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H01L 51/50 *(2006.01)*

(54) ORGANIC MATERIAL AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME

ORGANISCHES MATERIAL UND ORGANISCHE ELEKTROLUMINESZENZVORRICHTUNG DAMIT

MATÉRIAU ORGANIQUE ET DISPOSITIF ÉLECTROLUMINESCENT ORGANIQUE L'UTILISANT

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Description

FIELD OF INVENTION

[0001] The present invention generally relates to an organic material and organic electroluminescent (herein referred to as organic EL) device using the organic material. More specifically, the present invention relates to an organic material having general formula(A), an organic EL device employing the organic material as hole blocking layer(HBL), electron transport layer(ETL) or phosphorescent host can efficiently lower driving voltage, lower power consumption and increase the efficiency.

BACKGROUND OF THE INVENTION

[0002] Organic electroluminescent (organic EL) is a light-emitting diode (LED) in which the emissive layer is a film made by organic compounds which emits light in response to an electric current. The emissive layer of organic compound is sandwiched between two electrodes. Organic EL is applied in flat panel displays due to their high illumination, low weight, ultra-thin profile, self-illumination without back light, low power consumption, wide viewing angle, high contrast, simple fabrication methods and rapid response time.

[0003] The first observation of electroluminescence in organic materials were in the early 1950s by Andre Bernanose and co-workers at the Nancy -University in France. Martin Pope and his co-workers at New York University first observed direct current(DC) electroluminescence on a single pure crystal of anthracene and on anthracene crystals doped with tetracene under vacuum in 1963.

[0004] The first diode device was reported by Ching W. Tang and Steven Van Slyke at Eastman Kodak in 1987. The device used a two-layer structure with separate hole transporting and electron transporting layers resulted in reduction in operating voltage and improvement of the efficiency, that led to the current era of organic EL research and device production.

[0005] Typically organic EL is composed of layers of organic materials situated between two electrodes, which include a hole transporting layer(HTL), an emitting layer(EML), an electron transporting layer(ETL). The basic mechanism of organic electroluminescence involves the injection of the carrier, transport, recombination of carriers and exciton formed to emit light. When an external voltage is applied to an organic light-emitting device, electrons and holes are injected from a cathode and an anode, respectively, electrons will be injected from a cathode into a LUMO (lowest unoccupied molecular orbital) and holes will be injected from an anode into a HOMO (highest occupied molecular orbital). When the electrons recombine with holes in the emitting layer, excitons are formed and then emit light. When luminescent molecules absorb energy to achieve an excited state, an exciton may either be in a singlet state or a triplet state depending on how the spins of the electron and hole have been combined. 75% of the excitons form by recombination of electrons and holes to achieve a triplet excited state. Decay from triplet states is spin forbidden, Thus, a fluorescence electroluminescent device has only 25% internal quantum efficiency. In contrast to fluorescence electroluminescent device, phosphorescent organic light-emitting diodes make use of spin-orbit interactions to facilitate intersystem crossing between singlet and triplet states, thus obtaining emission from both singlet and triplet states and the internal quantum efficiency of electroluminescent devices from 25% to 100%.

[0006] Recently, a new type of fluorescent organic EL device incorporating mechanism of thermally activated delayed fluorescence (TADF) has been developed by Adachi and coworkers is a promising way to obtain a high efficiency of exciton formation by converting spin-forbidden triplet excitons up to the siglet level by the mechanism of reverse intersystem crossing(RISC).

[0007] The phosphorescent organic EL utilizes both triplet and singlet excitons. Cause of longer lifetime and the diffusion length of triplet excitons compared to those of singlet excitons, the phosphorescent organic EL generally need an additional hole blocking layer(HBL) between the emitting layer(EML) and the electron transporting layer(ETL) or the electron transporting layer with hole blocking ability instead of typical ETL. The purpose of the use of HBL or HBETL is to confine the recombination of injected holes and electrons and the relaxation of created excitons within the EML, hence the device's efficiency can be improved. To meet such roles, the hole blocking materials must have HOMO (highest occupied molecular orbital)and LUMO(lowest unoccupied molecular orbital)energy levels suitable to block hole transport from the EML to the ETL and to pass electrons from the ETL to the EML, in addition, lower power consumption, the good thermal and electrochemical stability of the materials are also needed. Similar organic materials are disclosed in US2014306207A1.

[0008] There continues to be a need for organic EL materials which is able to efficiently transport electrons and block holes, with lower power consumption , good thermal stability and high emitting efficiency. According to the reasons described above, the present invention has the objective of resolving such problems of the prior-art and offering an organic EL device which is excellent in its lower power consumption, thermal stability, high luminance and long half-life time. The present invention discloses a novel organic material having general formula(A), used as hole blocking lay-

er(HBL), electron transport layer(ETL) or phosphorescent host have good charge carrier mobility and excellent operational durability can efficiently lower driving voltage and power consumption, increasing efficiency of organic EL device.

SUMMARY OF THE INVENTION

[0009] In accordance with the present invention, the organic material for hole blocking material (herein referred to as HBM), electron transport material(herein referred to as ETM) or phosphorescent host and their use for organic EL device are provided. The organic can overcome the drawbacks of the conventional materials like as lower efficiency and higher power consumption.

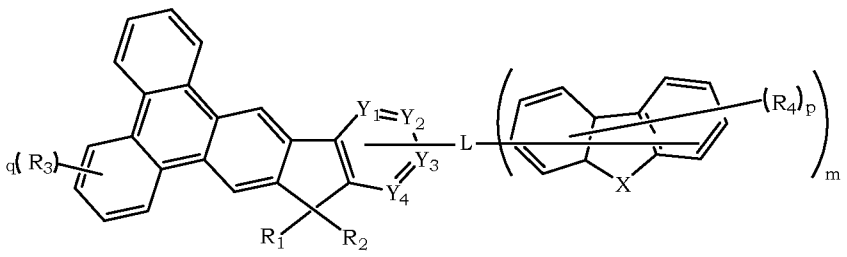
[0010] An object of the present invention is to provide the organic material which can be used as hole blocking material (HBM), hole blocking electron transport material(HBETM) for organic EL device and can efficiently confine excitons to transfer to electron transport layer.

[0011] An object of the present invention is to provide the organic material which can be used as electron transport material(ETM) for organic EL device.

[0012] An object of the present invention is to provide the organic material which can be used as phosphorescent host material of emitting layer for organic EL device.

[0013] Another object of the present invention is to apply the organic material for organic EL device and lower driving voltage, lower power consumption and increase the efficiency.

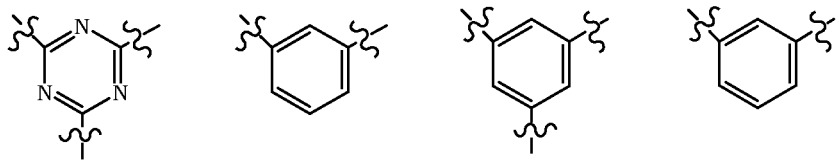
[0014] The present invention has the economic advantages for industrial practice. Accordingly the present invention, the organic material which can be used for organic EL device is disclosed. The mentioned the organic material is represented by the following formula(A) :

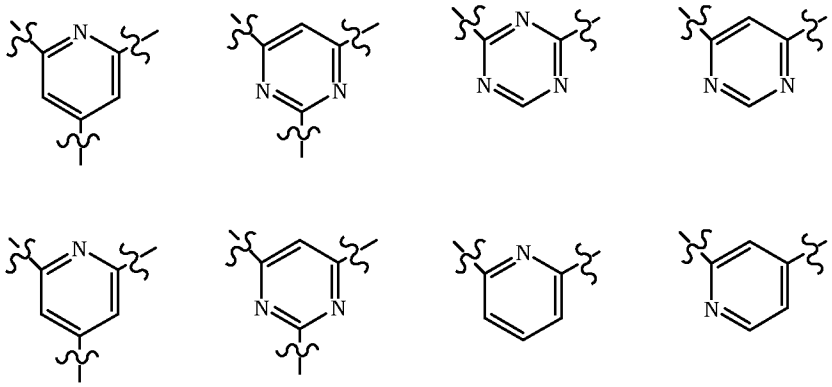


formula(A)

Wherein m represent 1 or 2, L represent a single bond, a substituted or unsubstituted arylene group having 6 to 40 ring carbon atoms, or a substituted or unsubstituted heterarylene group having 3 to 40 ring carbon atoms. X represent O, S, or NR_5; Y_1 to Y_4 each independently represent nitrogen atom or CR_6; R_5 and R_6 independently represent a hydrogen atom, a substituent, or a bond to L. p represent an integer of 0 to 7, q represent an integer of 0 to 10. R_1 to R_4 independently selected from the group consisting of a hydrogen atom, a halide, alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aralkyl group having 6 to 30 carbon atoms, and a substituted or unsubstituted heteroaryl group having 3 to 30 carbon atoms.

[0015] According to the formula (A), when L are not represented single bond, m represent 1 or 2, some preferable arylene group and heterarylene group for L are consisting of group represent as :

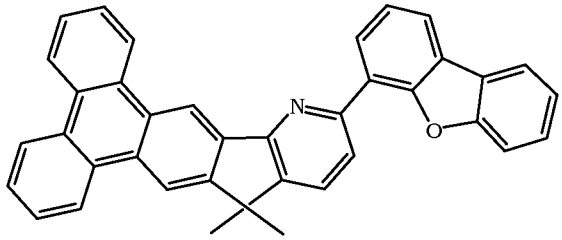




BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig.1 show one example of organic EL device in the present invention. 6 is transparent electrode, 13 is metal electrode, 7 is hole injection layer which is deposited onto 6, 8 is hole transporting layer which is deposited onto 7, 9 is fluorescent or phosphorescent emitting layer which is deposited onto 8, 10 is hole blocking layer or hole blocking electron transporting layerwhich is deposited onto 9, 11 is electron transporting layer which is deposited onto 10, 12 is electron injection layer which is deposited on to 11.

[0017] In this embodiment, some organic materials according formula (A) are shown below :



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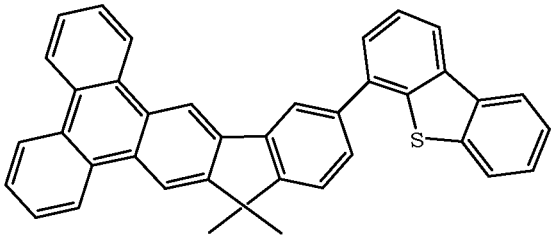

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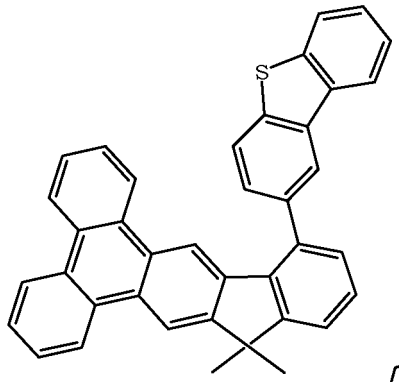

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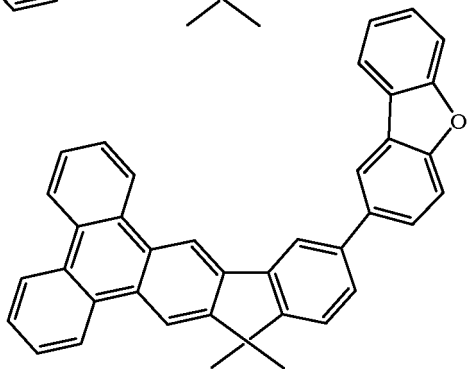

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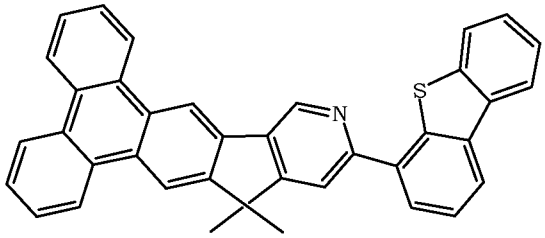

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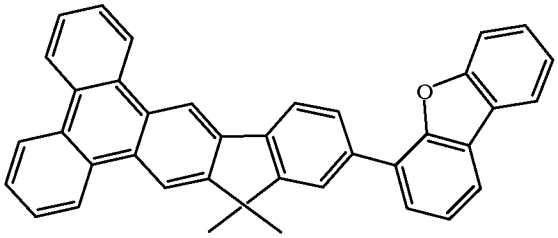

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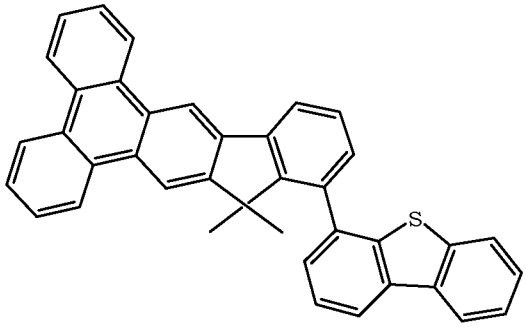

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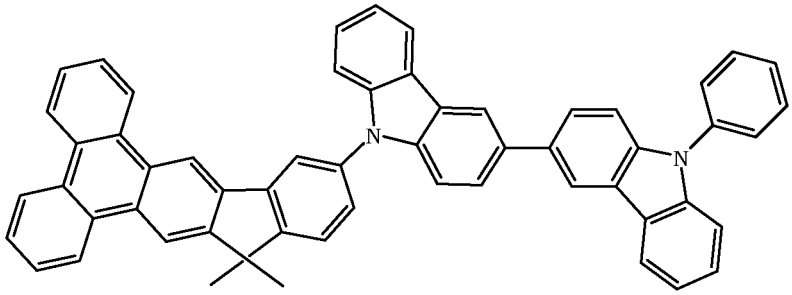

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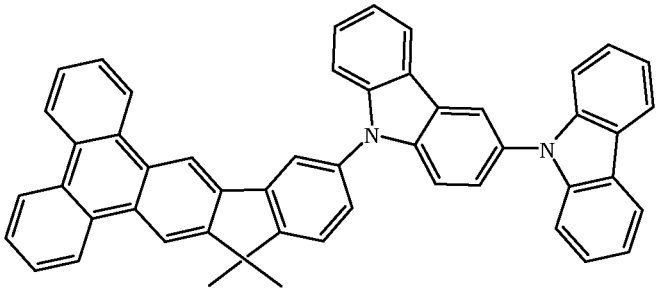

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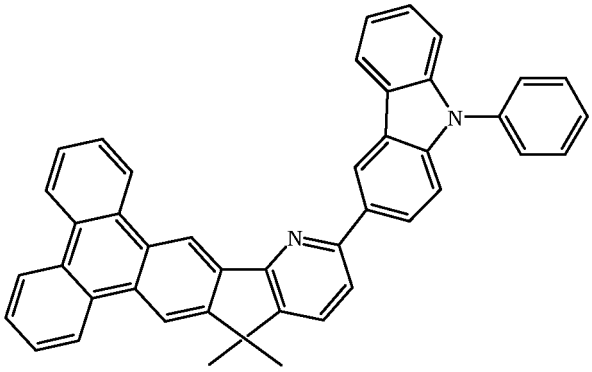

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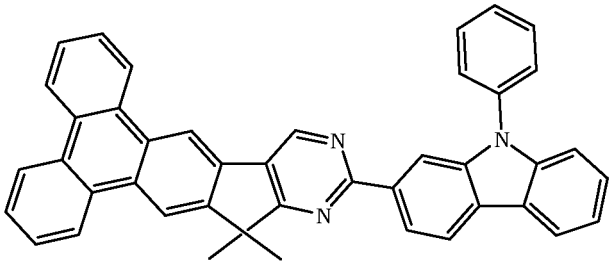

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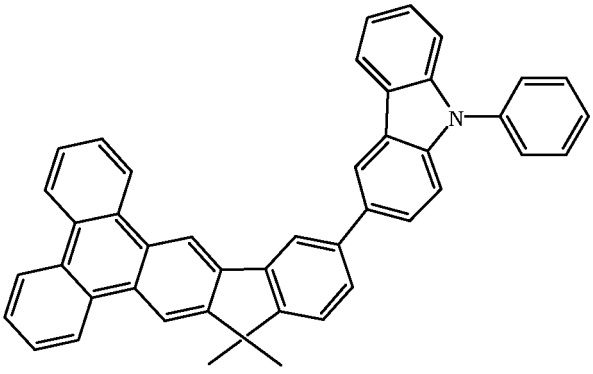

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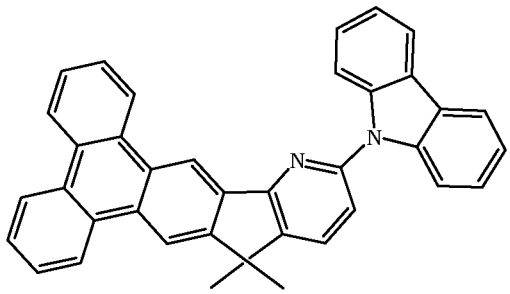

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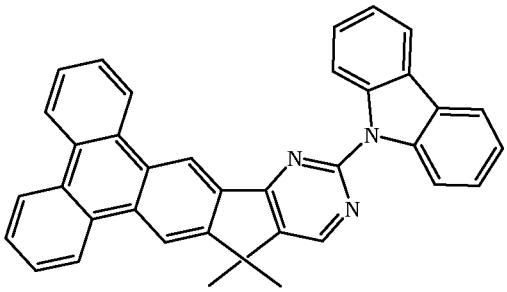

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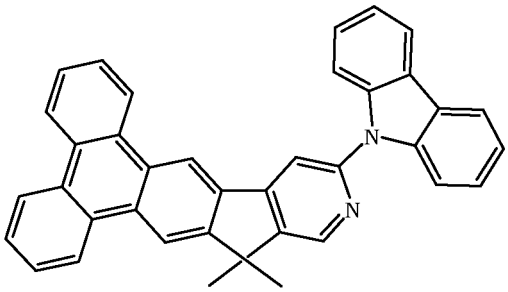

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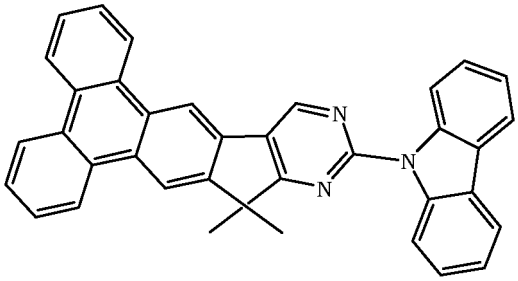

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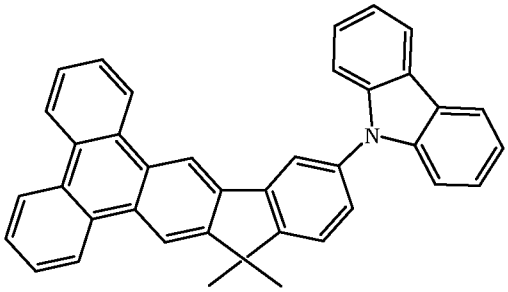

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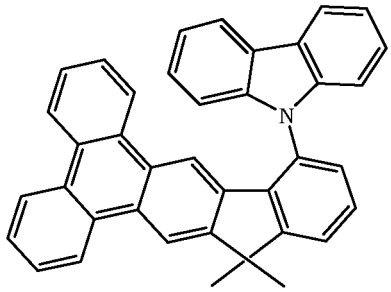

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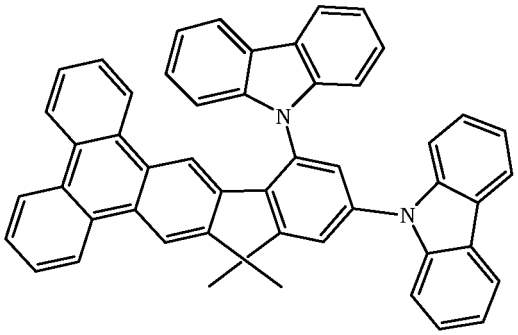

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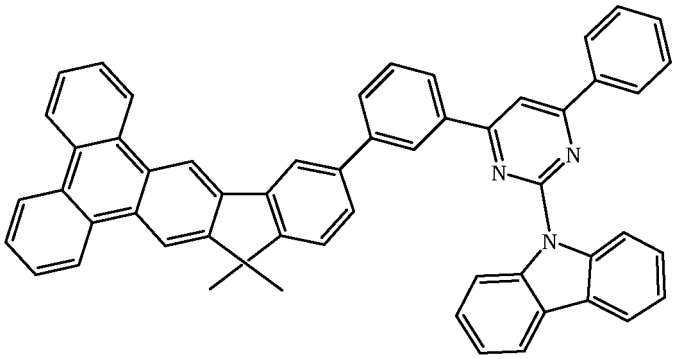

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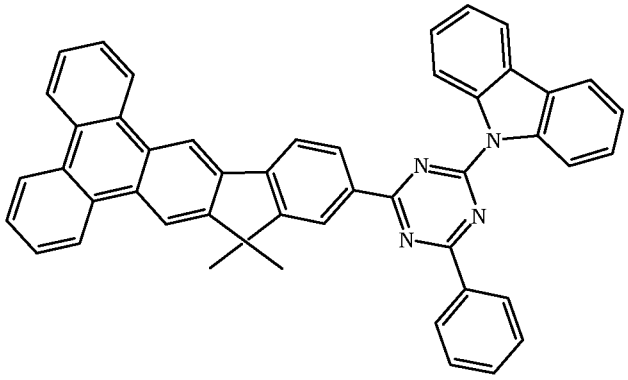

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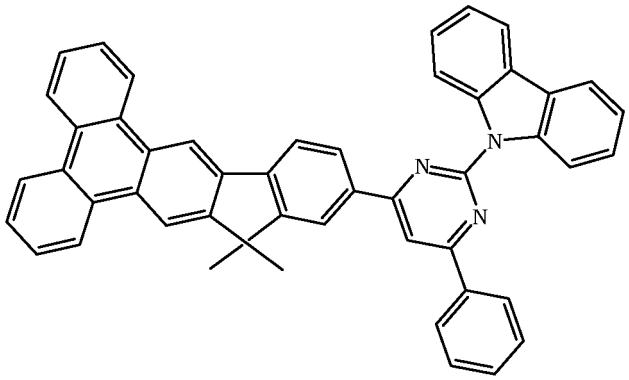

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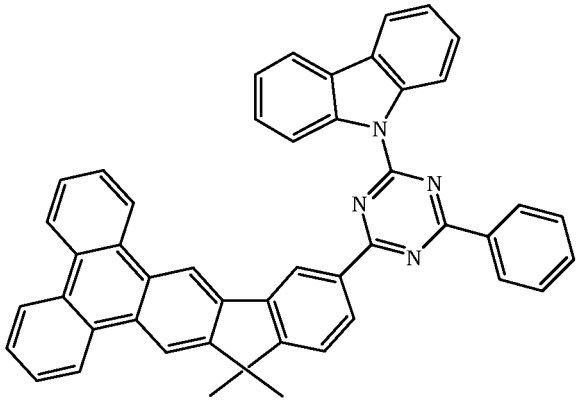

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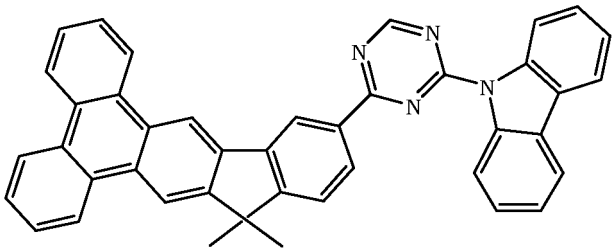

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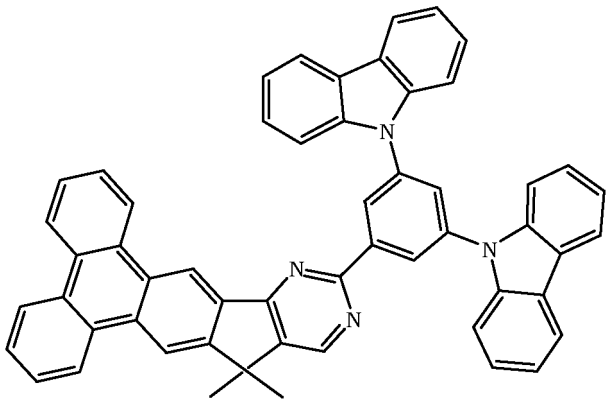

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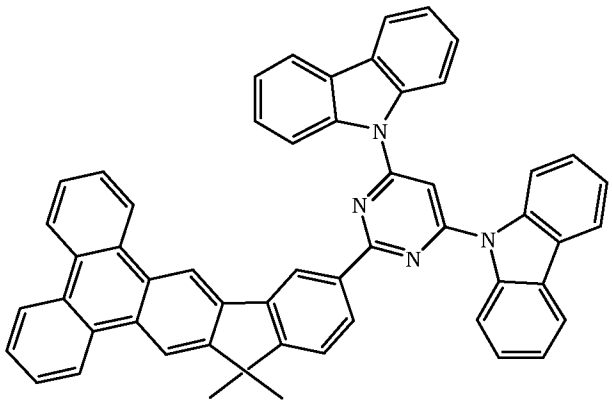

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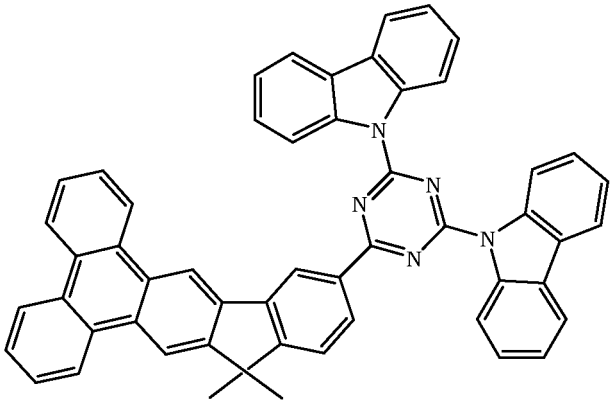

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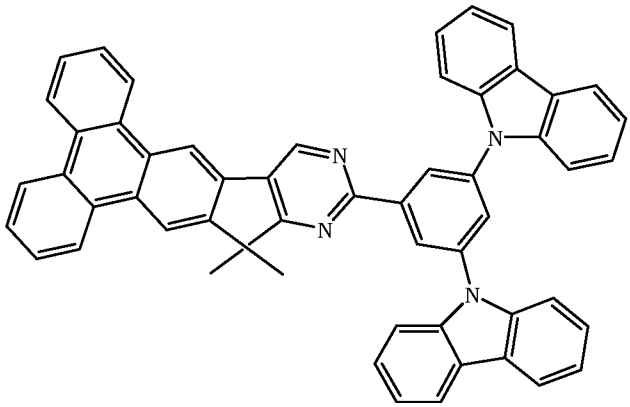

