High photovoltage achieved in low band gap polymer solar cells by adjusting energy levels of a polymer with the LUMOs of fullerene derivatives

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Solar cells based on organic molecules or conjugated polymers attract great attention due to their unique advantages, such as low cost, and their use in flexible devices, but are still limited by their low power conversion efficiency (PCE). To improve the PCEs of polymer solar cells, more efforts have been made to increase short-circuit current (J_{sc}) or open-circuit voltage (V_{oc}) . However, the trade-off between J_{sc} and V_{oc} in bulk heterojunctions solar cells makes it tricky to find a polymer with a low band gap to efficiently absorb photons in the visible and near infrared region of the solar spectrum, while maintaining a high V_{oc} in solar cells. Therefore, it is crucial to design and synthesize polymers with energy levels aligning with the LUMO (lowest unoccupied molecular orbital) of an electron acceptor to minimize the LUMO level difference between donor and acceptor to keep enough driving force for charge generation, thereby maximizing photovoltage in solar cells. Here a novel copolymer APFO-Green 9 was synthesized. Polymer solar cells based on APFO-Green 9 blended with a derivative of fullerene demonstrate high photovoltage by fine tuning the HOMO and LUMO level of APFO-Green 9. Solar cells based on APFO-Green 9 and [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM) present a photoresponse extended to 900 nm with J_{sc} of 6.5 mA cm⁻², V_{oc} of 0.81 V and PCE of 2.3% under illumination of AM1.5 with light intensity of 100 mW cm⁻². As a low band gap polymer with a V_{oc} bigger than 0.8 V, APFO-Green 9 is a promising candidate for efficient tandem solar cells.

Introduction

Impressive progress has been made in the field of polymer solar cells during the last decade. PCE of 5–6% has been demonstrated.^{1,2} To make polymer solar cells viable, more effort is needed to improve the PCE, which is proportional to photocurrent and photovoltage under illumination. To enhance photocurrent, many low band gap ($E_g < 2$ eV) polymers were synthesized to match solar spectrum, which generally resulted in reducing $V_{\rm oc}$ because the band gap of a material is the up-limit photogenerated potential in a solar cell.³ It is challenging to fabricate a single junction solar cell using a low band gap material to match solar spectrum, while maintaining a high $V_{\rm oc}$ due to the intrinsic conflict between maximum $J_{\rm sc}$ and maximum $V_{\rm oc}$.⁴

Unlike inorganic solar cells where the charge carriers are directly generated upon absorbing photons, the situation is more complicated in polymer solar cells because photocurrent is generated *via* excitons (bound electron and hole pairs). Upon absorbing photons in polymer solar cells, excitons are generated, which may be split into free charge carriers under strong electric field or at the interface between two components with different electron affinities and ionization potentials, thereby forming free charge carriers.⁵ Therefore, the most efficient polymer solar cells are based on heterojunctions with a large interface for facilitating exciton dissociation or charge generation. The two components used in polymer solar cells are polymers acting as electron donors (D) and derivatives of fullerene acting as electron acceptors (A), such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)⁶ or [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM).¹ The LUMO level of an acceptor divides the band gap of a polymer into two parts, LUMO(D)-LUMO(A) and LUMO(A)-HOMO (highest occupied molecular orbital) (D) where LUMO(D)-LUMO(A) determines the driving force for exciton dissociation LUMO(A)–HOMO(D) determines and photovoltage. LUMO(D)-LUMO(A) should be at least larger than the exciton binding energy of polymers (in the range of 0.1–0.4 eV) to dissociate excitons.⁷ Therefore, the photocurrent of a polymer solar cell relies on absorbance, electron affinity difference between two components, charge carrier mobility, morphology⁸ and thickness9 of active layer. Contrary to photocurrent, photovoltage of a polymer solar cell is fairly stable, which is mainly determined by LUMO(A)-HOMO(D) and the work function difference between two electrodes.4,10 Consequently, alignment of LUMO and HOMO levels of donor and acceptor plays an essential role in determining the performance of polymer solar cells. Small LUMO(D)-LUMO(A) benefits photovoltage, but

