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(54) **LIGHT EMITTING MATERIAL,
MANUFACTURE METHOD THEREOF AND
ORGANIC LIGHT EMITTING DIODE USING
THE LIGHT EMITTING MATERIAL**

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Foreign Application Priority Data

Jul. 20, 2016 (CN) 201610579646.9

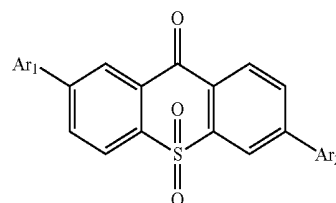
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C07D 339/08 (2006.01)

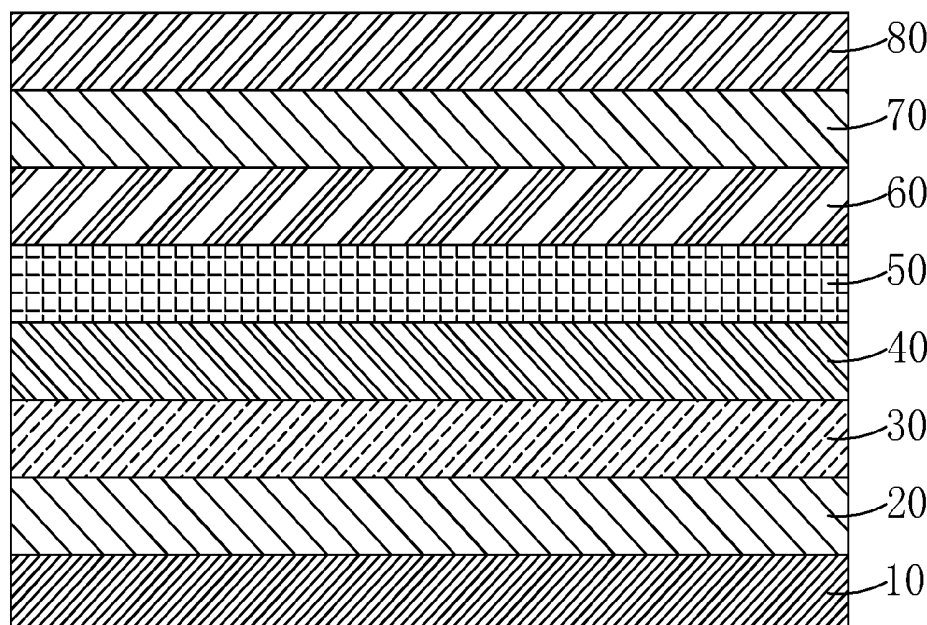
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(2013.01); **C07D 339/08** (2013.01); **C07D**
409/14 (2013.01)

(57) **ABSTRACT**

An organic light emitting diode includes a light emitting
layer that includes a light emitting material of the constitu-
tional formula



The structure is unitary, and the formula weight is deter-
mined, and the better solubility and film formation are
provided, and the thin film status is stable; it possesses a very
high decomposition temperature and a lower sublimation
temperature, and is easy to sublime to be light emitting
material of high purity, and can be applied for small mole-
cule organic light emitting diode. In the method for manu-
facturing the light emitting material, p-bromothiophenol and
4-Bromo-2-fluorobenzonitrile are employed to be starting
materials, and an intermediate of the light emitting material
is obtained with a series of simple reactions, and finally, the
light emitting material is obtained with Ullmann reaction or
Suzuki reaction, and these steps are simple and the produc-
tion is high.



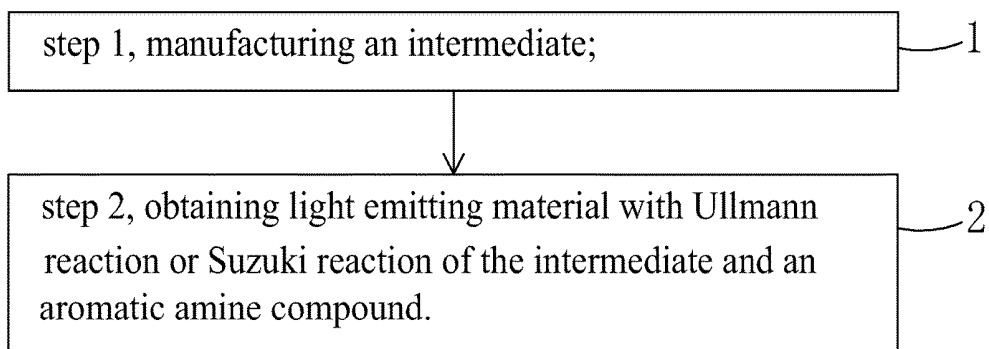


Fig. 1

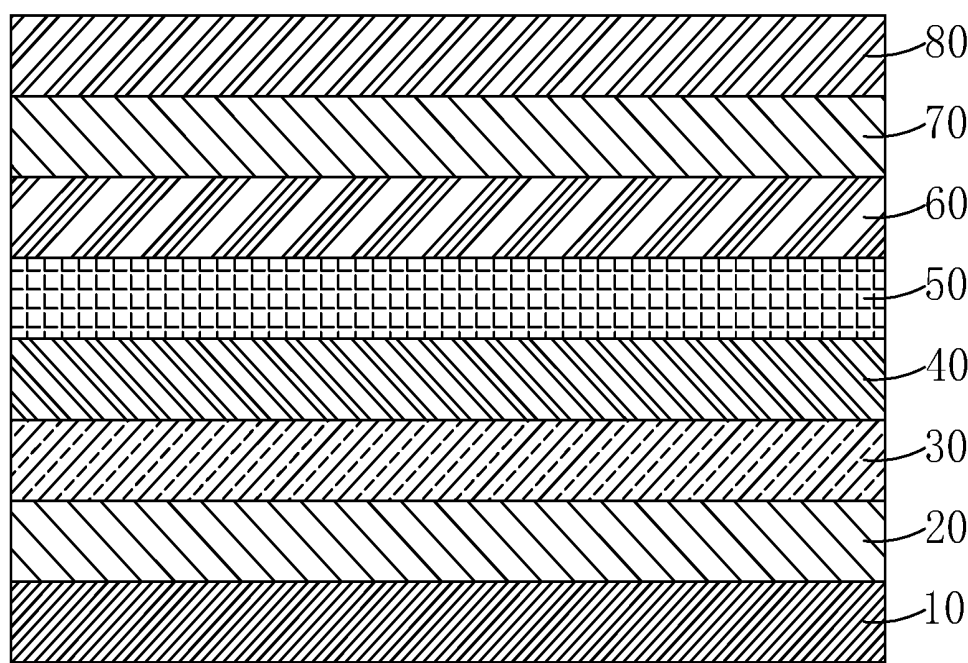


Fig. 2

LIGHT EMITTING MATERIAL, MANUFACTURE METHOD THEREOF AND ORGANIC LIGHT EMITTING DIODE USING THE LIGHT EMITTING MATERIAL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a divisional application of co-pending U.S. patent application Ser. No. 15/122,410, filed on Aug. 30, 2016, which is a national stage of PCT Application No. PCT/CN2016/095615, filed on Aug. 17, 2016, claiming foreign priority of Chinese Patent Application No. 201610579646.9, filed on Jul. 20, 2016.

FIELD OF THE INVENTION

[0002] The present invention relates to a display technology field, and more particularly to a light emitting material, a manufacture method thereof and an organic light emitting diode using the light emitting material.

BACKGROUND OF THE INVENTION

[0003] The OLED (Organic Light-Emitting Diode) display, which is also named as the Organic light emitting display, is a new flat panel display device. Because it possesses advantages of simple manufacture process, low cost, low power consumption, high light emitting brightness, wide operating temperature range, thin volume, fast response speed, and being easy to achieve the color display and the large screen display, and being easy to achieve the match with the integrated circuit driver, and being easy to achieve the flexible display. Therefore, it has the broad application prospects.

[0004] The OLED display utilizes the organic light emitting diode for light emission. Thus, it is extremely important to improve the efficiency and lifetime of the organic light emitting diode. Now, the organic light emitting diode has already made considerable progress. With the fluorescence phosphorescence hybrid, the white light element with the simple structure and high efficiency can be obtained. The efficiency of such fluorescence phosphorescence hybrid element significantly relies on the efficiency of the fluorescence. Therefore, it still has vital significant meaning to develop the high efficiency fluorescence material.

[0005] In comparison with polymer, the small molecule light emitting molecule has the simple steps, the stable structure and can be purified, and then the higher element efficiency can be obtained for the possible commercial application. The method of manufacturing multiple layer element by implementing evaporation or solution process with small molecule has already drawn the great attention and the great progress has been made. However, the traditional organic fluorescence material only can utilize 25% of singlet excitons. Thus, there is extreme big restriction to the efficiency of the element. Recently, the Japanese Adachi research group utilizes the thermally activated delayed fluorescence mechanism to make the exciton availability of all organic material reach up to 100%, and the organic fluorescence element efficiency progresses significantly. Nevertheless, there is few for such kind of materials. Therefore, the type expansion for such kind of material has the significant meaning for the application in the future. For now, the organic small molecule light emitting material of simple structure, and possessing well performance and satisfying

the commercialization requirement is still so limited. It is still profound to develop the light emitting material of low cost and excellent efficiency.

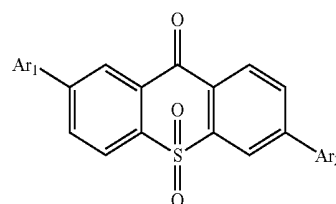
SUMMARY OF THE INVENTION

[0006] An objective of the present invention is to provide a light emitting material, in which the structure is unitary, and the formula weight is determined, and the better solubility and film formation are provided to be applied for small molecule organic light emitting diode.

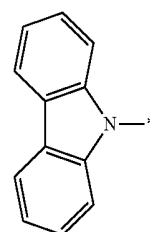
[0007] Another objective of the present invention is to provide a manufacture method of the light emitting material, in which the steps are simple, and the production is high.

[0008] Another objective of the present invention is to provide an organic light emitting diode, in which the light emitting layer comprises the aforesaid light emitting material that has higher light emission efficiency and stability.

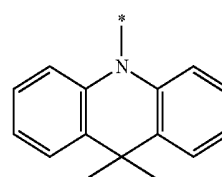
[0009] For realizing the aforesaid objectives, the present invention first provides a light emitting material, in which a constitutional formula is



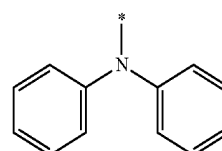
wherein Ar₁ and Ar₂ are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);



(1)



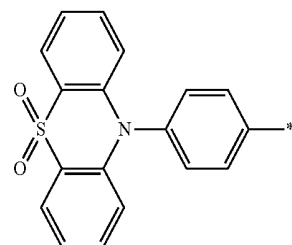
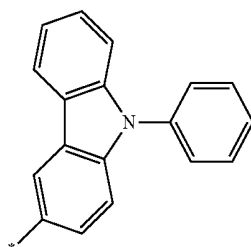
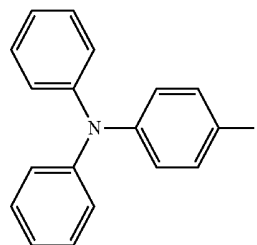
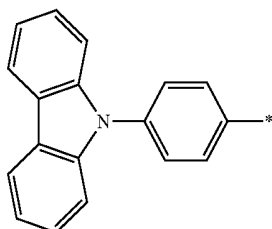
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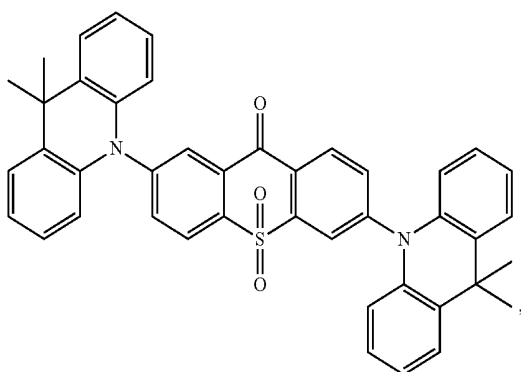
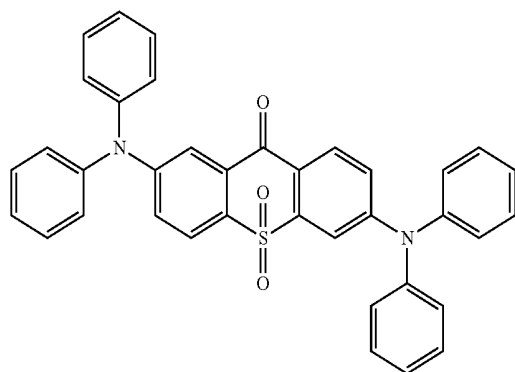
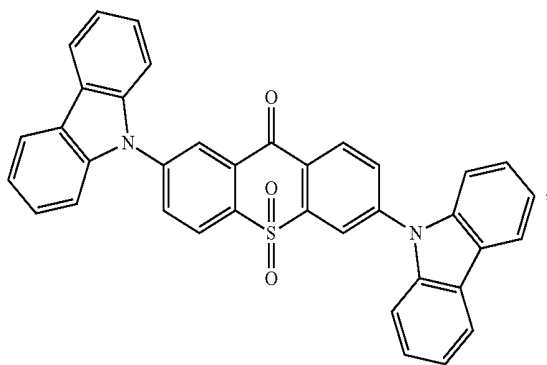
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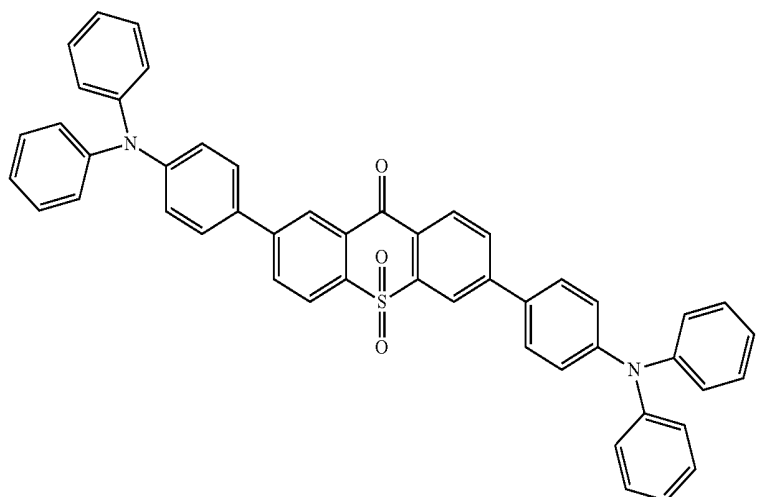
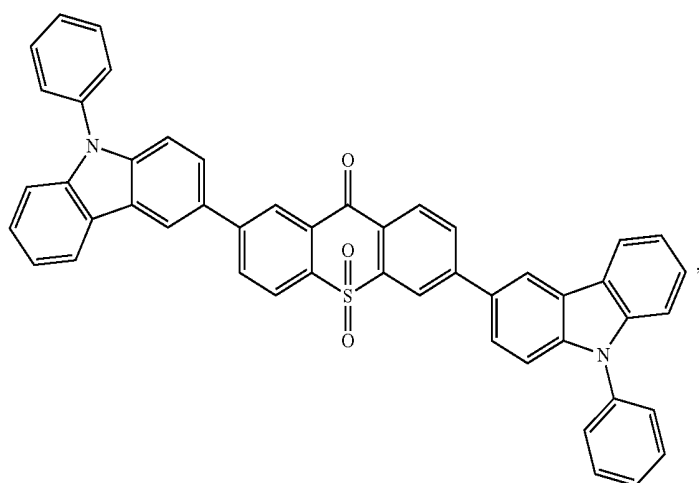
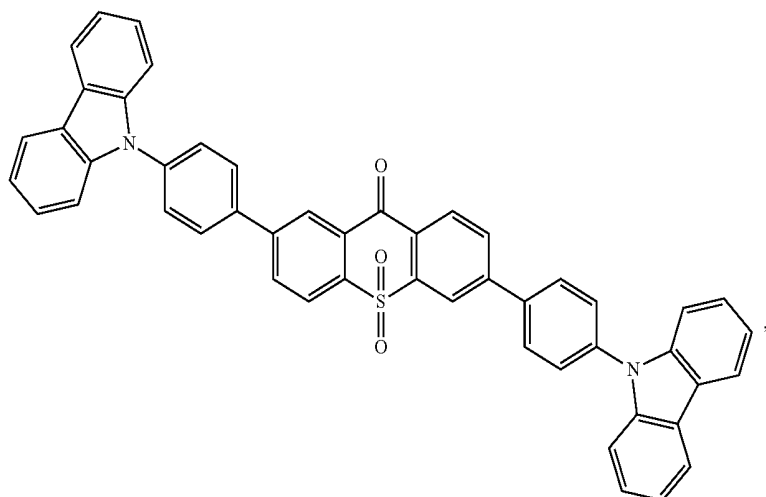


[0010] Ar₁ and Ar₂ are the same.

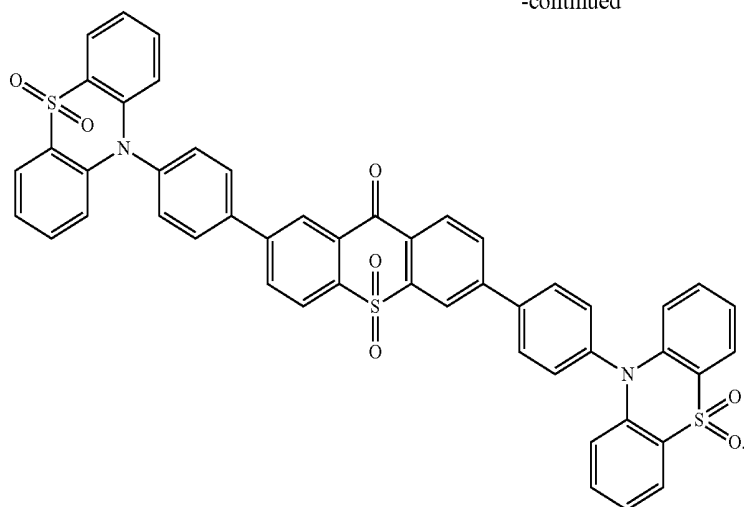
[0011] The light emitting material comprises one or more of following compounds:



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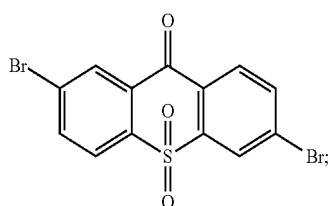


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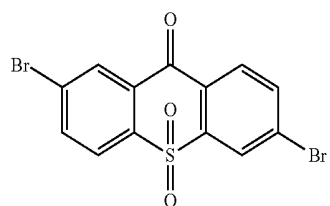


[0012] The present invention further provides a manufacture method of light emitting material, comprising steps of:

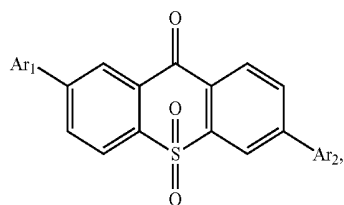
[0013] step 1, manufacturing an intermediate



[0014] step 2, obtaining light emitting material with Ullmann reaction or Suzuki reaction of the intermediate

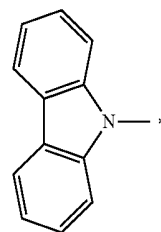


and an aromatic amine compound, in which a constitutional formula of the light emitting material is

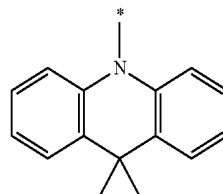


wherein Ar₁ and Ar₂ are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);

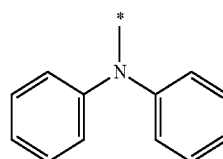
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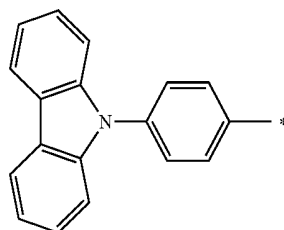
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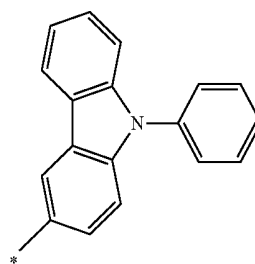
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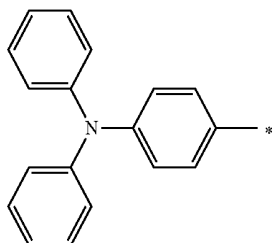
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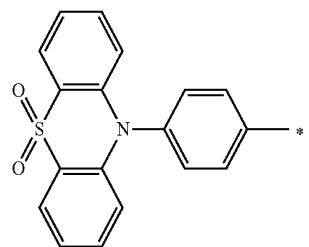


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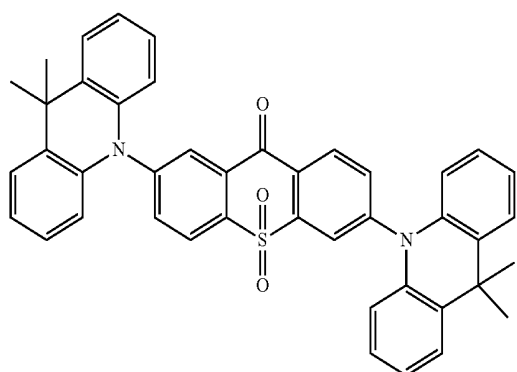
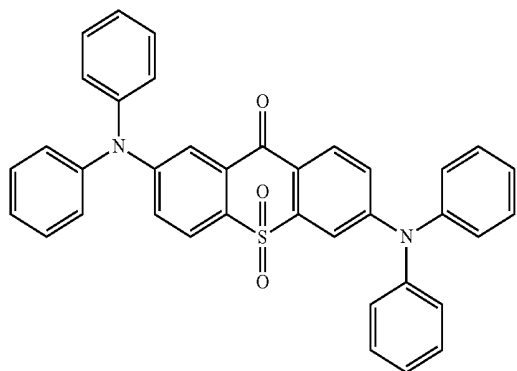
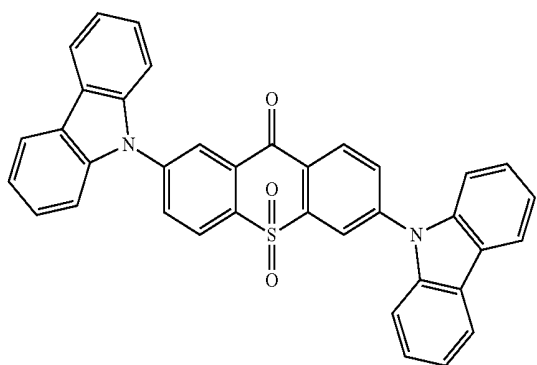
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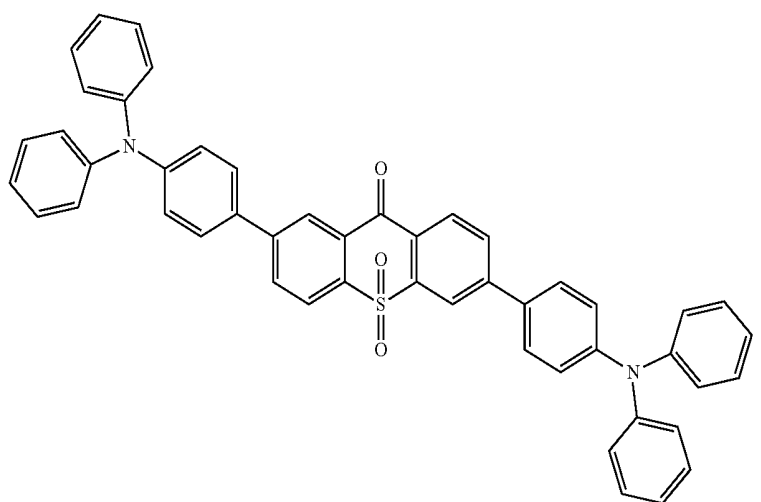
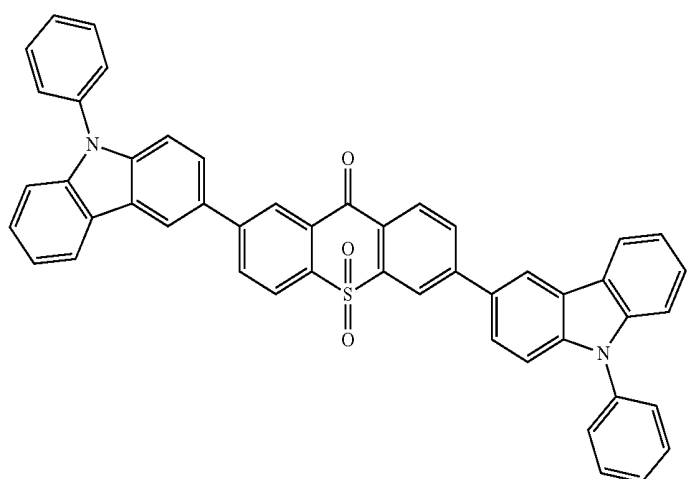
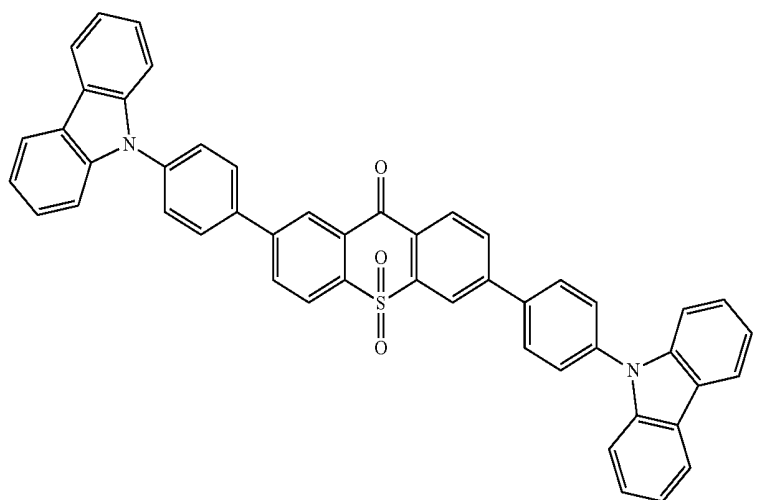
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[0015] Ar_1 and Ar_2 are the same.

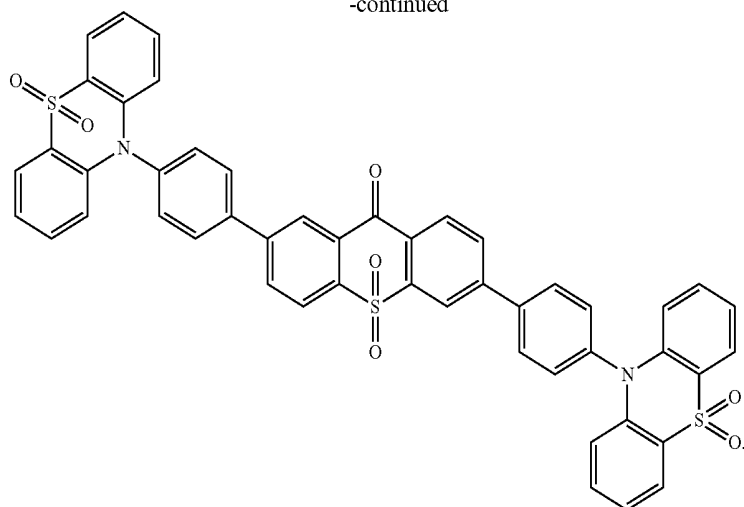
[0016] The light emitting material comprises one or more of following compounds:



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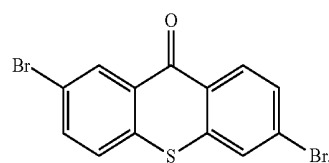
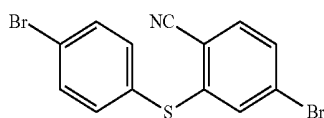
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[0017] The step 1 comprises:

to obtain

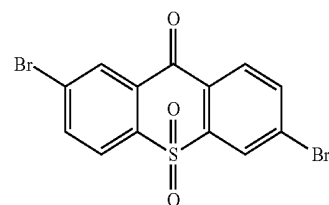
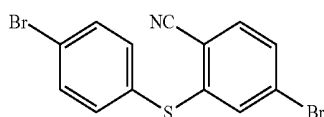
[0018] step 11, obtaining



with a reaction of p-bromothiophenol and 4-Bromo-2-fluorobenzonitrile;

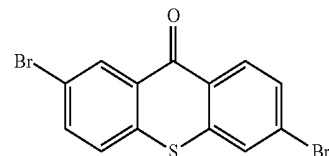
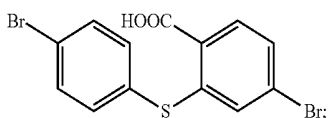
[0021] step 14, obtaining the intermediate

[0019] step 12, hydrolyzing



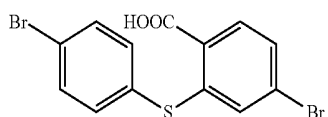
in an alkaline condition, and acidizing the same to obtain

with a reaction of



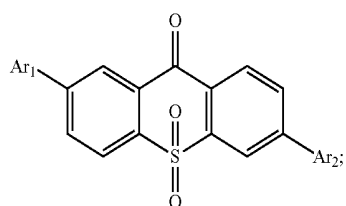
[0020] step 13, generating dehydration condensation reaction to

and hydrogen peroxide.

