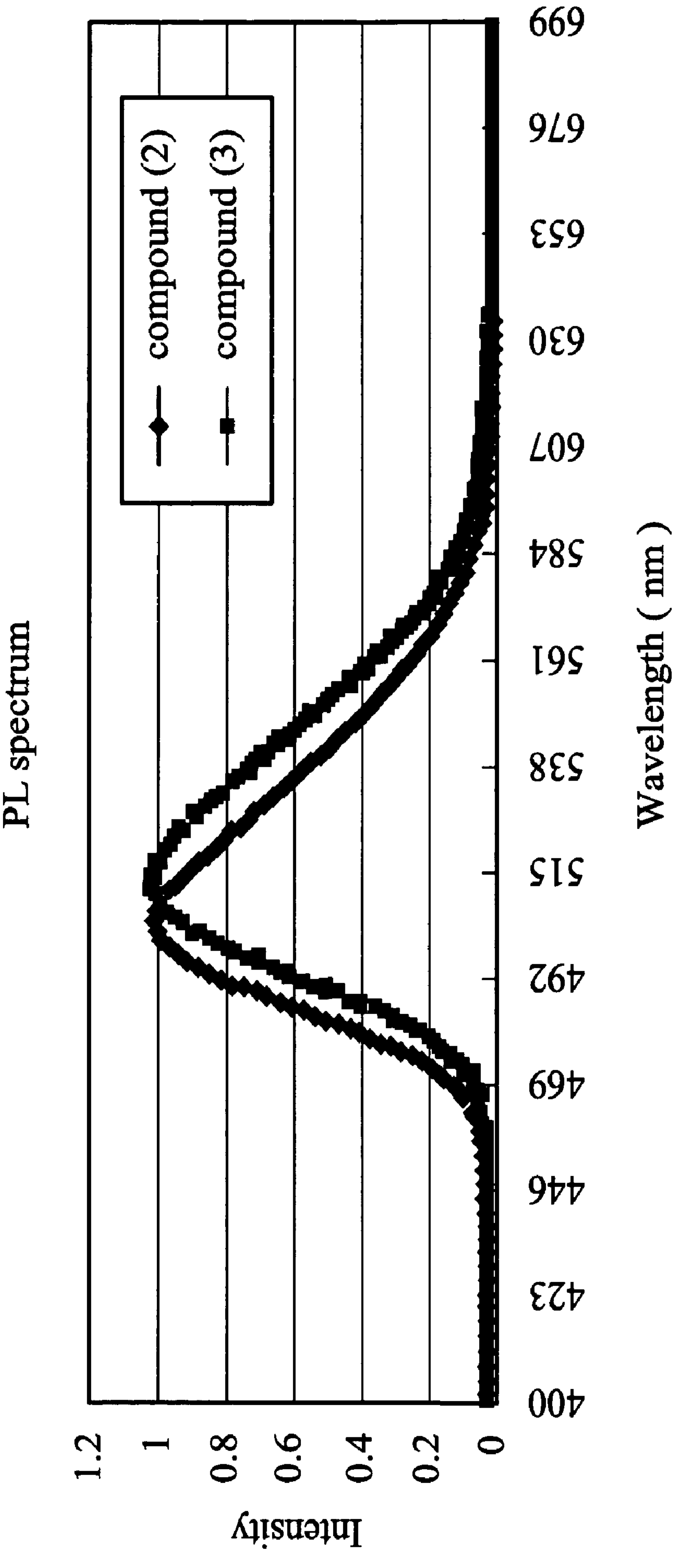

PL spectrum
compound (2)
compound (3)
Intensity
1.2
1
0.8
0.6
0.4
0.2
0
400
423
446
469
492
515
538
561
584
607
630
653
676
699
Wavelength (nm)

FIG. 1

ANTHRACENE COMPOUND FOR ORGANIC ELECTROLUMINESCENT DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

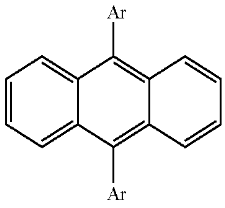
The present invention relates to an anthracene compound for an organic electroluminescent device, and more particularly to an anthracene compound serving as a light-emitting layer or hole transport layer of an organic electroluminescent device.

2. Description of the Related Art

An organic electroluminescent device (also referred to as organic light-emitting diode; OLED) is an LED with an organic layer acting as the active layer, increasingly applied in flat panel displays due to advantages, such as low voltage operation, high brightness, light weight, slim profile, wide viewing angle, and highly effective contrast ratio.

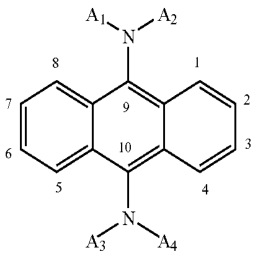
Generally, an OLED is composed of a light-emitting layer and a pair of electrodes sandwiching the light-emitting layer. Light emission is caused by the following phenomenon. When an electric field is applied to these two electrodes, the cathode injects electrons into the light-emitting layer and the anode injects holes into the light-emitting layer. When the electrons recombine with the holes in the light-emitting layer, their energy level shifts to a valence bond band which causes them to release energy as fluorescent light.

