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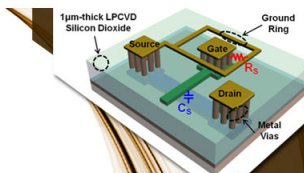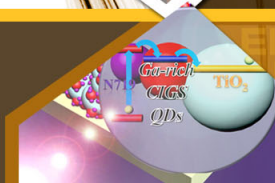
Efficient all-polymer solar cells based on blend of tris(thienylenevinylene)-substituted polythiophene and poly[perylene diimide-*alt*-bis(dithienothiophene)]

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A narrow band-gap alternating copolymer of perylene diimide and bis(dithienothiophene) (2) and a polythiophene derivative substituted by a tris(thienylenevinylene) conjugated side chain (4) are used as acceptor and donor, respectively, in all-polymer solar cells (SCs). The optimized device based on the blend of 4 and 2 in the ratio 3:1 (w/w) gives a short circuit current (J_{sc}) of 5.02 mA cm^{-2} and a power conversion efficiency of 1.48%, under simulated AM 1.5 illumination at 100 mW cm^{-2}. These values are among the highest values reported for all-polymer SCs. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975160]

Polymer solar cells (PSCs) have attracted considerable attention in recent years because of their potential application for low-cost solar energy conversion.[1–4] Power conversion efficiencies (PCEs) as high as 5%–6% have been reported for bulk heterojunction PSCs using regioregular poly(3-hexylthiophene) (P3HT) as donor and a solution-processable fullerene derivative (PCBM) as acceptor.[5,6] However, there are some drawbacks of PCBM for application in PSCs, including weak absorption in the visible region and the possibility of phase separation from the polymer donor. Therefore, nonfullerene hybrid devices[7,8] and all-polymer solar cells (SCs) in which a polymer donor is blended with a polymer acceptor have attracted interest recently.[9–14] However, the PCE of all-polymer devices remains relatively low at present. Until recently, the highest PCE of an all-polymer SC was 1% without thermal annealing;[13] this was further improved to 1.7% with optimized device structure and fabrication conditions, especially thermal annealing.[14] One of the reasons for the low efficiency of the all-polymer SCs is the lack of good polymer acceptors with high electron affinity, high electron mobility, and good sunlight-harvesting properties. For example, cyano-substituted poly(*p*-phenylenevinylene)s (PPVs), one of the widely used polymer electron acceptors in PSCs, exhibit low mobilities ($\sim 10^{-5}$ cm^2 V^{-1} s^{-1}).[15]

Recently, we reported a polymer acceptor [1, Fig. 1(a)] based on alternating dithienothiophene and perylene diimide units with high electron affinity (3.9 eV), high electron mobility (1.3×10^{-2} cm^2 V^{-1} s^{-1}), and broad absorption ranging from 250 to 850 nm.[16] A PCE of over 1%, under simulated AM 1.5, 100 mW cm^{-2}, was obtained for all-polymer SCs using this polymer as acceptor and a bis(thienylenevinylene)-substituted polythiophene [3, Fig. 1(a)] (Refs. 17 and 18) as donor. Here we report efficient all-polymer SCs based on a blend of two similar polymers [2

and 4, Fig. 1(a)]. By varying the composition of the blend, we have been able to achieve a PCE of 1.48% under illumination of simulated AM 1.5, 100 mW cm^{-2}.

Both polymers have good solution processability and are soluble in chloroform, tetrahydrofuran (THF), and chlorobenzene. The weight-average molecular weight, M_w (polydispersity index, M_w/M_n) of 2 and 4 were estimated by gel permeation chromatography, using polystyrene as the standard, to be 43 000 (2.2) and 50 000 (1.5), respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of 4 and 2 were measured by cyclic voltammetry. Both LUMO and
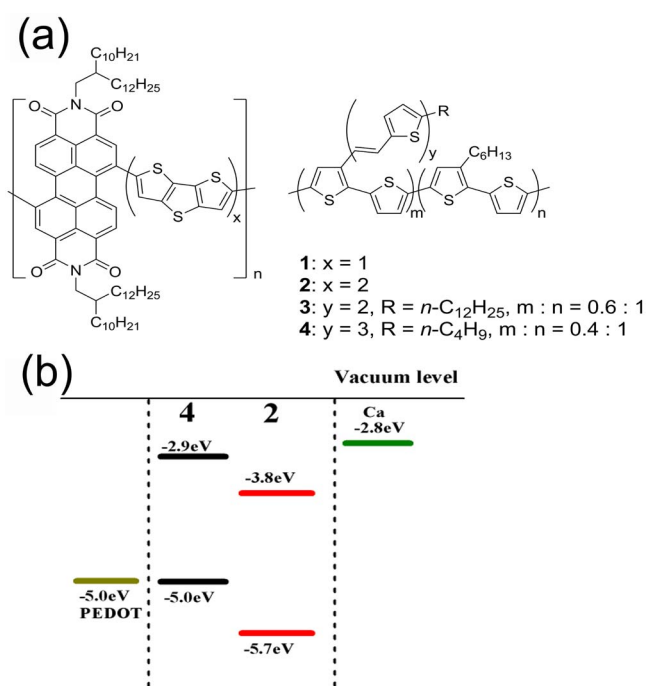

FIG. 1. (Color online) (a) Chemical structures of 2 and 4. (b) Schematic energy-level diagram for the PSC with the structure of ITO/PEDOT/4+2/Ca/Al.

