

COMMUNICATION

Wide band gap diketopyrrolopyrrole-based conjugated polymers incorporating biphenyl units applied in polymer solar cells†

Cite this: *Chem. Commun.*, 2014, 50, 679

Received 13th October 2013,
Accepted 6th November 2013

DOI: 10.1039/c3cc47868h

www.rsc.org/chemcomm

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Incorporating biphenyls as co-monomers in electron-deficient diketopyrrolopyrrole (DPP) conjugated polymers enables widening the optical band gap to 1.70 eV. Power conversion efficiencies of 3.7–5.7% and high open-circuit voltages of 0.80–0.93 V are obtained in solar cells based on these wide band gap DPP polymers.

Conjugated polymers that employ an electron-deficient diketopyrrolopyrrole (DPP) monomer in the main chain are frequently used in polymer solar cells and have provided power conversion efficiencies (PCEs) of up to 8%.^{1–4} A common feature of DPP-based conjugated polymers used for photovoltaic cells is the small optical band gap, typically in the range of 1.25–1.55 eV, that creates a broad spectral response of up to 1000 nm. The tendency of the polar DPP units to aggregate makes the DPP-based polymers form efficient interpenetrating networks in bulk heterojunction blends when mixed with fullerene derivatives such as [70]PCBM ([6,6]phenyl-C₇₁-butyric acid methyl ester). Additionally, DPP-polymers exhibit high charge carrier mobilities,⁵ which enhance formation and collection of free charges in solar cells and provide high photocurrents and fill factors (FF). In view of these advantages it is of interest to consider extending the family of DPP-polymers also to wider optical band gaps (>1.55 eV) that would possibly allow making more efficient single and multi-junction solar cells.

Within the ubiquitous donor-acceptor strategy of band gap control in conjugated polymers, strong electron donating and strong electron withdrawing units reduce the optical band gap.⁶ Commonly, the DPP units in these polymers are flanked by two five-membered heterocycles, such as thiophene (T). The DPP2T monomers provide optical absorption in the near-infrared region, even when combined with a weak donor such as a phenyl (P) ring. The resulting PDPPTPT polymer has an optical band gap of 1.53 eV.⁷ Replacing the central phenyl by stronger electron donors, such as thiophene,⁸ thienothiophene,⁹ benzodithiophene¹⁰ or dithienopyrrole¹¹ causes the optical

band gap to be further reduced to 1.25 eV. Other phenyl based derivatives, such as naphthalene,¹² fluorene¹³ and carbazole¹⁴ have band gaps at ~1.55 eV, similar to PDPPTPT. When the two thiophene rings in DPP2T are replaced by two phenyl rings, the optical band gap can be efficiently increased, but the performance of these polymers in polymer solar cells is low,¹⁵ due to the steric hindrance between the adjacent phenyl and DPP units. Recently, Jo *et al.* used DPP flanked by two pyridines, polymerized with bithiophene (2T) to afford a copolymer with an optical band gap of 1.71 eV that provides a PCE of 4.9% with [70]PCBM and a high open-circuit voltage (V_{oc}) of 0.92 V in solar cells.¹⁶

In this communication, biphenyl units are introduced into DPP2T polymers to increase the optical band gap (Fig. 1a). In our previous work, DPP-polymers with spatially extended electron donating parts afforded a blue-shifted absorption.¹⁷ This encouraged us to design wide band gap DPP-polymers with biphenyl (BP) units. Long and branched 2'-octyldodecyl (OD) solubilizing side chains are used to ensure solubility. We will show that the resulting polymer, PDPP2TBP (Fig. 1), indeed possesses a wider optical band gap of 1.63 eV and provides a PCE of 5.7% with a V_{oc} of 0.80 V in solar cells when blended with [70]PCBM. To increase V_{oc} , fluorine atoms on the biphenyl units are introduced into the 3,3' (F1-PDPP2TBP) and 2,2' (F2-PDPP2TBP) positions to lower HOMO and LUMO energy levels.¹⁸ As a result, a wide band gap (1.70 eV) DPP-polymer providing a high V_{oc} of 0.93 V and PCE of 4.1% in solar cells with [70]PCBM is obtained.

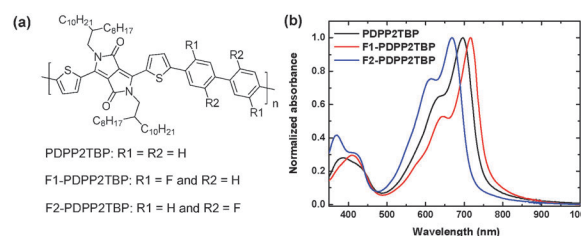


Fig. 1 (a) Diketopyrrolopyrrole based conjugated polymers with biphenyl donating units in this work. (b) Optical absorption spectra of the polymers in solid state films.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc47868h

The polymers were synthesized *via* Suzuki polymerization. The details of the synthesis of the monomers and polymers can be found in the ESI†. The reaction conditions, *i.e.* catalyst, ligand and reaction temperature, were carefully optimized to achieve high molecular weights that are generally beneficial for creating efficient blend morphologies of conjugated polymers with [70]PCBM. For PDPP2TBP and F2-PDPP2TBP polymerization with $\text{Pd}_2(\text{dba})_3/\text{PPh}_3$ (1 : 4) at 115 °C afforded high molecular weights of $M_n = 49 \text{ kg mol}^{-1}$ (PDPP2TBP) and $M_n = 72 \text{ kg mol}^{-1}$ (F2-PDPP2TBP). In contrast, only low molecular weights and low yields of F1-PDPP2TBP were obtained under these reaction conditions. However, polymerization using $\text{Pd}[\text{PPh}_3]_4$ as a catalyst at 80 °C afforded F1-PDPP2TBP in a high molecular weight of $M_n = 67.6 \text{ kg mol}^{-1}$.

The absorption spectra of the new DPP-polymers in films (Fig. 1b) and in chloroform solution (Fig. S1, ESI†) show increased optical band gaps (Table 1) compared to that of PDPPTPT at 1.53 eV. Compared to PDPP2TBP, the two fluorine atoms on the biphenyl unit reduce the band gap from 1.63 to 1.59 eV in F1-PDPP2TBP and increase the band gap to 1.70 eV in F2-PDPP2TBP. The increased band gap of F2-PDPP2TBP results from the increased torsion angle around the central carbon-carbon bond of the 2,2'-difluorobiphenyl linker compared to biphenyl and 3,3'-difluorobiphenyl.^{19,20} The energy levels were determined using cyclic voltammetry in *o*-DCB at 140 °C (Fig. S2 and Table S1, ESI†). The lowest unoccupied molecular orbital (LUMO) of PDPP2TBP was found at -3.59 eV. Upon introducing fluorine atoms the LUMO is lowered by only 0.04 eV. The fairly small effect of fluorine on the LUMO is attributed to the fact that fluorine is introduced into the biphenyl unit, while the LUMO of these polymers is mainly determined by the DPP acceptor unit. For all three polymers the LUMO-LUMO offset with [70]PCBM is larger than 0.5 eV, and above the ~0.35 eV threshold for efficient charge generation.²¹ The highest occupied molecular orbital (HOMO) levels shift to lower energies from -5.39 eV (PDPP2TBP), *via* -5.44 eV (F1-PDPP2TBP) to -5.48 eV (F2-PDPP2TBP) as a consequence of the electronegative fluorine and the increased torsion angle.^{19,20}

The crystallization of the DPP polymers was investigated using X-ray diffraction (XRD) on thin films prepared by drop casting of chloroform solutions onto a silicon wafer (Fig. S3, ESI†). The polymers show strong (100) diffraction peaks at $2\theta = 4.68^\circ$ (PDPP2TBP), 4.64° (F1-PDPP2TBP) and 4.91° (F2-PDPP2TBP) and the corresponding higher order reflections (*h*00) that are characteristic for a lamellar structure that is present in many π -conjugated polymers. The lamellar *d*-spacings are 1.89, 1.90 and 1.80 nm, respectively.

The charge carrier mobility of the polymers was determined in a field effect transistor (FET) in a bottom-gate bottom-contact

configuration and the results are summarized in Table 1. The new biphenyl polymers PDPP2TBP and F1-PDPP2TBP show only slightly reduced hole and electron mobilities compared to those of PDPPTPT with a single phenyl ring ($\mu_h = 0.04$ and $\mu_e = 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁷ This indicates that the biphenyl linker does not deteriorate charge transport compared to a phenyl linker. The mobilities of F2-PDPP2TBP are lower, possibly because the increased torsion angle reduces the three-dimensional order. Consistently the XRD of F2-PDPP2TBP is less intense and slightly broader (Fig. S3, ESI†). Low charge mobility reduces charge transport and increases bimolecular recombination in photovoltaic devices.

