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COMMUNICATION

A new type of organic photovoltaic materials: poly(rod-coil) polymers having alternative conjugated and non-conjugated segments†

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Hong-Jiao Li, Jin-Tu Wang, Chong-Yu Mei and Wei-Shi Li*

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A new type of organic photovoltaic materials, which is a kind of poly(rod-coil) polymers composed of alternatively definite conjugated and non-conjugated segments, has been proposed. The first five examples based on polyurethane chemistry showed photovoltaic performance surpassing the reference compound, but less dependent on their molecular weight.

Over the past decade, remarkable achievement has been made in organic photovoltaic donor materials, which have substantially improved power conversion efficiency (PCE) of organic solar cells (OSCs).¹ The so far reported donor materials can be categorized into two main classes: π -conjugated polymers^{1,2} and small molecular compounds.^{1,3} Conjugated polymers have a one-dimensional π -conjugated backbone, which is favourable to light acquisition and the transportation of excitons and charge carriers. Besides, polymer materials generally have a good film formation potential and adaptable to various solution processing technologies. However, all polymers have issues of average molecular weight and its polydispersity, which always vary from batch to batch. Since their photovoltaic properties are sensitive to these parameters,⁴ conjugated polymers usually suffer from poor batch-reproducibility, a severe problem for their real applications. On the other hand, small molecular compounds do not have such problem since they have a definite chemical structure and can be purified by means of many well-developed techniques. However, for the purpose of promising light absorption and good charge transportation, this kind of compounds usually has a large and rigid π -conjugated core. Consequently, they tend to aggregate or crystallize, and are hard to form a well-qualified homogenous film, particularly in a large size.

Herein, we propose a new type of polymeric photovoltaic materials with a structural feature between conventional conjugated polymers and small molecular compounds. As illustrated in Scheme 1a, this type of materials is a kind of poly(rod-coil) polymers composed of definite conjugated and non-conjugated segments in an alternative fashion. Conjugated rigid segments are photo-active

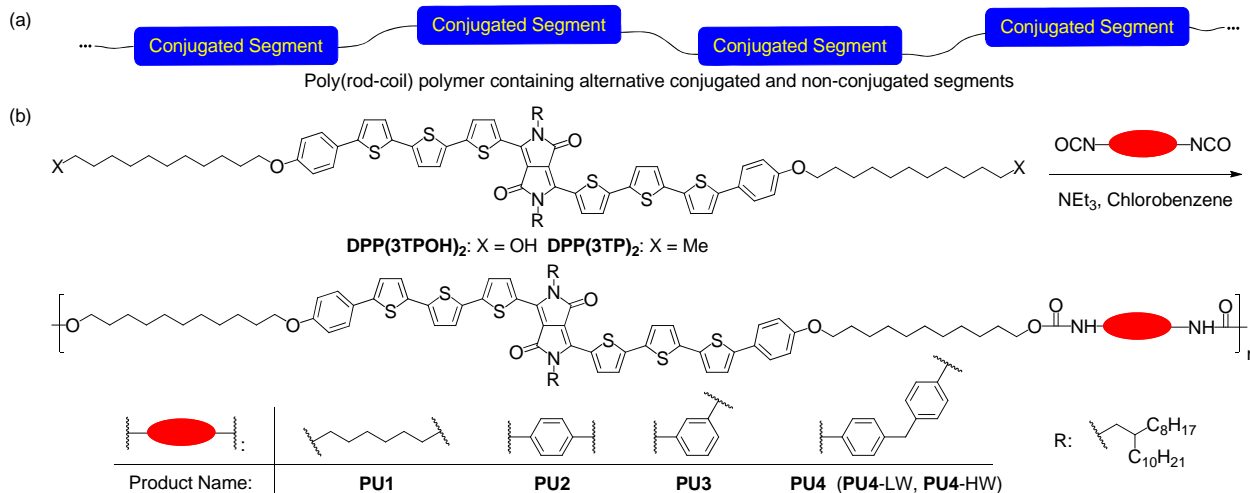
and basically determine optoelectronic properties of the material. For photovoltaic application, these segments are suggested to be made of donor-acceptor (D-A) and related structures for efficient light harvesting.¹⁻³ Since they have definite chemical structures, like conventional photovoltaic compounds, the final material would possess a performance less sensitive to its molecular weight and polydispersity. Furthermore, owing to its polymeric nature, good film formation potential could be expected for this kind of materials.

