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ARTICLE TYPE

Donor-acceptor alternating copolymers containing thienopyrroledione electron accepting units: Preparation, redox behaviour, and application to photovoltaic cells

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1. SEC Experimental

Analytical size exclusion chromatography (SEC) characterizations of the fractions of the four *push-pull* low band gap alternated copolymers **P1-P4** obtained after their initial purifications by soxhlet extraction and of the molecular weight-calibrated and low molar weight dispersity value's P1-F1/F9 sub-fractions were performed on a Chemstation 1260 (Agilent Technologies) equipped with a 300*7.5 mm PLgel Mixed-D 5 μ m/10⁴Å column (Varian), a diode array UV-Vis detector (DAD) and a fraction collector.

The molecular weight-calibrated and low molecular weight dispersity value's sub-fractions P1-F1/F9 sub-fractions were obtained by the SEC fractionation of the soluble fraction in chloroform of the copolymer P1. In a single analytical SEC fractionation cycle, up to 9 fractions of an equal 0.25 mL volume were collected with the fraction collector. Five consecutive analytical SEC fractionation cycles were then performed resulting in a cumulated volume of *ca.* 1.25 mL per sub-fraction (See Supporting Figure S2).

Typically *ca.* 1.0mg/g HPLC-grade of amylene-stabilized CHCl₃ (Acros, 99.8%) stock solutions of the fractions of P1-P4 after their initial purifications by soxhlet extraction were analyzed. As an example, see the elugram of the chloroform soluble fraction of the *push-pull* low band gap alternated copolymer P1 after its initial purification by soxhlet extraction given in the supporting figure S1. The obtained 1.25mL CHCl₃ solutions of the P1-F1/F9 sub-fractions were either concentrated or diluted in order to facilitate their analytical SEC characterizations. The column temperature and the flow rate were fixed to 313 K and 1 mL.min⁻¹, respectively. The calibration curve was built using 13 polystyrene (PS) narrow standards.

Two runs of 20 μ L injection of appropriately diluted or concentrated HPLC-grade of amylene-stabilized CHCl₃ (Acros, 99.8%) solutions were typically analyzed for each sample with an UV-Vis detection at 375 nm. Macromolecular parameters deduced from the analytical SEC characterizations of the fractions of *push-pull* low band gap alternated copolymers P1-P4 obtained after their initial purification by soxhlet extractions and of the molecular weight-calibrated and low molar weight dispersity index value's P1-F1/F9 sub-fractions are summarized in Table 1 and Table 2, respectively.

Supporting Figure S1

Supporting Figure S2

2. Fabrication of Photovoltaic Devices and Testing

The bulk-heterojunction organic solar cells, with the configuration of Glass/ITO/PEDOT:PSS/Polymer:[60]PCBM/Aluminum, were prepared on commercial (ITO)-coated glass substrate (25x25 mm²) with a sheet resistance of ≤ 10 Ohms/sq (Thin Film Devices Inc, USA). Each substrate was patterned using photolithography techniques before ITO was etched using warm hydrochloric acid for 20 min. Prior to use, the substrates were cleaned with detergent and deionized water. Then, they were ultrasonicated in deionized water and in isopropanol. ITO substrates were spin-coated (2000 rpm, 60 s) with a thin film (50 nm) of (PEDOT:

PSS, Baytron P, H. C. Starck) and dried at 120°C for one hour. A blend of [6,6]-phenyl C₆₁-butyric acid methyl ester ([60]PCBM) (Nano-C, USA) and P1 (1:2, 10 mg mL⁻¹) was solubilized overnight, filtered through a 0.45 μ m poly(tetrafluoroethylene) (PTFE) filter, spin-coated at 1000 rpm for 60 s (thickness = 82 nm). The devices were completed by deposition of a 100 nm Al layer. This layer was thermally evaporated at a pressure of 3 10⁻⁵ Torr at room temperature. The thicknesses of films were recorded by a profilometer (Dektak IIa).

