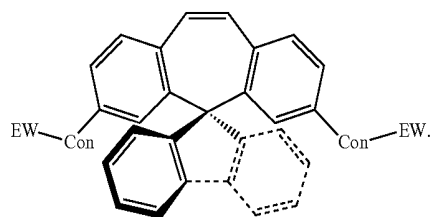




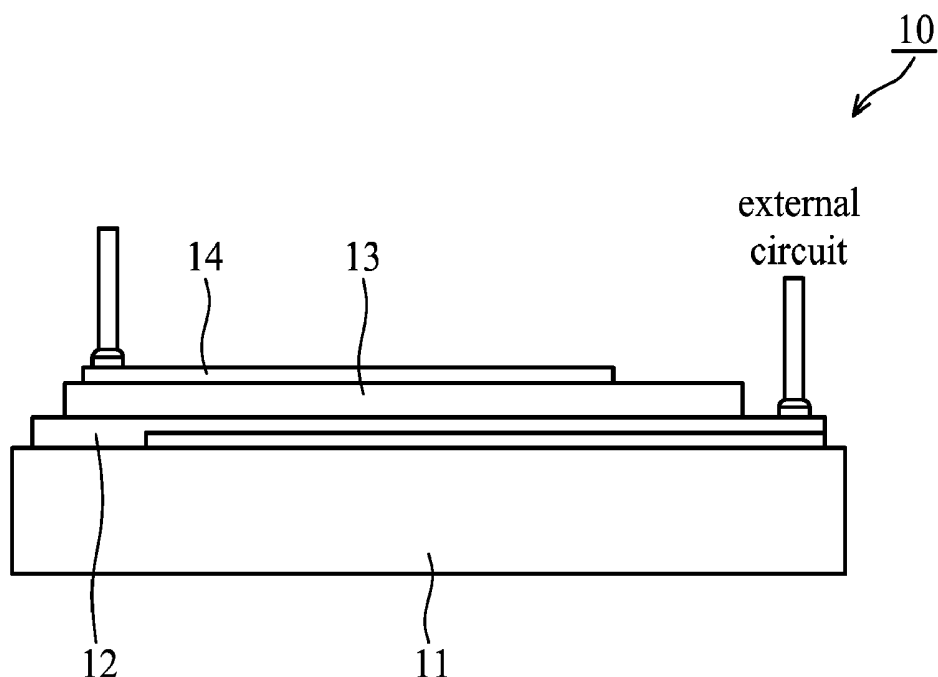
US 20140121386A1

(19) **United States**(12) **Patent Application Publication**
CHEN et al.(10) **Pub. No.: US 2014/0121386 A1**(43) **Pub. Date: May 1, 2014**(54) **P-TYPE ORGANIC SEMICONDUCTOR
MATERIAL AND OPTOELECTRONIC
DEVICE UTILIZING THE SAME**(71) Applicant: **INDUSTRIAL TECHNOLOGY
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CPC **H01L 51/0068** (2013.01)
USPC **549/59**(57) **ABSTRACT**Disclosed is a p-type organic semiconductor material having
the formula:

Each Con is the same and consists of a conjugated oligomer.
Each EW is the same and consists of an electron withdrawing
group. The p-type organic semiconductor material can be
applied in an active layer of an optoelectronic device, such as
an organic solar cell, an organic light-emitting diode, or an
organic thin-film transistor.



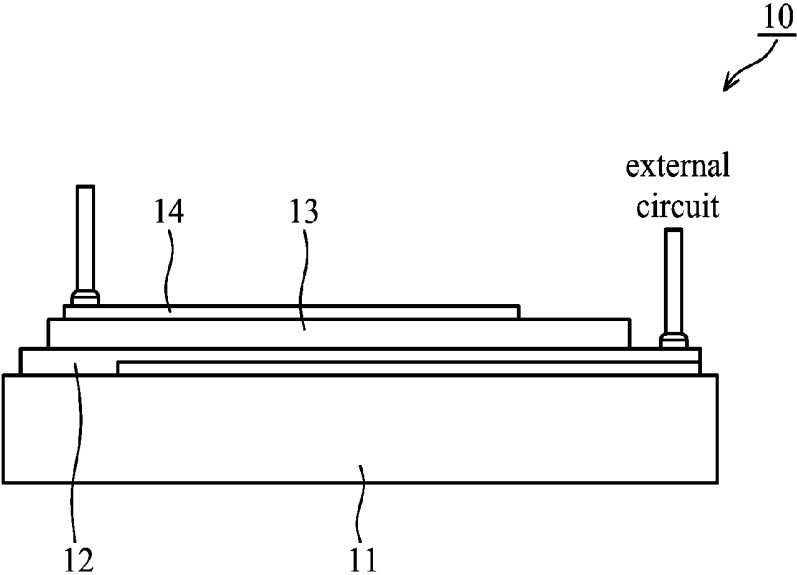


FIG. 1

P-TYPE ORGANIC SEMICONDUCTOR MATERIAL AND OPTOELECTRONIC DEVICE UTILIZING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is based on, and claims priority from, Taiwan Application Serial Number 101139632, filed on Oct. 26, 2012, the disclosure of which is hereby incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] The technical field relates to a p-type organic semiconductor material, and in particular to an optoelectronic device utilizing the same.

