A supramolecular polymer formed by the combination of crown ether-based and charge-transfer molecular recognitions

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Electronic Supplementary Information (11 Pages)

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds 3\textsuperscript{2a,31}, 4\textsuperscript{32} and 5\textsuperscript{33} were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298 K in CH\textsubscript{3}CN. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Electrospun supramolecular polymer nanofibers were obtained under the following conditions: 15 KV, 2.0 mL/h syringe flow rate, and 20 cm working distance, from a concentrated equimolar solution of 200 mM monomers 1 and 2.
2. Syntheses of monomers 1 and 2

2.1. Synthesis of monomer 1

A mixture of 3 (4.78 g, 10 mmol), 4-(pyren-1-yl)butanoic acid (2.88 g, 10 mmol), 1-(3’-dimethylaminopropyl)-3-ethylicarbodiimide hydrochloride (EDC, 3.85 g, 20 mmol) and 4-dimethylaminopyridine (DMAP, catalytic amount) in CH₂Cl₂ (50 mL) was stirred overnight at room temperature. After filtration, the solution was washed with water and brine. Then the organic layer was dried by MgSO₄ overnight. Dichloromethane was removed and the residue was purified by column chromatography (CH₂Cl₂/petroleum ether, 1:1, v/v) to afford 1 as a yellow solid (3.63 g, 48%). Mp: 144.2–146.5 ºC. The ¹H NMR spectrum of compound 1 is shown in Figure S1. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.15 (d, J = 8.0 Hz, 1H), 8.05 (dd, J₁ = 8.0 Hz, J₂ = 4.0 Hz, 2H), 7.98 (t, J = 8.0 Hz, 2H), 7.91 (s, 2H), 7.88 (d, J = 4.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 6.80–6.70 (m, 7H), 4.94 (s, 2H), 4.04–4.01 (m, 8H), 3.77–3.75 (m, 8H), 3.72 (s, 4H), 3.69 (s, 4H), 3.27 (d, J = 8.0 Hz, 2H), 2.39 (d, J = 8.0 Hz, 2H), 2.10 (d, J = 8.0 Hz, 2H). The ¹³C NMR spectrum of 1 is shown in Figure S2. ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm): 25.74, 31.64, 32.87, 65.18, 68.27, 68.29, 68.36, 68.73, 70.16, 75.80, 76.05, 76.31, 112.54, 112.98, 113.34, 120.36, 123.89, 126.42, 134.60, 147.78, 147.84, 147.91, 172.25. LRESIMS is shown in Figure S3: m/z 771.5 [M + Na]⁺ (100%). HRESIMS: m/z calcd for [M+ H]⁺ C₄₅H₄₉O₁₀, 748.3247; found 748.3242; error −0.7 ppm.
Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of 1.
Figure S2. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 1.
**Figure S3.** Electrospray ionization mass spectrum of 1.
2.2. Synthesis of monomer 2

A mixture of 4 (3.13 g, 10 mmol), K$_2$CO$_3$ (2.76 g, 20 mmol) and 1,10-dibromodecane (6.00 g, 20 mmol) in CH$_3$CN (100 mL) was stirred under reflux overnight. Then the solvent was removed and the residue was dissolved in 10% HCl/ethyl acetate (50 mL) and the mixture was stirred overnight at room temperature. The white solid was filtered, washed with ethyl acetate thoroughly, and dissolved in warm deionized water/acetonitrile (250 mL, 5:1, v:v). A saturated aqueous solution of NH$_4$PF$_6$ was added to afford a white precipitate, which was filtered and washed with deionized water. This white precipitate was added to a mixture of 5 (6.5 g, 9.1 mmol), CuSO$_4$•5H$_2$O (0.25 g, 1.0 mmol), Sodium L-ascorbate (VcNa, 0.40 g, 2.0 mmol) and DMF (25 mL). The mixture was stirred at 50 ºC overnight. Then the mixture was dropped to cold water to yield a light yellow solid. The solid was filtered and recrystallized from CH$_3$CN/MeOH/water to afford 2 as a gray solid (4.1 g, 37%). Mp: 189.8–192.3 ºC. The $^1$H NMR spectrum of compound 2 is shown in Figure S4. $^1$H NMR (400 MHz, CD$_3$SOCD$_3$, 298 K) $\delta$ (ppm): 9.45 (d, $J$ = 8.0 Hz, 4H), 8.69 (d, $J$ = 8.0 Hz, 4H), 7.59 (d, $J$ = 8.0 Hz, 2H), 7.45–7.36 (m, 8H), 7.21 (s, 2H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.08 (s, 1H), 6.96 (d, $J$ = 8.0 Hz, 2H), 5.83 (d, $J$ = 8.0 Hz, 2H), 5.14 (s, 2H), 4.34 (t, $J$ = 8.0 Hz, 2H), 3.95 (t, $J$ = 8.0 Hz, 2H), 2.27 (s, 6H), 1.79–1.69 (m, 4H), 1.39–1.25 (m, 12H). The $^{13}$C NMR spectrum of 2 is shown in Figure S5. $^{13}$C NMR (125 MHz, CD$_3$CN, 298 K) $\delta$ (ppm): 21.37, 26.85, 27.25, 29.79, 30.06, 30.16, 30.22, 30.31, 31.06, 51.27, 51.87, 52.00, 62.68, 65.54, 66.03, 69.21, 116.09, 116.92, 118.62, 123.67, 125.25, 126.07, 128.12, 128.53, 130.20, 130.60, 131.13, 132.13, 132.46, 132.64, 132.83, 133.68, 140.76, 144.13, 146.51, 146.69, 151.45, 151.50, 160.94, 161.36. LRESIMS is shown in Figure S6: $m/z$ 270.2 [M – 3PF$_6$]$^{3+}$ (100%), 480.1 [M – 2PF$_6$]$^{3+}$ (100%). HRESIMS: $m/z$ calcd for [M – PF$_6$]$^{3+}$ C$_{53}$H$_{63}$F$_{12}$N$_6$O$_2$P$_2$, 1105.4296; found 1105.4280; error –1.4 ppm.
**Figure S4.** $^1$H NMR spectrum (400 MHz, CD$_3$SOCD$_3$, 298 K) of 2.

**Figure S5.** $^{13}$C NMR spectrum (125 MHz, CD$_3$CN, 298 K) of 2.
Figure S6. Electrospray ionization mass spectrum of 2.
3. $^1$H NMR spectra and UV/vis spectra of model compounds

**Figure S7.** Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 298 K): a) paraquat (5.00 mM); b) paraquat and pyrene (both 5.00 mM); c) pyrene (5.00 mM).

**Figure S8.** UV/Vis spectroscopy of pyrene (red line) and pyrene-paraquat complexes (black line). The concentrations of pyrene and paraquat are $0.45 \times 10^{-4}$ M.
Figure S9. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 298 K): a) dibenzo-24-crown-8 and monomer 2 (1.00 mM for each); b) after adding pyrene (1.00 mM).

References:

