Poly(2,7-carbazole) and perylene tetracarboxydiimide: a promising donor/acceptor pair for polymer solar cells

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A highly soluble polycarbazole (PCz) has been synthesized, and used as a donor material with perylene tetracarboxydiimide (PDI) as an acceptor and light harvesting material in bulk-heterojunction solar cells. This donor/acceptor (D/A) pair shows a broad absorption fit within the solar spectrum, and balanced potential levels for charge separation at the D/A interface. The best photovoltaic device exhibits a high external quantum efficiency (EQE) of 16% at 490 nm and a power efficiency of 0.6% under illumination with solar light. The morphology of PCz/PDI films studied by SEM showed the formation of a favorable micro-phase separation, which is important in obtaining high efficiency. Incorporation of poly(3-hexyl)thiophene (P3HT) instead of PCz as donor produced a much lower V_{oc} and thus a lower efficiency in solar cells.

1. Introduction

Organic photovoltaic devices[1] are potentially one of the most important emerging new technologies, since the harvesting of energy by solar cells promises to be of increasing necessity as our reserves of fossil fuels dwindle. The most widely used design of organic solar cells are the so-called bulk-heterojunction devices in which the active layer consists of a blend of an electron-donating (p-type) and an electron-accepting (n-type) material. Already power efficiencies (η) up to 3% under sunlight have been achieved for devices using organic conjugated polymers as donors and with a substituted fullerene, such as PCBM, as acceptor.[2] Most work into such devices has used soluble polythiophenes[3] or derivatives of polyphenylenevinylene (PPV)[4] as the donors. These conjugated polymers have low band-gaps ($\sim$2 eV) which on the one hand complement the light absorption of PCBM, but on the other hand are susceptible to aerial oxidation due to their high HOMO energy levels.

A class of polymers that has to date received little attention as p-type materials for use in solar cells are polycarbazoles. Carbazole is a well-known electron-donating material and so poly(2,7-carbazoles)[5] are attractive candidates as p-type materials for solar cells. But the 2,7-homo-polymers of carbazole previously synthesized have low molecular weights due to their poor solubility, limiting their use in thin-film devices. The HOMO energy level of these polymers (-5.6 eV) is lower than that of polythiophene (*e.g.* -5.2 eV for P3HT[6]) and PPV-based materials (*e.g.* -5.3 eV for MDMO-PPV[7]) mentioned above, and so they are less easily oxidized. On the other hand, the band-gap in polycarbazoles is larger ($\sim$3 eV) and so their absorption is mainly in the violet or ultraviolet (UV), which forms only a small proportion of sunlight. In this case, a material with a stronger absorption in the 2–3 eV range than fullerenes would be required as acceptor in order to get high power conversion from solar irradiation. Dyes based on perylene tetracarboxydiimide (PDI) have been used as acceptors in solar cells since the pioneering work of Tang.[8] The perylene-based material has a low band-gap ($\sim$2 eV) and hence shows perfect absorption compensation for PCz and other wide band-gap donors. We have previously reported that the PDI **2** in combination with a discotic liquid crystalline hexa-*peri*-hexabenzocoronone (HBC) derivative (band-gap about 2.7 eV) showed a maximum external quantum efficiency (EQE) of 34% ($\eta = 1.95\%$) at 490 nm.[9] Here, we report on the synthesis of a new, soluble, high molecular weight poly(2,7-carbazole) (PCz, **1**) and its photovoltaic behavior upon incorporation into solar cells in combination with PDI **2**.

2. Experimental

Synthesis of PCz

PCz **1** was synthesized from 2,7-dibromocarbazole[10] by alkylation with 2-decyltetradecylbromide[11] followed by Ni(COD)$_2$ mediated Yamamoto polymerisation carried out in a DMF–toluene mixture under an argon atmosphere (Scheme 1).[12]

