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Synthesis and application of poly(flourene-*alt*-naphthalene diimide) as an n-type polymer for all-polymer solar cells†

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A new alternating copolymer of fluorene and naphthalene diimide, PF-NDI, was synthesized and characterized. The highest power conversion efficiency of all-polymer solar cells based on P3HT:PF-NDI reached 1.63% with a relatively high fill factor of 0.66 by using 1,8-diiodooctane as a solvent additive to optimize the mixing morphology.

Polymer solar cells (PSCs) have emerged as a promising alternative technology for producing clean and renewable energy, because inexpensive, light-weight, and large-area PSC devices can be fabricated through scalable solution-based processes.¹ The polymer-based bulk-heterojunction (BHJ)-type device first reported in 1995, consisting of conjugated polymers and fullerene derivatives, largely enhanced the power conversion efficiency (PCE) of PSCs under sunlight.² The highest efficiency for BHJ-type devices with fullerene derivatives has reached 8% through the development of the donor polymers and the optimization of device fabrication.³

Compared with the polymer–fullerene systems, all-polymer solar cells (all-PSCs), in which semiconducting polymers are used as the electron acceptor and conductor (n-type) instead of fullerene derivatives, have several advantages. Polymer structures are diverse, and thus the absorption spectra, energy levels, and the transport properties of the acceptors can be tuned to optimize optical properties, as well as charge transfer and collection processes.⁴ In addition, polymer–polymer blends could have an advantage in large-scale wet processes for film coating because of the better flexibility in controlling solution viscosity.

However, it is still a challenge to design and synthesize effective n-type polymers for photovoltaic use. One of the successful strategies for designing those polymers is to introduce strong electron-withdrawing groups onto the polymer backbone. Cyano (CN)-containing⁵ and 2,1,3-benzothiadiazole (BT)-containing⁶

n-type polymers are two kinds of important and successful systems for all-PSCs and have been extensively investigated.

Perylene diimide (PDI)-based polymers have recently emerged as a new class of n-type polymers for application in PSCs. A PDI-based polymer was first used in all-PSCs in 2007 by Zhan *et al.*⁷ After optimization in terms of both the materials and the device structures, the highest PCE of 2.23% was obtained.⁸

Compared with PDI-based polymers, naphthalene diimide (NDI)-based polymers show red-shifted absorption and higher electron mobility.⁹ However, all-PSCs based on NDI-based polymers have rarely been investigated and show poor photovoltaic performance. In 2011, several different groups used poly(NDI-*co*-dithiophene) (P(NDI2OD-T2)) as the electron acceptor material to fabricate all-PSCs. However, even after extensive device optimization with various donor materials, PCEs were still lower than 0.7%.¹⁰ One drawback of P(NDI2OD-T2) is the lower energy level of its lowest unoccupied molecular orbital (LUMO) (~4.0 eV), which results in lower open-circuit voltage (V_{OC}) of PSCs (~0.4 V) when combined with P3HT as the electron donor. Very recently, Neher *et al.* synthesized a new NDI-based polymer and the PCE of the all-PSC based on that polymer reached 1.4%; however, V_{OC} was still low (~0.56 V).¹¹ Thus, the design and synthesis of NDI-based polymers with a high-lying LUMO energy level is very important in order to improve the V_{OC} of all-PSCs.

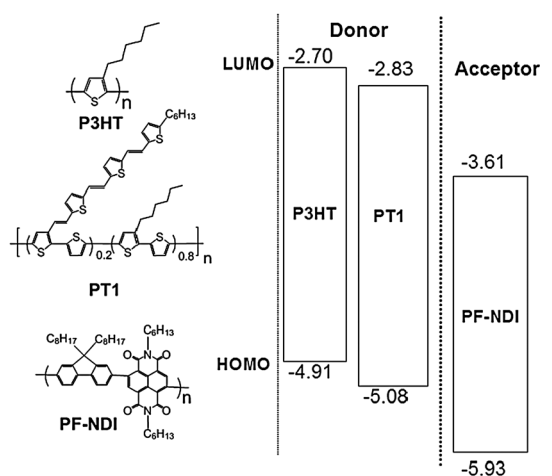
In the present study, we synthesized a new alternating copolymer of 1,4,5,8-naphthalene diimide (NDI) and fluorene (F), a common electron-donating building block. The resulting polymer (PF-NDI) could have a high-lying LUMO energy level due to the twisting of the connection between NDI and fluorene unit, resulting in the localization of LUMO density in the NDI groups. In addition to the common donor polymer P3HT, we investigate the combination with a conjugated-side-chain polythiophene (PT1) that has a lower highest occupied molecular orbital (HOMO) energy level of –5.08 eV as the electron donor. The structures of the three polymers and their HOMO and LUMO energy levels are shown in Scheme 1.