BACKGROUND

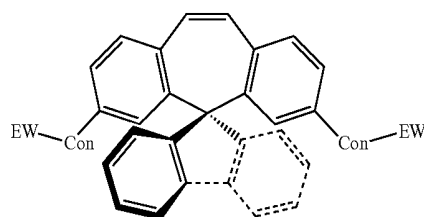
[0003] Because organic semiconductor materials have semiconducting and optoelectronic properties, they can be applied in many optoelectronic devices such as organic thin-film transistors (OTFT), organic solar cells, organic light-emitting diodes (OLED), and photo sensors. The organic semiconductor materials are utilized to form an active film on optoelectronic devices by solution coating. Optoelectronic devices utilizing organic semiconductor materials have advantages such as being lightweight, inexpensive, easy to fabricate, and flexible, in addition to their suitability for large-area fabrication. Conjugated polymers with a conjugated backbone are among the most popular organic semiconductor materials for use in optoelectronic devices. However, the conjugated polymer has disadvantages, such as low carrier mobility and a narrow absorption band of about 400 nm to 650 nm. As such, the application of conjugated polymers in optoelectronic devices is limited. Therefore, many conjugated polymers are synthesized to enhance carrier mobility and the absorption band thereof, to further improve photoelectric efficiency.

[0004] In solar cell applications, characteristics such as high electron/hole mobility and a wide absorption band are desirable for improving power-conversion efficiency. Photo-induced or electro-induced charges are easily recombined to dissipate in an improper active layer, thereby lowering the power-conversion efficiency of an organic solar cell, including the improper active layer. If the solar light absorption is increased and the carrier mobility is enhanced, the power-conversion efficiency of the organic solar cell can be greatly increased. Thus, an electron donor material such as polymer is often combined with an electron acceptor material such as C60 by heterojunction technology. For example, the electron donor material poly(3-hexylthiophene) (P3HT) blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) has a power-conversion efficiency of 3.5%.

[0005] Therefore, a novel p-type organic semiconductor material for replacing the P3HT to improve the organic solar cell performance (e.g. power-conversion efficiency) is still called-for.

SUMMARY

[0006] One embodiment of the disclosure provides a p-type organic semiconductor material, having the chemical formula:



wherein each Con is the same and consists of a conjugated oligomer; and each EW is the same and consists of an electron withdrawing group.

[0007] One embodiment of the disclosure provides an optoelectronic device, having an active layer, wherein the active layer includes the described p-type organic semiconductor material.

[0008] A detailed description is given in the following embodiments with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The disclosure can be more fully understood by reading the subsequent detailed description and examples with references made to the accompanying drawings, wherein:

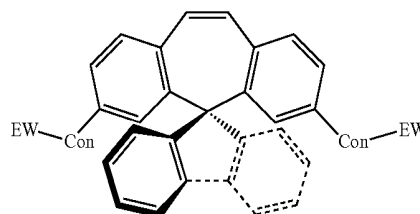
[0010] FIG. 1 shows an organic solar-cell device in one embodiment of the disclosure.

DETAILED DESCRIPTION

[0011] For the purposes of explanation, numerous specific details are set forth in the following detailed description to provide a thorough understanding of the disclosed embodiments. It will be apparent, however, that one or more embodiments may be practiced without these specific details. In other instances, well-known structures and devices are schematically shown in order to simplify the drawing.

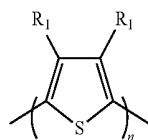
[0012] One embodiment of the disclosure provides a p-type organic semiconductor material as shown in Formula 1.

(Formula 1)



[0013] In Formula 1, each Con is the same and consists of a conjugated oligomer, and each EW is the same and consists of an electron withdrawing group. In one embodiment of the disclosure, the conjugated oligomer Con can be composed of a repeating unit such as thiophene, benzene, pyrene, pyrrole, furan, benzofuran, Benzothiophene, benzothiadiazole, pyridine, quinoline, iso-quinoline, pyrazine, pyrimidine, pyrrole, pyrazole, imidazole, indole, thiazole, isothiazole, oxazole, isoxazole, benzothiazole, benzoxazole, 1,2,4-triazole, 1,2,3-triazole, phenanthroline, oxadiazolopyridine, pyridopyrazine, benzooxadiazole, thiadiazolopyridine, selenophene, thiadiazoloquinoxaline, thienopyrazine,

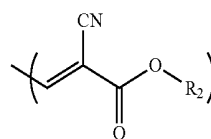
quinoxaline, or diketopyrrolopyrrole. For example, the conjugated thiophene oligomer has a chemical structure as shown in Formula 2.



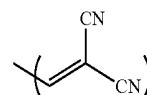
(Formula 2)

[0014] In Formula 2, each R¹ is independently selected from hydrogen or a C₃₋₁₀ alkyl group, and n is an integer of 2 to 20.

