• ARTICLES • • SPECIAL ISSUE • Organic photovoltaics

February 2015 Vol.58 No.2: 364–369 doi: 10.1007/s11426-014-5282-9

Synthesis, crystal structure, and application of an acenaphtho[1,2-*k*] fluoranthene diimide derivative

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Received August 8, 2014; accepted August 25, 2014; published online January 4, 2015

Organic electron acceptor materials play an important role in organic electronics. Recently, many organic electron acceptors have been developed, in which aromatic fused-imides have proved to be a promising family of excellent electron acceptors. We report the first synthesis of a novel aromatic fused-imide, acenaphtho[1,2-*k*]fluoranthene diimide derivative (**AFI**), using lithium-halogen exchange and Diels-Alder reactions. The construction of a large conjugated plane and the introduction of electron-withdrawing imide groups endow **AFI** with a low lowest unoccupied molecular orbital (LUMO) level of -3.80 eV. **AFI** exhibits a regular molecular arrangement and strong π - π interactions in the single-crystal structure, which indicates its potential application in organic electronic devices. Solar cell devices that were fabricated using **AFI** as the electron acceptor and P3HT as the electron donor achieved an energy conversion efficiency of 0.33%.

acenaphtho fluoranthene diimide, lithium-halogen exchange, Diels-Alder reaction, electron acceptor, solar cell

1 Introduction

Much attention has been paid to organic electron acceptor materials [1–3], which are indispensable components of organic electronics, due to their important role in p–n junction diodes, bipolar transistors, and complementary circuits [4–6]. Recently, organic electron acceptor materials such as fullerene and its derivatives [7–9], aromatic core-fused imides [2,10–12], perylene diimide derivatives [13,14], naph-thalene diimide [15,16], quinoid derivatives [17], and nitrogen heterocyclics [18,19] have been intensively investigated and have been shown to exhibit good performance in optoelectronic devices. However, the structural diversity and synthetic strategy of organic acceptors remain limited. Therefore, it is still a challenge to develop novel air-stable and solution-processable organic electron acceptors.

In our previous contribution, we developed a series of

fluoranthene-fused imides as good electron acceptors [20]. The introduction of imide unit in the fluoranthene-fused core plays an important role in tuning their electronic structures. In particular, the lowest unoccupied molecular orbital (LUMO) levels can be finely tuned by introducing other electron-withdrawing groups. Herein, we facilely synthesized a novel acenaphtho fluoranthene core using lithium-halogen exchange and Diels-Alder reactions as the main synthetic strategies. Two diimide substituents were introduced to lower the LUMO level, and long-branched alkyl chains were introduced at the nitrogen atoms to increase solubility. The target acceptor **AFI** (Figure 1) was obtained through six steps in a yield of 15% (Scheme 1).

2 Experimental

2.1 General method

All commercially available chemicals were used without further purification unless otherwise noted. Dichloromethane

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Figure 1 Molecular structure of acenaphtho[1,2-*k*]fluoranthene diimide derivative (**AFI**).



Scheme 1 Synthetic route to AFI.

was dried with calcium hydride and distilled under nitrogen. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica-gel-coated glass sheets with an F254/365 indicator. All yields refer to isolated yields. Nuclear magnetic resonance (NMR) spectra were recorded on 400 MHz Bruker spectrometers. Chemical shifts are reported in ppm and coupling constants (J values) are reported in Hertz. ¹H NMR chemical shifts are referenced to TMS (0 ppm) or CHCl₃ (7.26 ppm) and ¹³C NMR chemical shifts are referenced to CDCl₃ (77.23 ppm). Absorption spectra were recorded on a PerkinElmer Lambda 750 UV-Vis spectrometer. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS 55 Luminescence spectrometer. Cyclic voltammetry was performed using a BASI Epsilon workstation. Cyclic voltammetry was measured in dichloromethane containing 0.1 mol L^{-1} *n*-Bu₄NPF₆ as a supporting electrolyte. The glassy carbon electrode was used as a working electrode and a platinum sheet was used as a counter electrode. All potentials were recorded using Ag/AgCl as a reference electrode. The scan rate of cyclic voltammetry was 50 mV s⁻¹.

