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Supporting Information

69451 Weinheim, Germany

Supporting Information for

3D-Hybrid Networks with Controllable Electrical Conductivity by Electrochemical Deposition of Terthiophene-Functionalized Polyphenylene Dendrimers

Hermann John, Roland Bauer, Pamela Espindola, Prashant Sonar,
Jürgen Heinze and Klaus Müllen

General Information

Reagents were purchased from Aldrich and used without further purification unless otherwise noted. Tetrakis(triphenylphosphine)-palladium(0) ($Pd(PPh_3)_4$) catalyst was purchased from ABCR. Tetrabutylammonium hexafluorophosphate ($(C_4H_9)_4NPF_6$) was purchased from Fluka. The solvents were used of commercial p.a. quality; tetrahydrofuran (THF) was dried over potassium. Before use dichloromethane (CH_2Cl_2) was stirred with sulfuric acid (H_2SO_4) 95-97 %, distilled and passed through a cooled column filled with basic alumina. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 250 DPX (250 MHz and 62,5 MHz respectively) or Bruker AMX 300 (300 MHz and 75 MHz respectively). Mass spectra were recorded on a Bruker Reflex II mass spectrometer, equipped with a 337 nm N_2 laser at a pulse rate of 3Hz. UV/Vis data were obtained on a Perkin-Elmer Lambda 9 and fluorescence spectra were measured on a SPEX Fluorolog 2 Type 212 spectrometer.

The electrochemical experiments were carried out under argon atmosphere in specially constructed cells containing an internal drying column with highly activated alumina. The working electrode was a Pt disk sealed in soft glass (∅ 1.0 mm). A Pt wire, wrapped around the glass of the working electrode, served as counter electrode. The reference electrode was an Ag wire. Potentials were calibrated with ferrocene (Fc) ($E^{+}_{1/2}(Fc^{0} \mid Fc^{+}) = 0.38$ V versus Ag │ AgCl │ KCl aq.). The cyclic voltammograms were controlled and recorded with an EG&G PARC Model 175 Universal Programmer, Jaissle Potentiostat-Galvanostat IMP 88 PC and IMK PSO 8100 equipment.

In situ conductivity measurements were carried out on a microarray working electrode (5 µm gap). The working electrode was separated from the potentiostat by two 1 kΩ resistors. A bias of E = 10 mV was applied to the microarray electrode and a third 1 kΩ resistor at which the potential was measured. The conductivities of the polymers on the microarray electrode were calculated according to the ohmic rules. This set-up was controlled by an AMEL 553 potentiostat and the potential scans were performed with an EG&G PARC model 175 scan generator. Further details have been published previously [1, 2]. All values described as conductivity were calculated from the area and thickness of the films. The film thickness was determined with the help of a profilometer.

Materials

5-Methyl-[2,2´,5´,2´´ terthiophene] (2) as well as compounds **3a** and **3b** were prepared following the synthetic procedures reported in reference 20.

2,5-Diphenyl-3,4-bis-(4-[2,2';5',2'']terthiophen-5-yl-phenyl)-cyclopenta-2,4-dienone (5a): **3a** (0.65 g , 1.96 mmol) and **4** (0.42 g, 0.66 mmol) were dissolved in 4 ml toluene, 0.5 ml EtOH and 1.5 ml of a solution of 0.41g K_2CO_3 in H_2O (2 M) were added. The reaction mixture was degassed and flushed with argon. $Pd(PPh_3)_4$ as catalyst (4 mg 0.003 mmol) was added under argon flow and the reaction mixture was heated to 90 °C for 12 h. The resulting solution was washed repetitively with H_2O and CH_2Cl_2. The organic layer was separated and dried over $MgSO_4$. The reaction mixture was purified by flash column chromatography eluting with CH_2Cl_2 / petroleum ether 1:1 to yield **5a** **(**0.37g**,** 64 %**)** as a reddish brown powder. ^1H NMR (250 MHz, $C_2D_2Cl_4$):δ=7.43 (d, J(H,H)=7.22Hz, 4H), 7.31-7.22 ppm (m, 14H), 7.19 (d, J(H,H)=4.9Hz, 2H), 7.15 (d, J(H,H)=3,6Hz, 2H), 7.10 (s, 4H), 7.04(dd, JH,H=3.5,3.6Hz, 2H), 6.97 (d, J(H,H)= 7.5Hz, 4H), ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): δ=200.53, 153.85, 142.53, 137.09, 137.02, 136.66, 136.03, 134.11, 133.66, 132.08, 130.88, 130.14, 128.31, 126.13, 125.95, 125.6, 125.25, 125.1, 124.82, 123.58; MS (FD, 8kV) m/z (%) 876.5 (100 %) [M^+].