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may result in inefficient exciton dissociation or small photocurrent. On the other hand, large LUMO(D)-LUMO(A) benefits photocurrent, but may unnecessarily reduce V_{oc} , for instance, poly(3-hexylthiophene)(P3HT) has a similar band gap with APFO3 (about 2 eV), but very different V_{oc} in solar cells.^{11,3b} The $V_{\rm oc}$ of the solar cells based on P3HT:PCBM is smaller than 700 mV and the $V_{\rm oc}$ of the solar cells based on APFO3:PCBM is 1 V due to smaller LUMO(D)-LUMO(A) in APFO3:PCBM than in P3HT:PCBM.11 Therefore, from a materials point of view, the synthesis of polymers with low band gap absorbing visible and near infrared photons, with LUMO level aligning with that of an electron acceptor to retain a high photovoltage is a big challenge because there are only two ways to narrow the band gaps of polymers, either by moving the HOMO level toward vacuum level or the LUMO level away from vacuum level. The former will result in a reduction of photovoltage and the latter will attenuate the driving force for exciton dissociation at the interface. PCBM is commonly used as the most efficient electron acceptor both for charge generation and charge transport.¹² Therefore, the LUMO level of the polymer is generally limited by the LUMO of PCBM, and otherwise new acceptors are needed.13

Here we demonstrate that the goal of minimizing LUMO(D)-LUMO(A) for exciton dissociation at the interface between polymer and PCBM to maximum Voc in solar cells was achieved in a novel synthesized low band gap alternating polyfluorene copolymer APFO-Green 9 by fine tuning its HOMO and LUMO levels to match the LUMO level of PCBM. In this polymer we have chosen to introduce a pyrazino[2,3-g]quinoxaline unit inbetween two thiophene rings. The pyrazino[2,3-g]quinoxaline acts as an electron-accepting part and the thiophenes as electron donating, giving a partial charge transfer within the segment, which results in a relatively low band gap of the final polymer $(E_g \sim 1.8 \text{ eV})$. Solar cells composed of APFO-Green 9 and either PCBM or [70]PCBM (molecular structures shown in Fig. 1) present a photoresponse extended to 900 nm and a $V_{\rm oc}$ bigger than 0.8 V. The latter case demonstrated a $J_{\rm sc}$ of 6.5 mA cm⁻² and a PCE of 2.3% under illumination of AM1.5 (100 mW cm⁻²).

Results and discussion

Synthesis of APFO-Green 9

The synthetic route of the polymer is shown in Scheme 1. We have previously described a modified procedure of preparing the starting material.¹⁴ Attempts to reduce the starting material following a procedure described in the literature¹⁵ failed and we looked for other procedures for reducing the starting material. After testing several different alternatives we found that the



Fig. 1 The chemical structures of APFO-Green 9, PCBM and [70]PCBM.



Scheme 1 Synthetic route to APFO-Green 9.

described procedure in ref. 15 actually worked, but only after adding a few drops of water into the reaction mixture. The formed tetraamine was immediately condensed with benzil and compound 1 was formed. This compound was dibrominated with *N*-bromosuccinimide yielding dibromide 2. This compound was analyzed with MALDI-TOF (without addition of matrix) and the resulting mass spectrum and isotope pattern was in excellent agreement with the structure of 2. Compound 2 was polymerized together with 2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolane-2-yl)-9,9-dioctylfluorene,¹⁶ the color of the final polymer was green and the molecular weight was determined to $M_n = 13\ 000\ \text{g}\ \text{mol}^{-1}$ and $M_w = 30\ 000\ \text{g}\ \text{mol}^{-1}$, relative to polystyrene standards.

Energy levels and optical properties

To evaluate the HOMO and LUMO values of polymer, cyclic voltammetry was used. The LUMO and HOMO values of APFO-Green 9 were estimated using a cyclic voltammogram (CV) to be 3.9 and 5.7 eV, respectively, with a HOMO-LUMO gap of 1.8 eV, which corresponds to the peak of absorption spectrum.

