

THIAZOLOTHIAZOLE-BASED ORGANIC DYE FOR DYE-SENSITIZED SOLAR CELL AND DYE-SENSITIZED SOLAR CELL INCLUDING THE SAME

Field of the Invention

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The present invention relates to an organic dye for use in dye-sensitized solar cell. In particular, the invention relates to a thiazolothiazole-based organic dye for use in dye-sensitized solar cell.

10 Background of the Invention

As energy consumption increases, there has been a growing interest to provide alternative sources of renewable energy. One of the most common focuses of renewable energy is solar energy. In this regard, it has been well-established from prior art that a cost-saving alternative to the conventional silicon-based solar cells is dye-sensitized solar cells (DSSCs). This is attributed to several advantages of DSSCs such as relatively lower production cost as compared to conventional silicon-based solar cell, high efficiency and high stability.

20 A DSSC consists of four major components namely a conducting electrode coated with metal oxide semiconductor, for example, titanium dioxide (TiO_2), dye molecules (or photosensitizers) associated with the metal oxide semiconductor, an electrolyte and a catalyst counter electrode. Of particular interest are the dye molecules covering the metal oxide semiconductor. This is because the dye molecules contribute to the efficiency of absorbing light and converting the light energy to generate electrical energy.

Conventionally, dye sensitizers in DSSCs are made of noble metal complexes such as platinum and ruthenium. However, such dyes are disadvantageous because such metal complexes are limited and therefore costly. Further, these materials are associated with undesirable environmental consequences. Consequently, more recent researches have been focused on employing organic dyes which are relatively cheaper as compared to dyes containing platinum and/or ruthenium.

Examples of organic dyes known in the art include those disclosed in, for example, US Patent Publication no. 2010/0012930 A1, published on 21 January 2010 in the names of Hyeon Choi, *et al.*, US Patent Publication no.
5 2010/0137611 A1, published on 3 June 2010 in the names of Koji Horiba, *et al.*, and US Patent no. 7935828, published on 3 May 2011 in the name of Dai Nippon Printing Co., Ltd.

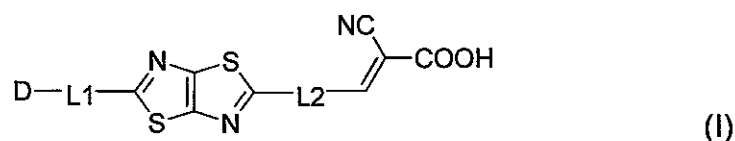
However, most organic dyes known in art have relatively lower solar energy-to-
10 electricity conversion efficiency and driving stability as compared to dyes containing ruthenium metal complex.

Therefore, there is a need to provide a novel organic dye for use in dye-sensitized solar cell that seeks to address at least one of the above problems, or
15 at least to provide an alternative.

Summary of the Invention

The above and other problems are solved and an advance in the art is made by
20 an organic dye for use in dye-sensitized solar cell in accordance with this invention. The organic dye in accordance with this invention has the advantage of having a large molar extinction coefficient which allows for high short circuit current J_{sc} , providing an improved molar absorption. A second advantage of the organic dye in accordance with this invention is that the organic dye has excellent
25 photoelectric conversion efficiency. A third advantage of the organic dye in accordance with this invention is that the organic dye can be prepared at a relatively lower cost. A fourth advantage of the organic dye in accordance with this invention is that the organic dye can be synthesized easily. A fifth advantage of the organic dye in accordance with this invention is that the molecular structure
30 of the organic dye can be facilely designed.

In accordance with an embodiment of this invention, an organic dye for use in dye-sensitized solar cell is provided. The organic dye is represented by the structure of formula (I):



wherein D is a donor group;

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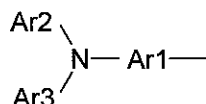
L1 is a single bond or an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings; and

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L2 is an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings.

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In accordance with an embodiment of this invention, the donor group D is represented by:



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wherein Ar1 represents a substituted or unsubstituted arylene group; and Ar2 and Ar3 each independently represent a substituted or unsubstituted aryl group.

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In accordance with some of the embodiments of this invention, Ar2 or Ar3 represents a substituted aryl group, a substituted group of the substituted aryl group is selected from the group comprising an alkyl having 1 to 12 carbon atom(s) and an alkoxy having 1 to 12 carbon atom(s).

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In accordance with some of the embodiments of this invention, Ar1 represents a substituted or unsubstituted 1,4-phenyl, 2,7-fluorene or 2,7-carbazole. A substituted group of the substituted or unsubstituted 1,4-phenyl, 2,7-fluorene or

2,7-carbazole is selected from the group comprising an alkyl having 1 to 12 carbon atoms and an alkoxy having 1 to 12 carbon atoms.

5 In accordance with some of these embodiments, Ar2 and Ar3 each independently represent a substituted or unsubstituted phenyl, 2-fluorenyl, 1-naphthyl, 9-anthracenyl, 1-pyrenyl or 2-carbazolyl.

10 In accordance with another embodiment of this invention, the donor group D is represented by D1, wherein D1 represents an alkyl-substituted carbazole, an alkyl or an aryl substituted indoline or an alkyl substituted phenothiazine. In accordance with some of these embodiments, L1 represents a single bond, a vinylene or an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any
15 combinations of the said rings; and L2 represents a vinylene or an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings.

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In accordance with another embodiment of this invention, a semiconductor film electrode comprising an organic dye in accordance with this invention is provided.

25 In accordance with some embodiments of this invention, a dye-sensitized solar cell comprising a semiconductor film electrode in accordance with this invention is provided.