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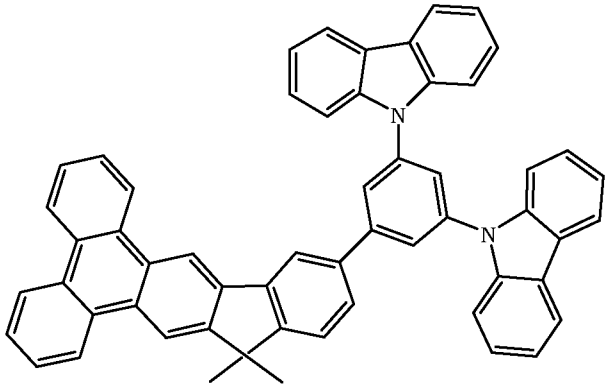

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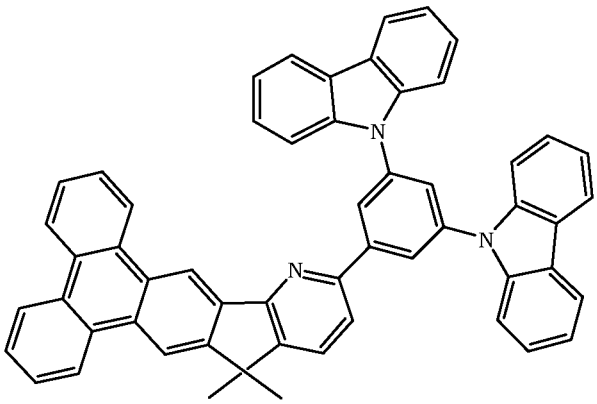

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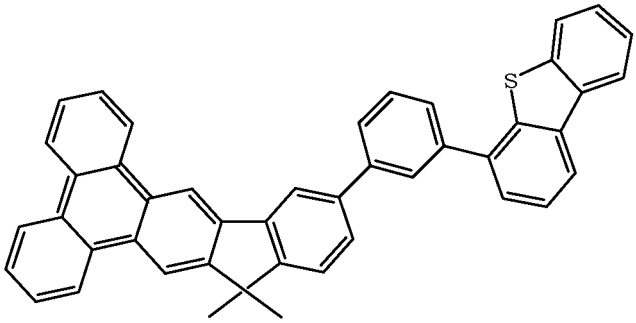

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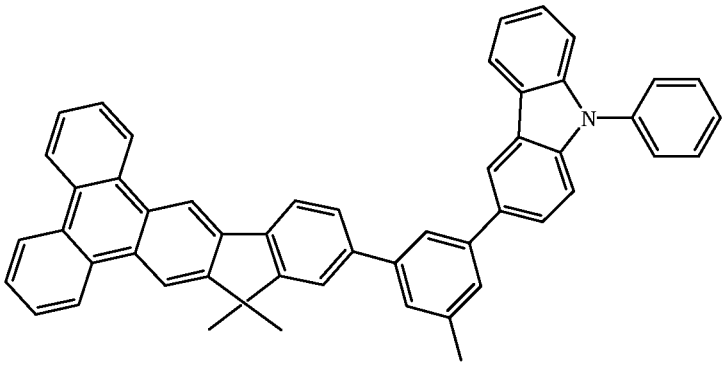

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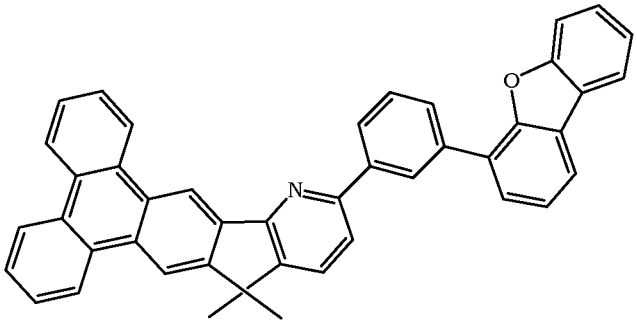

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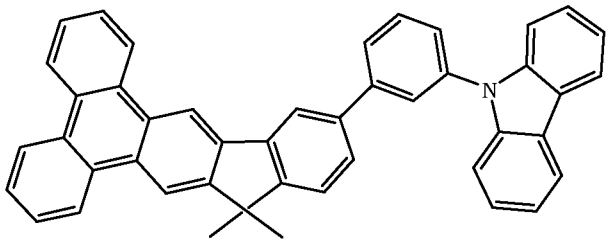

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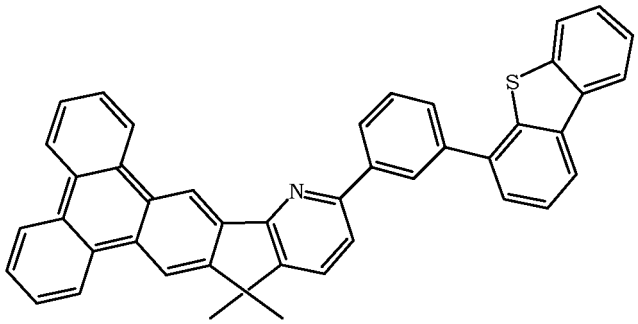

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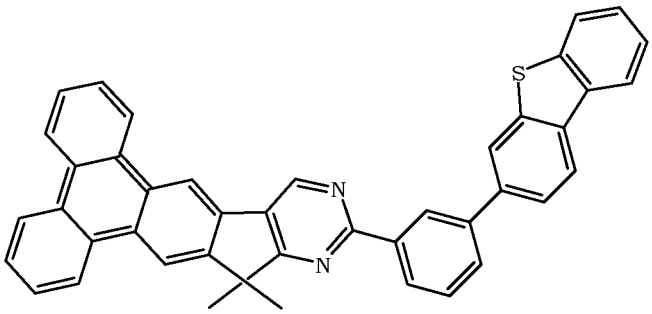

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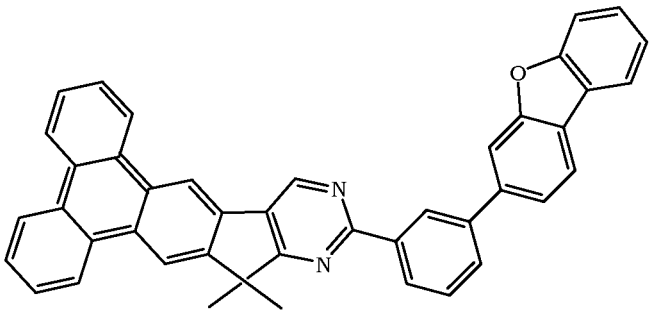


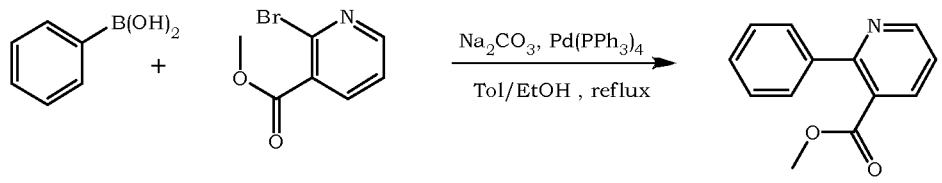
A37

[0018] Detailed preparation for the organic material in the present invention could be clarified by exemplary embodiments, but the present invention is not limited to exemplary embodiments. Intermediate Ia~Ig and EXAMPLE 1~17 show the preparation for some EXAMPLES of the organic material in the present invention. EXAMPLE 18 and 19 show the fabrication of organic EL device and I-V-B, half-life time of organic EL device testing report.

Synthesis of Intermediate Ia

Synthesis of methyl 2-phenylnicotinate

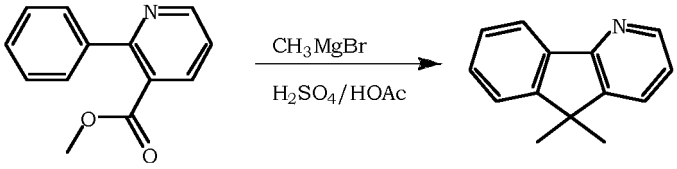
[0019]



[0020] A mixture of methyl 2-bromonicotinate(10.8g, 50mmol), phenylboronic acid(6.1g, 50mmol), 2M Na_2CO_3(100ml, 200mmol), and $Pd(PPh_3)_4$ (1.5g, Immol) was dissolved in 300ml toluene/ 100ml ethanol under N_2. After stirring for 24 h at 80°C, the mixture was allowed to cool to room temperature. The residue was extract using dichloromethane/water, and organic layer was evaporated to dryness. The residue was purified by column chromatography on silica gel to obtained 6.1g of methyl 2-phenylnicotinate. Yield 57.2%.

Synthesis of 5,5-dimethyl-5H-indeno[1,2-b]pyridine

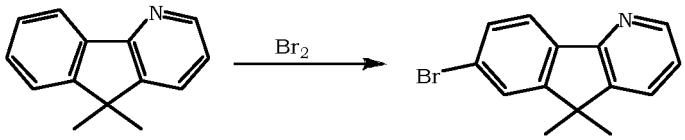
[0021]



[0022] The methyl 2-phenylnicotinate(10.6 g, 50mmol) is dissolved in THF(20ml), followed by adding 35ml of CH_3MgBr(3M in ether). The refluxing reaction is held for overnight then stopped. After extraction with ethyl acetate, drying with anhydrous magnesium sulfate, rotary evaporation to remove solvent, intermediate product is obtained. The intermediate product is then dissolved in mixed solution of acetic acid(100ml) and sulfuric acid(5ml). The refluxing reaction is held for 4 hours then stopped and cooled. After extraction with ethyl acetate, drying with anhydrous magnesium sulfate, rotary evaporation to remove solvent, the residue was purified by column chromatography on silica gel to obtain 3.1g of 5,5-dimethyl-5H-indeno[1,2-b] pyridine (31.8% yield)

Synthesis of 7-bromo-5,5-dimethyl-5H-indeno[1,2-b]pyridine

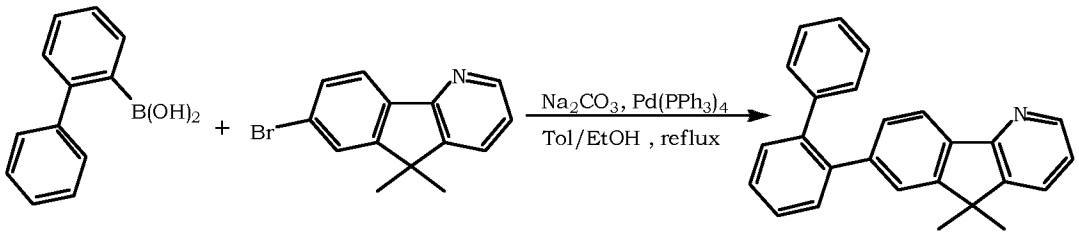
[0023]



[0024] 5,5-dimethyl-5H-indeno[1,2-b]pyridine(3.9g, 20mmol) was dissolved in chloroform(300ml), protected from light and bromine(3.2g, 20mmol) diluted in chloroform(10ml) was added drop wise. The mixture was stirred for 24 hours at room temperature, after which water(600ml) was added, then the precipitated product was filtered off with suction, washed with MeOH and recrystallized from chloroform to give the 7-bromo-5,5-dimethyl-5H-indeno[1,2-b]pyridine 3.7g. Yield 67.5%

Synthesis of 7-(biphenyl-2-yl)-5,5-dimethyl-5H-indeno[1,2-b] pyridine

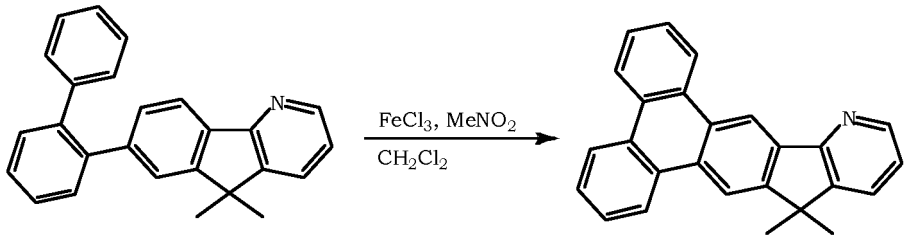
[0025]



[0026] A mixture of 7-bromo-5,5-dimethyl-5H-indeno[1,2-b]- pyridine (10g, 36.5mmol), biphenyl-2-ylboronic acid(7.2g, 36.5mmol), $Pd(PPh_3)_4$(0.43g, 0.368mmol), 2M Na_2CO_3(37ml), 50ml of EtOH and 150ml toluene was degassed and placed under nitrogen, and then heated at 90°C for 24h. After finishing the reaction, the reaction mixture was cool to room temperature. The organic layer was extracted with ethyl acetate and water, dried with anhydrous magnesium sulfate, the solvent was removed and the residue was purified by column chromatography on silica gel to obtain 7-(biphenyl-2-yl)-5,5-dimethyl-5H-indeno[1,2-b]pyridine 8.4g. Yield 66%.

Synthesis of Intermediate Ia

[0027]

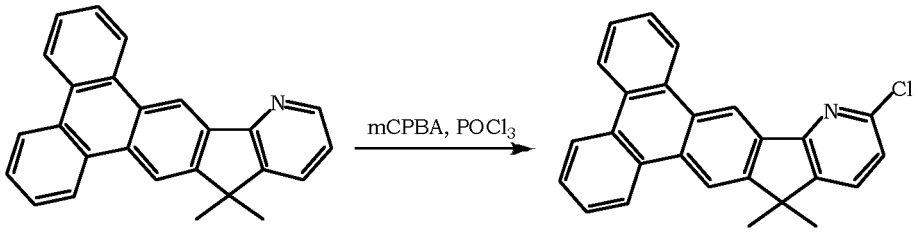


Intermediate Ia

[0028] Under nitrogen condition, 7-(biphenyl-2-yl)-5,5-dimethyl-5H-indeno[1,2-b]-pyridine(3.47g, 10mmol) was dissolved in anhydrous dichloromethane(250 ml), 1.62g(100mmol)Iron(III)chloride was then added, and the mixture was stirred one hour. Methanol 10ml were added to the mixture and the organic layer was separated and the solvent removed in vacuum. The residue was purified by column chromatography on silica gel to obtain 1.4 g of the product. Yield 40%.

Synthesis of Intermediate Ib

[0029]



Intermediate Ib

[0030] 13.82g(40mmol) of intermediate Ia was dissolved in 100ml of chloroform, 9.2g(52mmol) of mCPBA was added to the solution at 25° C, with stirring, and stirred at room temperature for 2 hours. After the reaction, sodium thiosulfate was added to the mixture, and dried over sodium sulfate and filtrated. The filtrate was concentrated and the slurry was washed with chloroform, the crude material was purified by chromatography on silica gel to obtain 5.8g of an N-oxide of Intermediate Ia. Yield 41 %.

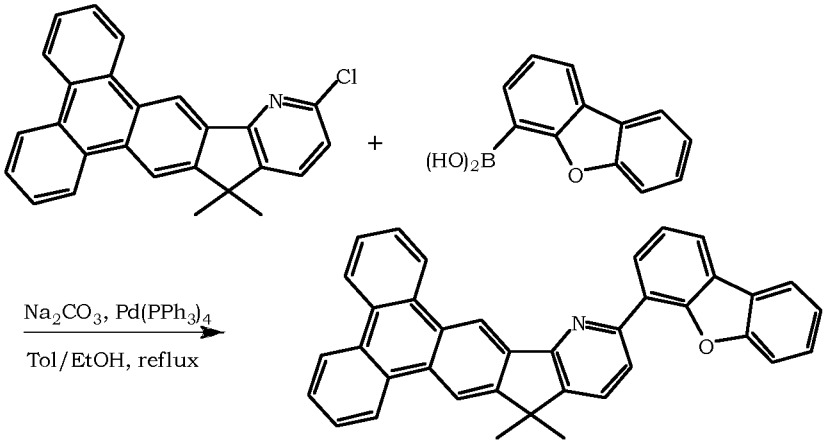
[0031] Subsequently, 15ml of phosphorus oxychloride was added to 5.8g(16mmol) of the above N-oxide, and heated and stirred at 95°C for 10hours. The reaction was concentrated, and then chloroform(200ml) was added to the concentrate. The chloroform solution was added dropwise to a saturated aqueous solution of sodium hydrogen carbonate, and

stirred for 1 hour. The mixture was extracted with chloroform, washed with sat. $NaCl_{(aq)}$, dried over sodium sulfate, and concentrated, the crude material was purified by chromatography on silica gel to give 3.1 g. Yield 51%. ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.75(s, 1H), 8.49~8.44(m, 3H), 8.32~8.28(m, 3H), 8.14~8.06(m, 4H), 7.77(d, J=8.0 Hz, 1H), 1.63(s, 6H).

EXAMPLE 1

Synthesis of Compound A1

[0032]



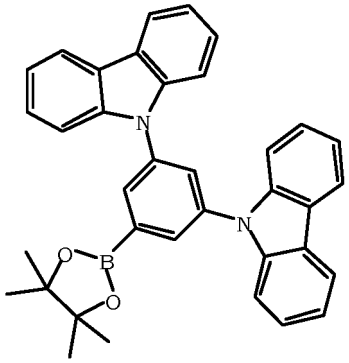
[0033] A three-necked 250ml flask was charged with Intermediate Ib (10mmol), dibenzo[b,d]furan-4-ylboronic acid(10mmol), $Pd(PPh_3)_4$(0.25 g, 0.21 mmol), aqueous Na_2CO_3(2M, 12ml, 24mmol), ethanol(15ml), and toluene(50 ml). The mixture was degassed and refluxed for 24h under nitrogen atmosphere. After being cooled, water(50ml) was added to the mixture. The crude product was collected as a solid powder by filtration and washed with methanol several times to remove impurity. It was dried at 60°C. under vacuum and gave a product in 52.1% yield. MS(m/z, FAB+): 511.2. ^{1}HNMR ($CDCl_3$, 400 MHz): chemical shift (ppm) 9.44(s, 1H), 8.90(m, 2H), 8.12~8.08(m, 4H), 7.92~7.81(m, 6H), 7.42~7.31(m, 5H), 7.10(d, J=8.0 Hz, 1H), 1.76(s, 6H).

EXAMPLE 2

Synthesis of Compound A30

Synthesis of 9,9'-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-phenylene)bis(9H-carbazole)

[0034]



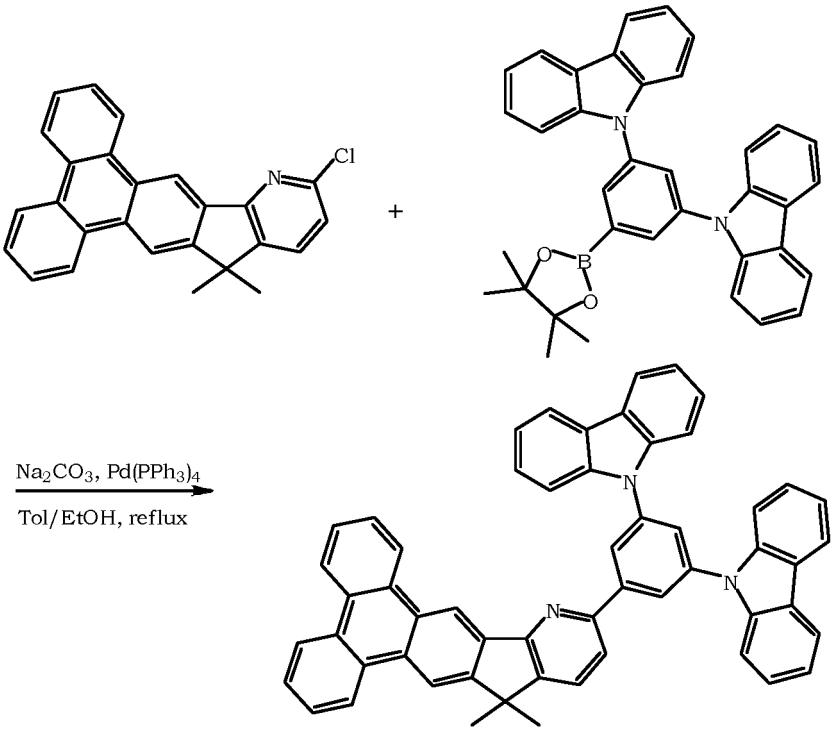
[0035] 1,3-dibromo chlorobenzene (8.11g, 39mmol), carbazole(13.7g, 82mmol), palladium acetate(450mg, 2mmol), t-butyl phosphine(6ml, 1M solution), sodium t-butoxide(15g, 156mmol) and dry o-xylene(250ml) were placed in a four-

necked flask. The mixture was reacted at 125°C for 30 hours under nitrogen. After cooling to room temperature, the reaction solution was poured into water, extracted with chloroform and washed with sat. $NaCl_{(aq)}$. Then, dried over anhydrous magnesium sulfate and the solvent were removed with an evaporator. The residue was purified by column chromatography and 4g of 3,5-di(carbazol-9-yl)chlorobenzene was obtained. Yield 23.2%.

[0036] In a four-necked flask, 3,5-di(carbazol-9-yl)chlorobenzene(4g, 9mmol), bis(pinacolato)diboron(2.4g, 9.4mmol), KOAc(2.5g, 25.8mmol), $Pd_2(dba)_3$(258mg, 0.284mmol), tricyclohexylphosphine(385mg, 1.4mmol) and anhydrous 1,4-dioxane(120ml) were placed. The mixture was reacted for overnight at 80 °C under nitrogen for 16hours. The reaction solution was poured into water, extracted with ethyl acetate and washed with sat. $NaCl_{(aq)}$. Then, dried over anhydrous magnesium sulfate and the solvent was removed with an evaporator. The residue was purified by column chromatography and 1.5g of product was obtained. Yield 32%.

Synthesis of compound A30

[0037]



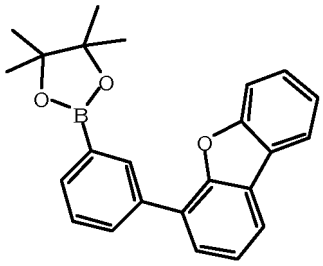
[0038] The synthesis of procedures are the same process with compound A1, the yield of the final product is 56.8%. MS (m/z, FAB+): 751.4 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.54(s, 1H), 8.92(d, J=8.0 Hz, 1H), 8.72~8.64(m, 4H), 8.19~8.13(m, 4H), 8.05(s, 1H), 7.96~7.86(m, 6H), 7.62~7.56(m, 5H), 7.35~7.28(m, 7H), 7.02(s, 1H), 1.66(s, 6H).

EXAMPLE 3

Synthesis of Compound A33

Synthesis of 2-(3-(dibenzo[b,d]furan-4-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

[0039]

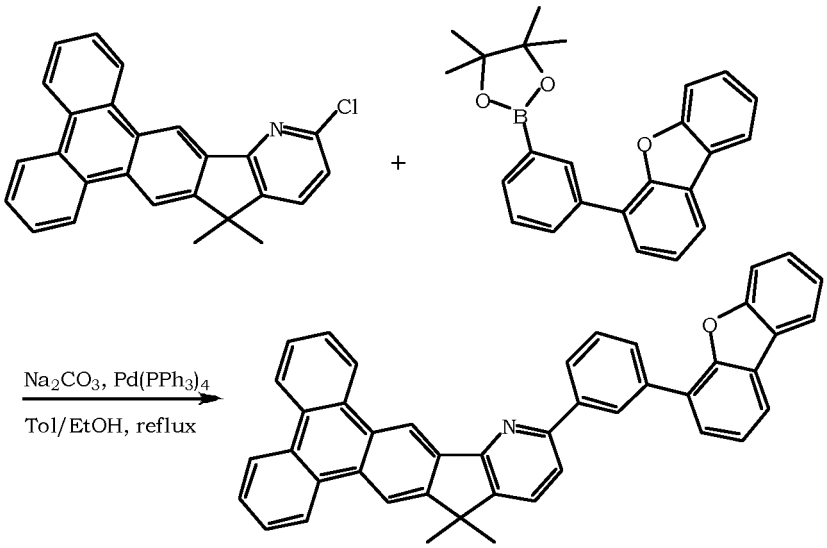


[0040] A mixture of 4-dibenzofuranboronic acid(10g, 47mmol), 1-Bromo-3-iodo-benzene(14.7g, 52mmol), and $Pd(PPh_3)_4$(0.55g) in 250mL of toluene and 150ml of ethanol was heated and degas for 30miniutes, then 2M $Na_2CO_{3(aq)}$(94ml) was added. The reaction mixture refluxed for overnight at 100°C. The mixture was then cooled to room temperature and diluted with 300ml ethyl acetate. The organic layer was washed with 2x300mL portions of water, 2×300ml portions of sat. $NaCl_{(aq)}$, and dried with anhydrous magnesium sulfate. After the solution was concentrated, the residue was purified by column chromatography to afford 4-(3-Bromo-phenyl)-dibenzofuran 8.5g. Yield 56%.

[0041] 5.76 g of 4-(3-Bromo-phenyl)-dibenzofuran(17.8mmol), 5.43g of bis(pinacolato)diboron(21.4mmol), and 0.582g of $Pd(dppf)Cl_2$(4%mol) were dissolved with heating in 100 ml 1,4-dioxane and then treated with KOAc (5.25g, 53.5mmol). The reaction mixture was stirred at reflux for 16hr, cooled to room temperature and diluted with ethyl acetate. The organic layer was washed with sat. $NaCl_{(aq)}$, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuum. The residue was purified by flash column chromatography with to yield the product 4.81g. Yield 73%.