In this contribution, we report the first set of examples based on well-known polyurethane chemistry. Firstly, we synthesized compound **DPP(3TPOH)₂** bearing one hydroxyl unit at both ends and a diketopyrrolopyrrole-centred D-A-D conjugated moiety⁵ (Scheme 1b and ESI†). Secondly, **DPP(3TPOH)₂** was copolymerized with various diisocyanate monomers, including hexamethylene diisocyanate, 1,4-phenylene diisocyanate, 1,3-phenylenediisocyanate, and methylene-diphenyl 4,4'-diisocyanate, and produced four kinds of polyurethane polymers named as **PU1**, **PU2**, **PU3**, and two **PU4** (**PU4-LW** and **PU4-HW**) with different molecular weight, respectively. The average number molecular weight (M_n) and polydispersity index (PDI) were determined to be 4.12 kDa and 1.08 for **PU1**, while 6.40 kDa and 1.15 for **PU2**, 6.66 kDa and 1.40 for **PU3**, 7.90 kDa and 1.39 for **PU4-LW**, and 16.7 kDa and 1.94 for **PU4-HW**. Obviously, **PU1**, **PU2**, **PU3** and **PU4-LW** have comparable molecular weight, while M_n of **PU4-HW** is doubled. Meanwhile, compound **DPP(3TP)₂** with saturated alkyl end chains were prepared as small molecular reference compound for comparison.

Compared with **DPP(3TP)₂**, polymer **PU1**, **PU2**, **PU3** and **PU4** have different thermal properties and solid-state structure. Thermogravimetric analysis (TGA, Fig. S10, ESI†) revealed that these polymers have a 5%-weight-loss decomposition temperature (T_d) in the range of 258–298 °C, lower than **DPP(3TP)₂** (383 °C). In the differential scanning calorimetry (DSC, Fig. S11, ESI†), only a glass transition around 60 °C and an weak endothermic peak at 160 °C were observed for **PU3** and **PU4** in the second heating procedure, while three small peaks around 88, 101, and 187 °C for **PU2**. In sharp

contrast, a couple of intense phase transition peaks (51, 102, 138 and 176 °C) appeared in the second heating DSC trace of **DPP(3TP)₂**. Especially, the endothermic enthalpy for the peak at 138 °C is extremely large, suggesting that **DPP(3TP)₂** is a crystalline material. X-ray diffraction analysis (XRD, Fig. S12, ESI†) further confirmed that

DPP(3TP)₂ is crystalline at room temperature while **PU2–PU4** are amorphous. Although a sharp phase transition was observed around 115 °C together with a weak one around 155 °C for **PU1** polymer, the non-structured XRD profile indicates it is also an amorphous material at room temperature.



Scheme 1 (a) Schematic representation of proposed poly(rod-coil) photovoltaic polymers. (b) Synthesis of photovoltaic polyurethanes.

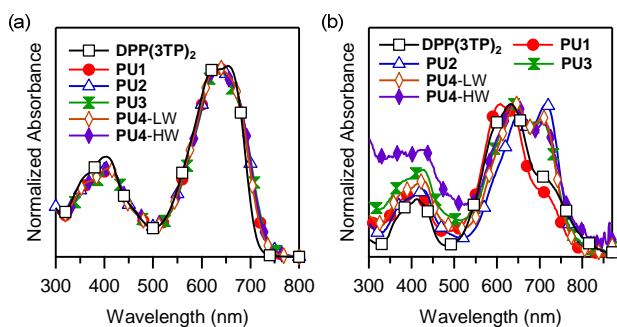


Fig. 1 Normalized UV-vis absorption spectra of **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW** in chloroform solutions with a concentration of 1×10^{-5} M (a) and in film state (b).