The three biphenyl polymers were blended with [70]PCBM as the electron acceptor and applied in organic photovoltaic devices on glass in a conventional layout with transparent ITO/PEDOT:PSS and reflecting LiF/Al metal electrodes. The photoactive polymer:[70]PCBM layers were deposited from chloroform, containing *o*-DCB or 1-chloronaphthalene (1-CN) as a co-solvent. For each polymer the donor to acceptor ratio, the amount of co-solvent and the thickness of active layers were carefully optimized. The optimized donor to acceptor weight ratio is 1 : 2 (w/w) and the optimized thickness 90–110 nm (Table 2). For PDPP2TBP and F2-PDPP2TBP, the best devices were obtained when casting the blends from chloroform solution with 1-CN as additive. Using *o*-DCB as additive gave slightly lower PCEs (Table S2, ESI†). For F1-PDPP2TBP, on the other hand, the optimized devices were processed with *o*-DCB as additive, while 1-CN resulted in a lower PCE (Table S2, ESI†).

PDPP2TBP:[70]PCBM solar cells achieve a PCE of 5.7% with $J_{sc} = 11.5 \text{ mA cm}^{-2}$, $V_{oc} = 0.80 \text{ V}$ and FF = 0.63. The maximum external quantum efficiency (EQE) in the absorption region of PDPP2TBP is 0.56 (Fig. 2b), which is similar to that of PDPPTPT (0.58),² demonstrating that the biphenyl unit does not result in less efficient charge generation and collection. However, the J_{sc} of the biphenyl-based polymer is lower than that of PDPPTPT (14.0 mA cm^{-2}). This is attributed to the wider optical band gap

Table 2 Solar cell parameters of optimized solar cells of the PDPP2TBP polymers with [70]PCBM cast from chloroform with co-solvent

Polymer	Co-solvent	Thickness (nm)	J_{sc}^a (mA cm ⁻²)	V_{oc} (V)	FF	PCE ^a (%)
PDPP2TBP	1-CN 3%	90	11.5	0.80	0.63	5.7
F1-PDPP2TBP	<i>o</i> -DCB 10%	105	6.7	0.89	0.62	3.7
F2-PDPP2TBP	1-CN 3%	100	7.7	0.93	0.56	4.1

^a J_{sc} and PCE were calculated by integrating the EQE spectrum with the AM1.5G spectrum.

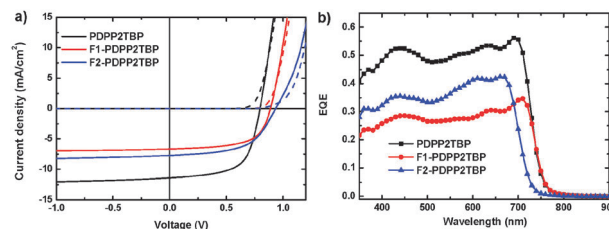


Fig. 2 (a) *J*-*V* characteristics in dark (dashed lines) and under white light illumination (solid lines) of optimized solar cells of the DPP polymers with [70]PCBM. (b) EQE of the same devices.

Table 1 Molecular weight, optical properties and charge carrier mobilities of the DPP Polymers

Polymer	M_n (kg mol ⁻¹)	PDI	E_g^{sol} (eV)	E_g^{film} (eV)	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)
PDPP2TBP ^a	49.0	3.61	1.67	1.63	3×10^{-2}	1×10^{-3}
F1-PDPP2TBP ^b	67.6	4.11	1.65	1.59	2×10^{-2}	2×10^{-2}
F2-PDPP2TBP ^b	72.0	1.98	1.74	1.70	1×10^{-4}	2×10^{-4}

^a Determined using GPC analysis at 140 °C using CHCl₃ as eluent.

^b Determined using GPC analysis at 80 °C using *o*-DCB as the eluent.

and the reduced coverage with the solar spectrum. Since V_{oc} and FF are comparable to that of PDPPTPT, the power conversion efficiency decreased from 7.4% for PDPPTPT to 5.7%. We note that for DPP-polymers that use fused planar biphenyl systems such as carbazole and fluorene lower PCEs of 1.60–3.64%^{14,22,23} and <1%^{13,22,23} have been reported compared to the 5.7% we find here for PDPP2TBP.