Anthracene has been used as material for a hole transport layer and a light-emitting layer. For example, U.S. Pat. No. 6,465,115 discloses an organic anthracene material as the hole transport layer, having the following formula:



wherein Ar is individually substituted or unsubstituted aryl having 5 to 20 carbon atoms.

In U.S. Pat. No. 5,759,444, an anthracene compound emitting light is disclosed, having the following formula:



wherein each of A_1 to A_4 is a substituted or unsubstituted aryl group having 6 to 16 carbon atoms. In the anthracene compound, the diarylamino group is introduced at positions 9 and 10 of the anthracene ring. It is found that the diarylamino group causes the anthracene light-emitting material to have a hole transport property. In addition, the stability at the interface between the light-emitting layer and the hole transport layer is increased, thus increasing the life of the device.

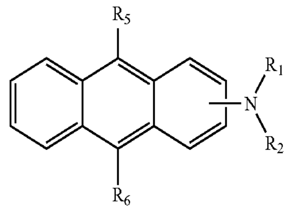
SUMMARY OF THE INVENTION

An object of the present invention is to provide a novel anthracene compound containing a diarylamino group, diheteroarylamino group, or dialkylamino group.

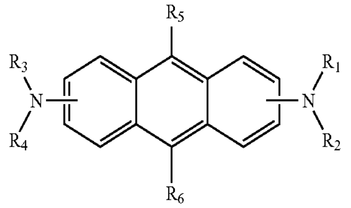
Another object of the present invention is to provide an organic electroluminescent device including the anthracene compound of the present invention. The anthracene compound of the present invention can serve as a light-emitting layer or a hole transport layer in the organic electroluminescent device.

To achieve the above objects, the anthracene compound of the present invention has formula (I) or (II)

(I)



(II)



wherein R_1, R_2, R_3, R_4, R_5, and R_6 are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is C_{1-10} alkyl, C_{1-10} alkoxy, or halogen.

The organic electroluminescent device of the present invention includes a pair of electrodes and a layer of organic light emitting medium disposed between the pair of electrodes. The layer of organic light emitting medium includes an anthracene compound having formula (I) or (II) as above.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawing, given by way of illustration only and thus not intended to be limitative of the present invention.

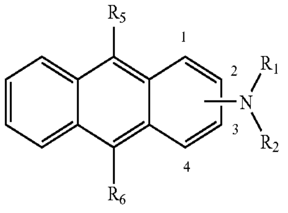
FIG. **1** is a diagram showing the photoluminescent (PL) intensity of compounds (2) and (3) at various wavelengths.

DETAILED DESCRIPTION OF THE INVENTION

The feature of the present invention resides in that in the anthracene compound of the present invention, at least one diarylamino group (or diheteroarylamino group or dialkyamino group) is introduced at one of the positions 1 to 4 and 5 to 8 of the anthracene ring.

Specifically, one diarylamino group (or diheteroarylamino group or dialkyamino group) can be introduced at one of the positions 1 to 4 of the anthracene ring. Thus, the anthracene compound of the present invention has formula (I)

(I)

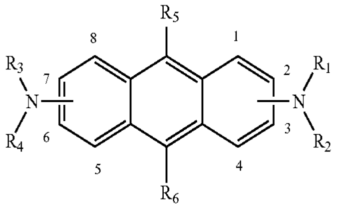


$$\text{(I)}$$

wherein R_1, R_2, R_5, and R_6 are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is C_{1-10} alkyl, C_{1-10} alkoxy, or halogen.

Any two of diarylamino groups, diheteroarylamino groups and dialkyamino groups can be introduced on the anthracene ring. One of the above amino groups is introduced at one of the positions 1 to 4, and the other at one of the positions 5 to 8. Thus, the anthracene compound of the present invention has formula (II)

(II)



wherein R_1, R_2, R_3, R_4, R_5, and R_6 are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is C_{1-10} alkyl, C_{1-10} alkoxy, or halogen.

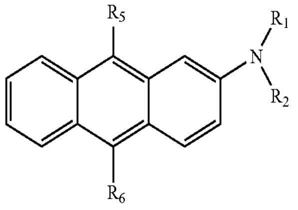
For each of R_1 to R_6 in the compounds of formulae (I) and (II), representative examples of the unsubstituted or substituted aryl groups include phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 4-ethylphenyl, biphenyl, 4-methylbiphenyl, 4-ethylbiphenyl, 4-cyclohexylbiphenyl, terphenyl, 3,5-dichlorophenyl, naphthyl, 5-methylnaphthyl, anthryl, and pyrenyl.