Fig. 1 displays UV-vis absorption spectra of the polymers and the reference compound in both solution and film state. In chloroform solution, all the polymers exhibited a similar electronic absorption spectrum to **DPP(3TP)₂**, with two featured bands in the regions of 300–500 nm and 500–750 nm for $\pi\text{-}\pi^*$ and intramolecular charge transfer (ICT) transition, respectively (Fig. 1a).⁵ It is valuable to point out that the two peaks around 622 and 654 nm observed for the ICT band of **DPP(3TP)₂** are due to the vibronic progression since they did not change upon dilution (Fig. S13, ESI†). In film state, **PU2–PU4** displayed a new intense peak in the range of 705–714 nm in addition to their 10–19 nm-red-shifted ICT bands (Fig. 1b). This suggests the occurrence of strong $\pi\text{-}\pi$ interactions among the conjugated segments in the film state. In comparison, **DPP(3TP)₂** only showed a relatively weak shoulder at this region, indicating its film structure is not favourable for $\pi\text{-}\pi$ interactions among the molecules. For **PU1** polymer film, a blue-shifted ICT band (606 nm) as referred to that in solution (630 nm), together with a weak shoulder at 708 nm, was observed, suggesting the formation of a different aggregation style,

probably H-aggregate. Although the differences were observed in the absorption peaks, the film state absorption spectra for either polymers or **DPP(3TP)₂** displayed a same onset point around 780 nm, giving an energy band gap of 1.59 eV for all the materials. Cyclic voltammetry further confirmed that all the materials have a similar highest occupied molecular orbital (HOMO) energy level at -5.3 eV (Fig. S14, ESI†). These results indicate the change from small molecule to polymer and the different urethane linkers, as well as polymer molecular weight, do not alter many basic optoelectronic properties of the materials, such as absorption bands in solution, energy band gap and molecular orbital energy levels, but does affect the aggregation-induced properties of the materials.

Bulk heterojunction OSCs with a conventional structure of ITO/PEDOT:PSS/active layer/Al using the synthesized polymers and **DPP(3TP)₂** as donor component while [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as acceptor component were fabricated. It was found that the best weight ratio of donor/PC₆₁BM varied with the checked donor materials, in which 1:2 for **DPP(3TP)₂**, 1:3 for **PU3**, 1:5 for **PU4-LW**, while 1:4 for the rest polyurethanes (Table S1–S6, ESI†). Other fabrication conditions, including solvent, concentration, spin-coating rate, annealing temperature, the addition of 1,8-diodooctane (DIO) were also optimized. Fig. 2 displays the device performance of all the checked systems under their respective optimized conditions, while their parameters are summarized in Table 1. From these data, one can find that all the polymers under optimized conditions displayed an improved photovoltaic performance than **DPP(3TP)₂** with an increasing factor of 29–73%.

Detailed comparison found that the change from **DPP(3TP)₂** to the polymers did not alter open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) a lot although in some cases slight enhancement or reduction was observed. This can be well understood since the optoelectronically active segments for all the polymers are the same as

that of **DPP(3TP)₂** and all polymers do possess a similar HOMO energy level like **DPP(3TP)₂**. As for J_{SC} , external quantum efficiency (EQE) spectroscopy revealed the photocurrent of the polymer-based cells decreased in the range of 550–750 nm but increased in the range of 300–550 nm (Fig. 2b). These two sides compensated each other and thus resulted in comparable J_{SC} values. Therefore, the performance improvement of the polymer-based solar cells finally came from the enhancement in FF value, which increased from 43.2% for **DPP(3TP)₂**-based cell to over 53% for the polymer-based ones. When the comparison was carried out among the polymer blend films, one could easily find that **PU2** showed the best photovoltaic output with a PCE near 1%. More importantly, the optimized solar cell based on **PU4-LW** or **PU4-HW** having a large difference in molecular weight displayed comparable performance. This result verified our initial expect that the molecular weight has less influence on the photovoltaic properties for this new kind of photovoltaic polymers and would be a merit for their real applications.