30 In accordance with yet another embodiment of this invention, a dye-sensitized solar cell comprising an organic dye in accordance with this invention, an electrolyte and photo-electrodes is provided.

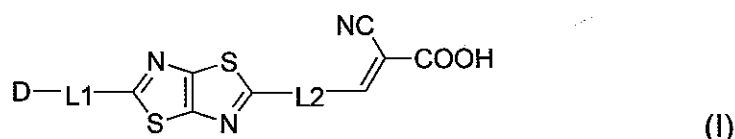
BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and advantages of the present invention will more clearly understood from the following detailed description taken in conjunction with the accompanying drawings:

- 5 Figure 1 is a graph showing the light-to-energy conversion efficiency of a dye-sensitized solar cell, fabricated using the organic dye of the present invention.

Detailed Description of the Invention

- 10 The present invention relates to an organic dye for use in a dye-sensitized solar cell. The organic dye is represented by the structure of formula (I):

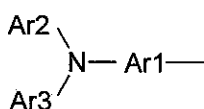


- 15 wherein D is a donor group;

L1 is a single bond or an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed
20 from any combinations of the said rings; and

L2 is an electron transfer linking group having at least one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any
25 combinations of the said rings.

In an embodiment of the invention, the donor group D is represented by:



wherein Ar1 represents a substituted or unsubstituted arylene group; and
Ar2 and Ar3 each independently represent a substituted or unsubstituted aryl
5 group.

In an embodiment where Ar2 or Ar3 represents a substituted aryl group, a
substituted group of the substituted aryl group is selected from the group
comprising an alkyl having 1 to 12 carbon atom(s) and an alkoxy having 1 to 12
10 carbon atom(s).

Preferably, Ar1 represents a substituted or unsubstituted 1,4-phenyl, 2,7-fluorene
or 2,7-carbazole. A substituted group of the substituted or unsubstituted 1,4-
phenyl, 2,7-fluorene or 2,7-carbazole is preferably selected from the group
15 comprising an alkyl having 1 to 12 carbon atoms and an alkoxy having 1 to 12
carbon atoms.

In a preferred embodiment, Ar2 and Ar3 each independently represent a
substituted or unsubstituted phenyl, 2-fluorenyl, 1-naphthyl, 9-anthracenyl, 1-
20 pyrenyl or 2-carbazolyl.

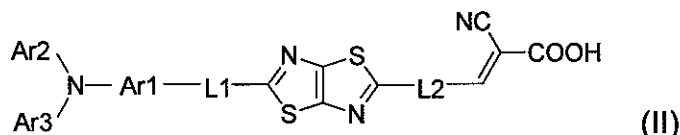
In another embodiment of the invention, the donor group D is represented by D1,
wherein D1 represents an alkyl substituted carbazole, an alkyl or an aryl
substituted indoline or an alkyl substituted phenothiazine.

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When the donor group D is represented by D1, L1 represents a single bond, a
vinylene or an electron transfer linking group having at least one heterocyclic ring
selected from the group comprising a thiophene ring, a furan ring, a benzene
ring, a pyrrole ring, and a condensed heterocyclic ring formed from any
30 combinations of the said rings; and L2 represents a vinylene or an electron
transfer linking group having at least one heterocyclic ring selected from the
group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring,

and a condensed heterocyclic ring formed from any combinations of the said rings.

In a selected embodiment of formula (I), an organic dye represented by the
5 following general formula (II) is provided:



10 wherein Ar1 represents a substituted or unsubstituted arylene group;
Ar2 and Ar3 each independently represent a substituted or unsubstituted aryl
group;
L1 represents a single bond or a spacer group; and
L2 represents a spacer group.

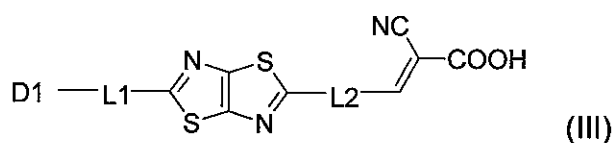
15 Preferably, Ar1 represents a substituted or unsubstituted 1,4-phenyl, 2,7-fluorene
or 2,7-carbazole. A substituted group of the substituted or unsubstituted 1,4-
phenyl, 2,7-fluorene or 2,7-carbazole is preferably selected from the group
comprising of an alkyl having 1 to 12 carbon atom(s) and an alkoxy having 1 to
20 12 carbon atom(s). More preferably, Ar1 is 1,4-phenyl.

Preferably, Ar2 and Ar3 each independently represent a substituted or
unsubstituted phenyl, 2-fluorenyl, 1-naphthyl, 9-anthracenyl, 1-pyrenyl or 2-
carbazolyl. More preferably, Ar2 and Ar3 each independently is a substituted or
25 unsubstituted phenyl. The substituted group of the substituted phenyl is
preferably an alkyl having 4 to 8 carbon atoms or an alkoxy having 4 to 8 carbon
atoms.

Preferably, the spacer group L1 represents a single bond, a vinylene or one
30 heterocyclic ring selected from the group comprising a thiophene ring, a furan
ring, a benzene ring, a pyrrole ring, and a condensed group formed from any
combinations of the said rings. The spacer group L2 represents a vinylene or

one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed group formed from any combinations of the said rings.