Representative examples of the unsubstituted or substituted heteroaryl groups include furanyl, thiophenyl, pyrrolyl, pyranyl, thiopyranyl, pyridinyl, thiazolyl, imidazolyl, pyrimidinyl, triazinyl, indolyl, quinolyl, purinyl and carbazolyl.

Representative examples of the unsubstituted or substituted alkyl groups include methyl, ethyl, propyl, butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, stearyl, 2-phenylisopropyl, trichloromethyl, and trifluoromethyl.

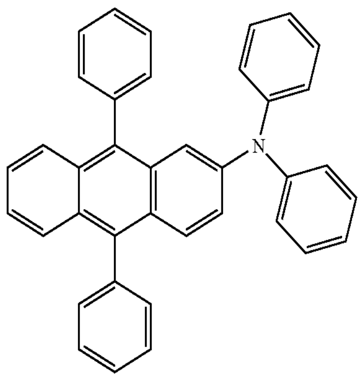
When only one diarylamino group (or diheteroarylamino group or dialkylamino group) is introduced at position 2 of the anthracene ring, the anthracene compound of the present invention has formula (III)

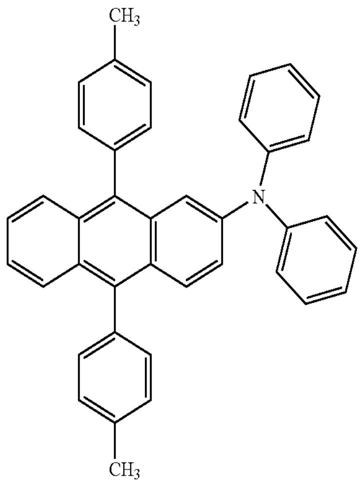
(III)



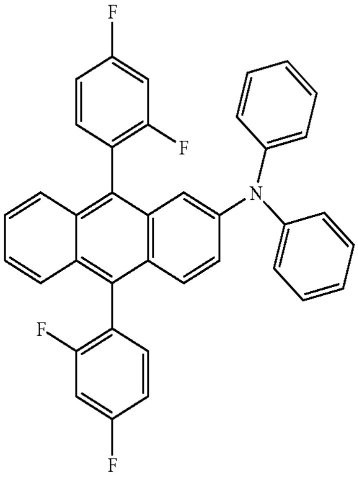
wherein R_1, R_2, R_5, and R_6 are defined above.

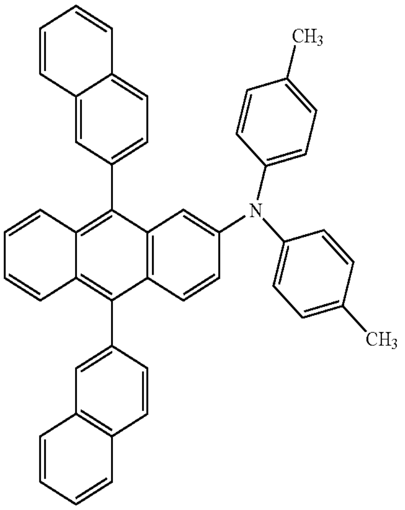
When R_1 and R_2 are unsubstituted or substituted aryl groups, representative examples of formula (III) include

