

SUPPLEMENTARY INFORMATION

Practical synthesis of an amphiphilic, non-ionic poly(*para*-phenyleneethynylene) derivative with a remarkable quantum yield in waterAnzar Khan,^{a,b} Stephan Müller,^a and Stefan Hecht*^{a,b}^a *Institut für Chemie / Organische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany*^b *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim and der Ruhr, Germany**E-mail: hecht@mpi-muelheim.mpg.de***General Methods**

Synthesis. 2,5-Diiodohydroquinone **1**¹ and 1,3-Bis(3,6,9-trioxadecyl)glycerol-2-toluenesulfonate **2**² were synthesized as described in the literature. Pd(PPh₃)₄ was freshly prepared,³ all other chemicals were commercial and used as received. Acetonitrile was distilled prior to use under N₂ atmosphere over calcium hydride. Column chromatography was carried out with 130-400 mesh silica gel.

Analytcs. NMR spectra were recorded on Bruker AC500 as well as Delta JEOL Eclipse 500 (500 and 126 MHz for ¹H and ¹³C, respectively) spectrometers at 23 ± 2 °C using residual protonated solvent signal as internal standard (¹H: δ(CHCl₃) = 7.24 ppm, δ(DMSO) = 2.49, δ(CH₃CN) = 1.94 ppm and ¹³C: δ(CHCl₃) = 77.0 ppm, δ(DMSO) = 39.7 ppm). Mass spectrometry was performed on Perkin-Elmer Varian Type CH5DF (FAB) instruments. IR spectra were recorded as KBr pellets on a Nicolet 5SXC FTIR-Interferometer. Elemental analyses were performed on a Perkin-Elmer EA 240. GPC measurements in THF as the mobile phase were performed on a Polymer Laboratories PL-GPC 120 system equipped with a built-in refractive index detector at 40 °C using a flow rate of 1 mL/min. The samples were separated through a series of three columns (l = 300 nm, d = 8 nm), PS-DVB gel with 10 μ bead sizes, which were calibrated with several narrow polydispersity polystyrene samples. The HPLC system consisted of a Knauer Eurosphere 7μm C18, 4·120 mm silica gel column and UV-detection at 254 nm with an eluent flow of 1 mL/min.

Optical spectroscopy. UV/visible absorption and fluorescence emission/excitation spectra were recorded in various solvents of spectroscopic grade using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer, respectively,

both equipped with Peltier thermostated cell holders ($\Delta T = \pm 0.05$ °C). Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C. For quantum-yield determinations using quinine sulfate ($9.98 \cdot 10^{-10}$ M in 2.0 M H_2SO_4) as standard, Melhuish's value⁴ of $\Phi_f = 0.546$ for 365 nm excitation was used. The samples were excited at $\lambda_{\text{exc}} = 365$ nm, slit widths were set to 2.5 nm bandpass for excitation and 5 nm bandpass for emission. Fluorescence spectra were corrected for variations in photomultiplier response over wavelength using correction curves generated on the instrument. The corrected fluorescence spectra were normalized by the exact optical density $\text{OD}_{365\text{nm}}$. For UV-visible absorption $\text{OD}(\lambda_{\text{max}}) \sim 0.8$ (~ 20 mg/L) and for fluorescence measurements $\text{OD}(\lambda_{\text{max}}) \sim 0.1$ were used. Influence of metal cations (Li^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+}) was investigated by adding varying amounts of the respective acetate salts to the aqueous solution. Variation of pH (4-11) was achieved by using buffer solutions.

Molecular Modeling. Molecular mechanics calculations were carried out using the MM2 force field. Reasonable starting geometries for the decamer resembling polymer **5** were obtained by minimization of shorter oligomer fragments that were obtained from monomer units minimized by molecular dynamics simulations.

