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

Abstract: 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: 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).
Improved Methods for Producing Organic Light Emitting Diode (OLED) materials

This invention relates to improved methods for producing Organic Light Emitting Diode (OLED) materials containing fluorene ring systems, such as those comprising spiros[5cycloalkane-1,9-fluorene], spiros[bicycloalkane-9-fluorene], and 9,9-Di[l,l-dimethylalk-l-yl]fluorenes, and condensed ring systems incorporating these structures.

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.

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

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:

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      X     X
   H2C       CH2
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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).

X may comprise an electron withdrawing group. Electron withdrawing groups that may be used include alkoxy-carbonyl, cyano, 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.

The invention comprises a synthesis (Synthesis 1) for previously unknown compound, fluorene-9,9-diacetic acid, dimethyl ester, which corresponds to Formula 1 with X = methoxycarbonyl.
An alternative pathway replaces step II with epoxidation with m-chloroperbenzoic acid followed by periodic acid oxidation to the dialdehyde. In either case the dialdehyde is, in fact, a polymeric hydrate similar to that formed by glutaraldehyde. Because of this the aldehyde and its imino or hydrazone derivatives are excluded from the list of candidate substituents X in Formula 1 since they do not, in fact, structurally exist.

The preferred X in Formula 1 is the 1,3-benzo[d]thiazol-2-yl radical. One reason for this is that the resulting compound (previously unknown), 2,2'(fluoren-9,9-diyldimethylene)bis-1,3-benzo[d]thiazole, is easily synthesised (Synthesis 2):
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 lithuims, e.g. 1,3-benzod-thiazol-2-yl, can yield complete deprotonation.

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
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.

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

![Formula 3](image1.png)  
![Formula 4](image2.png)

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

![Formula 5](image3.png)  
![Formula 6](image4.png)

All of the spiro materials in Figures 3, 4, 5, and 6 may be generically represented by the formula
A particularly preferred compound of this type is

In the synthesis of the compound with Formula 8, the deprotonation and alkylation process may proceed in two steps:
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 $\alpha,\omega$-dihaloalkane. If a monohaloalkane is used the resulting product will have the general formula:

![Formula 9]

A preferred example of compounds with Formula 9 is:

![Formula 10]

If the second intermediate of Formula 2 is deprotonated and then dialkylated with an $\alpha,\omega$-dihaloalkane the resulting product will have the general formula:

![Formula 11]
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 $\alpha,\omega$-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 11 Image]

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

![Formula 12 Image]

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,
the material with \( n = 3 \), \( m = 2 \), and \( X = \text{1,3-benzo[d]thiazol-2-yl} \), and

the material with \( n = 3 \), \( m = 3 \), and \( X = \text{1,3-benzo[d]thiazol-2-yl} \).
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.

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

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 -(CH₂)_n Y

In this synthesis Y is converted by a series of synthetic steps to a second intermediate with Formula 2 with R = -(CH₂)_m Y'
wherein $Y'$ is a leaving group such as iodo, bromo, chloro, p-toluenesulfonato, methanesulfonato, trifluoromethanesulfonato, etc.

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

A first example of this synthesis is:
1. 2-Aminobenzimidazole, polyphosphoric acid, 190 degrees C for 4 hours.
2. a. 1-Butyl lithium in dry THF at -78 degrees C for 3 hours; b. 1-Bromo-2-butylnaphthalene, hexane at -78 degrees C for 0.5 hours.
3. a. 1-Butyl lithium in dry THF at -78 degrees C for 3 hours; b. 1-Bromo-2-butylnaphthalene, hexane at -78 degrees C for 0.5 hours.
4. 5 Equivalents of tetraphenylammonium fluoride in THF at RT overnight.
5. Triphenylphosphine dibromide in DMF at 0 degrees C then allow to warm to RT overnight.
A second example synthesis is:

6. 1-Butyl lithium in dry THF at -78 degrees C and then let warm to RT overnight.
7. (CH₃)₂O·BF₄⁻ in dry dichloromethane at RT for 24 hours.
8. NaB₃H₆ in ethanol at RT with vigorous stirring for 2 hours.
9. a. AgNO₃ and pH 7 buffer in water CH₂CN at RT for 3 hours, b. triethylamine at 45 to 50 degrees C for 2 hours.
10. Methyleneetriphenylphosphorane in dry ether refluxed for 12 hours.
11. 3 atm. H₂ with 10% Pd on carbon in tetrahydrofuran for five hours in a Parr shaker.
1. a-t-Butyllithium in dry THF at -78 degrees C for 3 hours.
2. Sulfuryl chloride, catalytic pyridine, mercury(II) perchlorate, and pyridine solvent at room temperature.
3. LiAlH4 in tetrahydrofuran at 0 degrees C followed by 2 hours reflux.
4. Triphenylphosphine thiolate in DMF at 0 degrees C, then allow to warm to RT overnight.
5. a-t-Butyllithium in dry THF at -78 degrees C and then let warm to RT overnight.
A third example of the synthesis is:
1. t-Butyl lithium in dry THF at -78 degrees C for 3 hours, b. 1-Bromo-2-chloroethane at -78 degrees C for 0.5 hours then allow to warm to RT overnight;
2. t(\text{CH}_3)_2\text{O} \cdot \text{BF}_4^- \text{ 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_2CN 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 C for 3 hours, b. 1-Hydroxybutane at 0 degrees C for 15 min, and then

7. Warm to warm to RT overnight.

8. Methylene triphenylphosphorane in dry ether refluxed for 12 hours.

9. 3 atm. H₂ with 10% Pd on carbon in tetrahydrofuran for six hours in a Parr shaker.
Claims:

1. 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:

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\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{X} \\
\text{X} & \quad \text{CH}_2
\end{align*}
\]
```

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).

2. Methods according to claim 1, in which X comprises an electron withdrawing group.

3. Methods of producing OLED materials according to claim 1 or claim 2, including the step of Synthesis 1.

4. Fluorene-9,9-diacetic acid, dimethyl ester, produced by a method according to claim 4.

5. OLED materials comprising Formula 1, in which X is the 1,3-benzo[d]thiazol-2-yl radical.

6. Method of producing OLED materials according to claim 1 or claim 2, including the step of Synthesis 2.

7. Method of producing OLED materials according to claim 1 or claim 2, including the step of Synthesis 3.

8. Methods of producing OLED materials containing fluorene ring systems substantially as hereinbefore described.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/00 C07C13/567

According to International Patent Classification (IPC) onto both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search: 10 July 2013

Name and mailing address of the ISA:
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