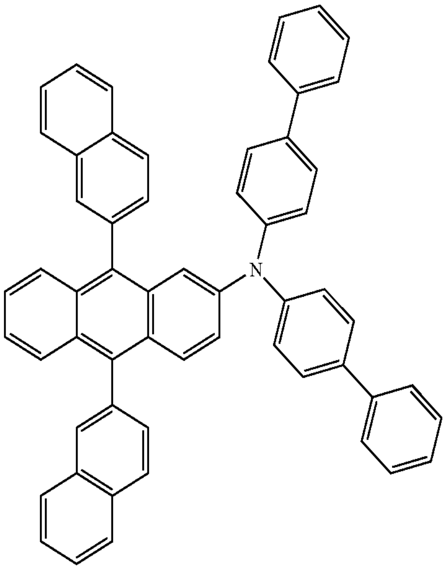




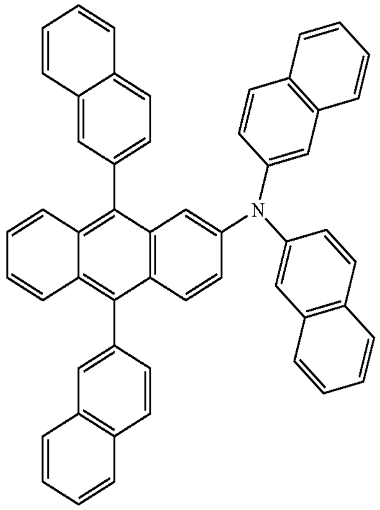
-continued





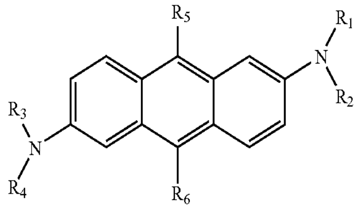


-continued



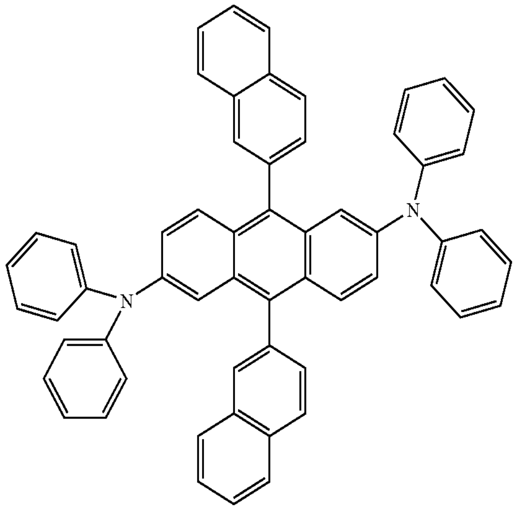
When one diarylamino group (or diheteroarylamino group or dialkylamino group) is introduced at position 2 and the other diarylamino group (or diheteroarylamino group or dialkylamino group) at position 6 of the anthracene ring, the anthracene compound of the present invention has formula (IV)

(IV)

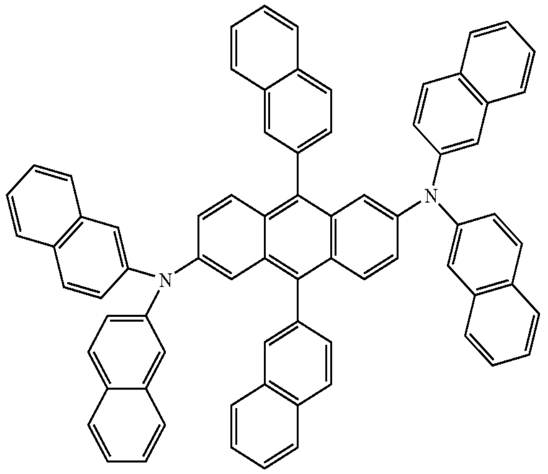


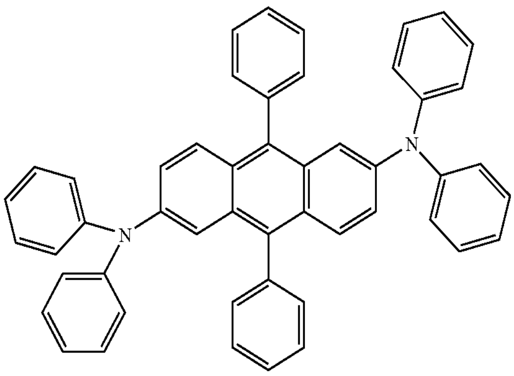
wherein R_1, R_2, R_3, R_4, R_5, and R_6 are defined above.

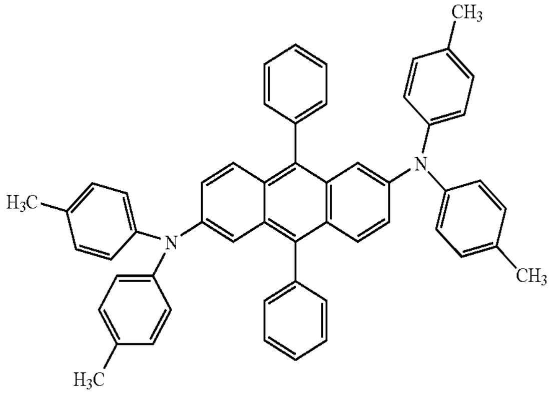
When R_1 to R_4 are unsubstituted or substituted aryl group, representative examples of formula (IV) include



