

ORGANIC LETTERS

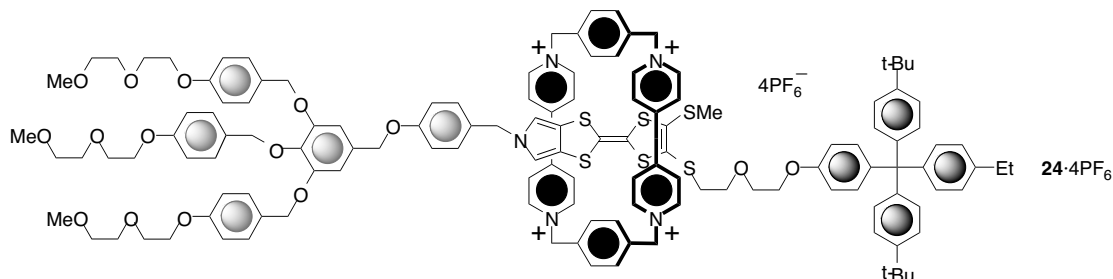
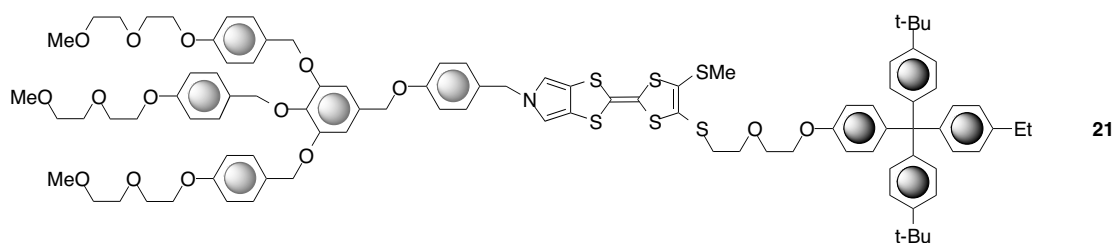
Self-Assembly of an Amphiphilic [2]Rotaxane Incorporating a Tetrathiafulvalene Unit

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SUPPORTING INFORMATION

(2 Pages)

EXPERIMENTAL PROCEDURES FOR **21** AND **24**•4PF₆



Experimental Section

Dumbbell **21**

Compound **20** (0.19 g, 0.21 mmol) and the chloride **18** (0.22 g, 0.24 mmol) were dissolved in anhydrous DMF (10 mL) and degassed (Ar, 10 min) before sodium hydride (0.021 g of a 60% suspension in mineral oil, 0.53 mmol) was added in one portion. The reaction mixture was stirred for 45 min at room temperature, causing the initially yellow solution to become more orange. H₂O (40 mL) was added dropwise (until no more gas evolution was observed), followed by addition of brine (40 mL). The yellow precipitate was filtered and dried. The crude product was purified by column chromatography (250 mL of silica gel, 6 cm Ø, eluent CH₂Cl₂/EtOAc 2:1). The yellow band (*R_f* = 0.35) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH₂Cl₂ (3 × 20 mL) and concentrated to give 0.29 g (80%) of the dumbbell **21** as an analytically pure yellow semisolid; ¹H NMR (400 MHz, CD₃COCD₃, 298 K) δ 1.17 (t, *J* = 7.6 Hz, 3H), 1.26 (s, 18H), 2.39 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 6.3 Hz, 2H), 3.26 (s, 9H), 3.44–3.49 (m, 6H), 3.59–3.64 (m, 6H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.76–3.81 (m, 8H), 4.05–4.13 (m, 8H), 4.88 (s, 2H), 4.97 (s, 2H), 5.00 (s, 2H), 5.01 (s, 4H), 6.70 and 6.72 (AB q, *J* = 2.1 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 4H), 6.84 (s, 2H), 6.89–6.94 (m, 6H), 7.03–7.16 (m, 12H), 7.25–7.33 (m, 6H), 7.37 (d, *J* = 8.8 Hz, 4H); MS(FAB) *m/z* 1736 (M⁺). Anal. Calcd for C₉₈H₁₁₃NO₁₅S₆ (1737.3): C, 67.75; H, 6.56; N, 0.81. Found: C, 67.61; H, 6.46; N, 0.80.

[2]Rotaxane **24•4PF₆**

A solution of the dumbbell **21** (0.26 g, 0.15 mmol), 1,4-bis(bromomethyl)benzene (**23**) (0.12 g, 0.45 mmol) and **22•2PF₆** (0.33 g, 0.47 mmol) in anhydrous DMF (10 mL) was stirred for 6 d at room temperature (after approx. one day the color changed to green and a white precipitate was formed). The green suspension was directly subjected to column chromatography (250 mL of silica gel 6 cm Ø) and unreacted dumbbell was eluted with Me₂CO, whereupon the eluent was changed to Me₂CO/NH₄PF₆ (1.0 g NH₄PF₆ in 100 mL Me₂CO) and the green band was collected. Most of the solvent was removed in vacuo (*T* < 30 °C) followed by addition of H₂O (30 mL). The resulting precipitate was collected by filtration, washed with Et₂O (20 mL) and dried affording 0.035 g (8%) of the [2]rotaxane **24•4PF₆** as a green solid: mp 135 °C (dec without melting); ¹H NMR (400 MHz, CD₃COCD₃, 298 K) δ 1.19 (t, *J* = 7.6 Hz, 3H), 1.28 (s, 18H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.64 (s, 3H), 3.28 (s, 6H), 3.29 (s, 3H), 3.29 (t, *J* = 6.4 Hz, 2H), 3.47–3.50 (m, 6H), 3.61–3.65 (m, 6H), 3.77–3.81 (m, 6H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.98–4.01 (m, 2H), 4.08–4.14 (m, 6H), 4.23–4.25 (m, 2H), 4.69 (s, 2H), 4.80 (s, 4H), 4.97 (s, 2H), 5.18 (s, 2H), 5.98–6.08 (m, 8H), 6.43 and 6.45 (AB q, *J* = 2.1 Hz, 2H), 6.78 (s, 2H), 6.83–6.85 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 4H), 7.07–7.12 (m, 10H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.26–7.31 (m, 10H), 7.38 (bs, 4H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.94–8.06 (m, 8H), 8.45 (bs, 4H), 9.16 (bs, 4H), 9.48 (bs,

4H); MS(FAB) m/z 2691 (M – PF₆)⁺, 2546 (M – 2PF₆)⁺, 2401 (M – 3PF₆)⁺, 1736 (dumbbell)⁺, 1273 (M – 2PF₆)²⁺, 1200.5 (M – 3PF₆)²⁺, 1128 (M – 4PF₆)²⁺; UV-vis (Me₂CO) λ_{max} 810 nm, (ϵ 1400 L mol⁻¹ cm⁻¹). Anal. Calcd for C₁₃₄H₁₄₅F₂₄N₅O₁₅P₄S₆·2H₂O (2837.6): C, 56.00; H, 5.23; N, 2.44. Found: C, 56.07; H, 5.06; N, 2.28.