Synthesis of compound A33

[0042]

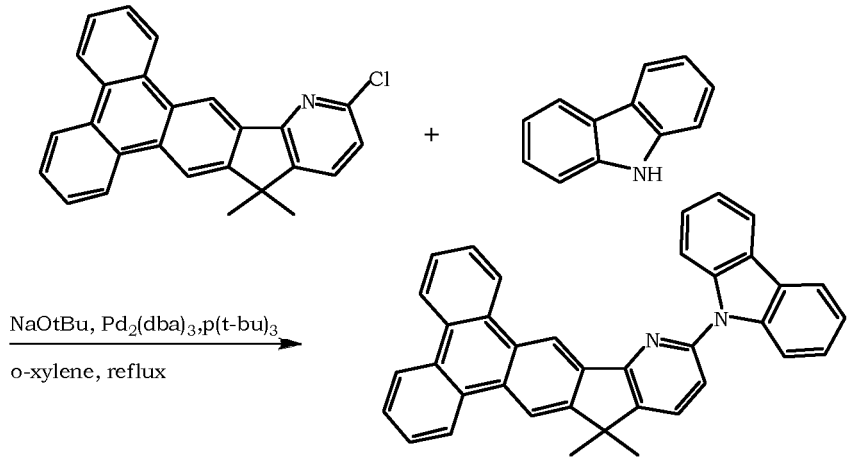


[0043] The synthesis of procedures are the same process with compound A1, the yield of the final product is 52.1%. MS (m/z, FAB+): 587.1 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.47(s, 1H), 8.91(m, 2H), 8.17~8.13(m, 2H), 8.07~8.01(m, 3H), 7.93~7.81(m, 8H), 7.62~7.51(m, 3H), 7.22~7.17(m, 3H), 7.04(d, J=8.0 Hz, 1H), 1.70(s, 6H).

EXAMPLE 4

Synthesis of Compound A13

[0044]

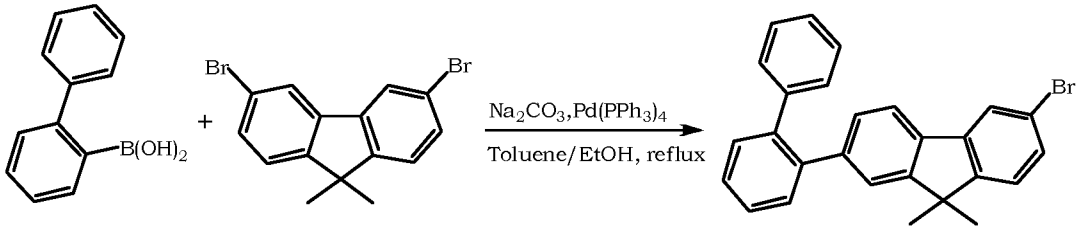


[0045] Carbazole(3.34g, 20mmol), intermediate Ib(3.80g, 10mmol), 18-Crown-6(0.32g, 1.96mmol), potassium carbonate(2.5g, 1.8mmol), $Pd_2(dba)_3$(0.1g, 0.12mmol) and tri-tert-butylphosphine(0.5ml, 0.5mmol, 1.0 M in toluene) were mixed in 50ml of o-xylene. The mixture was stirred under N_2 for 30 minutes, and the mixture was heated to reflux under N_2 for overnight. The o-xylene solution was decanted. The solvent was then evaporated and residue was purified by column chromatography. 2.65g of product was obtained. Yield 52%. MS(m/z, FAB+): 510.3 ^{1}HNMR($CDCl_3$, 400MHz): chemical shift(ppm) 9.04(s, 1H), 8.80~8.76(m, 2H), 8.73~8.66(m, 5H), 7.76~7.63(m, 5H), 7.38~7.31(m, 4H), 7.42~7.28(m, 2H), 7.20(d, J=8 Hz, 1H), 1.67(s, 6H).

Synthesis of intermediate Ic

Synthesis of 2-(biphenyl-2-yl)-6-bromo-9,9-dimethyl-9H-fluorene

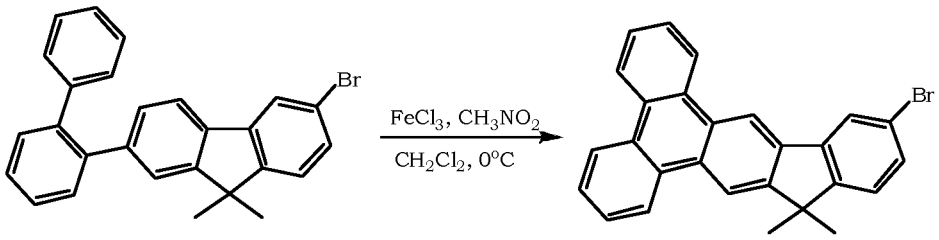
[0046]



[0047] A mixture of 35.2 g(100mmol) of 3,6-dibromo-9,9-dimethyl-9H-fluorene, 21.8 g(110mmol) of biphenyl-2-ylboronic acid, 2.31 g(2mmol) of $Pd(PPh_3)_4$, 75ml of 2M Na_2CO_3, 150ml of EtOH and 300ml toluene was degassed and placed under nitrogen, and then heated at 100°C. for 12h. After finishing the reaction, the mixture was allowed to cool to room temperature. The organic layer was extracted with ethyl acetate and water, dried with anhydrous magnesium sulfate, the solvent was removed and the residue was purified by column chromatography on silica to give product(26.8g, 63.0 mmol, 63%) as a white solid.

Synthesis of intermediate Ic

[0048]

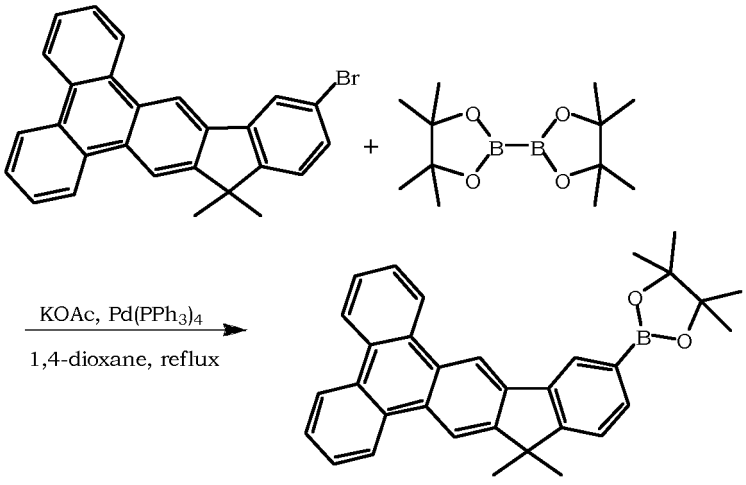


Intermediate Ic

[0049] In a 3000ml three-necked flask that had been degassed and filled with nitrogen, 26.8 g(60mmol) of 2-(biphenyl-2-yl)-7-bromo-9,9-dimethyl-9H-fluorene was dissolved in anhydrous dichloromethane(1500ml), 97.5g(600mmol)Iron(III) chloride was then added, and the mixture was stirred one hour. Methanol 500ml were added to the mixture and the organic layer was separated and the solvent removed in vacuo. The residue was purified by column chromatography on silica(hexane-dichloromethane) afforded a white solid (10.7g, 25.3mmol, 40%). ^{1}HNMR($CDCl_3$, 500 MHz): chemical shift(ppm) 8.93(s, 1H), 8.77~8.71(m, 2H), 8.67~8.65(m, 3H), 8.08(d, J=1.5 Hz, 1H), 7.71~7.64(m, 4H), 7.49(dd, J_1=8.5Hz, J_2=1.5Hz, 1H), 7.37(d, J=8.5Hz, 1H), 1.62(s, 6H).

Synthesis of intermediate Id

[0050]



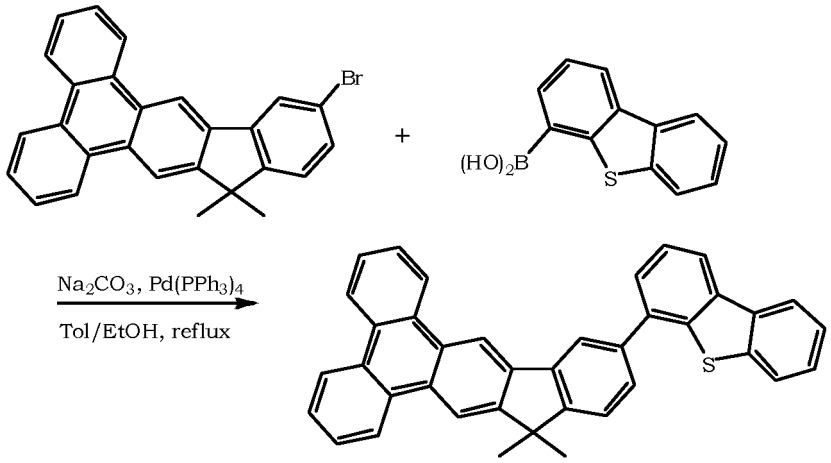
Intermediate Id

[0051] A mixture of 10.7g(25.3mmol) of intermediates Ic, 7.7g(30.3 mmol) of bis(pinacolato)diboron, 0.3g(0.26mmol) of $Pd(PPh_3)_4$, 7.4g(75.4mmol) of potassium acetate, and 500ml 1,4-dioxane was degassed and placed under nitrogen, and then heated at 90°C. for 16h. After finishing the reaction, The mixture was allowed to cool to room temperature. The organic phase separated and washed with ethyl acetate and water. After drying over magnesium sulfate, the solvent was removed in vacuum. The residue was purified by column chromatography on silica to give product(9.5 g, 20.2mmol, 80%) as a light-yellow solid; ^{1}HNMR($CDCl_3$, 500 MHz): chemical shift(ppm) 8.93(s, 1H), 8.77~8.71(m, 2H), 8.67~8.65(m, 3H), 7.88(d, J=1.5 Hz, 1H), 7.71~7.64(m, 4H), 7.29(dd, J_1=8.5Hz, J_2=1.5Hz, 1H), 7.42(d, J=8.5Hz, 1H), 1.62(s, 6H), 1.42(s, 12H).

EXAMPLE 5

Synthesis of Compound A2

[0052]

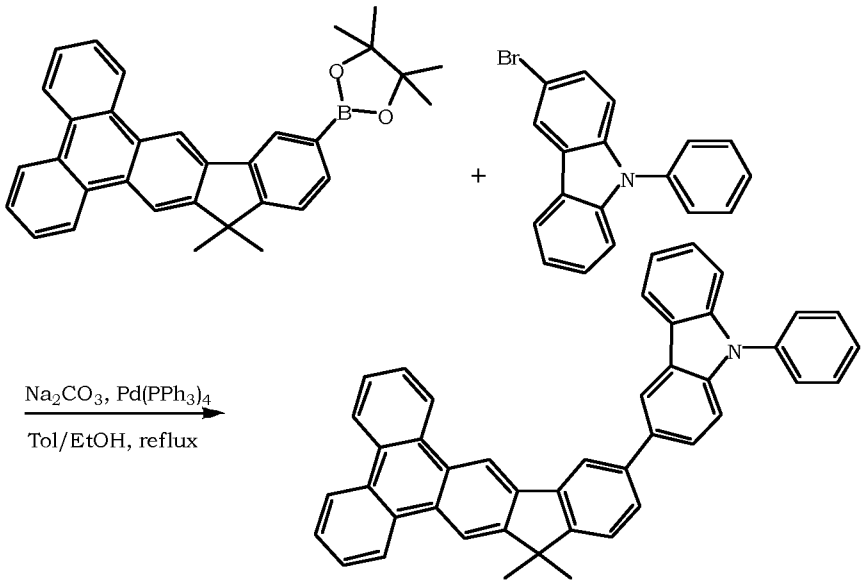


[0053] A three-necked 250ml flask was charged with intermediate Ic 4.2g(10mmol), dibenzo[b,d]thiophen-4-ylboronic acid 2.3g(10mmol), $Pd(PPh_3)_4$(0.25g, 0.21mmol), aqueous Na_2CO_3 (2M, 12ml, 24mmol), ethanol(15ml), and toluene (50ml). The mixture was degassed and refluxed for 24h under nitrogen atmosphere. After being cooled, water(50ml) was added to the mixture. The crude product was collected as a solid powder by filtration and washed with methanol several times to remove impurity. The residue was purified by column chromatography on silica(hexane-dichloromethane) afforded a white solid (2.1g, 40%). MS (m/z, FAB+): 526.2 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.94(s, 1H), 8.80(m, 2H), 8.62~8.51(m, 4H), 7.92~7.84(m, 6H), 7.55~7.45(m, 5H), 7.29(d, J=8.0 Hz, 1H), 1.69(s, 6H).

EXAMPLE 6

Synthesis of Compound A12

[0054]



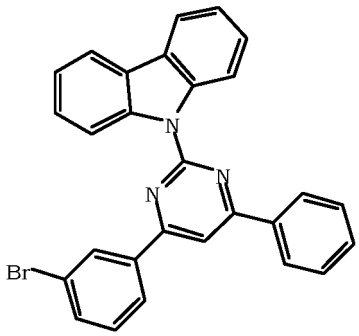
[0055] A mixture of 4.4g(10mmol) of intermediate Id, 3.2g(10mmol) of 3-bromo-9-phenyl-9H-carbazole, 0.23g(0.2mmol) of tetrakis(triphenyl phosphine)palladium, 15ml of 2M Na_2CO_3, 20ml of EtOH and 40ml toluene was degassed and placed under nitrogen, and then heated at 90°C overnight. After finishing the reaction, the mixture was allowed to cool to room temperature. Than 100ml of MeOH was added, while stirring and the precipitated product was filtered off with suction. To give 3.7g(yield63%) of yellow product which was recrystallized from toluene. MS(m/z, FAB+): 585.3 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.96(s, 1H), 8.81(d, J=8 Hz, 1H), 8.76(d, J=8 Hz, 1H), 8.67~8.60(m, 4H), 7.73~7.66(m, 6H), 7.53~7.43(m, 10H), 7.21~7.16(m, 2H), 1.66(s, 6H).

EXAMPLE 7

Synthesis of Compound A20

Synthesis of 9-(4-(3-bromophenyl)-6-phenylpyrimidin-2-yl)-9H-carbazole

[0056]



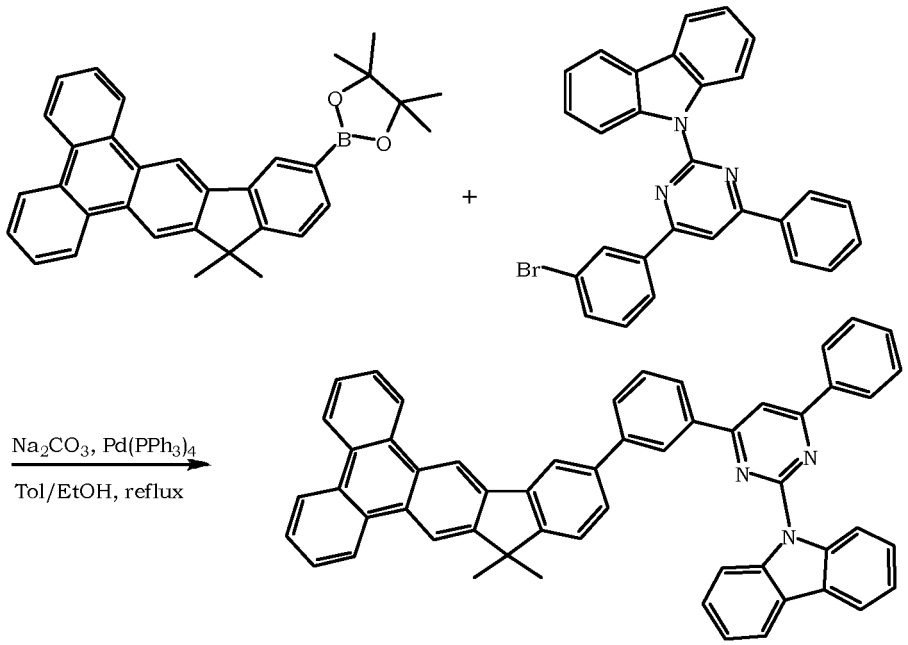
[0057] A mixture of 4,6-diiodo-2-chloropyrimidine(18.3g, 50mmol), phenylboronic acid(6.1 g, 50mmol), K_2CO_3(13.8g, 100mmol), and $Pd(PPh_3)_4$ (1.16g, 1mmol) was dissolved in 500ml 1,4-dioxane/20ml H_2O under N_2. After stirring for 24 h at 80°C, the mixture was allowed to cool to room temperature. The solid was removed by filtration, and the filtrate was evaporated to dryness. The residue was purified by column chromatography on silica gel to obtained 8.3g of 2-chloro-4-iodo-6-phenylpyrimidine. Yield 52.3%

[0058] A mixture of 2-chloro-4-iodo-6-phenylpyrimidine(8.3g, 26.2 mmol), 3-bromo-phenylboronic acid(3.2 g, 26.2mmol), K_2CO_3(7.2g, 52.4mmol), and $Pd(PPh_3)_4$(0.58g, 0.5mmol) was dissolved in 200ml 1,4-dioxane/ 10ml H_2O under N2. After stirring for 24 h at 80°C, the mixture was allowed to cool to room temperature. The solid was removed by filtration, and the filtrate was evaporated to dryness. The residue was purified by column chromatography on silica gel to obtained 4.1g of 4-(3-bromophenyl)-2-chloro-6-phenyl-pyrimidine. Yield 45.2%

[0059] A mixture of 4-(3-bromophenyl)-2-chloro-6-phenyl-pyrimidine (4.1g, 11.9mmol), carbazole(2.2g, 13mmol), tri-tert-butylphosphonium tetra fluoroborate(0.7g, 2.4mmole) and $Pd_2(dba)_3$(0.55g, 5mol%) were dissolved in 300ml of o-xylene and 2.9g of sodium-tert-butoxide, under N_2. The resulting solution was heated to reflux for overnight. After cooled to room temperature, the residue was extract for 3 times using CH_2Cl_2/water. The organic layer was collected and evaporated. The resulting crude product was purified by chromatography to obtained 2.6g of product. Yield 45.9%.

Synthesis of compound A20

[0060]



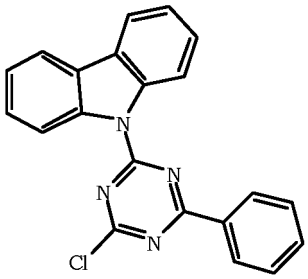
[0061] The synthesis of procedures are the same process with compound A12, the yield of the final product is 48.4%. MS(m/z, FAB+): 739.3 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.14(s, 1H), 8.86(d, J=8 Hz, 1H), 8.80(d, J=8 Hz, 1H), 8.73(s, 1H), 8.63~8.48(m, 6H), 7.84~7.67(m, 13H), 7.42~7.28(m, 8H), 1.66(s, 6H).

EXAMPLE 8

Synthesis of Compound A23

Synthesis of 9-(4-chloro-6-phenyl-1,3,5-triazin-2-yl)-9H-carbazole

[0062]

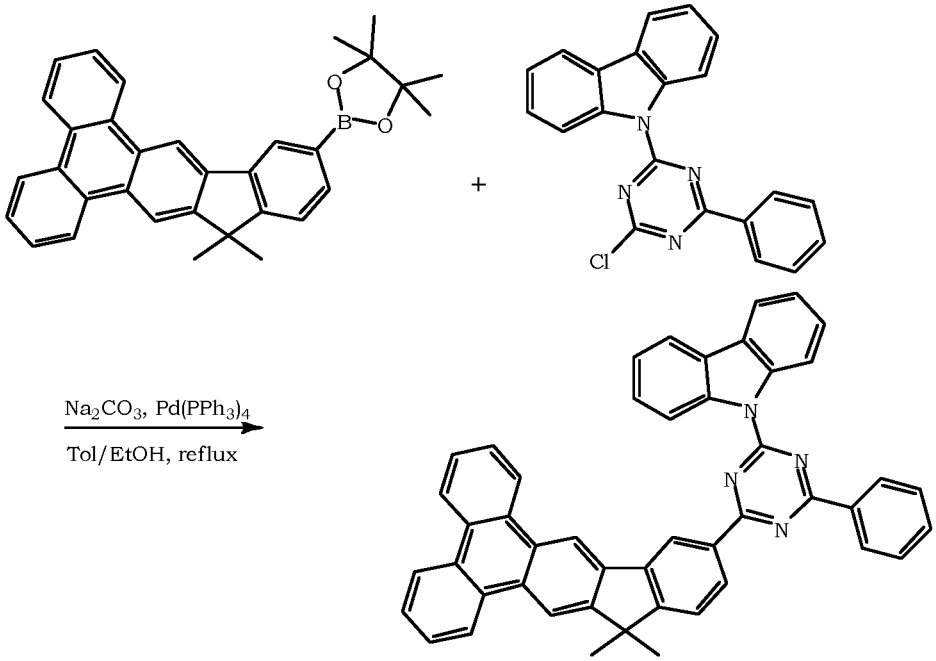


[0063] 10g(54mmol) of cyanuric chloride was added 50 ml of dry THF, then 54 ml of phenylmagnesium bromide(1.0mol in THF) was added dropwise at 0°C, and the mixture was stirred at 0°C for 3hours. The reaction solution were added 50ml of water and 100ml of toluene, the organic layer was dried over anhydrous magnesium sulfate, and the solvent was distilled off under reduced pressure. The solid thus washed with hexane and 6g of 2,4-dichloro-6-phenyl-1,3,5-triazine was obtained. Yield 49.2%.

[0064] Under a N_2 condition, 80ml of THF was added to 3.9g(102mmol) of sodium hydride(62.2% dispersion in oil) and stirred at room temperature for 30 minutes. To the suspension thus obtained was added a solution of 16.5g (96mmol) of carbazole in DMF(100ml), the reaction mixture was stirred at room temperature for 1 hour. The resulting suspension was added 20.3g(90 mmol) of 2,4-dichloro-6-phenyl-1,3,5-triazine and stirred at 60°C. for 40 minutes. The reaction mixture was cooled to room temperature, 300ml of water was added with stirring, and the precipitated solid was collected by filtration. The solid was purified by silica gel column chromatography to obtained 14g of product. Yield 43.6%.

Synthesis of compound A23

[0065]



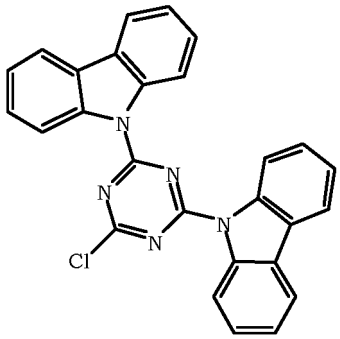
[0066] The synthesis of procedures are the same process with compound A12, the yield of the final product is 48.4%. MS(m/z, FAB+): 664.3.^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.96(s, 1H), 8.83(d, J=8Hz, 1H), 8.74(d, J=8Hz, 1H), 8.75~8.57(m, 10H), 7.78~7.59(m, 4H), 7.44~7.23(m, 7H), 7.16~7.14(m, 2H), 1.66(s, 6H).

EXAMPLE 9

Synthesis of Compound A27

Synthesis of 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole)

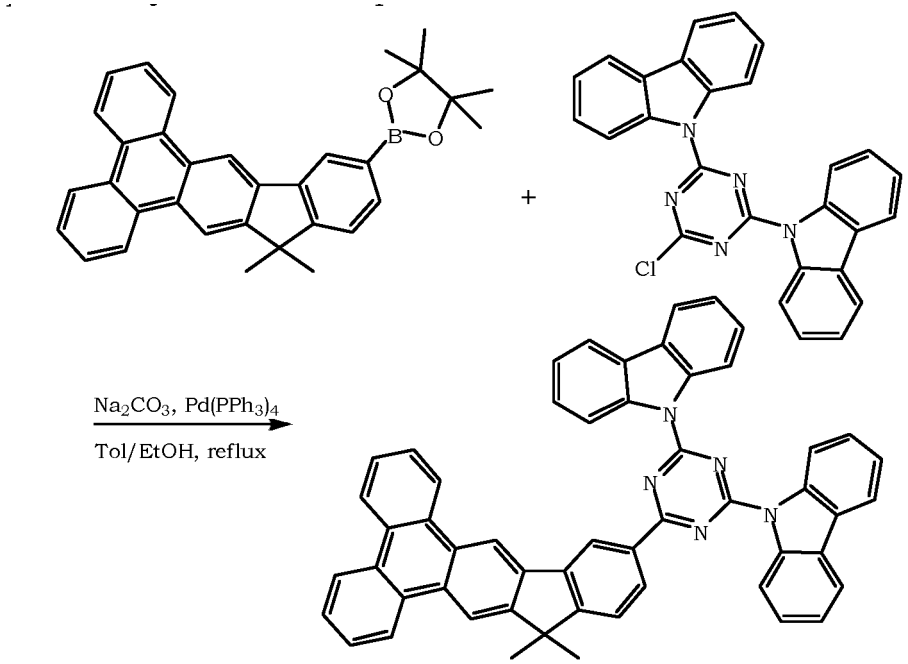
[0067]



[0068] Under N_2, carbazole (28.4g, 170mmol) was dissolved in 800ml of dry THF in a 4-neck round-bottom flask. n-Buthyllithium(1.6M in hexane solution)(100ml, 160mmol) was added dropwise to the carbazole solution and the mixture was stirred for 15 minutes. In another three-necked, round-bottom flask, cyanuric chloride(14.8g, 80mmol) was dissolved in 400ml of dry THF in an N_2 atmosphere. The carbazole lithium solution was added dropwise to the cyanuric chloride solution using a transfer canula within 30 minutes. The reaction mixture was refluxed for 6h. After the solution was cooled to room temperature, 500ml of water was added. The product was filtered off, washed with water, hexane, and diethyl ether and further purified by hot filtration from ethanol. 20g of product was obtained. Yield 56.1 %.

Synthesis of compound A27

[0069]

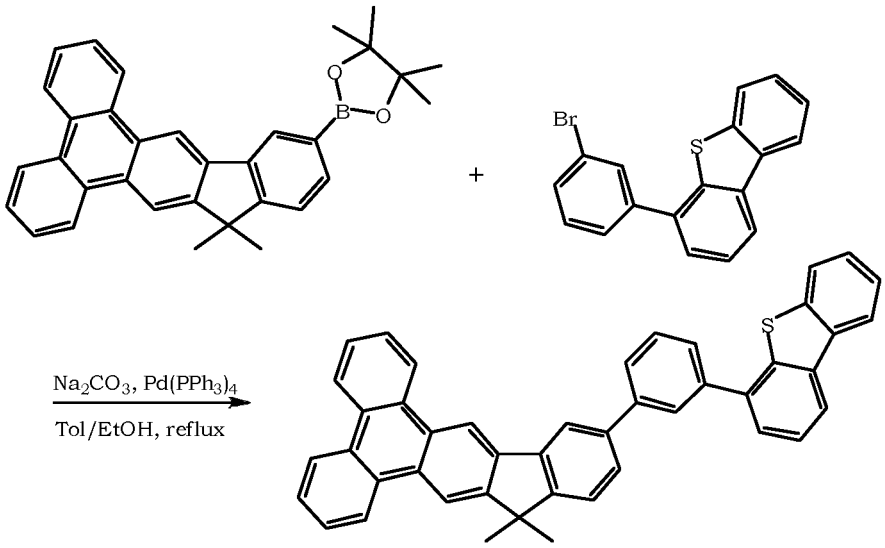


[0070] The synthesis of procedures are the same process with compound A12, the yield of the final product is 52.2%. MS(m/z, FAB+): 753.4 .^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.04(s, 1H), 8.84(d, J=8Hz, 1H), 8.82(d, J=8Hz, 1H), 8.69~8.58(m, 8H), 8.07~8.02(m, 6H), 7.76~7.67(m, 6H), 7.40~7.36(m, 3H), 7.14~7.08(m, 3H), 1.62(s, 6H).

EXAMPLE 10

Synthesis of Compound A31

[0071]



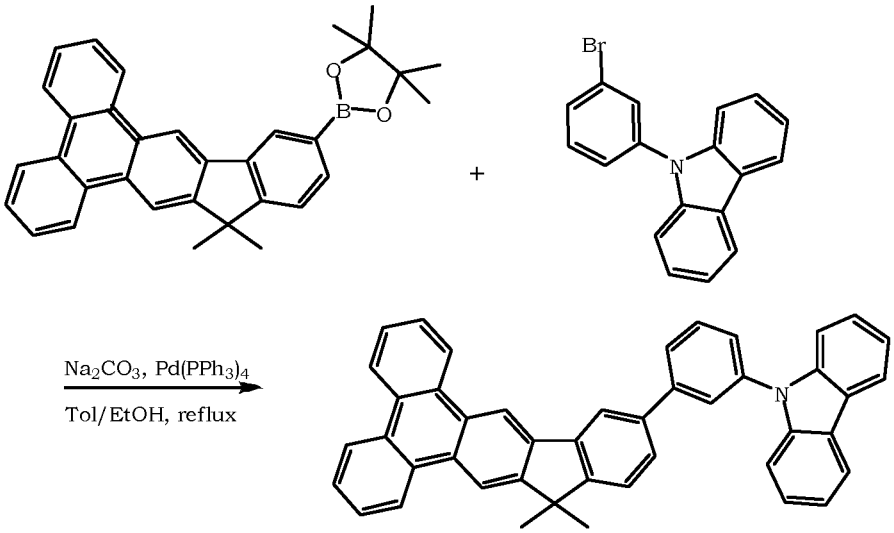
[0072] The synthesis of procedures are the same process with compound A12, the yield of the final product is 41%. MS(m/z, FAB+): 602.4.^{1}H NMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.94(s, 1H), 8.80(d, J=8Hz, 1H), 8.74(d, J=8Hz,

1H), 8.72~8.64(m, 7H), 8.52~8.49(m, 2H), 7.78~7.59(m, 6H), 7.42~7.28(m, 5H), 7.16(d, J=8Hz, 1H), 1.67(s, 6H).

EXAMPLE 11

Synthesis of Compound A34

[0073]

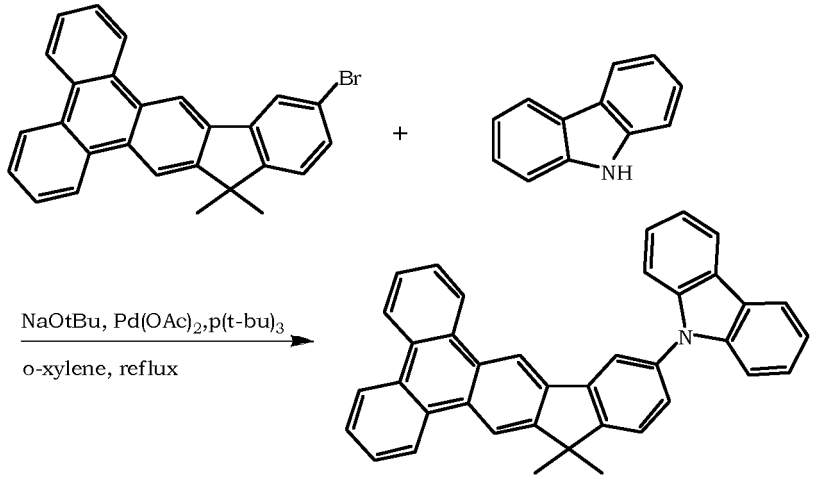


[0074] The synthesis of procedures are the same process with compound A12, the yield of the final product is 47%. MS (m/z, FAB+): 585.8. ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.93(s, 1H), 8.81(d, J=8Hz, 1H), 8.74(d, J=8Hz, 1H), 8.76~8.64(m, 7H), 7.78~7.59(m, 7H), 7.44~7.23(m, 6H), 7.16~7.14(m, 2H), 1.66(s, 6H).

EXAMPLE 12

Synthesis of Compound A17

[0075]

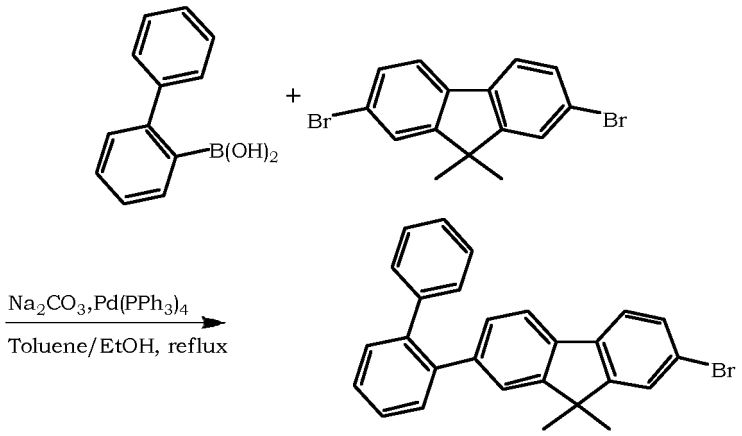


[0076] The synthesis of procedures are the same process with compound A13, the yield of the final product is 47%. MS(m/z, FAB+): 509.3.^{1}H NMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.03(s, 1H), 8.83(d, J=8 Hz, 1H), 8.73(d, J=8 Hz, 1H), 8.63~8.53(m, 6H), 8.23~8.14(m, 6H), 7.79~7.65 (m, 4H), 7.12~7.08(m, 2H), 1.76(s, 6H).

Synthesis of intermediate Ie

Synthesis of 2-(biphenyl-2-yl)-7-bromo-9,9-dimethyl-9H-fluor-ene

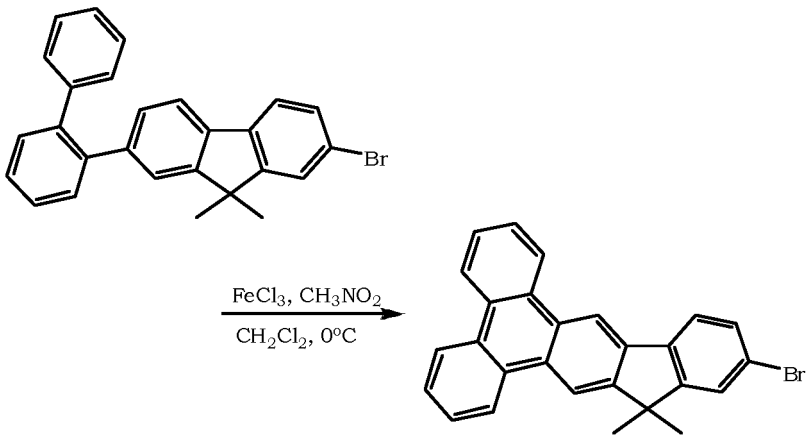
[0077]



[0078] A mixture of 35.2g (100mmol) of 2,7-dibromo-9,9-dimethyl-9H-fluorene, 21.8g (110mmol) of biphenyl-2-ylboronic acid, 2.31g (2mmol) of $Pd(PPh_3)_4$, 75ml of 2M Na2CO3, 150ml of EtOH and 300ml toluene was degassed and placed under nitrogen, and then heated at 100°C. for 12 h. After finishing the reaction, the mixture was allowed to cool to room temperature. The organic layer was extracted with ethyl acetate and water, dried with anhydrous magnesium sulfate, the solvent was removed and the residue was purified by column chromatography on silica to give product (26.8g, 63.0 mmol, 63%) as a white solid.

Synthesis of 12-bromo-10,10-dimethyl-10H-indeno[2,1-b] triphenylene

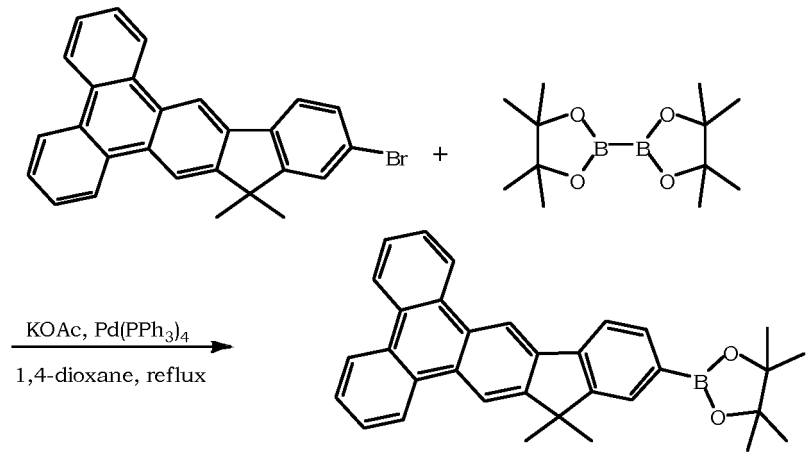
[0079]



[0080] In a 3000 ml three-necked flask that had been degassed and filled with nitrogen, 26.8g(60mmol) of 2-(biphenyl-2-yl)-7-bromo-9,9-dimethyl-9H-fluorene was dissolved in anhydrous dichloromethane(1500ml), 97.5g(600mmol) Iron(III) chloride was then added, and the mixture was stirred one hour. Methanol 500ml were added to the mixture and the organic layer was separated and the solvent removed in vacuo. The residue was purified by column chromatography on silica(hexane-dichloromethane) afforded a white solid (10.7g, 25.3mmol, 40%). ^1H NMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.95(s, 1H), 8.79~8.74(m, 2H), 8.69~8.68(m, 3H), 7.84(d, J=8.0 Hz, 1H), 7.72~7.65(m, 5H), 7.57(d, J=8.0 Hz, 1H), 1.66(s, 6H).

Synthesis of intermediate Ie

[0081]



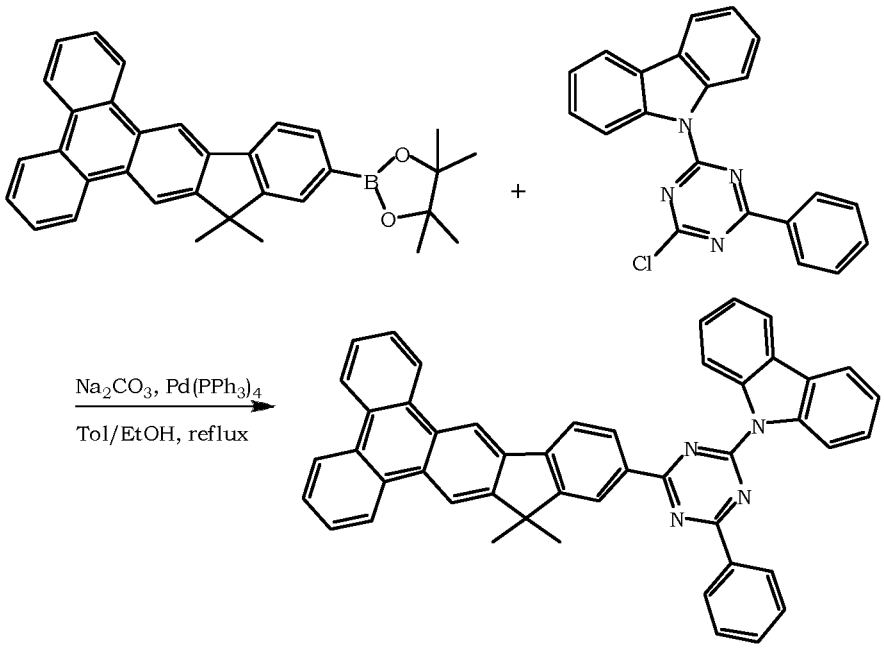
Intermediate Ie

[0082] A mixture of 10.7g(25.3mmol) of 12-bromo-10,10-dimethyl-10H-indeno-[1,2-b]triphenylene, 7.7g(30.3mmol) of bis(pinacolato)diboron, 0.3g (0.26mmol) of $Pd(PPh_3)_4$, 7.4g(75.4mmol) of potassium acetate, and 300 ml 1,4-dioxane was degassed and placed under nitrogen, and then heated at 90°C. for 16h. After finishing the reaction, the mixture was allowed to cool to room temperature. The organic phase separated and washed with ethyl acetate and water. After drying over magnesium sulfate, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (hexane-dichloromethane) to give product (9.5g, 20.2mmol, 80%) as a light-yellow solid; ^{1}HNMR(CDCl3, 400 MHz): chemical shift(ppm) 9.03(s, 1H), 8.81(d, J=7.84 Hz, 1H), 8.77(d, J=7.88 Hz, 1H), 8.70~8.67(m, 3H), 8.02~7.93 (m, 3H), 7.71~7.67(m, 4H), 1.69(s, 6H), 1.42(s, 12H)

EXAMPLE 13

Synthesis of Compound A21

[0083]



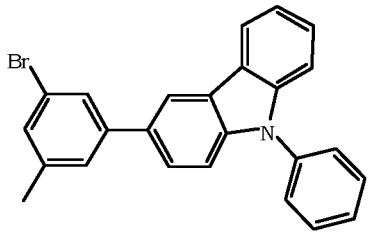
[0084] The synthesis of procedures are the same process with compound A23, the yield of the final product is 61%. MS (m/z, FAB+): 664.3. ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.97(s, 1H), 8.82(d, J=8Hz, 1H), 8.75 (d, J=8Hz, 1H), 8.73~8.55(m, 10H), 7.73~7.55(m, 4H), 7.34~7.20(m, 7H), 7.15~7.10(m, 2H), 1.65(s, 6H).

EXAMPLE 14

Synthesis of Compound A32

Synthesis of 3-(3-bromo-5-methylphenyl)-9-phenyl-9H-carbazole

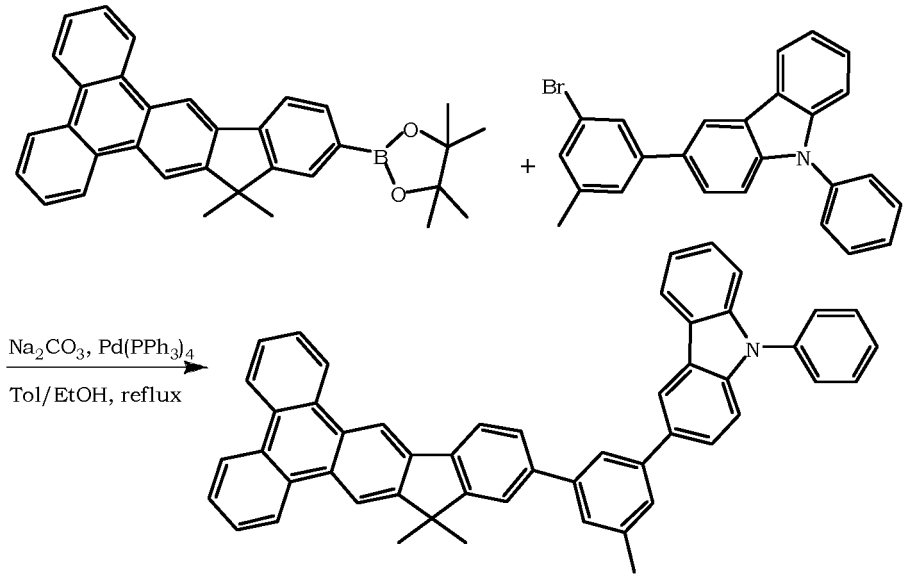
[0085]



[0086] Under N_2 condition, A mixture of 3-(N-phenylcarbazole)boronic acid(20mmol, 5.74g), 3-bromo-5-methyl-iodo-benzene(24mmol, 7.13g), 2M $Na_2CO_{3(aq)}$(20ml, 40mmol), ethanol(40ml) and toluene(40ml), $Pd(PPh_3)_4$(1.16g, 1mmol) was added and refluxed for 16 hours. After completion of the reaction, the mixture was extracted with ethyl acetate in a separating funnel, dried over anhydrous magnesium sulfate, filtered and concentrated. The concentrate was purified by silica gel column chromatography to give 5g of product. Yield 61%.

Synthesis of compound A32

[0087]

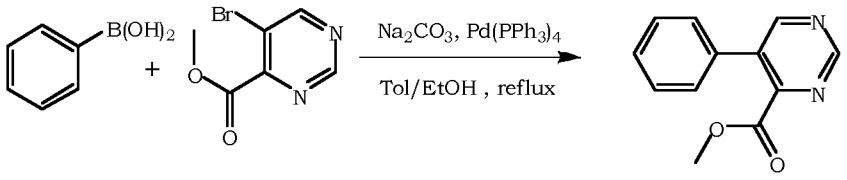


[0088] The synthesis of procedures are the same process with compound A12, the yield of the final product is 45%. MS(m/z, FAB+): 675.4. ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 8.96(s, 1H), 8.82(d, J=8 Hz, 1H), 8.75(d, J=8 Hz, 1H), 8.73~8.61(m, 8H), 8.23~8.15(m, 4H), 7.73~7.55(m, 6H), 7.34~7.20(m, 5H), 7.15~7.10(m, 2H), 2.24(s, 3H), 1.65(s, 6H).

Synthesis of Intermediate If

Synthesis of methyl 5-phenylpyrimidine-4-carboxylate

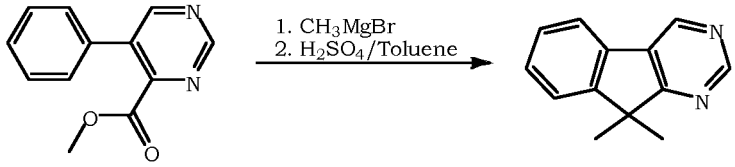
[0089]



[0090] A mixture of methyl 5-bromopyrimidine-4-carboxylate(13g, 60mmol), phenylboronic acid(7.3g, 60mmol), 2M $Na_2CO_{3(aq)}$(120ml, 240mmol), and $Pd(PPh_3)_4$(1.8g, 1.2mmol) was dissolved in 400ml toluene/ 130ml ethanol under N_2. After stirring for 24h at 80°C, the mixture was allowed to cool to room temperature. The residue was extract using dichloromethane/water, and organic layer was evaporated to dryness. The residue was purified by column chromatography on silica gel to obtained 5.9g of methyl 5-phenylpyrimidine-4-carboxylate. Yield 45.4%.

Synthesis of 9,9-dimethyl-9H-indeno[2,1-d]pyrimidine

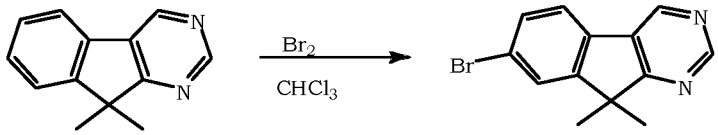
[0091]



[0092] Methyl 5-phenylpyrimidine-4-carboxylate(8.6g, 40mmol) is dissolved in dry THF(160ml), followed by adding 30ml of CH_3MgBr(3M in ether). The reaction is reflux for overnight then stopped. After extraction with ethyl acetate, drying with anhydrous magnesium sulfate, rotary evaporation to remove solvent, intermediate product is obtained. The intermediate product is then dissolved in mixed solution of acetic acid(100mL) and sulfuric acid (5ml). The refluxing reaction is held for 4 hours then stopped and cooled. After extraction with ethyl acetate, drying with anhydrous magnesium sulfate, rotary evaporation to remove solvent, the residue was purified by column chromatography on silica gel to obtain 2.5g of 9,9-dimethyl-9H-indeno [2,1-d]pyrimidine. Yield 32%.

Synthesis of 7-bromo-9,9-dimethyl-9H-indeno[2,1-d] pyrimidine

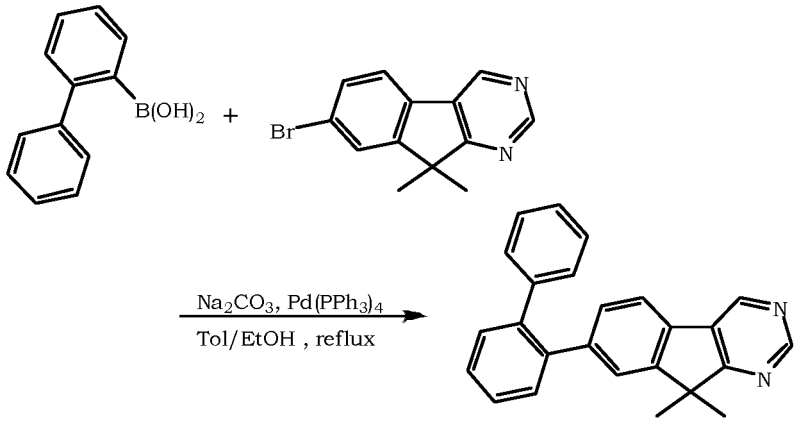
[0093]



[0094] 9,9-dimethyl-9H-indeno[2,1-d]pyrimidine(5.9g, 30mmol) was dissolved in chloroform (300ml), protected from light and bromine(4.8g, 30mmol) diluted in chloroform(10ml) was added drop wise. The mixture was stirred for 24 hours at room temperature, after which water(600ml) was added, then the precipitated product was filtered off with suction , washed with MeOH and recrystallized from chloroform to give the 7-bromo-9,9-dimethyl-9H-indeno[2,1-d]pyrimidine 5.4g. Yield 66%

Synthesis of 7-(biphenyl-2-yl)-9,9-dimethyl-9H-indeno[2,1-d] pyrimidine

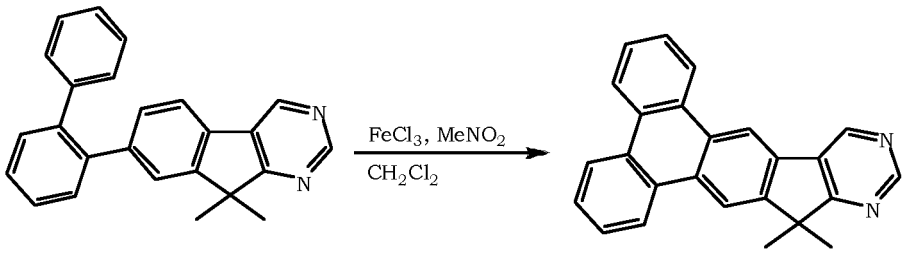
[0095]



[0096] A mixture of 7-bromo-9,9-dimethyl-9H-indeno[2,1-d]pyrimidine (5g, 18.3mmol), biphenyl-2-ylboronic acid(3.6g, 18.3mmol), $Pd(PPh_3)_4$(0.22g, 0.184mmol), 2M Na_2CO_3(19ml), 30ml of EtOH and 100ml toluene was degassed and placed under nitrogen, and then heated at 90°C for 24h. After finishing the reaction, the reaction mixture was cool to room temperature. The organic layer was extracted with ethyl acetate and water, dried with anhydrous magnesium sulfate, the solvent was removed and the residue was purified by column chromatography on silica gel to obtain 7-(biphenyl-2-yl)-9,9-dimethyl-9H-indeno[2,1-d]pyrimidine 3.5g. Yield 56%.

Synthesis of Intermediate If

[0097]

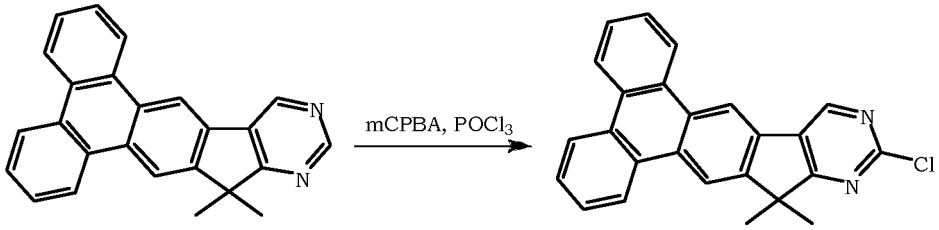


[0098] Under nitrogen condition, 7-(biphenyl-2-yl)-5,5-dimethyl-5H-indeno[1,2-b]-pyridine(3.48g, 10mmol) was dissolved in anhydrous dichloromethane(250ml), 1.62g(100mmol) Iron(III) chloride was then added, and the mixture was stirred one hour. Methanol 10ml were added to the mixture and the organic layer was separated and the solvent removed in vacuum. The residue was purified by column chromatography on silica gel to obtain 1.35g of the product. Yield 39%.

Synthesis of Intermediate Ig

Synthesis of Intermediate Ig

[0099]



Intermediate Ig

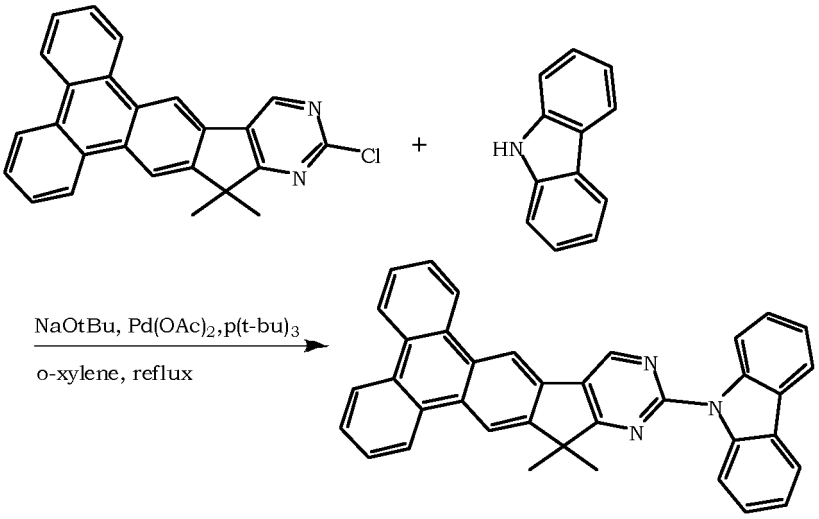
[0100] 5.0g(14.4mmol) of intermediate If was dissolved in 100ml of chloroform, 3.2g(18.7mmol) ofmCPBAwas added to the solution at 25°C. with stirring, and stirred at room temperature for 2hours. After the reaction, sodium thiosulfate was added to the mixture, and dried over sodium sulfate and filtrated. The filtrate was concentrated and the slurry was washed with chloroform, the crude material was purified by chromatography on silica gel to obtain 3.9g of an N-oxide of intermediate. Yield 74.5%.

