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## **A propeller-like uranyl metallomesogen**

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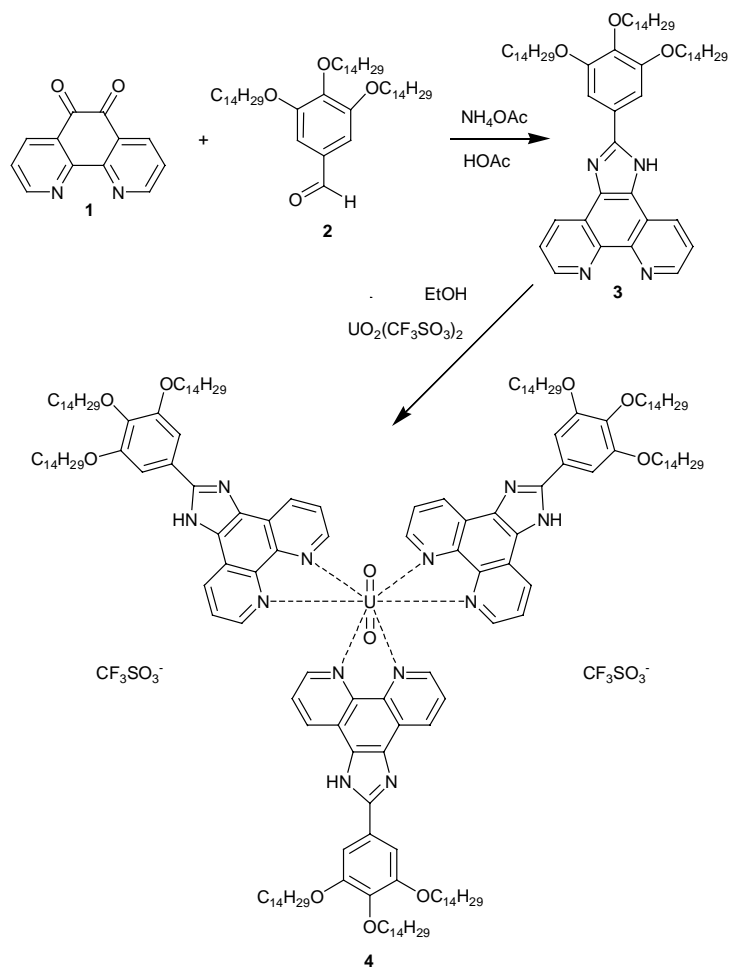
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### **Experimental Techniques:**

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz) or a Bruker AMX-400 (operating at 400 MHz). FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method. Elemental analyses were obtained on a CE-Instrument EA-1110 elemental analyzer. Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature-controller. DSC traces were recorded with a Mettler-Toledo DSC821e module.

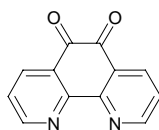
The XRD patterns were obtained with two different experimental set-ups, and in all cases, the powdered sample was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic  $\text{CuK}\alpha_1$  beam ( $\lambda = 1.5405 \text{ \AA}$ ) obtained with a sealed-tube generator (900 W) and a bent quartz monochromator were used (both generator and monochromator were manufactured by Inel). One set of diffraction patterns was registered with a curved counter Inel CPS 120, for which the sample temperature is controlled within  $\pm 0.05 \text{ }^\circ\text{C}$ ; periodicities up to  $60 \text{ \AA}$  can be measured. The other set of diffraction patterns was registered on Image Plate. Periodicities up to  $90 \text{ \AA}$  can be measured, and the sample temperature is controlled within  $\pm 0.3 \text{ }^\circ\text{C}$ .

