Conjugated alternating copolymers containing both donor and acceptor moieties in the main chain†

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A straightforward synthesis toward two conjugated alternating copolymers consisting of 2,7-linked carbazole donor (2,7-Cz) and ladderized pentaphenylene with diketone bridge (LPPK) acceptor chromophores is reported: the copolymers differ by the repeat unit ratio between the 2,7-Cz and LPPK units within the backbone; energy and charge transfer properties and supramolecular organizations of donor–acceptor moieties in these copolymers have been studied *via* optical spectroscopy and two-dimensional wide-angle X-ray scattering (2D-WAXS); preliminary results such as the efficient energy and charge transfer and π-stacking character in the solid state suggest that the copolymers are potentially useful for photovoltaic devices.

Polymer solar cells attract considerable attention due to their unique advantages, such as low cost, light weight, and potential use in flexible devices.[1–5] They are often based on polymer donors and molecular acceptors in blends, so-called bulk heterojunctions. A general drawback of the bulk heterojunction design is the fact that the transport and collection of charges in a disordered nanoscale blend can be hindered by phase boundaries and discontinuities. One way to overcome this drawback is to covalently link the donor and acceptor in a single polymer chain.[6] This method has important advantages because the intrinsic tendency of each segment in copolymers to aggregate in an individual phase provides a means to create a well-ordered nanoscale morphology (*e.g.*, spheres, cylinders, lamellar), governed by the relative volume fractions. Moreover, the built-in intramolecular charge transfer can facilitate ready manipulation of the electronic structure, and lead to low band gap semiconducting polymers.[7–13] In particular, through design and synthesis of new polymer structures, donor–acceptor conjugated polymers can extend to systems with efficient photoinduced charge-transfer, -separation, and -transport processes for photovoltaic devices.[14–16] While this principle has been utilized in engineering various materials to create fascinating architectures, conjugated polymers containing donor–acceptor units in the main chain have received limited attention.[17–21]

Recently our group has reported the photovoltaic device based on a poly(2,7-carbazole) derivative as an electron-donor material in combination with PCBM acceptor yielding a good efficiency of 0.6%.[22] Furthermore, we have previously synthesized a ladder-type pentaphenylene with two ketone groups at the bridges as an excellent electron-accepting (n-type) material.[23] In these regards, herein is presented the synthesis and characterization of a new class of donor–acceptor (D–A) copolymers, represented by **P1** and **P2** (Chart 1), which consist of alternating 2,7-linked carbazole (2,7-Cz) and ladderized pentaphenylene with diketone bridge (LPPK) segments. **P1** comprises 2,7-Cz and LPPK chromophores in a 1 : 1 ratio whereas **P2** contains a 2 : 1 ratio in backbone. The basic photophysics and supramolecular organization of the copolymers (**P1** and **P2**) in solid state have been studied.

The covalently linked D–A system 2,7-Cz–LPPK has been synthesized according to the route depicted in Scheme 1 utilizing the synthetic approach previously developed for **1** and **3**.[22–24] The diboronic ester **2** as an acceptor unit was prepared by the palladium-catalyzed Suzuki coupling reaction of **1** with bis(pinacolato)diboron under Pd(dppf)Cl_2–KOAc–dioxane conditions. Since poly(2,7-carbazole) derivatives have been known to have limited solubility in organic solvents, the introduction of the bulky solubilizing group (4-[tris-(4-octyloxyphenyl)methyl]phenyl) at the nitrogen on the carbazole unit was carried out. In addition, the solubilizers with alkoxy-side chains can improve the electron-donating characteristics. The coupling of **3a** and *p*-fluorobenzoicacidmethylester gave *N*-arylcarbazole derivative **4a** under sodium hydride as a strong base and subsequent addition of 4-octyloxybromobenzene generated the carbazole alcohol compound **5a**. The corresponding phenol **6a** was obtained by the treatment with acetyl chloride followed by phenol, which then underwent nucleophilic substitution of **6a** with octylbromide to produce the desired *N*-alkoxyaryl-2,7-dibromocarbarzole derivative **7a** as a