2,7-Dibromo-*N*-(2-decyltetradecyl)carbazole): To 2,7-dibromocarbazole (4 g, 12.3 mmol) and anhydrous DMF (40 mL) was added slowly NaH (680 mg, 60% in mineral oil, 17.1 mmol). After 30 min 2-decyltetradecylbromide (6.6 g, 15.8 mmol) was added under argon and the solution was stirred at 70 °C for 18 h. The reaction was quenched with water and extracted with dichloromethane. The organic fractions were dried over MgSO$_4$ and the solvent was removed *in vacuo*. The product was purified by column chromatography (hexane) to yield the title product as a colourless oil, which slowly solidified (7.19 g, 88%). *m/z* = 661.2 [M$^+$] (calcd. 661.65). Mp = 55 °C. ^{1}H-NMR (250 MHz, CD$_2$Cl$_2$): δ = 7.91 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 1.58 Hz, 2H), 7.34 (dd, *J* = 8.2 Hz, *J* = 1.58 Hz, 2H), 4.07 (d, *J* = 7.58 Hz, 2H), 2.09 (m, 1H), 1.21 (m, 40H), 0.88 (t, *J* = 6.65, 6H, CH$_3$). ^{13}C-NMR (62.89 MHz, CD$_2$Cl$_2$): δ = 142.30, 122.77, 121.78, 121.60, 119.91, 112.79, 48.32, 37.92, 32.33, 32.30, 32.01, 30.27, 30.03, 29.98, 29.90,

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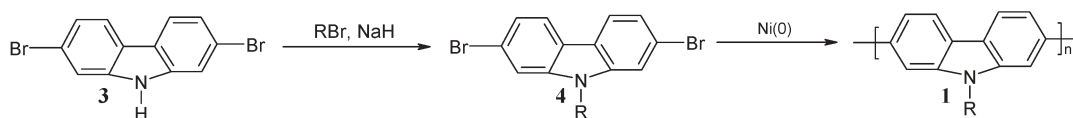
Scheme 1 Synthesis of PCz.

29.75, 29.71, 26.74, 23.08, 14.27. Anal. Calcd for $C_{36}H_{55}Br_2N$: C, 65.35; H, 8.38; N, 2.12. Found: C, 65.34; H, 8.43; N, 2.10%.

Poly[*N*-(2′-decyltetradecyl)carbazole]-2,7-diyl: Bis-(1,5-cyclooctadiene)nickel(0) (515 mg, 1.87 mmol), cyclooctadiene (0.23 mL, 1.87 mmol), and 2,2′-bipyridyl (293 mg, 1.87 mmol) were dissolved in dry DMF (3 mL) and dry toluene (3 mL) under argon. This mixture was heated for 30 min at 80 °C and then 2,7-dibromo-*N*-(2-decyltetradecyl)carbazole (1 g, 1.08 mmol) and bromobenzene (2.6 µL, 0.025 mmol) dissolved in toluene (6 mL) were added. The reaction was stirred for 3 d under argon at 80 °C. The reaction mixture was poured into methanol–conc. HCl (1 : 1) and the precipitated product was filtered off. The polymer was dissolved in chloroform, washed with a saturated EDTA solution, and the oligomers were extracted in a Soxhlet apparatus using acetone as solvent to give the title polymer as a light-yellow solid (318 mg, 84%). ^{1}H-NMR (250 MHz, THF-d_8): δ = 8.22(d, J = 7.28 Hz, 2H), 7.86–7.32 (m, 4H), 4.46 (s, 2H), 2.37 (s, 1H), 1.51–1.21 (m, 40H), 0.86 (m, 6H). Anal. Calcd for $(C_{36}H_{55}N)_n$: C, 86.16; H, 11.05; N, 2.79. Found: C, 86.13; H, 11.04; N, 2.65%. GPC (PS standard): M_n = 39100 g mol^{-1}, M_w = 75500 g mol^{-1}, D = 1.93.

PDI and P3HT (M_n 3.07 × 10^4 g mol^{-1}, D 1.80) were purchased from Sensient Imaging Technologies (Germany) and American Dye Source (Canada), respectively. Both were used without further purification.