## Synthesis



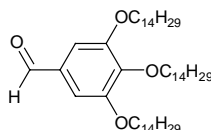
Scheme 1

**(a) 1,10-phenanthroline-5,6-dione (1)**



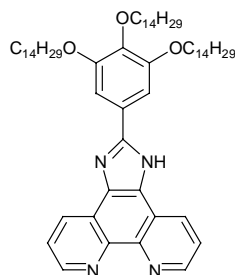
1,10-Phenanthroline monohydrate (0.0504 mol, 10.00 g) was added in small portions under stirring to 60 mL of concentrated sulfuric acid in a round-bottom flask (500 mL) equipped with a reflux condenser. After the solid compound was dissolved, sodium bromide (0.0504 mol, 5.19 g) was added, followed by 30 mL of 70% nitric acid. The mixture was heated to 105 °C for 6 hours. The temperature was then lowered to 95 °C and the reflux condenser was removed to allow the bromine vapors to escape for a period of 16 hours. After being cooled, the mixture was poured onto 800 g of ice and was carefully neutralized to pH 7 with about 300 mL of a 10 M solution of sodium hydroxide. The turbid solution was filtered and the solid residue was extracted with 5 × 200 mL of boiling water. The insoluble material was removed from the cooled extraction liquid by filtration and the combined aqueous solutions were extracted with dichloromethane, dried over anhydrous MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was recrystallized from toluene to obtain orange crystals. Yield: 30% (3.18 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 7.58–7.62 (dd, 2H, H-aryl, *J*<sub>o</sub> = 8.1 Hz, *J*<sub>o</sub> = 4.8 Hz), 8.53 (dd, 2H, H-aryl, *J*<sub>o</sub> = 8.1 Hz, *J*<sub>m</sub> = 1.8 Hz), 9.12 (dd, 2H, H-aryl, *J*<sub>o</sub> = 4.8 Hz, *J*<sub>m</sub> = 1.8 Hz). Calcd. for C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>·0.25H<sub>2</sub>O: C 67.13, H 3.05, N 13.05. Found: C 67.25, H 2.77, N 12.99. M.p.: 257 °C.

**(b) Aldehyde 2**



Aldehyde **2** was prepared by adding tetradecylbromide (0.0180 mol, 4.99 g) to a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (0.0058 mol, 1.00 g) and potassium carbonate (0.0180 mol, 2.49 g) in DMF (50 mL). A catalytic amount of potassium iodide was added and the mixture was refluxed for 3 hours under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was poured into 150 mL of a H<sub>2</sub>O/HCl (100:50) solution. The solution was extracted with dichloromethane and the combined organic layers were washed with brine, dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified on a silica column with hexane/ethyl acetate (95:5) as the eluent. The product was recrystallized from ethanol. Yield: 41% (1.72 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 0.89 (t, 9H, CH<sub>3</sub>), 1.27–1.49 (m, 66H, CH<sub>2</sub>), 1.72–1.88 (m, 6H, –CH<sub>2</sub>–CH<sub>2</sub>–O–), 4.02–4.17 (m, 6H, –CH<sub>2</sub>–O–), 7.09 (s, 2H, H-aryl), 9.84 (s, 1H, CH=O). Calcd for C<sub>49</sub>H<sub>90</sub>O<sub>4</sub>·0.5(CH<sub>3</sub>CH<sub>2</sub>OH): C 78.37, H 12.23. Found: C 78.52, H 12.22. M.p.: 58 °C.

