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Synthesis, Characterization, and Physical Properties of a Conjugated Heteroacene: 2-Methyl-1,4,6,7,8,9-hexaphenylbenz(g)isoquinolin-3(2H)-one (BIQ)

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Abstract: We report the synthesis and characterization of a novel, stable and blue heteroacene, 2-methyl-1,4,6,7,8,9-hexaphenylbenz(g)isoquinolin-3(2H)- one (BIQ 3). BIQ 3, with its relatively small π framework, has an absorption λ_{max} at 620 nm, which is larger than that of pentacene (λ_{max} =582 nm), but BIQ 3 is more stable. The solutions of BIQ 3 are observed without any noticeable photobleaching on the order of days. In the solid state, it is very

Introduction

The pursuit of low-cost, mechanically flexible, and highly efficient organic semiconductor devices has strongly motivated chemists to rationally design and synthesize novel small conjugated organic molecules and polymers.^[1] As one family of polycyclic aromatic hydrocarbons (PAHs),^[2] linear oligoa-

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stable at ambient conditions and can be stored indefinitely. Owing to its pyridone end unit, BIQ **3** can display different resonance structures in different solvents (aprotic and protic) or Lewis acids to give different colors. The attractive stability exhibited by BIQ **3** is

Keywords: absorption • heteroacenes • photovoltaics • semiconductors • solvent effects very desirable in organic semiconductor devices. Herein, we investigated a simple heterojunction photovoltaic device based on BIQ **3** as an electron donor and [6,6]-phenyl- C_{61} butyric methyl ester as an electron acceptor. Our results show that this type of heteroacene could be a good candidate as a charge-transport material in organic semiconductor devices.

cenes **1** (Scheme 1) and their derivatives have created a great deal of interest not only in fundamental science but also in potentially technological applications, such as organic



Scheme 1. The structure of oligoacenes (1), isoquinolinones (2), and 2-methyl-1,4,6,7,8,9-hexaphenylbenz(g)isoquinolin-3(2H)-one (3).

light-emitting diodes (OLEDs), organic photovoltaic devices, organic photodetectors, and field-effect transistors (FETs).^[3] Their excellent electronic performance encourages us to examine their similar analogues, heteroacenes,^[4] the conjugated frameworks of which have at least one heteroatom, such as N, P, O, and S atoms. Currently, several types of heteroacenes, such as thienobis(benzothiophenes),^[5] anthradithiophene and its derivates,^[6] pentathienopentacenes,^[7] carbazole-based heteroacenes,^[8] and azapentacenes^[9] have been synthesized and applied in organic semiconductor devices. Their promising performance has stimulated us to look at another class of heteroacenes, isoquinolinones **2** (Scheme 1), the structures of which contain at least one lactam unit. Although isoquinolinones **2** have attracted some interest on account of their electronic properties and sometimes unusual photophysics,^[10] their applications in organic semiconductor devices remain largely undeveloped.

To enrich the family of organic semiconducting materials and enhance the performance of organic electronic devices, we are vigorously engaged in synthesizing a series of isoquinolinones 2 and examining their performance in organic semiconducting devices.

Generally, quinolinones and their derivatives contain many biologically active alkaloids and can serve as bases in nucleosides or building units in the synthesis of many alkaloids.^[11] Many methods, which are very important in synthetic and medicinal chemistry, have been developed.^[12] However, in our research, isoquinolinones **2**, which are different from biologically active quinolinones, are a family of conjugated heterocyclic compounds. It is worth noting that the nitrogen atom in BIQ **2** is in the 2-position, not the 1-position as reported in many papers. This feature makes the synthetic work more challenging.

In addition, isoquinolinones are very important building blocks to challenge longer polyacenes through [4+2] cyclic addition. However, it is well-known that longer polyacenes (more than pentacene) become extremely insoluble and unstable. To overcome these problems, one possible way is to increase more phenyl-substituted groups in these systems to protect the conjugated system and increase the solubility.

Herein, we report a new method to synthesize a stable, blue compound, 2-methyl-1,4,6,7,8,9-hexaphenylbenz(g)isoquinolin-3(2H)-one (BIQ **3**, Scheme 1). Surprisingly, BIQ **3**, with its relatively small π framework, has an absorption λ_{max} at 620 nm, which is larger than that of pentacene (n=5 in **1**, Scheme 1, $\lambda_{max}=582$ nm).^[13] However, BIQ **3** is more stable under atmospheric conditions. Interestingly, the structure of BIQ **3** can be transformed into its resonant type—*meso*-ion formation (Scheme 2)—with a significant color change if it is dissolved in different solvents (aprotic and protic) or is treated with Lewis acids.



