The present invention provides PHPIT and fabrication thereof. PHPIT has a side-chain-tethered with hexylphenanthryl-imidazole polythiophene. The visible light absorption of the PHPIT/PCBM blend is enhanced by the presence of the electron-withdrawing hexylphenanthryl-imidazole. The PHPIT/PCBM blend experienced more-balanced electron and hole mobilities and solvability.
Figure 1
<table>
<thead>
<tr>
<th>Polymer blend annealed at 120°C</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>Fill Factor (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PHPIT/PCBM</strong> (w/w=1:1) annealed for 20 min</td>
<td>0.6</td>
<td>8.3</td>
<td>62</td>
<td>3.1</td>
</tr>
<tr>
<td><strong>PHPIT/PCBM</strong> (w/w=1:1) annealed for 30 min</td>
<td>0.61</td>
<td>11.3</td>
<td>60</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Figure 2**
Figure 3
<table>
<thead>
<tr>
<th>Polymer blend annealed at 120°</th>
<th>hole mobility($\mu_h$) (cm²/Vs)</th>
<th>electron mobility($\mu_e$) (cm²/Vs)</th>
<th>$\mu_e/\mu_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P3HT/PCBM (w/w=1:1)</strong></td>
<td>$1.8 \times 10^{-6}$</td>
<td>$2.5 \times 10^{-5}$</td>
<td>13.8</td>
</tr>
<tr>
<td>annealed for 30 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PHPIT/PCBM (w/w=1:1)</strong></td>
<td>$6.6 \times 10^{-6}$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>2.4</td>
</tr>
<tr>
<td>annealed for 20 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PHPIT/PCBM (w/w=1:1)</strong></td>
<td>$1.8 \times 10^{-5}$</td>
<td>$3.7 \times 10^{-5}$</td>
<td>2.0</td>
</tr>
<tr>
<td>annealed for 30 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PHPIT/PCBM</strong></td>
<td>$4.4 \times 10^{-6}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>3.2</td>
</tr>
</tbody>
</table>

**Figure 5**
PHOTOT R AND FABRICATION THEREOF

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention provides a polythiophene derivative polymer, particularly a polythiophene derivative polymer applied to solar cell.

[0003] 2. Description of the Prior Art

[0004] In recent years, for the application of polymer to solar cell, there are several problems that have to be improved, such as insufficient light absorption range, shorter wavelength of adsorbed light (only about 700 nm), low charge transferring speed, and easy recombination phenomenon and so on.

[0005] Thus, there are many research results about the improvement of solar cell efficiency have been published in recent years. It means to use different annealing temperature and different time to reduce the resistance of components, or introduce the electrode having low work function as the technological means. On the other hand, there are few researches that discuss the introduction of different conjugated monomers to change the structure of polymer.

[0006] As for the polymerization of donor-acceptor polymer, for example, there is significant progress for the addition of polyfluorene on the main chain. The introduction of polyfluorene can change the highest occupied molecular orbital (HOMO) energy level but reduce electron mobility and hole mobility. Therefore, the new introduced material can improve the electron and hole mobility and the efficiency.

[0007] Obviously, under the circumstance that the existing technology is unable to reach effective light absorption and charge transferring, it is more important for the research and development of the advanced material to the solar cell technology.

SUMMARY OF THE INVENTION

[0008] The present invention provides a polythiophene derivative polymer applied to solar cell and its fabrication method thereof. The hexyl group is introduced to the end of polymer on order to improve solubility of the polymer.

[0009] Moreover, the present invention provides a polythiophene derivative polymer applied to solar cell and its fabrication method thereof, such as a method for fabricating organic polymer of solar cell. The phenanthryl-1,3-imidaazole group is introduced to the polymer for generating the donor-acceptor effect in intramolecular of polymers. The charge separation of molecule can accelerate the charge separation of polymer, and improve the photovoltaic conversion efficiency.

[0010] According to the above-mentioned description, a polythiophene derivative polymer is developed. This polythiophene derivative polymer has a side-chain tethered with hexylphenanthryl-1,3-imidaazole polythiophene, and have a hexyl group at its end. The fabrication method comprises: Reacting 3,6-dibromophenanthrene-9,10-dione with 3-thiopheneacarboxaldehyde, 4-hexylaniline, ammonium acetate, and acetic acid to form Compound 1 firstly.

[0011] Consequently, reacting Compound 1 with hexyl magnesium bromide and Ni(dppp)Cl₂ to form Compound 2. Then reacting Compound 2 with N-bromosuccinimide (NBS), tetrahydrofuran (THF), and acetic acid to form 2-(2,5-dibromophenyl-3-yl)-6,9-dihexyl-1-(4-hexylphenyl)-1H-phenanthro[9,10-d]-imidazole (HPIT). Finally, reacting HPIT with tetrahydrofuran, methyl magnesium bromide, and Ni(dppp)Cl₂ to form polymer for solar cell applications.