3,4-Bis-[4-(5''-methyl-[2,2';5',2'']terthiophen-5-yl)-phenyl]-2,5-diphenyl-cyclopenta-2,4-dienone (5b): Identical synthetic procedure as in the case of **5a,** starting from 0.43 g (1.26 mmol**)** **3b** and 0.26 g (0.41 mmol) of **4** yielded in **5b** (0.34g, 61%). ^1H NMR (500 MHz, $C_2D_2Cl_4$):δ=7.44 (d, J(H,H)=7.9Hz, 4H), 7.31-7.22 ppm (m, 12H), 7.12 (d, J(H,H)=3.5Hz, 2H), 7.06 (d, J(H,H)=3,5Hz, 2H), 7.00-6.96 (m, 8H), 6.68 (d, J(H,H)= 3.5, Hz, 2H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$): δ=200.3, 154.65, 142.4, 141.43, 141.24, 137.98, 137.69, 135.04, 133.66, 133.36, 133.17, 132.68, 130.34, 126.13, 125.95, 125.8, 125.6, 125.3, 125.1, 124.98, 123.45, 122.72, 114.73, 15.4; MS (FD, 8kV) m/z (%) 904.5 (100 %) [M^+].

Dendrimer 7a: 0.016g (0.007 mmol) of **6** and 0.115g (0.131 mmol) of **5a** were heated in a mixture of 1 ml o-xylene and 2 ml diphenyl ether for 3-4 days at 190°C under argon atmosphere. After verification of the reaction mixture by means of matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, it was allowed to cool down to room temperature. The reaction mixture was then precipitated in MeOH, filtrated and washed with a mix of CH_2Cl_2 and MeOH, 1:4. The obtained yellow powder (0.051g, 69%) was dried under reduced pressure and used for characterization. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$):δ=7.76-6.8 (unresolved overlapping aromatic signals); ^{13}C NMR (62.5 MHz, $C_2D_2Cl_4$): δ=144.5, 142.4, 142.3, 141.6, 141.43, 141.24 140,8. 140,3. 139,5. 139,1. 138,5. 138,2. 137,9. 137,69. 133,66. 133,3. 133,17. 132,9; 132.8, 131.9, 131.3, 130.2, 128.8, 127.8, 127.0, 126.2, 125.8, 125.6, 124.98, 123.45, 122.72, 115.85, 112.7, 112.4; 55,4.; MALDI-TOF (TCNQ) m/z [ue^{-1}]: 8827 (M^+); 6626 (¾ M^+), 2190 (¼M^+); Calcd for $C_{577}H_{356}S_{48}$: 8828.34 (M^+), 6625.27 (¾ M^+), 2204,08 (¼M^+).

Dendrimer 7b: 0.014g (0.006 mmol) of **6** and 0.106g (0.116 mmol) of **5b** were subjected to the same procedure as in the case of **7a**. The reaction yielded 0.047g (71%) of an amorphous powder which was subsequently dried under reduced pressure and used for characterization. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$):δ=7.79-6.9 (m, 298H), 6.84 (d,J(H,H)=7,9Hz,16H), 6.68 (d,J(H,H)=3.5, Hz,16H), 2.46 (s, 48H); ^{13}C NMR (62.5 MHz, $C_2D_2Cl_4$): δ=144.5, 142.3, 141.6, 141.43, 141.24 140,8. 140,3. 139,5. 139,1. 138,5. 138,2. 137,9. 137,69. 133,66. 133,3. 133,17. 132,9; 132.8, 131.9, 131.3, 130.2, 129,54, 128.8, 127.8, 127.0, 126.2, 125.6, 125,01 123.5, 122.65, 115.9, 112.5, 112.2; 55,3. 15,0 ; MALDI-TOF (TCNQ) m/z [ue^{-1}]: 9053 (M+); Calcd for $C_{593}H_{388}S_{48}$: 9052,78.