Current versus potential curves (*I-V* characteristics) were measured with a Keithley 2400 Digital Source Meter under a collimated beam. Illumination of the cells was done through the ITO side using light from 150 W Oriol Instruments Solar Simulator and xenon lamp with AM1.5G filter (No. 81094) to provide an intensity of 100 mW cm⁻² which was calibrated with a photodiode OSI-optoelectronics UV-013D. All fabrications and characterizations were performed in an ambient environment without a protective atmosphere.

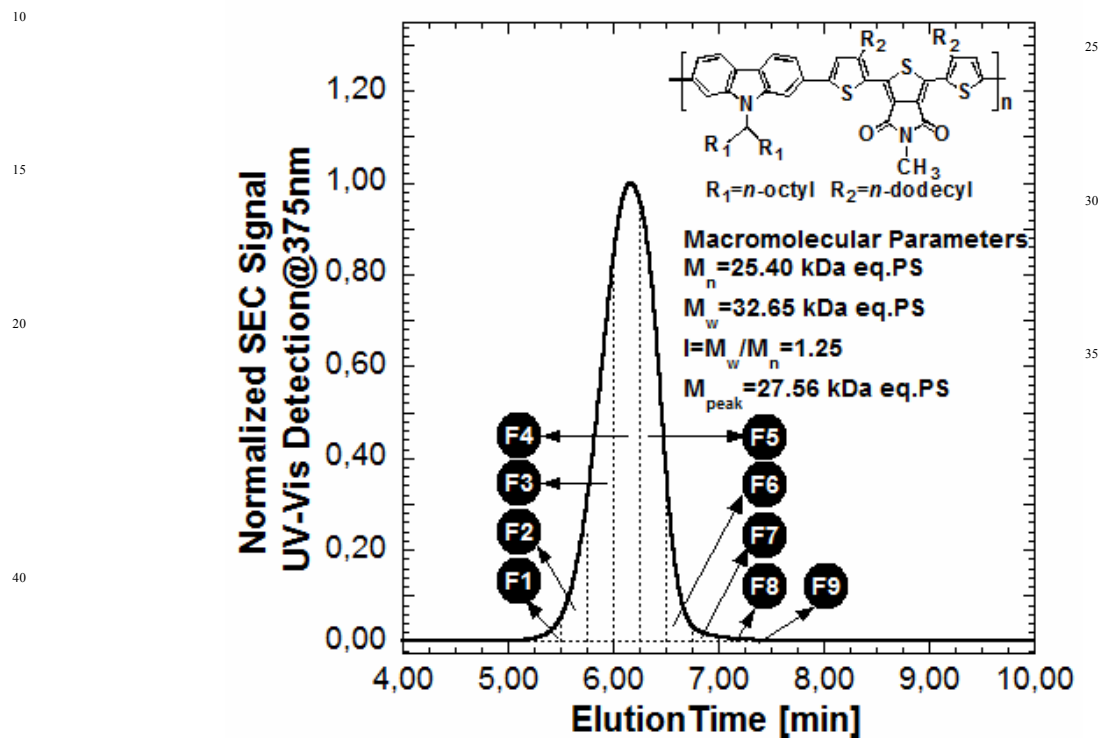
3. Oxidation potential of carbazole-thienopyrroledione *push-pull* copolymer