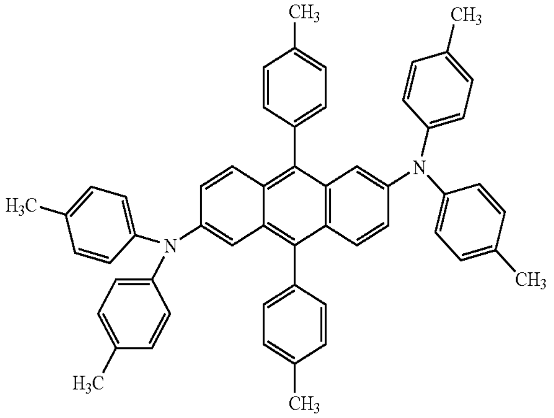
-continued

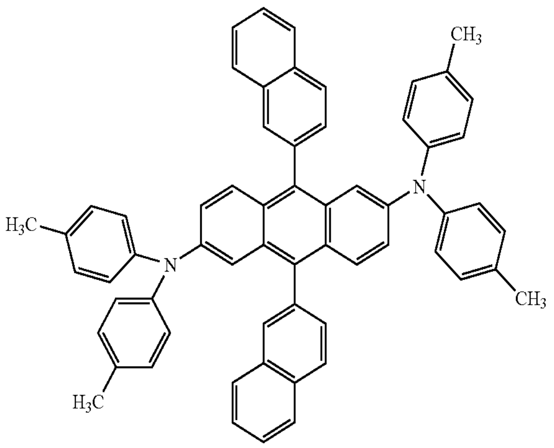






-continued

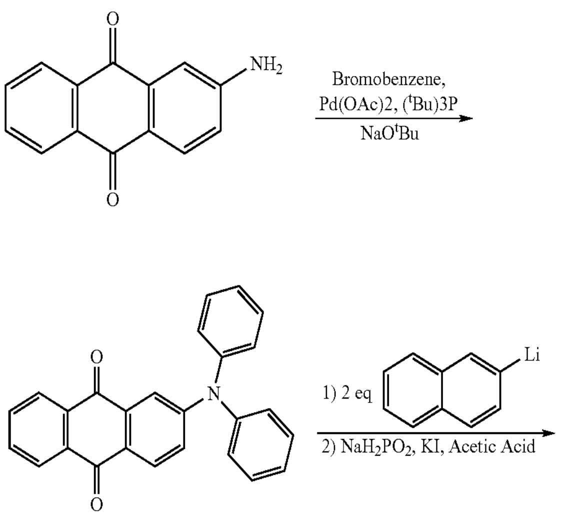




The following examples are intended to illustrate the process and the advantages of the present invention without limiting its scope, since numerous modifications and variations will be apparent to those skilled in the art.

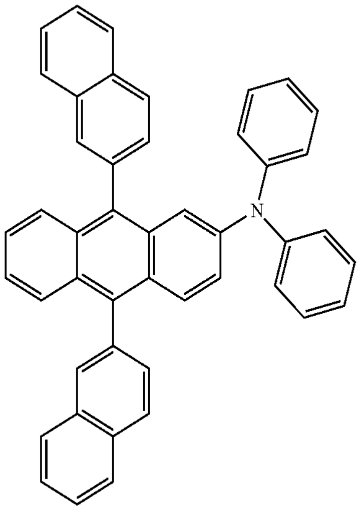
EXAMPLE 1

The synthesis pathway is shown below.



Compound (1)

-continued



Compound (2)

Method of Synthesis of Compound (1)

To a suspension of anthraquinone (1 g, 4.8 mmol), bromobenzene (1.66 g, 10.6 mmol), NaOtBu (1.1 g, 11.52 mmol) and $Pd(OAc)_2$ (71 mg, 0.32 mmol) were dissolved in 50 mL dry toluene, tri-tert-butylphosphine (257 mg, 1.28 mmol) was added through a syringe. The reaction mixture was heated to reflux for 36 hours. After cooling, the reaction was added with 50 mL of water, then extracted with ethyl acetate. After being dried over $MgSO_4$, and then purified by column chromatography to give the compound (1) (1.04 g).

Method of Synthesis of Compound (2)

2-Bromonaphthalene (2.3 g, 11 mmole) was dissolved in 100 mL THF, the 4.8 mL n-BuLi (11 mmol, 2.5M) was slowly added into the solution at −78° C. After 30 minutes, the above mixture was added to the compound (1) (1.7 g, 4.7 mmol) in 30 mL THF dropwise at −78° C. The mixture was left to reach room temperature. Cold water (100 mL) was added and the organic phase separated. The water phase was extracted with ethyl acetate. The organic fractions were dried over $MgSO_4$, and then the solvent was removed by a rotary evaporator. KI (2.8 g, 17 mmole), sodium hypophosphite monohydrate (3.8 g, 32 mmole), and 30 mL acetic acid were added to the crude residue. The mixture was heated under reflux for 2 hours. After cooling, the white precipitate was collected, then purified by column chromatography to give the compound (2) (2.5 g).

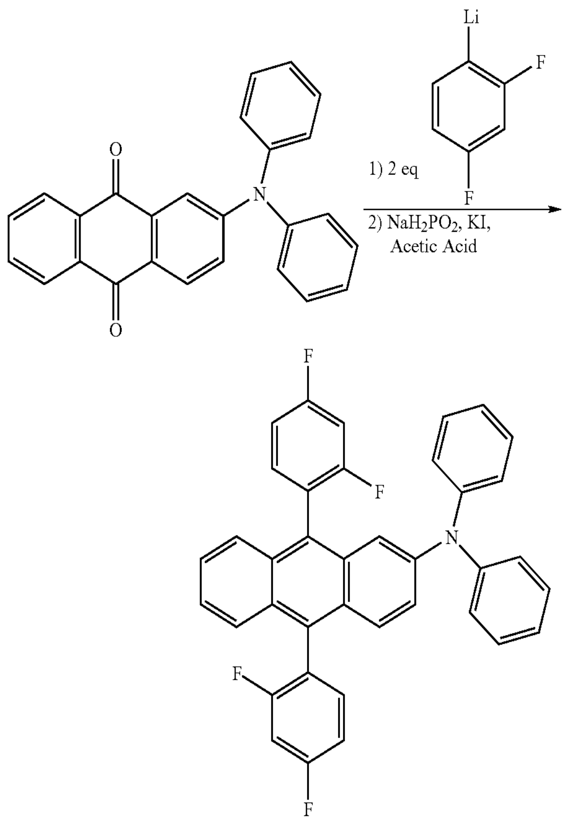
FIG. **1** is a diagram showing the photoluminescent (PL) intensity of compounds (2) and (3) at various wavelengths. It shows that for compound (2), the wavelength at the maximum intensity is 504 nm, indicating that compound (2) emits green light.