PF-NDI was synthesized by Suzuki coupling between *N,N'*-dihexyl-2,6-dibromo-1,4,5,8-naphthalene diimide and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Scheme S1, ESI†). The polymer exhibited good solubility in common organic solvents such as chloroform, chlorobenzene (CB),

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Scheme 1 Chemical structures of PF-NDI and two p-type polythiophene derivatives (*P3HT* and *PT1*) and their energy level diagrams.

o-dichlorobenzene (DCB), and xylene. The number average molecular weight (M_n) of the polymer was 12.2 kg mol^{-1} with a polydispersity index (PDI: M_w/M_n) of 1.59 measured by gel permeation chromatography (GPC).

The absorption spectra of PF-NDI in CHCl_3 and in film are shown in Fig. S1, ESI.† In CHCl_3 solution, PF-NDI showed two main absorption bands with maxima at 322 nm and 513 nm in addition to two small peaks at 362 and 368 nm. The peak at 513 nm could be attributed to the intramolecular charge-transfer (ICT) transition, and the others were possibly the result of higher energy transitions. In film, the peak of maximum ICT absorption was at 520 nm, which was slightly red-shifted by 7 nm compared with that in CHCl_3 solution. The optical band gap of the PF-NDI film was estimated as 2.1 eV from the absorption onset (590 nm).

Cyclic voltammetry (CV) was performed to determine the energy levels of the HOMO and LUMO of PF-NDI. The CV curve is shown in Fig. S2, ESI.† Based on the onset values of oxidation potential (+1.13 V) and reduction potential (−1.19 V) of the polymer vs. Fc/Fc^+ , the HOMO and LUMO levels of the polymer were calculated to be −5.93 and −3.61 eV, respectively.

We investigated the photovoltaic properties for the P3HT:PF-NDI and PT1:PF-NDI combinations. All-PSCs were fabricated with a typical sandwich structure of glass/ITO/PEDOT:PSS/active layer/Ca/Al. The ratio of the donor to the acceptor polymers was optimized from 3 : 1 to 1 : 3, and the device with the ratio of 2 : 1 showed the best performance for both P3HT and PT1.

Many works have shown that the solvents strongly affect the final photovoltaic performance. First, we tested three traditional solvents, namely, CB, DCB, and xylene. Fig. S3 (ESI†) shows the J - V curves for the P3HT:PF-NDI and PT1:PF-NDI combinations that were spin-coated from the abovementioned three solvents. The photovoltaic data are summarized in Table S1, ESI.† V_{OC} of photovoltaic devices based on P3HT:PF-NDI was 0.66–0.70 V, higher than that of P3HT:P(NDI2OD-T2) devices (~ 0.4 V). This could be attributed to the high-lying LUMO of PF-NDI. When PT1 was used as the donor material, the V_{OC} was increased to

0.84–0.88 V higher than that of P3HT. Although the solvents for the coating were changed, all the devices show comparable J_{SC} (1.95 – 2.26 mA cm^{-2}) and PCE (0.64–0.78%).

The morphology of the six blend films was observed by atomic force microscopy (AFM), and the results are presented in Fig. S4, ESI.† All the blend films of P3HT:PF-NDI had a rough surface with arithmetic mean roughness (R_a) of 3.6–5.7 nm and coarse phase separation between the polymers. In contrast, all the PT1:PF-NDI films had a rather smooth surface with R_a of 0.35–0.41 nm and more uniform mixing. This difference may be related to the high crystallinity of the regioregular P3HT. The rougher morphology of P3HT:PF-NDI blend films compared with PT1:PF-NDI blend films indicates that there is still considerable room for improvement in terms of the charge separation interface in the P3HT:PF-NDI system.

It has been reported that a small amount of 1,8-diiodooctane (DIO) can significantly enhance the interpenetrating nanoscale morphology and thus improved the PCE of PSCs for polymer–fullerene systems,¹² molecular materials–fullerene systems,¹³ and polymer–molecular materials systems.¹⁴ However, there have been few reports on the use of DIO in all-PSC systems. Although the general mechanism of the improvement is not clear yet, the change of the aggregation kinetics due to the difference in the miscibility between the materials and DIO could be a reason for the morphological change. We added DIO as an additive to the P3HT:PF-NDI system and expected that it could improve the film morphology. Three different volume ratios of DIO to CB (0.3%, 0.5% and 1%) were tested for P3HT:PF-NDI devices. The J - V curves and corresponding photovoltaic data are shown in Fig. 1. With the introduction of DIO, the V_{OC} decreased slightly but J_{SC} and FF improved substantially, resulting in higher PCE. With the optimum amount of DIO (0.5%), the PCE reached 1.63%, which is the highest to date for all-PSCs based on NDI polymers. The average PCE of five devices was 1.59% with a standard deviation of 0.03%. It is noteworthy that the FF increased from 0.54 to 0.66 upon the addition of DIO. This value is quite high for polymer–polymer blend systems and is even comparable with polymer–fullerene systems.