2.2 Synthesis of the acenaphtho[1,2-*k*]fluoranthene diimide derivative (AFI)

2.2.1 6,7-Dihydroindeno[6,7,1-def]isochromene-1,3-dione(2)

Compound 1 [21] (10 mmol) was dissolved in anhydrous THF (50 mL) at hydrogen atmosphere. To the solution, *t*-butyl lithium (40 mmol) was added slowly at -78 °C and allowed to react for 30 min. The dianion was formed through lithium-halogen exchange. Nucleophilic addition reaction took place between dianion and excess dry CO₂ for 20 min. After being warmed to room temperature, the solvent was removed by reduced-pressure distillation. The residue was dissolved by water, then concentrated hydrochloric acid was added and a white solid precipitated. The precipitate was obtained by filtration and dried in vacuum. After being treated with reflux acetic anhydride, the crude product was used in the subsequent reaction without further purification.

2.2.2 2-(2-Octyldodecyl)-6,7-dihydro-1*H*-indeno[6,7,1-def]isoquinoline-1,3(2*H*)-dione (**4**)

A mixture of compound 2 (2.24 g, 10.0 mmol) and compound 3 (7.43 g, 25.0 mmol) was dissolved in acetic acid (100 mL), and heated at 130 °C for 3 days. After cooling to room temperature, the reaction mixture was extracted with chloroform 3 times, washed with water, and dried with anhydrous sodium sulfate. The crude product was evaporated under reduced pressure. The resulting solid was purified by column chromatography (silica gel, petroleum ether/chloroform=4:1) to give product as a yellow solid. Yield: 4.68 g, 73% for the three steps. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.48 (2H, d, J=7.2 Hz), 7.55 (2H, d, J=7.2 Hz), 4.11 (2H, d, J=7.2 Hz), 3.56 (4H, s), 1.98 (1H, m), 1.40-1.21 (32H, m), 0.88–0.83 (6H, m); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 164.8, 153.6, 137.8, 132.8, 126.5, 120.9, 119.3, 44.4, 36.7, 31.9, 31.8, 31.7, 30.1, 29.63, 29.57, 29.3, 29.3, 26.6, 22.7, 14.1. Anal: calcd. for C₃₄H₄₉NO₂: C, 81.06; H, 9.80; N, 2.78; found: C, 80.93; H, 9.81; N, 2.67.

2.2.3 2-(2-Octyldodecyl)-1*H*-indeno[6,7,1-def]isoquinoline-1,3(2*H*)-dione (**5**)

A mixture of compound **4** (1.51 g, 3.0 mmol), NBS (0.641 g, 3.6 mmol), and AIBN (0.098 g, 0.60 mmol) was dissolved in CCl₄ (50 mL), and heated at 80 °C overnight. After being cooled to room temperature, the residue was removed by filtrating and the filtrate was evaporated under reduced pressure. The crude solid was used in the subsequent reaction without further purification. The crude solid was mixed with anhydrous lithium bromide (0.905 g, 10.4 mmol) and

dissolved in dry DMAc (20 mL) in nitrogen atmosphere, and then heated at 80 °C overnight. After being cooled to room temperature, the mixture was extracted with chloroform twice and washed with dilute hydrochloric acid. The organic layer was combined and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane=6:1) to give product as an orange solid. Yield: 0.47 g, 31% for two steps. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.31 (2 H, d, J=6.8 Hz), 7.71 (2 H, d, J=6.8 Hz), 7.07 (2 H, s), 4.07 (2 H, d, J=7.2 Hz), 1.94(1 H, m), 1.39-1.21 (30 H, m), 0.86 (6 H, m); ¹³H NMR (CDCl₃, 100 MHz, ppm): δ 164.3, 144.3, 132.9, 131.6, 127.5, 125.0, 123. 3, 122.9, 44.4, 36.9, 31.93, 31.90, 31.7, 30.1, 29.64, 29.58, 29.34, 29.31, 26.6, 22.7, 14.1. HRMS (ESI): calcd. for C₃₄H₄₈NO₂ (M+H)⁺: 502.3680; found: 502.3675.

2.2.4 2-(2-Octyldodecyl)-1H-indeno[6,7,1-def]isoquinoline-1,3,6,7(2H)-tetraone (**6**)

Compound **5** (3.0 mmol) was dissolved in acetic anhydride (100 mL), and heated to 110 $^{\circ}$ C. Chromium trioxide powder (15.0 mmol) was slowly added into the solution in batches and allowed to react for 20 min. Without prior cooling, the reaction mixture was poured into ice (300 g), and dilute hydrochloric acid (30 mL) was added slowly to quench the reaction under stirring. The solid was filtrated and washed with a little ethyl alcohol. A light yellow product was obtained and used in the subsequent condensation reaction without further purification.

