

## SUPPORTING INFORMATION

### **Self-Assembled Structures of Semiconductor Nanocrystals and Polymers for Photovoltaics. 2. Multilayers of CdSe Nanocrystals and Oligo(poly)thiophene-Based Molecules. Optical, Electrochemical, Photoelectrochemical and Photoconductive Properties.**

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## Synthesis of oligothiophenes, polythiophenes and nanocrystals

All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions (Fluka) were absolute and stored over molecular sieves. NMR spectra were recorded on a Bruker FT 300 (300 MHz for  $^1\text{H}$ ); chemical shifts value are given in parts per million.

3',3''-dihexyl-2,2':5',2''-terthiophene (He2T3) and 5,5''-dibromo-3',3''-dihexyl-2,2':5',2''-terthiophene were prepared according to the literature [1].

### ***5,5''-(3',3''-dihexyl-2,2':5',2''-terthiophene)-dicarboxylic acid (CAHe2T3CA).***

Butyllithium (1.6 M in hexane, 0.6 mmol) was added dropwise to a solution of 3',3''-dihexyl-2,2':5',2''-terthiophene (He2T3) (100 mg, 0.24 mmol) in THF (10mL)  $-78^\circ\text{C}$ . The reaction was maintained at  $-78^\circ\text{C}$  for 1 h before purging with dried  $\text{CO}_2$  gas for 30 min. The mixture was then stirred vigorously for 2 h at  $-78^\circ\text{C}$ . The temperature was then raised slowly to room temperature and stirred for 24 h. The resulting mixture was neutralized carefully by the addition of an aqueous solution of NaOH (3%) and then filtered. Diethyl ether (20 mL) was added to the filtrate and the organic layer was washed sequentially with 3% aqueous HCl (3x5 ml) and water (3x10 ml). After drying with  $\text{MgSO}_4$ , the solvent was removed by rotary evaporator. Flash chromatography of the residue (silica gel, acetone/n-hexane 1:9) afforded the title compound ( yield was 64.2% yield). Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{O}_4\text{S}_3$  : C, 61.90; H, 6.35; S, 19.05. Found: C, 61.98; H, 6.43; S, 18.99. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3066, 2924, 1691, 1625, 1465, 696.18. UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 374 \text{ nm}$   $^1\text{H}$  NMR(*d*-TCE):  $\delta$  0.81 (t, 6H,  $J=6.7 \text{ Hz}$ ), 1.14-1.34 (br, 12H), 1.60 (br, 4H), 2.72 (m, 4H), 7.14 (s, 2H), 7.61 (s, 2H). MS,  $m/e$  504 ( $\text{M}^{++}$ ).

***[5''-(Diethoxy-phosphoryl)-3',3''-dihexyl-2,2':5',2''-terthiophene-5-yl]-phosphonic acid diethyl ester.*** A mixture of 5,5''-dibromo- 3',3''-dihexyl-2,2':5',2''-terthiophene (207 mg, 0,36 mmol), triethyl phosphite (145 mg, 0.86 mmol), and  $\text{NiCl}_2$  was stirred overnight at  $135^\circ\text{C}$ . Flash chromatography (silica gel,  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  8:2) of the obtained product afforded the title compound (129 mg, 52%yield). Anal. Calcd for  $\text{C}_{32}\text{H}_{50}\text{O}_6\text{P}_2\text{S}_3$ : C, 55.79; H, 7.32%. Found: C, 55.63; H, 7.25%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.85 (t, 6H), 1.30 (m, 12H), 1.33 (t, 12H), 1.61 (m, 4H), 2.75 (m, 4H), 4.15 (m, 8H), 7.13 (s, 2H), 7.46 (d, 2H).