In addition, the HOMO level of compound (2) was measured to be 5.40 eV, which is very close to the HOMO level (5.5 eV) of NPB (a commonly-used material for the hole transport layer). Thus, compound (2) of the present invention is suitable for use as a hole transport layer.

EXAMPLE 2

Method of Synthesis of Compound (3)

The synthesis pathway is shown below.



Compound (3)

2,4-difluorobromobenzene (2.5 g, 13 mmole) was dissolved in 100 mL THF, and 5.2 mL nBuLi (13 mmol, 2.5M) was then slowly added into the mixture at −78° C. After 30 minutes, the above mixture was added to the compound (1) (2.1 g, 5.8 mmol) in 30 mL THF dropwise at −78° C. The mixture was left to reach room temperature. Cold water (100 mL) was added and the organic phase was separated. The water phase was extracted with ethyl acetate. The organic fractions were dried over $MgSO_4$ and the solvent was then removed by rotary evaporator. KI (3.4 g, 20.5 mmole), sodium hypophosphite monohydrate (4.9 g, 41.2 mmole), and 30 mL acetic acid were added to the crude residue. The mixture was heated under reflux for 2 hours. After cooling, the white precipitate was collected, then purified by column chromatography to give the compound (3) (1.6 g).

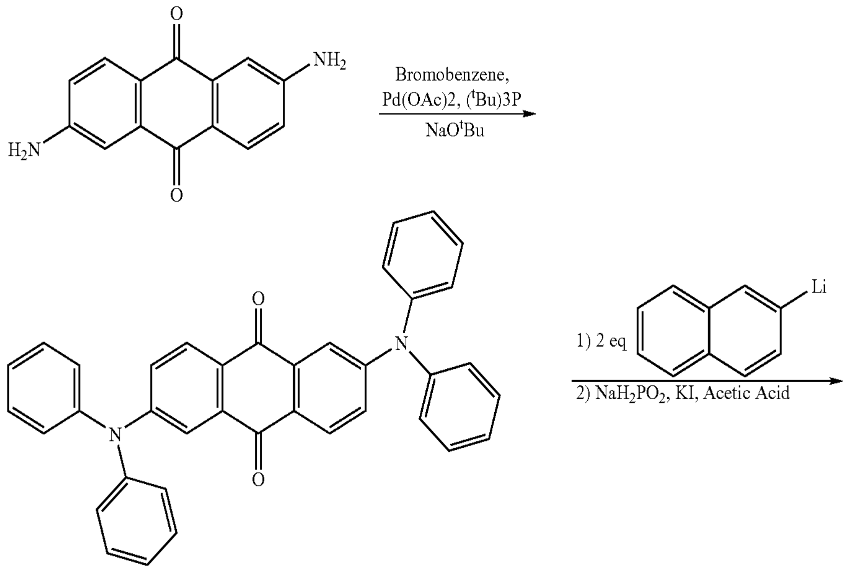
FIG. **1** is a diagram showing the photoluminescent (PL) intensity of compounds (2) and (3) at various wavelengths. It shows that for compound (3), the wavelength at the maximum intensity is 513 nm, indicating that compound (3) emits green light.

In addition, the HOMO level of compound (3) was measured to be 5.85 eV, which is very close to the HOMO level (5.5 eV) of NPB (a commonly-used material for the hole transport layer). Thus, compound (3) of the present invention is suitable for use as a hole transport layer.

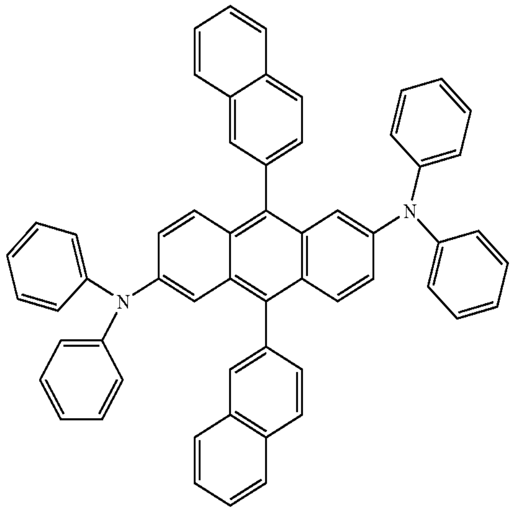
EXAMPLE 3

Method of Synthesis of Compound (4)

The synthesis pathway is shown below.



