

SUPPORTING INFORMATION

Main-chain Poly(fullerene) Multiblock Copolymers as Organic Photovoltaic Donor-Acceptors and Stabilizers

Mahfoudh Raissi,^{1,2a*} Harikrishna Erothu,^{3b} Emmanuel Ibarboure,³ Habiba Bejbouji,¹ Henri Cramail,³ Eric Cloutet,^{3,4*} Laurence Vignau^{1,2*}, Roger C. Hiorns,^{4,5*}

1. Bordeaux INP, IMS, CNRS UMR 5218, F-33400, Talence, France.
2. Université de Bordeaux, IMS, CNRS UMR 5218, F-33400, Talence, France
3. Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques (LCPO), (UMR 5629), ENSCBP, IPB, 16 avenue Pey Berland, 33607 Pessac Cedex, France.
4. CNRS, Laboratoire de Chimie des Polymères Organiques (LCPO), (UMR 5629), ENSCBP, IPB, 16 avenue Pey Berland, 33607 Pessac Cedex, France.
5. CNRS/Univ Pau & Pays Adour, Institut des Science Analytiques et Physico-Chimie pour l'Environnement et les Matériaux, UMR5254, 64000, Pau, France.

Current Addresses:

- a. CEISAM, Nantes University, 123 rue de la houssinière, 44322, Nantes, France
- b. Center for Advanced Energy Studies (CAES), Koneru Lakshmaiah University, Green Fields, Vaddeswaram, Guntur, Andhra Pradesh, India - 522 502

*Corresponding authors: Roger C. Hiorns (roger.hiorns@univ-pau.fr); Eric Cloutet (cloutet@enscbp.fr); Laurence Vignau (laurence.vignau@ims-bordeaux.fr)

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Apparatus

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker[®] Avance 400 spectrometer. Gel permeation chromatography (GPC) was performed using THF as eluant at 40 °C and flow rate of 1 mL min⁻¹ through 4 columns (TSK G5000HXL (9 μm), G4000HXL (6 μm), G3000HXL (6 μm), and G2000HXL (5 μm)) and connected to Varian refractometer and UV-visible spectrophotometer calibrated against linear polystyrene (PS) standards for use with P3HT and P3HT-containing copolymers. AFM was performed under air at 25 °C using a Nanoscope IIIa microscope operating in tapping-mode. The probes were commercially available silicon tips with a spring constant of 42 N m⁻¹, a resonance frequency of 285 kHz, and a typical radius of curvature in the 8-10 nm range. Both topography and phase signal images were recorded at a resolution of 512 × 512 data points. TEM was performed using with a Philips EM400 microscope at an accelerating voltage of 80 kV. BF-TEM measurements were prepared by floating the photoactive layer on water, transferring the film to a TEM copper grid and recording under slightly defocused conditions. Current density and voltage (*J-V*) characterisations of devices were conducted by a computer-controlled Keithley 4200 SCS and under AM 1.5G (100 mW cm⁻²) illumination (KHS Solarcell) calibrated against an IL1400BL radiometer.

Materials

C₆₀ (99.9 %) was obtained from MER Corporation (USA). PCBM (99%) was obtained from Solenne BV. Other materials were obtained from Aldrich (France), unless otherwise stated. Solvents were distilled from over their respective drying agents under dry nitrogen. K₂CO₃ was dried at 135 °C under reduced pressure for 24 h. Where possible, air and light were excluded from the handling of polymers, and reactions were performed in flame dried, dry nitrogen flushed glassware.