Characterization

Gel permeation chromatography (GPC) analysis was performed using PS columns (500, 10^5 and 10^6 Å pore widths) connected to a UV/refractive index detector and THF as solvent. Electrochemical measurements were performed on a Voltammetric Analyzer (AutoLab PGSTAT-30, Potentiostat/Galvanostat) in a three-electrode cell with a working electrode of indium tin oxide (ITO) glass (sheet resistance of 20 Ω □$^{-1}$), a silver quasi-reference electrode (AgQRE, calibrated with the Fc/Fc$^+$ redox couple E° = −4.8 eV) and a Pt counter electrode. Films were spin-coated on the pre-treated ITO glass. Tetrabutylammonium perchlorate (TBAClO$_4$, 0.1 M), and acetonitrile were used as electrolyte and solvent, respectively. Absorption measurement of the thin film was recorded using a spectrometer (Perkin Elmer, Lambda 900). Scanning Electron Microscopy (SEM, LEO 1530 Gemini) was performed to observe the morphology of the thin film. For the cross-section view, the film was first immersed into liquid nitrogen, and then taken out and quickly broken in half. The fresh fracture side was subsequently observed by SEM. 2-D X-ray diffraction of oriented fibers was conducted using a rotating anode (Rigaku, 18 kw) X-ray beam (CuKα, pinhole collimation, double graphite monochromator) with the beam perpendicular to the fiber axis and a CCD camera.

Device fabrication and testing

The devices were fabricated by spin coating PCz : PDI solutions or P3HT : PDI solutions (15 mg ml^{-1}) onto ITO substrates pre-treated with acetone and isopropanol in an ultrasonic bath followed by cleaning for 10 min with oxygen plasma. 100 nm thick silver was subsequently evaporated through a mask on the surface to form the cathode. The effective area of the device was approximately 6 mm^2 defined by overlap of etched ITO and the top electrode, which was accurately measured by an optical microscope for subsequent calculations.

Incident light was focused on the effective area of each device through a lens. Current–wavelength (I–λ) curves were recorded with a Keithley 236 Source-Measure Unit. A tungsten halogen lamp was employed as light source, supplying monochromatic light from 300 nm to 800 nm through a TRIAX 180 monochromator. Incident light intensity was determined by a calibrated silicon diode. The maximum intensity was 6 W m^{-2} at *ca.* 600 nm. Solar light was obtained from a solar simulator (Lichttechnik, Germany) using a 575 W metal halide lamp, in combination with an ODF filter, to produce a spectral distribution close to the global radiation AM1.5. The light intensity was set to around 100 W m^{-2}. Devices were tested under a nitrogen atmosphere.

3. Results and discussion

In the synthesis of PCz, the 'long dove-tail' alkyl chains were introduced to improve the processability of the material. It has been shown that this is an efficient way to increase the solubility of perylene based dyes[13] and two-dimensional polycyclic aromatic hydrocarbons.[11] The resulting PCz is highly soluble in common organic solvents such as chloroform or toluene, and shows excellent film-forming properties. Thin films of PCz spin-coated from chloroform solution are quite smooth, with a typical root mean square (RMS) roughness of less than 3 nm for 100 nm thick films.

PDI shows absorption maxima at 490 nm and 530 nm, while those for PCz are at 395 nm and 270 nm. When they are blended, a broad absorption between 300 nm and 600 nm coinciding with the strongest emission part of the solar spectrum is achieved (Fig. 1), which is highly desirable in a solar cell.

The potential suitability of the PCz : PDI combination for solar cell applications was further confirmed by determination of the molecular orbital energy levels from cyclic voltammetry on thin films of PCz (**1**) and PDI (**2**) on ITO referenced with Ag/Ag$^+$ and calibrated against ferrocene. It was found that PDI had its highest occupied molecular orbital (HOMO) energy level at −5.8 eV, (cf literature value of −5.35 eV[9]) which was below the HOMO level of PCz (−5.6 eV). The corresponding LUMO values were estimated to be −2.6 eV (**1**)
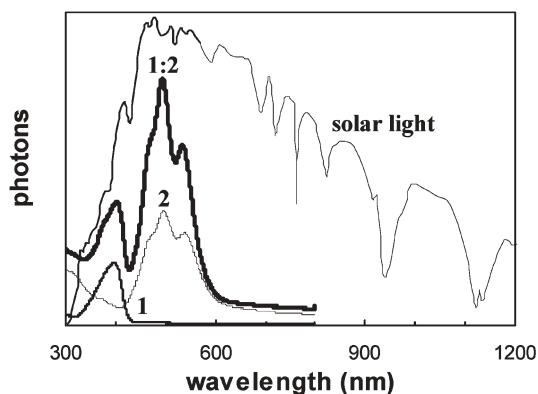
Fig. 1 Absorption spectra of **1**, **2** and their blend as thin films compared with AM1.5 global solar spectrum.