**[3',3''-Dihexyl-5''-phosphono-2,2':5',2''-terthiophene-5-yl)-phosphonic acid (PAHe2T3PA).**

A solution of trimethylbromosilane (103 mg, 0.67 mmol) in CH<sub>2</sub>Cl<sub>2</sub> ( 1 mL) was added dropwise to a solution of [5''-(diethoxy-phosphoryl)-3',3''-dihexyl-2,2':5',2''-terthiophene-5-yl]-phosphonic acid diethyl ester (85 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> ( 5 mL), and the resulting solution was stirred overnight. The solvent and excess trimethylbromosilane were evaporated at reduced pressure leaving a product which was shown to be the silyl ester by <sup>1</sup>H NMR. The silyl ester was dissolved in methanol (30 mL) and the solution was stirred for 5 min, followed by removal of methanol under reduced pressure. The hydrolysis procedure was repeated three times yielding the title compound as a yellow solid (69 mg, 97% yield). Anal. Calcd for C<sub>24</sub>H<sub>34</sub>O<sub>6</sub>P<sub>2</sub>S<sub>3</sub>: C, 49.99; H, 5.94%. Found: C, 49.77; H, 5.91%. <sup>1</sup>H NMR (CD<sub>3</sub>OD) : δ 0.86 (t, 6H), 1.33 (m, 12H), 1.62 (m, 4H), 2.76 (m, 4H), 7.15 (s, 2H), 7.37 (d, 2H). <sup>31</sup>P NMR (CD<sub>3</sub>OD) δ 25.32 vs 85% H<sub>3</sub>PO<sub>4</sub>. MS, *m/e* 576 (M<sup>++</sup>).

**Electrosynthesis of poly(CPDT-SO) tetrabutylammonium salt**

The monomer 4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithien-4-yl)butanesulfonate) lithium salt (CPDT-SO) was prepared according to literature [2].

The synthesis of poly(CPDT-SO) tetrabutylammonium salt (PCPDT-SO) is a modification of that reported previously [2,3]. Bulk oxidized PCPDT-SO is deposited in the sulfonic acid form at a 2x5 cm<sup>2</sup> platinum sheet electrode by potentiostatic oxidation at 0.7 V of a ca 2x10<sup>-3</sup> M solution of CPDT-SO lithium salt (17 mg, 0.053 mmol) in acetonitrile + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> (25 ml) after conversion of the monomer to the acid form by addition of one equivalent of HClO<sub>4</sub>. After completion of the electrolysis, with the passage of 2.4 F mol<sup>-1</sup>, the deposit was washed with acetonitrile and then dissolved in 1:1 water/ethanol to give a blue-green solution. After compensation of the doping charge with a tenfold excess of hydrazine and addition of one equivalent of Bu<sub>4</sub>NOH to produce the undoped tetrabutylammonium salt, the dark violet solution was filtered from the insoluble polymer fraction and evaporated under vacuum to yield ca 25 mg of polymer.

**Electrosynthesis of poly(CPDT-C5CA) tetrabutylammonium salt**

The monomer 6-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithien-4-yl)hexanoic acid (CPDT-C5CA) was prepared according to literature [4].

Bulk poly(CPDT-C5CA) tetrabutylammonium salt (PCPDT-C5CA) was obtained as the acid form by exhaustive electrolysis of CPDT-C5CA in acetonitrile + 0.1 M NaClO<sub>4</sub> at a 2x5 cm<sup>2</sup> platinum sheet electrode and 0.7 V applied voltage. Thus 13.4 mg dissolved in 25 ml required the passage of 10 C (2.3 F mol<sup>-1</sup>) with production of a dark blue precipitate which turned immediately violet upon reduction with a drop of hydrazine. Filtered, washed three times with acetonitrile and added with one equivalent of Bu<sub>4</sub>NOH (to produce the undoped tetrabutylammonium salt) in boiling 3:1 ethanol/water, the 12.3 mg of crude polymer give a red solution (maximum absorption at 480 nm) containing ca 4 mg of red polymer (yield: 30%). The FTIR spectrum of the soluble polymer confirms the suggested formulation showing,, besides the strong -CH<sub>2</sub>- stretching bands around 2900 cm<sup>-1</sup>, two strong bands at 1561 and 1412 cm<sup>-1</sup> due to the asym and sym stretching of the carboxylate anion.