[0012] Therefore, the advantage and spirit of the invention can be further understood by the following detailed description and figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as well becomes better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

[0014] FIG. 1 shows the preparation process for the embodiment of the present invention.

[0015] FIG. 2 shows the photovoltaic conversion efficiency for the embodiment of the present invention.

[0016] FIG. 3 is a relationship diagram of wavelength versus EQE, which describes the comparison for the embodiment of the present invention and the conventional P3HT/PCBM.

[0017] FIGS. 4A, FIG. 4B and FIG. 4C show the image of PHIT/PCBM film taken by the atomic force microscope under 20, 30, and 45 minutes, respectively.

[0018] FIG. 5 shows the electron mobility, hole mobility, and their ratio of PHIT/PCBM and P3HT/PCBM for different temperature keeping time.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] The present invention provides a polymer applied to solar cell and its fabrication method thereof. The 3,6-dibromophenanthrene-9,10-dione is prepared by a suitable method firstly. In an embodiment, N-bromosuccinimide (NBS) is dropped into a solution composed of 9,10-dihydrophenanthrene, tetrahydrofuran (THF), and acetic acid gradually, and agitate the mixture for 20 minutes. Add the saturated NaHCO₃, and use water to rinse the solution. Use ethyl acetate to extract the solution. Use MgSO₄ to dry the organic layer, and concentrate it to obtain 3,6-dibromophenanthrene. Then dissolve 3,6-dibromophenanthrene and chromic trioxide in acetic anhydride, and react at room temperature for several hours. Pour the solution into 1N HCl solution. Use ethyl acetate to extract the solution. Use MgSO₄ to dry the organic layer, and concentrate it to obtain 3,6-dibromophenanthrene-9,10-dione.

[0020] Please refer to FIG. 1, after 3,6-dibromophenanthrene-9,10-dione is reacted with 3-thiopheneacarboxaldehyde, 4-hexylaniline, ammonium acetate, and acetic acid is separated the Compound 1 (6,9-dibromo-1-phenyl-2-(thiophen-3-yl)-1H-phenanthro[9,10-d]-imidazole) from the products.

[0021] Then please refer to FIG. 1, after Compound 1 is reacted with hexyl magnesium bromide and Ni(dppp)Cl₂ to form Compound 2. Then reacting Compound 2 with N-bromosuccinimide (NBS), tetrahydrofuran (THF), and acetic acid to form 2-(2,5-dibromophenyl-3-yl)-6,9-dihexyl-1-(4-hexylphenyl)-1H-phenanthro[9,10-d]-imidazole from the products.

[0022] As shown in FIG. 1, after Compound 2 is reacted with N-bromosuccinimide (NBS), tetrahydrofuran (THF) and acetic acid, separate the formed HPIT (2-(2,5-dibromophenyl-3-yl)-6,9-dihexyl-1-(4-hexylphenyl)-1H-phenanthro[9,10-d]-imidazole) from the products.

[0023] Then please refer to FIG. 1 again, after HPIT is reacted with tetrahydrofuran (THF), methyl magnesium bro-
mide and Ni(dppp)Cl₂. PHPIT (poly(hexylphenanthryl-
imidazole thiophene) (poly[2-(thiophen-3-yl)-6,9-dihexyl-
1-(4-hexylnyl)-1H-phenanthro[9,10-d]imidazole]) is formed.

[0024] According to PHPIT prepared in the above-men-
tioned process, the solvability of polymer is improved, due to
the introduction of three hexyl groups. Furthermore, after
phenanthryl-1,3-imidazole group is introduced, the char-
ges in molecule are separated due to the donor-acceptor
effect, that can accelerate the charge separation of polymer
and obtain more-balanced electron mobility and hole mobi-
ity, and improve the photovoltaic conversion efficiency.

[0025] Then, blend PHPIT and [6,6]-phenyl-C₆₁-butyric
acid methyl ester (PCBM) to form a component. Thus, the
structure of component prepared in the present invention is
ITO/PEDOT:PSS/PHPIT:PCBM (1:1, w/w)/Ca/Al solar cell.
And then, the measurement of photovoltaic current can be
conducted, wherein the photovoltaic current density is altered
with the keeping temperature.

[0026] Referring to the embodiment shown in FIG. 2, when
the temperature is kept at 120°C, the best photovoltaic
conversion efficiency can be obtained. When the tempera-
ture is kept for 20 minutes, the photovoltaic current density is 8.3
mA/cm² and the photovoltaic conversion efficiency is 3.1%.
When the temperature is kept for 30 minutes, the photovoltaic
current density is 11.5 mA/cm² and the photovoltaic conver-
sion efficiency is 4.1%, which is increased 32% compared to
the condition at 20 minutes.

