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(54) IMPROVED METHODS FOR PRODUCING ORGANIC LIGHT EMITTING DIODE (OLED) MATERIALS

VERBESSERTES VERFAHREN ZUR HERSTELLUNG VON ORGANISCHEN LEUCHTDIODEN (OLED)-MATERIALIEN

PROCÉDÉS PERFECTIONNÉS POUR LA PRODUCTION DE MATÉRIAUX DE DIODE ÉLECTROLUMINESCENTE ORGANIQUE (DELO)

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EP 2 847 808 B1

Description

[0001] This invention relates to improved methods for producing Organic Light Emitting Diode (OLED) materials containing fluorene ring systems, such as those comprising spiro[cycloalkane-1,9-fluorene]s, spiro[bicycloalkane-9-fluorene]s, and 9,9-Di(1,1-dimethylalk-1-yl)fluorenes, and condensed ring systems incorporating these structures.

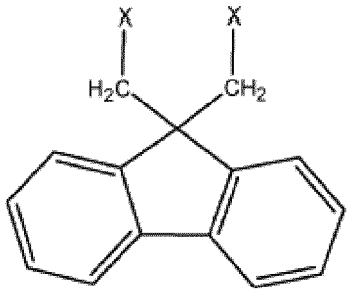
[0002] Organic Light Emitting Diode (OLED) materials containing fluorene ring systems in which two alkyl substituents at the 9-position of fluorene ring are alkyl substituted are desirable components for use in OLEDs because of their high oxidative stability. Previous methods of producing these materials were very low yielding.

[0003] The present invention provides methods by which these materials may be produced with higher yields.

[0004] Document EP 1 215 192 A discloses in Examples 5-9 a method of producing materials through 9,9-disubstituted fluorene derivatives as intermediates.

[0005] The invention provides a method and product as defined by the claims.

[0006] The invention comprises methods of producing OLED materials containing fluorene ring systems in which two alkyl substituents at the 9-position of fluorene ring are alkyl substituted through key intermediates generically represented by the formula:

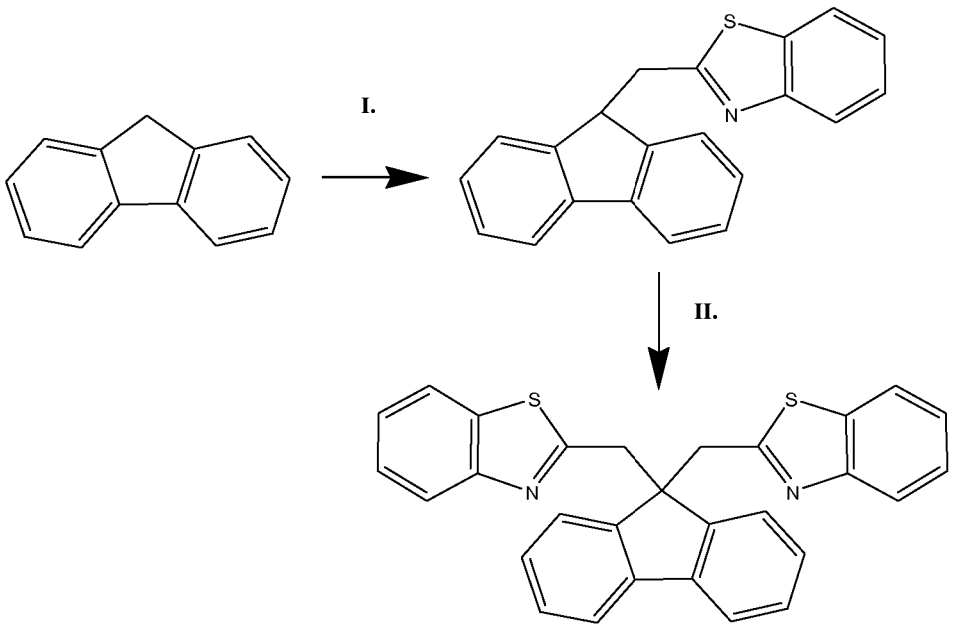


Formula 1

where X represents a substituent that increases the acidity of the hydrogen atoms on the adjoining methylene group (which is immediately adjacent the fluorene ring systems 9-position).

[0007] X represents 1,3-benzo[d]thiazol-2-yl.

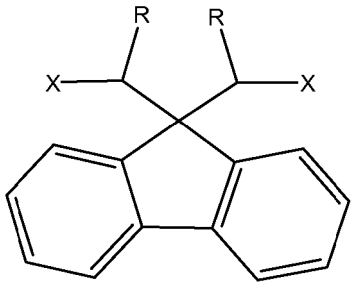
[0008] There is also disclosed a synthesis (Synthesis 1) for previously unknown compound, fluorene-9,9-diacetic acid, dimethyl ester, which corresponds to Formula 1 with X = methoxycarbonyl :



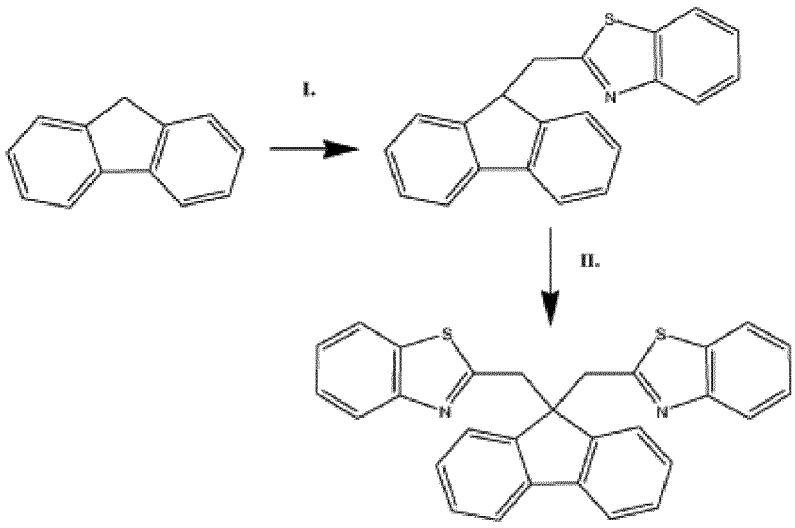
I. 1. lithium diisopropylamide, THF, 2. 2-bromomethyl-1,3-benzo[d]thiazole;
II. 1. lithium diisopropylamide, THF, 2. 2-bromomethyl-1,3-benzo[d]thiazole.