[0101] Subsequently, 20ml of phosphorus oxychloride was added to 3.9g(10.7mmol) of the above N-oxide, and heated and stirred at 95°C for 10hours. The reaction was concentrated, and then chloroform(200ml) was added to the concentrate. The chloroform solution was added dropwise to a saturated aqueous solution of sodium hydrogen carbonate, and stirred for 1 hour. The mixture was extracted with chloroform, washed with sat. $NaCl_{(aq)}$, dried over sodium sulfate, and concentrated, the crude material was purified by chromatography on silica gel to give 1.8 g. Yield 43.9%, ^{1}HNMR($CDCl_3$, 400MHz): chemical shift(ppm) 8.99(s, 1H), 8.90(d, J=8.0 Hz, 1H), 8.79~8.72 (m, 4H), 7.80(m, 1H), 7.72~7.60(m, 4H), 1.65(s, 6H).

EXAMPLE 15

Synthesis of Compound A16

[0102]

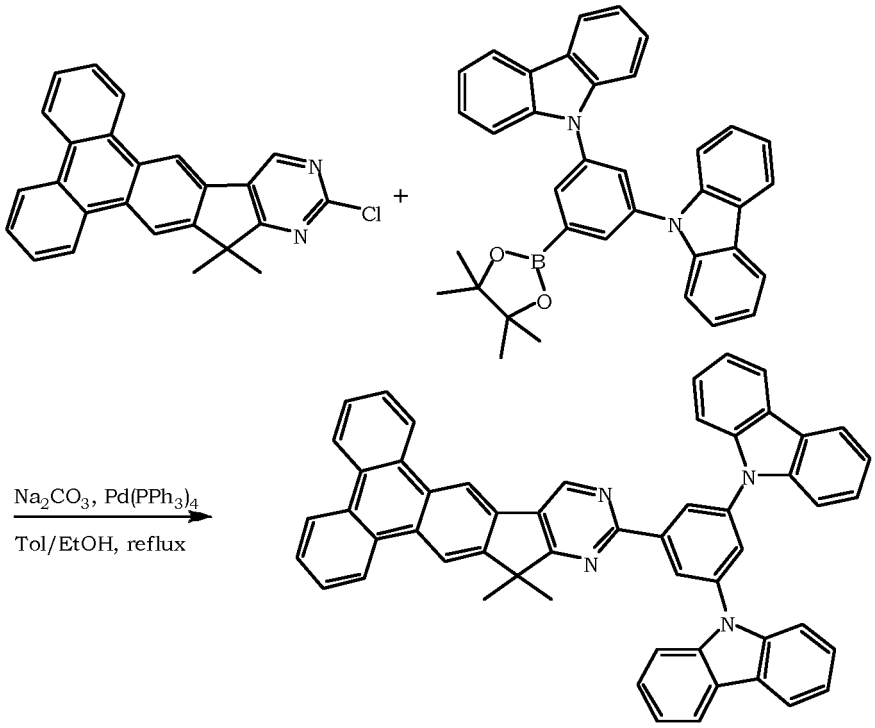


[0103] The synthesis of procedures are the same process with compound A13, the yield of the final product is 61%. MS(m/z, FAB+): 511.6. ^{1}HNMR ($CDCl_3$, 400 MHz): chemical shift(ppm) 9.12(s, 1H), 9.05(s, 1H), 8.91(d, J=8 Hz, 1H), 8.82(d, J=8 Hz, 1H), 8.73~8.66(m, 5H), 8.13~7.98(m, 4H), 7.68~7.59(m, 4H), 7.20~7.17(m, 2H), 1.66(s, 6H).

EXAMPLE 16

Synthesis of Compound A28

[0104]

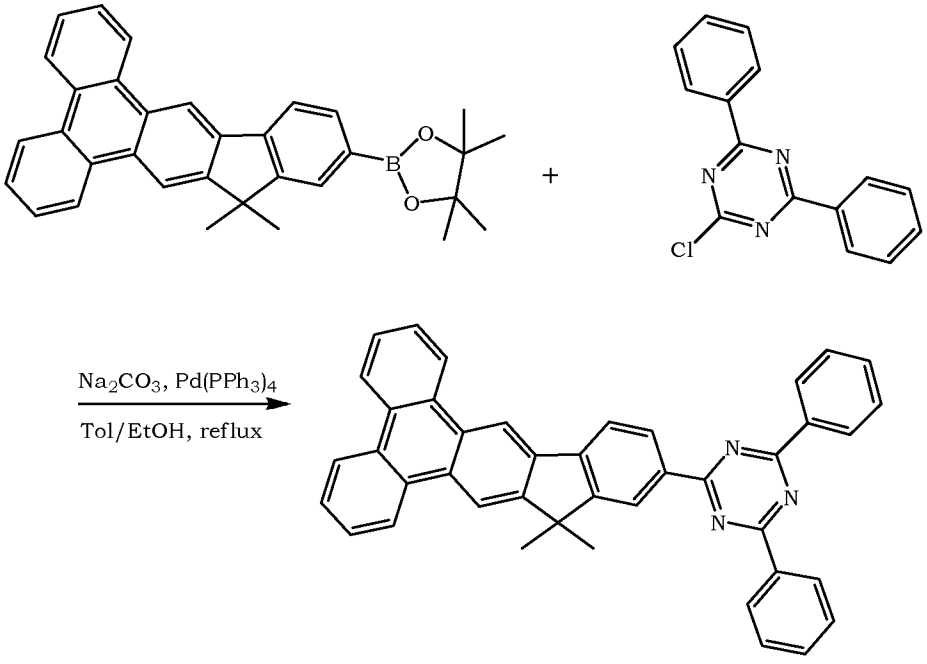


[0105] The synthesis of procedures are the same process with compound A1, the yield of the final product is 36%. MS (m/z, FAB+): 752.3. ^{1}HNMR ($CDCl_3$, 400 MHz): chemical shift(ppm) 9.08(s, 1H), 8.90(m, 2H), 8.82(d, J=8 Hz, 1H), 8.74~8.62(m, 8H), 8.23~8.14(m, 8H), 7.69~7.48(m, 4H), 7.34~7.28(m, 4H), 7.20~7.14(m, 2H), 1.66(s, 6H).

EXAMPLE 17

Synthesis of Compound A38

[0106]



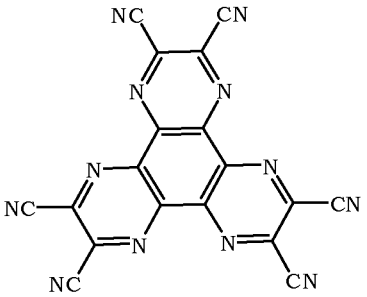
[0107] The synthesis of procedures are the same process with compound A23, the yield of the final product is 67%. MS(m/z, FAB+):575.3 ^{1}HNMR($CDCl_3$, 400 MHz): chemical shift(ppm) 9.04(s, 1H), 8.88~8.86(m, 2H), 8.82~8.79(m, 5H), 8.76(d, J=8Hz, 1H), 8.72(s, 1H), 8.67~8.65(m, 2H), 8.11(d, J=8Hz, 1H), 7.73~7.58(m, 10H), 1.79(m, 6H).

GENERAL METHOD OF PRODUCING ORGANIC EL DEVICE

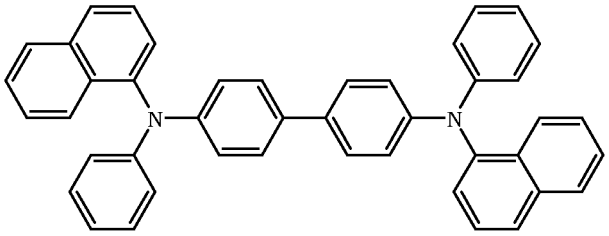
[0108] ITO-coated glasses with 9~12 ohm/square in resistance and 120~160nm in thickness are provided(hereinafter ITO substrate) and cleaned in a number of cleaning steps in an ultrasonic bath(e.g. detergent, deionized water). Before vapor deposition of the organic layers, cleaned ITO substrates are further treated by UV and ozone. All pre-treatment processes for ITO substrate are under clean room(class 100).

[0109] These organic layers are applied onto the ITO substrate in order by vapor deposition in a high-vacuum unit(10^{-7} Torr), such as: resistively heated quartz boats. The thickness of the respective layer and the vapor deposition rate (0.1~0.3 nm/sec) are precisely monitored or set with the aid of a quartz-crystal monitor. It is also possible, as described above, for individual layers to consist of more than one compound, i.e. in general a host material doped with a dopant material. This is achieved by co-vaporization from two or more sources.

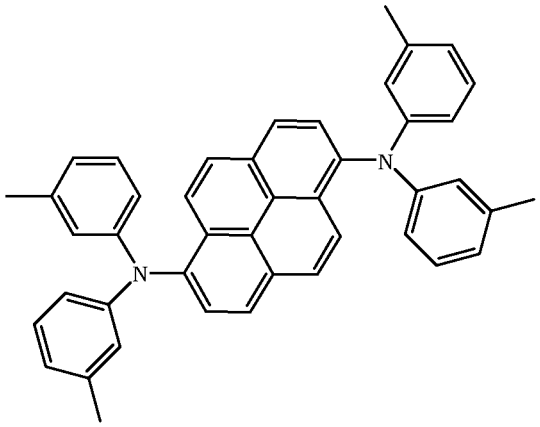
[0110] Dipyrazino[2,3-f:2,3-]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) is used as hole injection layer in this organic EL device. N,N-Bis(naphthalene-1-yl)-N,N-bis(phenyl)-benzidine(NPB) is most widely used as the hole transporting layer. 10,10-Dimethyl-12-(4-(pyren-1-yl)phenyl) -10H-indeno[1,2-b]triphenylene(PT-312,US20140175384)are used as blue emitting host and N1,N1,N6,N6-tetram-tolylpyrene-1,6-diamine(D1) is used as blue guest. 4,7-Diphenyl-2,9-bis(4-(1-phenyl-1H-benzo[d]imidazole -2-yl)phenyl)-1,10-phenanthroline(LT-N8001,US Pat. No 7,754,348) is used as electron transporting material(ETM) to co-deposit with 5% Li or co-deposit with 8-hydroxyquinolato-lithium(LiQ) in organic EL device. Bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium(BAlq) is used as hole blocking material(HBM) and phosphorescent host for phosphorescent system, Bis(2-phenylpyridinato)(2,4-diphenylpyridinato)iridium(III)(D1) are used as phosphorescent dopant. The prior art of OLED materials for producing standard organic EL device control and comparable material in this invention shown its chemical structure as following:



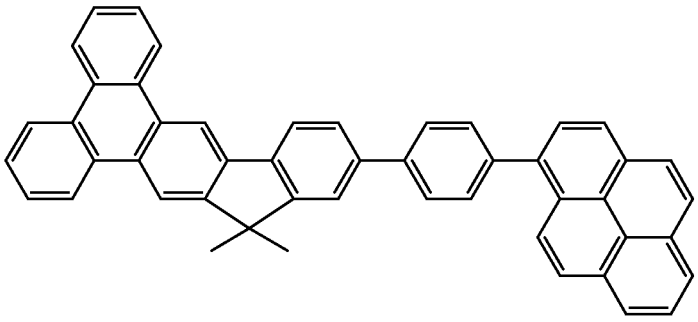
HAT-CN



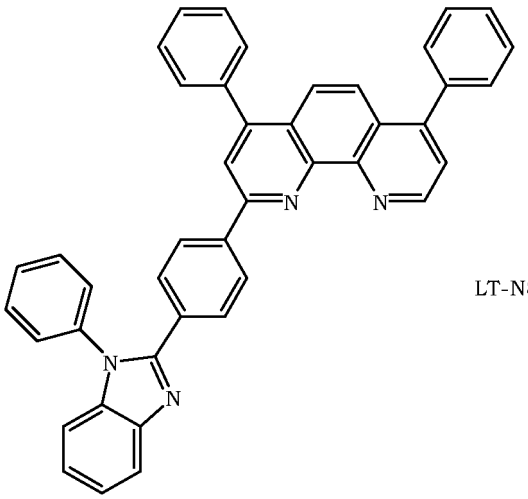
NPB



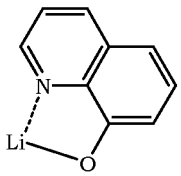
D1



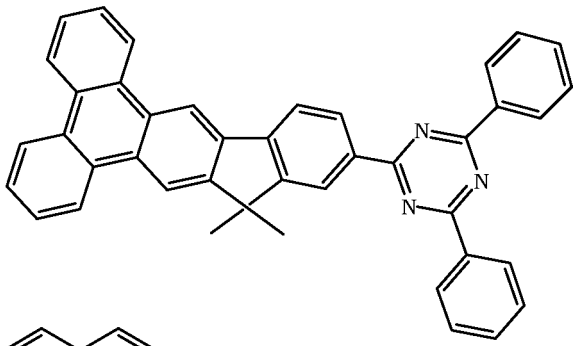
PT-312



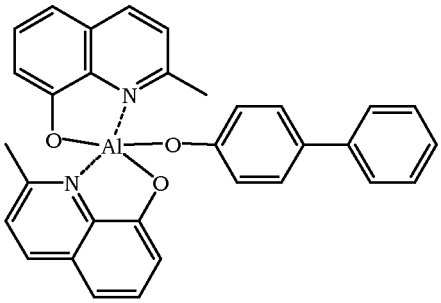
LT-N8001



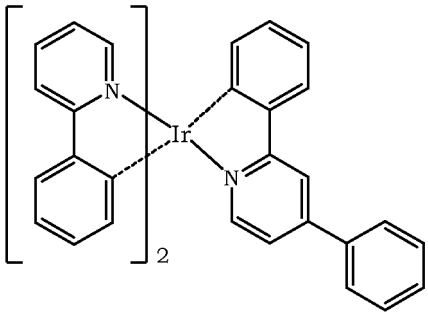
LiQ



A38



BAlq



D2

[0111] A typical organic EL device consists of low work function metals, such as A1, Mg, Ca, Li and K, as the cathode by thermal evaporation, and the low work function metals can help electrons injecting the electron transporting layer from cathode. In addition, for reducing the electron injection barrier and improving the organic EL device performance, a thin-film electron injecting layer is introduced between the cathode and the electron transporting layer. Conventional materials of electron injecting layer are metal halide or metal oxide with low work function, such as: LiF, LiQ, MgO, or Li_2O. On the other hand, after the organic EL device fabrication, EL spectra and CIE coordination are measured by using a PR650 spectra scan spectrometer. Furthermore, the current/voltage, luminescence/voltage and yield/voltage characteristics are taken with a Keithley 2400 programmable voltage-current source. The above-mentioned apparatuses are operated at room temperature(about 25 °C) and under atmospheric pressure.

EXAMPLE 18

[0112] Using a procedure analogous to the above mentioned general method, fluorescent blue-emitting organic EL device having the following device structure were produced(See Fig.1) : ITO/HAT-CN(20nm)/NPB(130nm) /PT-312 doped 5% D1(30nm)/HBM(10nm)/ETM co-deposit LiQ(ETM : LiQ , ratio=1:1(40nm)/LiQ(1nm)/Al(160nm). The I-V-B(at 1000nits) and half-life time of fluorescent blue-emitting organic EL device testing report as Table 1, The half-life time is defined that the initial luminance of 1000cd/m^2 has dropped to half.

Table 1

HBM	ETM	Voltage (V)	Efficiency (lm/w)	CIE(y)	Half-lifetime (hour)
----	LT-N8001	5.6	2.8	0.183	140
BAlq	LT-N8001	5.8	3.1	0.184	220
----	A15	4.8	2.6	0.189	200

(continued)

HBM	ETM	Voltage (V)	Efficiency (lm/w)	CIE(y)	Half-lifetime (hour)
----	A21	5.3	3.3	0.187	180
----	A25	5.1	3.2	0.177	280
----	A31	4.5	3.7	0.180	300
BAlq	A31	4.8	4.0	0.178	250
----	A38	4.0	4.7	0.189	290
BAlq	A38	4.2	4.9	0.189	330

EXAMPLE 19

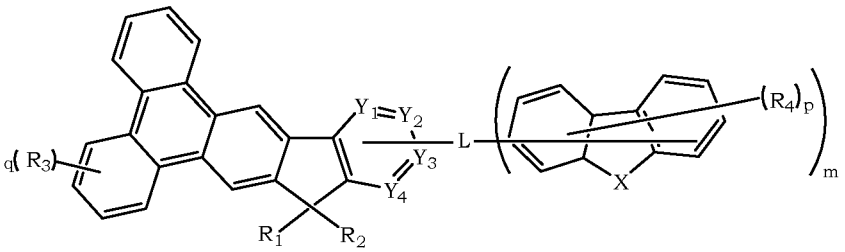
[0113] Using a procedure analogous to the above mentioned general method, phosphorescent emitting organic EL device having the following device structures are produced(See Fig1.) : ITO/HAT-CN(20nm)/NPB(130nm) /phosphorescent host(PHhost) +15% D2(30nm)/HBM(15nm)/A38 co-deposit LiQ(A38 : LiQ , ratio=1:1)(40nm)/LiQ(1nm)/Al(160nm).The I-V-B (at1000nits) and half-life time of phosphorescent emitting organic EL device testing report as Table 2. The half-life time is defined that the initial luminance of 3000cd/m^2 has dropped to half.

Table 2

PHhost(H1+H2) H1:H2=1:1	HBM	Voltage (V)	Efficiency (lm/w)	CIE(x,y)	Half-life time (hour)
BAlq	BAlq	6.8	12	0.45,0.58	350
A2+A27	BAlq	5.3	26	0.43,0.58	400
A2+A27	A27	3.8	37	0.42,0.56	650
A12+A27	A27	4.1	21	0.42,0.56	350
A17+A28	A27	4.2	18	0.42,0.56	400
A31+A28	A27	3.7	22	0.42,0.56	380
A33+A27	A27	3.9	18	0.42,0.56	200
A34+A28	A27	4.2	24	0.42,0.57	110
A2+A23	A27	3.4	30	0.42,0.57	560
A2+A28	A27	3.5	38	0.41,0.56	800
A2+A21	A27	3.9	29	0.41,0.56	750
A2+A33	A27	3.7	16	0.42,0.56	180
A2+A23	A28	3.3	31	0.43,0.57	600
A2+A28	A28	3.2	36	0.43,0.57	750
A2+A21	A28	3.0	32	0.42,0.56	650
A2+A30	A28	3.8	29	0.43,0.56	250
A2+A31	A28	3.4	14	0.42,0.56	200

[0114] In the above preferred embodiments for organic EL device test report(see Table1 and Table2), we show that the organic material formula(A) in the present invention used as hole blocking material, electron transport material or phosphorescent host display good performance than the prior art of organic EL materials.

[0115] To sum up, the present invention discloses a novel organic material which can be used for organic EL device is disclosed. The mentioned organic material are represented by the following formula(A):

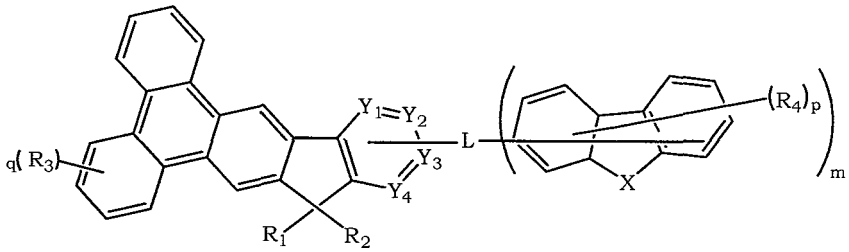


formula(A)

Wherein m represent 0 to 2, and when m represent 1 or 2, L represent a single bond, a substituted or unsubstituted arylene group having 6 to 40 ring carbon atoms, or a substituted or unsubstituted heterarylene group having 3 to 40 ring carbon atoms. When m represent 0, L represent a substituted or unsubstituted heterarylene group having 3 to 40 ring carbon atoms. X represent O, S, NR_5. Y_1 to Y_4 each independently represent nitrogen atom or CR_6. R_5 and R_6 independently represent a hydrogen atom, a substituent, or a bond to L. p represent an integer of 0 to 7, q represent an integer of 0 to 10. R_1 to R_4 independently selected from the group consisting of a hydrogen atom, a halide, alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aralkyl group having 6 to 30 carbon atoms, a substituted or unsubstituted heteroaryl group having 3 to 30 carbon atoms.

Claims

1. A organic material with a general formula(A) as following:

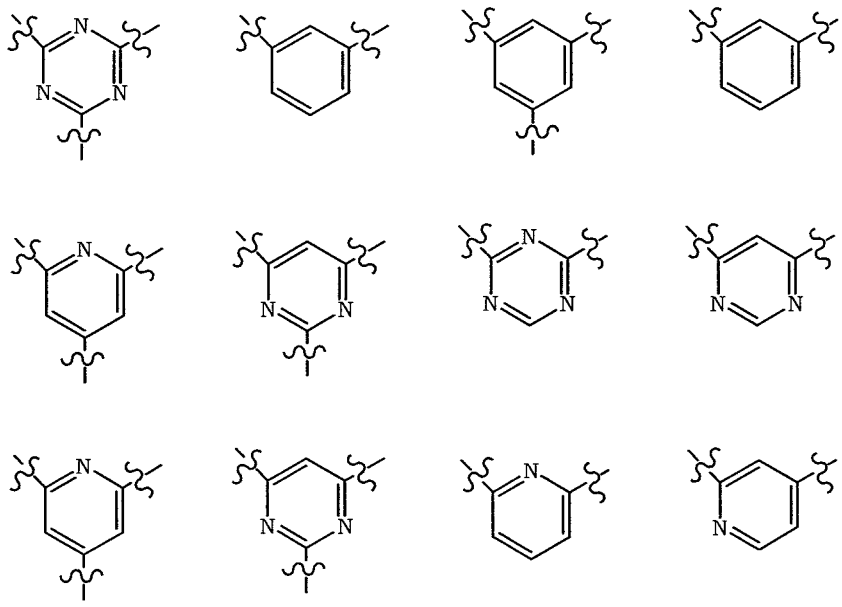


formula(A)

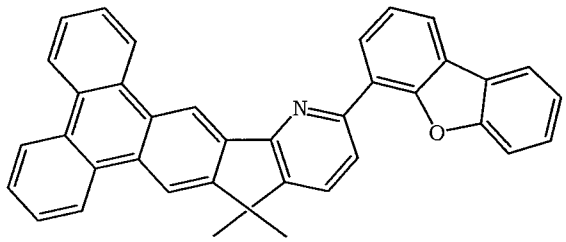
wherein:

m represent 1 or 2;
L represent a single bond, a substituted or unsubstituted arylene group having 6 to 40 ring carbon atoms, or a substituted or unsubstituted heterarylene group having 3 to 40 ring carbon atoms;
X represent O, S, or NR_5;
Y_1 to Y_4 each independently represent nitrogen atom or CR_6;
R_5 and R_6 independently represent a hydrogen atom, a substituent, or a bond to L;
p represent an integer of 0 to 7;
q represent an integer of 0 to 10;
R_1 to R_4 independently selected from the group consisting of a hydrogen atom, a halide, alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aralkyl group having 6 to 30 carbon atoms, and a substituted or unsubstituted heteroaryl group having 3 to 30 carbon atoms.