- 5 In another selected embodiment of formula (I), an organic dye represented by the following general formula (III) is provided:



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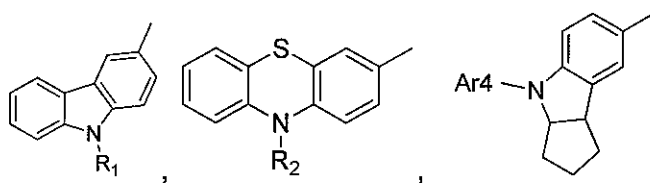
wherein D1 represents an alkyl substituted carbazole, an alkyl or an aryl substituted indoline or an alkyl substituted phenothiazine;

L1 represents a single bond or a spacer group; and

L2 represents a spacer group.

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In a preferred embodiment, D1 is an alkyl having 4 to 8 carbon atoms substituted carbazole, an alkyl having 4 to 8 carbon atoms or aryl substituted indoline or an alkyl having 4 to 8 carbon atoms substituted phenothiazine as shown below:



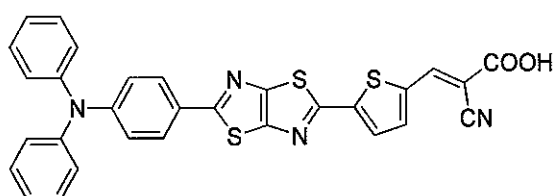
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wherein R₁ and R₂ each independently represent an alkyl having 4 to 8 carbon atoms; and

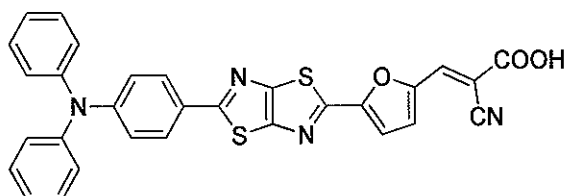
- 25 Ar₄ represents a substituted or unsubstituted phenyl. Preferably, the substitute group of the substituted phenyl is an alkyl having 1 to 8 carbon atom(s) or an alkoxy group having 1 to 8 carbon atom(s).

Preferably, the spacer group L1 represents a single bond, a vinylene or one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed group formed from any combinations of the said rings. The spacer group L2 represents a vinylene or one heterocyclic ring selected from the group comprising a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed group formed from any combinations of the said rings. More preferably, L1 is a single bond or a vinylene; L2 is a thiophene ring, a furan ring or a benzene ring.

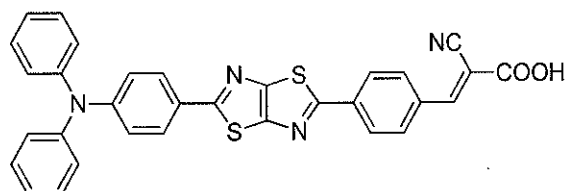
- Some illustrative examples of the organic dye represented by formula (I) include, but are not limited to, the following formulae.



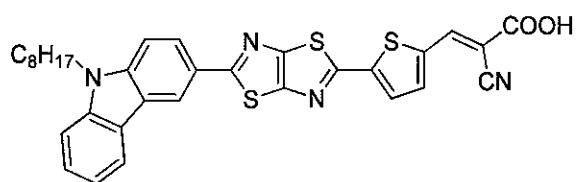
(T1)



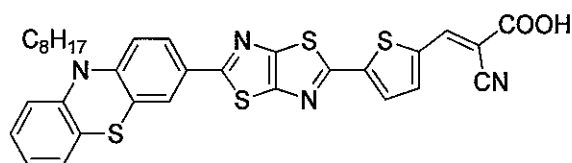
(T2)



(T3)

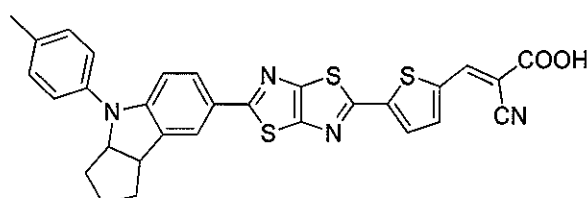


(T4)



(T5)

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(T6)

The organic dye of the present invention has several advantages. The organic dye has a large molar extinction coefficient which can lead to a high short circuit current J_{SC} . The organic dye has excellent photoelectric conversion efficiency and the performance of the dye is comparable to that of a ruthenium-based dye (as shown in Example 3 as described herein below). The cost of the organic dye of the present invention is relatively lower than that of a ruthenium-based dye and therefore, the dye can be prepared at a relatively lower cost. The molecular structure of the dye can be facilely designed and the dye can be synthesized easily as will be illustrated in the examples below.

In another embodiment of the invention, a semiconductor film electrode comprising the organic dye in accordance with the present invention is provided. In one embodiment, the semiconductor film electrode may comprise a substrate having an electrically conductive surface, an electron transporting layer disposed on the electrically conductive surface and an organic dye of formula (I) disposed on the electron-transporting layer.

In a further embodiment of the invention, a dye-sensitized solar cell comprising the organic dye in accordance with the present invention is provided. In one embodiment, the dye-sensitized solar cell may comprise a semiconductor film electrode, the semiconductor film electrode comprising a substrate having an electrically conductive surface, an electron transporting layer disposed on the electrically conductive surface and an organic dye of formula (I) disposed on the electron-transporting layer; a counter electrode; and a hole transporting layer in contact with the semiconductor film electrode and the counter electrode.

The dye-sensitized solar cell of the present invention uses the organic dye of the present invention which contains thiazolothiazole moiety. As the cost of the organic dye is relatively lower than that of a ruthenium-based dye as described hereinabove, the cost of manufacturing the dye-sensitized solar cell using the organic dye of the present invention is also relatively lower than that of a ruthenium-based dye-sensitized solar cell.

