Supporting Information

Photoinduced Charge-Separation and Charge-Recombination of Oligothiophene-Viologen Dyads in Polar Solvent

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Received April 14, 2004

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General. All chemicals are of reagent grade. Melting points are uncorrected. ^{1}H-NMR spectra were measured on a JEOL Lambda 400 spectrometer using deuteriochloroform or deuteriodimethyl sulfoxide as solvent and tetramethylsilane as internal standard. MS spectra were recorded on a Shimadzu KOMPACT-MALDI PROBE spectrometer using a dithranol matrix.

5-(3-Chloropropyl)-3,3"'-dihexyl-2,2';5',2";5",2"'-quaterthiophene (2a). Into a stirred solution of 3,3"'-dihexyl-2,2';5',2";5",2"'-quaterthiophene[RS1] (**1a**, 3.4 g, 6.8 mmol) in tetrahydrofuran (35 mL) cooled at –40 °C was dropwise added a hexane solution of butyllithium (1.59 *N*, 3.5 mL, 5.6 mmol) over a period of 0.5 h under a nitrogen atmosphere. The mixture was stirred at 0 °C for 0.5 h and cooled to –30 °C. After 1-bromo-3-chloropropane (1.7 mL, 17 mmol) was added, the mixture was stirred at RT for 5 h, treated with water (50 mL) with ice-cooling, and extracted with hexane (30 mL x 3). The extract was washed with water and dried on anhyd. magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 9:1 hexane-dichloromethane, Rf 0.3) to give a yellow oil (1.7 g, 52%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87-0.88 (m, 6H), 1.30-1.37 (m, 12H), 1.60-1.66 (m, 4H), 2.13 (quint, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 8.3 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 6.67 (s, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 6.96 (d, *J* = 3.7 Hz, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 5.4 Hz, 1H); MS (MALDI-TOF) *m/z* 573.3 (M^+); Anal. Calcd for $C_{31}H_{39}ClS_4$: C, 64.71; H, 6.83%. Found: C, 64.69; H, 6.83%.

RS1 Yamashiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem. Lett*. **1999**, 443.

5-(3-Chloropropyl)-3,3"',4"",3"""-tetrahexyl-2,2';5',2";5",2"';5"",2""';5"",2""';5"",2""";5"",2""";5"",2"""'-octithiophene (2b). This compound was obtained in 34% yield from 3,3"',4"",3"""-tetrahexyl- 2,2';5',2";5",2"';5"",2""';5"",2""';5"",2""";5"",2""";5"",2"""'-octithiophene (1b) [RS1] in a similar manner as above-stated: red oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87-0.92 (m, 12H), 1.26-1.40 (m, 24H), 1.58-1.69 (m, 8H), 2.14 (quint, J = 7.1 Hz, 2H),

2.70-2.81 (m, 8H), 2.95 (t, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 6.68 (s, 1H), 6.94 (d, *J* = 5.4 Hz, 1H), 6.97 (d, *J* = 3.9 Hz, 1H), 7.01 (s, 2H), 7.03 (d, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 3.9 Hz, 2H), 7.05 (d, *J* = 3.9 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 7.14 (d, *J* = 3.9 Hz, 2H), 7.19 (d, *J* = 5.1 Hz, 1H); MS (MALDI-TOF) *m/z* 1069.2 (M^+); Anal. Calcd for $C_{59}H_{71}ClS_8$: C, 66.09; H, 6.67%. Found: C, 66.04; H, 6.71%.

3,3'''-Dihexyl-5-(3-iodopropyl)-2,2';5',2'';5'',2'''-quaterthiophene (3a). A solution of **2a** (1.6 g, 2.8 mmol) and sodium iodide (11 g, 73 mmol) in acetone (180 mL) was refluxed for 24 h. After water (100 mL) was added, the mixture was extracted with hexane (30 mL x 3). The extract was washed with water and dried on anhyd. magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography to give a yellow oil (1.8 g, 94%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87-0.91 (m, 6H), 1.30-1.38 (m, 12H), 1.59-1.68 (m, 4H), 2.16 (quint, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 8.1 Hz, 2H), 2.77 (t, *J* = 8.1 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.6 Hz, 2H), 6.68 (s, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 6.96 (d, *J* = 3.7 Hz, 1H), 7.10 (d, *J* = 3.9 Hz, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 5.1 Hz, 1H); MS (MALDI-TOF) *m/z* 667.4 (M^+); Anal. Calcd for $C_{31}H_{39}IS_4$: C, 55.84; H, 5.90%. Found: C, 56.20; H, 5.95%.

3,3''',4'''',3''''''-Tetrahexyl-5-(3-iodopropyl)-2,2';5',2'';5'',2''';5''',2'''';5'''',2''''';5'''',2'''''';5''''',2'''''''-octithiophene (3b). This compound was obtained in 90% yield from **2b** in a similar manner as above-stated: red oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87-0.92 (m, 12H), 1.28-1.450 (m, 24H), 1.58-1.69 (m, 8H), 2.16 (quint, *J* = 7.31 Hz, 2H), 2.710-2.81 (m, 8H), 2.90 (t, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 6.698 (s, 1H), 6.94 (d, *J* = 5.14 Hz, 1H), 6.97 (d, *J* = 3.69 Hz, 1H), 7.01 (s, 2H), 7.03 (d, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 3.9 Hz, 2H), 7.05 (d, *J* = 3.9 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.13 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 3.9 Hz, 2H), 7.19 (d, *J* = 5.41 Hz, 1H); MS (MALDI-TOF) *m/z* 1161.3 (M^+); Anal. Calcd for $C_{59}H_{71}IS_8$: C, 60.09; H, 6.15%. Found: C, 60.95; H, 6.16%.