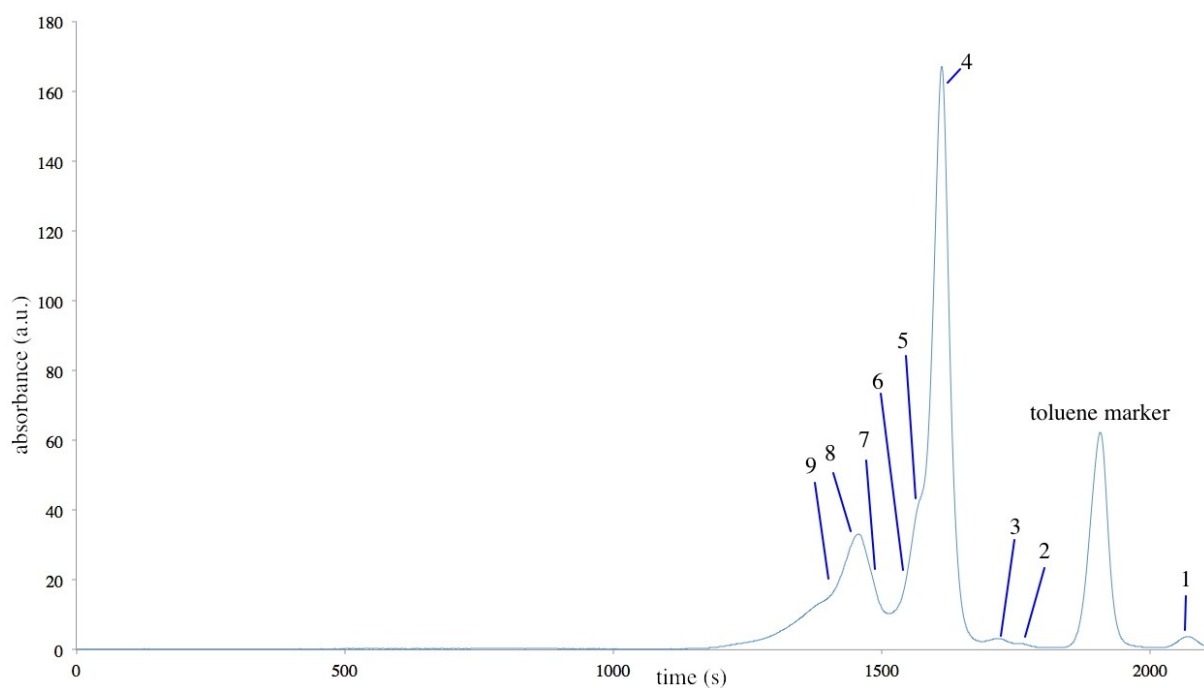


Figure S1. GPC of brut unwashed sample of PFDP (UV-254 nm) where each peak and shoulder is labelled to indicate the assumed appearance of a molecule with one more additional C_{60} group (see A. Gügel, P. Belik, M. Walter, A. Kraus, E. Harth, M. Wagner, J. Spickermann and K. Müllen, *Tetrahedron* 1996, **52**, 5007 for more details on this methodology). Note, in accordance with prior work i.e., F. Audouin *et al.*, *J. Polym. Sci. Pt A: Polym. Chem.* 2004, **42**, 3456, the fullerene (labelled 1 here) elutes after the toluene marker due to its well known retention in the column.