2.2.5 6,8-Bis(4-methoxyphenyl)-2-(2-octyldodecyl)cyclopenta[2,3]indeno[6,7,1-def]isoquinoline-1,3,7(2*H*)-trione (**8**) A mixture of 1,3-bis(4-methoxyphenyl)propan-2-one (compound **7**) [22] (0.20 mmol) and compound **6** (0.20 mmol) was dispersed in isopropyl alcohol (2 mL), and heated to 80 °C. KOH sheets (0.10 mmol) were added into the mixture and allowed to react for 30 min. After cooling in an ice bath, the product as a reddish brown solid was obtained by filtration and was used in the subsequent Diels-Alder reaction without further purification.

2.2.6 AFI

A mixture of compound **5** (0.198 g, 0.26 mmol) and compound **8** (0.130 g, 0.26 mmol) in nitrobenzene (2 mL) was stirred at 180 °C overnight. After being cooled to room temperature, the crude solution was then loaded onto a silica gel column. The nitrobenzene was removed by petroleum ether and dichloromethane with the ratio of 5:1 and the product as an orange solid was eluted by petroleum ether and dichloromethane at a ratio of 2:1. Yield: 0.104 g, 20% for the three steps. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.21 (4H, d, *J*=7.2 Hz), 7.55 (4H, d, *J*=8.8 Hz), 7.29 (4H, d, *J*=8.8 Hz), 6.88 (4H, d, *J*=7.2 Hz), 4.09 (6H, s), 4.00 (4H, d, *J*=3.2 Hz), 1.95–1.92 (2H, m), 1.37–1.19 (64H, m), 0.87–0.82 (12H, m); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 164.0, 160.2,

141.3, 139.6, 136.8, 132.0, 132.0, 129.8, 129.1, 124.8, 124.2, 122.1, 115.4, 55.5, 44.4, 36.7, 31.9, 31.7, 30.0, 29.6, 29.6, 29.5, 29.3, 29.3, 26.5, 22.7, 14.1. HRMS (ESI): calcd. for $C_{84}H_{105}N_2O_6[M+H]^+$: 1237.7967; found: 1237.7967.

2.3 Single-crystal X-ray diffraction

A single crystal suitable for X-ray structural analysis was obtained by slow evaporation of the mixed solvents (ethyl alcohol/dichloromethane) containing **AFI**. Diffraction data were collected on a Ragaku mm007 diffractometer using the ω -scan mode with graphite-monochromatic Mo-K α radiation (λ =0.71073 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic software package [23,24]. Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated and refined isotropically.

3 Results and discussion

3.1 Photophysical property of AFI

The photophysical property of **AFI** was investigated in the dilute CHCl₃ solution (Figure 2). The absorption spectrum of **AFI** reveals three main bands that peaked at 328 nm, 376 nm, and 484 nm. Compared with **FAI** we had synthesized previously [25], the maximum absorption peak of **AFI** red-shifted by 70 nm, which can be attributed to the additional imide group and the extension of the conjugated backbone. The fluorescence spectrum of **AFI** reveals an emission maximum at 613 nm, which red-shifted over 60 nm compared with **FAI**.

3.2 Electrochemical property

The electrochemical property of **AFI** was measured by using cyclic voltammetry (CV). **AFI** was dissolved in dichloromethane containing 0.1 mol L^{-1} *n*-Bu₄NPF₆ as supporting electrolyte at a concentration of 10^{-3} mol L^{-1} . Ag/AgCl was used as reference electrode and ferrocene was the standard compound. Three reversible reduction waves were observed (Figure 3), which indicated its excellent electron-acceptor property. The LUMO level of **AFI** estimated from the onset of its reduction wave showed a value of -3.80 eV, which indicated strong electron-withdrawing ability of **AFI**. The introduction of the imide group and the extension of the conjugated skeleton obviously lowered the LUMO level of **AFI**.

3.3 Single-crystal analysis

The molecular configuration of **AFI** is shown in Figure 4. The two *p*-methoxyphenyl groups were nearly perpendicular to the flat acenaphtho fluoranthene-fused core, and the torsion angle was measured to be 78.2° . Two acenaphtho



Figure 2 Absorption spectra (a) and photoluminescence (PL) spectra (b) of **AFI** in CHCl₃ solutions $(1.0 \times 10^{-5} \text{ mol L}^{-1})$.