Synthesis

Monomer: 1,4-Bis(1,3-bis(3,6,9-trioxadecyl)-2-glyceryl)-2,5-diiodobenzene (3): Compound **1**¹ (1.44 g, 4.0 mmol), **2**² (5.1 g, 9.6 mmol), and K_2CO_3 (2.21 g, 16 mmol) were dissolved in 8 mL of dry DMF and heated at 65 °C for 2 days. Then the reaction mixture was diluted with dichloromethane and washed with saturated ammonium chloride and brine solutions. The resulting crude product was purified by column chromatography (10 % methanol in ethyl acetate) to give **3** as orange oil (3.0 g, 69 % yield). ¹H-NMR (500 MHz, CDCl_3): δ 7.22 (s, 2 H, Ar-H), 4.20-4.10 (m, 2 H, O- CH_2), 3.50-3.40 (m, 48 H, O- CH_2), 3.30-3.28 (m, 8 H, O- CH_2), 3.13 (s, 6 H, O- CH_3), 3.11 (s, 6 H, O- CH_3); ¹³C NMR (500 MHz, CDCl_3): δ 153.09, 125.78, 87.67, 80.57, 71.72, 70.97, 70.61, 70.45, 70.42, 70.36, 70.28, 58.77; FAB-MS (MNBA, 3 kV): $m/z = 1117.3$ (calcd 1117.27 for $\text{C}_{40}\text{H}_{72}\text{O}_{18}\text{I}_2\text{Na}^+$), Anal. C: 45.26, H: 6.79 (calcd C: 43.88, H: 6.63); HPLC (85 % MeOH / 15 % H_2O , 1 mL/min): 98.6 % peak area.

Polymer 5: Monomer **3** (0.438 g, 0.40 mmol), CuI (0.008 g, 0.04 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.028 g, 0.02 mmol) were loaded in a flame-dried 10 mL Schlenk tube, which was evacuated and refilled with argon. Dry and degassed acetonitrile (1.7 mL) was submitted to the tube via a syringe, then

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.36 mL, 2.40 mmol) and trimethylsilylacetylene **4** (TMSA, 0.057 mL, 0.40 mmol) were added, immediately followed by addition of distilled water (0.070 mL, 4.0 mmol). The tube was covered with aluminum foil and the reaction mixture was allowed to stir at rt for 3 d. The reaction mixture was precipitated in 500 mL of diethyl ether, the resulting solid was dissolved in chloroform and washed with water, brine, saturated ammonium chloride, 1 M HCl, water, and NaHCO₃ solution to give the desired polymer **5** (0.29 g, 83 %) as yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 7.10 (broad s, 2 H, Ar-H), 4.47 (broad s, 2 H, O-CH), 3.71 (broad s, 8H O-CH), 3.62-3.46 (broad m, 48 H, O-CH), 3.30 (broad s, 6 H, O-CH₃), 3.28 (broad s, 6H, O-CH₃); ¹³C-NMR (500 MHz, CDCl₃): δ 133.74, 131.88, 131.60, 131.28, 128.71, 128.65, 128.56, 106.32, 105.41, 84.53, 71.10, 70.29, 69.70, 69.61, 69.44, 61.18, 57.84; GPC (THF, 40 °C): M_w = 46500, M_n = 22700, PDI (M_w/M_n) = 2.0; Anal. C: 57.74, H: 7.50 (calcd for (C₄₂H₇₂O₁₈)_n C: 58.32, H: 8.39); IR (KBr): 3419, 2924, 2872, 2811, 2724, 2200, 2143, 1642, 1488, 1421, 1350, 1271, 1210, 1108, 1041, 851, 543 cm⁻¹.

References

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- 2 U. Lauter, W. H. Meyer, V. Enkelmann and G. Wegner, *Macromol. Chem. Phys.*, 1998, **199**, 2129-2140.
- 3 D. R. Coulson, *Inorg. Syn.*, 1971, **13**, 121-124.
- 4 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.