Electrochemistry

Cyclic voltammograms of the oxidation of **7a** in CH_2Cl_2 are shown in figure 1. As can be seen, the oxidation of the terthiophene moiety begins at a potential of +0.85 V. In a multisweep-experiment the formation of hexathiophene oligomers can be detected as new voltammetric waves appearing in the potential range between +0.5 V and +1.0 V.

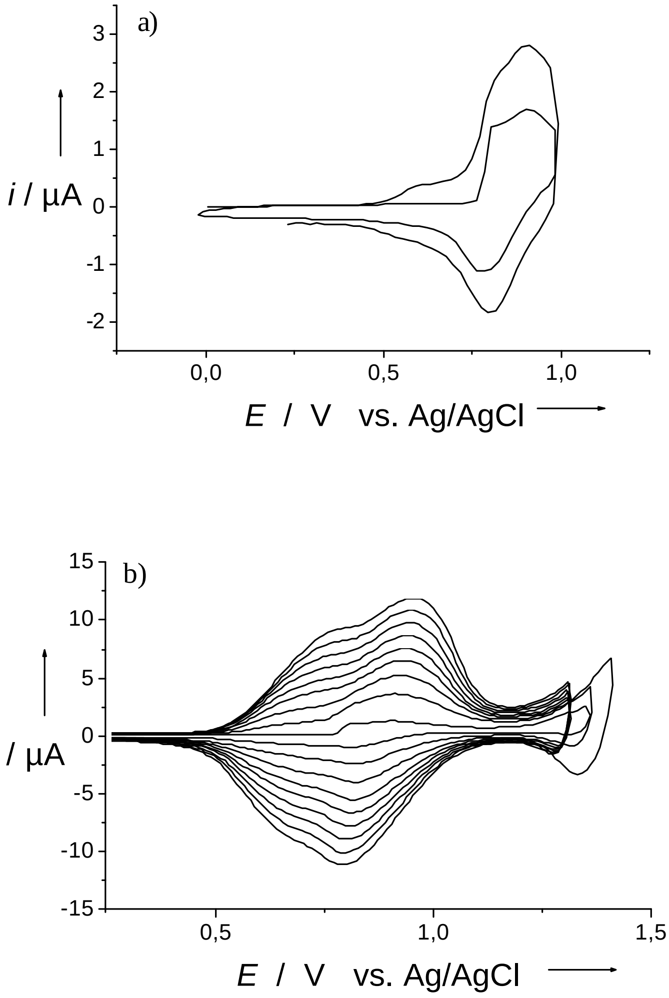

Figure 1: Multisweep cyclic voltammograms of **7a** in CH_2Cl_2 / $TBAPF_6$,

$c = 10^{-4}$ mol l^{-1}, room temperature, Pt-electrode, 1 mm ∅.,

a) $v = 0.2$ Vs^{-1}, freshly polished electrode, $E_\lambda = 1.0$ V

b) $v = 0.1$ Vs^{-1}, continuation of the experiment, E_λ around 1.3 V.

In contrast to **7a, 7b** is blocked at the highly reactive α-position of the terthiophene units. The oxidation of the terthiophene does not generate irreversible covalent bonding of these units. Thus, multisweep cyclic voltammogramms below E = +1.0V in CH_2Cl_2 give no changes between the successive cycles indicating no follow-up reactions (Figure 2a). Nevertheless, the formation of a film can be obtained by applying a higher switching potential of E_λ = +1.7 V (Figure 2b).