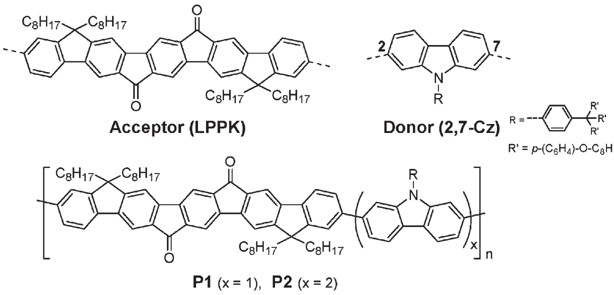

Chart 1 Structures of 2,7-Cz and LPPK alternating copolymers (**P1** and **P2**).

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† Electronic supplementary information (ESI) available: Synthesis, UV-vis absorption and PL spectra of **P1**, the concentration dependent PL spectra of the LPPK monomer and the measurement of the 2D-WAXS. See DOI: 10.1039/b617931b

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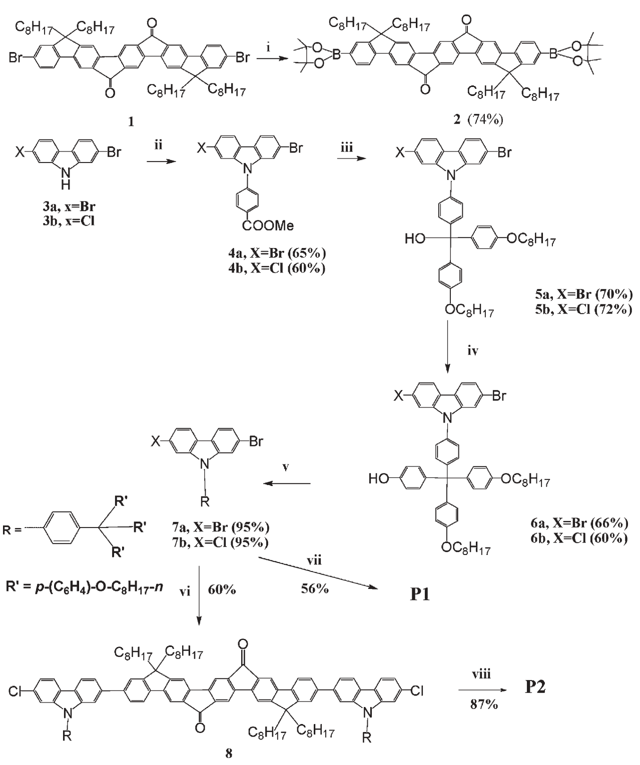

Scheme 1 Synthesis of the D–A copolymers **P1** and **P2**. (i) bis(pinacolato)diboron, KOAc, Pd(dppf)Cl_2, dioxane, 80 °C, overnight; (ii) NaH, *p*-fluorobenzoicacidmethylester, DMF, 70 °C, 3 d; (iii) 4-octyloxybromobenzene, n-BuLi, THF, RT, overnight; (iv) acetyl chloride, 80 °C , 1 day, then phenol, 120 °C, 3 d; (v) KOH, octylbromide, RT, 1 day; (vi) **7a**, **2**, K_2CO_3, tetrakis(triphenylphosphine)palladium, Toluene, H_2O, Argon, 85 °C, 3 d; (vii) 7b, **2**, K_2CO_3, tetrakis(triphenylphosphine)palladium, THF, H_2O, Argon, 80 °C, overnight; (viii) Bis(cyclooctadiene)nickel, cyclooctadiene, 2,2′-bipyridine, dry toluene and dry DMF, 60 °C, 30 min, then monomer **8**, 75 °C, 2 d.

donor building unit. The copolymer **P1** was synthesized by Suzuki polycondensation of **2** and **7a** under palladium(0) catalysed condition.