Scheme 2. Resonance structures of BIQ 3.

Given that the molecular-electronic properties of pentacene have been shown to be desirable for electronic applications,^[14] it is promising to envision similar functions for BIQ **3** as its electronic properties are quite similar, as reported here. As a proof of concept, a heterojunction photovoltaic device based on BIQ **3** and [6,6]-phenyl-C₆₁ butyric methyl ester (PCBM) (weight ratio 1:1) was fabricated, and our preliminary results demonstrated that isoquinolinones can be used as p-type charge-transport materials in organic electronic devices.

Results and Discussion

Although many synthetic routes have been reported in the literature to prepare various types of isoquinolinones,^[15] a quicker and more-practical way to approach a benzoisoquinolinone, in which n=3, is through a [4+2] cycloaddition involving in situ arynes as dienophiles and *meso*-ionic pyrimidines **5**^[16] as dienes (Scheme 3). BIQ **3** was obtained in



Scheme 3. The synthetic route to BIQ 3.

quantitative yield from its precursor 1,4-dihydro-1,4,6,7,8,9hexaphenyl-2,12-dimethyl-1,4-(iminomethano)benz(g)isoquinoline-2,12-dione (**4**) through thermal elimination of lactam bridges at 220 °C. The precursor **4** was obtained in 65 % yield through slow addition of a suspension of 3-amino-5,6,7,8-tetraphenylnaphthalene-2-carboxylic acid (**6**) in dichloroethane into a boiling solution of *meso*-ionic compound **5** in the presence of isoamyl nitrite (Scheme 4).



Scheme 4. The synthetic route to 3-amino-5,6,7,8-tetraphenylnaphthalene-2-carboxylic acid (6). DCE = 1,2-dichloroethane.

The novel naphthalyne precursor **6** was synthesized by reacting a step-by-step bis-benzyne precursor 2-amino-5-nitrotetrephthalic acid 4-methyl ester (**7**) with tetraphenylcyclopentadienone (**8**), followed by reduction and hydroxylation (Scheme 4). The step-by-step bis(benzyne) precursor **7** was synthesized from a commercially available product, aminoterephalic dimethyl ester, in four steps according to the reported procedures.^[17]

As we had difficulties in establishing a full ¹³C NMR spectrum of the precursor **4**, light-yellow single crystals suitable for X-ray diffraction analysis were grown from a mixed solution of dichloromethane/methanol (1:1) through slow evaporation. Its structure with atomic labeling and crystal data and structure refinement are shown in Figure 1 and Table 1.

The UV/Vis absorption spectrum of BIQ **3** was recorded in THF at room temperature. As shown in Figure 2a, BIQ **3**



Figure 1. X-ray structure of **4**.

Table 1. Crystal data and structure refinement for compound **4**.

	$\frac{\text{Compound 4}}{\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_2}$		
empirical formula			
M _r	722.84		
crystal system	monoclinic		
space group	P21/n		
a [Å]	11.9918(8)		
b [Å]	22.3878(16)		
c [Å]	14.3440(10)		
α [°]	90		
β [°]	92.1810(10)		
γ [°]	90		
absorption coefficient [mm ⁻¹]	0.075		
F(000)	1520		
crystal size [mm ³]	$0.60 \times 0.20 \times 0.10$		
2θ [°]	1.69 to 28.39		
index ranges	$-15 \le h \le 15, -29 \le k \le 29, -18 \le l \le 19$		
reflns collected	34476		
independent reflns	9373		
R(int)	0.0696		
completeness [%]	97.1		
max/min transmission	0.990/0.9550		
final R indices $(I > 2\sigma(I))$	R1 = 0.0556, wR2 = 0.1051		
R indices (all data)	R1 = 0.1708, wR2 = 0.1368		



Figure 2. a) UV/Vis spectrum of **3** in THF. b) Cyclic voltammogram of 10^{-5} M BIQ **3** in 0.1 M TBAP/CH₃CN (first three cycles vs. Ag/AgCl).