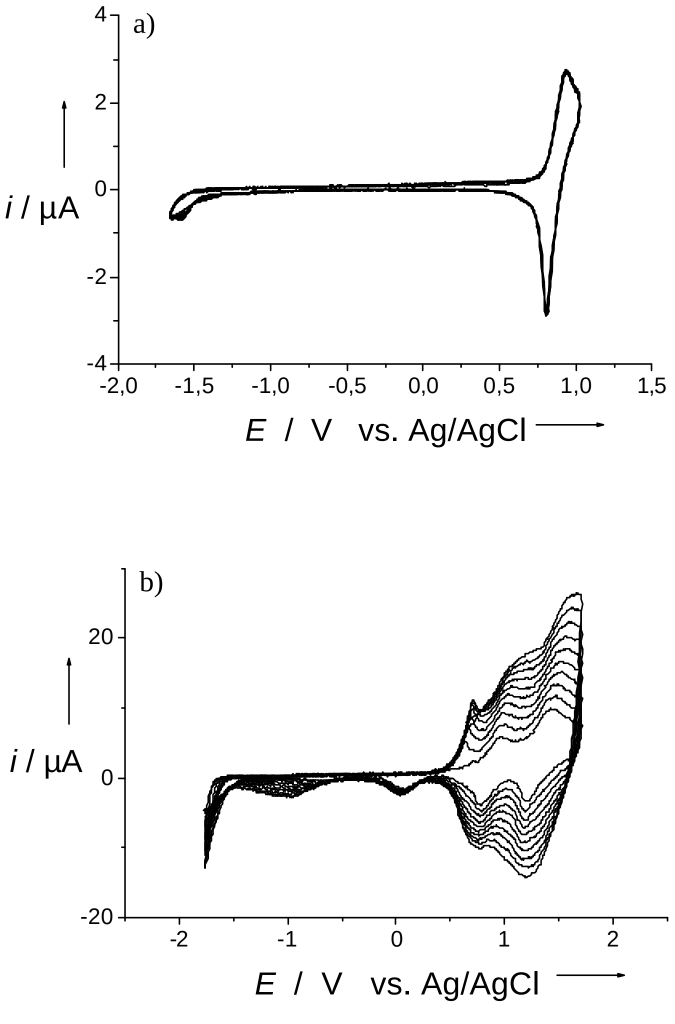

Figure 2: Multisweep cyclic voltammograms of **7b** in CH_2Cl_2 / $TBAPF_6$, $c = 5\cdot10^{-5}$ mol l^{-1}, v = 0.1 Vs^{-1}, T = 34 °C, Pt-electrode, 1 mm ∅, a) 11 scans, E_λ = 1.0 V, b) 10 scans, E_λ = 1.7 V.

Optical Properties

UV/Vis spectra taken from **3b**, **5a**, **5b**, **7a** and **7b** in chloroform solutions in the diluted regime (10^{-6} M) are presented in figure 3. The absorption spectra reflect the electronic structures possible due to the different mutual arrangements of the terthiophene relative to the connected phenyl ring in the molecule. The red shift in the π-π*-transition maxima reflects the π-delocalization increasing from **3b** to **5b** the absorption maxima of which are peaked at 360 (9213 $M^{-1}cm^{-1}$) and 391 (20955 $M^{-1}cm^{-1}$) nm respectively. This is in accordance with a relative small torsion of the bond between the terthiophene unit and the α-phenyl ring of the cyclopentadienone which would be favorable for broader π-delocalisation. The absorption spectra of the terthiophene-functionalized dendrimers **7a** and **7b** are depicted in the same figure and exhibit the absorption maxima at 386 (135211 $M^{-1}cm^{-1}$) and 390 (140684 $M^{-1}cm^{-1}$) nm indicating no remarkable change in the relative arrangement of the terthiophene units and the connected phenyl rings, compared with the case of the functional cyclopentadienones **5a** and **5b**. The fluorescence emissions of the two terthiophene functionalized dendrimers are well structured showing two peaks and a shoulder. Of these the 0-0 bands are observed at 457 (7b) and 462 (7a) nm which is characteristic for phenyl substituted terthiophene / phenylene cooligomers [3].