[0015] In one embodiment of the disclosure, the electron withdrawing group can be alkyl α-cyanoacrylate, 1,1-dicyanoethylene, halogen, nitro group (—NO₂), or another suitable electron withdrawing group. For example, the alkyl α-cyanoacrylate has a chemical structure as shown in Formula 3, and the 1,1-dicyanoethylene has a chemical structure as shown in formula 4.



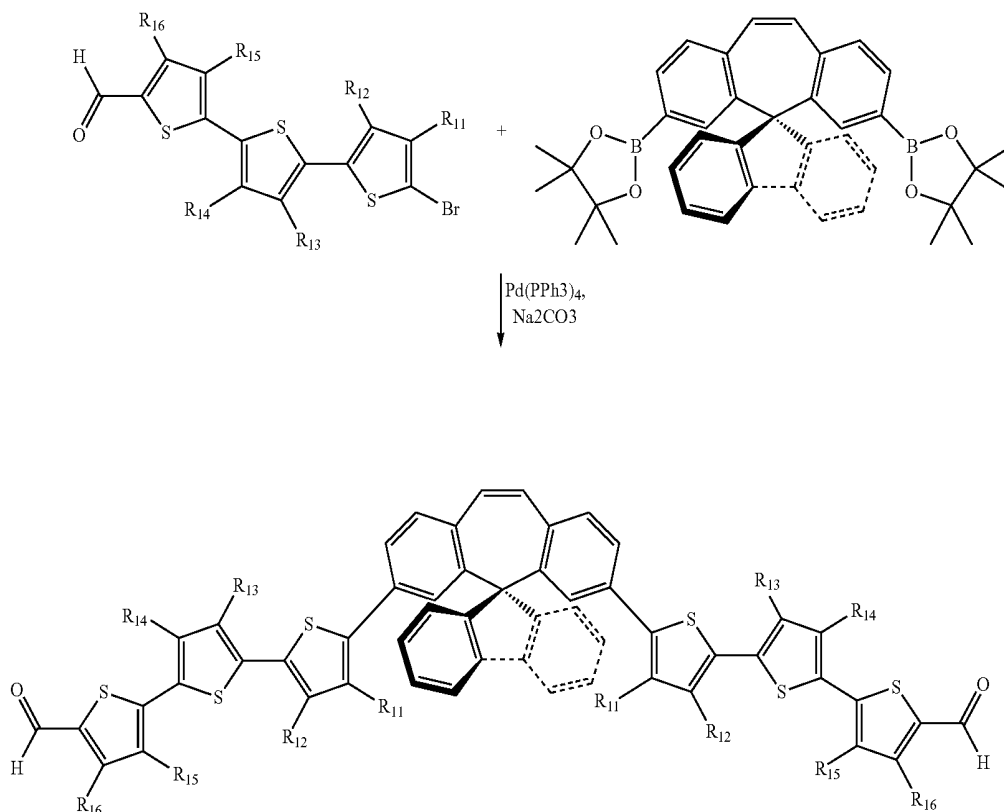
(Formula 3)



(Formula 4)

[0016] In Formula 3, R² is a C₃₋₁₀ alkyl group. In one embodiment, the p-type organic semiconductor material is synthesized as below. Note that the p-type organic semiconductor material of the disclosure can be synthesized by other steps and is not limited by the following steps. Those skilled in the art may change the synthesis steps according to their equipment and starting materials.

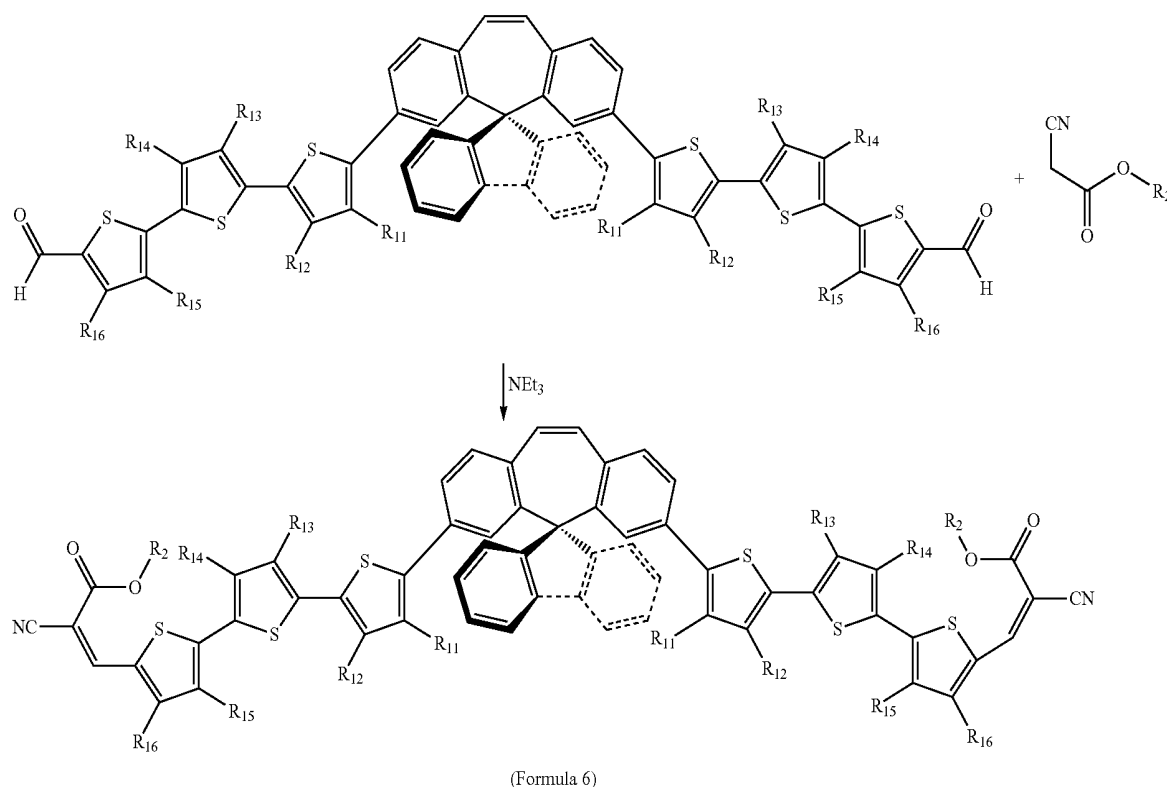
[0017] First, a cis-stilbene boride is reacted with a conjugated oligomer (e.g. a conjugated thiophene oligomer), as shown in Formula 5. Note that the conjugated thiophene oligomer in Formula 5 is merely illustrative rather than limiting the scope of the disclosure. In other words, the conjugated oligomer can be other suitable conjugated oligomers.