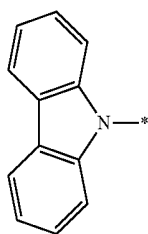


[0022] The present invention provides an organic light emitting diode, comprising a substrate, and an anode, a Hole Injection Layer, a Hole Transporting Layer, a light emitting layer, an Electron Transport Layer, an Electron Injection Layer and a cathode stacking up on the substrate from bottom to top in order;

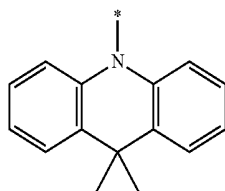
[0023] the light emitting layer comprises light emitting material, in which a constitutional formula is



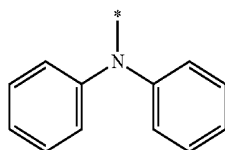
[0024] wherein Ar₁ and Ar₂ are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);



(1)

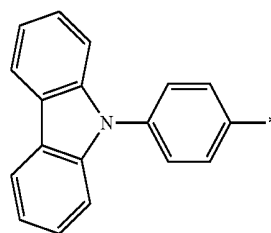


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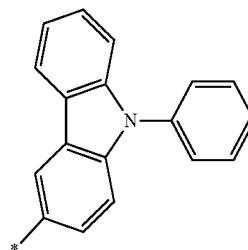


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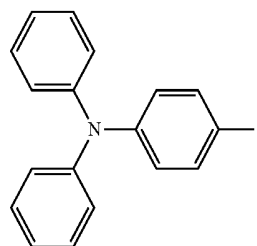
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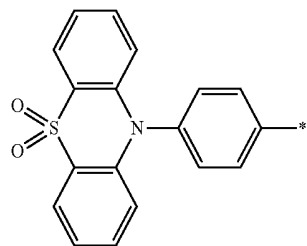
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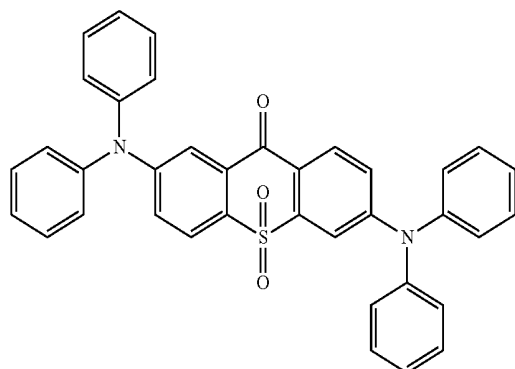
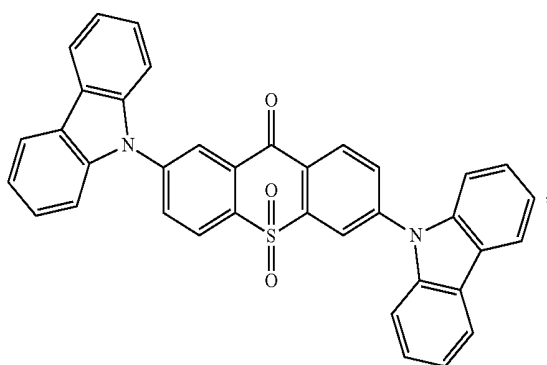
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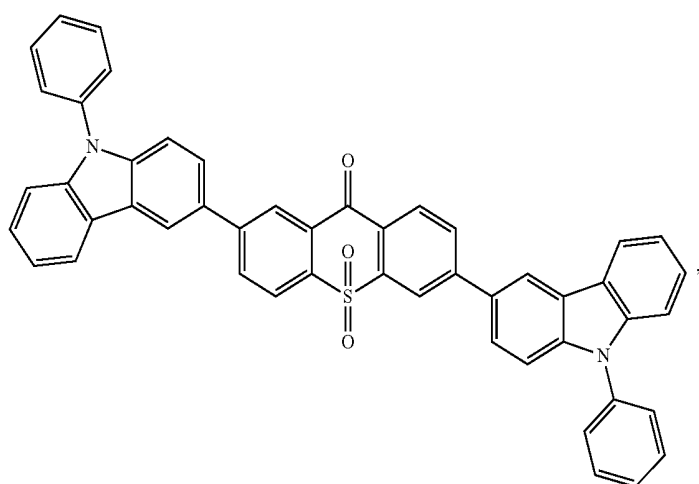
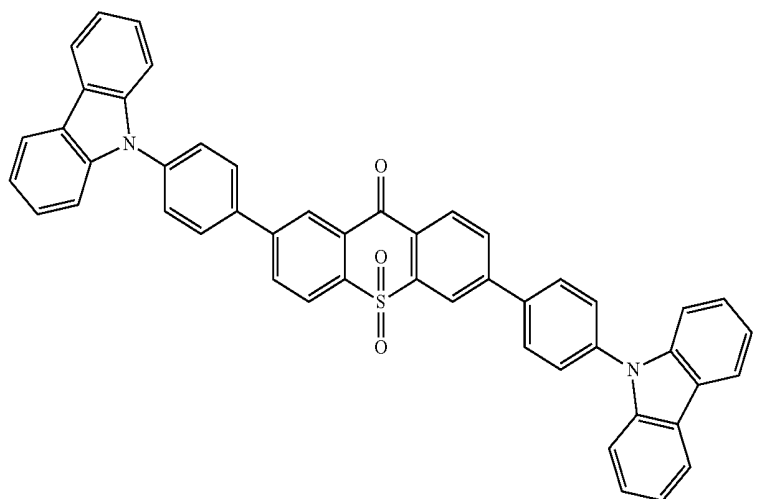
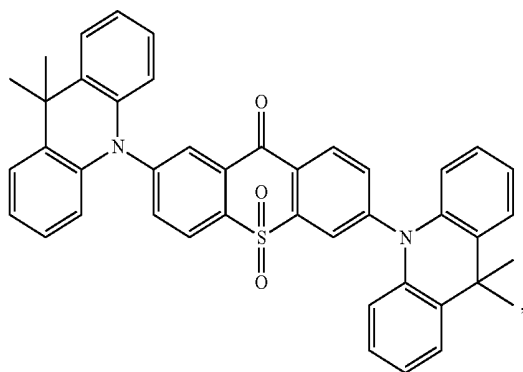
(7)

[0025] Ar₁ and Ar₂ are the same.

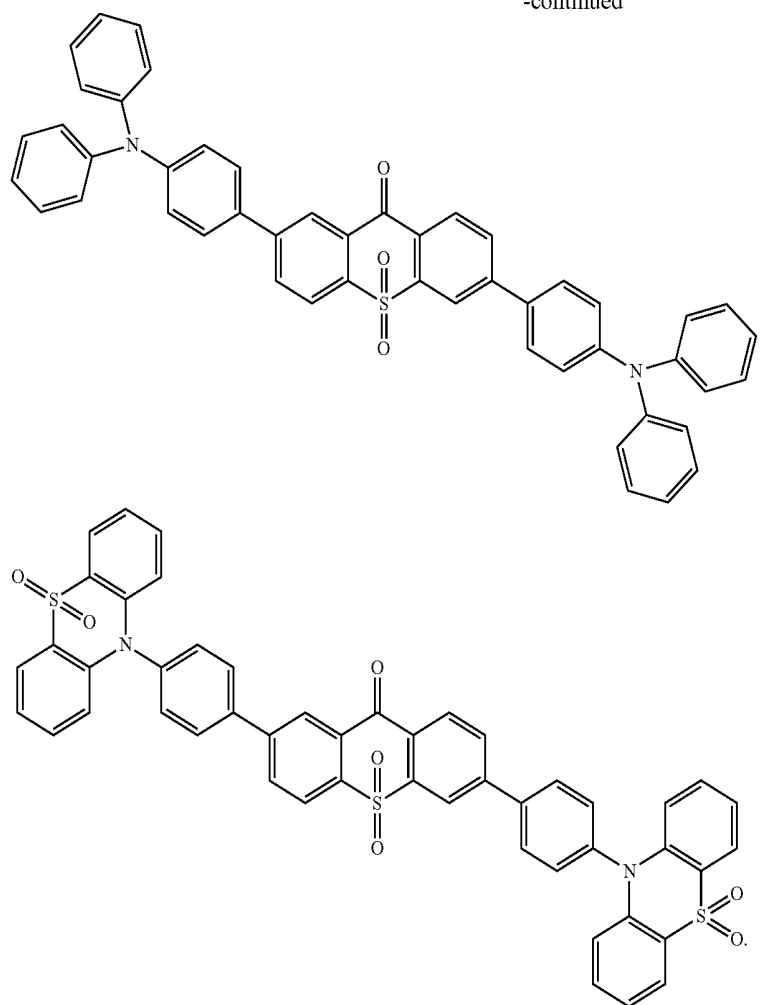
[0026] The light emitting material comprises one or more of following compounds:



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[0027] The benefits of the present invention are: the present invention provides a light emitting material, in which the structure is unitary, and the formula weight is determined, and the better solubility and film formation are provided, and the thin film status is stable; it possesses a very high decomposition temperature and a lower sublimation temperature, and is easy to sublime to be light emitting material of high purity, and can be applied for small molecule organic light emitting diode; by changing the aromatic amine group, which is connected, the physical property can be improved in advance to promote the performance of the photoelectric element of the light emitting material. The present invention provides a manufacture method of the light emitting material. p-bromothiophenol and 4-Bromo-2-fluorobenzonitrile are employed to be starting materials, and the intermediate of the light emitting material is obtained with a series of simple reactions, and finally, the light emitting material is obtained with Ullmann reaction or Suzuki reaction, and the steps are simple and the production is high. The present invention provides an organic light emitting diode, in which the light emitting layer comprises the aforesaid light emitting material that has higher light emission efficiency and stability.

[0028] In order to better understand the characteristics and technical aspect of the invention, please refer to the follow-

ing detailed description of the present invention is concerned with the diagrams, however, provide reference to the accompanying drawings and description only and is not intended to be limiting of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The technical solution and the beneficial effects of the present invention are best understood from the following detailed description with reference to the accompanying figures and embodiments.

[0030] In drawings,

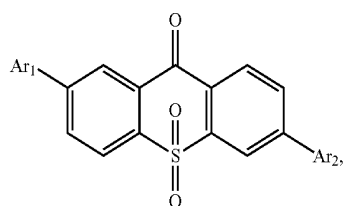
[0031] FIG. 1 is a flowchart of a manufacture method of light emitting material according to the present invention;

[0032] FIG. 2 is a structure diagram of an organic light emitting diode according to the present invention.

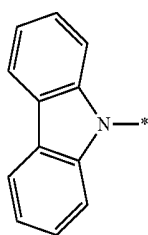
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0033] For better explaining the technical solution and the effect of the present invention, the present invention will be further described in detail with the accompanying drawings and the specific embodiments.

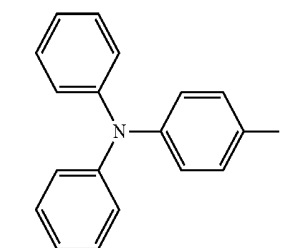
[0034] The present invention first provides a light emitting material, in which a constitutional formula is



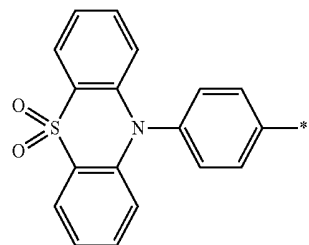
wherein Ar_1 and Ar_2 are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);



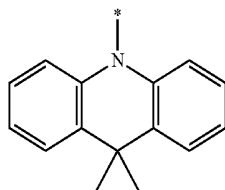
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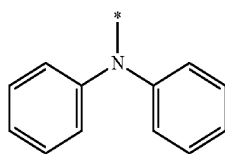
(6)



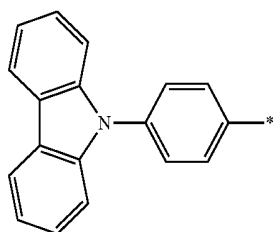
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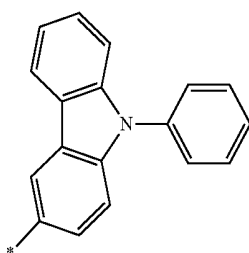
(2)



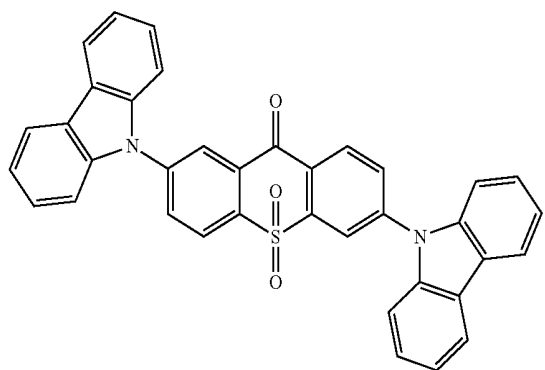
(3)



(4)

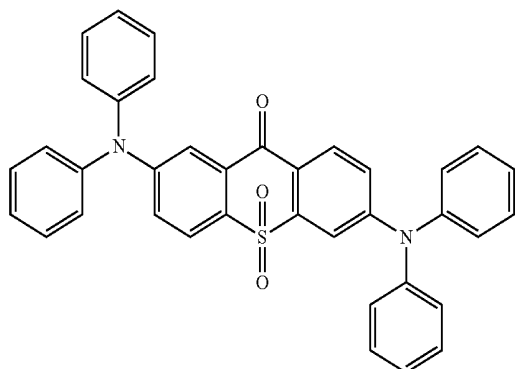


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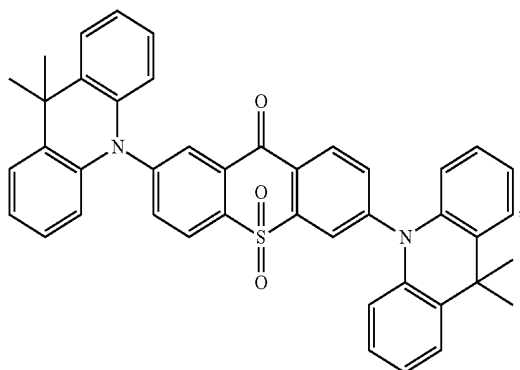


[0035] Preferably, Ar_1 and Ar_2 are the same.