Compound (4)



Compound (5)

To a suspension of 2,6-diaminoanthraquinone (1.2 g, 5 mmol), bromobenzene (3.5 g, 22 mmol), NaOtBu (1.2 g, 12 mmol) and $Pd(OAc)_2$ (149 mg, 0.66 mmol) were dissolved in 50 mL dry toluene, tri-tert-butylphosphine (533 mg, 2.64 mmol) was added through a syringe. The reaction mixture was heated to reflux for 36 hours. After cooling, the reaction mixture was added with 50 mL water, then extracted with ethyl acetate. After dry over $MgSO_4$, the reaction mixture was purified by column chromatography to give the compound (4) (1.1 g).

Method of Synthesis of Compound (5)

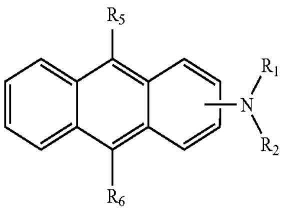
2-Bromonaphthalene (2.3 g, 11 mmole) was dissolved in 100 mL THF, then 4.8 mL nBuLi (11 mmol, 2.5M) was slowly added into the mixture at −78° C. After 30 minutes, the compound (4) (2.7 g, 5 mmol) in 30 mL THF was added dropwise at −78° C. The mixture was left to reach room temperature. Cold water (100 mL) was added and the organic phase was separated. The water phase was extracted with ethyl acetate. The organic fractions were dried over $MgSO_4$ then the solvent was removed by rotary evaporator. Kl (3.0 g, 18 mmole), sodium hypophosphite monohydrate (4.1 g, 34 mmole), and 30 mL acetic acid were added to the crude residue. The mixture was heated under reflux for 2 hours. After cooling, the white precipitate was collected, then purified by column chromatography to give compound (5) (3.1 g).

The foregoing description of the preferred embodiments of this invention has been presented for purposes of illustration and description. Obvious modifications or variations are possible in light of the above teaching. The embodiments chosen and described provide an excellent illustration of the principles of this invention and its practical application to thereby enable those skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the present invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

What is claimed is:

1. An anthracene compound having formula (I)

(I)

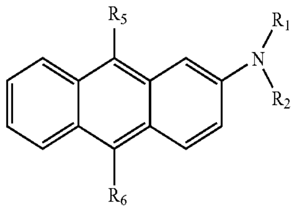


wherein R_1, and R_2, are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, wherein the substituent is $C_{1\text{-}10}$ alkyl, $C_{1\text{-}10}$ alkoxy, or halogen; and

R_5, and R_6 are each individually an unsubstituted or substituted phenyl group, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is $C_{1\text{-}10}$ alkyl, $C_{1\text{-}10}$ alkoxy, or halogen.

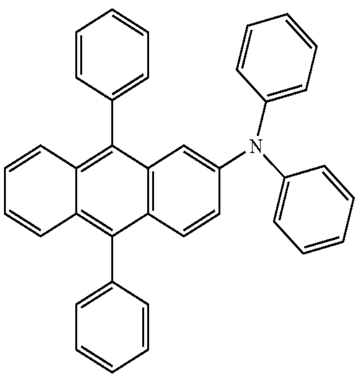
2. The anthracene compound as claimed in claim **1**, which has formula (III)

(III)

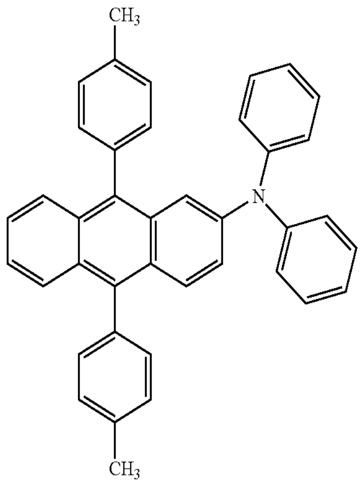


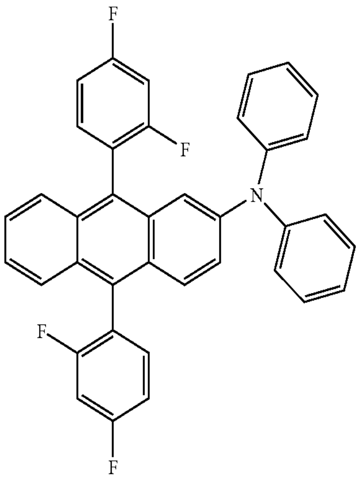
wherein R_1, R_2, R_5, and R_6 are defined above.

3. The anthracene compound as claimed in claim **2**, which is selected from the following formulae



-continued





.