### **Electrosynthesis and characterization of sexithiophene CAHe4T6CA**

Bulk sexithiophene CAHe4T6CA has been produced by exhaustive electrolysis (1.5 F mol<sup>-1</sup>) at 0.8 V vs Ag/Ag<sup>+</sup> of 10 mg of the terthiophene He2T3CA in 25 ml of acetonitrile + 0.1 M NaClO<sub>4</sub> using a 2x5 cm<sup>2</sup> platinum sheet electrode. The resulting dark blue suspension of the oxidized product was reduced with one drop of hydrazine to an orange suspension which was filtered, washed with acetonitrile and dried. The solid was then extracted with a warm chloroform/0.1 M HClO<sub>4</sub> 1:1 v/v mixture, the yellow organic phase was washed with water to neutral pH, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give the desired compound as a red material (yield: >90%). MS (MALDI) [M+H]<sup>+</sup> *m/e*: 921.

The sexithiophene CAHe4T6CA is soluble both in scarcely polar solvents such as chloroform (<10<sup>-4</sup> M) and in polar solvents such as ethanol (>10<sup>-3</sup> M). Thus it appears that both the lipophilic core and the hydrophylic ends of the linear molecule can be used to bring the material into solution. The electronic spectrum (fig.S1) follows in fact the solvation. In the solid state the strong bathochromic position at 488 nm of the maximum absorption and the vibronic structure of the signal evidence in fact a noticeable solid state effect, which is attributable to a specific coplanarizing and rigidifying effect of the hexyl substituents [5]. The maximum is heavily shifted to 426 nm in CHCl<sub>3</sub> and even 409 nm in EtOH as a consequence of solvation.

CAHe4T6CA as film shows a CV (fig.S2) with the regular two processes of two reversible one-electron oxidation processes to radical cation and dication [6].

### Synthesis of CdSe-NCs

A mixture of Cd(Ac)<sub>2</sub> (115 mg), stearic acid (573 mg), hexadecylamine (5 g) and trioctylphosphine oxide (10 g) was heated under vacuum at 110 °C for 1 h. A solution of Se (158 mg) in 2 ml of trioctylphosphine was swiftly injected into the reaction mixture heater at 305 °C. The mixture turned dark immediately and after 3 minutes it was cooled down and CHCl<sub>3</sub> was added. Methanol was added and, after centrifugation, the obtained solid was dissolved in CHCl<sub>3</sub> and reprecipitated with methanol. After centrifugation and drying ca 90 mg of CdSe-NCs are obtained. ( $\lambda_{\max}$  = 620-625 nm in CHCl<sub>3</sub>; diameter 6.0 nm).

Absorbance and PL spectra are shown in fig.S3. The PL maximum is characterized by a small Stokes shift (ca 6 nm) and is narrow (ca 25 nm at half width).

### References

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S1

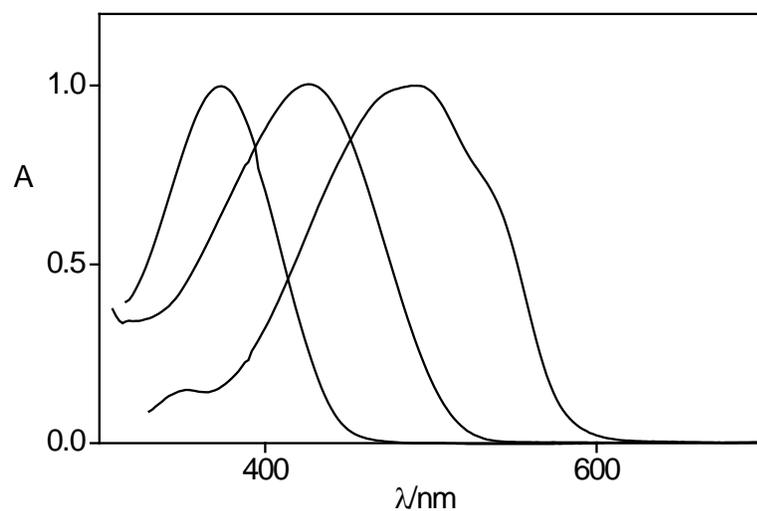


fig.S1 – UV-vis spectra of (a) CAHe2T3CA in  $\text{CHCl}_3$ , (b) CAHe4T6CA in  $\text{CHCl}_3$  and (c) CAHe4T6CA film on ITO.