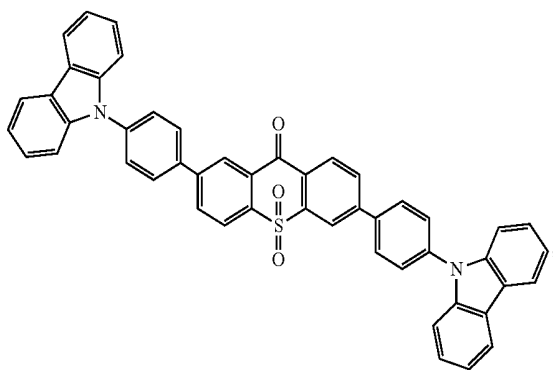
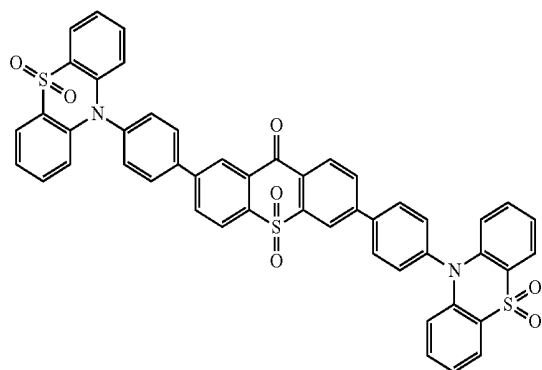
[0036] Specifically, the light emitting material comprises one or more of following compounds:



-continued



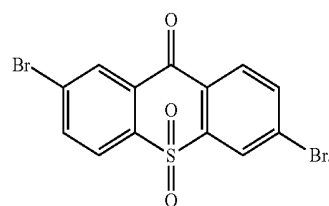
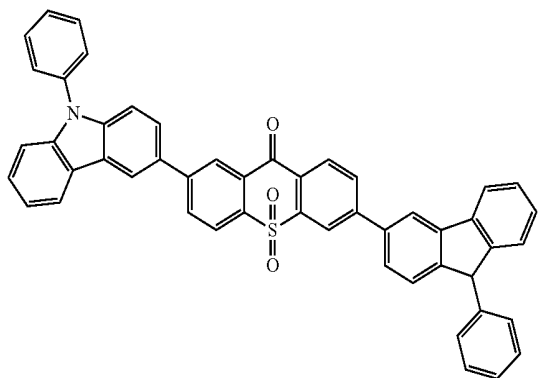
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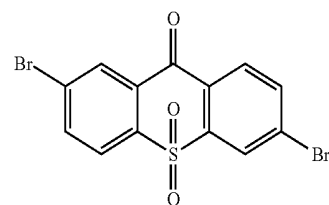
[0037] In the aforesaid light emitting material, the structure is unitary, and the formula weight is determined, and the better solubility and film formation are provided, and the thin film status is stable; it possesses a very high decomposition temperature and a lower sublimation temperature, and is easy to sublime to be light emitting material of high purity, and can be applied for small molecule organic light emitting diode; by changing the aromatic amine group, which is connected, the physical property can be improved in advance to promote the performance of the photoelectric element of the light emitting material.

[0038] Please refer to FIG. 1. The present invention further provides a manufacture method of light emitting material, comprising steps of:

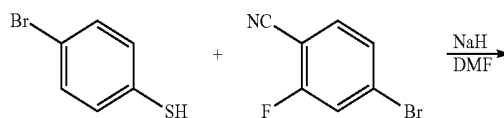
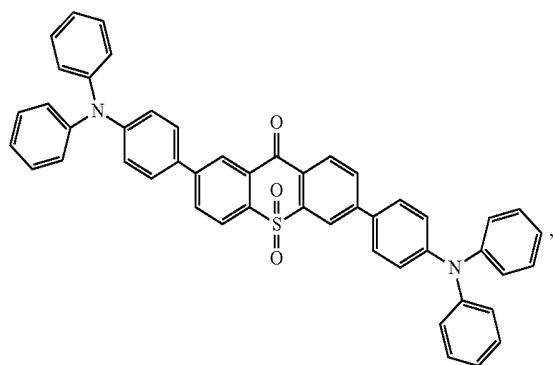
[0039] step 1, manufacturing an intermediate

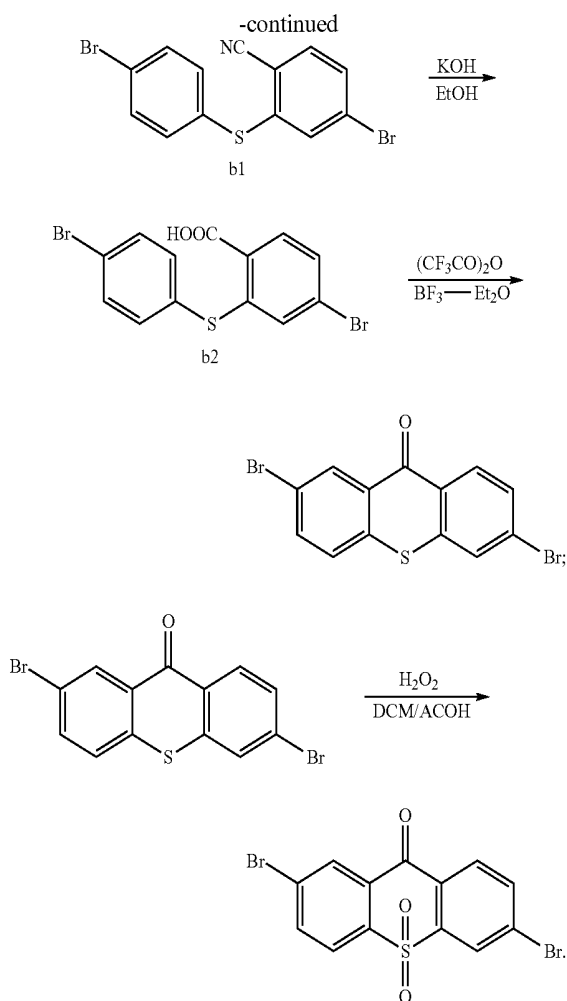


[0040] A synthetic route of the intermediate



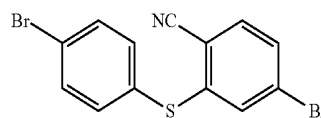
is:



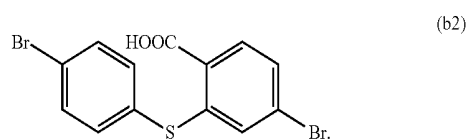


color solid 5.2 g, i.e. the compound b1 is obtained. Molecular formula: $C_{13}H_7Br_2NS$, and MS: 366.87, and elemental analysis: C, 42.31; H, 1.91; Br, 43.30; N, 3.80; S, 8.69.

[0045] step 12, hydrolyzing



in an alkaline condition, and acidizing the same to obtain



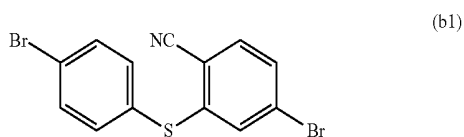
[0046] The specific implementing steps of the step 12 are:

[0047] In 250 ml boiling flask-3-neck, 80 ml deionized water, 15 g KOH and 80 ml alcohol are added, and 5.2 g compound b1 is added in reaction bottle to reflux overnight under protection of nitrogen. After the reaction is completed, the reaction solution is cooled to the room temperature, and added in 100 ml 6M hydrochloric acid, the white solid is separated out with ice bath, and extracted and filtered, and then dried to obtain white solid 5.1 g, i.e. the compound b2. Molecular formula: $C_{13}H_8Br_2O_2S$, and MS: 385.86, and elemental analysis: C, 40.23; H, 2.08; Br, 41.18; O, 8.25; S, 8.26.

[0048] step 13, generating dehydration condensation reaction to

[0041] Specifically, the step 1 comprises steps of:

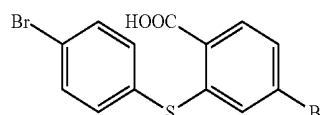
[0042] step 11, obtaining



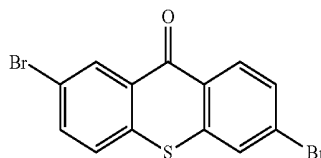
with a reaction of p-bromothiophenol and 4-Bromo-2-fluorobenzonitrile.

[0043] The specific implementing steps of the step 11 are:

[0044] In 250 ml boiling flask-3-neck, 0.73 g (30 mmol) NaH is slowly added in 20 ml dry dimethylformamide (DMF) dissolved with 4.6 g (25 mmol) p-bromothiophenol, and then 20 ml dry dimethylformamide dissolved with 5 g (25 mmol) 4-Bromo-2-fluorobenzonitrile is dropped into it. Under the protection of nitrogen, 20 h heating reflux reaction is implemented, and the temperature drops to the room temperature after the reaction is completed, and then the reaction fluid is poured in 50 ml 1M NaOH solution, and extracted in dichloromethane (DCM) to be decompressed to remove the solvent, and through silicagel column, white

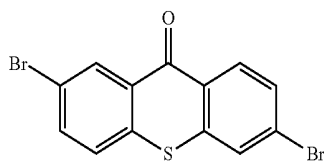


to obtain



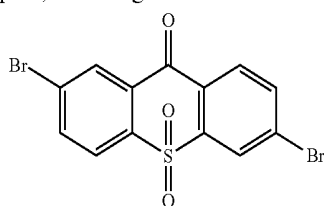
[0049] The specific implementing steps of the step 13 are:

[0050] In 500 ml boiling flask, 2.75 g (10 mmol) compound b2 is added, and 500 ml chloroform is added to be solvent, and 3.2 g (20 mmol, 2 equ) trifluoroacetic anhydride is dropped, and stirred 10 min in the room temperature, and then 0.5 g Boron trifluoride etherate is added, and the ice bath is removed for reacting 12 h at the room temperature. After the reaction is completed, sodium sulfite saturated aqueous solution is added to quench redundant trifluoroacetic anhydride, and separated, and reduced pressure distilled to remove the solvent, and through column,

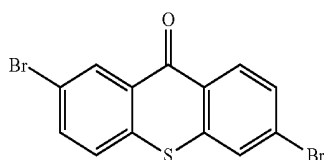


is obtained. Molecular formula: $C_{13}H_8Br_2O_2S$; MS: 385.86; elemental analysis: C, 40.23; H, 2.08; Br, 41.18; O, 8.25; S, 8.26.

[0051] step 14, obtaining the intermediate



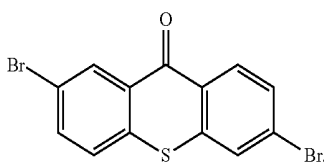
with a reaction of



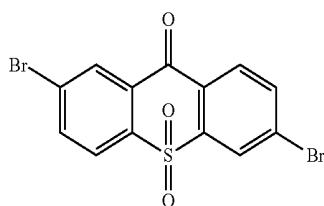
and hydrogen peroxide.

[0052] The specific implementing steps of the step 14 are:

[0053] In 250 ml boiling flask-3-neck, 5 g (13.59 mmol), 50 mL dichloromethane

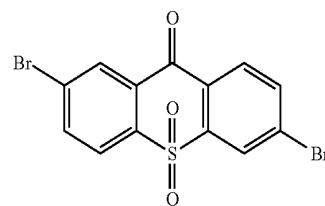


20 mL ethylic acid, 3 mL (5 equ) hydrogen peroxide are added. The reaction last 8 hours at 80° C., and the temperature is lowered after the reaction is completed, and water is used to remove redundant hydrogen peroxide for extraction. Through column, 4.6 g intermediate

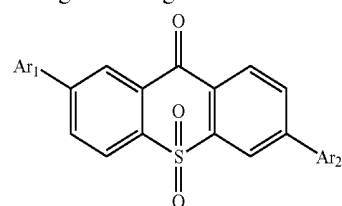


is obtained, and productivity is 85%. Molecular formula: $C_{13}H_6Br_2O_3S$; M/Z=399.84; theoretic value: 402.06; elemental analysis: 401.84 (100.0%), 399.84 (50.0%), 403.84 (48.1%), 402.84 (15.0%), 404.84 (7.8%), 400.84 (7.5%), 403.83 (4.4%), 405.83 (2.2%).

[0054] step 2, obtaining light emitting material with Ullmann reaction or Suzuki reaction of the intermediate

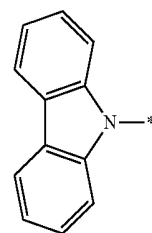


and an aromatic amine compound, in which a constitutional formula of the light emitting material is

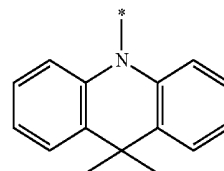


wherein Ar₁ and Ar₂ are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);

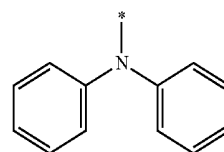
(1)



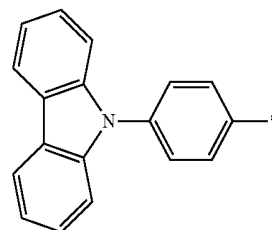
(2)



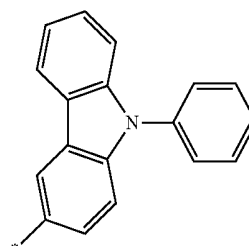
(3)



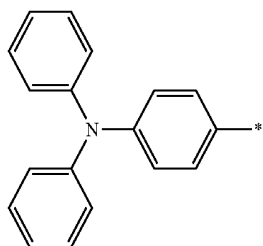
(4)



(5)

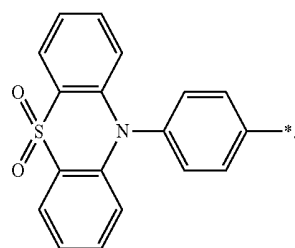


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(6)

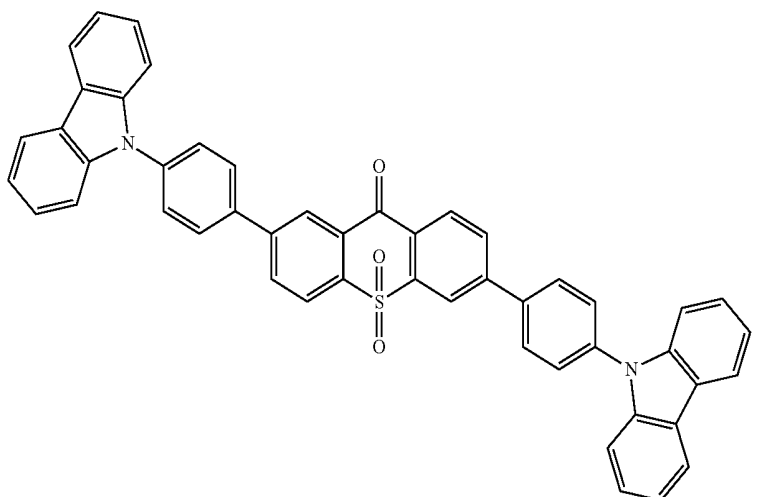
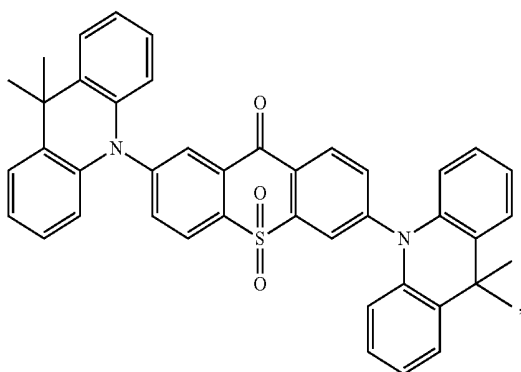
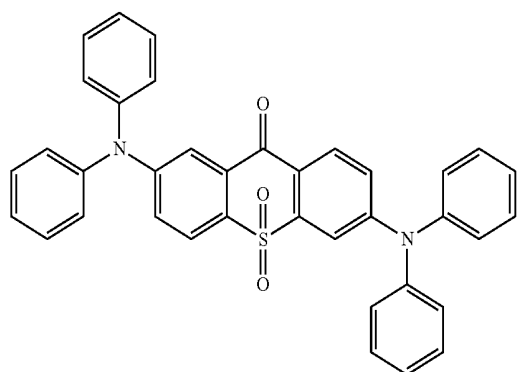
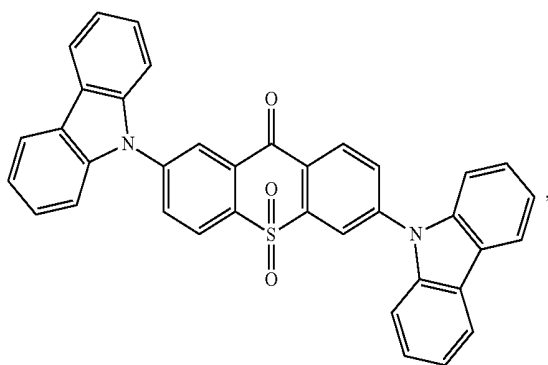
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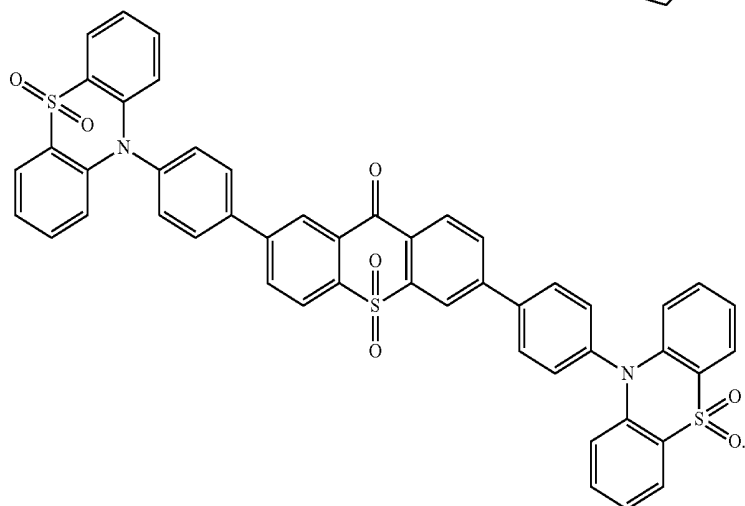
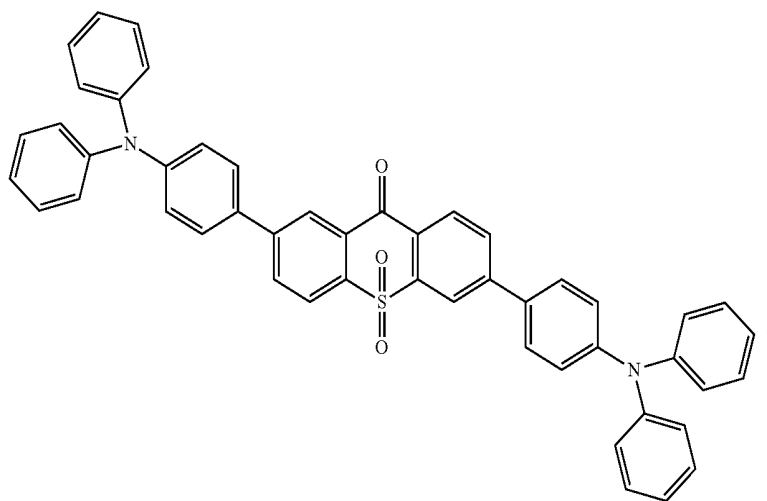
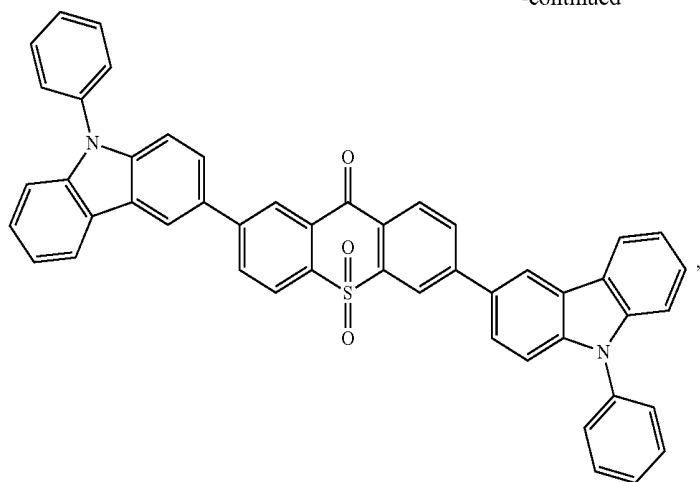
(7)

[0055] Preferably, Ar₁ and Ar₂ are the same.

[0056] Specifically, the light emitting material comprises one or more of following compounds:

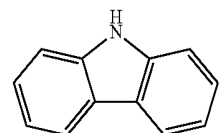


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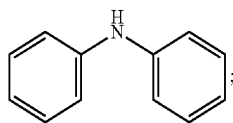


[0057] Specifically, in the step 2, the aromatic amine compound comprises one or more of carbazol, diphenylamine, 9,9-dimethylacridan, 4-carbazoleBenzene borate ester, 4-phenylcarbazole borate ester, 4-triphenylamine borate ester, 4-phenylthiophene-S,S-dioxide borate ester;

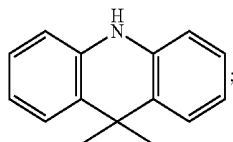
[0058] a constitutional formula of the carbazol is



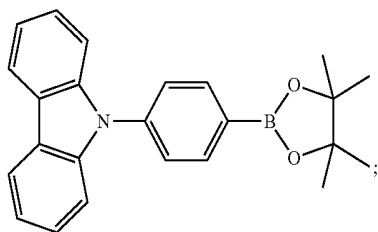
[0059] a constitutional formula of the diphenylamine is



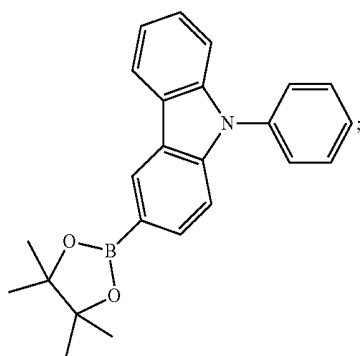
[0060] a constitutional formula of the 9,9-diMethylacridan is



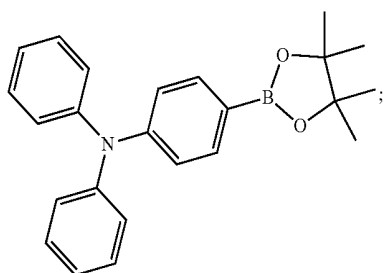
[0061] a constitutional formula of the 4-carbazoleBenzene borate ester is



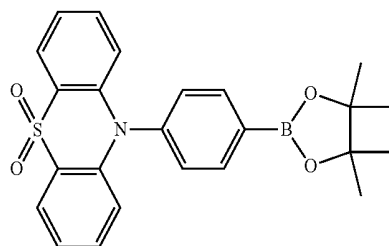
[0062] a constitutional formula of the 4-phenylcarbazole borate ester is



[0063] a constitutional formula of the 4-triphenylamine borate ester is



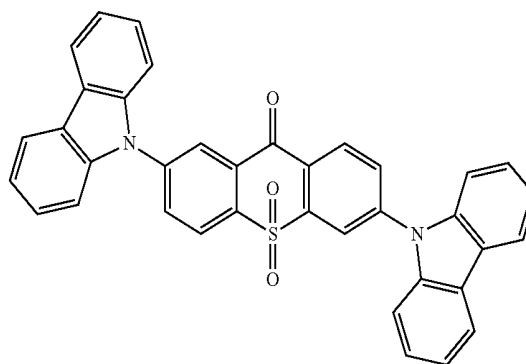
[0064] a constitutional formula of the 4-phenylthiophene-S,S-dioxide borate ester is



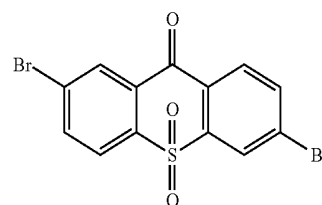
[0065] The specific implementing method of the step 2 is described below in detail with combination of the specific embodiment.

Embodiment 1

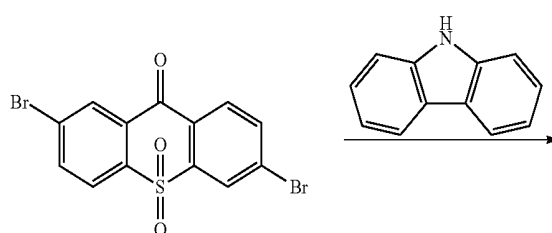
[0066]



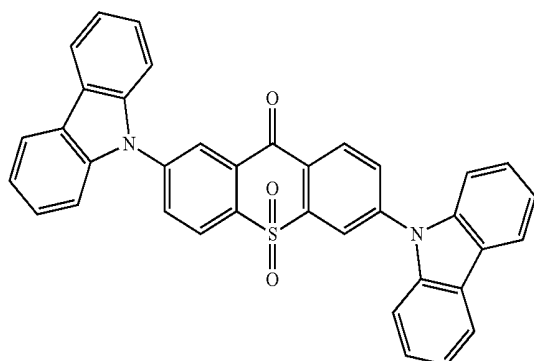
is obtained with Ullmann reaction of intermediate



and carbazol, and the reaction formula is:

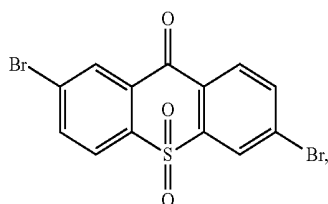


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[0067] The specific implementing steps are:

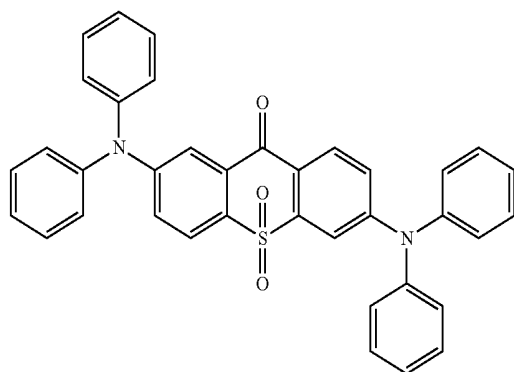
[0068] Under the protection of nitrogen, in boiling flask-3-neck, 100 ml methylbenzene, 0.72 g (2 mmol) intermediate



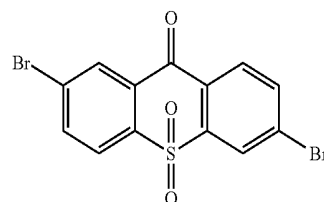
0.67 g (4 mmol) carbazole are added, and 0.3 g sodium tert-butoxide is added in stirring, and then 20 mg tris (dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) is added, and then 0.3 ml 10% tri-tert-butylphosphine hexane solution is added, and heated reflux to react overnight. The temperature is lowered, and extracted in dichloromethane in organic phase, and spin dried, and through column. White color solid product 0.81 g is obtained, and productivity is 75%. Molecular formula: $\text{C}_{37}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$; $\text{M/S}=574.14$; theoretic value: 574.65; elemental analysis: 574.14 (100.0%), 575.14 (40.4%), 576.14 (9.2%), 576.13 (4.5%), 577.13 (1.8%), 575.13 (1.5%), 577.15 (1.0%).

Embodiment 2

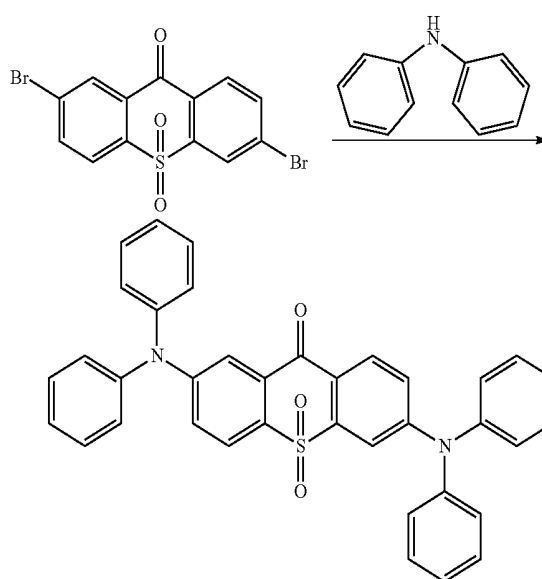
[0069]



is obtained with Ullmann reaction of intermediate

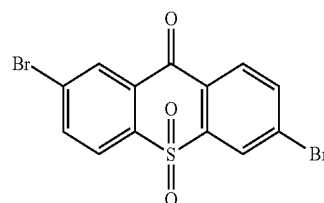


and diphenylamine, and the reaction formula is:



[0070] The specific implementing steps are:

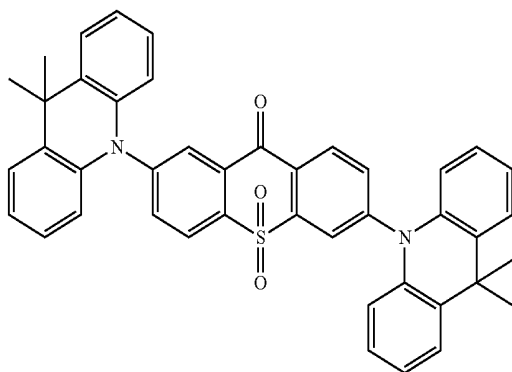
[0071] Under the protection of nitrogen, in boiling flask-3-neck, 100 ml methylbenzene, 0.72 g (2 mmol) intermediate



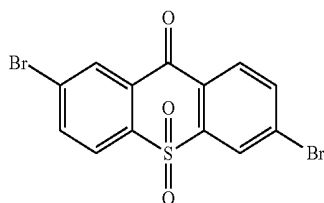
0.84 g (4 mmol) diphenylamine are added, and 0.3 g sodium tert-butoxide is added in stirring, and then 20 mg tris (dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) is added, and then 0.3 ml 10% tri-tert-butylphosphine hexane solution is added, and heated reflux to react overnight. The temperature is lowered, and extracted in dichloromethane in organic phase, and spin dried, and through column. White color solid product 0.81 g is obtained, and productivity is 75%. Molecular formula: $\text{C}_{37}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$; $\text{M/S}=578.17$; theoretic value: 578.68; elemental analysis: 578.17 (100.0%), 579.17 (41.2%), 580.17 (9.1%), 580.16 (4.5%), 581.17 (2.2%), 581.18 (1.0%).

Embodiment 3

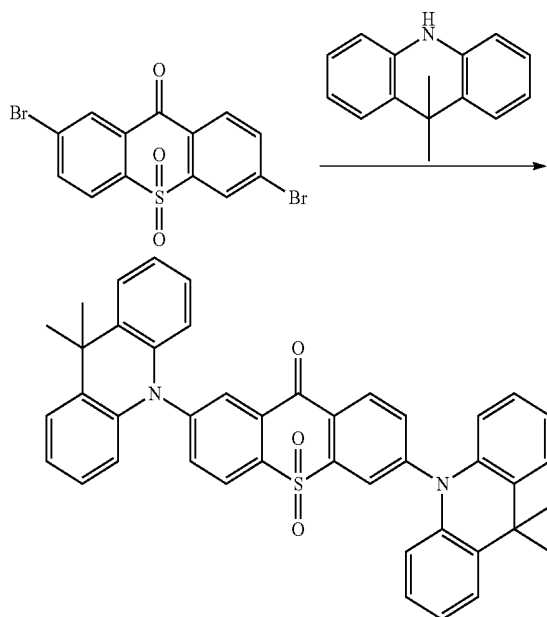
[0072]



is obtained with Ullmann reaction of intermediate

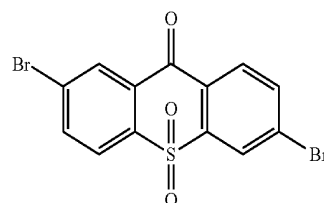


and 9,9-diMethylacridan, and the reaction formula is:



[0073] The specific implementing steps are:

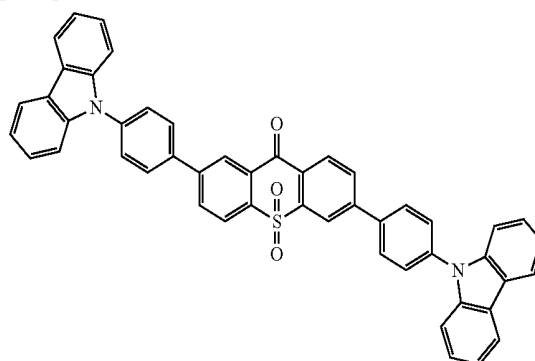
[0074] Under the protection of nitrogen, in boiling flask-3-neck, 100 ml methylbenzene, 0.72 g (2 mmol) intermediate



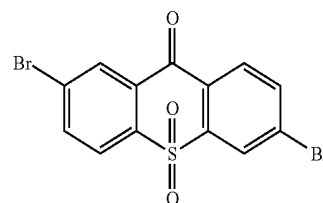
0.84 g (4 mmol) 9,9-diMethylacridan are added, and 0.3 g sodium tert-butoxide is added in stirring, and then 20 mg tris(dibenzylideneacetone)dipalladium (Pd2(dba)3) is added, and then 0.3 ml 10% tri-tert-butylphosphine hexane solution is added, and heated reflux to react overnight. The temperature is lowered, and extracted in dichloromethane in organic phase, and spin dried, and through column. White color solid product 0.85 g is obtained, and productivity is 79%. Molecular formula: $C_{43}H_{34}N_2O_3S$; M/S=658.23; theoretic value: 658.81; elemental analysis: 658.23 (100.0%), 659.23 (48.2%), 660.24 (10.8%), 660.22 (4.5%), 661.23 (2.2%), 661.24 (2.0%), 660.23 (1.3%).

Embodiment 4

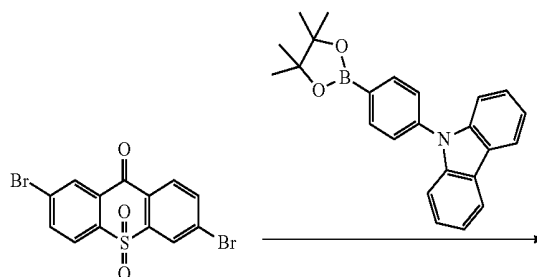
[0075]



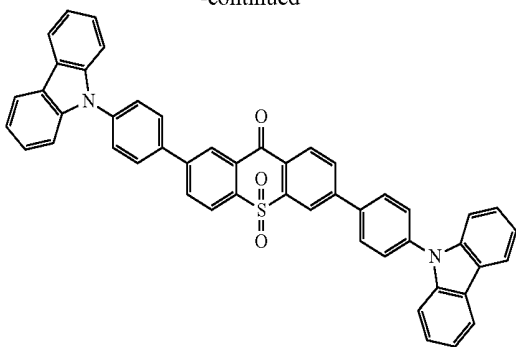
is obtained with Suzuki reaction of intermediate



and 4-carbazoleBenzene borate ester, and the reaction formula is:

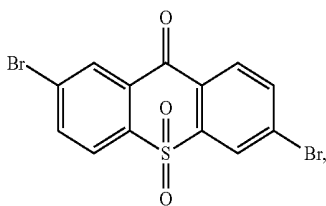


-continued



[0076] The specific implementing steps are:

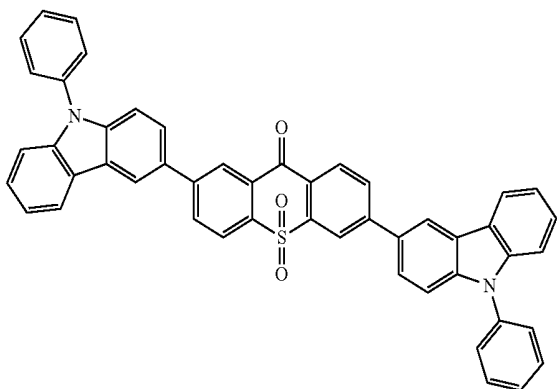
[0077] Under the atmosphere of nitrogen, in 250 ml boiling flask, 96 ml methylbenzene, 32 ml alcohol, 16 ml 2M potassium carbonate aqueous solution, 0.72 g (2 mmol) intermediate



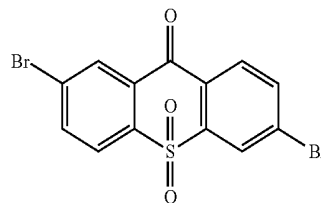
2.06 g (1.2 equ) 4-carbazoleBenzene borate ester are added, and stirred at the room temperature, and then 100 mg triphenylphosphineplatinum (catalyzer) is added and 96° C. reflows for 24 hours. It is cooled to the room temperature, and extracted in dichloromethane, and dried in anhydrous magnesium sulfate. White color solid product 0.86 g is obtained, and productivity is 79%. Molecular formula: $C_{49}H_{30}N_2O_3S$; M/S=726.2; theoretic value: 726.84; elemental analysis: 726.20 (100.0%), 727.20 (54.3%), 728.20 (15.2%), 728.19 (4.5%), 729.21 (2.7%), 729.20 (2.6%).

Embodiment 5

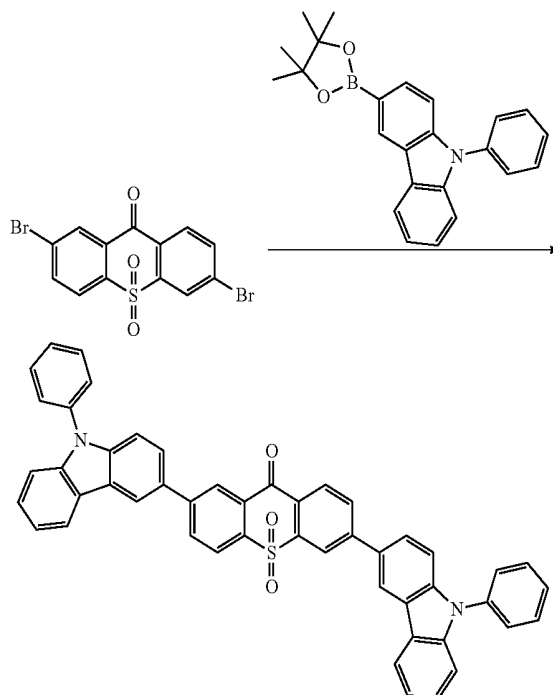
[0078]



is obtained with Suzuki reaction of intermediate

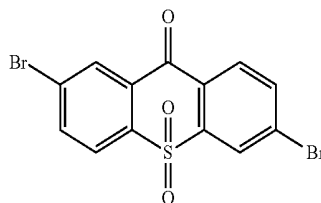


and 4-phenylcarbazole borate ester, and the reaction formula is:



[0079] The specific implementing steps are:

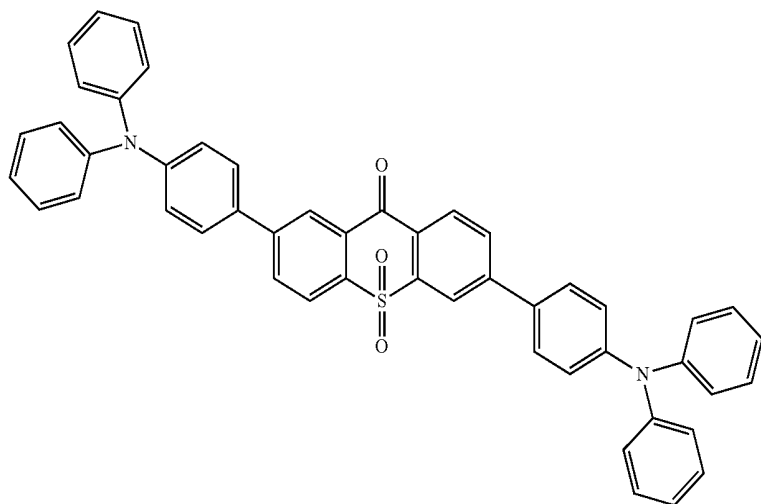
[0080] Under the atmosphere of nitrogen, in 250 ml boiling flask, 96 ml methylbenzene, 32 ml alcohol, 16 ml 2M potassium carbonate aqueous solution, 0.72 g (2 mmol) intermediate



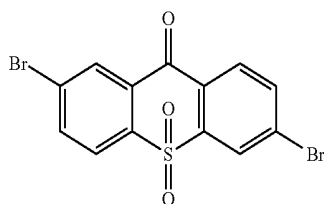
2.32 g (1.2 equ) 4-phenylcarbazole borate ester are added, and stirred at the room temperature, and then 100 mg triphenylphosphineplatinum (catalyzer) is added and 96° C. reflows for 24 hours. It is cooled to the room temperature, and extracted in dichloromethane, and dried in anhydrous magnesium sulfate. White color solid product 0.92 g is obtained, and productivity is 83%. Molecular formula: $C_{49}H_{30}N_2O_3S$; M/S=726.2; theoretic value: 726.84; elemental analysis: 726.20 (100.0%), 727.20 (54.3%), 728.20 (15.2%), 728.19 (4.5%), 729.21 (2.7%), 729.20 (2.6%).