Normalized optical absorbance of APFO-Green 9, PCBM, [70]PCBM and blends of APFO-Green 9 with PCBM, and [70]PCBM with the ratio of 1 : 4 (by weight) are shown in Fig. 2. The absorption spectrum of pure APFO-Green 9 displays two peaks at 400 and 710 nm, which extend to 900 nm. There is one peak at 335 nm in pure PCBM film and three peaks at 320, 380 and 475 nm in pure [70]PCBM film. The peak of optical absorption of APFO-Green 9 at 710 nm (1.75 eV) is a measure of the band gap in a 1D semiconductor, and corresponds to the gap from electrochemical study (*vide infra*) (1.8 eV). The long wavelength absorption peak of APFO-Green 9 is greatly



Fig. 2 The normalized absorptions of APFO-Green 9 (squares), PCBM (filled circles), [70]PCBM (filled triangles) and the blends of APFO-Green 9 with PCBM (open-circles) and [70]PCBM (open triangles) in the ratio of 1 : 4 (by weight).

attenuated in blends (and in devices) by adding 80% PCBMs. Absorption of [70]PCBM complements the valley in the absorption spectrum of APFO-Green 9, which gives a contribution to photocurrent in the devices.

Neat APFO-Green 9 film presents broad photoluminescence (PL) peaking at 900 nm when excited at 450 or 650 nm. The photoluminescence (PL) of APFO-Green 9 was significantly quenched, but not completely in blend films with 80% PCBM or [70]PCBM and 20% APFO-Green 9, which indicates incompletely electron transfer from APFO-Green 9 to PCBMs. However, the PL quenching in APFO-Green 9:[70]PCBM blend is more pronounced than that in APFO-Green 9:PCBM. The incomplete PL quenching may be partly due to small driving forces at the interfaces between the two components. The offset of LUMOs between APFO-Green 9 and PCBMs is only about 0.1 eV (LUMO of PCBM ~ -4.0 eV). It was observed that PL quenching depends on pumping wavelength, and more quenching appears when the film was excited by long wavelength photons rather than short wavelength ones. On the other hand, the emission from both PCBM (720 nm) and [70]PCBM (710 nm) were quenched in blend films, which indicates efficient hole transfer from PCBMs to APFO-Green 9. Hole transfer from [70]PCBM to APFO-Green 9 was also confirmed by the fact that the photocurrents of the devices do come from both components with very pronounced contribution from [70]PCBM in EQE, due to the high absorption in the visible range, compared to PCBM.

Device characterization

First, solar cells based on APFO-Green 9 and PCBM with different thicknesses (from 70 to 140 nm) and stoichiometries (1:2, 1:3 and 1:4) were fabricated and characterized. External quantum efficiencies (EQEs) of all cells under monochromatic light are presented in Fig. 3a and the *J*–*V* characteristics under illumination of AM1.5 are shown in Fig. 3b. Almost identical profiles between the EQEs of the cells and the absorbance of APFO-Green 9 (Fig. 2) indicates that excitons are mainly generated in polymer phase. It was observed that contributions from long wavelength photons are pronounced in thick active layers and contributions from short wavelength photons are enhanced in thin active layers (Fig.3a). The



Fig. 3 (a) EQEs of the cells under illumination of monochromatic light, (b) J-V characteristics under AM1.5 (100 mW cm⁻²) where 1 : 2 (squares), 1 : 3 (circles), 1 : 4 (triangles), filled symbols for cells spin-cast at 1000 rpm, open symbols at 2000 rpm.

Table 1 Summary of the performances of all the diodes

Ratio and thickness of active layer	$J_{ m sc}/ m mA~ m cm^{-2}$	V _{oc} /V	FF	PCE (%)
1 : 2 (70 nm)	3.9	0.85	0.39	1.3
1 : 2 (90 nm)	4.2	0.83	0.38	1.3
1 : 3 (75 nm)	4.4	0.84	0.43	1.6
1 : 3 (140 nm)	4.9	0.83	0.41	1.7
1 : 4 (80 nm)	4.6	0.82	0.44	1.6
1 : 4 (110 nm)	4.8	0.82	0.42	1.7

parameters of the performance of these diodes are summarized in Table 1.