and −3.8 eV (**2**) from the band-gap calculated from the absorption spectrum. This indicates in principle when composing a solar cell that, PDI (**2**) form excitons (**2***), and the 0.2 eV difference in HOMO energies allows for a ready hole migration from PDI excited states to PCz to complete the charge separation. The 0.8 eV energy difference between the LUMOs of PCz and PDI means electron migration from PCz to PDI can also be expected to occur readily.

Thin films of PDI prepared by spin-coating show high crystallinity confirmed by electron diffraction.[9] A high charge carrier mobility of 0.2 cm^2 V^{-1} s^{-1} has been reported in its crystalline phase.[14] X-ray diffraction studies on an extruded PCz fiber reveal that at room temperature the polymer chains are aligned with the long molecular axis along the extrusion direction. We assigned a reflection peak of 8.1 Å in the meridional direction to the length of the repeating unit and another reflection peak of 2.3 nm in the equatorial direction to the inter-chain distance. Due to the lack of more reflection peaks, the three-dimensional correlation of the polymer chains could not be exactly determined. In addition, the halo at 4.7 Å is a typical correlation between alkyl chains. Thus both components in the blend tend to form ordered nano-phases, which are essential for an efficient charge transfer.

Photovoltaic devices were prepared to test the performance of the PCz : PDI pair (Fig. 2). Blends (PCz : PDI) with weight ratios of 1 : 1 to 1 : 5 were tested and the best performance was obtained for ratios of 1 : 4 and 1 : 5, as shown in Fig. 3. The highest EQE of 16% was achieved at 490 nm for a blend containing 20 wt% of PCz and 80 wt% of PDI (**1** : **2** = 1 : 4), corresponding to an efficiency of 3.2% at 0.6 W m^{-2} incident light. At monochromatic light of 470 nm, the cell showed a V_{oc} of 0.7 V, a short circuit current (I_{sc}) of 6.7 µA cm^{-2}, and an FF of 0.43. In order to compare PCz with widely applied P3HT
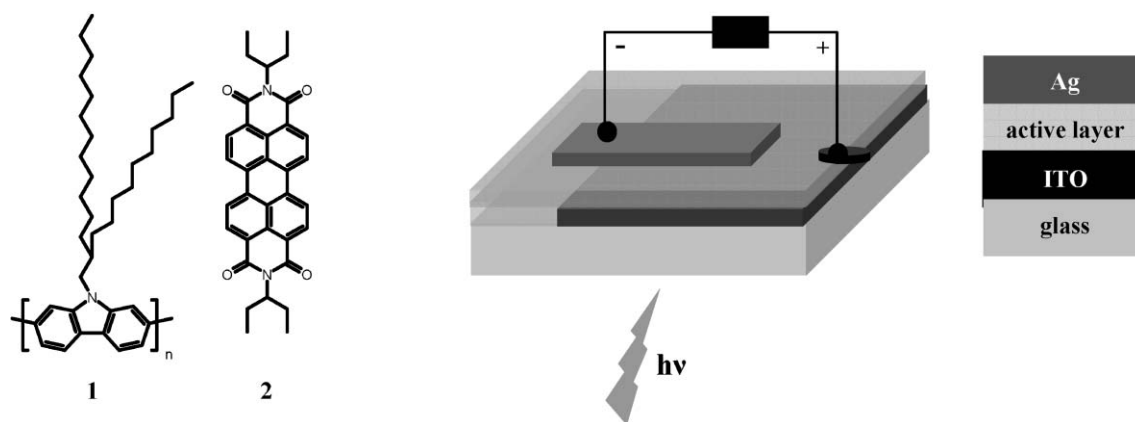