S2

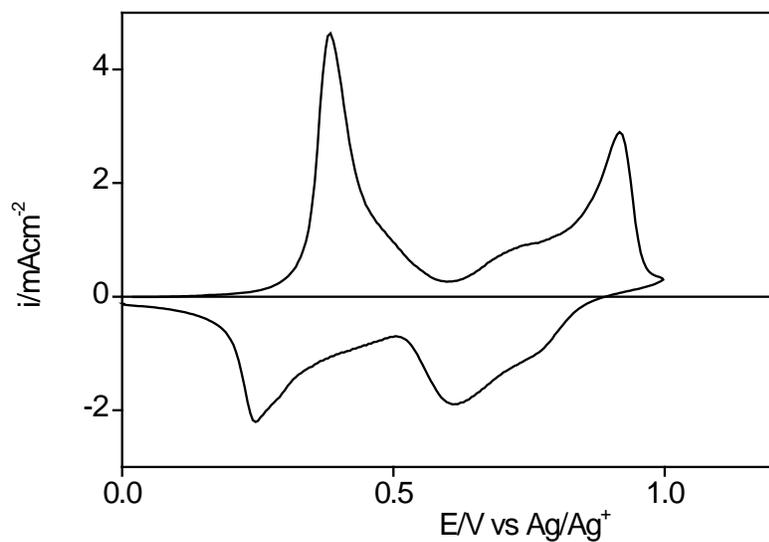


fig.S2 – Cyclic voltammogram of CAHe4T6CA film in acetonitrile + 0.1 M  $\text{NaClO}_4$ . Scan rate:  $0.1 \text{ V s}^{-1}$ .

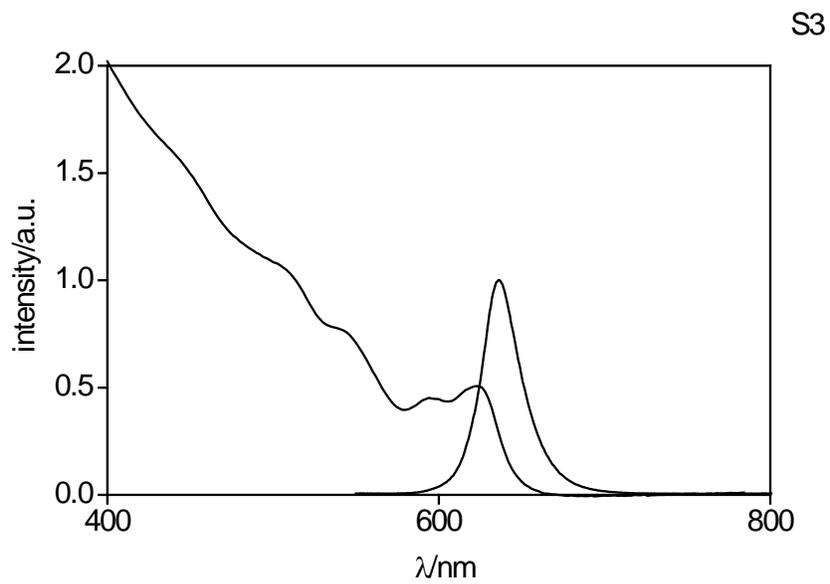


fig.S3 – UV-vis absorption and PL spectra of 6-nm CdSe-NCs in CHCl<sub>3</sub>.