(Formula 5)

[0018] In Formula 5, each R^{11} is the same, each R^{12} is the same, each R^{13} is the same, each R^{14} is the same, each R^{15} is the same, and each R^{16} is the same. R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} are independently selected from hydrogen or a C_{3-10} alkyl group.

[0019] As shown in Formula 6, the product in Formula 5 is then reacted with an electron withdrawing group (e.g. alkyl α -cyanoacrylate). Note that the alkyl α -cyanoacrylate in Formula 6 is merely illustrative rather than limiting the scope of the disclosure. In other words, the electron withdrawing group can be another suitable electron withdrawing group.



[0020] In Formula 6, each R^2 is the same and consists of a C_{3-10} alkyl group. As described above, the p-type organic semiconductor material is a symmetric structure with an intramolecular mirror plane. Therefore, the p-type organic semiconductor material is easily regularly stacked to form a film. If different conjugated oligomers and/or electron withdrawing groups are substituted on two sides of the cis-stilbene, the asymmetric p-type organic semiconductor material will not be regularly stacked as the symmetric p-type organic semiconductor material of the disclosure. As such, the asymmetric p-type organic semiconductor material is limited in the application of the optoelectronic devices due to worse optoelectronic properties.

[0021] The p-type organic semiconductor material may serve as an active layer material of an OTFT device, an OLED device, or an organic solar-cell device. For example, the active layer of the organic solar cell includes the p-type organic semiconductor material of the disclosure and an electron acceptor material such as [6,6]-phenyl-C61-butyric acid methyl ester (abbreviated PC₆₁BM) or [6,6]-phenyl-C71-butyric acid methyl ester (abbreviated PC₇₁BM). In one embodiment, the p-type organic semiconductor material of

the disclosure and the electron acceptor material have a weight ratio of 1:0.5 to 1:2, such that the organic solar-cell device has high power-conversion efficiency.

[0022] Below, exemplary embodiments will be described in detail with reference to accompanying drawings so as to be easily realized by a person having ordinary knowledge in the art. The inventive concept may be embodied in various forms without being limited to the exemplary embodiments set forth herein. Descriptions of well-known parts are omitted for clarity, and like reference numerals refer to like elements throughout.