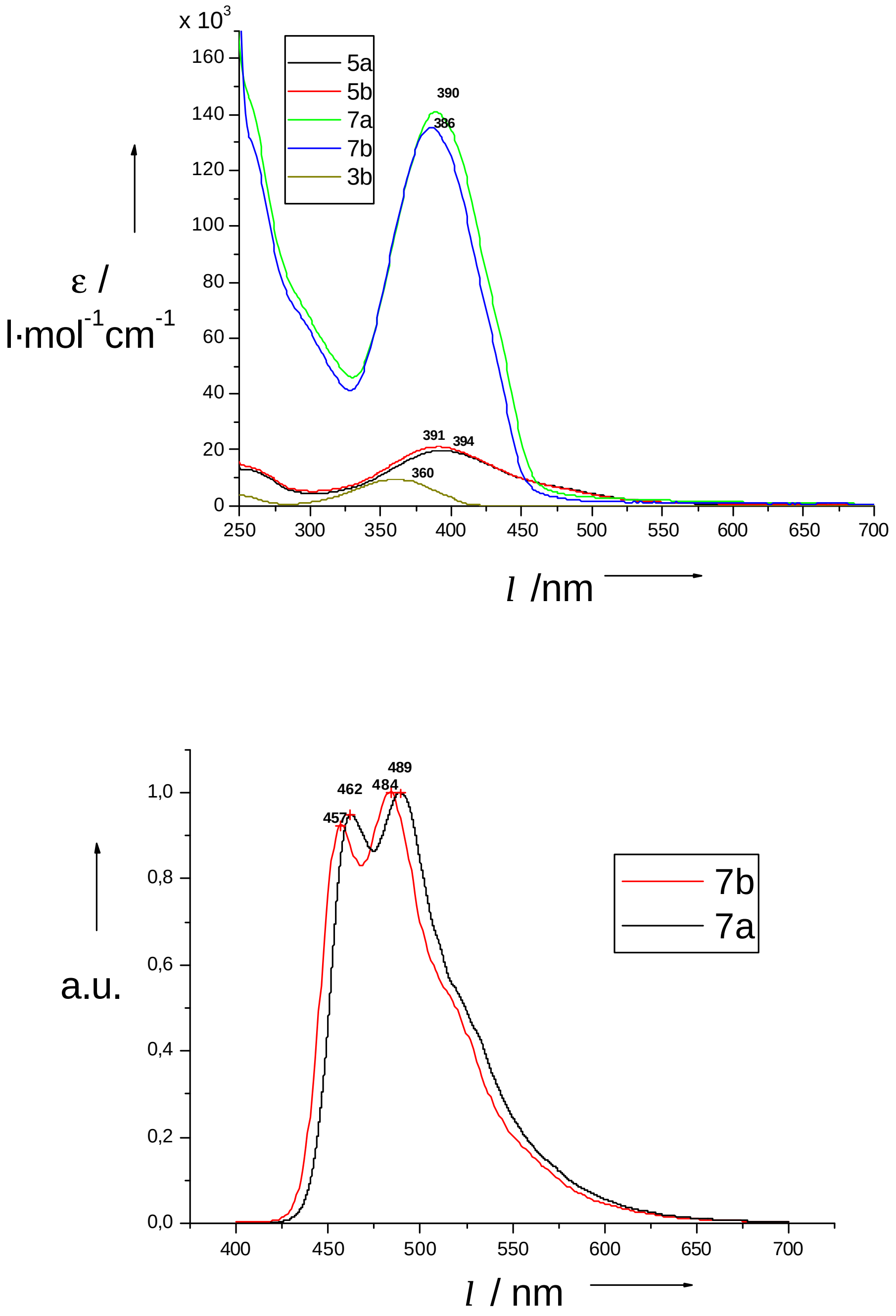

Figure 3: UV/Vis absorption spectra of **3b**, **5a**, **5b**, **7a** and **7b** (top, $CHCl_3$, c = 10^{-6} mol l^{-1}) as well as the fluorescence emission spectra of **7a** and **7b** (bottom).

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