The film surface morphologies spin-coated from pristine CB and CB with DIO are compared in Fig. 2. The images show

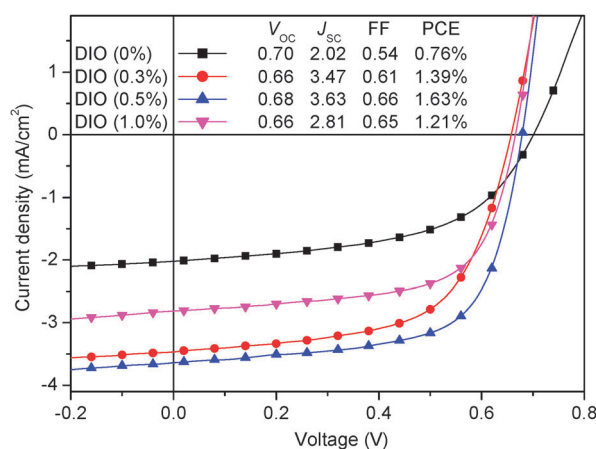


Fig. 1 J - V curves of all-PSCs based on P3HT:PF-NDI, with different ratios of DIO as additive.

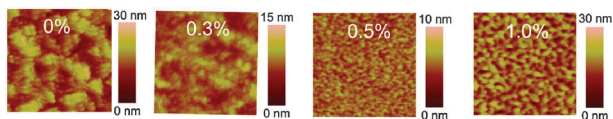


Fig. 2 AFM height images of P3HT:PF-NDI composite films, spin-coated from chlorobenzene solutions with different ratios of DIO additive.

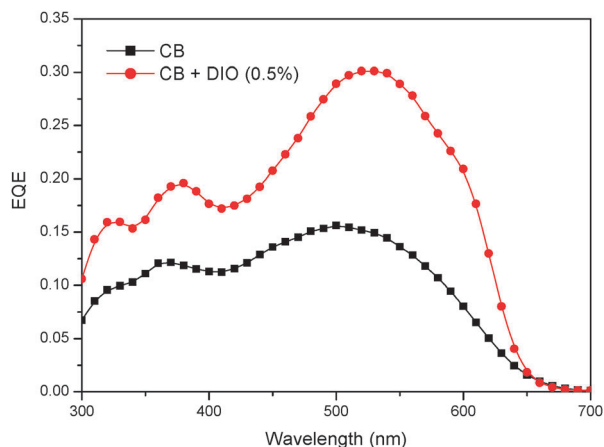


Fig. 3 EQE plots of polymer solar cells based on P3HT:PF-NDI blended under different conditions.

obvious improvement of polymer mixing by the use of DIO; the surface roughness decreased upon addition of 0.5 vol% DIO but increased slightly upon 1.0 vol% DIO addition. The domain sizes observed by AFM were correlated to J_{SC} of the devices, assuming that the donor–acceptor interface governed the charge separation efficiency. The same tendency has been observed for all-PSC with PDI-based n-type polymers.⁸ For the PT1:PF-NDI system, we also tested the additive effect of DIO at different ratios, but no improvement of photovoltaic performance was observed. This may be because the film morphology without DIO was already optimal, as suggested by AMF images, and further improvement through this approach could be difficult.

Fig. 3 shows the external quantum efficiency (EQE) plots of two photovoltaic devices under monochromatic light illumination. The shapes of the EQE curves of these devices are similar, but the device prepared with 0.5 vol% DIO exhibited higher values than the one prepared from pristine CB. The highest EQE values of the two cases were 0.30 and 0.15, below the value for P3HT:fullerene devices (~ 0.65), which could be inferior hole and/or electron transport. Further research on the charge transport properties in both the pristine PF-NDI film and blend films is in progress.

In conclusion, an n-type polymer, PF-NDI, was synthesized by Suzuki coupling. The polymer had good solubility and a high LUMO energy level of -3.61 eV. Two polythiophene derivatives, P3HT and PT1, were chosen as p-type polymers

and combined with PF-NDI, and photovoltaic performance was investigated systematically. P3HT:PF-NDI and PT1:PF-NDI showed similar photovoltaic performance when spin-coated from three different solvents, namely, CB, DCB, and xylene. By adding DIO as a solvent additive to optimize the mixing morphology of the P3HT:PF-NDI combination, the PCE and fill factor (FF) reached values of 1.63% and 0.66, respectively.

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