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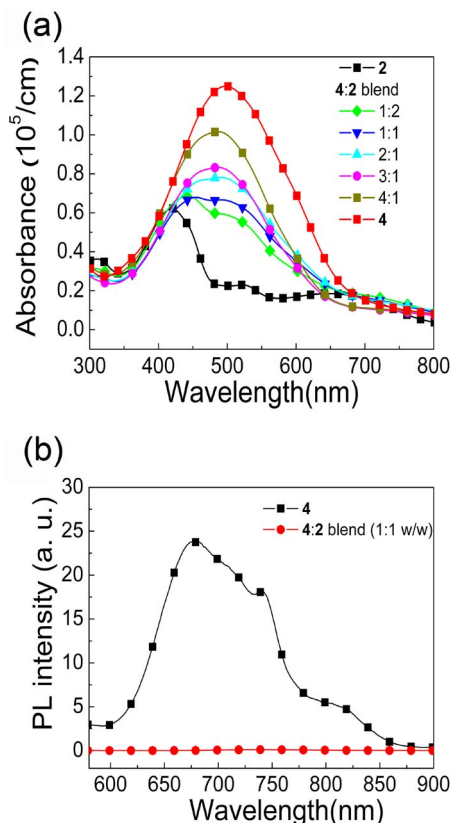
FIG. 2. (Color online) (a) Absorption spectra of the polymer films of 4, 2, and their blends with different weight ratios. (b) PL spectra of the polymer films of 4 and the blend of 4/2 (1:1, w/w).

FIG. 3. (Color online) (a) J-V curves and (b) IPCE spectra of the PSCs with different weight ratios of 4/2 under illumination of simulated AM 1.5, 100 mW cm^{-2}.

HOMO levels of the donor 4 are more than 0.7 eV higher than that of the acceptor 2, as shown in Fig. 1(b), indicating that the energy-level positions of the donor and acceptor are suitable for efficient charge transfer and separation at the interface between these two polymers.[19]

Figure 2(a) shows the UV-visible absorption spectra of thin films of 2, 4, and their blends with different weight ratios. 2 shows a broad absorption throughout the visible and extending into the near-IR region (to approximately 800 nm) although the absorbance in the range of 470–800 nm is relatively weak. The absorption of 4 is broad extending from 300 to 680 nm and stronger than that of 2. The absorption of the blend films is also broad extending from 300 to 800 nm and increasing in strength as the weight ratio of 4 is increased.

Photoluminescence (PL) quenching in donor/acceptor composites is a symptom of efficient photoinduced charge transfer between the donor and acceptor.[20] Figure 2(b) gives an example for PL of a blend of 4 and 2 in a ratio of 1:1(w/w) as well as that of neat 4. 4 exhibits a broad emission peaked at 680 nm. The PL of the blend of 4 and 2 with different weight ratios of 4:2 (1:2, 1:1, 2:1, 3:1, 4:1) was completely quenched, indicating that photoinduced charge transfer occurred between 4 and 2.[21] This result suggests that the blend of 4/2 is suitable to be used as the photovoltaic materials in the PSCs from a view point of exciton charge separation.

All-polymer SCs were fabricated in nitrogen filled gloveboxes with the traditional sandwich structure, indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate (PEDOT:PSS) (30 nm)/2:4 blended film (60 nm)/Ca (10 nm)/Al (150 nm), using blends of 4 (electron
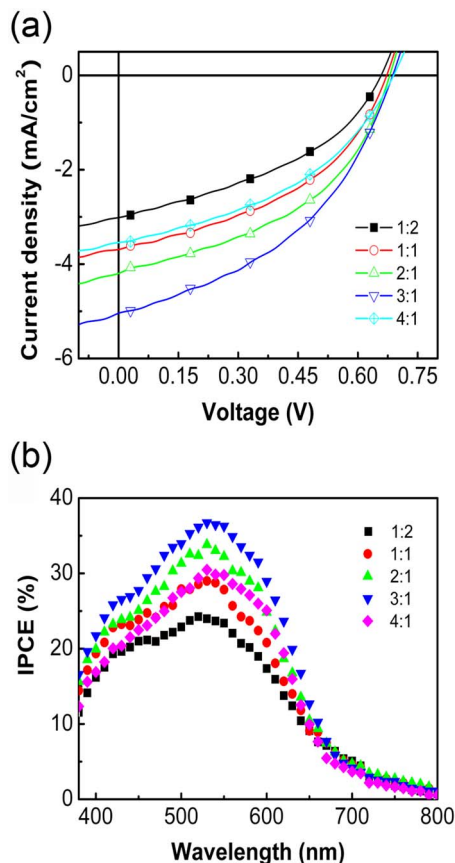
donor) and 2 (electron acceptor) with different weight ratios. The active area of one cell was 4 mm^2. We examined different thicknesses of the active layer varying from 40 to 100 nm and found that a thickness of 60 nm resulted in the highest device efficiency. Thus, we chose 60 nm as the active layer thickness for subsequent experiments. Figure 3(a) shows the current density (J) versus voltage (V) curves of the PSCs with an active layer thickness of 60 nm, under illumination of simulated AM 1.5 at 100 mW cm^{-2}. The current density-voltage (J-V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with an AM 1.5 filter was used as the light source. The optical power on the sample was 100 mW cm^{-2}. All the measurements were performed under ambient atmosphere at room temperature. The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and the PCE of the devices are summarized in Table I. V_{oc} (0.66–0.69 V) and FF (0.40–0.44) of the devices changed only a little with the donor to acceptor weight ratio. However, J_{sc}