EXAMPLES

Example 1

Synthesis of p-type Organic Semiconductor Material

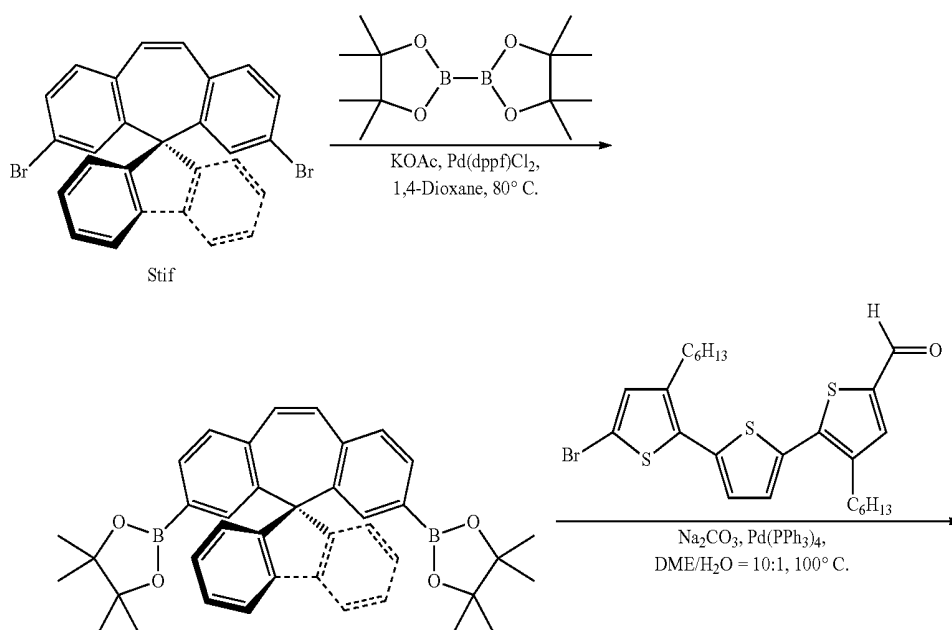
[0023] A reflux condenser was connected to a 50 mL two-necked round bottom bottle, and a stirrer bar was put into the bottle. The bottle was vacuum dried and then filled with nitrogen. 2501 mg of 3,7-dibromo-5,5-spirofluorenyl[a,d]cycloheptene (Stif, 5 mmole, prepared as *J. Am. Chem. Soc.* 2007, 129, 7478), 2666 mg of bis(pinacolato)diboron (10.5 mmole), 2356 mg of potassium acetate (24 mmole), and 163 mg of catalyst Pd(dppf)Cl₂ (0.2 mmole) were sequentially added into the bottle. 100 mL of deoxygenated 1,4-dioxane was injected into the bottle. The mixture in the bottle was heated to reflux for 18 hours, and then cooled to room temperature. The cooled reaction was bubbled by oxygen to be quenched. The quenched reaction was extracted by 20 mL of dichloromethane 3 times. The extraction was dried by anhydrous magnesium sulfate, filtered by celite, and then condensed by a rotatory condenser to obtain a crude. The crude

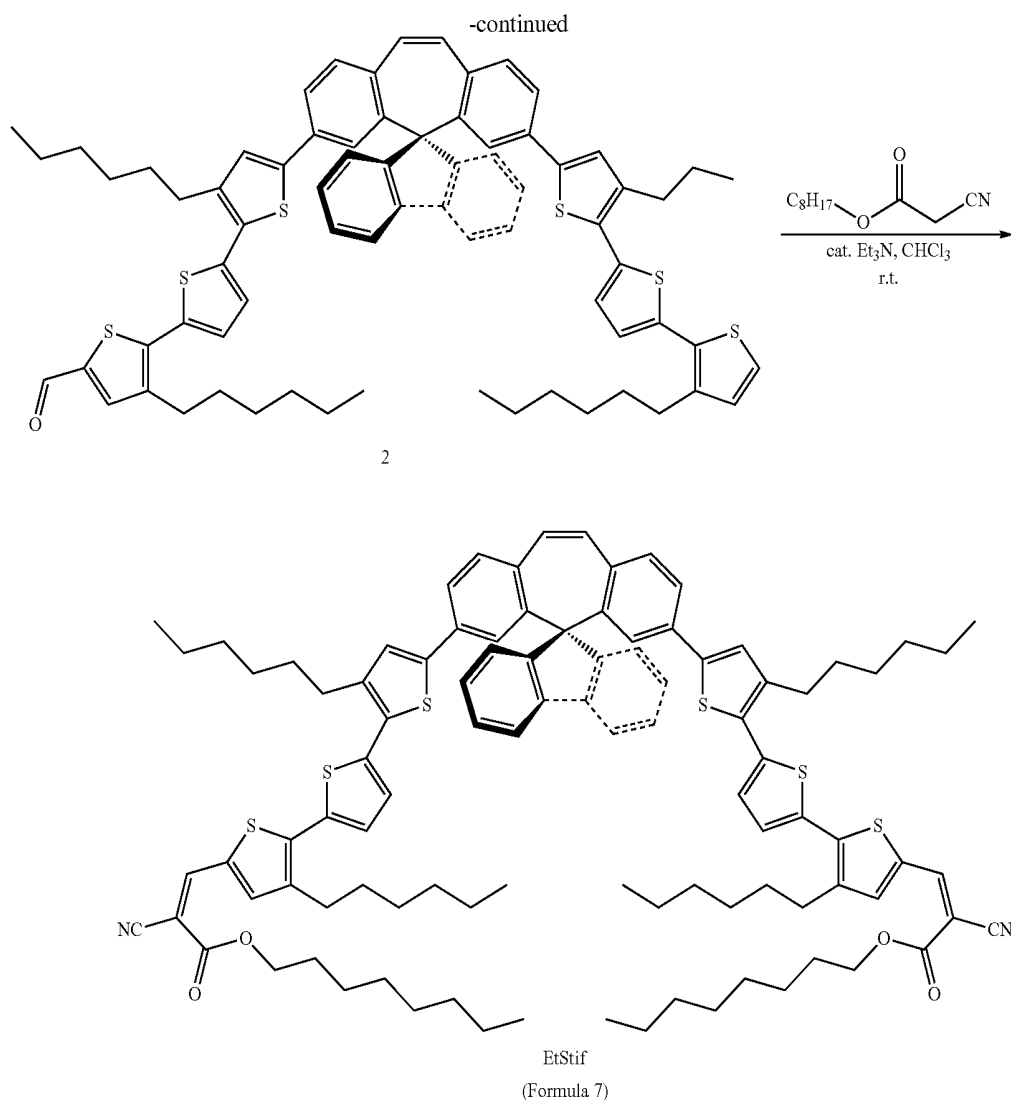
was washed by 20 mL of methanol 3 times to obtain 2427 mg of the white solid compound 1 (4.08 mmole, yield=82%), as shown in Formula 7. The white solid compound 1 had a ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum as: δ 7.97 (d, $J=7.8$ Hz, 2H), δ 7.73 (d, $J=7.6$ Hz, 2H), δ 7.70 (dd, $J=7.5$, 1.0 Hz, 2H), δ 7.38 (d, $J=7.3$, 2H), δ 7.35 (t, $J=7.6$ Hz, 2H), δ 7.23 (td, $J=7.7$, 1.1 Hz, 2H), δ 7.01 (s, 2H), δ 1.19 (s, 24H); and a ^{13}C NMR (100 MHz, CDCl_3) spectrum as: δ 152.4, 141.2, 139.0, 138.8, 135.3, 134.3, 133.3, 131.4, 127.7, 127.1, 127.0, 120.2, 83.4, 66.0, 24.7.