[0009] A further reason why this compound is the preferred intermediate is that the hydrogens on the methylenes adjacent to the groups X appear to have unusually low acidities for hydrogens located next to these activating groups, likely due to the effect of the fluorene ring. The nitrogenous bases such as lithium diisopropylamide (LDA) that are normally used to deprotonate such materials appear to only partially deprotonate the materials represented by Figure 1 resulting in low yields. Sufficient deprotonation is only achieved by carbon-based bases like n-butyl lithium and t-butyl lithium. Thus only groups X which are stable to alkyl lithiums, e.g. 1,3-benzo[d]thiazol-2-yl, can yield complete deprotonation.

[0010] Following deprotonation the intermediate (Formula 1) is dialkylated to form a second intermediate. If monohaloalkanes are used for the alkylation , the second intermediate has the formula



Formula 2



I. 1. lithium diisopropylamide, THF, 2. 2-bromomethyl-1,3-benzo[d]thiazole;
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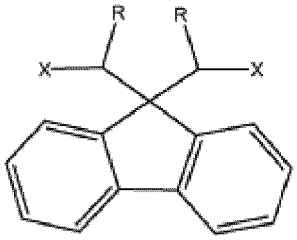
[0011] A further reason why this compound is the preferred intermediate is that the hydrogens on the methylenes adjacent to the groups X appear to have unusually low acidities for hydrogens located next to these activating groups, likely due to the effect of the fluorene ring. The nitrogenous bases such as lithium diisopropylamide (LDA) that are normally used to deprotonate such materials appear to only partially deprotonate the materials represented by Formula 1 resulting in low yields. Sufficient deprotonation is only achieved by carbon-based bases like n-butyl lithium and t-butyl lithium. Thus only groups X which are stable to alkyl lithiums, e.g. 1,3-benzo[d]thiazol-2-yl, can yield complete deprotonation.

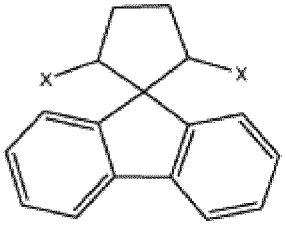
[0012] Following deprotonation the intermediate (Formula 1) is dialkylated to form a second intermediate. If monohaloalkanes are used for the alkylation, the second intermediate has the formula



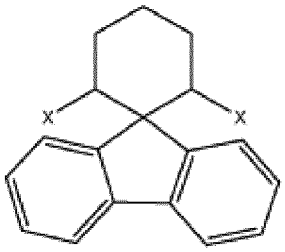
Formula 2

[0013] Here X has the same meaning as in Formula 1 and R is an alkyl group, most commonly n-alkyl, but branched chain alkyl groups may be used as well. 1-Bromo-n-alkanes are most commonly used in this synthetic step except that iodomethane is used if R is to be methyl. The Rs may be different. However, this introduces the problem of optical isomers in the final product. Aside from monohaloalkanes, alkanes substituted with other leaving groups such as methylsulphonates and p-toluenesulphonates may also be used.

[0014] If α,ω-dihaloalkanes are used spiro[cycloalkane-1,9-fluorenes] are the resulting second intermediates. In particular, dialkylation with l-bromo-2-chloroethane and with l-bromo-3-chloropropane result in spiro[cyclopentane-1,9-fluorene]s (Formula 3) and spiro[cyclohexane-1,9-fluorene]s (Formula 4) respectively.

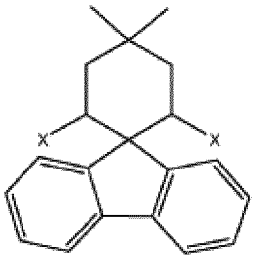


Formula 3

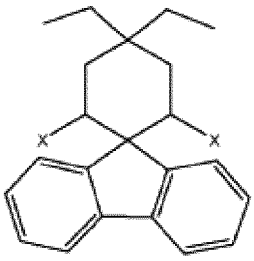


Formula 4

[0015] In addition, dialkylation of the deprotonated material of Formula 2 with 1-bromo-3-chloro-2,2-dimethylpropane and 3-bromomethyl-3-chloromethyl-n-pentane result in 4,4-dimethylspiro[cyclohexane-1,9-fluorene]s (Formula 5) and 4,4-diethylspiro[cyclohexane-1,9-fluarene]s (Formula 6) respectively.



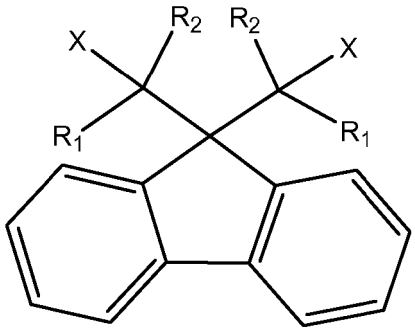
Formula 5



Formula 6

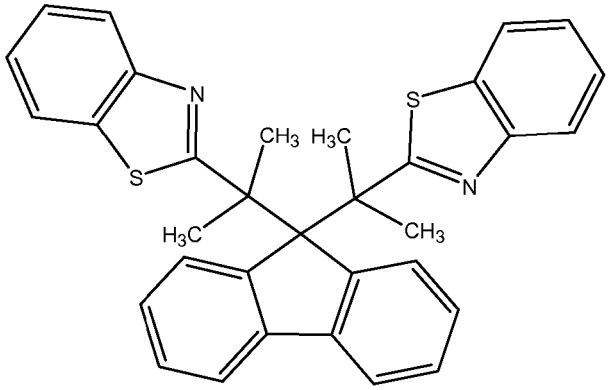
[0016] All of the spiro materials in Formulae 3,4,5, and 6 may be generically represented by the formula

[0017] In the next step of this synthetic method, if the second intermediate has the structure shown in Formula 2, it may again be deprotonated with a strong base (e.g. t-butyl lithium) and then dialkylated with a monohaloalkane or an α,ω-dihaloalkane. If a monohaloalkane is used the resulting product will have the general formula



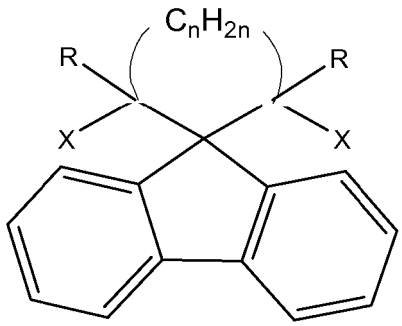
Formula 9

[0018] A preferred example of compounds with Formula 9 is



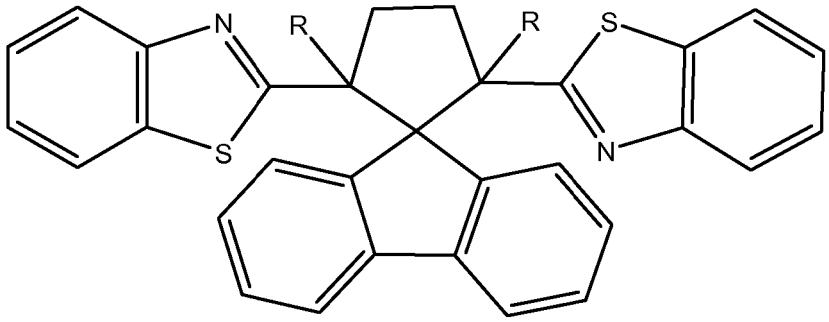
Formula 10

[0019] If the second intermediate of Formula 2 is deprotonated and then dialkylated with an α,ω-dihaloalkane the resulting product will have the general formula