Larger J_{sc} and lower FF were achieved in the diodes with thicker active layer than thinner ones in all three stoichiometries. V_{oc} decreases with increasing amount of PCBM in the active layers, which results in a maximum power conversion efficiency (PCE) of 1.7% in the diodes with both stoichiometries of 1 : 3 and 1 : 4. V_{oc} of all diodes, despite the thickness or stoichiometries, are above 0.8 V, which is a remarkable number for low band gap polymer solar cells.

To compensate the valley around 500 nm in the absorbance of APFO-Green 9 and to enhance J_{sc} , [70]PCBM was used to replace PCBM as electron acceptor to harvest the photons in that region. The EQE of the diode based on APFO-Green 9:[70]PCBM (1 : 3) is presented in Fig. 4a. The pronounced contribution of [70]PCBM to EQE in visible range makes the



Fig. 4 (a) EQEs of the cells based on APFO-Green 9:[70]PCBM (squares) and PCBM (circles) with stoichiometry of 1:3 under illumination of monochromatic light, (b) *I*–*V* characteristics of the cells based on APFO-Green 9:[70]PCBM under illumination of AM1.5 (100 mW cm⁻²).

peak of APFO-Green 9 in EQE at 700 nm invisible. For comparison, the EQE of the diode based on APFO-Green 9:PCBM (1 : 3) is also depicted in the same figure. By optimizing the thickness and stoichiometry of the active layers, J_{sc} of 6.5 mA cm⁻², V_{oc} of 0.81 V, FF of 0.44 and PCE of 2.3% were achieved for the diodes with 1 : 3 and thickness of 70 ± 10 nm (see Fig. 4b). As shown in Fig. 4a, the [70]PCBM indeed makes a great contribution for harvesting the photons from 400 nm to 650 nm, which results in an enhancement of J_{sc} by 33% compared to PCBM under illumination of AM1.5.

To know the limitation of the performance of the solar cells, EQEs of the cells based on APFO-Green 9:[70]PCBM and PCBM (1 : 3) were recorded under applied reverse electric field (Fig. 5). The fact that EQE was increased by applied a reverse bias of 1 V indicates that strong electric field was needed to extract photoinduced charge carriers. Therefore one of the most important loss mechanisms of the diodes was charge recombination due to less efficient extraction of charges from the active layers after they were generated. The small FF and the field dependence of the photocurrent also suggest that the PCE is limited by transport, even though the charge generation is also less efficient in this combination, due to smaller driving force at the interface between two components as indicated by incomplete PL. Therefore, not only absorption coefficient and HOMO, LUMO values, but also the transport property should be



Fig. 5 The EQEs of the diodes of APFO-Green 9:PCBM (circles) and APFO-Green 9:[70]PCBM (squares) with (open symbols) and without (filled symbols) applied electric field.

optimized when synthesizing new polymers. The transport properties of APFO-Green 9 are under investigation.

Morphology studies

Photocurrent of polymer solar cells is sensitive to morphology. We imaged the surface of the active layer to know whether the incomplete PL quenching in blend films is due to phase separation hindering electron transfer from APFO-Green 9 to PCBMs, in addition to the small driving force at the interface between APFO-Green 9 and PCBM. The morphology of the blends APFO-Green9:[70]PCBM with the ratio of 1:3 spin-coated from pure chloroform solution (CF) or from co-solvent (chloroform (CF) mixed with dichlorobenzene (DCB) in ratio of 10 : 1 by volume) were recorded using atomic force microscopy (AFM). The topography images of these two films are shown in Fig. 6. The images indicate a strong dependence of the structure on the nature of the solvent. Some small phase-separated domains are present in the film spin-coated from CF solution (rms roughness of 0.54 nm) while the one elaborated from the CF:DCB solution presents a very smooth surface with an rms roughness of 0.39 nm. The morphological difference is explained by the higher solubility of [70]PCBM in DCB compared to CF, resulting in the formation of smoother films.



Fig. 6 AFM topography of APFO-Green9:[70]PCBM (1 : 3) films spincoated from CF solution (a) and from a CF–DCB solvent mixture solution with a ratio of 10 : 1 in volume (b). The scan size is $2 \times 2 \mu m$ and the Z-range is 10 nm.



Fig. 7 (a) PL of blend films coated from CF solution (thick line) and from CF:DCB solution (thin line). (b) the *I*–*V* characteristics of the solar cells fabricated from CF solution (squares) and from CF:DCB solution (circles).

