Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Polythiophene Derivatives by Step-growth Polymerization via Photoinduced Electron Transfer Reactions

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Experimental Part

Materials

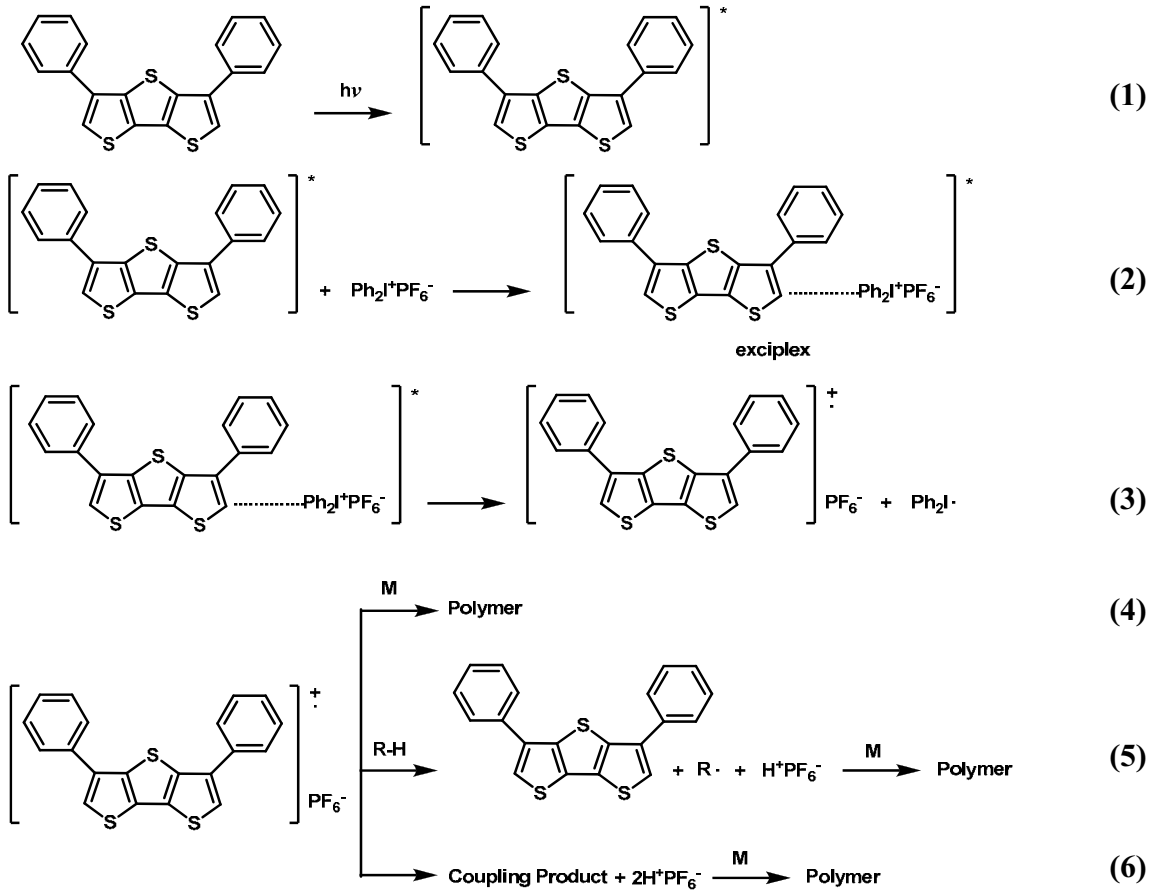
3,5-Diphenyldithieno[3,2-b:2,3-d]thiophene (DDT) was synthesized as described in literature.[1] Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 98%, Alfa Aesar) was used as received. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous $CaCl_2$ and CaH_2 and finally distilled with a fractionation column. Methanol (Fluka) was used as received.

Polymerization Procedure

Photopolymerization was carried out under nitrogen atmosphere. A typical photopolymerization reaction was performed as follows: prior to irradiation, the appropriate solution of dithienothiophene (0.040 g, 1.15×10^{-4} mol) containing predetermined amounts of onium salt (0.098 g, 2.30×10^{-4} mol) and dichloromethane as the solvent (5 mL) were placed in a pyrex tube and irradiated in a Rayonet merry-go-round type photoreactor equipped with 16 lamps emitting light nominally at λ= 350 nm and a cooling system. At the end of irradiation, the dark solution was poured into methanol. The precipitate was isolated by filtration and dried for 24 hours in vacuum oven at 25°C ($M_{n,GPC}$= 1147, M_w/M_n= 1.76).