TABLE I. Photovoltaic performance of the PSCs.

4:2 (w/w)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1:2	3.02	0.66	0.40	0.80
1:1	3.71	0.67	0.43	1.08
2:1	4.22	0.68	0.44	1.27
3:1	5.02	0.69	0.43	1.48
4:1	3.54	0.69	0.43	1.04

and PCE of the devices were strongly dependent on the donor to acceptor weight ratio in the active blend layers. With increasing the ratio of 4 to 2 from 1:2 to 3:1, J_{sc} increased from 3.02 to 5.02 mA cm^{-2}, and the PCE increased from 0.8% to 1.48%. When the composition of the active layer was 75% 4 (3:1), the PSC device exhibited the best performance; V_{oc}, J_{sc}, FF, and PCE reached 0.69 V, 5.02 mA cm^{-2}, 0.43%, and 1.48%, respectively. The J_{sc} is the highest reported and the PCE of 1.48% is among the highest values reported for the all-polymer SCs.[9–14] When we further increased the content of 4 to 4:1, J_{sc} and PCE decreased to 3.54 mA cm^{-2} and 1.04%, respectively. Thus, the most effective weight ratio of donor/acceptor examined was 3:1. It should be noted that this blend ratio is quite different from that commonly used in P3HT/PCBM (typically 1:1) or MEH-PPV/PCBM (typically 1:4) systems. It should also be noted that the 1:1 device shows similar behavior to that previously reported for a 1:1 blend of 1 and 3,[16] consistent with the similarity of the electrochemical and optical properties of 2 and 4 to those of 1 and 3, respectively.

The dependence of the photovoltaic performance on the weight ratios of donor/acceptor was further confirmed by the incident photon to converted current efficiency (IPCE) measurements of the devices, as shown in Fig. 3(b). The IPCE was measured by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a calibrated silicon photovoltaic cell. As the weight ratio is increased from 1:2 to 3:1 then to 4:1, the IPCE at 530 nm increased from 24% to 37%, and then dropped to 30%. In addition, the IPCE curves of the devices show a main peak at approximately 530 nm and a shoulder at approximately 430 nm, corresponding to the absorption maxima of donor 4 and acceptor 2, respectively. However, the relative insensitivity of the shape of the IPCE curve upon the ratio change of 4:2 suggests that excitation of the donor is the dominant contributor to the photocharge generation in the devices, although the shoulder at 430 nm may suggest a small contribution from the acceptor as well.

The dependence of the photovoltaic performance on the weight ratios of 4:2 could be explained in terms of the absorption and an interpenetrating network of donor and acceptor in the blend films. Since the absorption coefficient of 4 in the visible region from 450 to 650 nm is much larger than that of 2 [see Fig. 2(a)], the increase in J_{sc} and PCE with the concentration of 4 in the blend film can mainly be ascribed to the enhanced light absorption of the polymer blend. When further increasing the 4 content to 4:1, the decrease in J_{sc} and PCE may be attributed to a disruption of the acceptor-polymer network in the polymer blend, which could adversely affect electron transport.

We must mention that in our all-polymer SCs, we used low work function calcium and aluminum bilayer cathode. The calcium used here would potentially decrease the lifetime and the stability of the device.[22–24] Further work concerning selecting proper cathode, proper cathode modifier, and encapsulation of the device to increase the stability and the lifetime needs to be done.

In summary, all-polymer SCs were fabricated based on the blend of the donor 4 and acceptor 2. The PCE of the device was significantly increased by changing the donor/acceptor weight ratios. The optimized device gave a J_{sc} of 5.02 mA cm^{-2} and a PCE of 1.48%, under illumination of simulated AM 1.5, 100 mW cm^{-2}, with 25 wt % acceptor, different from that commonly used in P3HT/PCBM (50 wt % PCBM) or MEH-PPV/PCBM system (80 wt % PCBM). The short circuit current and PCE are among the highest values for all-polymer SCs, indicating that 4 and 2 are promising electron donor and acceptor materials, respectively, for all-polymer solar cells.

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