The increased optical band gap and similar V_{oc} of PDPP2TBP:[70]PCBM increases the energy loss ($E_g - eV_{oc} = 0.83$ eV) compared to 0.73 eV for PDPPTPT:[70]PCBM. This would ultimately limit the PCE and to increase V_{oc} fluorine atoms were introduced into the 3,3' or 2,2' positions of the biphenyl unit to lower the HOMO and LUMO levels of polymers. For F1-PDPP2TBP this results in a slight red-shifted absorption and an increased V_{oc} of 0.89 V such that the $E_g - eV_{oc}$ energy loss drops to 0.70 eV. F2-PDPP2TBP provides an even higher V_{oc} of 0.93 V, but the $E_g - eV_{oc}$ energy loss drops only to 0.77 eV because of the wider band gap. Despite these reduced energy losses, the PCEs of solar cells based on F1-PDPP2TBP (3.7%) and F2-PDPP2TBP (4.1%) are less than that of PDPP2TBP:[70]PCBM (5.7%) because the EQE and J_{sc} are decreased. For F2-PDPP2TBP also the fill factor is lower, which could be related to the lower hole mobility of this polymer.

Comparing the morphologies of the photoactive layers gives some indication why the EQE differs among the three biphenyl DPP polymers. TEM (Fig. 3) and AFM (Fig. S5, ESI†) analyses of the photoactive layers reveal a fibrillar structure in the blend films that is common to many DPP-based polymers. In the blends of PDPP2TBP and F2-PDPP2TBP with [70]PCBM the fibrils have a width of around 10 nm, which is similar to the exciton diffusion length in conjugated polymers and would allow for efficient dissociation of excitons into electrons and holes. However, for the F1-PDPP2TBP:[70]PCBM blend, the phase separation is more coarse, and wider fibrils and bundled fibrils with large diameters are present. This will reduce formation of charges, because excitons that are created in the middle of these wider fibrils need to diffuse over a longer distance to reach the interface with the fullerene phase, where they can dissociate and produce charges. This can explain why F1-PDPP2TBP has a lower J_{sc} than PDPP2TBP. The reason that F2-PDPP2TBP has a lower J_{sc} than PDPP2TBP is likely related to the much lower mobility of this material that causes more bimolecular recombination and results in a lower J_{sc} and lower FF.

In conclusion, wide band gap conjugated polymers based on electron deficient diketopyrrolopyrrole units incorporating biphenyl units were successfully designed and synthesized. Organic photovoltaic devices based on these polymers achieve

power conversion efficiencies of 5.7% with a spectral response of up to 760 nm. Further structure engineering by adding fluorine atoms on the biphenyl units increases the V_{oc} up to 0.93 V, but results in a somewhat lower efficiency of 4.1%. These results represent a successful example of incorporating biphenyl units in wide band gap conjugated polymers for polymer solar cells. Additionally, the results show that non-planar biphenyl units in conjugated polymers are not detrimental and in fact provide higher performance compared to planar and fused biphenyl systems such as fluorene and carbazole.

We thank Ralf Bovee and Xianwen Lou for GPC analysis. The work was performed in the framework of the Largecells and X10D projects that received funding from the European Commission's Seventh Framework Programme (Grant Agreement No. 261936 and No. 287818). The work was further supported by the "Europees Fonds voor Regionale Ontwikkeling" (EFRO) in the Interreg IV-A project "Organext". The research forms part of the Solliance OPV programme and has received funding from the Ministry of Education, Culture and Science (Gravity program 024.001.035).

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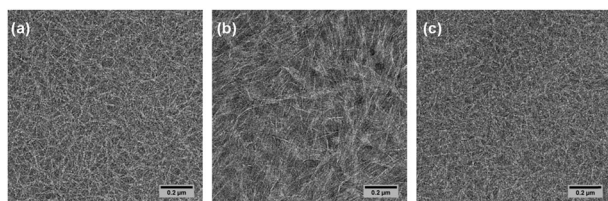


Fig. 3 (a–c) Bright field TEM images ($1.2 \times 1.2 \mu\text{m}^2$) of the optimized biphenyl-DPP polymer:[70]PCBM blend films. (a) PDPP2TBP (b) F1-PDPP2TBP and (c) F2-PDPP2TBP.