displays two broad absorption bands at around 300 and 620 nm. We were very surprised by the fact that BIQ **3**, with its relatively small π framework (three rings), has an absorption at 620 nm, with two shoulders at 582 and 670 nm. It is worth noting that the absorption at 670 nm is longer than that at the longest wavelength for pentacene ($\lambda_{max} = 582$ nm, five rings).^[13] When excited at 620 nm, it displays an emission peak at 710 nm (Figure 2b) with a low quantum yield ($\Phi_f = 0.3\%$, using 9,10-diphenylanthracene (ethanol solution, $\Phi_f = 0.95$) as a reference) at room temperature.^[18]

Cyclic voltammetry (CV) of BIQ **3**, recorded at room temperature in dry CH₃CN that contained 0.1 M tetrabutylammonium perchlorate (TBAP), shows that the oxidation and reduction processes are chemically and electrochemically reversible (Figure 4, discussed in more detail below). The HOMO–LUMO gap calculated from the difference between the half-wave redox potentials ($E_{1/2}^{ox} = +0.15 \text{ eV}$ and $E_{1/2}^{red} =$ -1.80 eV) is 1.95 eV. This value is in good agreement with the band gap, 2.0 eV, derived from the UV/Vis absorption data. Like the UV/Vis data, the CV measurement collected for BIQ **3** reinforces the similarity in electronic properties to that of pentacene.

The electronic states of BIQ 3 are strongly governed by its pyridone end unit. There are two possible major contributing resonance structures in BIQ 3 (Scheme 2). On the left is the neutral polyene state and on the right is the charge-separated state (meso-ion state). Either electronic state can be readily favored through the choice of solvents. In aprotic solvents, shown in Figure 3 with tetrahydrofuran as well as other solvents (CH₂Cl₂, DMF, DMSO), the longest absorption maxima center is around 620 nm. In protic solvents such as methanol, BIQ 3 is hydrogen-bonded to clearly establish a different electronic species and the absorption has been blueshifted to 575 nm, whereas in strongly acidic solvents such as trifluoroacetic acid (TFA), the absorption spectrum narrowed and the λ_{max} is drastically blueshifted to 505 nm. In a relatively weaker acid such as acetic acid (AcOH), the absorption spectrum falls between dichloromethane and trifluoroacetic acid at $\lambda_{max} = 540$ nm. In contrast to the trifluoroacetic acid solution, in which BIQ is completely protonated, the electronic spectrum of BIQ 3 in AcOH suggested an acid-base equilibrium between protonated BIQ 3 and the acetate anion. Based on the two acidic media studied, the acidity of protonated BIQ 3 is roughly



Figure 3. UV/Vis absorption spectra of BIQ 3 $(3.0 \times 10^{-5} \text{ M})$ in different solvents: a) CH₂Cl₂, b) THF, c) CH₃OH, d) DMF, e) DMSO, f) CH₃COOH, g) CF₃COOH. The inset shows the color changes in different solvents.

between AcOH and trifluoroacetic acid. The colors of these solutions are also distinctly different (inset in Figure 3).

The dynamic structure of BIQ 3 from the solvent-dependence studies demonstrated the importance of its amide bond observed in the static structure. The drastic shift in the absorption spectrum clearly distinguishes the polyene and aromatic structure. In trifluoroacetic acid, the electronic spectrum of BIQ 3 is blueshifted due to the shortening of its N-CO bond through protonation, which locked the structure into a lower-energy aromatic system. The same phenomenon was also observed when BIQ 3 was treated with either BF₃·Et₂O or methyl triflate. In both cases, the strong Lewis or Brønsted acidity locked the structure into a charge-separated state. This suggested that in aprotic solvents in which BIQ 3 is not protonated, the electronic arrangement adopts exclusively the higher-energy polyene resonance structure, thereby reflecting a longer amide bond. Interestingly, in methanol, the solution spectrum suggested an intermediate bond length between the two structures since hydrogen bonding is the only governing effect. This may be better elucidated by the absorption exhibited in AcOH.

The close resemblance in electronic properties between BIQ and 5,7,12,14-tetraphenylpentacene (TPP)^[17b] is demonstrated in Table 2. The results obtained from UV/Vis and CV for both molecules are strikingly similar. The UV/Vis data of BIQ **3** and TPP show absorption maxima at approximately 620 nm (2.0 eV) and 622 nm (1.99 eV), respectively. The $\Delta E_{\text{HOMO-LUMO}}$ obtained from CV data for BIQ **3** and TPP are 1.95 and 1.94 eV, respectively. These results are highly suggestive that the electronic properties of BIQ **3** are closely related to pentacene ($\Delta E_{\text{HOMO-LUMO}} = 2.1 \text{ eV}$).