[0024] A reflux condenser was connected to a 25 mL two-necked round bottom bottle, and a stirrer bar was put into the bottle. 406 mg of the white solid compound 1 (0.35 mole), 223 mg of sodium carbonate (2.1 mmole), 209 mg of 5''-(4-bromo)-3,3''-di-n-hexyl-2,2':5',2''-terthiophene-5-carbaldehyde (0.77 mmole), and 35 mg of catalyst $\text{Pd}(\text{PPh}_3)_4$ (0.03 mmole) were sequentially added into the bottle. The bottle was degassed to remove the oxygen therein, and then filled with nitrogen. 10 mL of deoxygenated 1,2-dimethoxyethane and 1 mL were then injected into the bottle. The mixture in the bottle was then heated to reflux for 18 hours, and then cooled to room temperature. The cooled reaction was bubbled by oxygen to be quenched. The quenched reaction was extracted by 20 mL of dichloromethane 3 times. The extraction was dried by anhydrous magnesium sulfate, filtered by celite, and then condensed by a rotatory condenser to obtain a crude. The crude was purified by chromatography with an eluent (CH_2Cl_2 /hexane, $v/v=1/2$) to obtain 384 mg of the compound 2 (0.31 mmole, yield=89%), as shown in Formula 7. The compound 2 had a ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum as: δ 9.82 (s, 2H), δ 8.03 (d, $J=7.7$ Hz, 2H), δ 7.80 (d, $J=7.5$ Hz, 2H), δ 7.58 (s, 2H), δ 7.44 (t, $J=7.3$ Hz, 2H), δ 7.41 (dd, $J=8.1$, 1.6 Hz, 2H), δ 7.36 (d, $J=7.8$ Hz, 2H), δ 7.33 (t, $J=7.4$ Hz, 2H), δ 7.23 (d, $J=1.4$ Hz, 2H), δ 7.22 (d, $J=3.9$ Hz, 2H), δ 7.04 (d, $J=3.8$ Hz, 2H), δ 6.96 (s, 2H), δ 6.79 (s, 2H), δ 2.81 (t, $J=7.7$ Hz, 4H), δ 2.68 (t, $J=7.6$ Hz, 4H), δ 1.72-1.55

(m, 8H), δ 1.43-1.31 (m, 24H), δ 0.92-0.88 (m, 12H); and a ^{13}C NMR (CDCl_3 , 100 MHz, ppm) spectrum as: δ 182.48, 152.18, 142.16, 141.96, 141.16, 141.06, 140.25, 140.18, 139.04, 139.01, 138.32, 135.90, 134.37, 133.60, 132.92, 132.70, 129.49, 128.23, 127.75, 127.53, 126.95, 126.30, 126.05, 123.98, 120.53, 66.01, 31.66, 31.61, 30.28, 29.51, 29.46, 29.16, 29.12, 22.57, 22.57, 14.10, 14.05.