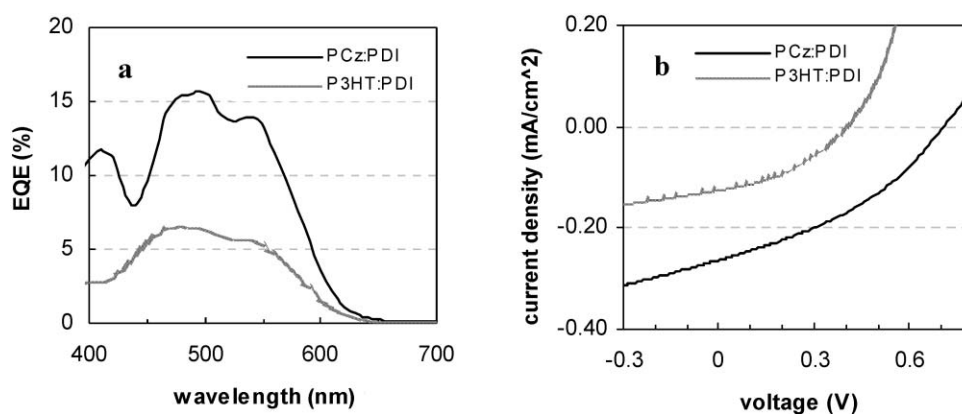**Fig. 2** Device architecture for the thin film bulk heterojunction photovoltaic device.

Fig. 3 EQE–wavelength curves (a) and I–V curves (b) under solar light at light intensity of 100 W m^{-2} for ITO/**1** : **2** (1 : 4)/Ag device (solid line). Curves for ITO/P3HT : PDI (1 : 4)/Ag device (dotted line) are also shown as reference.

as a donor material for PDI, a device using P3HT : PDI (1 : 4) was also prepared. The P3HT based device displayed a highest EQE of 6.6% and an efficiency of 0.39%, under identical irradiation conditions to the PCz-based device. These values are comparable to those reported by Dittmer *et al.* for P3HT : PDI (1 : 4) device,[15] which produced a highest EQE of 7% and an efficiency of 0.4% at 540 nm with light intensity of 1.6 W m^{-2}.

When illuminated with simulated solar light (AM1.5 Global, light intensity about 100 W m^{-2}), the PCz : PDI (1 : 4) cell displayed an I_{sc} of 0.26 mA cm^{-2}, a V_{oc} of 0.71 V, an FF of 0.37, and an efficiency of 0.63%, which to the best of our knowledge is the highest efficiency yet reported for a polymer-based solar cell not incorporating PCBM. Furthermore, an efficiency of 0.04% was obtained for the 1 : 1 blend and of 0.62% for the 1 : 5 blend. By contrast the P3HT : PDI (1 : 4) device showed an I_{sc} of 0.12 mA cm^{-2}, V_{oc} of 0.40 V, FF of 0.39, and efficiency of 0.19%. It is clear that the PCz device has almost twice the I_{sc} and V_{oc} in comparison with the P3HT device, which in turn triples the efficiency of the PCz device. As previously reported for this type of donor–acceptor bulk-heterojunction cell,[16] the open circuit voltage is related directly to the energy difference between the HOMO level of the donor and the LUMO level of the acceptor. As such, a PCz based device should exhibit a higher V_{oc} than a P3HT based device, as the HOMO level of PCz (−5.6 eV) is lower than the HOMO level of P3HT (−5.2 eV). This is consistent with the experimental results of about 0.3 V larger V_{oc} for a PCz device despite voltage losses at all interfaces. On the other hand, I_{sc} of the PCz device is much higher, indicating a possible better photon–electron transition. In principle, since P3HT has a broad absorption from 400 nm to 650 nm, it can be expected to absorb more photons which can contribute to the photocurrent than can PCz. But we clearly observed that the photocurrent for the PCz based device is much higher. One can expect that more ideal morphology is achieved for the PCz device, so as to improve charge separation and charge transfer. Further investigations are under way to elucidate this matter.