The present invention will be further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

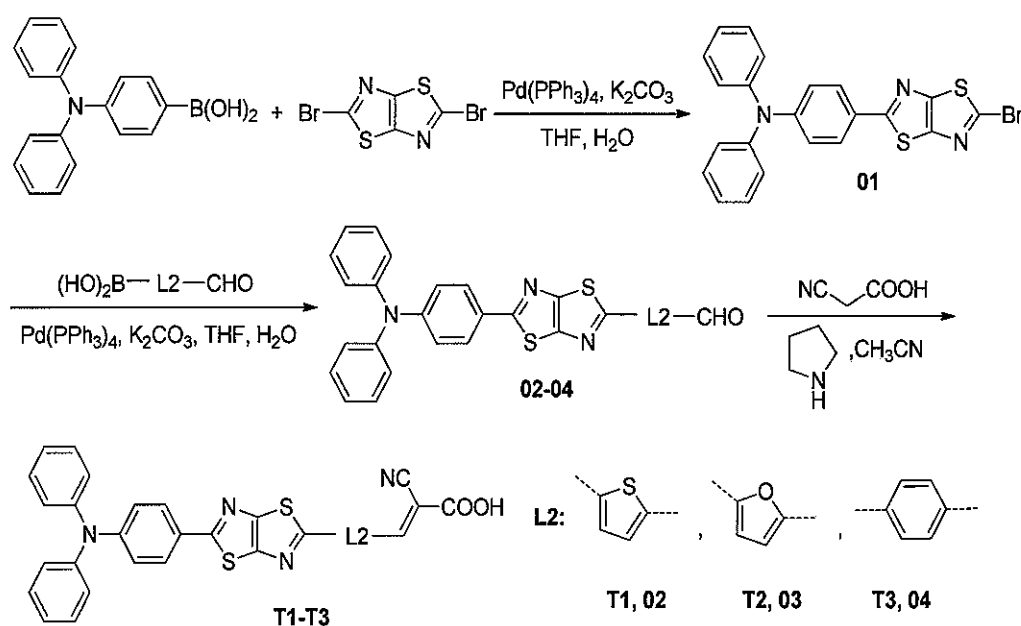
EXAMPLES

In order to clearly illustrate the method for preparing the organic dyes according to the invention, the preparation of some compounds disclosed in the invention are described in detail as below.

Example 1

Synthesis of Exemplary Compounds T1, T2 and T3

The synthetic route to the three organic dyes T1, T2 and T3 is depicted in Scheme 1.

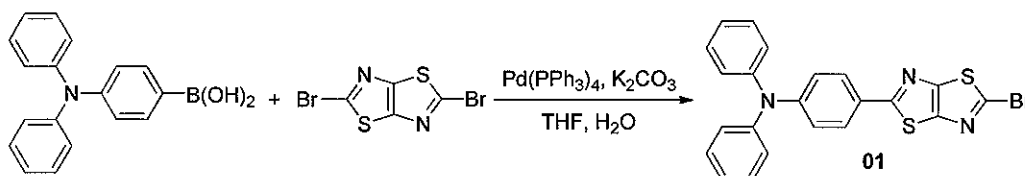


Scheme 1: Synthetic route of thiazolothiazole dyes (T1-T3)

- 5 The synthesis began with reacting 2,5-dibromothiazolo[5,4-d]thiazole with 4-(diphenylamino)phenylboronic acid via Suzuki coupling to afford the mono-substituted side product 01. This is followed by reacting the mono-substituted side product 01 with 5-formylthiophen-2-yl-boronic acid, 5-formylfuran-2-ylboronic acid and 4-formyl phenylboronic acid via Suzuki coupling to afford compound 02, 03 and 04, respectively. The desired products T1, T2 and T3 were then obtained from the subsequent Knoevenagel condensation of aldehydes 02, 03 and 04 with cyanoacetic acid in the presence of pyrrolidine and acetonitrile respectively.

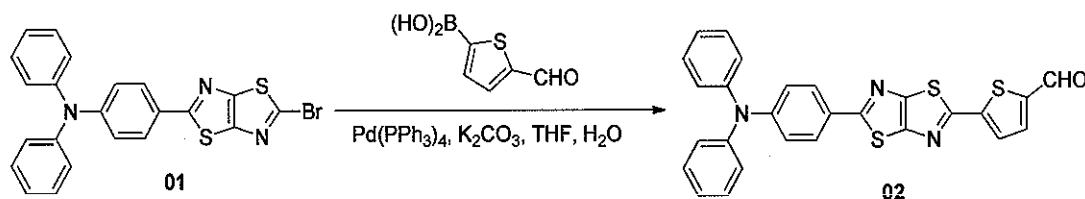
Synthesis of Compound (01) - 4-(5-bromothiazolo[5,4-d]thiazol-2-yl)-N,N-diphenylaniline

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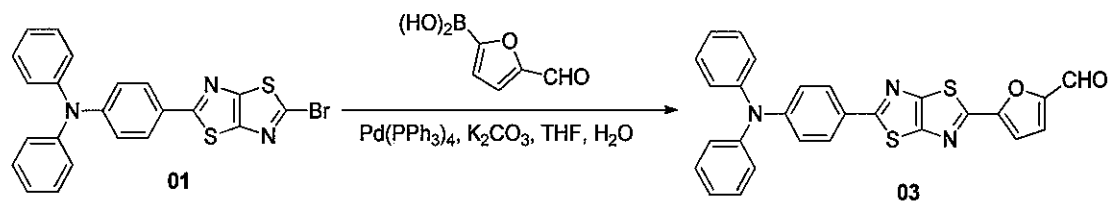
A mixture of 2,5-dibromothiazolo[5,4-d]thiazole, (4-(diphenylamino)phenyl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed from the mixture via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were then dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (02) - 5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde



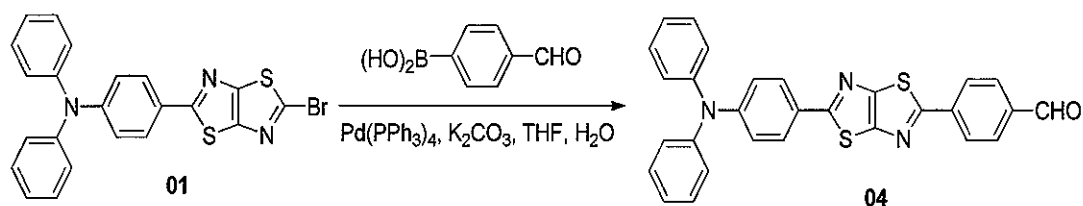
A mixture of 4-(5-bromothiazolo[5,4-d]thiazol-2-yl)-N,N-diphenylaniline, (5-formylthiophen-2-yl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed from the mixture via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (03) - 5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)furan-2-carbaldehyde



A mixture of 4-(5-bromothiazolo[5,4-d]thiazol-2-yl)-N,N-diphenylaniline, (5-formylfuran-2-yl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd(PPh}_3)_4$), and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed from the mixture via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (04) - 4-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)benzaldehyde



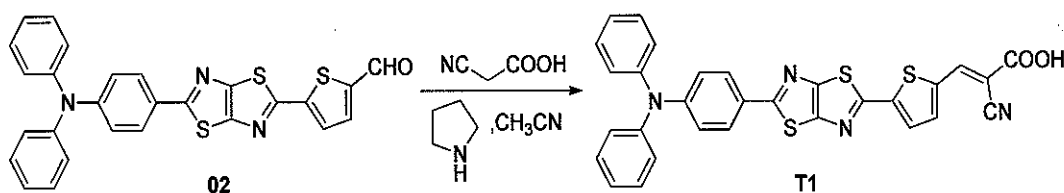
A mixture of 4-(5-bromothiazolo[5,4-d]thiazol-2-yl)-N,N-diphenylaniline, (4-formylphenyl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd(PPh}_3)_4$) and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed from the mixture via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was

evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Exemplary Compound (T1)

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(i) 2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)thiophen-2-yl)acrylic acid



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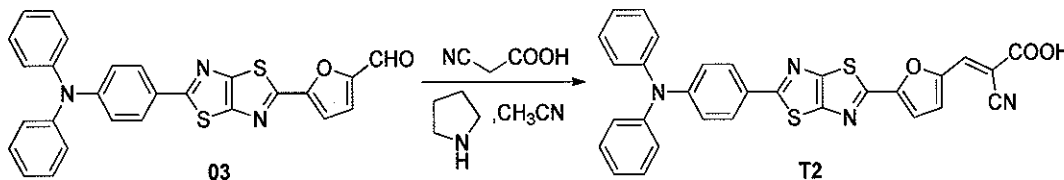
A mixture of 5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hour. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

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Synthesis of Exemplary Compound (T2)

(ii) 2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)furan-2-yl)acrylic acid

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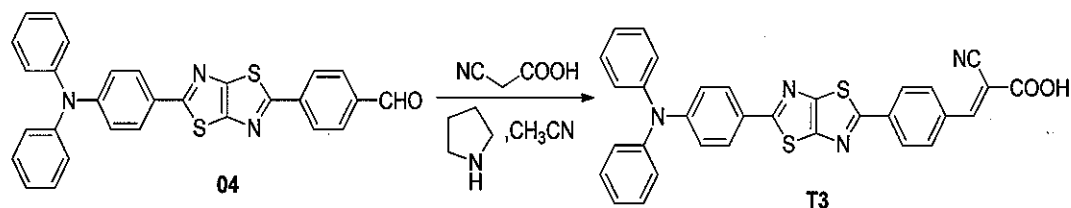


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A mixture of 5-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)furan-2-carbaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hours. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

Synthesis of Exemplary Compound (T3)

- (iii) 2-cyano-3-(4-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)phenyl)acrylic acid

