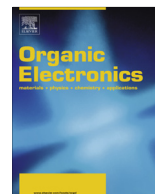




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Synthesis and characterizations of poly(3,6-thienophenanthrene) and poly(2,7-thienophenanthrene) and their applications in polymer light-emitting devices and solar cells

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ABSTRACT

Here we report the synthesis of two novel phenylene-based polymers—poly(3,6-thienophenanthrene) (PTP36) and poly(2,7-thienophenanthrene) (PTP27) via base-free Suzuki–Miyaura reaction. The structure and electroluminescent properties of the meta-linked PTP36 and para-linked PTP27 are fully characterized. The obtained polymers were found to be liquid-crystalline, with broad band gap of 2.72 eV and 2.49 eV, respectively, which are much smaller than those of corresponding polyphenanthrenes. On the basis of PTP36 and PTP27, copolymers of 2,7-thienophenanthrene and 3,6-thienophenanthrene with 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole (DBT), namely PTP36-DBT and PTP27-DBT were prepared and be investigated as a potential donor material for polymer solar cells. The preliminary data show that the maximal power conversion efficiencies (PCEs) of the PTP27-DBT- and PTP36-DBT-based polymer solar cells are 3.5% and 0.9%, respectively.

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1. Introduction

Conjugated polymers are currently attracting a great deal of attention as they can be used as novel organic semiconductors in many kinds of organic optoelectronics, such as polymer light-emitting devices (PLEDs), organic

photovoltaic cells (OPVs) and organic field effect transistors (OFETs), organic lasers, and memory cells in recent years [1–6]. These polymer-based devices can be fabricated by solution-processed process, thus will continue to gain importance in view of their immense potential as promising, lightweight and low-cost lighting source, energy source or integrated circuits. Recent developments in the processing and patterning for active optical and optoelectronic devices via ink-jet printing, roll-to-roll manufacturing, and other soft lithography techniques have verified the potential of these devices as low-cost, large-area optoelectronic devices, while the development of novel semiconducting polymer continue to be the central issue towards the realization of high performance organic

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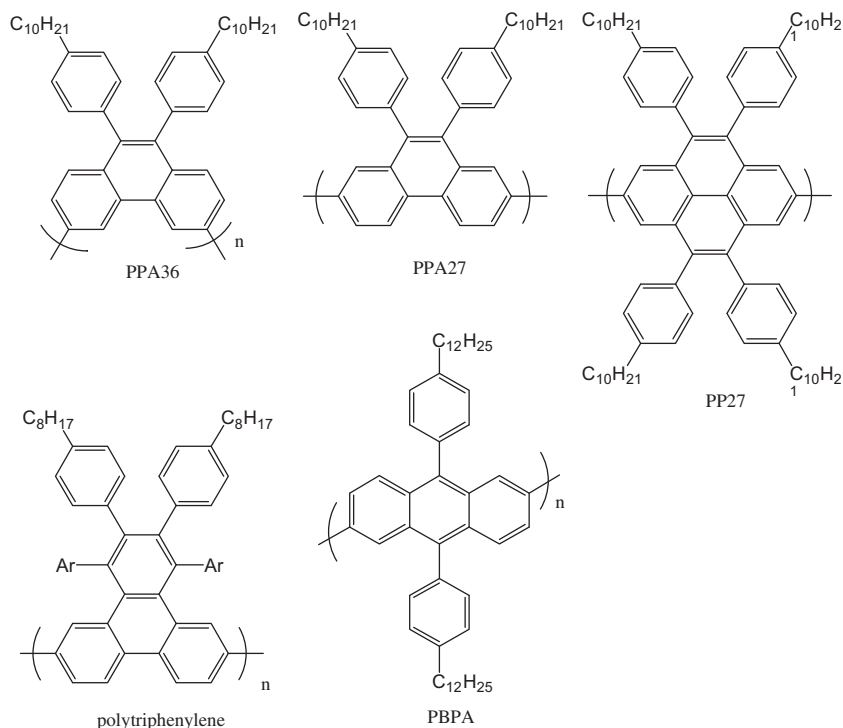
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optoelectronics. Among the material catalogs of conjugated polymers, polyphenylene-based materials are one of the most intensively studied since the synthesis of poly-p-phenylenevinylene (PPV) can be tracked back to 1968 (reported by Wessling and Zimmermanin) [7], especially when polymer light-emitting diodes were invented in 1990 [8]. So far, poly-p-phenylenevinylene (PPV), in conjunction with polyfluorene (PF) [9], are the most famous conjugated polymers for PLEDs applications.

However, heterocyclic polymers and fused-ring containing polymers are becoming more and more important with the rapid development of applications in OPVs and OFETs. Typically, polyfluorenes (PFs), poly(2,7/3,6-phenanthrylene)s (PPAs) [10–12] and polypyrene (PP) [13] (as shown in Scheme 1), are blue light-emitting polymers in common and thus unsuitable for the solar conversion purpose due to their relatively smaller absorption overlap with the solar spectrum. In order to broaden the absorption range of polyphenylenes, the most straight-forward strategy is to introduce donor-acceptor moieties and form copolymers with low band-gap polymers. This strategy have been verified in a great volume of literatures including the early report of poly(9,9-dioctylfluorene-co-4,7-di-2-thienyl-2,1,3-benzothiadiazole) (PFO-DBT) with PCE of 2.24% in 2004 [14] and the recent reported poly[2,7-(5,5-bis-(3,7-dimethyloctyl)-5H-dithieno[3,2-b:2',3'-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothia diazole)] with a PCE of 10.6% in a tandem cells [15]. Usually, these two donor-acceptor copolymers are composed of electron-rich (thiophene and/or phenylene) and electron-deficient (benzothiadiazole) units, and both of them determine the band gaps and energy levels

of the copolymers, eventually affect the PCEs of the resulting solar cells. Although phenylene-based polymers are inferior to polythiophenes for OPVs at present in device performance, the PSCs from which usually exhibits higher open-circuit voltages (V_{oc}) than those from polythiophenes since V_{oc} is thought to be associated with the differences between the HOMO (highest occupied molecular orbital) of the donor and the LUMO (lowest unoccupied molecular orbital) of the acceptor [16]. As polyphenylenes usually have lower HOMO level, it is expected that there is still some potential to get high PCEs with them [17].

In order to fully exploit the competitive advantages of phenylene-based polymers and improve their photovoltaic properties, novel phenylene derivatives with broad absorption range are highly desired. Therefore, it is essential to delocalize the π systems of the repeating units. Usually the bandgap of conjugated polymers decrease with the increasing numbers of fused rings in their repeating units, for example, the band gaps of polytriphenylenes and polyphenanthrylenes were reported to be 2.87–2.9 eV [18] and 3.1 eV [10–12], respectively, as a results of having one more ring in triphenylene. To date, there is no report on the photovoltaic properties of these broad bandgap polymers, mainly due to unfavourable absorption for light harvest purpose. In order to extend the promising electron donor material catalog to phenylene-based polymers and decrease their band gap, we propose to combine a thiophene ring with two long chain esters and phenanthrylene to form a novel monomer, namely thienophenanthrene, which is indeed a rarely studied repeating unit for electron polymers donors. Here we synthesized two homopolymers



Scheme 1. Structure of some phenylene-based polymers and polyanthracene (PBPA).

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