Embodiment 6

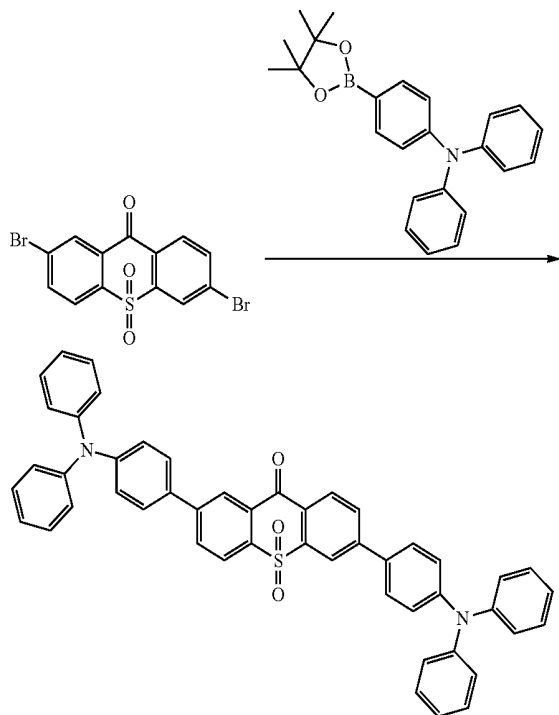
[0081]



is obtained with Suzuki reaction of intermediate

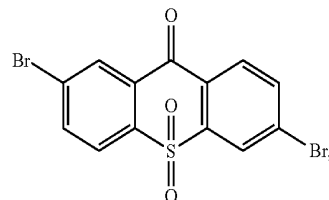


and 4-triphenylamine borate ester, and the reaction formula is:



[0082] The specific implementing steps are:

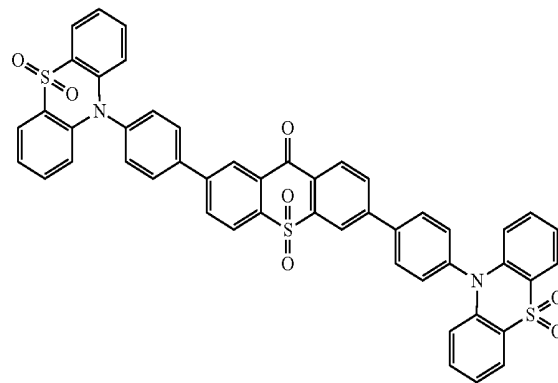
[0083] Under the atmosphere of nitrogen, in 250 ml boiling flask, 96 ml methylbenzene, 32 ml alcohol, 16 ml 2M potassium carbonate aqueous solution, 0.72 g (2 mmol) intermediate



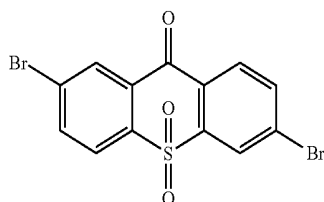
2.32 g (1.2 equ) 4-triphenylamine borate ester are added, and stirred at the room temperature, and then 100 mg triphenylphosphineplatinum (catalyzer) is added and 96° C. reflows for 24 hours. It is cooled to the room temperature, and extracted in dichloromethane, and dried in anhydrous magnesium sulfate. White color solid product 0.96 g is obtained, and productivity is 87%. Molecular formula: C₄₉H₃₄N₂O₃S; M/S=730.23; theoretic value: 730.87; elemental analysis: 730.23 (100.0%), 731.23 (54.7%), 732.24 (14.0%), 732.22 (4.5%), 733.24 (2.8%), 733.23 (2.5%), 732.23 (1.4%).

Embodiment 7

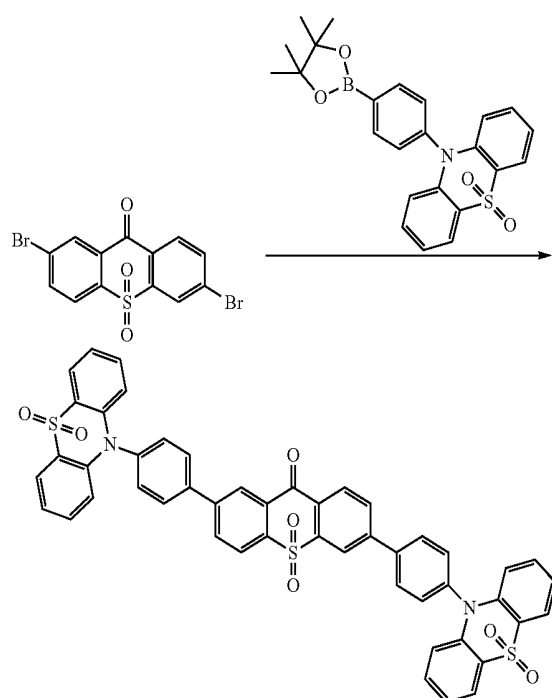
[0084]



is obtained with Suzuki reaction of intermediate

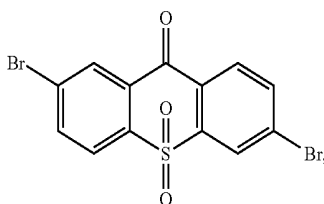


and 4-phenylthiophene-S,S-dioxide borate ester, and the reaction formula is:



[0085] The specific implementing steps are:

[0086] Under the atmosphere of nitrogen, in 250 ml boiling flask, 96 ml methylbenzene, 32 ml alcohol, 16 ml 2M potassium carbonate aqueous solution, 0.72 g (2 mmol) intermediate



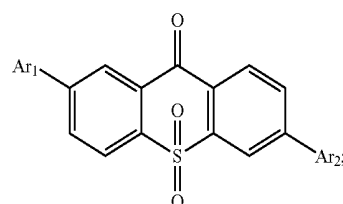
2.06 g (1.2 equ) 4-phenylthiophene-S,S-dioxide borate ester are added, and stirred at the room temperature, and then 100 mg triphenylphosphineplatinum (catalyzer) is added and 96° C. refluxes for 24 hours. It is cooled to the room temperature, and extracted in dichloromethane, and dried in anhydrous magnesium sulfate. White color solid product 0.96 g is obtained, and productivity is 87%. Molecular formula:

$C_{49}H_{30}N_2O_7S_3$; $M/S=854.12$; theoretic value: 854.97; elemental analysis: 854.12 (100.0%), 855.12 (56.1%), 856.13 (15.5%), 856.12 (15.3%), 857.12 (7.5%), 857.13 (3.7%), 858.12 (2.3%).

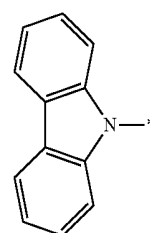
[0087] In the aforesaid manufacture method of the light emitting material, p-bromothiophenol and 4-Bromo-2-fluorobenzonitrile are employed to be starting materials, and the intermediate of the light emitting material is obtained with a series of simple reactions, and finally, the light emitting material is obtained with Ullmann reaction or Suzuki reaction, and the steps are simple and the production is high.

[0088] Please refer to FIG. 2. The present invention further provides an organic light emitting diode, comprising a substrate 10, and an anode 20, a Hole Injection Layer 30, a Hole Transporting Layer 40, a light emitting layer 50, an Electron Transport Layer 60, an Electron Injection Layer 70 and a cathode 80 stacking up on the substrate 10 from bottom to top in order;

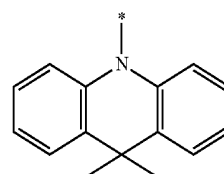
[0089] the light emitting layer 50 comprises light emitting material, in which a constitutional formula is



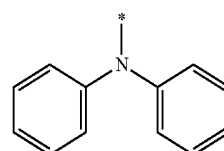
[0090] wherein Ar_1 and Ar_2 are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);



(1)

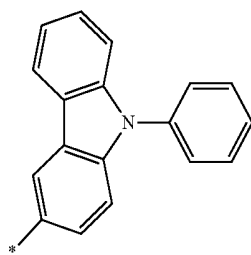
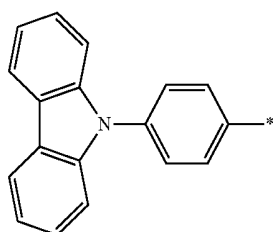


(2)

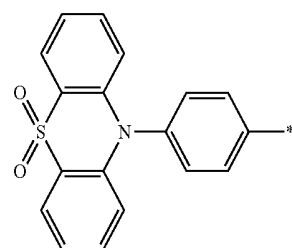
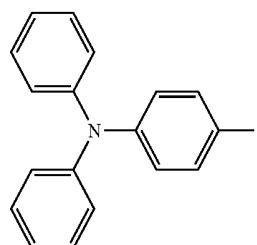


(3)

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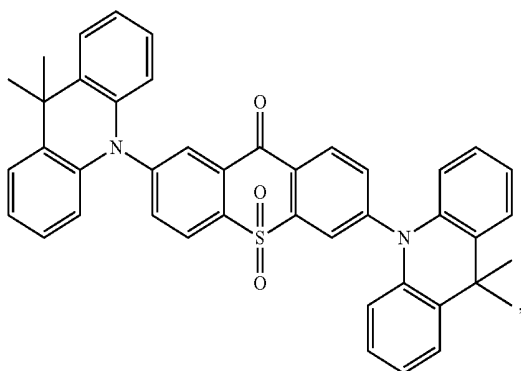
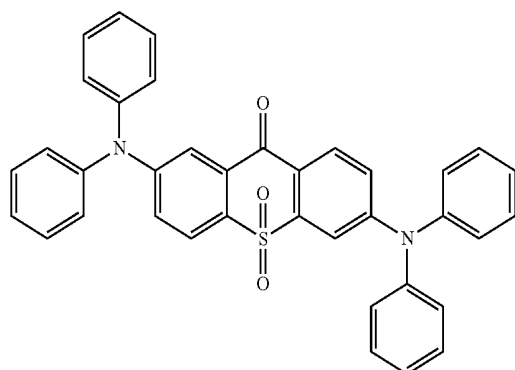
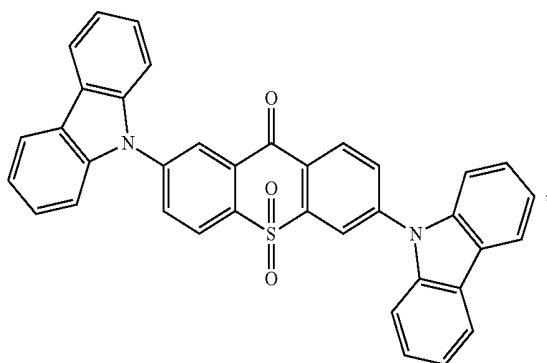


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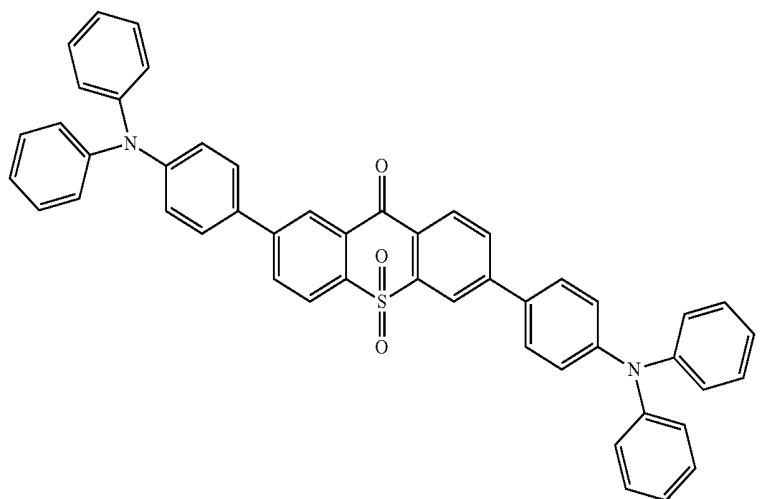
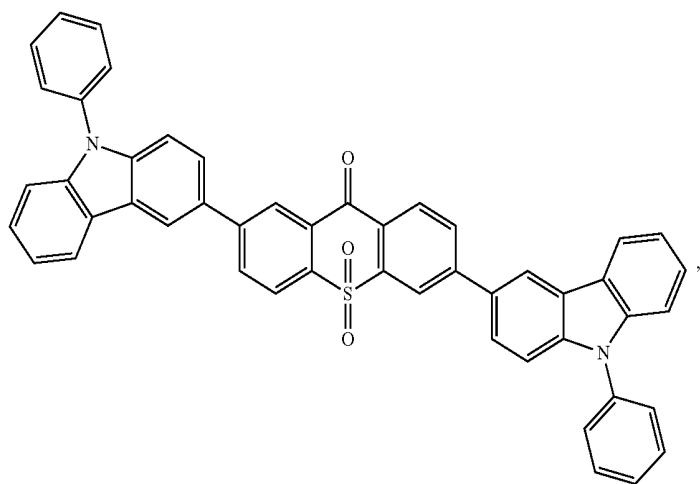
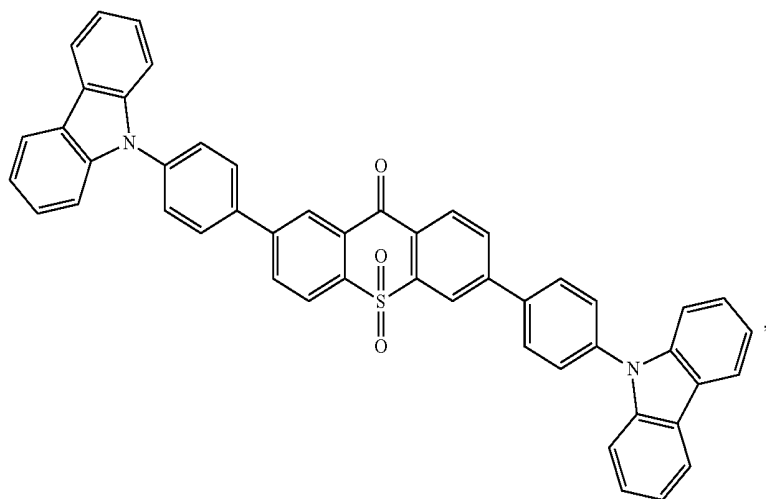


[0091] Preferably, Ar₁ and Ar₂ are the same.

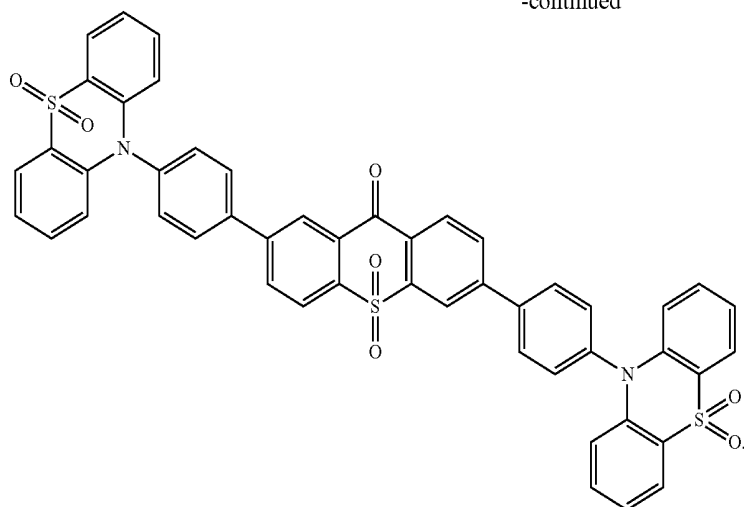
[0092] Specifically, the light emitting material comprises one or more of following compounds:



-continued



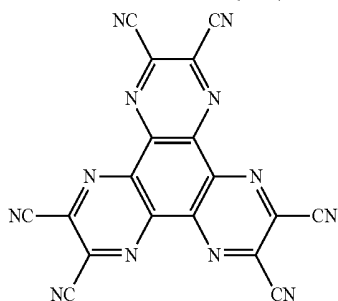
-continued



[0093] Preferably, in material of the light emitting layer **50**, a mass percentage of the light emitting material is 1%.