Characterization

^{1}H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), a Viscotek UV detector and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni–01 software. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 ºC min under nitrogen flow.



(1)

(2)

(3)

(4)

(5)

(6)

Scheme S1. Photoinitiated cationic polymerization mechanism based on electron transfer between excited 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) and iodonium ion.

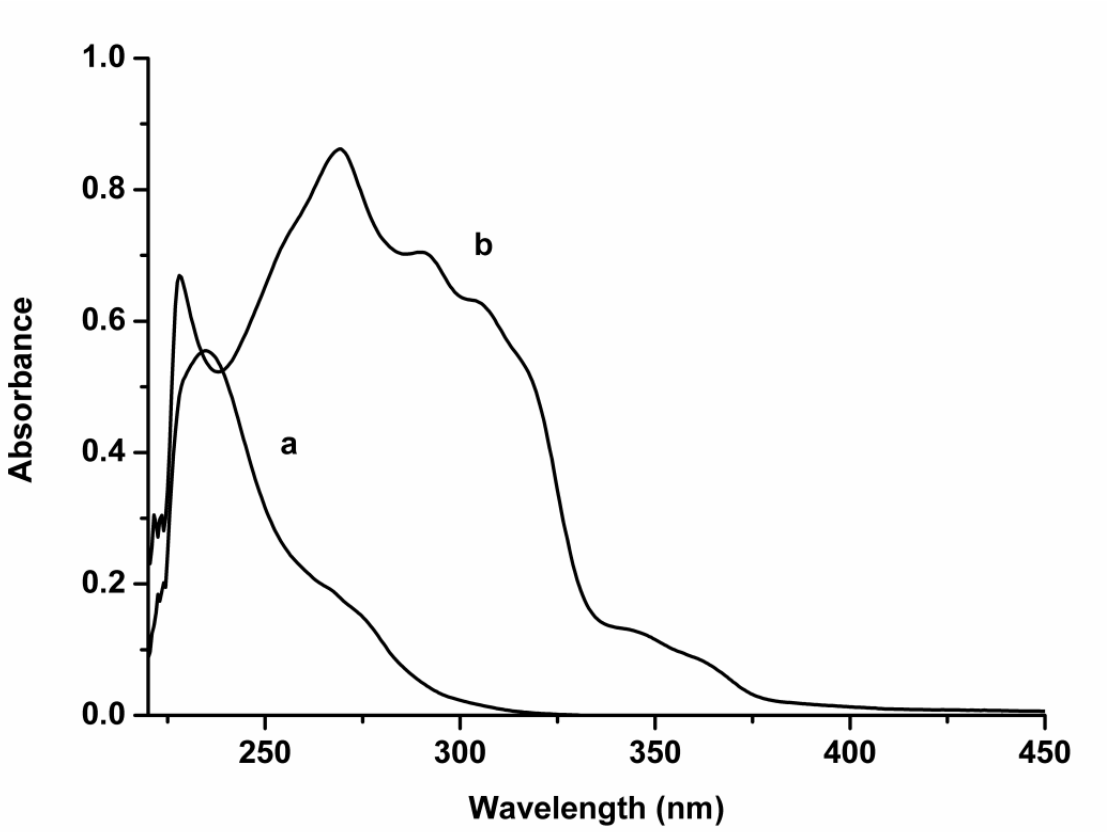


Figure S1. Optical absorption spectra of a) $Ph_2I^+PF_6^-$ (3.5 x 10^{-5} M) and b) DDT (3.5 x 10^{-5} M) in CH_2Cl_2.