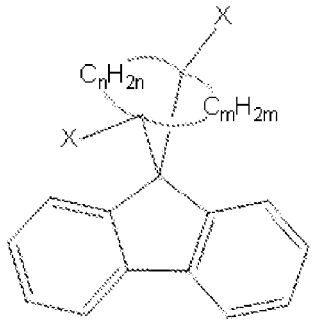
Formula 11

[0020] If the second intermediate has the structure shown in Formula 7, it may also be deprotonated with a strong base and then be dialkylated with a monohaloalkane or an α,ω-dihaloalkane. If it is dialkylated with a monohaloalkane the resulting product will have the structure shown in Formula 11. A preferred series of compounds of Formula 11 are



Formula 12

[0021] If the dialkylation of the deprotonated material with structure shown in Figure 7 is carried out using an α,ω-dihaloalkane, the resulting product will be a spiro[bicycloalkane-9-fluorene] of the general formula

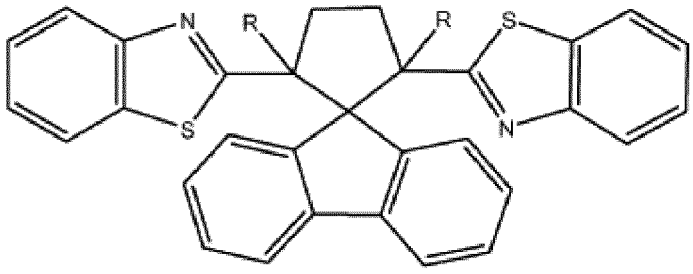


Formula 13

[0022] Preferred compounds with a structure shown in Figure 13 are the material with n = 2, m = 2, and X = 1,3-benzo[d]thiazol-2-yl,

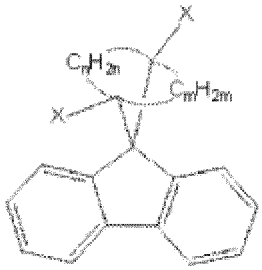
Formula 11

[0023] If the second intermediate has the structure shown in Formula 7, it may also be deprotonated with a strong base and then be dialkylated with a monohaloalkane or an α,ω-dihaloalkane. If it is dialkylated with a monohaloalkane the resulting product will have the structure shown in Formula 11. A preferred series of compounds of Formula 11 are



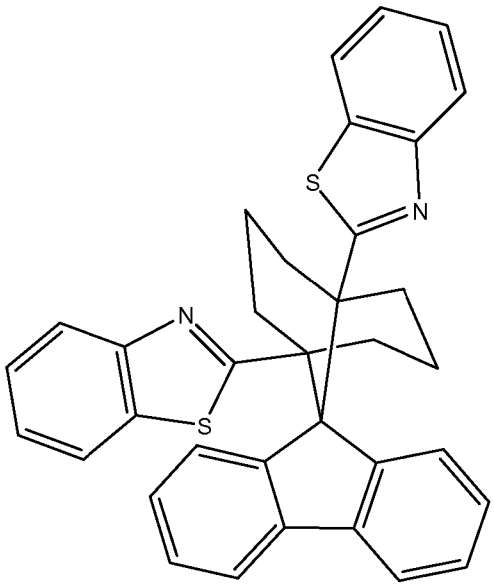
Formula 12

[0024] If the dialkylation of the deprotonated material with structure shown in Formula 7 is carried out using an α,ω-dihaloalkane, the resulting product be a spiro[bicycloalkane-9-fluorene] of the general formula



Formula 13

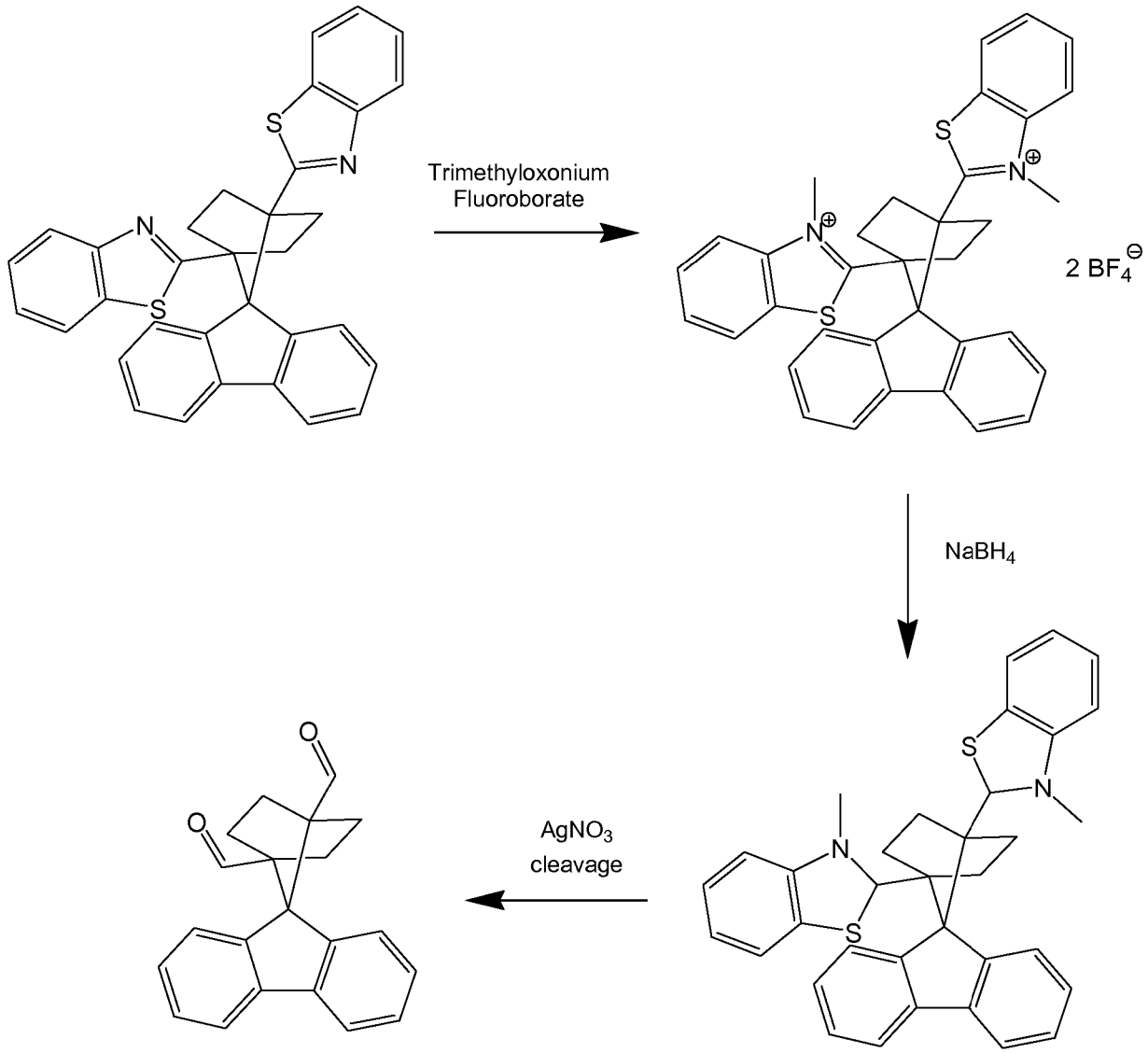
[0025] Preferred compounds with a structure shown in Formula 13 are the material with n = 2, m = 2, and X = 1,3-benzo[d]thiazol-2-yl,