Table 2. Comparative electronic properties of BIQ **3** with TPP.

	UV/Vis		Cyclic voltammetry ΔF	
	[nm]	([eV])	[eV]	[nm]
BIQ 3 TPP	620 622	(2.0) (1.99)	1.95 1.94	(636.4) (639)

The physical properties of BIQ **3** are equally noteworthy. BIQ **3**, as demonstrated in the solvent-dependent electronic spectroscopy study, is readily soluble. In solution, it is several orders of magnitudes less sensitive than pentacene. Solutions of BIQ **3** are observed without any noticeable photobleaching on the order of days. In the solid state, it is very stable at ambient conditions and can be stored indefinitely. Given the very good performance of pentacene, but poor stability in molecular electronics,^[19] we were very interested in replacing pentacene with BIQ **3** and examine its behavior in semiconductor devices.

The structure and current density-voltage (J-V) characteristic of a typical organic photovoltaic (OPV) is shown in Figure 4. No current response in the dark was observed.



Figure 4. *J–V* characteristic of an ITO/PEDOT:PSS/BIQ:PCBM/Al OPV device. Inset: schematic illustration of the solar-cell structure.

However, under simulated 100 mW cm⁻² 1.5 AM illumination, the results show that as-fabricated devices with an open-circuit voltage (V_{oc}) of 0.35 V, short-circuit current density (J_{sc}) of 0.27 mA cm⁻², and a fill factor (*FF*) of 0.24 were obtained. The V_{oc} of this hybrid cell structure (≈ 0.4 V) is smaller than the difference (1.25 eV) in energy between the LUMO of PCBM (3.7 eV)^[20] and HOMO of BIQ **3** (4.95 eV) on account of the barrier heights for electrons going from Al (4.35 eV) into the LUMO level of PCBM determined by investigation of the injection limited electron current (ILC).^[21] At present, a relatively low-power conversion efficiency (≈ 0.08 %) is observed without optimization. However, a strong endeavor to improve the power conversion efficiency through optimization of the fabrication parameters is on the way.

In conclusion, a stable, blue heteroacene 2-methyl-1,4,6,7,8,9-hexaphenyl-benz(g) isoquinolin-3(2H)-one (BIQ 3) has been successfully synthesized and its optical property and cyclic voltammetry have been studied. Interestingly, BIQ 3 displays different colours in different solvents (aprotic and protic) owing to its pyridone end unit, which can have different resonance structures in various solvents. Moreover, the fact that BIQ 3 has a low HOMO-LUMO gap (1.95 eV), which is comparable to that of pentacene, makes it a potential candidate for organic electronic applications. A heterojunction photovoltaic device based on BIQ 3 and PCBM has been fabricated. Our preliminary results

demonstrated a proof of concept that heteroacenes, such as BIQ **3**, can act as charge-transport materials in organic semiconductor devices. Further works such as enhancing the power conversion efficiency through optimizing the photovoltaic devices' fabrication parameters, synthesizing highlyconjugated heteroacenes with longer π -frameworks, and their applications on organic semiconductor devices are under investigation.

Experimental Section

All starting materials were used as received without further purification. Compounds 5 and 7 were synthesized according to the reported procedure.^[16,17]

9 (Scheme 4): Compound 7 (2.0 g, 8.4 mmol, precipitated in CH₂ClCH₂Cl (30 mL)) was added dropwise to a boiling solution of tetraphenylcyclopentadienone 8 (3.2 g, 8.4 mmol) and isoamyl nitrite (3.5 mL, 25.0 mmol) in CH2ClCH2Cl (50 mL) under an Ar atmosphere. The reaction was heated at reflux overnight. Then the solution was cooled down, and the solvent was evaporated under vacuum. After passing through a silica column using dichloromethane as a solvent, a pale yellow product was obtained after washing with ether. Yield: 74%; m.p. 268-270°C; $^1\mathrm{H}$ NMR (CDCl_3, 500 MHz): $\delta\!=\!8.15$ (s, 1 H), 7.98 (s, 1 H), 7.31–7.29 (m, 6H), 7.22-7.21 (m, 4H), 6.90-6.89 (m, 10H), 3.82 ppm (s, 3H); ¹³C NMR $(CDCl_3, 125 \text{ MHz}): \delta = 165.8, 145.3, 143.1, 142.6, 140.0, 139.5, 139.4,$ 139.3, 137.7, 137.5, 132.5, 131.8, 130.86, 130.84, 130.71, 130.70, 130.25, 127.82, 127.76, 127.2, 127.1, 126.64, 126.62, 125.78, 125.77, 123.85, 123.42, 53.3 ppm; IR (drift): $\tilde{\nu} = 3058$, 3027, 2977, 2867, 1735, 1549, 1439, 1347, 1300, 1131, 1052, 913, 848, 748, 703, 531 cm⁻¹; MALDI-TOF: *m/z*: calcd: 535.20; found: 535.14.