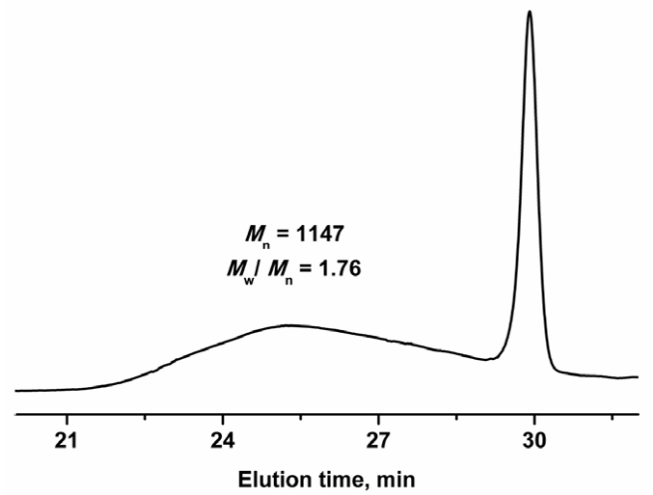


Figure S2. The GPC profile of PDDT formed after irradiation of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) in the presence of $Ph_2I^+PF_6^-$.

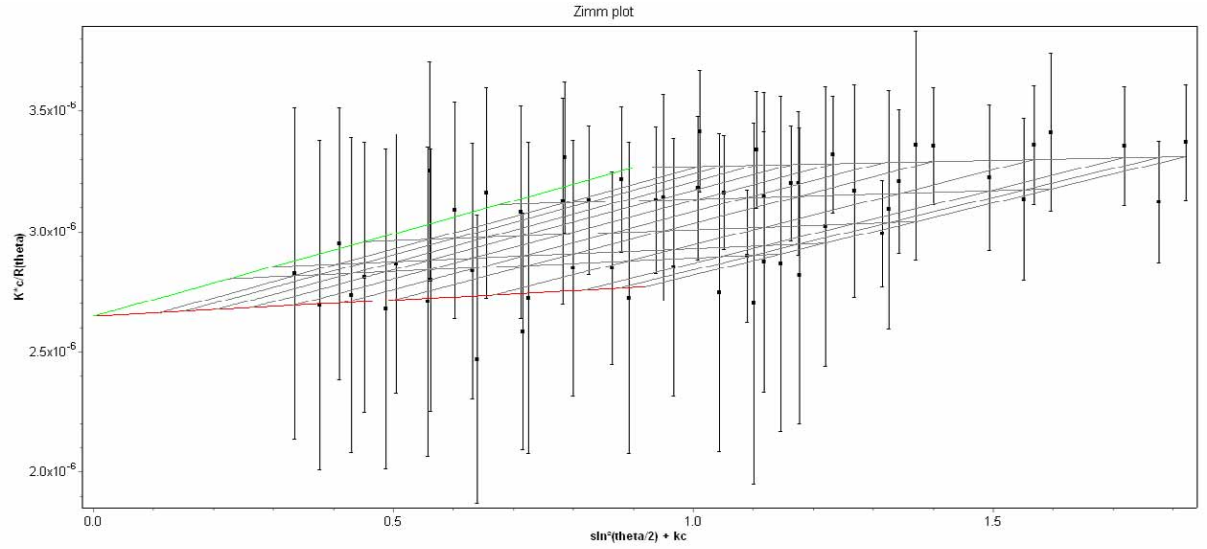


Figure S3. Zimm plot for PDDT in THF.