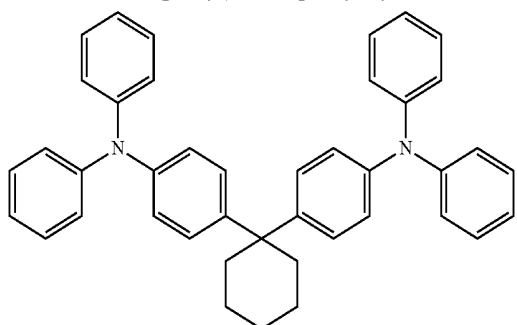
[0094] Specifically, the light emitting layer **50** can emit red light, yellow light, green light or blue light.

[0095] Specifically, material of the anode **20** comprises transparent metal oxide. The transparent metal oxide is preferably to be Indium Tin Oxide (ITO).

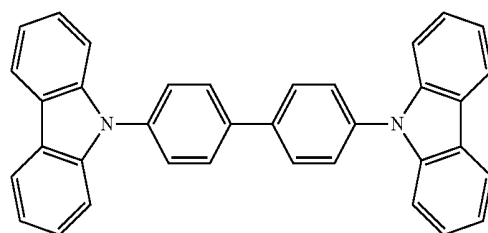


Specifically, material of the Hole Injection Layer **30** comprises 2,3,6,7,10,11-Hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN), and a constitutional formula of the 2,3,6,7,10,11-Hexacyano-1,4,5,8,9,12-hexaazatriphenylene is.

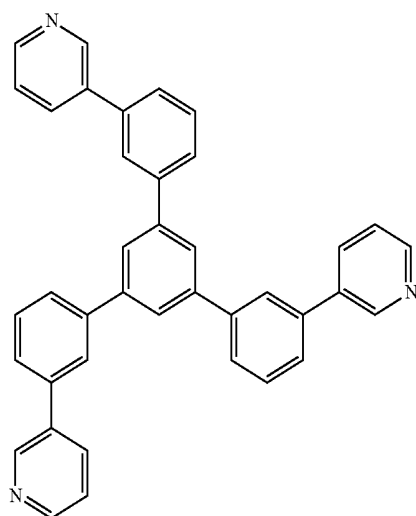
[0096] Specifically, material of the Hole Transporting Layer **40** comprises 1,1-Bis[4-[N,N-di(p-tolyl)amino]phenyl]cyclohexane (TAPC), and a constitutional formula of the 1,1-Bis[4-[N,N-di(p-tolyl)amino]phenyl]cyclohexane is



[0097] Specifically, material of the light emitting layer **50** further comprises 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP), and a constitutional formula of the 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl is



[0098] Specifically, material of the Electron Transport Layer **60** comprises 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), and a constitutional formula of the 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene is



[0099] Specifically, material of the Electron Injection Layer **70** comprises Lithium fluoride (LiF).

[0100] Specifically, material of cathode **80** comprises aluminum (Al).

[0101] Preferably, a thickness of the anode **20** is 95 nm, and a thickness of the Hole Injection Layer **30** is 5 nm, and a thickness of the Hole Transporting Layer **40** is 20 nm, and a thickness of the light emitting layer **50** is 35 nm, and a thickness of the Electron Transport Layer **60** is 55 nm, and a thickness of the Electron Injection Layer **70** is 1 nm, and a thickness of the cathode **80** is larger than 80 nm.

[0102] The manufacture process of the organic light emitting diode is: putting Indium Tin Oxide transparent conductive glass in the cleaner for the ultrasonic process, and using the deionized water for cleaning to employ ultrasound to remove oil in the mixture solution of acetone/ethanol, and then, baking the same in the clean environment until the water is completely removed, and then, using ultraviolet light and ozone for cleaning, and employing low energy cation to bombard the same to obtain the anode **20**, and putting the transparent conductive glass with the anode **20** in the vacuum chamber, and vacuuming to 1×10^{-5} – 9×10^{-3} Pa, and next, sequentially evaporating the Hole Injection Layer **30**, the Hole Transporting Layer **40**, the plurality of light emitting layer **50**, the Electron Transport Layer **60**, the Electron Injection Layer **70** and the cathode **80** on the anode **20**, and ultimately obtaining the organic light emitting diode of this embodiment.

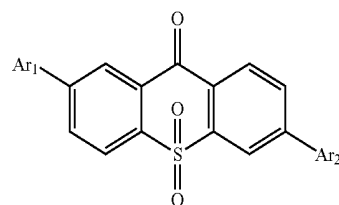
[0103] In conclusion, the present invention provides a light emitting material, in which the structure is unitary, and the formula weight is determined, and the better solubility and film formation are provided, and the thin film status is stable; it possesses a very high decomposition temperature and a lower sublimation temperature, and is easy to sublime to be light emitting material of high purity, and can be applied for small molecule organic light emitting diode; by changing the aromatic amine group, which is connected, the physical property can be improved in advance to promote the performance of the photoelectric element of the light emitting material. The present invention provides a manufacture method of the light emitting material. p-bromothiophenol and 4-Bromo-2-fluorobenzonitrile are employed to be starting materials, and the intermediate of the light emitting material is obtained with a series of simple reactions, and finally, the light emitting material is obtained with Ullmann reaction or Suzuki reaction, and the steps are simple and the production is high. The present invention provides an organic light emitting diode, in which the light emitting layer comprises the aforesaid light emitting material that has higher light emission efficiency and stability.

[0104] Above are only specific embodiments of the present invention, the scope of the present invention is not limited to this, and to any persons who are skilled in the art, change or replacement which is easily derived should be covered by the protected scope of the invention. Thus, the protected scope of the invention should go by the subject claims.

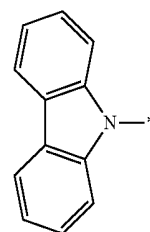
What is claimed is:

1. An organic light emitting diode, comprising a substrate, and an anode, a hole injection layer, a hole transporting layer, a light emitting layer, an electron transport layer, an electron injection layer and a cathode stacked in sequence on the substrate from bottom to top;

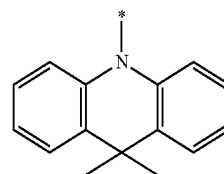
wherein the light emitting layer comprises a light emitting material having the following constitutional formula:



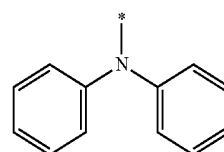
wherein Ar₁ and Ar₂ are respectively selected from aromatic amine groups shown in formula (1), formula (2), formula (3), formula (4), formula (5), formula (6), formula (7);



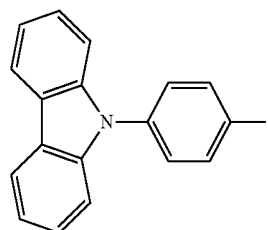
(1)



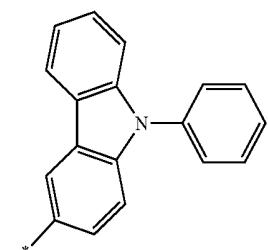
(2)



(3)

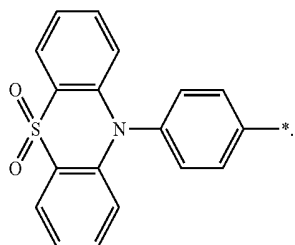
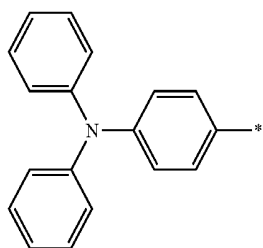


(4)



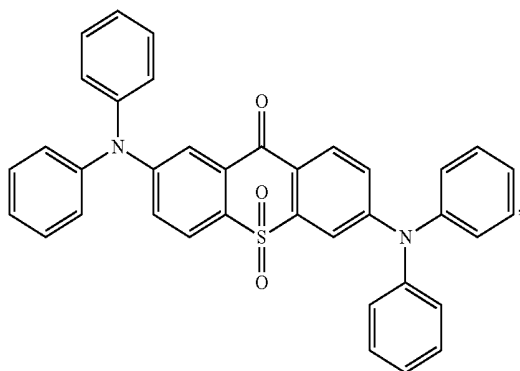
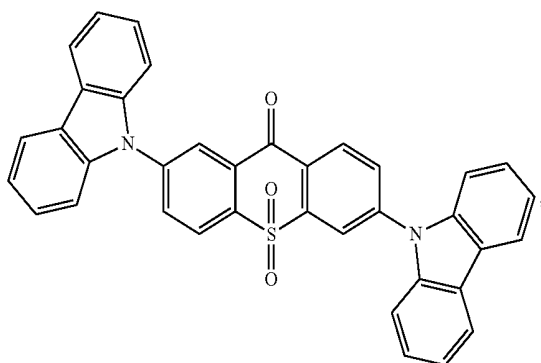
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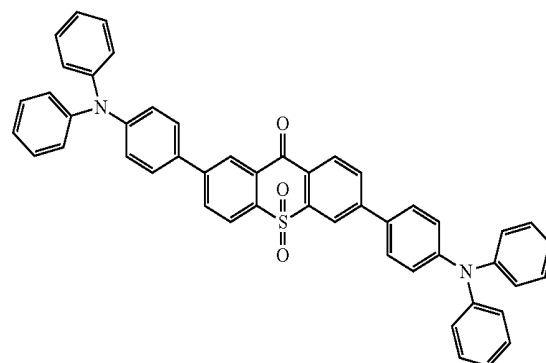
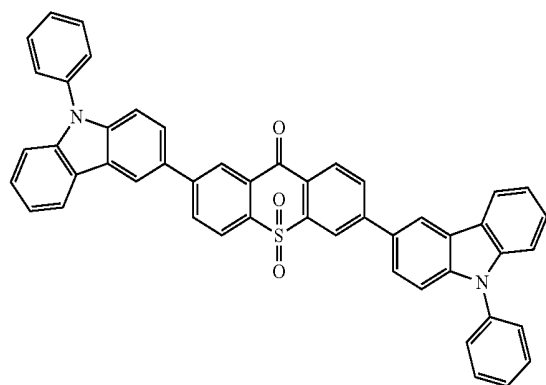
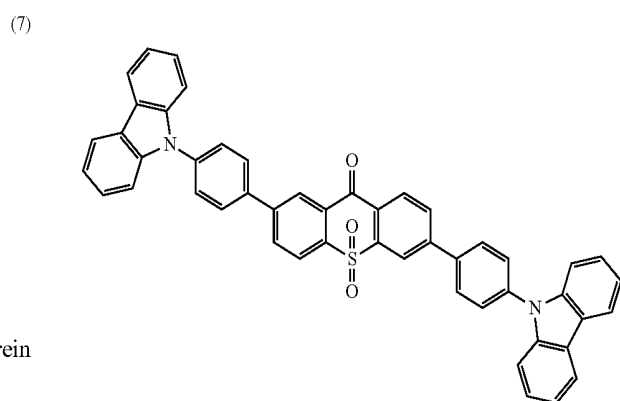
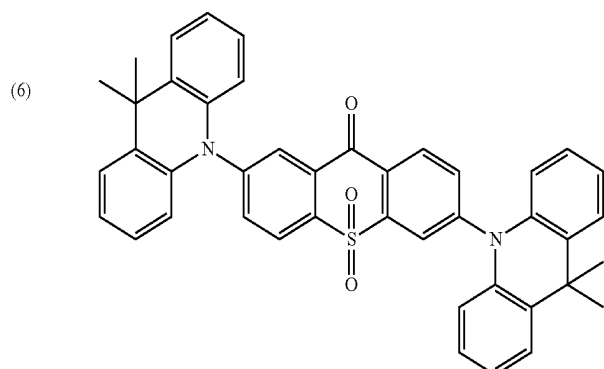


2. The light emitting diode according to claim 1, wherein Ar_1 and Ar_2 are the same.

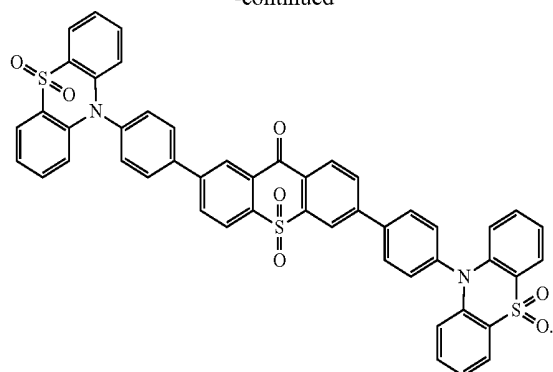
3. The light emitting diode according to claim 2, wherein the light emitting material is selected from one of the following compounds:



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* * * * *

专利名称(译)	发光材料，其制造方法和使用该发光材料的有机发光二极管		
公开(公告)号	US20190177610A1	公开(公告)日	2019-06-13
申请号	US16/278720	申请日	2019-02-19
[标]申请(专利权)人(译)	深圳市华星光电技术有限公司		
申请(专利权)人(译)	深圳市中国星光电科技有限公司.		
当前申请(专利权)人(译)	深圳市中国星光电科技有限公司.		
[标]发明人	LI XIANJIE WU YUANCHUN SU SHIJIAN LI YUNCHUAN		
发明人	LI, XIANJIE WU, YUANCHUN SU, SHIJIAN LI, YUNCHUAN		
IPC分类号	C09K11/06 H01L51/00 C07D409/14 C07D417/14 C07D335/16 C07D339/08		
CPC分类号	C09K11/06 H01L51/0074 H01L51/0061 H01L51/0072 C07D409/14 C07D417/14 C07D335/16 C07D339/08 H01L51/5072 H01L51/5056 H01L51/56 C09K2211/1037 H01L51/5206 H01L51/5221 H01L51/5092 H01L51/5012 C09K2211/1029 C09K2211/1092 H01L51/0071		
优先权	201610579646.9 2016-07-20 CN 15/122410 2016-08-30 US		
其他公开文献	US10626327		
外部链接	Espacenet USPTO		

摘要(译)

有机发光二极管包括发光层，该发光层包括构成式的发光材料 结构单一，确定配方重量，提供更好的溶解性和成膜性，薄膜状态稳定;它具有很高的分解温度和较低的升华温度，易于升华成高纯度的发光材料，可用于小分子有机发光二极管。在制造发光材料的方法中，使用对溴苯硫酚和4-溴-2-氟苄腈作为起始材料，并通过一系列简单反应获得发光材料的中间体，最后，光采用Ullmann反应或Suzuki反应得到发光材料，这些步骤简单，生产率高。