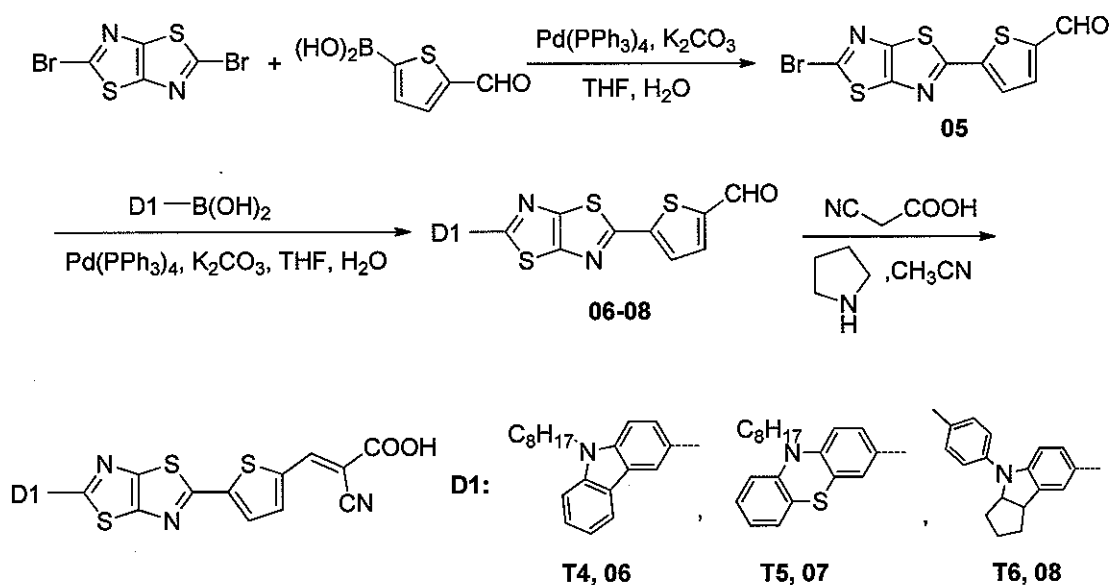


- A mixture of 4-(5-(4-(diphenylamino)phenyl)thiazolo[5,4-d]thiazol-2-yl)benzaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hours. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

15 EXAMPLE 2

Synthesis of Exemplary Compounds T4, T5 and T6

- The synthetic route to the three organic dyes T4, T5 and T6 is depicted in Scheme 2.

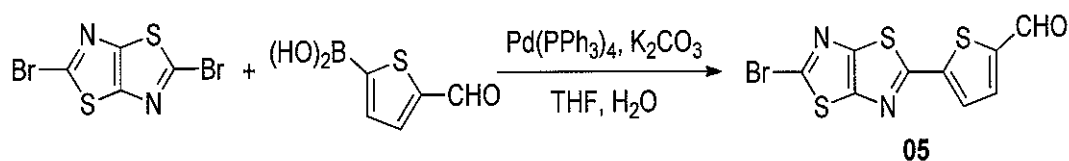


Scheme 2: Synthetic route of thiazolothiazole dyes (T4-T6)

- 5 The synthesis began with reacting 2,5-dibromothiazolo[5,4-d]thiazole with 5-formylthiophen-2-yl-boronic acid via Suzuki coupling to afford the mono-substituted side product 05. This is followed by reacting the mono-substituted side product 05 with (9-octyl-9H-carbazol-3-yl)boronic acid, (10-octyl-10H-phenothiazin-3-yl)boronic acid and (4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid via Suzuki coupling to afford compound 06, 07 and 08 respectively. The desired products T4, T5 and T6 were then obtained from the subsequent Knoevenagel condensation of aldehydes 06, 07 and 08 with cyanoacetic acid in the presence of pyrrolidine and acetonitrile respectively.

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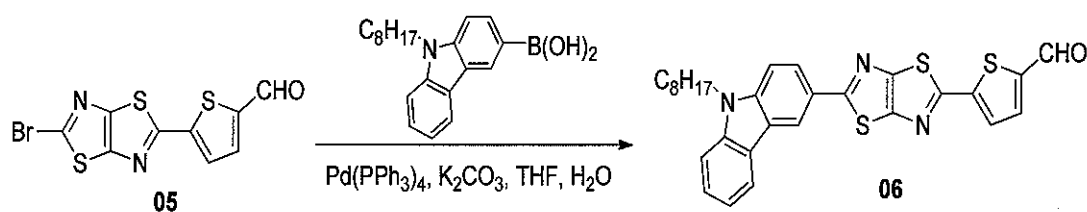
Synthesis of Compound (05)- 5-(5-bromothiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde



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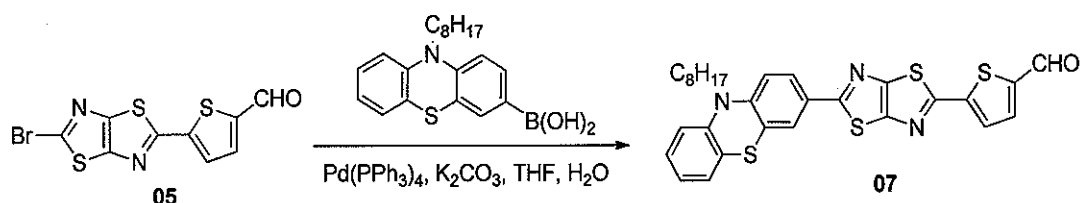
A mixture of 2,5-dibromothiazolo[5,4-d]thiazole, (5-formylthiophen-2-yl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed from the mixture via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (06)- 5-(5-(9-octyl-9H-carbazol-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde



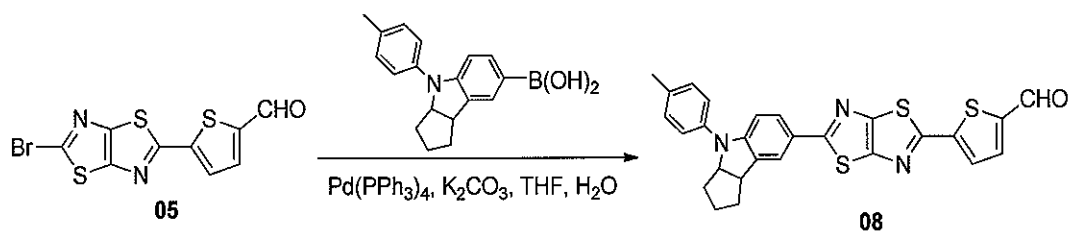
A mixture of 5-(5-bromothiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, (9-octyl-9H-carbazol-3-yl)boronic acid, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and 2M of aqueous potassium carbonate (K_2CO_3) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH_2Cl_2). The combined organic layers were dried with anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (07)- 5-(5-(10-octyl-10H-phenothiazin-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde



A mixture of 5-(5-bromothiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, (10-octyl-10H-phenothiazin-3-yl)boronic acid, tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) and 2M of aqueous potassium carbonate (K₂CO₃) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH₂Cl₂). The combined organic layers were dried with anhydrous sodium sulfate (Na₂SO₄). The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Compound (08)- 5-(5-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde



A mixture of 5-(5-bromothiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, (4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid, tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) and 2M of aqueous potassium carbonate (K₂CO₃) was prepared under a nitrogen atmosphere. Tetrahydrofuran (THF) was injected into the mixture and the mixture was refluxed for 24 hours. The mixture was then cooled to room temperature before THF was removed via evaporation. The mixture was then extracted with 3 x 20 ml of dichloromethane (CH₂Cl₂). The combined organic layers were dried with anhydrous sodium sulfate

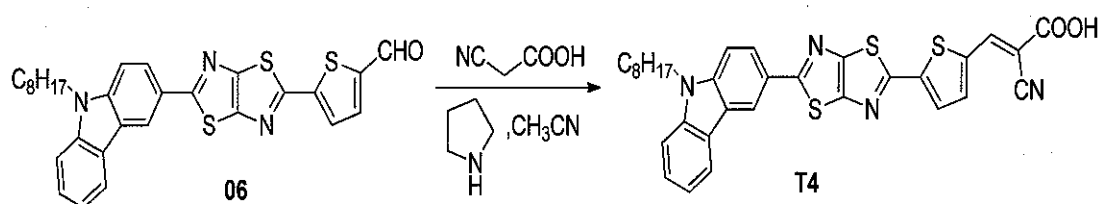
Na_2SO_4 . The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Synthesis of Exemplary Compound (T4)

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(iv) 2-cyano-3-(5-(5-(9-octyl-9H-carbazol-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophen-2-yl)acrylic acid

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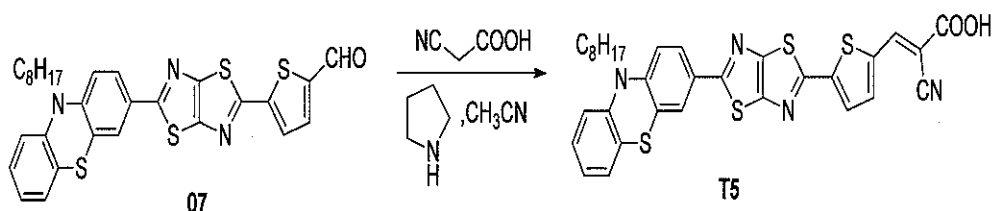
A mixture of 5-(5-(9-octyl-9H-carbazol-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hours. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

Synthesis of Exemplary Compound (T5)

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(v) 2-cyano-3-(5-(5-(10-octyl-10H-phenothiazin-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophen-2-yl)acrylic acid

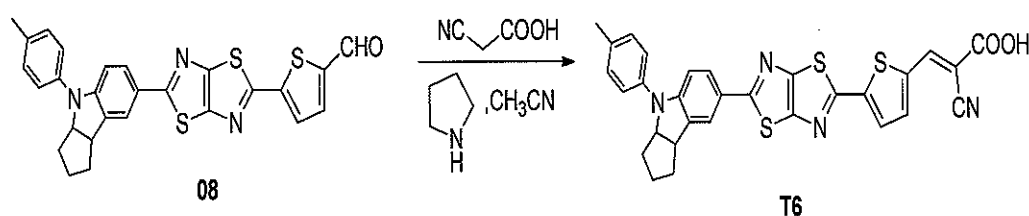
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A mixture of 5-(5-(10-octyl-10H-phenothiazin-3-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hours. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

Synthesis of Exemplary Compound (T6)

(vi) 2-cyano-3-(5-(5-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)thiazolo[5,4-d]thiazol-2-yl)thiophen-2-yl)acrylic acid



A mixture of 5-(5-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)thiazolo[5,4-d]thiazol-2-yl)thiophene-2-carbaldehyde, 2-cyanoacetic acid, pyrrolidine and acetonitrile was refluxed for 18 hours. The mixture was then cooled to room temperature before it was added to water. The precipitate formed was then filtered and washed with water. The residue was purified by column chromatography on silica gel.

EXAMPLE 3

Fabrication of dye-sensitized solar cell

Device fabrication: The titanium dioxide (TiO_2) films were fabricated using a screen printing method according to the published method known in the art. The thickness of the films is about 15 μm . The tri-layer TiO_2 electrodes were heated under an air flow at 450 $^\circ\text{C}$ for 15 min and 500 $^\circ\text{C}$ for 15 min. The sintered films were further treated with 40 mM of titanium tetrachloride (TiCl_4) aqueous solution at 70 $^\circ\text{C}$ for 40 min and washed with water and ethanol, which can significantly increase the short-circuit photocurrent. The films were then annealed at 450 $^\circ\text{C}$

for 30 min. After the titanium tetrachloride pretreated films were cooled down at around 50 °C, it was immersed into a 5×10^{-4} M dye bath in dichloromethane (CH_2Cl_2) solutions and maintained under dark for 18 hours at room temperature. The electrode was then rinsed with CH_2Cl_2 and ethanol and then dried.