[0025] A stirrer bar was put into a 50 mL round bottom bottle. 256 mg of the compound 2 (0.20 mmole), 400 mg of octylcyanoacetate (2.2 mmole), 20 mL of anhydrous chloroform solvent were sequentially added into the round bottom bottle. 2 drops of triethylamine was then added into the round bottom bottle. The mixture was reacted at room temperature for 18 hours, and then extracted by water and dichloromethane. The dichloromethane extraction was dried by anhydrous magnesium sulfate, filtered, and then condensed by a rotatory condenser to obtain a crude. The crude was purified by chromatography with a eluent (CH_2Cl_2 /hexane, $v/v=1/1$) to obtain 284 mg of the dark red solid compound EtStif (0.18 mmole, yield=90%), as shown in Formula 7. The compound EtStif had a ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum as: δ 8.20 (s, 1H), δ 8.03 (d, $J=7.8$ Hz, 2H), δ 7.80 (d, $J=7.4$ Hz, 2H), δ 7.58 (s, 2H), δ 7.45 (t, $J=7.4$ Hz, 2H), δ 7.41 (dd, $J=7.9$, 1.7 Hz, 2H), δ 7.37-7.32 (m, 4H), δ 7.27 (d, $J=4.0$ Hz, 2H), δ 7.23 (d, $J=1.6$ Hz, H), δ 7.05 (d, $J=3.9$ Hz, 2H), δ 6.97 (s, 2H), δ 6.79 (s, 2H), δ 4.29 (t, $J=6.8$ Hz, 4H), δ 2.82 (t, $J=7.8$ Hz, 4H), δ 2.69 (t, $J=7.5$ Hz, 4H), δ 1.78-1.57 (m, 12H), δ 1.41-1.25 (m, 44H), δ 0.92-0.87 (m, 18H); and a ^{13}C NMR (CDCl_3 , 100 MHz, ppm) spectrum: δ 63.09, 152.36, 145.85, 142.18, 141.9, 141.72, 141.2, 140.69, 140.37, 139.02, 138.77, 135.89, 133.91, 133.53, 32.92, 132.82, 132.68, 129.49, 128.23, 128.08, 127.53, 126.94, 126.22, 126.05, 123.96, 120.52, 115.98, 97.59, 77.20, 66.50, 65.99, 31.75, 31.66, 31.58, 30.19, 30.14, 29.55, 29.33, 29.17, 29.15, 29.12, 28.54, 25.78, 22.61, 22.58, 22.55, 14.09, 14.06, 14.04.





Example 2

Organic Solar-cell Device

[0026] An organic solar-cell device **10** was prepared as shown in FIG. 1, it included an ITO anode **11**, a hole transport layer **12** composed of poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) overlying the anode **11**, an active layer **13** including the p-type organic semiconductor material of the disclosure or the commercially available P3HT overlying the hole transport layer **12**, and a cathode **14** composed of Ca/Al.

[0027] The active layer **13** was composed of the EtStif in Example 1 (or commercially available P3HT) and [6,6]-phenyl-C-butyric acid methyl ester (PCBM) with a blend ratio of 1:0.8, wherein the “-C-” could be C61 or C71 derivatives. The organic solar-cell device efficiency was measured under a solar luminance of AM 1.5.

[0028] The processes of manufacturing the organic solar-cell device are described below.

[0029] (1) The active layer solutions of EtStif/PCBM and P3HT/PCBM (10 mg/mL) were prepared and then stirred overnight.

[0030] (2) The ITO glass was washed by ultrasonic vibration in acetone and isopropanol for 15 minutes, respectively. The washed glass was blow-dried by nitrogen and baked on a heat plate for 5 minutes.

[0031] (3) The baked ITO glass was put under oxygen plasma for 5 minutes.

[0032] (4) The PEDOT:PSS (P-VP A14083, commercially available from Baytron) was spun (at 3000 rpm/30 sec.) on the ITO-glass to form the hole transport layer, and then baked at 150° C. in a dry box for 1 hour.

[0033] (5) The active layer solutions in step (1) were spun (for 1000 rpm/60 sec.) on the hole transport layer in the dry box, respectively.

[0034] (6) The ITO glass was charged on the 140° C. heat plate to anneal for 20 minutes, and then stood and cooled.

[0035] (7) The ITO glass was put on the photomask to evaporate a Ca/Al electrode.

[0036] (8) The device was sealed to measure its properties such as power-conversion efficiency, short-circuit current, open-circuit voltage, and filling factor as shown in Table 1.

TABLE 1

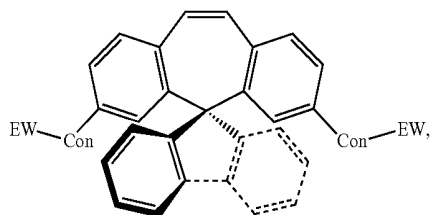
Active layer	Short-circuit current (J_{SC} , mA/cm ²)	Open-circuit voltage (V_{OC} , mV)	Filling factor (FF)	Power-conversion efficiency (%)
P3HT/PC ₆₁ BM	9.9	0.64	62.0	3.9
EtStif/PC ₆₁ BM	6.1	1.00	67.2	4.1
EtStif/PC ₇₁ BM	7.3	0.97	68.0	4.8

[0037] Compared to the organic solar-cell device including the conventional active layer of P3HT/PCBM, the organic solar-cell device including the active layer of the p-type organic semiconductor material of the disclosure (e.g. EtStif) has a lower short-circuit current, a higher open-circuit voltage, a higher filling factor, and a higher power-conversion efficiency.

[0038] It will be apparent to those skilled in the art that various modifications and variations can be made to the disclosed methods and materials. It is intended that the specification and examples be considered as exemplary only, with the true scope of the disclosure being indicated by the following claims and their equivalents.