The same procedures as described above were adopted for the synthesis of the 2-bromo-7-chloro-9-{4-[tris-(4-octyloxyphenyl)-methyl]phenyl}carbazole (**7b**) starting from carbazole **3b** (Scheme 1). Suzuki coupling of **2** and **7b** under palladium catalysis generated the target dichloride monomer **8**. The analogous copolymer **P2** was prepared *via* a nickel(0)-mediated Yamamoto polycondensation. Both copolymers (**P1** and **P2**) were readily soluble in common organic solvents, tetrahydrofuran (THF), toluene, dichloromethane (DCM), *etc.*. Gel-permeation chromatography (GPC) analysis with PPP standard exhibited a number-average molecular mass (M_n) of 1.0 × 10^4 g mol^{-1} and 4.4 × 10^4 g mol^{-1}, for **P1** and **P2**, respectively with a polydispersity of 1.38 and 1.91.

The optical properties of **P1** and **P2** were similar. Here, we took **P2** as an example (**P1** is shown in the supporting information†). Fig. 1 shows the UV-vis absorption spectra of **P2** in a dilute chloroform solution and a drop-casted film on quartz glass at room temperature, together with the absorption spectra in different solvents. **P2** showed two absorption maxima at around 345 nm and 408 nm in solution, which correspond to the π–π* transition of the copolymer's backbone. An absorption band at 560 nm corresponding to the n–π* transition in the carbonyl of LPPK was weak.[23,25] The effect of the solvent polarity on **P2** absorption was displayed in Fig. 1(b). By changing the solvent from toluene to chloroform, the peak at around 550 nm shifted to 560 nm. Comparing the UV-vis spectra of **P2** thin film with that of the dilute solution, it can be clearly seen that the absorption spectra of thin films were apparently broader, the position of the main absorption peaks were red-shifted and the absorption intensity at 560 nm was stronger, which may be due to the stronger π–π stacking of the LPPK units in the main chain. It is postulated that this feature is associated with the formation of close-packed self-organized layers by a strong interchain interaction in this π-conjugated system in the solid state.[26] Comparing **P1** with **P2**, it could be found that the absorption maximum at 560 nm of **P1** was stronger than that of **P2** relative the intensity of the copolymer backbone, which can be due to the higher 2,7-Cz content in **P2**.

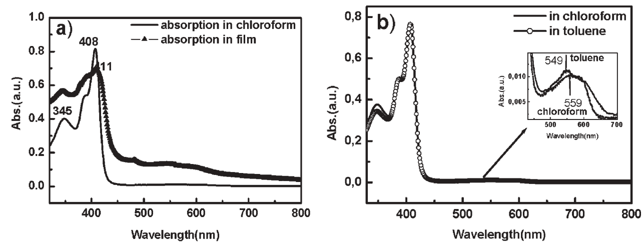

Fig. 1 (a) UV-vis absorption of **P2** in a dilute chloroform solution and drop-casted film on quartz glass; (b) absorption spectra of **P2** in different solvents.

The PL of **P2** in solution was very weak. The emission spectra of **P2** showed only one maximum at 696 nm, which was attributed to LPPK units in these copolymers. This was supported by concentration dependent photoluminescence spectroscopy of pentaphenylene diketone monomer, which demonstrated a red-shift from 620 nm to 633 nm with increasing concentration, and finally the emission in solid state was at around 720 nm (supporting information†). There was no emission from the 2,7-Cz subunits, implying complete energy transfer from 2,7-Cz donor to LPPK acceptor moieties,[27,28] while the luminescence quenching of the acceptor moiety in **P2** compared to pure acceptor LPPK monomer indicated the charge transfer involved: when the **P2** has the same concentration as the pure monomer LPPK, stronger emission quenching of **P2** was found (supporting information†), which supports the existence of a charge separated state upon photoexcitation in the D–A polymer.