Janssen *et al.*[17] and Sariciftci *et al.*[18] have shown the importance of morphology for the performance of solar cells based on phase-separated active layers. Here SEM was used to study the morphology of thin films of the active layers. Both the top surface and cross-section of the film were analyzed. For the latter, the film was first immersed in liquid nitrogen, and then taken out and quickly broken in half. The fresh fracture side was subsequently observed by SEM. As shown in Fig. 4, PDI crystals can be seen on the film surfaces. From a comparison of thin film blends of **1** and **2** at two different ratios, 1 : 2 and 1 : 5, it is clear that with increasing PDI content, a bilayer structure at the ratio of 1 : 2 is gradually replaced by a more homogeneous morphology at the ratio of 1 : 5 (the 1 : 4 blend resembles the 1 : 5 blend but the PDI crystals are more clearly distinguishable). The higher efficiencies for the 1 : 4 and 1 : 5 blends suggests that a more intimate molecular contact is desirable for achieving high power efficiency.

It has been reported[18] that a hierarchical build-up of two cooperative interpenetrating networks on different length scales is necessary in well performing PPV/PCBM devices,
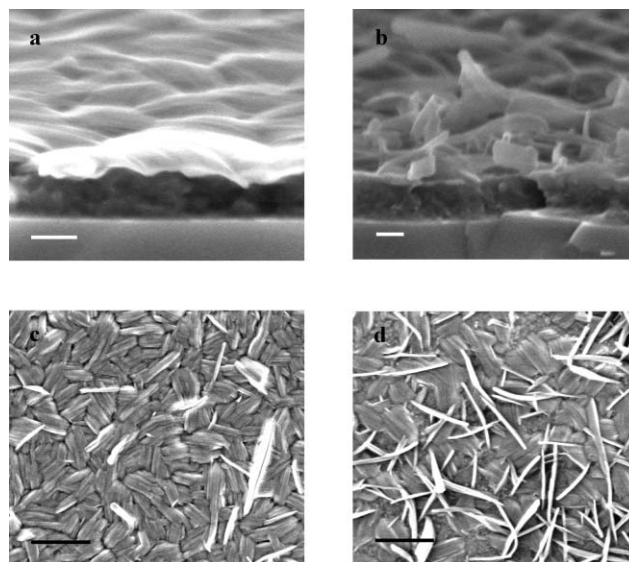

Fig. 4 SEM pictures for cross-section (a and b) and top view (c and d) of PCz : PDI blends **1** : **2** = 1 : 2 (a and c) and 1 : 5 (b and d) thin films spin-coated from chloroform solution. The scale bars are 100 nm for a and b, and 500 nm for c and d.

i.e., molecularly dispersed blends (50 wt% PCBM) or tiny domains for efficient charge separation, and one order of magnitude larger domains of pure PCBM for reducing charge recombination and better percolation pathways. In the case of PCz : PDI, the monotonic increase of efficiency from 0.04% (**1** : **2** = 1 : 1) to 0.6% (**1** : **2** = 1 : 5) with decreasing phase separation scale (corresponding to a change from an observable bilayer to a homogeneous film) indicates that charge separation is far from saturated, and there is still much space to develop the morphology of the thin film. For optimal efficiency a minimized phase separation scale would be desired. Further investigations into the effect of different processing conditions upon the morphology of PCz : PDI films are under way.

4. Conclusion

A new soluble poly(2,7-carbazole) has been applied in bulk-heterojunction cells using a PDI dye as electron acceptor. The good fit in orbital energy levels and absorption spectra led to high efficiency. This result indicates that conjugated polymers with high band-gap can also be applied as materials in efficient solar cell if appropriate electron acceptors are chosen. Replacing PCz with P3HT led to a drop in V_{oc} and efficiency mainly due to the improper energy level between the low band-gap donor and acceptor. Correlating the morphology of the active thin film with efficiency suggests that the dominating factor for high efficiency in PCz : PDI devices is charge separation. There also appears to be considerable scope for further optimization of the efficiency for carbazole-based solar cells. At the same time, the system of PCz : PDI has great potential to be developed by blending PCz with other dyes having broader absorption spectra. This work thus extends the range of applicable materials for efficient organic solar cells.

Acknowledgements

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