10 (Scheme 4): A solution of compound **9** (6.0 g, 11.4 mmol) and Pd/C (500 mg) in CH₂Cl₂/methanol (1:1) was stirred under hydrogen gas administered with a balloon for 5 h. The inorganic residue was removed by vacuum filtration and the filtrate was concentrated. The red residue was purified by column chromatography over silica gel using chloroform to afford amine (83.3 %), then recrystallization from methanol/methylene chloride (1:1) to give yellow powder. M.p: 293–295 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 8.31 (s, 1H), 7.25–7.18 (m, 10H), 6.84–6.82 (m, 10H), 6.81 (s, 1H), 3.79 ppm (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ = 168.2, 141.5, 140.4, 140.3, 139.45, 139.38, 139.0, 136.0, 132.5, 131.4, 131.2, 131.1, 130.9,127.5, 127.4, 126.4, 126.3, 125.3, 125.1, 114.4, 51.8 ppm; IR (drift): $\hat{\nu}$ = 3489, 3379, 3028, 2953, 2950, 1700, 1616, 1576, 1492, 1440, 1303, 1255, 1223, 1073, 749, 699, 568 cm⁻¹; MALDI-TOF: *m*/*z*: calcd: 505.20; found: 505.2034.

6 (Scheme 4): A solution of **10** (3.00 g, 5.94 mmol) and NaOH (2 g, 50 mol) in MeOH/isopropanol (20 mL, 1:1) was heated at reflux overnight under an Ar atmosphere. Solvent was removed and the yellow residue was taken up in water (20 mL). Concentrated HCl was added and stirred at room temperature for 0.5 h. The participate was filtered and dried to give compound **6** (92%) as a yellow solid. m.p. > 300°C; ¹H NMR (DMSO, 400 MHz): δ = 8.58 (br, 2H), 8.04 (s, 1H), 7.23–7.12 (m, 10H), 6.81–6.59 (m, 10H), 6.34 ppm (s, 1H); ¹³C NMR (DMSO, 125 MHz): δ = 168.9, 141.5, 140.5, 140.3, 140.2, 140.0, 139.3, 139.27, 139.0, 136.1, 135.8, 135.6, 132.4, 131.4, 131.15, 131.12, 130.9, 129.2, 128.5, 128.1, 127.9, 127.0, 126.9, 126.80, 126.78, 125.8, 125.7 ppm; IR (drift): $\tilde{\nu}$ = 3492, 3384, 3057, 3042, 3300–2200 (br), 1700, 1618, 1584, 1494, 1426, 1314, 1266, 1217, 1087, 919, 701 cm⁻¹; MALDI-TOF: *m/z*: calcd: 491.19; found: 491.1865.

4 (Scheme 3): The solution of *meso*-ionic compound **5** (292 mg, 1 mmol) and the corresponding acid **6** (490 mg, 1 mmol) with isoamyl nitrite (1 mL) in 1,2-dichloroethylene (DCE; 15 mL) was stirred at 90 °C overnight. After DCE was removed, the residue was purified by column chromatography on silica gel using dichloromethane to give the corresponding cycloadduct **4** (65%). m.p. 210 °C (decomp); ¹H NMR (CDCl₃, 500 MHz): δ =8.03 (d, 2H), 7.84 (s, 1H), 7.75 (m, 2H), 7.48 (m, 3H),