The supramolecular structures of both polymers **P1** and **P2** have been investigated by two-dimensional wide-angle X-ray scattering (2D-WAXS) on extruded filaments.[29] Fig. 2 shows a characteristic 2D X-ray pattern of **P2**. The distinct and strong reflections were related to a well-aligned macroscopic organization in the extruded sample, which was also obvious for **P1**, confirming no influence of the chemical structure difference on the ordering of both copolymers. The equatorial small-angle reflections indicated a lateral distance between the conjugated polymer chains of 1.8 nm for **P1** and 1.92 nm for **P2**. Since this value was determined by the length of the substitutions, these distances were in a good agreement with the difference in the attached units of **P1** and **P2**. The equatorial wide-angle reflections corresponded to the

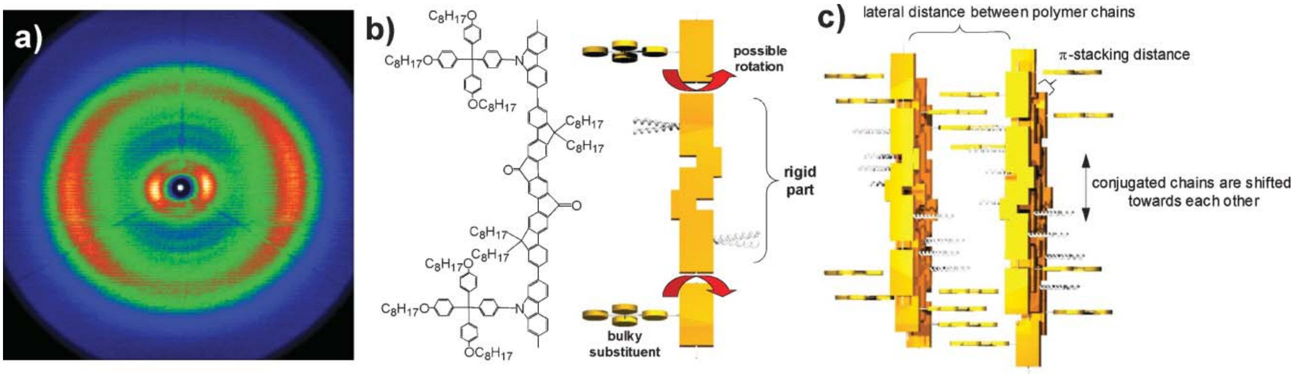

Fig. 2 (a) 2D-WAXS of **P2** at room temperature, schematic illustration of the (b) polymer conformation and (c) supramolecular organization.

π-stacking period of 0.45 nm and were in a typical range for conjugated polymers. On the other hand, the appearance of a strong scattering intensity indicating π-stacking interactions between the macromolecules in both the case of **P1** and **P2** is quite surprising. One might assume initially that the 4-[tris-(4-octyloxyphenyl)methyl]phenyl substituents hindered a stacking. However, the packing during self-assembly takes place due to a most probable flipping of the polymers. Additionally, the backbones of **P1** and **P2** were not very rigid and planar allowing a spontaneous twisting during stacking and thus diminishing in this way the sterically demanding influence of the 4-[tris-(4-octyloxyphenyl)methyl]phenyl. Furthermore, the relatively weak intensity scattering correlated to 0.73 nm, which was in accordance to the monomer repeating distance along the conjugated backbone, suggested that the polymer chains were shifted towards each other, supporting the self-assembly.

In summary, we have described the synthesis and characterization of soluble conjugated D–A copolymers (**P1** and **P2**) containing electron-donating 2,7-Cz and electron-accepting LPPK subunits. The resulting copolymers exhibited efficient energy and charge transfer between D and A moieties in the solid state, as proved by optical spectroscopy. Furthermore, both the copolymers revealed an alignment well due to a pronounced π-stacking interaction between the conjugated polymer chains. These attractive properties such as energy and charge transfer and macroscopic organization establish them as good candidates for photovoltaic devices.

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