Figure 3 CV curve of AFI in CH_2Cl_2 (1.0×10⁻³ mol L⁻¹).



Figure 4 Molecular configuration of AFI in single crystal.

-diimide segments are exposed for intermolecular stacking. The crystal data and structure refinement for **AFI** are summarized in Table 1. Figure 5 illustrates the single-crystal packing diagram of **AFI**. It adopts a brickwork packing structure, which leads to slipped face-to-face π - π stacking that is quite similar to rubrene [26]. No displacement along the short axis of the molecular backbone was observed. There is a close slipped π - π overlap between adjacent acenaphtho-diimide cores with a distance of 3.72 Å. In this crystal structure, sufficient and successive π - π orbital overlap is achieved. The π - π stacking distance may be further decreased by using shorter linear alkyl chains at the nitrogen atoms.

3.4 Device performance in solar cells

In order to investigate the electron-acceptor property of **AFI**, bulk-heterojunction solar cells were fabricated and tested in

Table 1 Crystal data and structure refinement for AFI

Parameters	Value
empirical formula	$C_{86}H_{106}Cl_6N_2O_6$
formula weight	1476.43
$T(\mathbf{K})$	293 (2)
λ (Å)	0.71073
crystal system	triclinic
space group	<i>P</i> 1
<i>a</i> (Å)	10.229 (7)
<i>b</i> (Å)	12.374 (9)
<i>c</i> (Å)	16.608 (12)
α (°)	78.82 (3)
β (°)	80.15 (4)
γ (°)	81.91 (4)
$V(\text{\AA}^3)$	2019 (2)
Z	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	4.857
$\mu (\mathrm{mm}^{-1})$	1.061
GOF on F^2	1.113
R_1^{a} $[I > 2\sigma(I)]$	0.1482
$wR_2^{(b)} [I > 2\sigma(I)]$	0.4166
θ range (°)	1.69 to 24.88
<i>F</i> (000)	3144
Data/restraints/parameters	7000/3/451

a) $R_1 = \sum ||F_0| - |F_C|| / \sum |F_0|$; b) $wR_2 = \sum [w(F_0^2 - F_C^2)^2] / \sum [w(F_0^2)^2]^{1/2}$.



Figure 5 Single-crystal packing diagram of AFI.

a configuration of ITO/PEDOT:PSS/P3HT:AFI/LiF/A1. P3HT was chosen as the electron donor and AFI as the electron acceptor. Devices with various P3HT/AFI weight ratios were fabricated. Before the device fabrication, 40 mg of AFI and 40 mg of P3HT were dissolved into 1 mL of o-dichlorobenzene, respectively, to serve as the stock solutions. Both solutions were heated to 100 °C for 1 h, filtered through 0.2 µm filter, and then cooled to room temperature. Mixing the stock solutions in different volume ratios provided various weight-blend ratios of donor/acceptor. After spin-coating the blended solution onto the ITO/PEDOT: PSS substrate, the solvent in the pristine wet film was allowed to evaporate slowly in a petridish. All the devices were measured in ambient conditions under 100 mW cm⁻² AM 1.5G-simulated solar illumination. After careful optimization, a weight ratio of 1:2 (w/w) for donor/acceptor was adopted and all the devices underwent pre-annealing at 100 °C for 15 min. The devices yielded power conversion efficiencies (PCEs) up to 0.33%, with an open circuit voltage $(V_{\rm oc})$ of 0.65 V (Figure 6), a short circuit current $(J_{\rm sc})$ of 1.37 mA cm^{-2} , and a fill factor (FF) of 0.45.

4 Conclusions

We have developed a convenient synthetic strategy to construct a new type of aromatic fused diimide **AFI**. The construction of a large conjugated plane and the introduction of electron-withdrawing imide groups significantly lowered its LUMO level, which makes **AFI** a promising electron-acceptor material. The molecular configuration and packing structure in solid state were investigated through single-crystal analysis, which indicated strong π - π interactions between adjacent molecules. BHJ solar cells based on **AFI**/P3HT blend achieved PCEs up to 0.33%. Improved electron-acceptor performance is expected after rational structure modification and device-processing optimization.



Figure 6 Device performance of AFI in solar cells.

This work was financially supported by the National Basic Research Program of China (2013CB933501), and the National Natural Science Foundation of China. It was also supported by a General Financial Grant (2013M530135) from the China Postdoctoral Science Foundation.

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