Figures

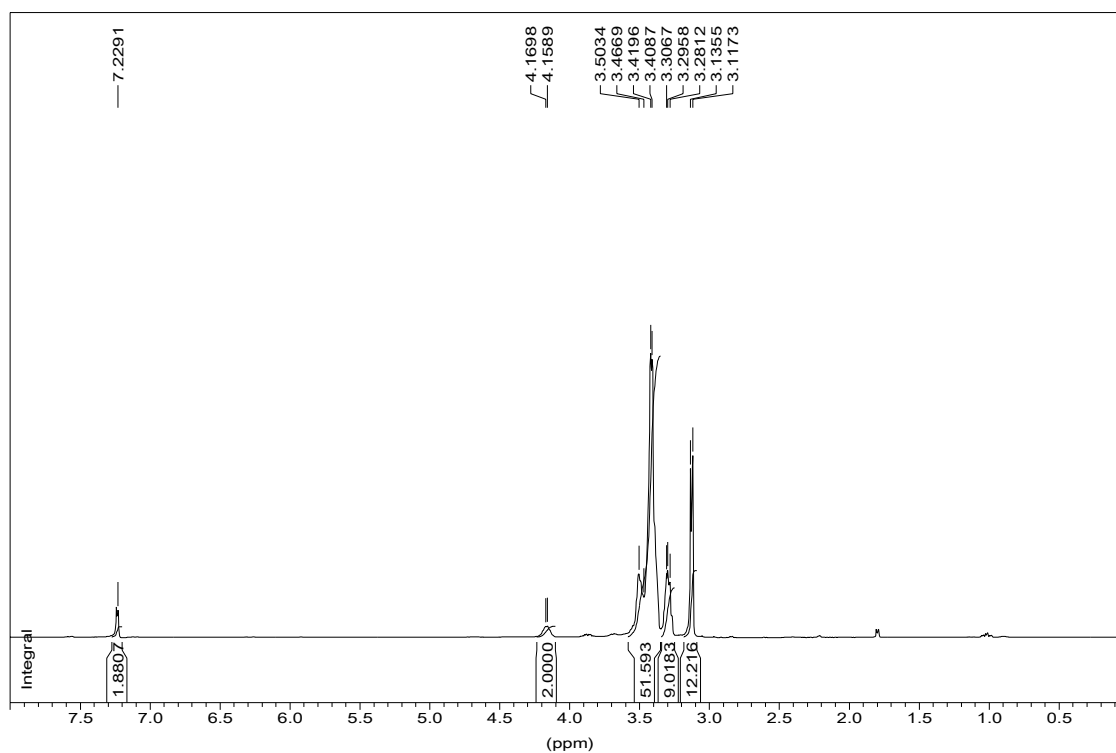


Figure 1. ¹H NMR spectrum of monomer **3** (500 MHz, CDCl₃, 25 °C).

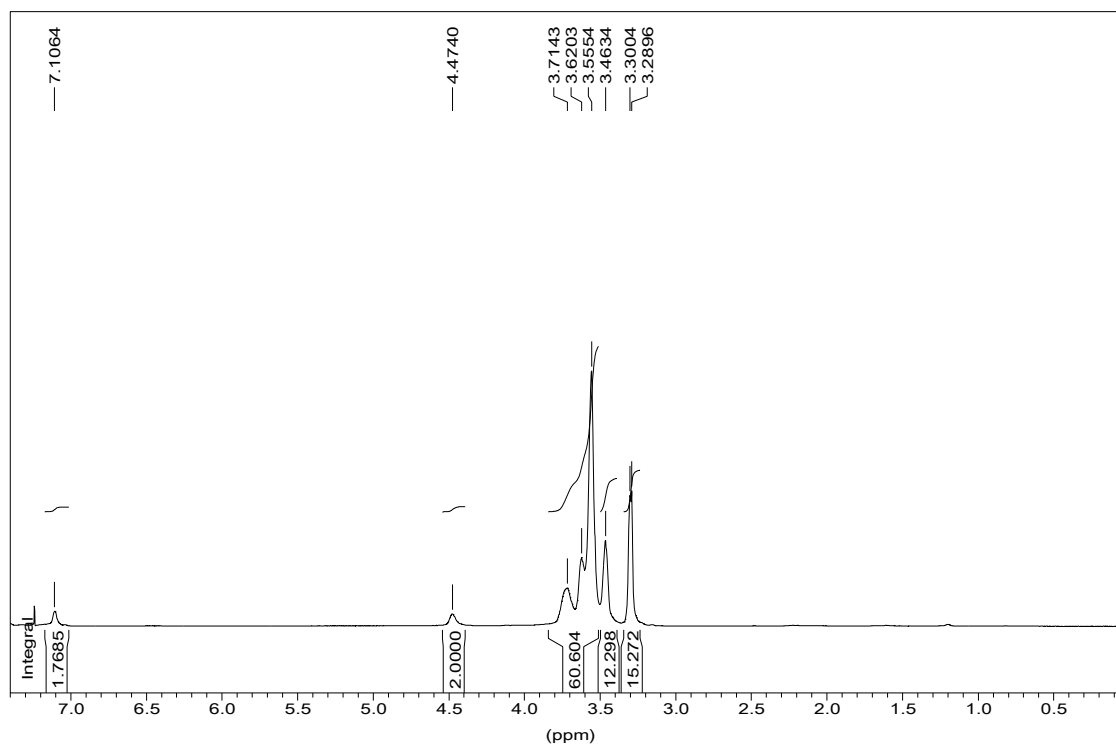


Figure 2. ¹H NMR spectrum of polymer **5** (500 MHz, CDCl₃, 25 °C).