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To prepare the counter electrode, platinum catalyst was deposited on the cleaned fluorine doped tin oxide (FTO) glass by spinning with a drop of platinum chloride (H_2PtCl_6) solution (20 mM 2-propanol solution) and treated with heat at 400 °C for 15 min. Two holes were drilled on the counter electrode using a drill-press. The perforated sheet was cleaned with ultrasound in an ethanol bath for 10 min. For the assembly of DSSCs, the dye-covered TiO_2 electrode and platinum-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (DuPont). The electrolyte (0.1 M LiI, 0.05 M I_2 , 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M TBP in a mixture of acetonitrile and methoxypropionitrile (volume ratio, 7 : 3)) was introduced into the cell from a hole in the back of the counter electrode. Finally, the hole was sealed using a hot-melt gasket.

The dye-sensitized solar cell fabrication was then completed. A high light-to-energy conversion efficiency of about 5.0% was achieved under solar simulator test (AM 1.5, 1 Sun condition) (see Figure 1 and Table 1 below). The results obtained are comparable to that of a N719-sensitized TiO_2 solar cell containing ruthenium-based dye, which showed an efficiency of about 6.98% when tested under the same experimental conditions as the solar cell of the invention.

25

Table 1

	Measurements
Voc (V)	0.60175
Isc (A)	0.0023477
Vmax (V)	0.42498
Imax (A)	0.0017697
Pmax (W)	0.00075209
Efficiency, η (%)	5.0352

Fill Factor (%)	53.236
Jsc (mA/cm ²)	14.775
Cell Temperature (deg. C)	23.560
Rsh (Ohm)	1381.0

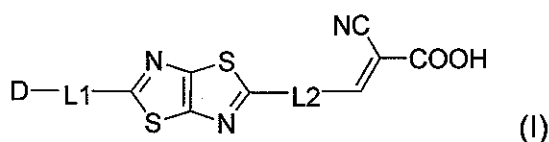
The above is a description of the subject matter the inventor regards as the invention. It is foreseeable that those skilled in the art can and will design alternative methods and compounds that include this invention based on the

5 above disclosure.

CLAIMS:

1. An organic dye for use in dye-sensitized solar cell, the organic dye represented by the structure of formula (I):

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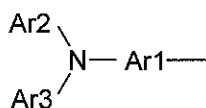


wherein D is a donor group;

10 L1 is a single bond or an electron transfer linking group having at least one heterocyclic ring selected from the group consisting of a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings; and

15 L2 is an electron transfer linking group having at least one heterocyclic ring selected from the group consisting of a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings.

20 2. The organic dye according to claim 1, wherein the donor group D is represented by:



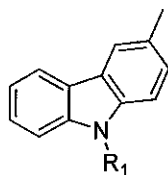
wherein Ar1 represents a substituted or unsubstituted arylene group; and

25 Ar2 and Ar3 each independently represent a substituted or unsubstituted aryl group.

30 3. The organic dye according to claim 2, wherein Ar2 or Ar3 represents a substituted aryl group, a substituted group of the substituted aryl group is selected from the group consisting of an alkyl having 1 to 12 carbon atom(s) or an alkoxy having 1 to 12 carbon atom(s).

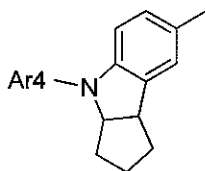
4. The organic dye according to claim 2, wherein Ar1 is a substituted or unsubstituted 1,4-phenyl, 2,7-fluorene or 2,7-carbazole.
5. The organic dye according to claim 4, wherein a substituted group of the substituted or unsubstituted 1,4-phenyl, 2,7-fluorene or 2,7-carbazole is selected from the group consisting of an alkyl having 1 to 12 carbon atom(s) and an alkoxy having 1 to 12 carbon atom(s).
6. The organic dye according to claim 4, wherein Ar1 is 1-4-phenyl.
7. The organic dye according to claim 2, wherein Ar2 and Ar3 each independently represent a substituted or unsubstituted phenyl, 2-fluorenyl, 1-naphthyl, 9-anthracenyl, 1-pyrenyl or 2-carbazolyl.
8. The organic dye according to claim 7, wherein Ar2 and Ar3 each independently is a substituted or unsubstituted phenyl.
9. The organic dye according to claim 1, wherein the donor group D is represented by D1, wherein D1 represents an alkyl substituted carbazole, an alkyl or an aryl substituted indoline or an alkyl substituted phenothiazine.
10. The organic dye according to claim 9, wherein L1 represents a single bond, a vinylene or an electron transfer linking group having at least one heterocyclic ring selected from the group consisting of a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings; and L2 represents a vinylene or an electron transfer linking group having at least one heterocyclic ring selected from the group consisting of a thiophene ring, a furan ring, a benzene ring, a pyrrole ring, and a condensed heterocyclic ring formed from any combinations of the said rings.

11. The organic dye according to claim 9, wherein D1 is an alkyl substituted carbazole represented by the following formula:



5 wherein R₁ represents an alkyl having 4 to 8 carbon atoms.

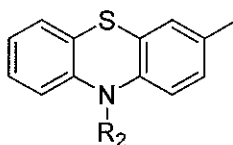
12. The organic dye according to claim 9, wherein D1 is an alkyl substituted indoline represented by the following formula:



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wherein Ar₄ represents a substituted or unsubstituted phenyl.

13. The organic dye according to claim 9, wherein D1 is an alkyl substituted
15 phenothiazine represented by the following formula:



wherein R₂ represents an alkyl having 4 to 8 carbon atoms.

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14. A semiconductor film electrode comprising an organic dye according to claim 1.

15. A dye-sensitized solar cell comprising a semiconductor film electrode
25 according to claim 14.

16. A dye-sensitized solar cell comprising an organic dye according to claim 1, an electrolyte and photo-electrodes.