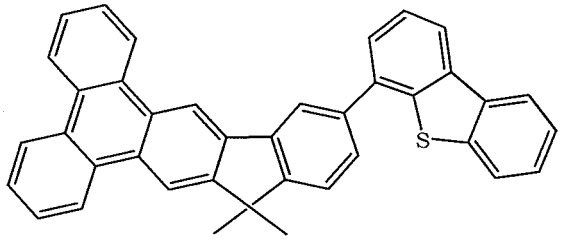
2. The organic material according to claim 1, wherein L is selected from one of the following groups:



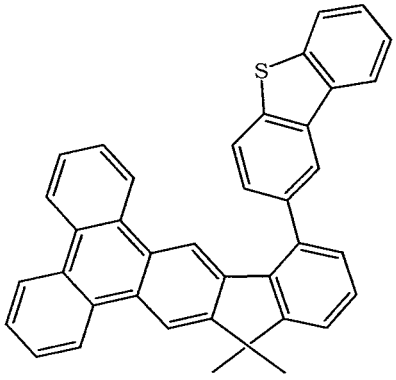
3. The organic material according to claim 1, wherein the organic material with a general formula (A) is selected from the group consist of A1 to A37:



A1



A2



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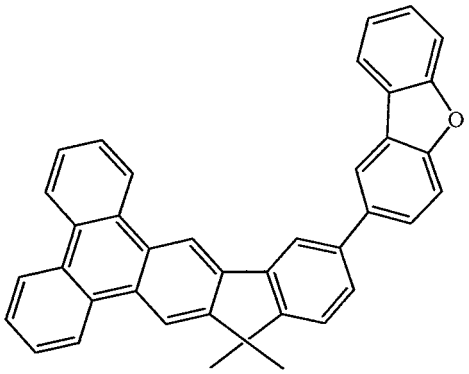

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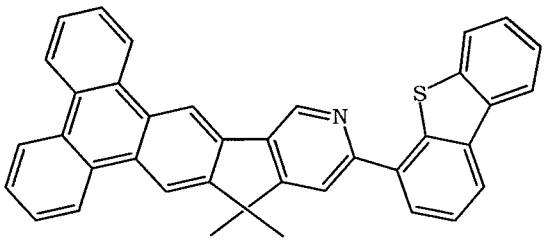

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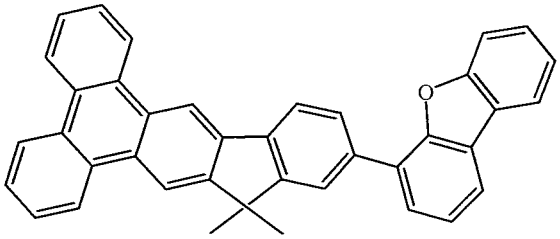

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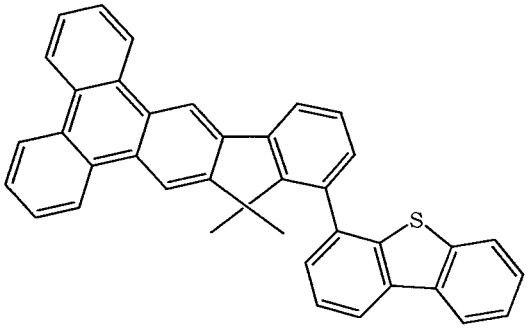

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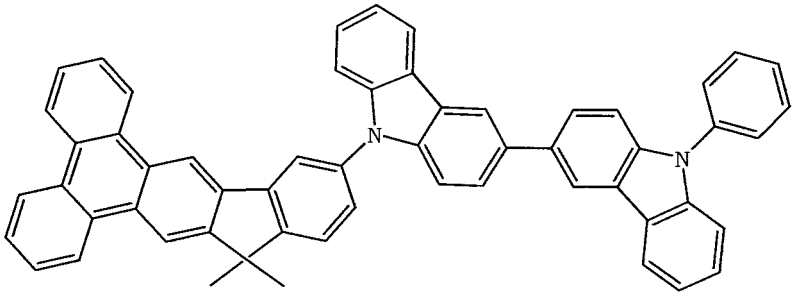

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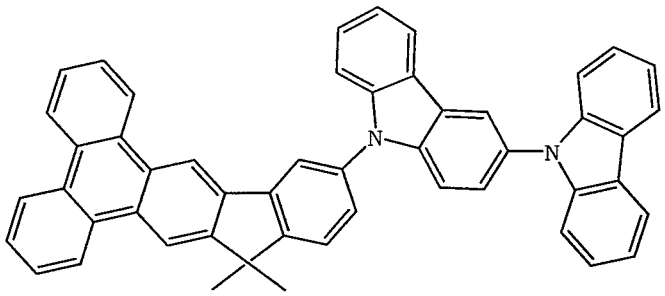

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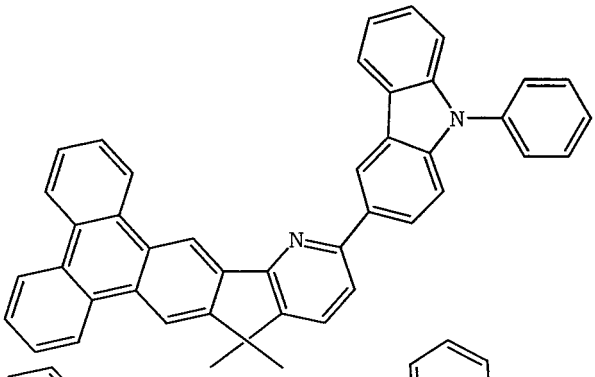

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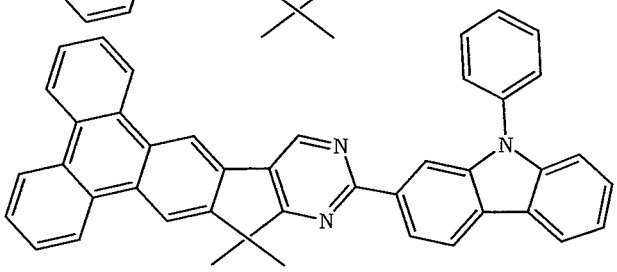

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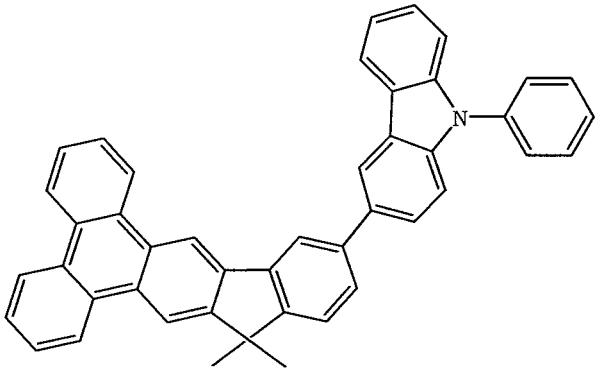

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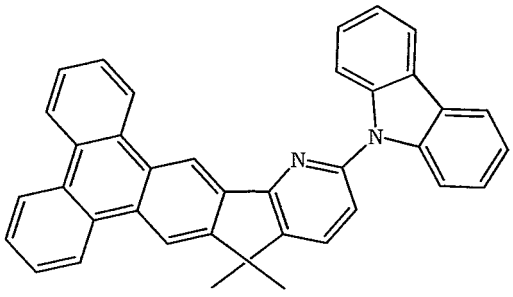

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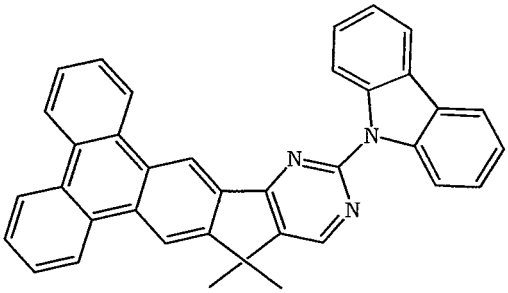

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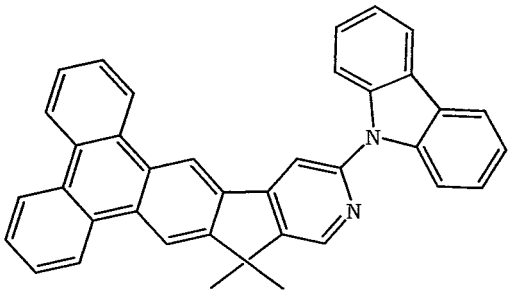

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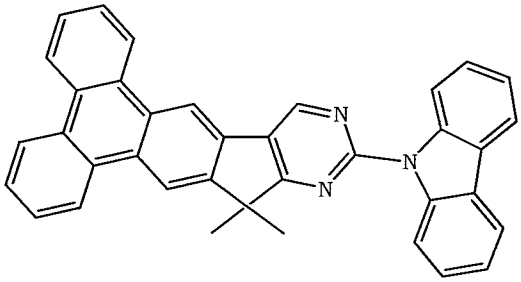

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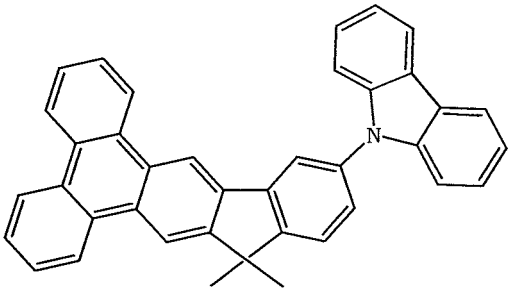

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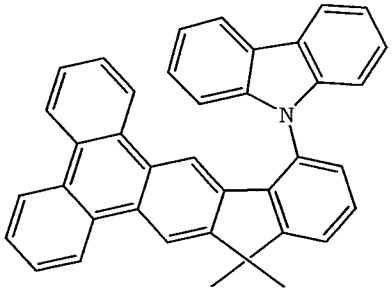

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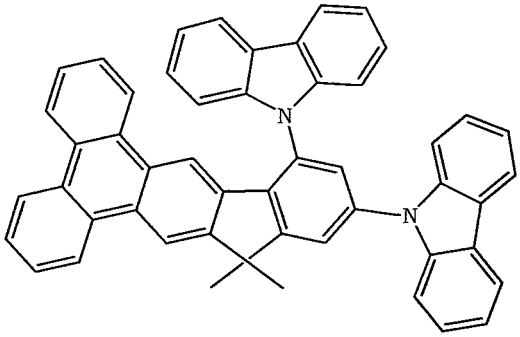

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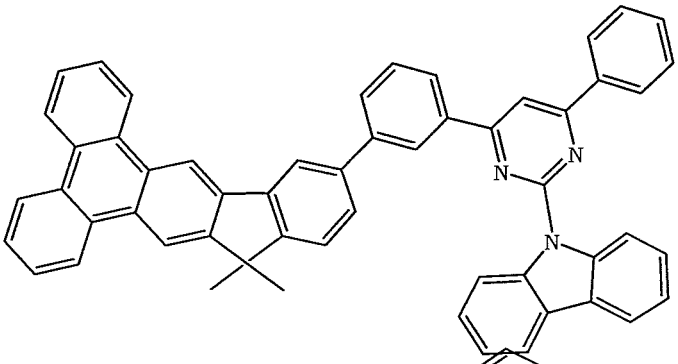

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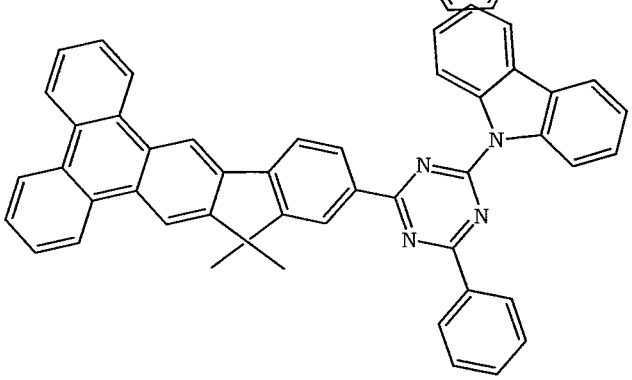

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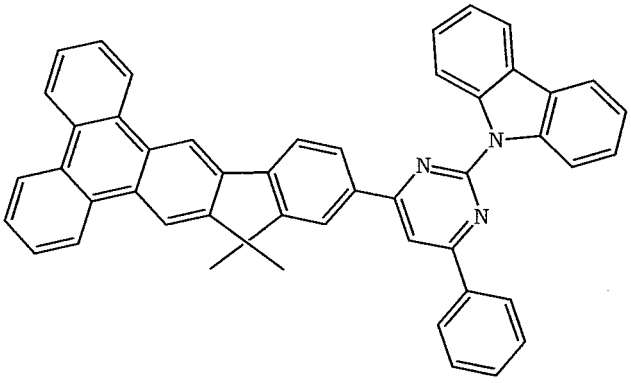

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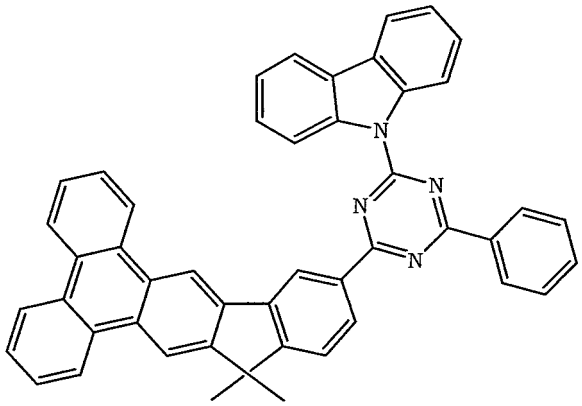

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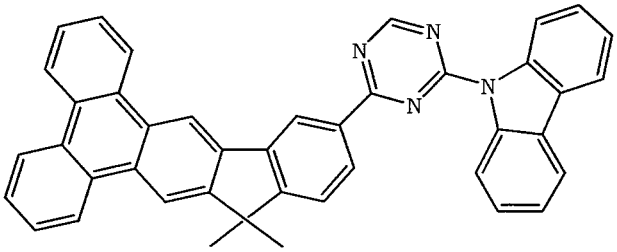

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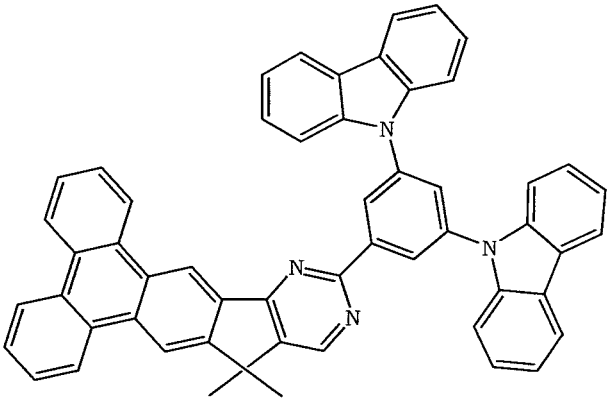

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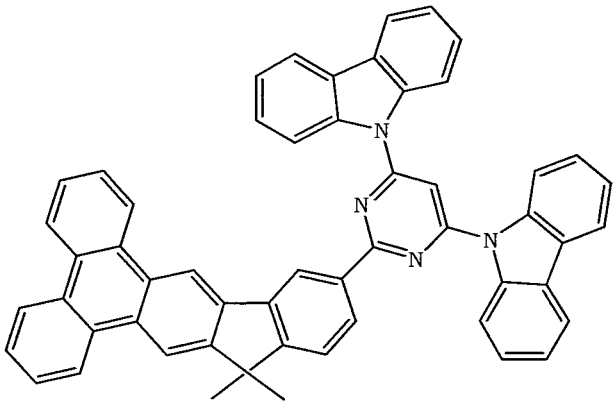

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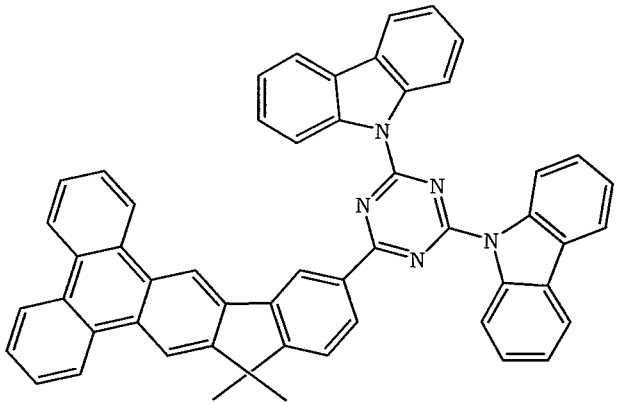

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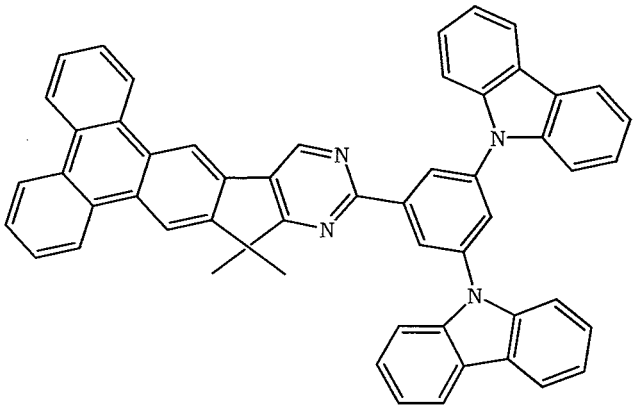

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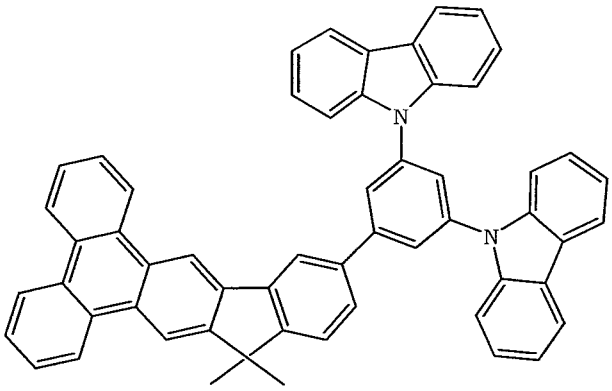

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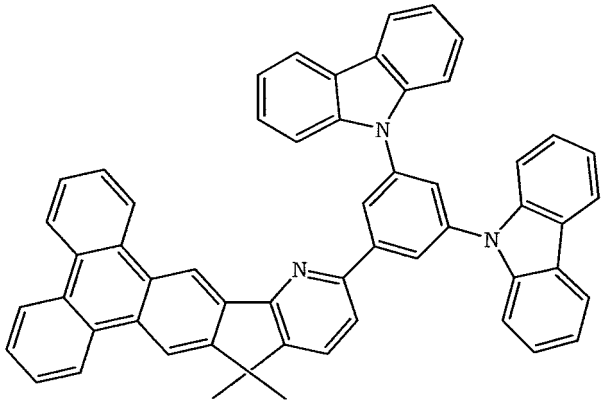

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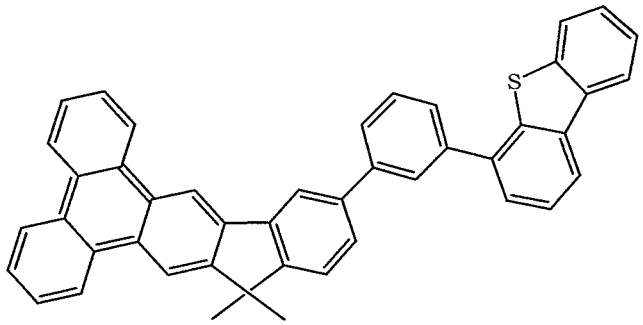

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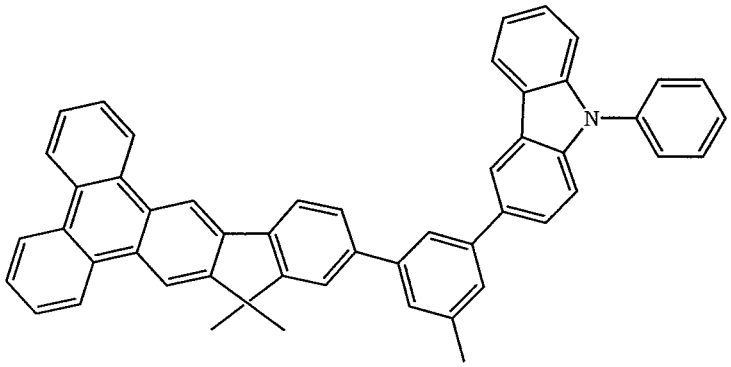

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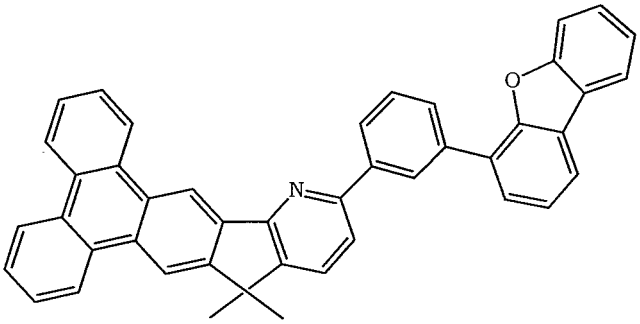

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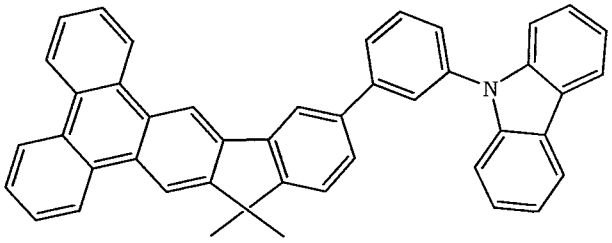

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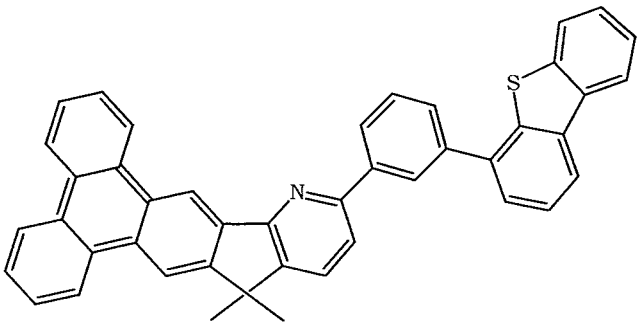

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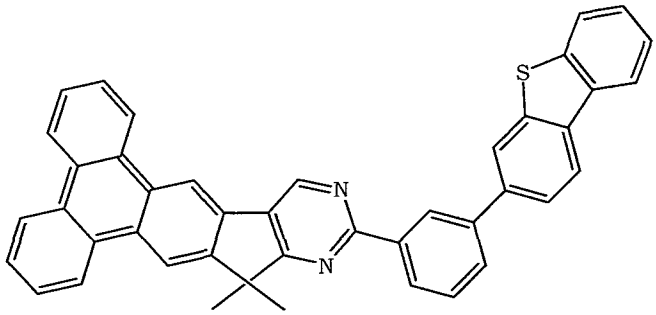

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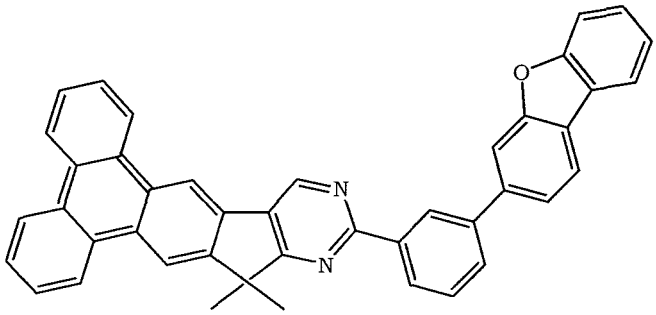


A37

4. A organic electroluminescent device comprising a pair of electrodes consisting of a cathode and an anode and between the pairs of electrodes comprising at least a layer of the organic material with a general formula(A) according to any of the claims 1 to 3.

5. The organic electroluminescent device according to claim 4, wherein the emitting layer comprising the organic material with a general formula(A).

6. The organic electroluminescent device according to claim 5, wherein the emitting layer comprising the organic material with a general formula(A) is a phosphorescent host material or thermally activated delayed fluorescence host material.

7. The organic electroluminescent device according to claim 5 or 6, wherein the emitting layer comprising phosphorescent dopant or thermally activated delayed fluorescence dopant.

8. The organic electroluminescent device according to claim 7, wherein the phosphorescent dopant are iridium(Ir) complexes.

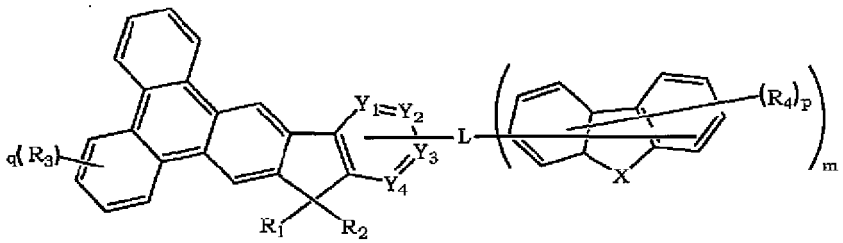
9. The organic electroluminescent device according to any of the claims 4 to 8, wherein the electron transport layer comprising the organic material with a general formula(A).

10. The organic electroluminescent device according to any of the claims 4 to 9, wherein the electron transport layer comprising Li, Ca, 8-hydroxyquinolinolato-lithium.

11. The organic electroluminescent device according to any of the claims 4 to 10, wherein the hole blocking electron transport layer comprising the with a general formula(A).

Patentansprüche

1. Ein organisches Material mit einer allgemeinen Formel (A) wie folgt:

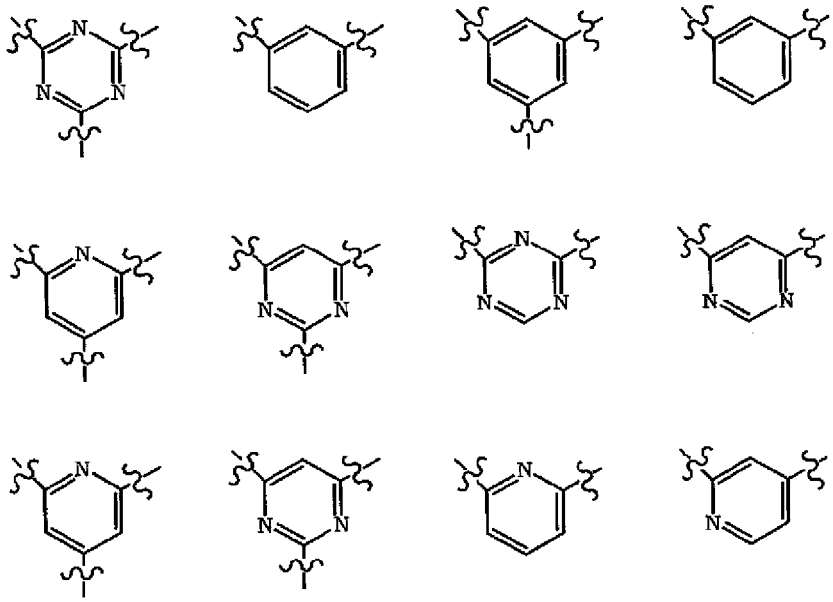


Formel (A)

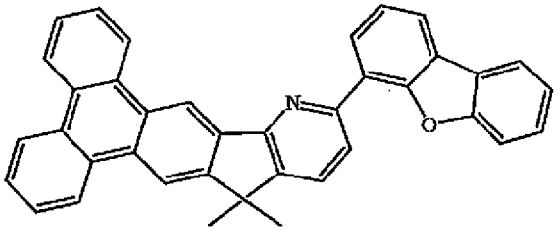
worin:

m steht für 1 oder 2;
L steht für eine Einfachbindung, eine substituierte oder unsubstituierte Arylengruppe mit 6 bis 40 Ringkohlenstoffatomen oder eine substituierte oder unsubstituierte Heterarylengruppe mit 3 bis 40 Ringkohlenstoffatomen;
X steht für O, S oder NR_5;
Y_1 bis Y_4 stehen jeweils unabhängig voneinander für Stickstoffatom oder CR_6;
R5 und R6 stehen unabhängig voneinander für ein Wasserstoffatom, einen Substituenten oder eine Bindung an L;
p steht für eine ganze Zahl von 0 bis 7;
q steht für eine ganze Zahl von 0 bis 10;
R_1 bis R_4, unabhängig ausgewählt aus der Gruppe bestehend aus einem Wasserstoffatom, einem Halogenid, einer Alkylgruppe mit 1 bis 20 Kohlenstoffatomen, einer substituierten oder unsubstituierten Arylgruppe mit 6 bis 30 Kohlenstoffatomen, einer substituierten oder unsubstituierten Aralkylgruppe mit 6 bis 30 Kohlenstoffatomen Atomen und einer substituierten oder unsubstituierten Heteroarylgruppe mit 3 bis 30 Kohlenstoffatomen.