The PL quenching of these two films and the corresponding device performance were compared. Similar PL quenching was observed and shown in Fig. 7a. The I-V characteristics of the two devices (Fig. 7b) present comparable performance, irrespective of morphology difference, which indicates that domain size in the blends has insignificant influence on exciton dissociation. The main limitation for electron transfer from APFO-Green 9 to PCBMs is the small offset of LUMO values between APFO-Green 9 and PCBMs. Accordingly, the maximum V_{oc} of the solar cells made from the low band gap APFO-Greens was reached. A further moving of the LUMO level of the polymer away from vacuum level (towards the LUMO of PCBM) will result in loss of photocurrent. Thus, with APFO-Green 9 optimized HOMO and LUMO levels were realized to balance V_{oc} and J_{sc} and to match the LUMO level of PCBM.

Potential application

It is challenging to reach 10% power conversion efficiency with a single material due to the trade-off between J_{sc} and V_{oc} . In order to increase PCE of polymer solar cells, more efforts have been made to build tandem diodes composed of one polymer or two polymers, but few of them show bigger PCE than single cells because the increase of V_{oc} cannot usually compensate for the loss of J_{sc} in series connection of tandem cells.^{1,17} To harvest photons in a broad range of the solar spectrum, using polymers with complementary absorbance are preferred, that is, combining low band gap and high band gap polymer.¹ However, Experimental

Synthetic procedure

a promising polymer for tandem solar cells.

2,3,6,7-Tetraphenyl-9,10-dithien-2-ylpyrazino[2,3-g]quinoxaline. A suspension of zinc dust (498 mg, 7.6 mmol) and 1,4-dithien-2-yl-2,3-dinitrobenzo[2,1,3]thiadiazole¹⁴ (100 mg, 0.25 mmol) in acetic acid (10 ml) and a few drops of water was kept at 60 °C for one hour and the reaction mixture turned white–pink. The mixture was filtered and benzil (214 mg, 1.0 mmol) was added to the pink solution. The solution was stirred for 48 hours at room temperature, after which it was filtered and the residue was washed with acetic acid to remove the excess benzil. The product, 80 mg (49%) was collected as a brown–black solid.

most solar cells based on low band gap polymers present lower

 $V_{\rm oc}$ and smaller $J_{\rm sc}$ than those of high band gap polymers, which

either limits the J_{sc} in series connection tandem cells or limit the V_{oc} in parallel connection tandem cells.¹⁸ APFO-Green 9

combined with [70]PCBM demonstrates decent J_{sc} and remarkable V_{oc} , which are crucial requirements for low band gap polymers employed in efficient tandem solar cells. A high PCE of 6.5 % was achieved in the stacked tandem solar cells composed

of P3HT and PCPDTBT with a V_{oc} of 1.24 V.¹ We have demonstrated that $V_{oc} = 1.8$ V in folded reflective tandem solar

cells based on APFO-Green 9 and APFO3.18 As a low band gap

polymer with a $V_{\rm oc}$ bigger than 0.8 V, APFO-Green 9 is

¹H NMR: (*δ*, ppm) 8.48 (2H, dd, *J* 3.9 Hz), 7.82 (8H, m), 7.76 (2H, dd, *J* 5.1 Hz), 7.39 (14H, m)

2,3,6,7-Tetraphenyl-9,10-di(1'-bromothien-2-yl)pyrazino[2,3-g]quinoxaline. To a solution of 2,3,6,7-tetraphenyl-9,10-dithien-2-ylquinazoline (1) (80 mg, 0.12 mmol) in chloroform (25 ml) and of acetic acid (25 ml), *N*-bromosuccimide (44 mg, 0.48 mmol) was added. This mixture was stirred for 3 hours at room temperature in darkness after which TLC proved that the reaction was finished. The reaction mixture was filtered and the precipitate was collected. This yielded 70 mg (70%) of a black solid.

¹H NMR: (δ, ppm) 8.48 (2H, d, J 4.2 Hz), 7.82 (8H, m), 7.43 (12H, m), 7.29 (2H, d, J 4.5 Hz), MS (MALDI), *m*/*z* 805.8 (M⁺).