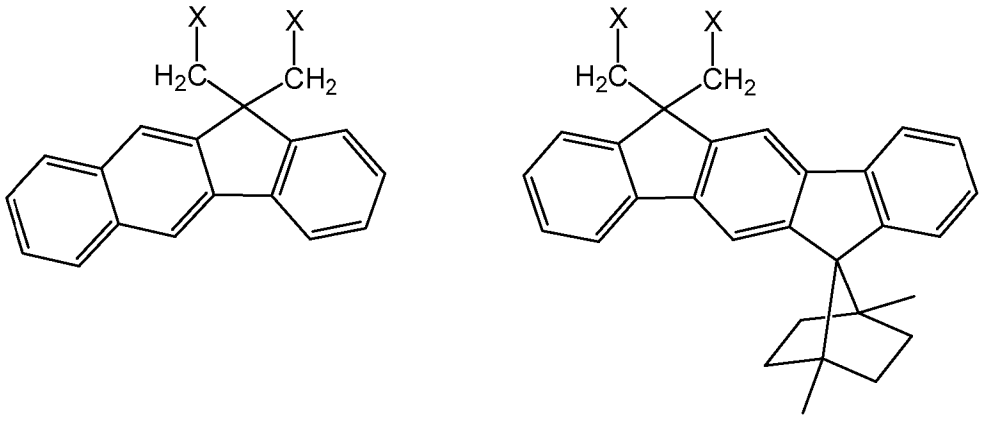
Formula 16

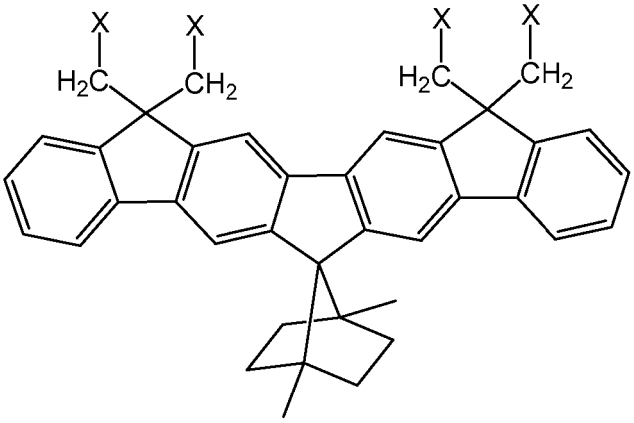
[0026] Electron withdrawing groups that may be used in compounds with formulae 2 and 7 so as to allow further deprotonation and alkylation include 1,3-thiazol-2-yl, 1,3-benzo[d]oxazol-2-yl, and 1,3-benzo[d]thiazol-2-yl and N-alkylimino.

[0027] The 1,3-oxazol-2-yl, 1,3-thiazol-2-yl, 1,3-benzo[d]oxazol-2-yl, and 1,3-benzo[d]thiazol-2-yl functions in compounds of formulae 7, 9, 11, and 13 may be converted into aldehyde functions by a previously known series of steps, for instance,



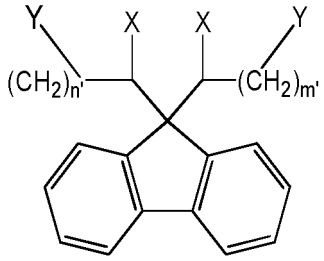
[0028] The intermediates of Formula 1 may be substituted at any of the positions on the fluorene ring system. In particular, the fluorene may fused to further aromatic rings, e.g.



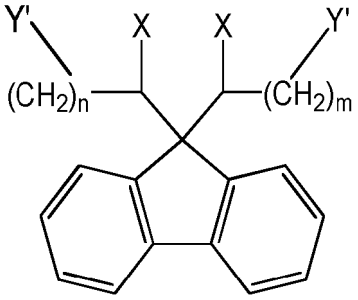


[0029] Compounds with formulae 2,7,9,11, and 13 may be similarly substituted or fused.

[0030] A further preferred synthetic variation of this method (Synthesis 3) utilises a variant of the intermediate with Formula 2 in which R has the formula - $(CH_2)_nY$

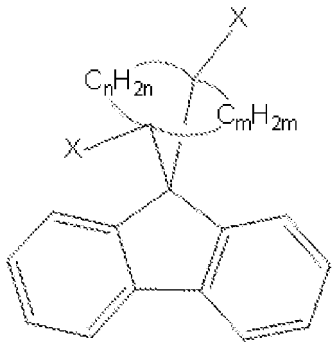


[0031] In this synthesis Y is converted by a series of synthetic steps to a second intermediate with Formula 2 with R = $-(CH_2)_mY'$