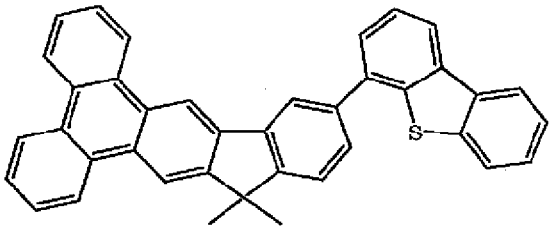
2. Das organisches Material nach Anspruch 1, wobei L ausgewählt ist aus einer der folgenden Gruppen:



3. Das organisches Material nach Anspruch 1, wobei das organische Material mit einer allgemeinen Formel (A) aus der Gruppe bestehend aus A1 bis A37 ausgewählt ist:



A1



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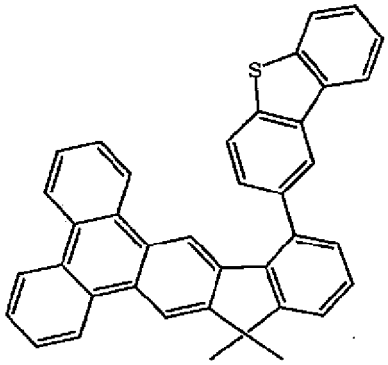

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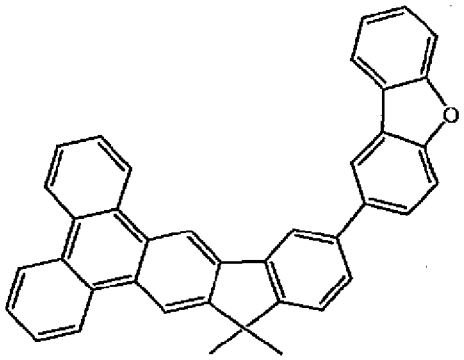

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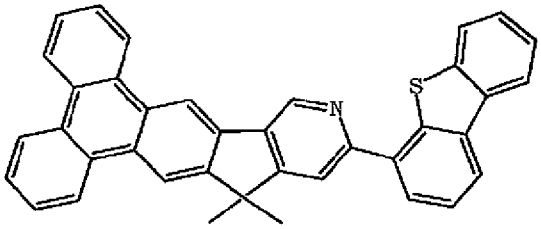

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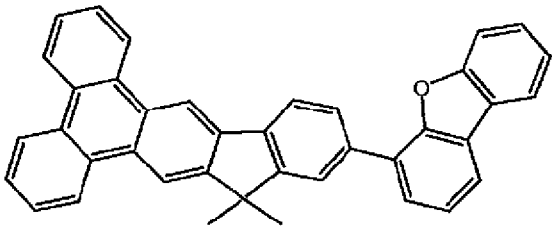

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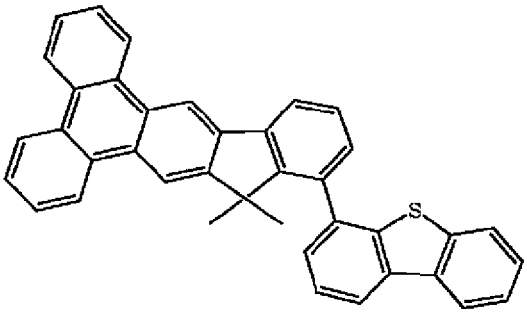

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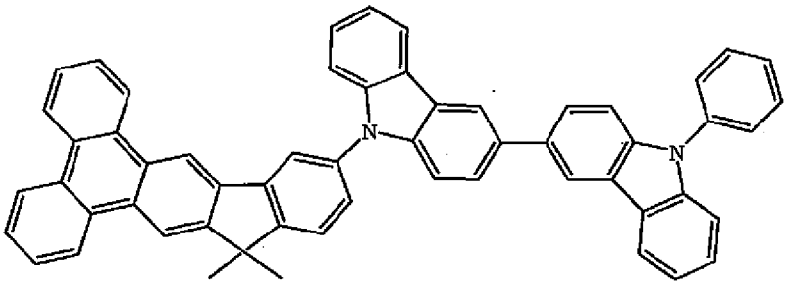

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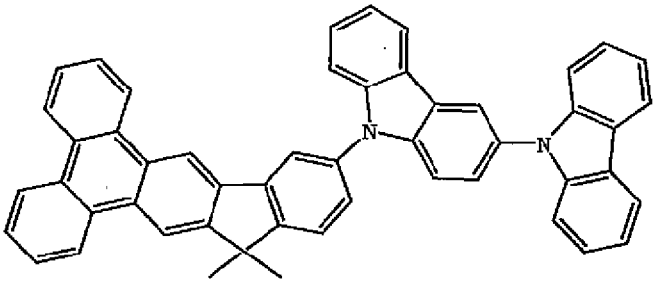

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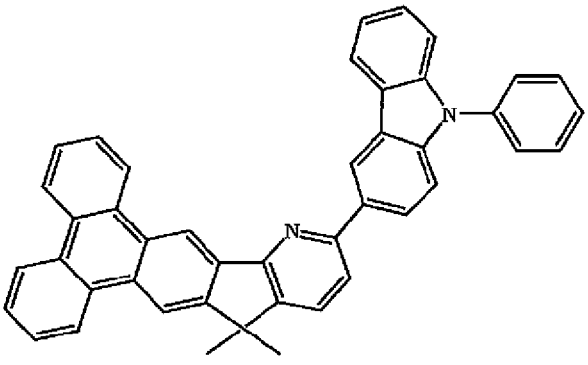

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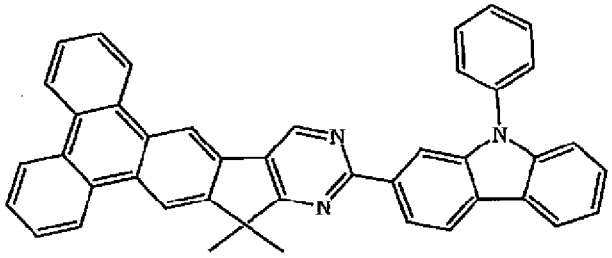

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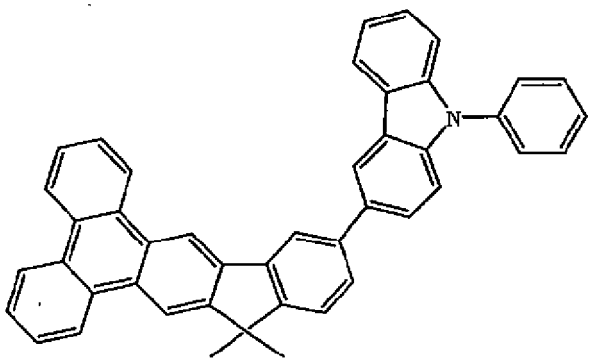

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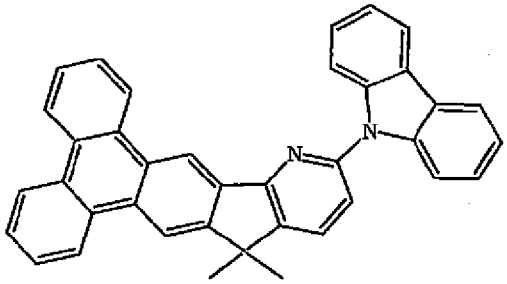

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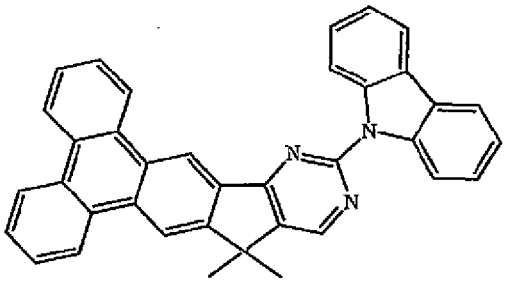

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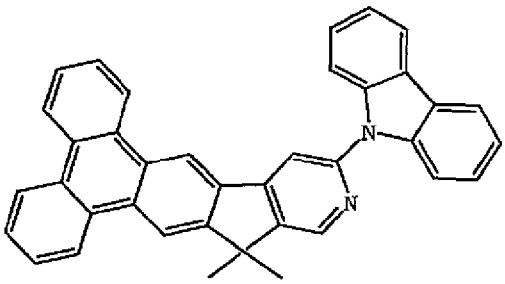

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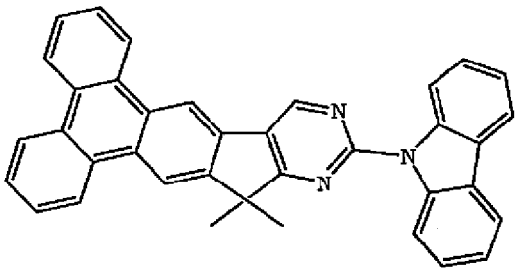

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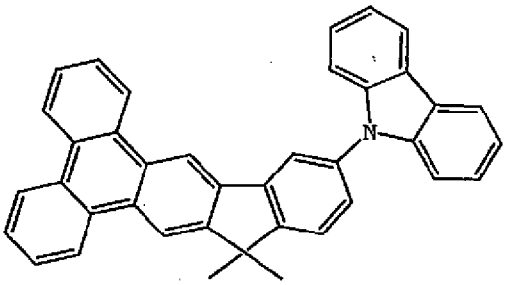

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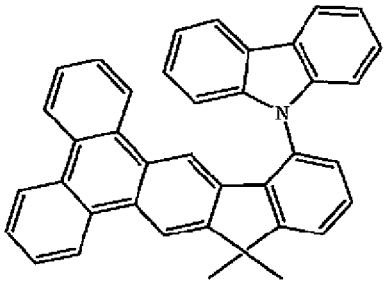

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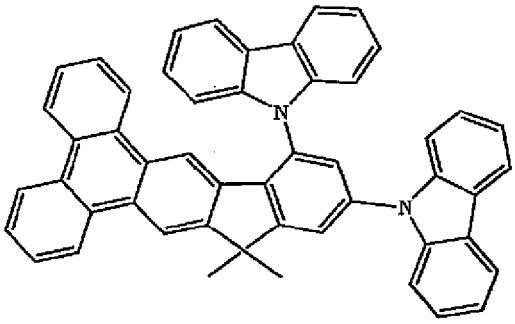

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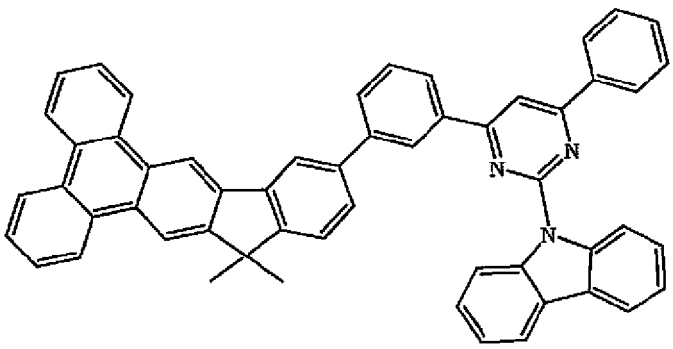

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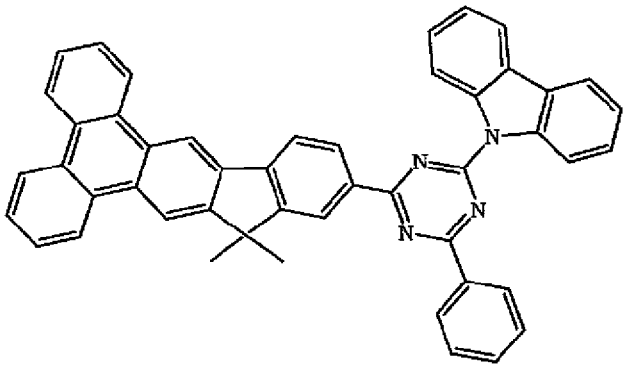

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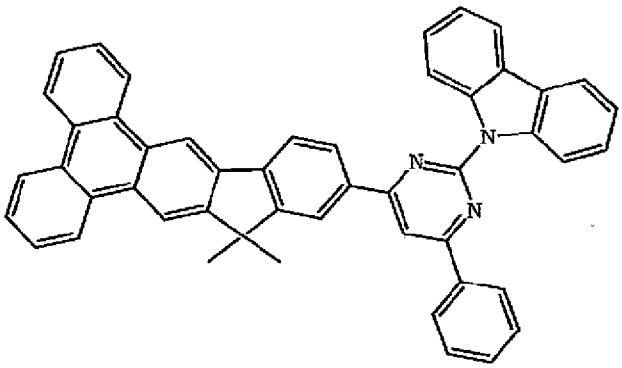

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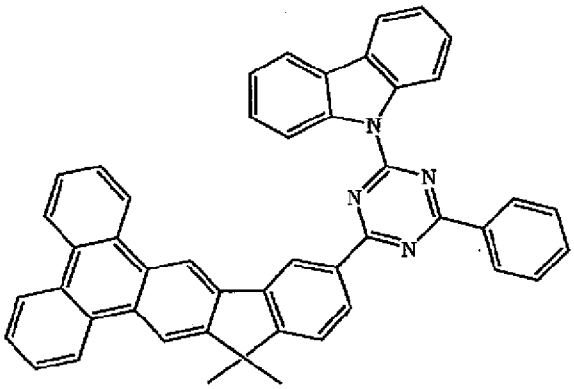

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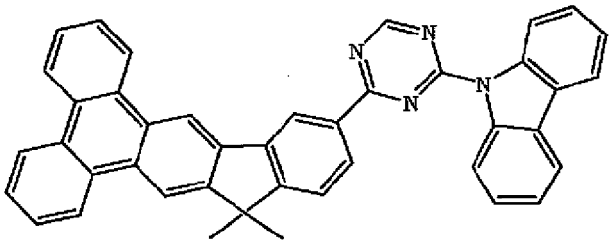

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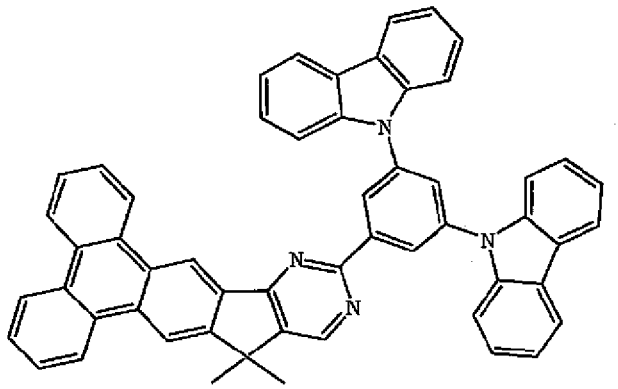

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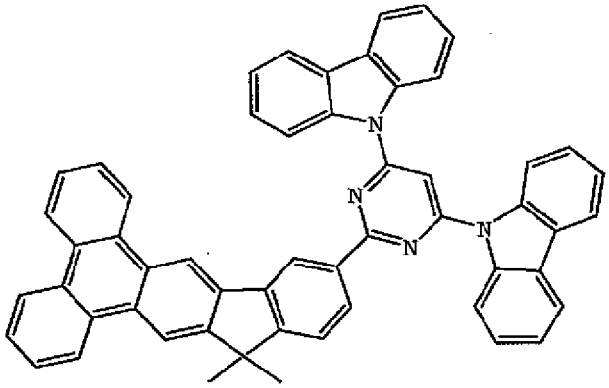

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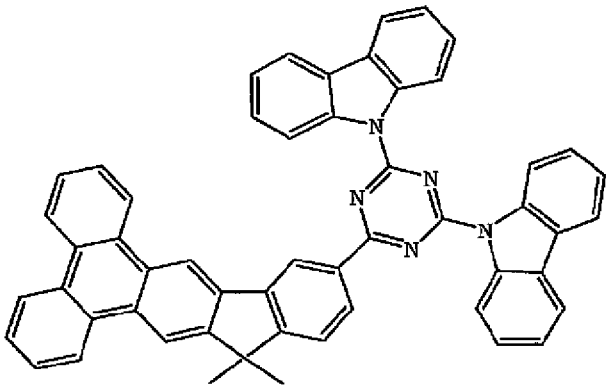

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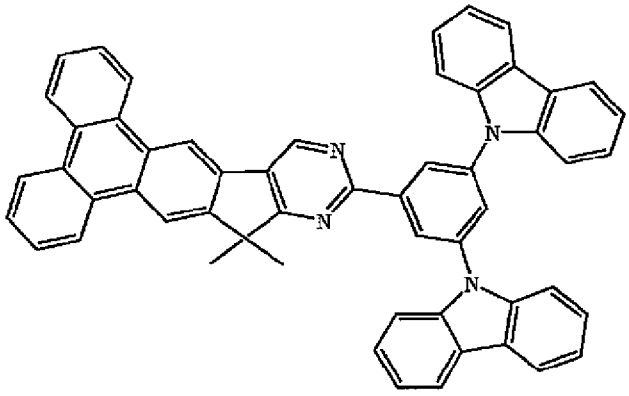

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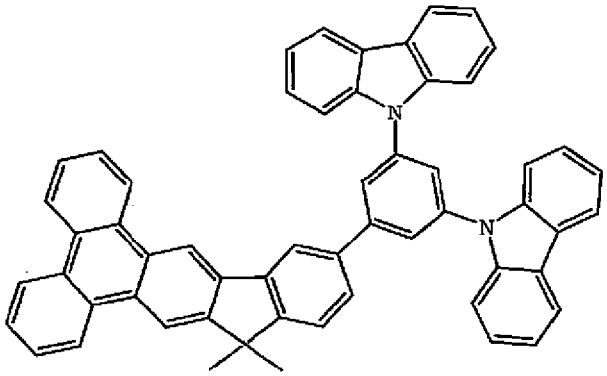

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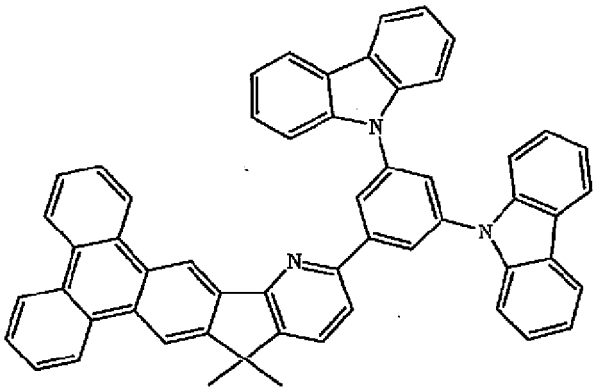

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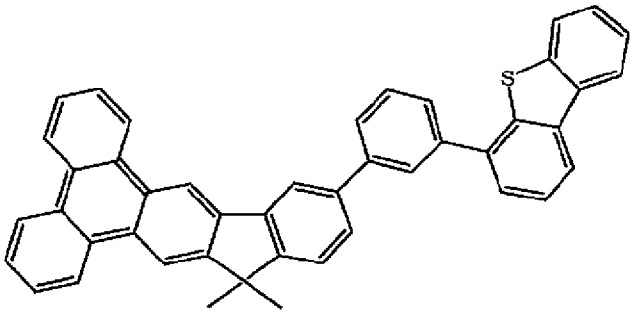

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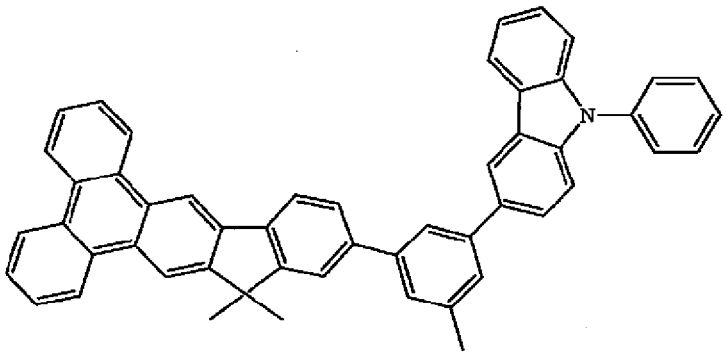

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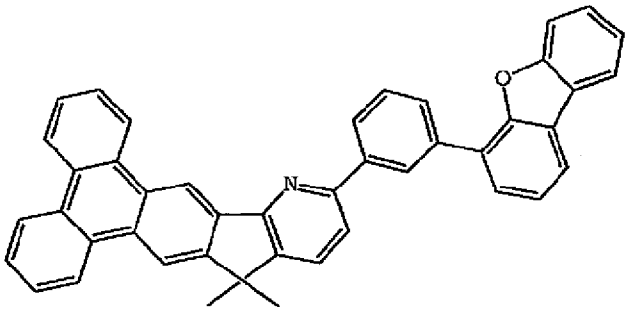

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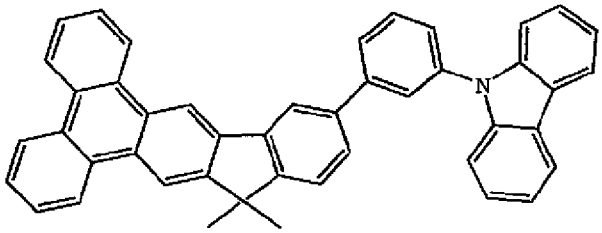

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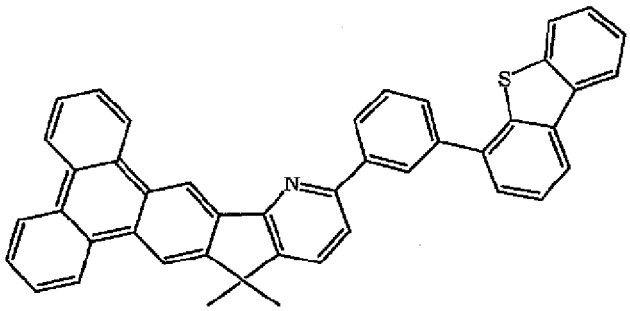

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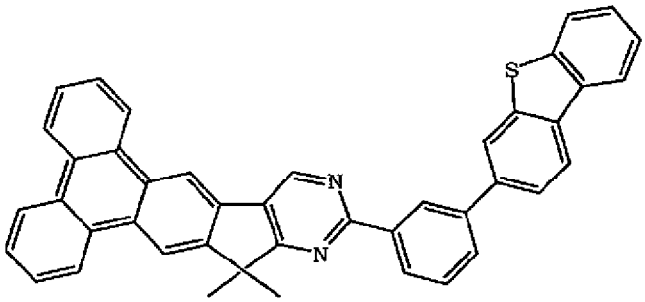

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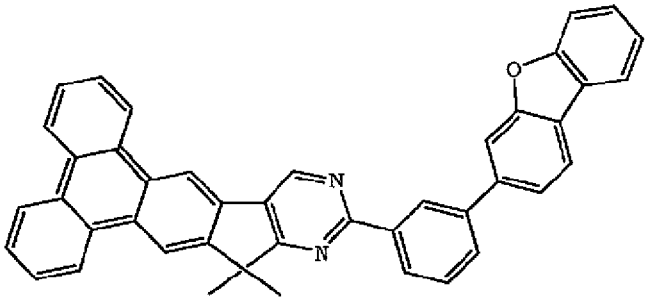


A37

4. Eine organische Elektrolumineszenzvorrichtung umfassend ein Paar von Elektroden, bestehend aus einer Kathode und einer Anode und zwischen den Paaren von Elektroden, umfassend mindestens eine Schicht des organischen Materials mit einer allgemeinen Formel (A) nach einem der Ansprüche 1 bis 3.

5. Die organische Elektrolumineszenzvorrichtung nach Anspruch 4, wobei die emittierende Schicht das organische

Material mit der allgemeinen Formel (A) umfasst.

6. Die organische Elektrolumineszenzvorrichtung nach Anspruch 5, wobei die emittierende Schicht, die das organische Material mit der allgemeinen Formel (A) umfasst, ein phosphoreszierendes Wirtsmaterial oder thermisch aktiviertes verzögertes Fluoreszenzwirtsmaterial ist.

7. Die organische Elektrolumineszenzvorrichtung nach Anspruch 5 oder 6, wobei die emittierende Schicht einen phosphoreszierenden Dotierstoff oder einen thermisch aktivierten verzögerten Fluoreszenzdotierstoff enthält.

8. Die organische Elektrolumineszenzvorrichtung nach Anspruch 7, wobei der phosphoreszierende Dotierstoff Iridium (Ir) -Komplexe sind.

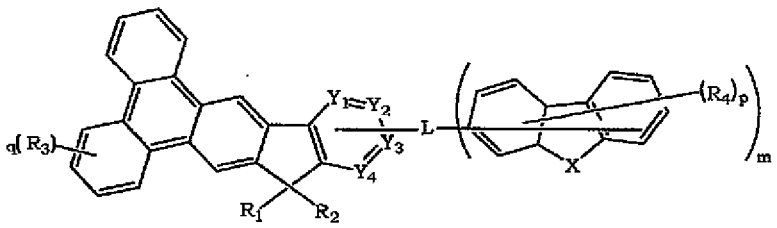
9. Die organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 4 bis 8, wobei die Elektronentransportschicht das organische Material mit der allgemeinen Formel (A) umfasst.

10. Die organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 4 bis 9, wobei die Elektronentransportschicht Li, Ca, 8-Hydroxychinolinolatolithium umfasst.

11. Die organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 4 bis 10, wobei die Lochblockierelektronentransportschicht, die allgemeine Formel (A) umfasst.