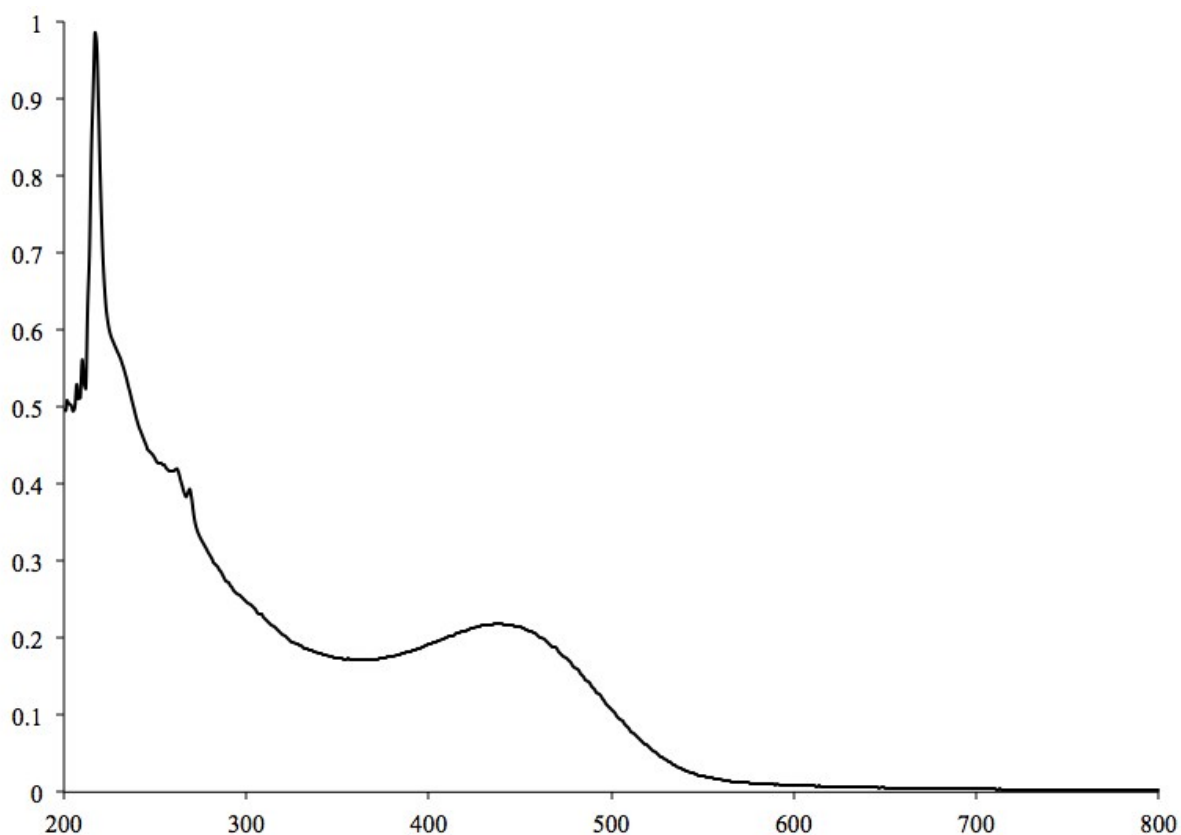


Figure S2. UV-visible spectrum of PFDP in THF at 0.01125 g L⁻¹.

Note: using Lambert-Beer's law, i.e., $A = \epsilon Cl$ where A is absorbance at the peak position, C the molar concentration, l the cell length in cm and ϵ the molar extinction coefficient, we find that at 254 nm:

$$\epsilon_{\text{PFDP}} = A/Cl = 0.426/[(0.01125 / 9930) \times 1] = 0.426 / 1.133 \times 10^{-6} = 376\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$$

To calculate the molar concentration, a value of $M_n = 9930 \text{ g mol}^{-1}$ was assumed based on the average chain containing 9 repeating units. See text of main article for details.