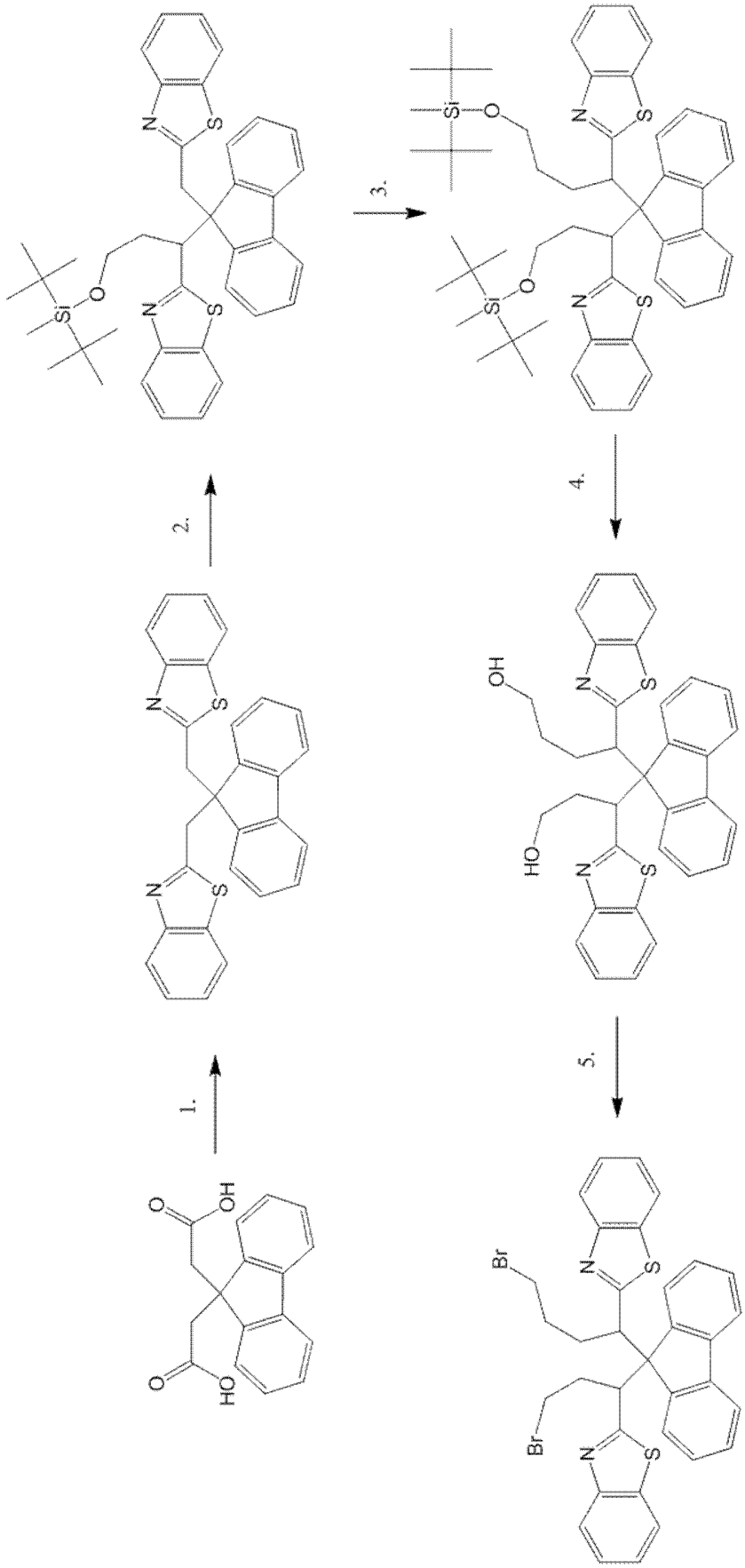


wherein Y' is a leaving group such as iodo, bromo, chloro, p-toluenesulfonato, methanesufonato, trifluoromethanesulfonato, etc.

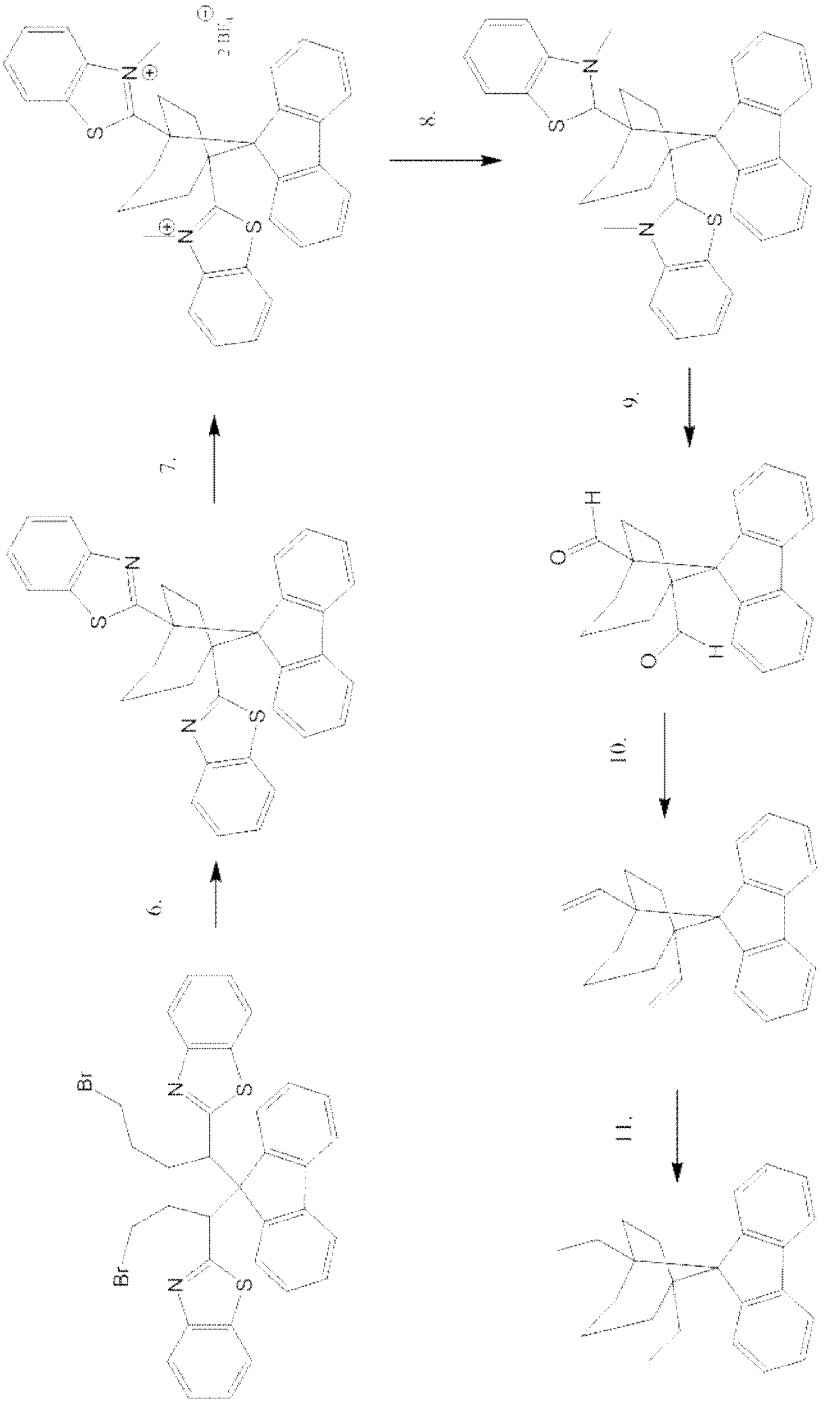
[0032] Treatment of this second intermediate with a strong base converts the material to a product with Formula 13:



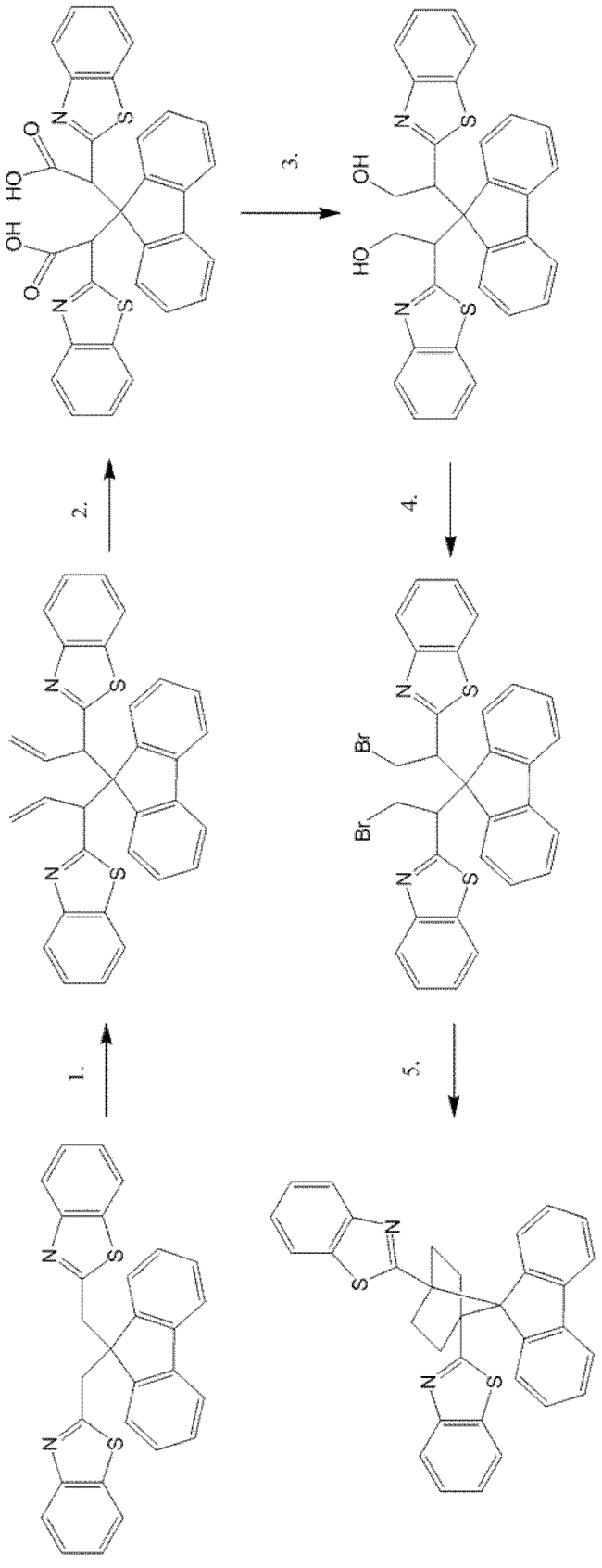
[0033] A first example of this synthesis is :



1. 2-Aminobenzenethiol, polyphosphoric acid, 190 degrees C for 4 hours;
2. a. t-Butyl lithium in dry THF at -78 degrees for 3 hours, b. 1-Bromo-2-(Di-t-butylmethylsilyloxy)ethane at -78 degrees C for 0.5 hours;
3. a. t-Butyl lithium in dry THF at -78 degrees for 3 hours, b. 1-Bromo-3-(Di-t-butylmethylsilyloxy)propane at -78 degrees C for 0.5 hours;
4. 5 Equivalents of tetrabutylammonium fluoride in THF at RT overnight.
5. Triphenylphosphine dibromide in DMF at 0 degrees C then allow to warm to RT overnight.



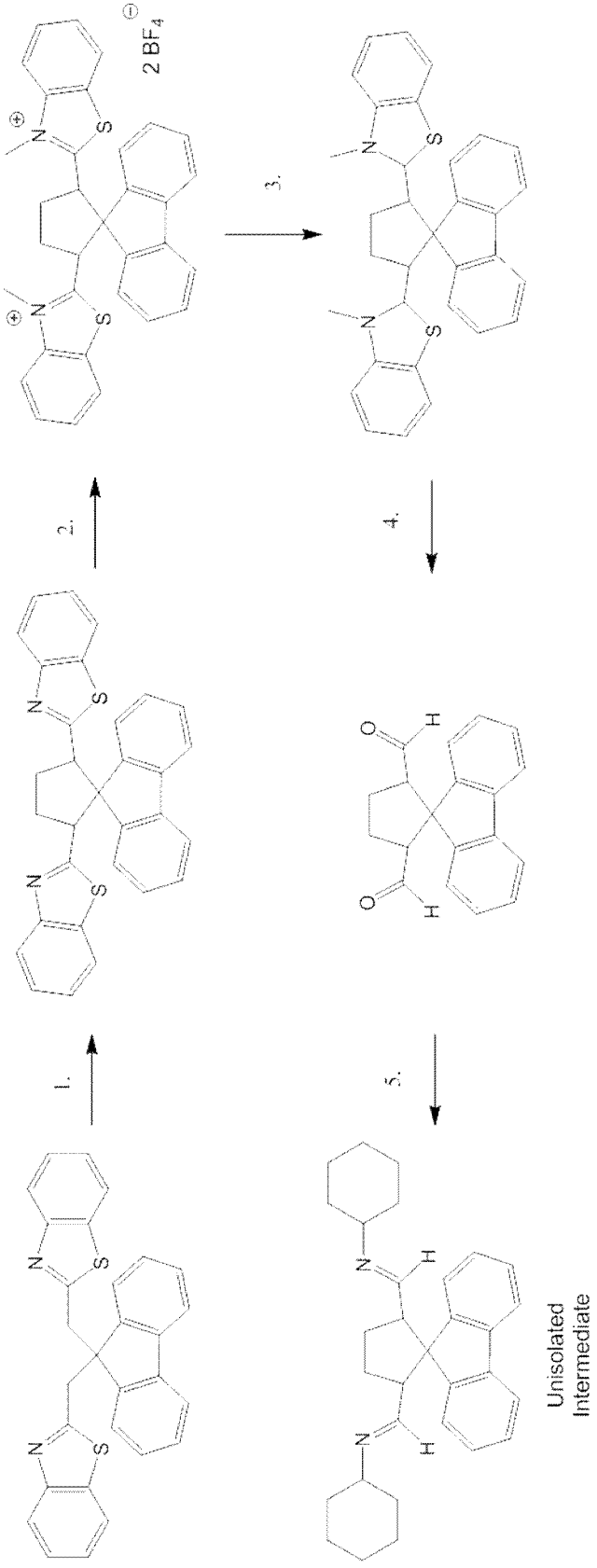
[0034] A second example synthesis is:



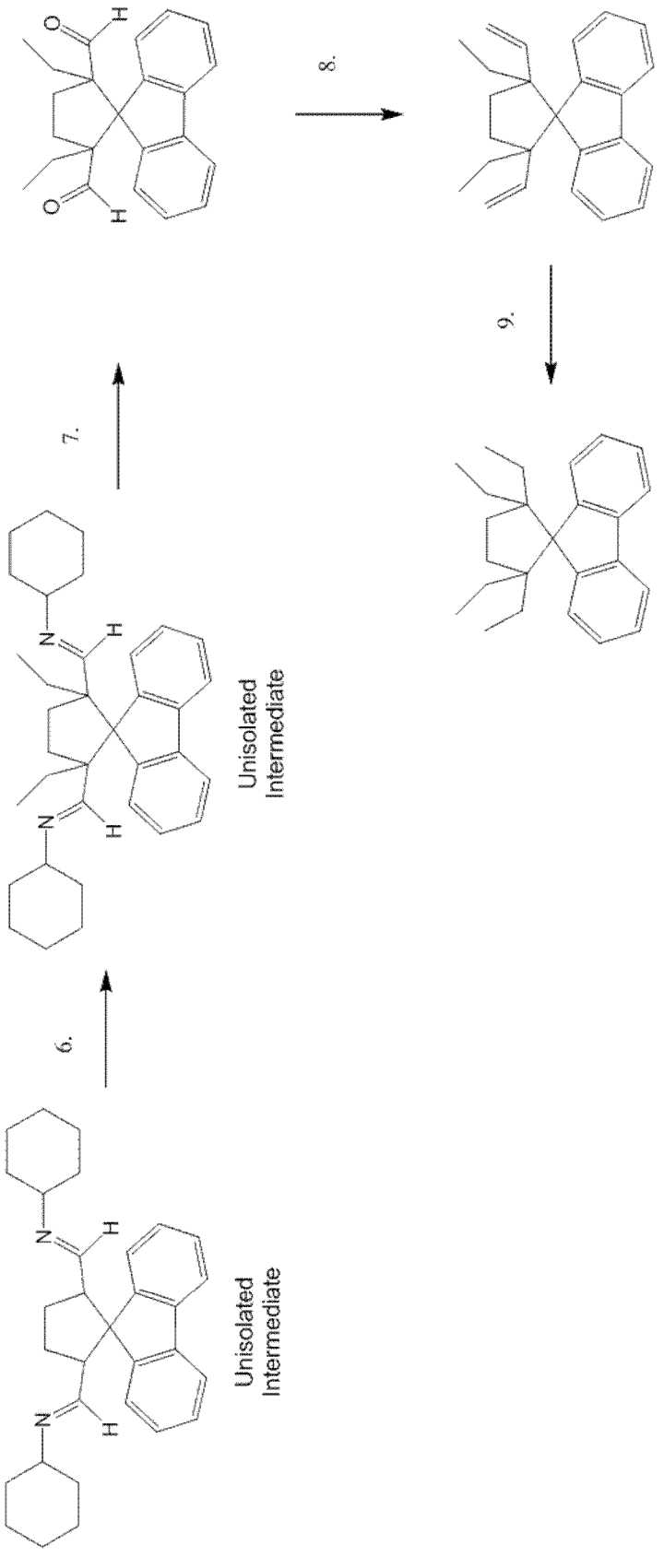
1. a. t-Butyl lithium in dry THF at -78 degrees for 3 hours, b. Allyl bromide at -78 degrees C for 0.5 hours;
2. Sodium metaperiodate, catalytic potassium permanganate, and sodium carbonate in pyridine/water solvent at room temperature.
3. $LiAlH_4$ in tetrahydrofuran at 0 degrees C followed by 2 hours reflux.
4. Triphenylphosphine dibromide in DMF at 0 degrees C then allow to warm to RT overnight.
5. t-Butyl lithium in dry THF at -78 degrees C and then let warm to RT overnight.

[0035] A third example of the synthesis is:

iisis:



1. a. t-Butyl lithium in dry THF at -78 degrees for 3 hours, b. 1-Bromo-2-chloroethane at -78 degrees C for 0.5 hours then allow to warm to RT overnight;
2. $(CH_3)_3O^+ BF_4^-$ in dry dichloromethane at RT for 24 hours;
3. $NaBH_4$ in ethanol at RT with vigorous stirring for 2 hours;
4. a. $AgNO_3$ and pH 7 buffer in water/CH_3CN at RT for 3 hours, b. triethylamine at 45 to 50 degrees C for 2 hours;
5. Cyclohexylamine an benzene solvent, azeotrope for 6 hours.

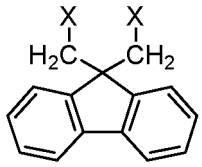


6. a. Lithium diisopropylamide and hexamethylphosphoramide in dry THF at 0 degrees for 3 hours, b. 1-Iodobutaneat at 0 degrees for 15 min. and then allow to warm to RT overnight;
7. 1 Molar oxalic acid at RT for 2 hours;
8. Methylenetriphenylphosphorane in dry ether refluxed for 12 hours;
9. 3 atm. H_2 with 10% Pd on carbon in tetrahydrofuran for five hours in a Parr shaker.

Claims

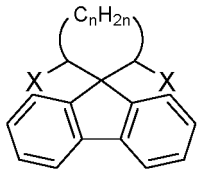
1. A method of producing fluorene OLED materials comprising the steps of:

(a) deprotonation and alkylation of a compound of Formula 1:



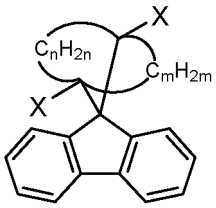
Formula 1

to produce a compound of Formula 7:



Formula 7

(b) deprotonation and alkylation of the compound of Formula 7 to produce an OLED material of Formula 13:



Formula 13

wherein X represents 1,3-benzo[d]thiazol-2-yl, and wherein the deprotonation is with an alkyl lithium base, wherein the alkylation is with an α,ω-dihaloalkane, and wherein n and m are 2 or 3.