What is claimed is:

1. A p-type organic semiconductor material, having the chemical formula:



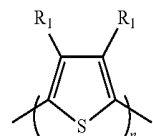
wherein each Con is the same and consists of a conjugated oligomer; and

each EW is the same and consists of an electron withdrawing group.

2. The p-type organic semiconductor material as claimed in claim 1, wherein the conjugated oligomer is composed of a repeating unit selected from a group consisting of thiophene, benzene, pyrene, pyrroline, furan, benzofuran, Benzothiophene, benzothiodiazole, pyridine, quinoline, isoquinoline, pyrazine, pyrimidine, pyrrole, pyrazole, imidazole, indole, thiazole, isothiazole, oxazole, isoxazole, benzothiazole, benzoxazole, 1,2,4-triazole, 1,2,3-triazole, phenanthroline, oxadiazolopyridine, pyridopyrazine, ben-

zooxadiazole, thiadiazolopyridine, selenophene, thiadiazoloquinoxaline, thienopyrazine, quinoxaline, or diketopyrrol-
opyrrole.

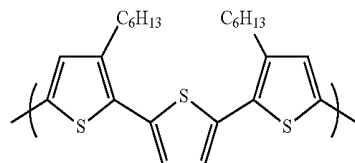
3. The p-type organic semiconductor material as claimed in claim 1, wherein the conjugated oligomer has the chemical formula:



wherein each R¹ is independently selected from hydrogen or a C₃₋₁₀ alkyl group; and

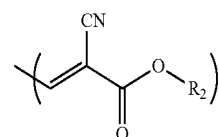
n is an integer of 2 to 20.

4. The p-type organic semiconductor material as claimed in claim 3, wherein the conjugated oligomer has the chemical formula:



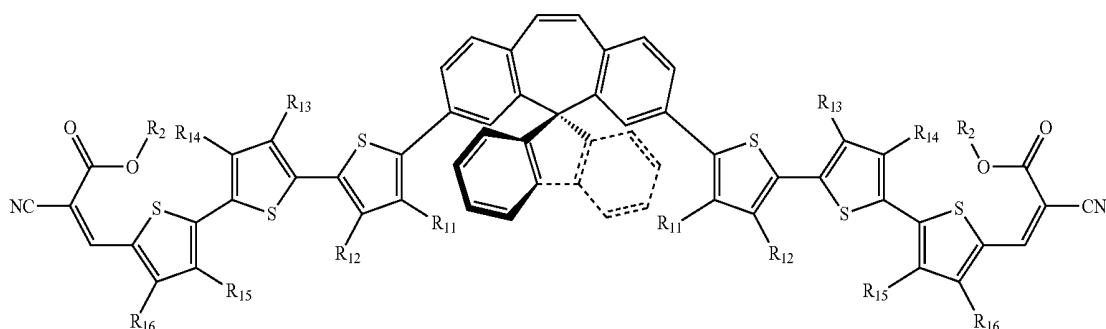
5. The p-type organic semiconductor material as claimed in claim 1, wherein the electron withdrawing group EW consists of alkyl α -cyanoacrylate, 1,1-dicyanoethylene, halogen, or nitro group ($-\text{NO}_2$).

6. The p-type organic semiconductor material as claimed in claim 5, wherein the alkyl α -cyanoacrylate has the chemical formula:



wherein R² consists of a C₃₋₁₀ alkyl group.

7. The p-type organic semiconductor material as claimed in claim 1, having the chemical formula:



wherein each R^2 is the same and consists of a C_{3-10} alkyl group;

each R^{11} is the same, each R^{12} is the same, each R^{13} is the same, each R^{14} is the same, each R^{15} is the same, and each R^{16} is the same; and

R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} are independently selected from hydrogen or a C_{3-10} alkyl group.

8. An optoelectronic device, having an active layer, wherein the active layer includes the p-type organic semiconductor material as claimed in claim 1.

9. The optoelectronic device as claimed in claim 8, comprising an organic solar cell, an organic light-emitting diode, or an organic thin-film transistor.

* * * * *

专利名称(译)	P型有机半导体材料和利用其的光电器件		
公开(公告)号	US20140121386A1	公开(公告)日	2014-05-01
申请号	US13/871087	申请日	2013-04-26
[标]申请(专利权)人(译)	财团法人工业技术研究院		
申请(专利权)人(译)	工业技术研究院		
当前申请(专利权)人(译)	工业技术研究院		
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发明人	CHEN, CHIH-PING TSAI, FANG-YUAN CHEN, CHIEN-TIEN HWANG, GUE-WUU		
IPC分类号	H01L51/00		
CPC分类号	H01L51/0068 B82Y10/00 H01L51/0036 H01L51/0047 H01L51/4253 Y02E10/549		
优先权	1020101139632 2012-10-26 KR		
其他公开文献	US8907108		
外部链接	Espacenet USPTO		

摘要(译)

公开了一种具有下式的p型有机半导体材料：每个Con是相同的并且由共轭低聚物组成。每个EW是相同的并且由吸电子基团组成。p型有机半导体材料可以应用于光电器件的有源层，例如有机太阳能电池，有机发光二极管或有机薄膜晶体管。