Supporting Figure S3

Figures

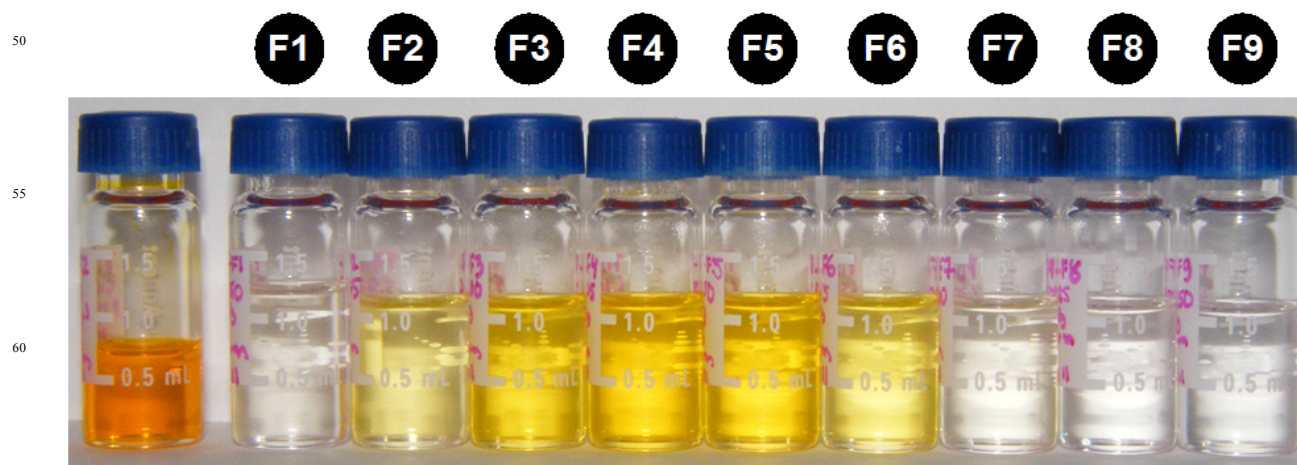
Supporting Figure S1

- 5 SEC Elugram, Macromolecular parameter (M_n , M_w , $I=M_w/M_n$ & M_{peak} (mass @ apex of the elugram), and fractionation scheme into its nine P1-F1/F9 sub-fractions of the soluble fraction in *n*-hexane of the DA low band gap alternated copolymer **P1** after its initial purification by soxhlet extraction. Inset: chemical structure of the repeating unit of the D/A low band gap alternated copolymer **P1**.



Supporting Figure S2

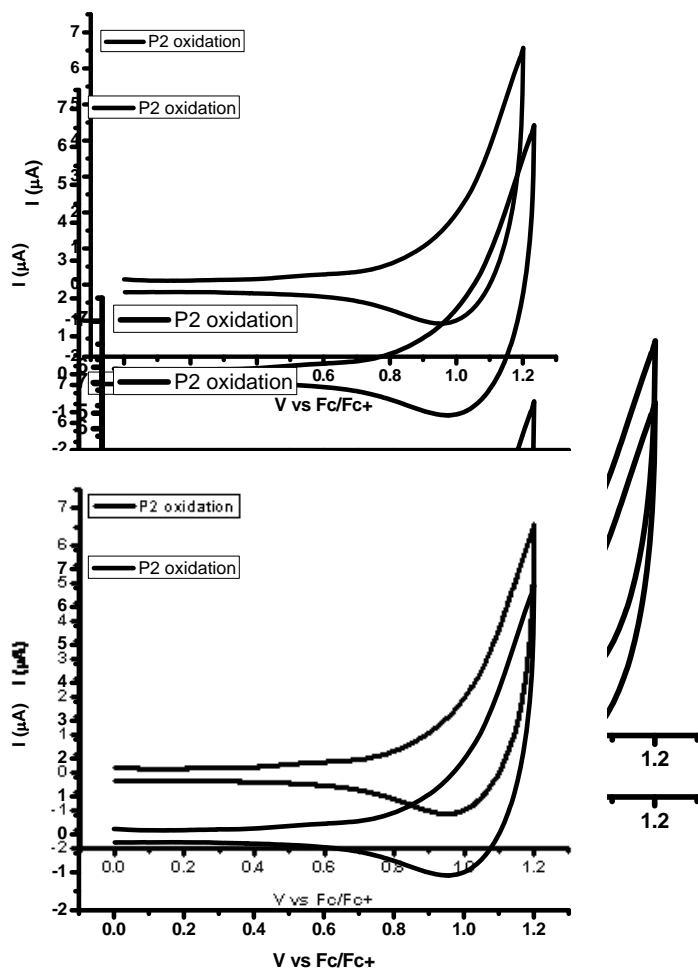
- 45 (from the left to the right): Optical picture (daylight condition with flash) of $CHCl_3$ solutions of the DA low bandgap alternated copolymer **P1** soluble fraction in *n*-hexane after its initial purification by soxhlet extraction vs. its molecular weight-calibrated and low polymolecularity index value's P1-F1/F9 sub-fractions obtained after 5 consecutive analytical SEC fractionation cycles.



Supporting Figure S3

3. Oxidation potential of carbazole-thienopyrroledione *push-pull* copolymer

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