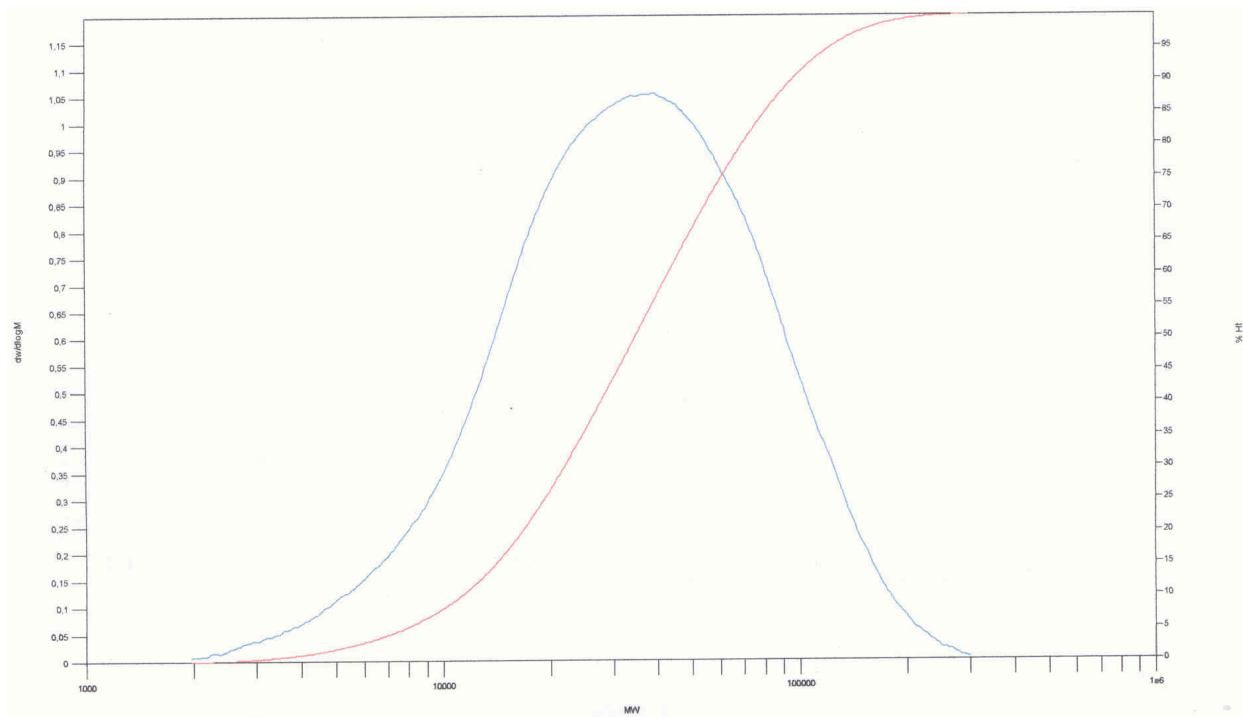


Figure 3. GPC trace of polymer **5** (THF, 40 °C).