7.32–7.21 (m, 8H), 7.17 (s, 1H), 7.09–7.07 (m, 3H), 7.0 (m, 2H), 6.87– 6.79 (m,10H), 2.63 ppm (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ =171.8, 140.08, 140.01, 139.96, 139.89, 139.08, 138.9, 138.7, 138.2, 136.0, 134.8, 131.4, 131.2, 131.0, 130.9, 130.7, 130.6, 129.9, 129.8, 128.6, 127.6, 127.4, 127.3, 127.2, 126.6, 126.58, 126.55, 126.3, 125.48, 125.44, 120.0, 80.8, 65.8, 33.7 ppm; IR (drift): $\bar{\nu}$ =3054, 2979, 2973, 1687, 1603, 1492, 1444, 1198, 1008, 920, 886, 755, 703, 539 cm⁻¹; MALDI-TOF: *m*/*z*: calcd: 722.29; found: 723.3025 [*M*+H].

3 (Scheme 3): The corresponding precursor **4** was heated at 220 °C for 6 h. Blue compound **3** was obtained in quantitative yield. m.p. > 300 °C; ¹H NMR (CD₂Cl₂, 500 MHz): δ =7.48 (d, 1H), 7.45–7.40 (m, 5H), 7.33–7.21 (m, 6H), 7.15–6.98 (m, 10H), 6.86–6.82 (m, 10H), 1.58 ppm (s, 3H); ¹³C NMR (CD₂Cl₂, 125 MHz): δ =158.0, 154.3, 140.78, 140.2, 140.1, 138.7, 138.6, 138.5, 137.2, 136.7, 136.5, 136.1, 135.6, 132.9, 131.0, 130.9, 130.7, 130.6, 130.1, 129.4, 128.67, 128.65, 127.66, 127.34, 127.1, 126.4, 126.3, 126.1, 126.08, 125.3, 125.2, 119.6, 117.0, 114.6, 36.8 ppm; IR (drift): $\tilde{\nu}$ = 3056, 3030, 1685, 1602, 1523, 1484, 1441, 1331, 1222, 1072, 1028, 887, 750, 698 cm⁻¹; MALDI-TOF: *m*/*z*: calcd: 665.27; found: 666.2761 [*M*+H].

Cyclic Voltammetry (CV) Measurements

Cyclic voltammetry was performed with a three-electrode cell in a solution of acetonitrile and tetrabutylammonium perchlorate (0.1 M, Bu₄ClO₄, abbreviated as TBAP) at a scan rate of 100 mVs⁻¹. A Pt wire was used as a counter electrode, and glassy carbon was used as the working electrode with an Ag/AgCl electrode used as reference electrode. Its potential was corrected to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple in this system (0.44 V vs. SCE).^[22]

X-Ray Crystal Structure

Single-crystal data was collected at 298 K with graphite-monochromatized $Mo_{K\alpha}$ radiation (λ =0.71073 Å). The cell parameters were obtained from the least squares refinement of the spots using the SMART program. The structure was solved by direct methods using SHELXS-97, which revealed the positions of all non-hydrogen atoms. This is followed by several cycles of full-matrix least-squares refinements. Absorption corrections were applied by using SADABS.^[23] Hydrogen atoms were included as fixed contributors to the final refinement cycles. The position of hydrogen atoms were calculated on the basis of idealized geometry and bond length. In the final refinement, all non-hydrogen atoms were refined with anisotropic thermal coefficients.

CCDC 742124 (4) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Fabrication and Evaluation of Photovoltaic Devices

The photovoltaic devices were fabricated on indium tin oxide (ITO)coated glass substrates. The ITO glass was thoroughly cleaned by an ultrasonic treatment in acetone, ethanol, and deionized water sequentially and dried before use. A layer of poly(3,4-ethylenedioxythiophene)/poly-(styrenesulfonate) (PEDOT/PSS) was spin-coated at 3000 rps for 60 s on the ITO substrate, followed by heating for 15 min at 140 °C in an annealing oven. Afterwards, the active layer that contained a mixture of this new material and PCBM (1:1 wt%) were spin-coated from *o*-dichlorobenzene onto the substrates, respectively. Finally, the aluminum top electrodes were evaporated by thermal evaporation in vacuum (2×10^{-4} Pa) through a shadow mask. Post-device annealing was carried out at 150 °C for 15 min in a nitrogen-filled glovebox. The photovoltaic characteristics of cells were determined by a SourceMeter (Keithley, model 2400) under Xe-lamp illumination with a power density of 100 mW cm⁻² (1.5 AM).

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