[0027] FIG. 3 is a relationship diagram of wavelength ver-
sus external quantum efficiency (EQE), which describes
the comparison for the embodiment of the present invention
and the conventional P3HT/PCBM. It is understood from
the diagram that the EQE of PHPIT/PCBM of the present inven-
tion is higher than that of the conventional P3HT/PCBM. It is
the most significant case when the temperature is kept for 30
minutes. According to the above-mentioned description, the
solvability for the embodiment of the present invention is
very well, which can raise the value of fill factor (FF).
Moreover, the internal charge separation ability and the visible
light absorption ability of polymer are increased, thus the
photovoltaic conversion efficiency is improved.

[0028] FIG. 4A, FIG. 4B and FIG. 4C show the image of
PHPIT/PCBM film taken by the atomic force microscope under
20, 30, and 45 minutes, respectively. When the tem-
perature is kept for 30 minutes, the R.M.S. roughness is
increased to 2.27, which describes the possibility for the
increase of internal light absorption of the component.

[0029] FIG. 5 shows the electron mobility, hole mobility,
and their ratio of PHPIT/PCBM and P3HT/PCBM for different
temperature keeping time. It is shown when more-bal-
anced electron and hole mobility is achieved, a higher short-
circuit current density will be produced.

[0030] It is understood that various other modifications will
be apparent to and can be readily made by those skilled in
the art without departing from the scope and spirit of this inven-
tion. Accordingly, it is not intended that the scope of the
claims appended hereto be limited to the description as set
forth herein, but rather that the claims be construed as encoun-
tering all the features of patentable novelty that reside in the
present invention, including all features that would be treated
as equivalents thereof by those skilled in the art to which this
invention pertains.

What is claimed is:
1. A polythiophene derivative polymer having a side-chain
tethered with hexylphenanthryl-1,3-imidazole poly-

2. The material according to claim 1, wherein the poly-
thiophene derivative polymer comprises a hexyl group at
its end.

3. The material according to claim 2, wherein the poly-
thiophene derivative polymer comprises PHPIT (poly(hexyl-
phenanthryl-imidazole thiophene)).

4. A polymer for solar cell applications, comprised blended
by [6,6]-phenyl-C₆₁-butyric acid methyl ester and poly-
thiophene derivative polymer, wherein the polythiophene
derivative polymer having a side-chain tethered with hexyl-
phenanthryl-1,3-imidazole polyythiophene.

5. The material according to claim 4, wherein the poly-
thiophene derivative polymer comprises a hexyl group at
its end.

6. The material according to claim 5, wherein the poly-
thiophene derivative polymer comprises PHPIT (poly(hexyl-
phenanthryl-imidazole thiophene)).

7. A method for fabricating organic polymer of solar cell,
comprising:
reacting 3,6-dibromophenanthrene-9,10-dione with
3-thiophenecarboxaldehyde, 4-hexylnalnine, ammo-
nium acetate and acetic acid to form as a Compound 1;
reacting the Compound 1 with hexyl magnesium bromide
and Ni(dppp)Cl₂ to form as a Compound 2;
reacting the Compound 2 with N-bromosuccinimide
(NBS), tetrahydrofuran (THF), and acetic acid to form a
2-(2,5-dibromothiophen-3-yl)-6,9-dihexyl-1-(4-hexyl-
phyen)-1H-phenanthro[9,10-d]imidazole (HPIT); and
reacting the HPT with tetrahydrofuran, methyl magne-
sium bromide and Ni(dppp)Cl₂ to form the organic polymer
of solar cell.

8. The method according to claim 7, wherein the polymer
comprises polythiophene derivative polymer.

9. The method according to claim 8, wherein the poly-
thiophene derivative polymer comprises a side-chain tethered
having hexylphenanthryl-1,3-imidazole polythiophene.

10. The method according to claim 9, wherein the poly-
thiophene derivative polymer comprises a hexyl group at
its end.

11. The method according to claim 8, wherein the poly-
thiophene derivative polymer comprises PHPIT (poly(hexyl-
phenanthryl-imidazole thiophene)).

12. A method for fabricating PHPIT, comprising:
reacting 3,6-dibromophenanthrene-9,10-dione with
3-thiophenecarboxaldehyde, 4-hexylnalnine, ammo-
nium acetate and acetic acid to form as a Compound 1;
reacting the Compound 1 with hexyl magnesium bromide
and Ni(dppp)Cl₂ to form as a Compound 2;
reacting the Compound 2 with N-bromosuccinimide
(NBS), tetrahydrofuran (THF), and acetic acid to form a
HPIT; and
reacting the HPIT with tetrahydrofuran, methyl magne-
sium bromide and Ni(dppp)Cl₂ to form a PHPIT (poly
(hexylphenanthryl-imidazole thiophene).

13. The PHPIT according to claim 12, wherein the PHPIT
is applied to solar cell.

* * * * *