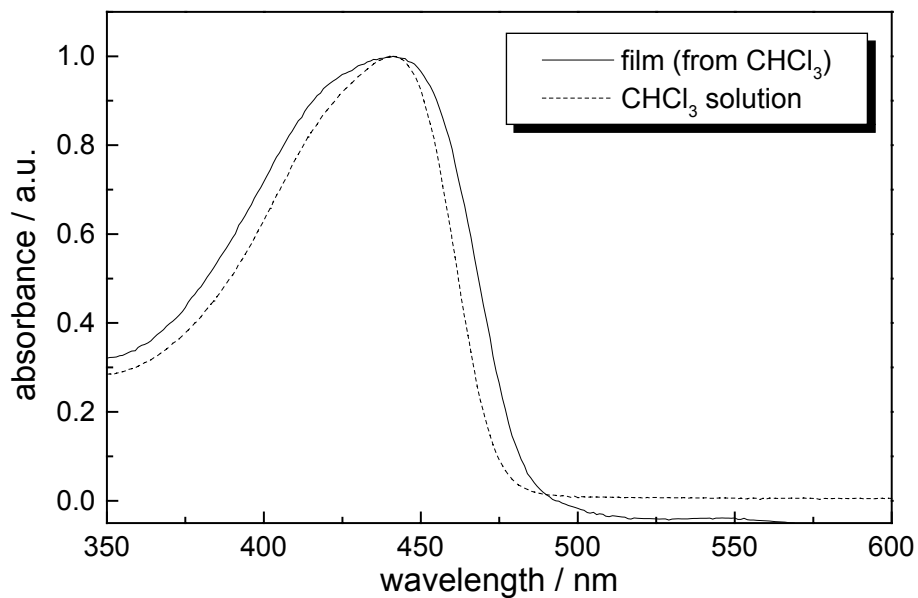


Figure 4. UV/vis absorption spectra of polymer **5** in CHCl₃ solution and in the annealed, i.e. heated, film prepared by drop casting from CHCl₃ (25 °C).

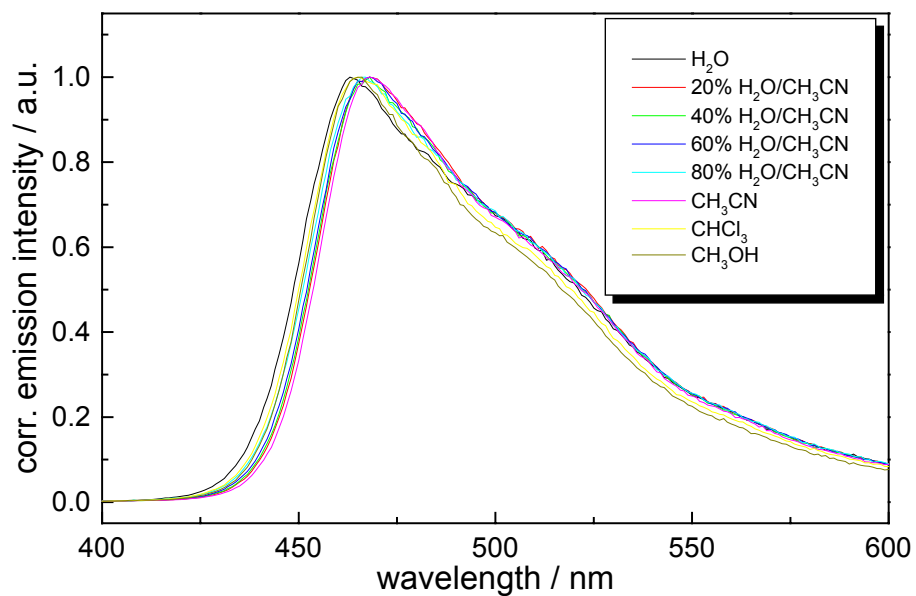


Figure 5. Corrected fluorescence emission spectra of polymer **5** in various solvents. The spectra have been normalized to their emission maximum in order to compare spectral shape.

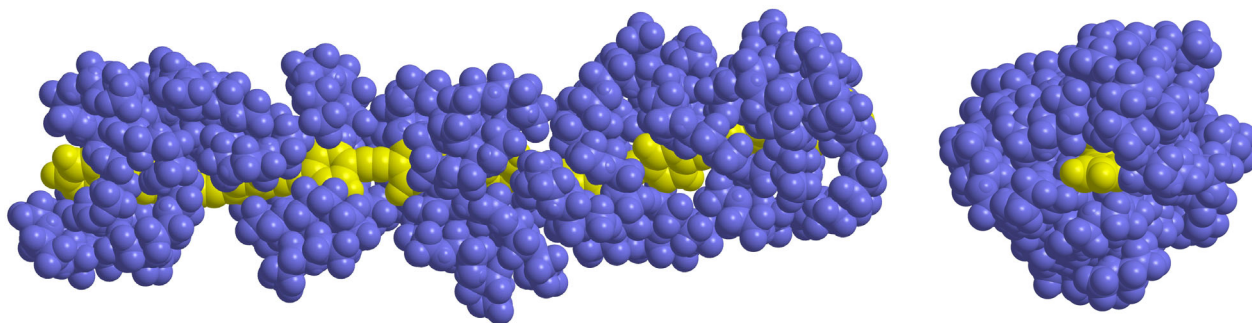


Figure 6. Molecular model (MM2) of decamer resembling polymer **5** (side and top views; PpPE-backbone is shown in yellow, branched OEG side chains in blue).