Revendications

1. Un matériau organique de formule générale (A) comme suit:

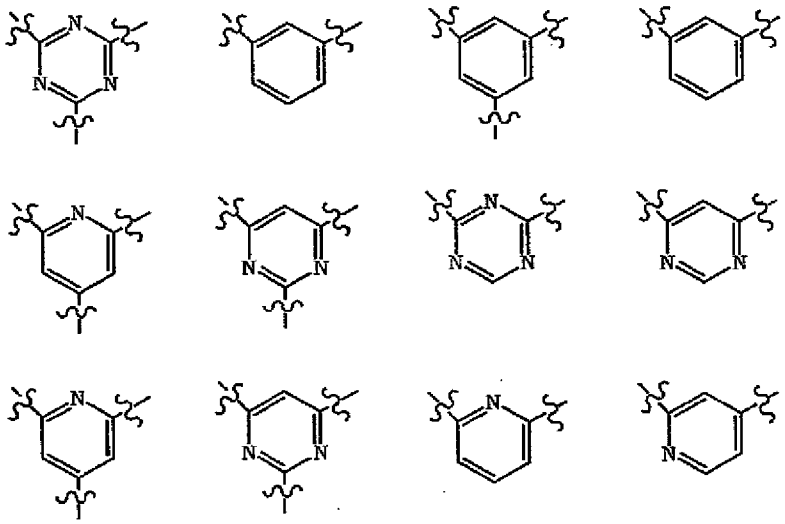


formule (A)

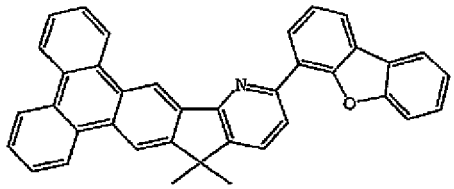
dans laquelle :

m représente 1 ou 2,
L représente une liaison simple, un groupe arylène substitué ou non substitué ayant 6 à 40 atomes de carbone du cycle, ou un groupe hétérolénylène substitué ou non substitué ayant 3 à 40 atomes de carbone du cycle ;
X représente O, S, NR_5 ;
Y1 à Y4 représentent chacun indépendamment l'atome d'azote ou CR_6 ;
R_5 et R_6 représentent indépendamment un atome d'hydrogène, un substituant ou une liaison à L ;
p correspond à un nombre entier de 0 à 7,
q correspond à un nombre entier de 0 à 10 ;
R_1 à R_4 choisis indépendamment dans le groupe comportant un atome d'hydrogène, un groupe halogénure, un groupe alkyle ayant 1 à 20 atomes de carbone, un groupe aryle substitué ou non substitué ayant 6 à 30 atomes de carbone, un groupe aralkyle substitué ou non substitué ayant 6 à 30 atomes de carbone.

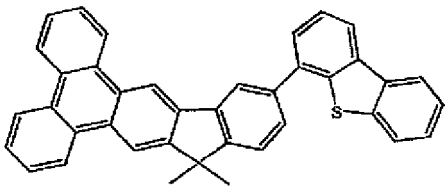
2. Le matériau organique selon la revendication 1, dans lequel L est choisi parmi l'un des groupes suivantes :



3. Le matériau organique selon la revendication 1, dans lequel le matériau organique avec la formule générale (A) est choisi au sein du groupe comportant A1 à A37 :



A1



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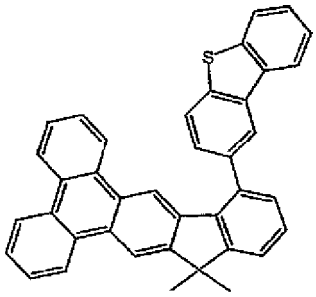

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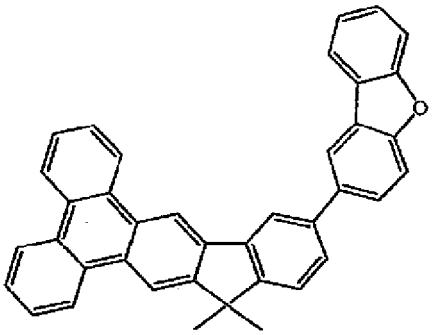

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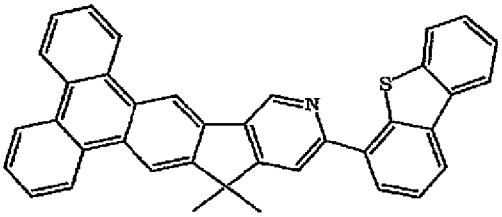

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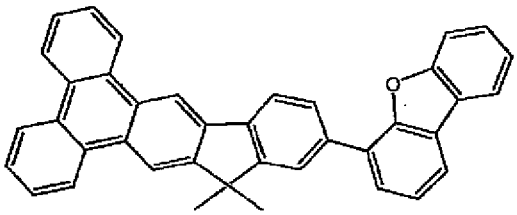

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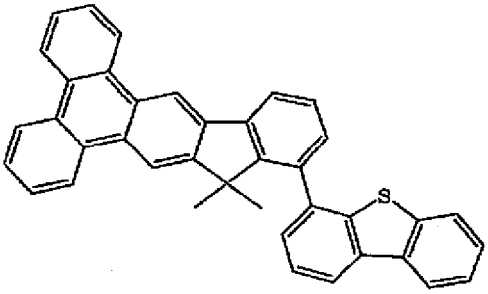

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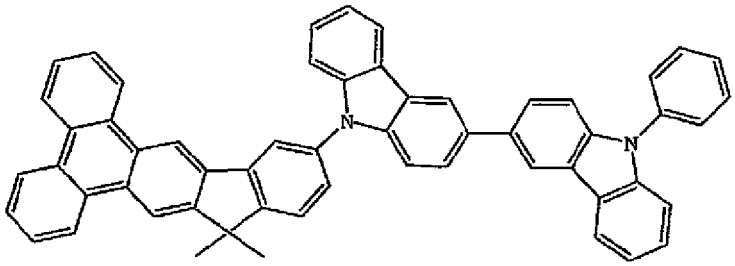

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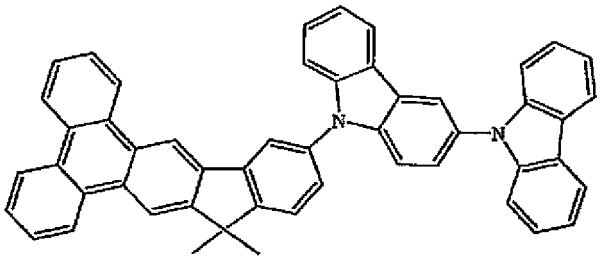

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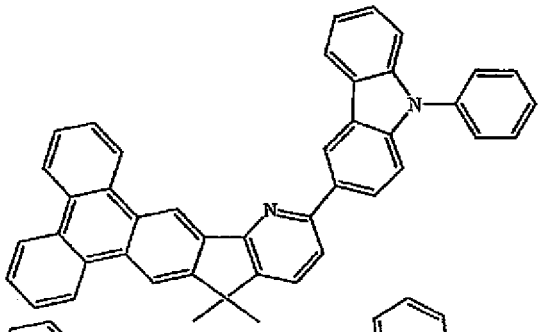

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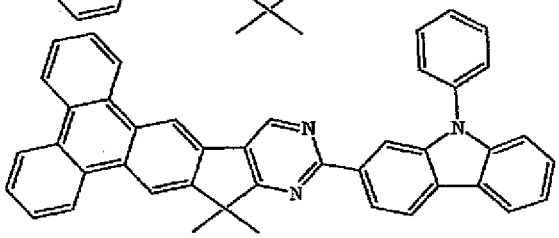

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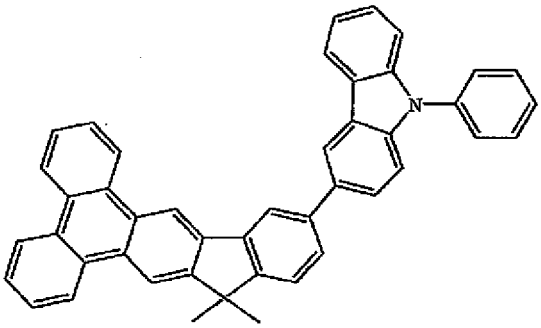

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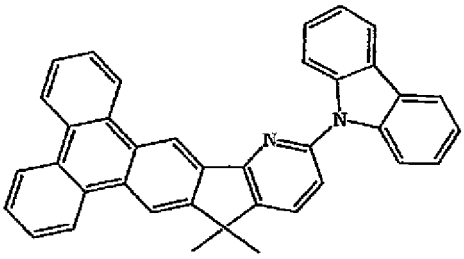

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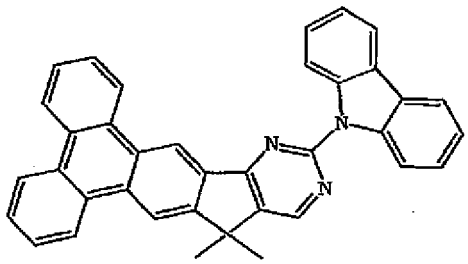

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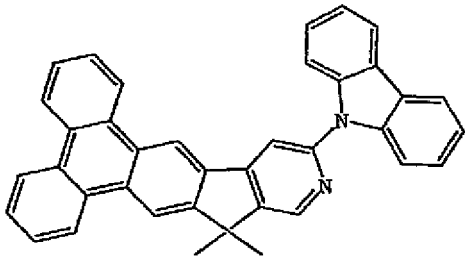

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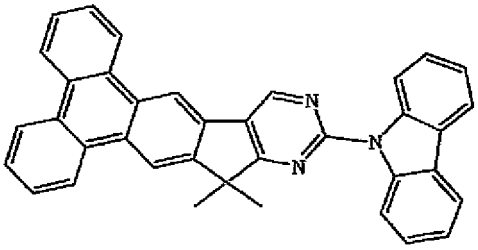

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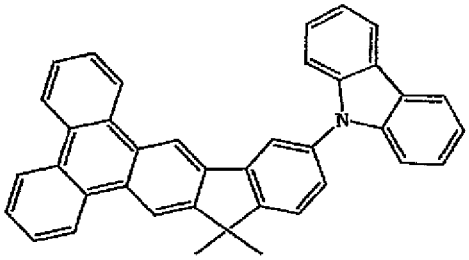

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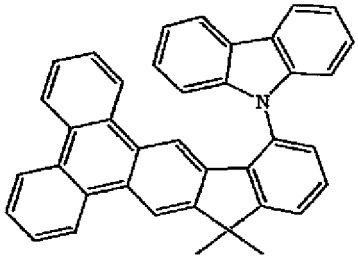

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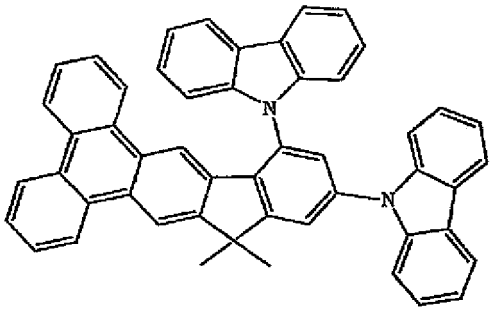

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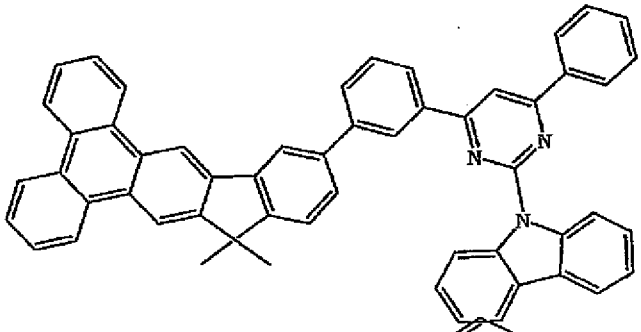

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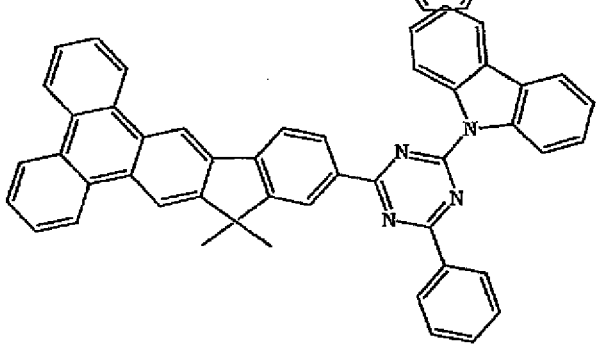

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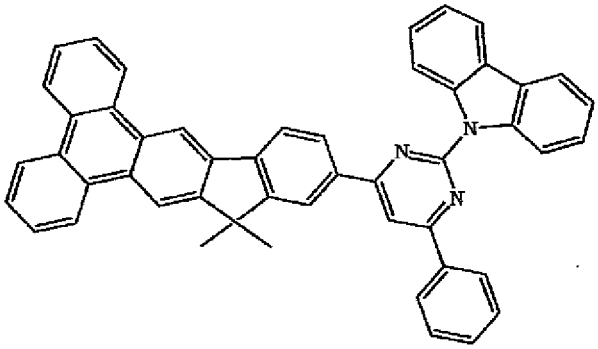

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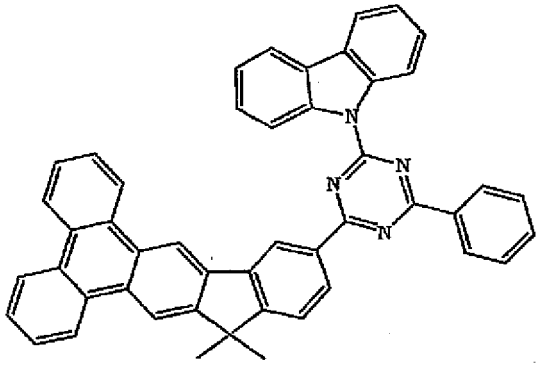

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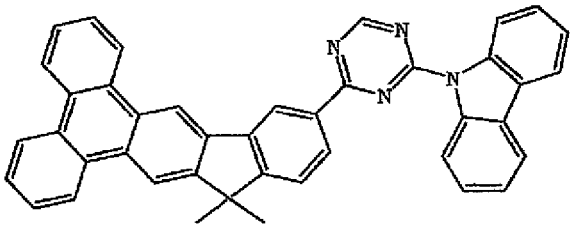

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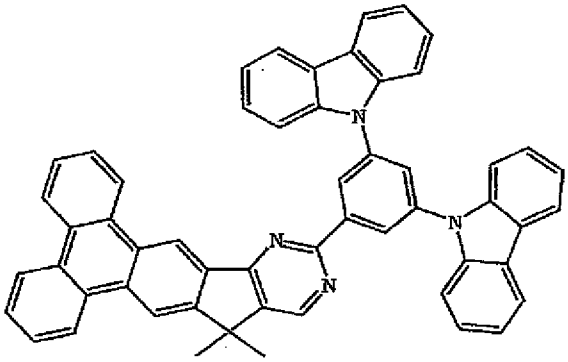

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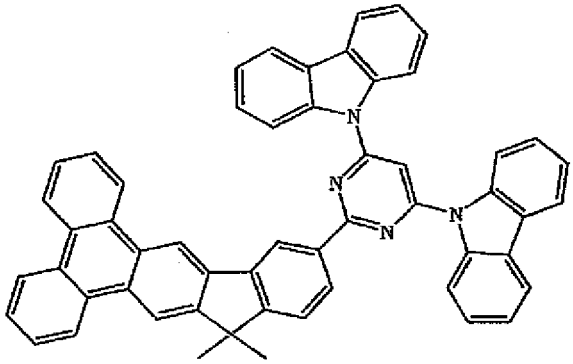

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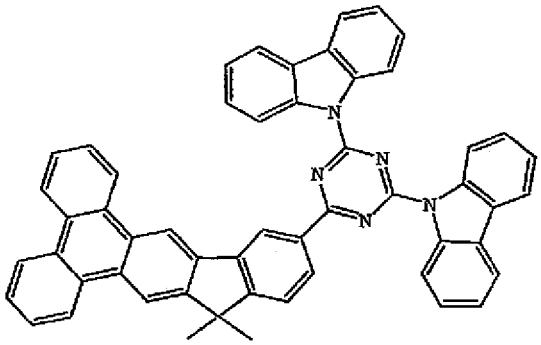

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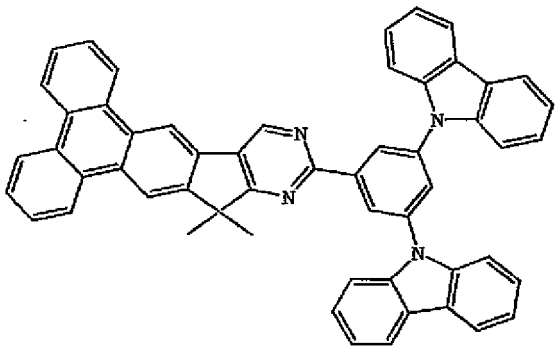

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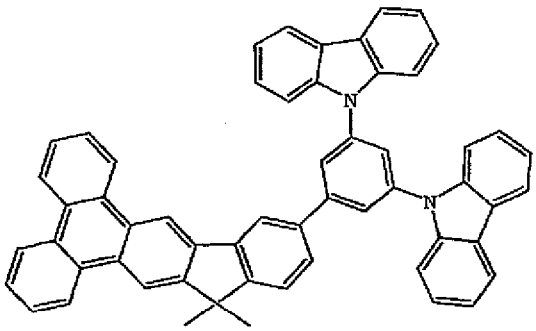

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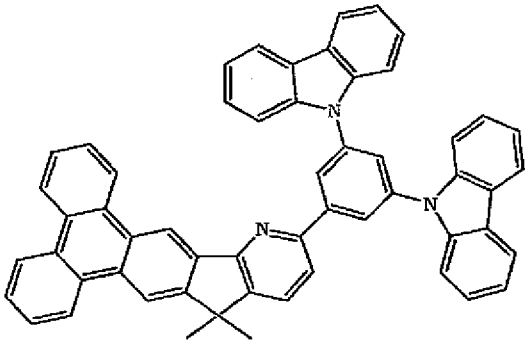

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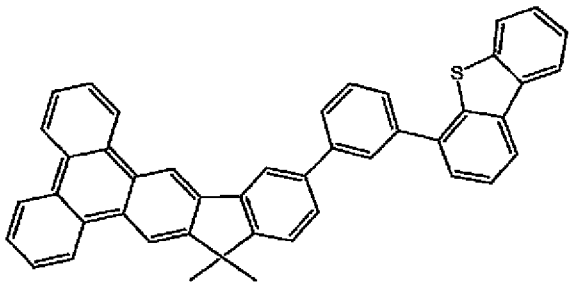

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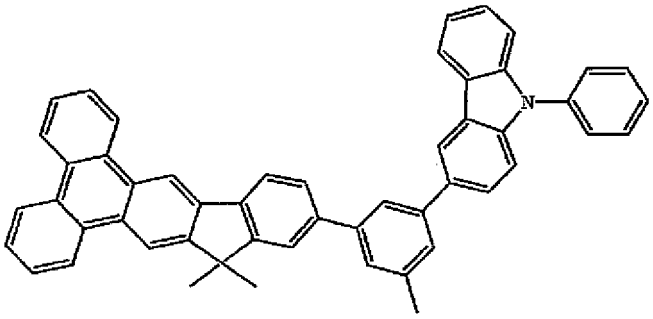

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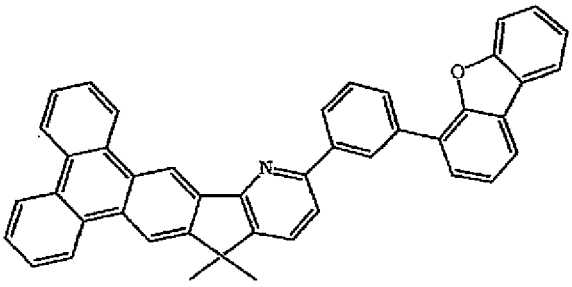

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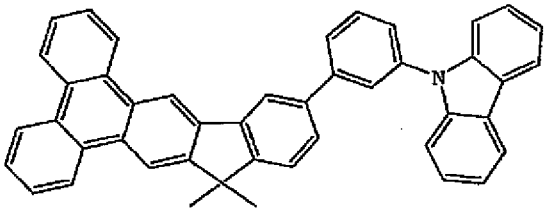

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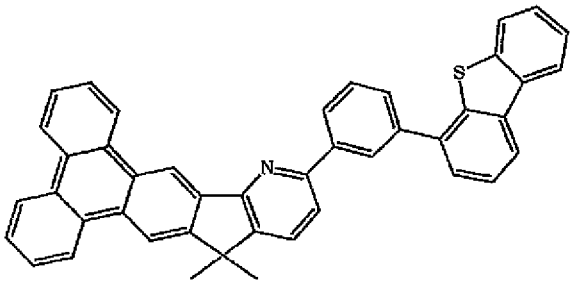

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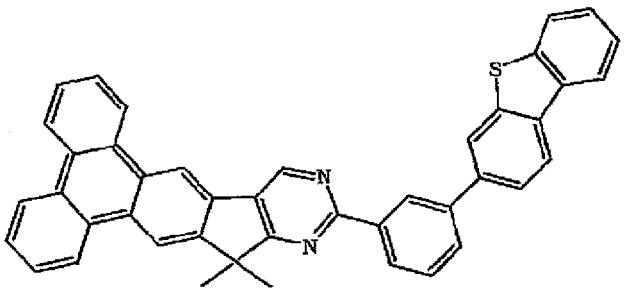

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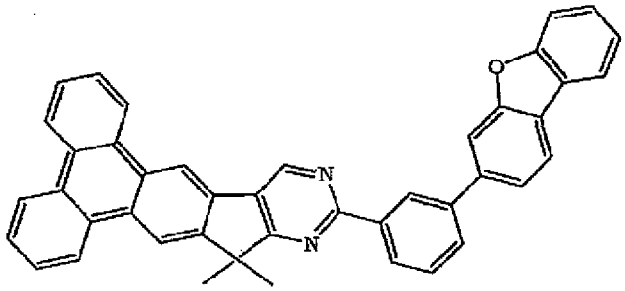


A37

4. Un dispositif électroluminescent organique comprenant une paire d'électrodes constituées d'une cathode et d'une anode et entre les paires d'électrodes comprenant au moins une couche de matière organique de formule générale (A) selon l'une quelconque des revendications 1 à 3.

5. Le dispositif électroluminescent organique selon la revendication 4, dans lequel la couche émettrice comprenant la matière organique de formule générale (A).

6. Le dispositif électroluminescent organique selon la revendication 5, dans lequel la couche émettrice comprenant la matière organique de formule générale (A) est un matériau hôte phosphorescent ou un matériau hôte à fluorescence retardée activé thermiquement.

7. Le dispositif électroluminescent organique selon la revendication 5 ou 6, dans lequel la couche émettrice comprend un dopant phosphorescent ou un dopant à fluorescence retardée activé thermiquement.

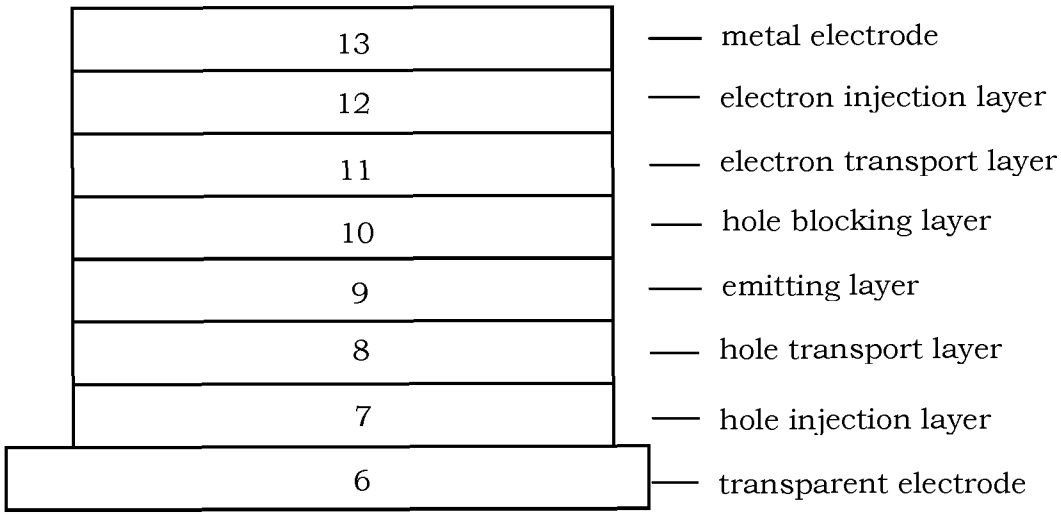
8. Le dispositif électroluminescent organique selon la revendication 7, dans lequel le dopant phosphorescent est constitué de complexes iridium (Ir).

9. Le dispositif électroluminescent organique selon l'une quelconque des revendications 4 à 8, dans lequel la couche de transport d'électrons comprend le matériau organique de formule générale (A).

10. Le dispositif électroluminescent organique selon l'une quelconque des revendications 4 à 9, dans lequel la couche de transport d'électrons comprend Li, Ca, et 8-hydroxyquinolinolato-lithium.

11. Le dispositif électroluminescent organique selon l'une quelconque des revendications 4 à 10, dans lequel la couche de transport d'électrons à blocage de trou comprend la formule générale (A).

Fig. 1


13
12
11
10
9
8
7
6
metal electrode
electron injection layer
electron transport layer
hole blocking layer
emitting layer
hole transport layer
hole injection layer
transparent electrode

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 2014306207 A1 **[0007]**
- US 20140175384 A **[0110]**
- US 7754348 B **[0110]**

专利名称(译)	有机材料和使用其的有机电致发光器件		
公开(公告)号	EP3040395B1	公开(公告)日	2017-10-18
申请号	EP2015198385	申请日	2015-12-08
申请(专利权)人(译)	发光科技股份有限公司.		
当前申请(专利权)人(译)	发光科技股份有限公司.		
[标]发明人	YEN FENG WEN CHANG CHENG HAO		
发明人	YEN, FENG-WEN CHANG, CHENG-HAO		
IPC分类号	C09K11/06 H01L51/00 C07D401/14 C07D333/76 C07D401/04 C07D403/04 C07D403/14 C07D405/04 C07D251/24 C07D209/82 H01L51/50		
CPC分类号	H01L51/0072 C07D209/82 C07D251/24 C07D333/76 C07D401/04 C07D401/14 C07D403/04 C07D403/14 C07D405/04 C09K11/06 C09K2211/1011 C09K2211/1029 C09K2211/1044 C09K2211/1059 C09K2211/1088 C09K2211/1092 H01L51/0056 H01L51/0067 H01L51/0073 H01L51/0074 H01L51/5016 H01L51/5072 H01L51/5096 H01L2251/5384		
优先权	14/585219 2014-12-30 US		
其他公开文献	EP3040395A1		
外部链接	Espacenet		

摘要(译)

本发明公开了一种新型有机材料，由下式（A）表示，有机EL器件采用有机材料作为空穴阻挡层（HBL），电子传输层（ETL）或磷光主体可有效降低驱动电压，降低功率消费，提高效率。与本发明中描述的定义相同。