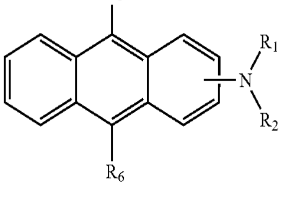
4. The anthracene compound as claimed in claim **1**, which is light emitting.

5. The anthracene compound as claimed in claim **1**, which has hole transport property.

6. An organic electroluminescent device, comprising a pair of electrodes and a layer of organic light emitting medium disposed between the pair of electrodes,

wherein the layer of organic light emitting medium includes an anthracene compound having formula (I)

(I)

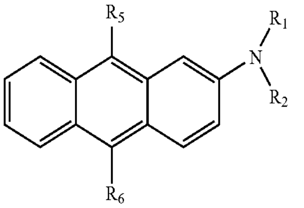


wherein R_1, and R_2, are each individually an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, wherein the substituent is $C_{1\text{-}10}$ alkyl, $C_{1\text{-}10}$ alkoxy, or halogen; and

R_5, and R_6 are each individually an unsubstituted or substituted phenyl group, an unsubstituted or substituted heteroaryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted alkyl group having 1 to 12 carbon atoms, wherein the substituent is C_{1-10} alkyl, C_{1-10} alkoxy or halogen.

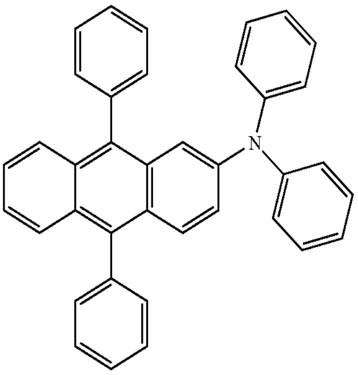
7. The organic electroluminescent device as claimed in claim **6**, wherein the anthracene compound has formula (III)

(III)

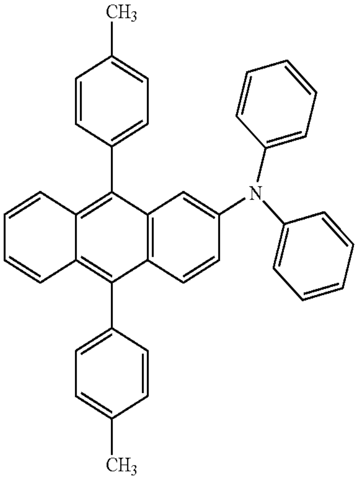


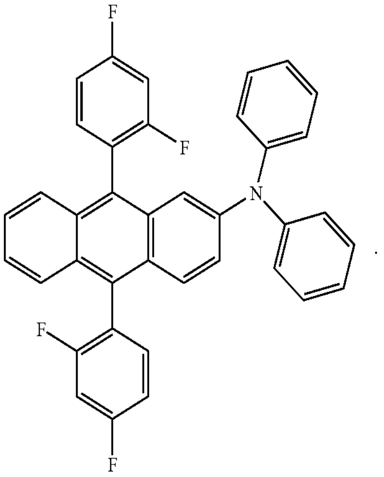
wherein R_1, R_2, R_5, and R_6 are defined above.

8. The organic electroluminescent device as claimed in claim **7**, wherein the anthracene compound is selected from the following formulae



-continued





9. The organic electroluminescent device as claimed in claim **6**, wherein the layer of organic light emitting medium includes a light emitting layer, and the light emitting layer includes an anthracene compound having formula (I).

10. The organic electroluminescent device as claimed in claim **6**, wherein the layer of organic light emitting medium includes a light emitting layer and a hole transport layer, and the hole transport layer includes an anthracene compound having formula (I).

* * * * *

专利名称(译)	用于有机电致发光器件的蒽化合物		
公开(公告)号	US7252894	公开(公告)日	2007-08-07
申请号	US10/946895	申请日	2004-09-22
[标]申请(专利权)人(译)	友达光电股份有限公司		
申请(专利权)人(译)	友达光电.		
当前申请(专利权)人(译)	友达光电.		
[标]发明人	YU CHEN PING KO CHUNG WEN		
发明人	YU, CHEN-PING KO, CHUNG-WEN		
IPC分类号	H01L51/50 C07C211/00 C09K11/06 C07C211/61 H01L51/00 H05B33/12 H05B33/14		
CPC分类号	C07C211/61 C09K11/06 H01L51/006 H05B33/14 H01L51/0058 C09K2211/1011 C09K2211/1014 Y10S428/917 H01L51/5012 H01L51/5048 C09B57/008		
优先权	093114612 2004-05-24 TW		
其他公开文献	US20050260442A1		
外部链接	Espacenet USPTO		

摘要(译)

用于有机电致发光器件的蒽化合物，具有式（I）或（II） 其中R1，R2，R3，R4，R5和R6各自独立地是具有6-20个碳原子的未取代或取代的芳基，具有6-20个碳原子的未取代或取代的杂芳基，或具有未取代或取代的烷基。 1至12个碳原子，其中取代基是C1-10烷基，C1-10烷氧基或卤素。