b

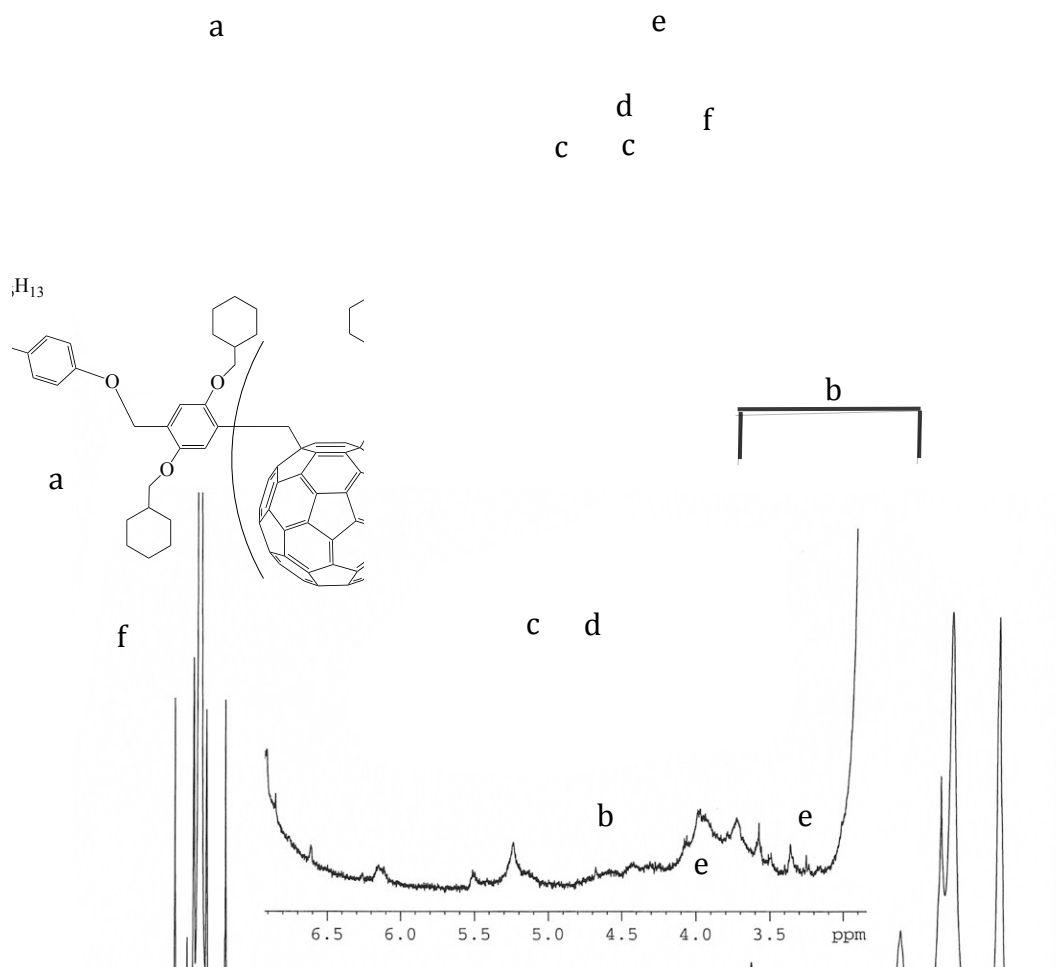


Figure S3.

Representative ¹H NMR of P3HT-*b*-PFDP (5 mg per mL, C₆D₆, ambient temperature, D1 = 6 s). Due to the long experiment times, imposed by the low solubility of the material, minor impurities such as CH₂Cl₂ (5.3 ppm) are picked up.

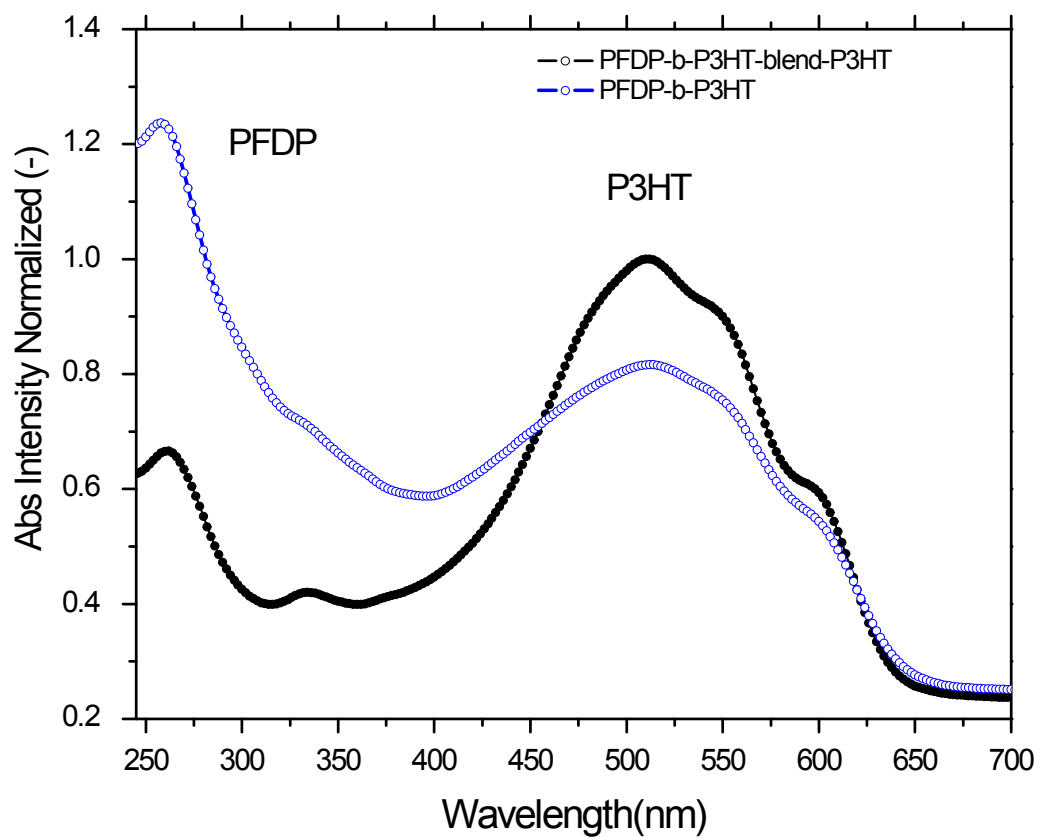


Figure S4. UV-visible spectra of annealed (180 °C, 10 min) solid state films of (P3HT-*b*-PFDP) and (P3HT-*b*-PFDP)-*blend*-P3HT showing peaks at *ca* 320 nm characteristic of modified (1,4-addition) C₆₀ in PFDP, and the increase in P3HT absorptions on addition of that material.