2. The method of claim 1, wherein the alkyl lithium base is n-butyl lithium.

3. The method of claim 1, wherein the alkyl lithium base is t-butyl lithium.

4. The method of any preceding claim, wherein the α,ω-dihaloalkane is 1-bromo-2-chloroethane.

5. The method of any one of claims 1 to 3, wherein the α,ω-dihaloalkane is 1-bromo-3-chloropropane.

6. The method of any preceding claim, wherein n is 2 and m is 2.

7. The method of any one of claims 1 to 5, wherein n is 3 and m is 2.

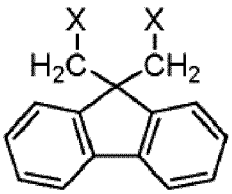
8. The method of any one of claims 1 to 5, wherein n is 3 and m is 3.

9. The compound 2,2'(fluoren-9,9-diyldimethylene)bis-1,3-benzo[d]thiazole.

Patentansprüche

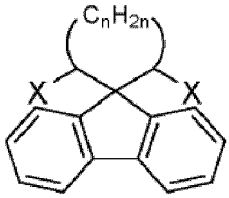
1. Verfahren zur Herstellung von Fluoren OLED Materialien umfassend die Schritte:

(a) Deprotonierung und Alkylierung einer Verbindung der Formel 1:



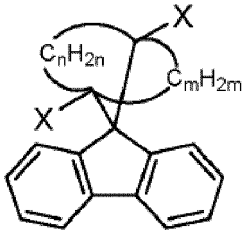
Formel 1

um eine Verbindung der Formel 7 herzustellen:



Formel 7

(b) Deprotonierung und Alkylierung der Verbindung der Formel 7, um ein OLED Material der Formel 13 herzustellen:



Formel 13

wobei X 1,3-Benzo[d]thiazol-2-yl darstellt und wobei die Deprotonierung mit einer Alkyl-Lithium-Base ist, wobei die Alkylierung mit einem α,ω-Dihaloalkan ist und wobei n und m 2 oder 3 sind.

2. Verfahren nach Anspruch 1, wobei die Alkyl-Lithium-Base n-Butyl-Lithium ist.

3. Verfahren nach Anspruch 1, wobei die Alkyl-Lithium-Base t-Butyl-Lithium ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das α,ω-Dihaloalkan 1-Brom-2-Chlorethan ist.

5. Verfahren nach einem der Ansprüche 1 bis 3, wobei das α,ω-Dihaloalkan 1-Brom-3-Chlorpropan ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei n 2 ist und m 2 ist.

7. Verfahren nach einem der Ansprüche 1 bis 5, wobei n 3 ist und m 2 ist.

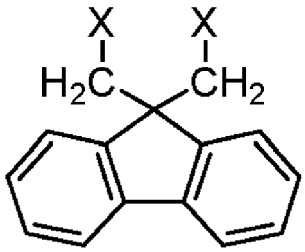
8. Verfahren nach einem der Ansprüche 1 bis 5, wobei n 3 ist und m 3 ist.

9. Verbindung 2,2'(Fluoren-9,9-diyldimethylen)bis-1,3-benzo[d]thiazol.

Revendications

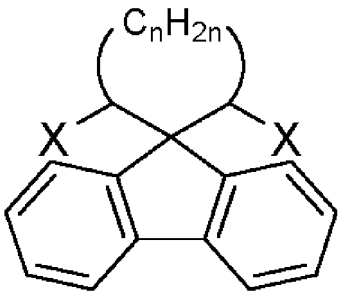
1. Procédé de production de matériaux OLED à base de fluorène comprenant les étapes de :

(a) déprotonation et alkylation d'un composé répondant à la Formule 1 :



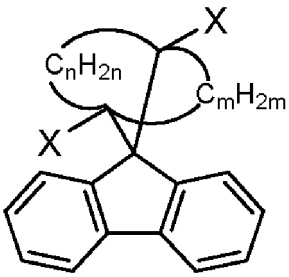
Formule 1

pour produire un composé répondant à la Formule 7 :



Formule 7

(b) déprotonation et alkylation du composé répondant à la Formule 7 pour produire un matériau OLED répondant à la Formule 13 :



Formule 13

où X représente le 1,3-benzo[d]thiazol-2-yle, et où la déprotonation est effectuée avec une base alkyllithium, où l'alkylation est effectuée avec un α,ω-dihalogénoalcane, et où n et m valent 2 ou 3.

2. Procédé de la revendication 1, dans lequel la base alkyllithium est le n-butyllithium.

3. Procédé de la revendication 1, dans lequel la base alkyllithium est le tert-butyllithium.

4. Procédé de l'une des revendications précédentes, dans lequel le α,ω-dihalogénoalcane est le 1-bromo-2-chloroéthane.

5. Procédé de l'une quelconque des revendications 1 à 3, dans lequel le α,ω-dihalogénoalcane est le 1-bromo-3-

chloropropane.

6. Procédé de l'une des revendications précédentes, dans lequel n vaut 2 et m vaut 2.

7. Procédé de l'une quelconque des revendications 1 à 5, dans lequel n vaut 3 et m vaut 2.

8. Procédé de l'une quelconque des revendications 1 à 5, dans lequel n vaut 3 et m vaut 3.

9. Composé de 2,2'(fluorène-9,9-diyldiméthylène)bis-1,3-benzo[d]thiazole.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1215192 A **[0004]**

专利名称(译)	用于制造有机发光二极管（OLED）材料的改进方法		
公开(公告)号	EP2847808B1	公开(公告)日	2018-09-19
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[标]申请(专利权)人(译)	洛马克斯有限公司		
申请(专利权)人(译)	LOMOX有限公司		
当前申请(专利权)人(译)	LOMOX有限公司		
[标]发明人	KOCH GENE CARL		
发明人	KOCH, GENE CARL		
IPC分类号	H01L51/00 C07C13/567		
CPC分类号	C07D417/08 C07C1/2076 C07C1/34 C07C5/03 C07C45/56 C07C45/68 C07C57/50 C07C69/616 C07C2601/08 C07C2603/18 C07C2603/78 C07C2603/94 C07D277/64 C07F7/0827 C09K11/06 C09K2211/1011 C09K2211/1018 H01L51/0052 H01L51/0058 H01L51/0071 H01L51/50 H01L51/5012 C07C13/72		
优先权	2012008136 2012-05-10 GB		
其他公开文献	EP2847808A1		
外部链接	Espacenet		

摘要(译)

制备含有芴环系统的OLED材料的方法，其中在芴环的9位上的两个烷基取代基是通过通式表示的关键中间体取代的烷基：其中X表示增加邻接的氢原子的酸性的取代基。亚甲基（紧邻芴环系统9-位）。