APFO-Green 9

To a degassed toluene (5 ml) mixture of 2,3,6,7-tetraphenyl-9,10-di(1-bromothien-2-yl)quinazoline (2) (70 mg, 0.086 mmol), 9,9-dioctyl-2,7-di(4',4',5',5'-tetramethyldioxyboralane)fluorene (58 mg, 0.91 mmol) and tetrakis(triphenylphosphine)palladium (5 mg, 4 μ mol) under nitrogen a tetraethylammonium hydroxide solution (0.37ml, 20 wt% in water) was added. This mixture was boiled under reflux for 3 hours after which bromobenzene (20 mg, 0.12 mmol) was added. This was again refluxed for one hour, then phenylboronic acid (15 mg, 0.12 mmol) was added. After one additional hour of refluxing the mixture was left stirring overnight. The reaction mixture was precipitated in methanol (150 ml) and filtered. The crude polymer was dissolved in boiling chloroform (50 ml) and extracted with NH₄OH solution (50 ml, 28%). This extraction was repeated four times, but the last time pure water was used. The organic layer was again precipitated in methanol (150 ml), and filtered. The resulting solid was soxhlet extracted overnight with diethyl ether, after which the ether soaked thimble was allowed to dry in ambient conditions. The thimble was then soxhlet extracted with chloroform. The chloroform solution was reduced in volume and the polymer was precipitated with methanol (70 ml) and collected by filtration. The solid was dried in a vacuum oven overnight (40 $^{\circ}$ C). This yielded 57 mg (64 %) of a black–green solid.

¹H NMR: (δ, ppm) 8.73 (2H, m), 7.95 (8H, m), 7.84 (6H, m), 7.71 (2H, m), 7.48 (12H, m), 2.18 (4H, m), 1.13 (24H, m), 0.76 (6H, m).

Physical property characterization

Absorption spectra were recorded using a spectrophotometer (Lambda 950) and the PL spectra were characterized with an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector). The samples for absorption and photoluminescence measurements were prepared on glass substrates. Electrochemical experiments were done as reported in the literature.¹⁹ The film surface morphology was investigated using atomic force microscopy (AFM) with a Dimension 3100 system (Digital Instruments/Veeco) operating in tapping mode. Silicon cantilevers (NSG10) with a force constant of 5.5–22.5 N m⁻¹, a resonance frequency of 190–325 kHz and a tip curvature radius of 10 nm were used. For observations, the films were prepared under the same conditions as the devices.

Diode fabrication and characterization

The solar cells are fabricated by spin-coating. First a polymer anode of PEDOT-PSS (EL grade) was spin-coated on ITO coated on glass substrate following annealing at 120 °C for 5 minutes. The active layer of mixed APFO-Green 9 and PCBM was spin-coated from chloroform on top of PEDOT-PSS. LiF (1nm) and Al (60nm) as top electrode were deposited under vacuum on the active layer. The thickness of the active layer is about 60–140 nm. The size of the diode is defined by a mask when depositing Al under vacuum, and is about 5 mm².

The spectral response was recorded by a Keithley 485 picoammeter under short circuit condition when devices were illuminated through the ITO side with a monochromatic light from a halogen lamp. Current–voltage characteristics were recorded using a Keithley 2400 Source Meter under illumination of AM 1.5 with intensity of 100 mW cm⁻² from a solar simulator (Model SS-50A, Photo Emission Tech., Inc.). All fabrication and characterizations were performed in an ambient environment.

Conclusions

A low band gap polymer APFO-Green 9 was synthesized. Solar cells based on APFO-Green 9 combined with PCBM or [70]PCBM were fabricated and characterized. Decent J_{sc} (6.5 mA cm⁻²), impressive V_{oc} (0.81 V) and PCE (2.3%) were obtained under AM1.5 (100 mW cm⁻²) by aligning the HOMO and LUMO levels of the polymer to match the LUMO of PCBM, extending absorption to harvest photons in near infrared region and maintain V_{oc} . The V_{oc} (0.8 V) is among the largest value for low band gap polymer solar cells, which makes the APFO-Green 9 a very competitive candidate for tandem solar cells.

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