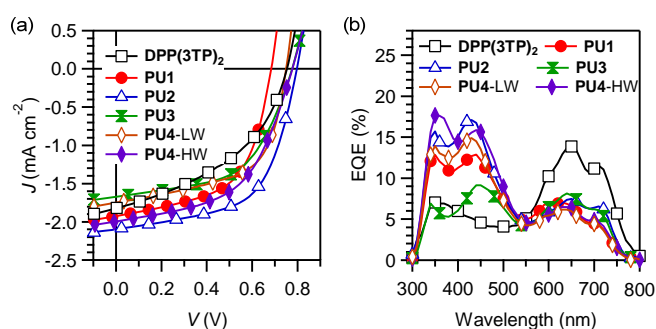


Fig. 2 (a) J - V curves under AM 1.5 G illumination with a density of 100 mW cm^{-2} and (b) EQE spectra of the best OSCs based on **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW** as donor component while PC_{61}BM as acceptor component under the optimized conditions shown in Table S1–S6 (ESI[†]).

Table 1 Device parameters of the organic solar cells shown in Fig. 2.

Donor	V_{OC} (V)	J_{SC}^a (mA cm^{-2})	FF (%)	PCE ^b (%)	μ_n^c ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_p^c ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
DPP(3TP)₂	0.76	1.82 (1.98)	43.2	0.59 (0.55)	1.3×10^{-4}	5.6×10^{-4}
PU1	0.68	1.92 (1.62)	57.0	0.75 (0.71)	1.4×10^{-4}	1.8×10^{-5}
PU2	0.80	2.09 (1.87)	58.8	0.98 (0.95)	1.8×10^{-5}	2.5×10^{-5}
PU3	0.77	1.67 (1.49)	55.1	0.71 (0.68)	6.1×10^{-5}	1.5×10^{-4}
PU4-LW	0.75	1.75 (1.57)	58.4	0.77 (0.76)	4.7×10^{-5}	5.8×10^{-4}
PU4-HW	0.78	1.99 (1.78)	53.0	0.82 (0.77)	6.0×10^{-5}	2.1×10^{-4}

^a Data in parentheses are the J_{SC} values calculated from EQE spectra shown in Fig. 2b. ^b Data in parentheses are the average values.

In order to penetrate the origination of the performance difference, the morphology and charge transportation of the blend films for the best devices were studied. As revealed by transmission electron microscopy (Fig. S15, ESI[†]), the **DPP(3TP)₂**/ PC_{61}BM blend film presented a large island-sea phase separation microstructure, while those of polymer blend films appeared homogeneous without clear phase separation. Obviously, the latter is favour to device performance since it could provide much smaller phase domains and larger heterojunction interface. On the other hand, the mobility measurements by space-charge-limited method indicate that the **DPP(3TP)₂**/ PC_{61}BM blend film possess hole and electron mobilities larger than the most polymer blend films, but comparable to some cases (Table 1). These results obviously suggest the morphology

change would be the main account for the above performance improvement observed for the polymers.

In summary, we have demonstrated a new type of polymeric photovoltaic materials, which contain multiple conjugated rigid segments but linked by non-conjugated soft chains. Compared with their small molecular reference, the present five photovoltaic polyurethane examples exhibited the performance improvement by a factor of 29–73%. Moreover, the molecular weight seems no longer to be one of the important factors that affect the material properties. Although PCE in the present examples is low, this work opens an avenue for the development of new photovoltaic materials with the features of both small molecular compounds and polymers. For improving the performance of this kind of materials, there are a lot of things that can be done, for example, the well design and optimization either on the opto-electronically active segments, or on the non-conjugated soft linking segments, including the type of linking functionalities and pattern, the nature and length of linking chains. Furthermore, this material design strategy is not only limited to the OPV materials, but also can be applied in the fields of organic field-effect transistors and organic light-emitting diodes.

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Notes and references

Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling road, Shanghai 200032, China. E-mail: liws@mail.sioc.ac.cn.

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