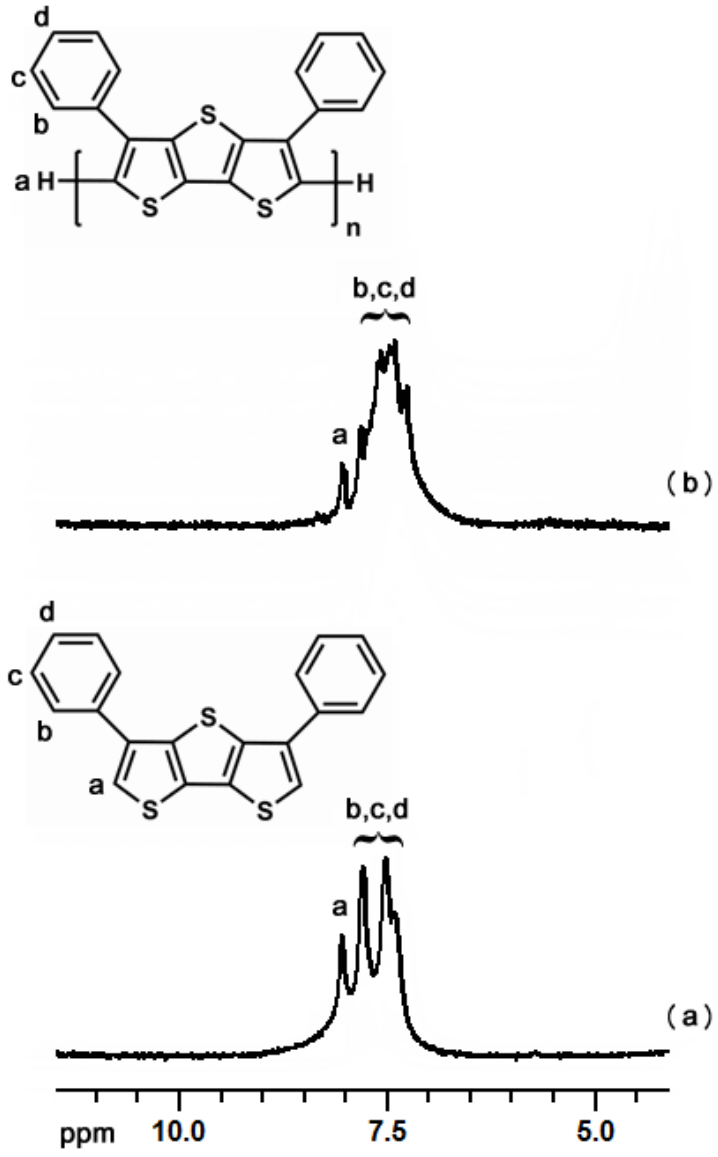


Figure S4. ^{1}H NMR spectra of a) DDT and b) PDDT in d_6-DMSO.

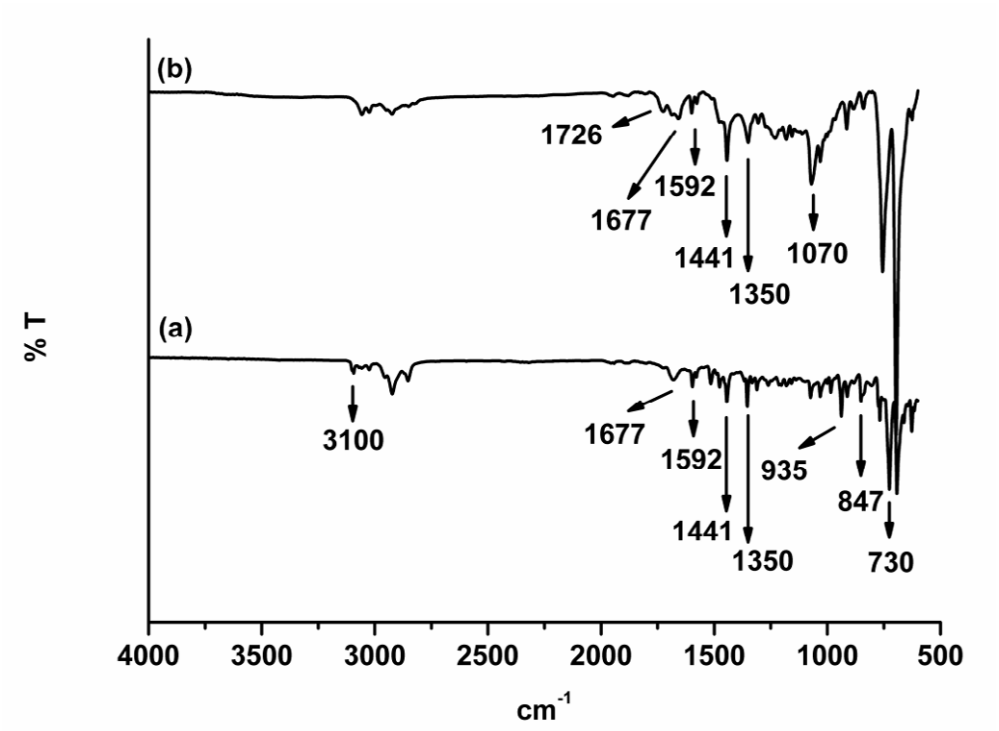


Figure S5. FT-IR spactra of a) DDT and b) PDDT.

References

(1) Mert, O.; Sahin, E.; Ertas, E.; Ozturk, T.; Aydin, E. A.; Toppare, L. *J. Electoanal. Chem.* **2006**, 591, 53- 58