**(c) Ligand 3**

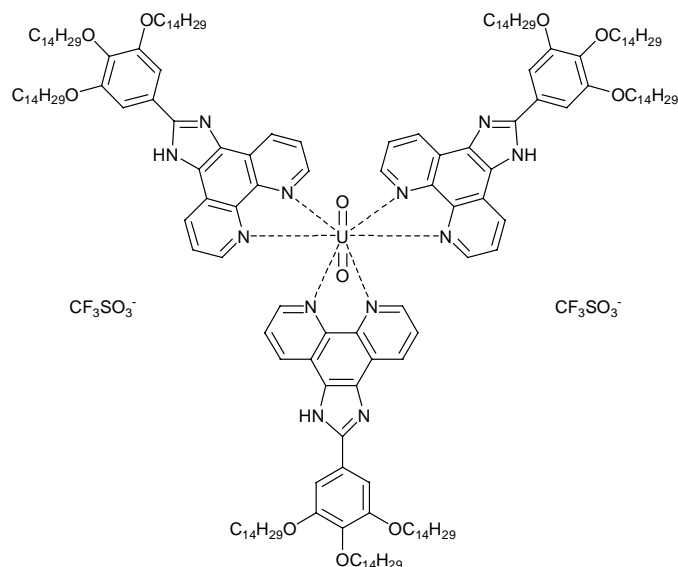


Ligand **3** was prepared by adding aldehyde **2** (0.0020 mol, 1.50 g) to a warm solution of 1,10-phenanthroline-5,6-dione (0.0020 mol, 0.42 g) and ammonium acetate (0.0170 mol, 1.32 g) in 20 mL of glacial acetic acid. The mixture was heated to 85 °C for 5 hours. After the reaction mixture was cooled to room temperature, it was poured into 100 mL of water and neutralized to pH 7 with an aqueous ammonia solution. The precipitate was filtered, washed with distilled water and dried. The crude product was purified on a silica column with  $\text{CHCl}_3$ /hexane/MeOH (50:50:10) as the eluent. Since the compound holds solvents firmly, it was dried in a vacuum oven at 50 °C. Yield: 55% (1.03 g).  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ ,  $\delta$  ppm): 0.87 (t, 9H,  $\text{CH}_3$ ), 1.25–1.67 (m, 72H,  $\text{CH}_2$ ), 3.60 (m, 4H,  $-\text{CH}_2-\text{O}-$ ), 3.88 (t, 2H,  $-\text{CH}_2-\text{O}-$ ), 7.30 (m, 1H, H-aryl), 7.68 (s, 2H, H-aryl), 7.74 (m, 1H, H-aryl), 8.66 (d, 1H, H-aryl), 8.80 (d, 1H, H-aryl), 8.97 (d, 1H, H-aryl), 9.19 (d, 1H, H-aryl), 14.82 (s, 1H, N–H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{THF-d}_8$ ,  $\delta$  ppm): 14.36, 23.46, 26.91, 27.03, 30.23, 30.59, 31.26, 32.79, 69.25, 73.51, 105.86, 121.15, 123.68, 124.17, 125.88, 126.39, 127.92, 131.02, 131.42, 137.57, 140.35, 144.67, 144.94, 147.75, 148.24, 152.80, 154.24. Calcd for  $\text{C}_{61}\text{H}_{96}\text{N}_4\text{O}_3$ : C 78.49, H 10.37, N 6.00. Found: C 78.77, H 10.63, N 5.50. ESI-MS (Methanol,  $m/z$ ): 933.9,  $[\text{M} + \text{H}]^+$ . M.p.: 83 °C.

**(d) Uranyl triflate**

Triflic acid (0.0663 mol, 11 mL) was added into a 100 mL round-bottomed flask containing  $\text{UO}_3$  (0.0024 mol, 0.7 g) and the mixture was refluxed for 24 hours under a nitrogen atmosphere. The excess of triflic acid was removed under vacuum into a trap connected between the flask and the vacuum line and cooled in liquid nitrogen. The compound was dried under vacuum at 80 °C. Yield: 73% (1.00 g). Calcd for  $\text{C}_2\text{F}_6\text{O}_8\text{S}_2\text{U} \cdot 3\text{H}_2\text{O}$ : C 3.86, H 0.97. Found: C 3.81, H 1.17.

**(e) Uranyl complex 4**



The uranyl complex **4** was prepared by slowly adding a solution of  $\text{UO}_2(\text{CF}_3\text{SO}_3)_2$  (0.036 mmol, 0.020 g) in ethanol to a warm solution of the ligand **3** (0.107 mmol, 0.100 g) in ethanol. The mixture was stirred for 30 minutes at 65 °C. The orange precipitate was filtered off, washed with ethanol and dried in a vacuum oven at 50 °C. Yield: 83% (0.100 g).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ ,  $\delta$  ppm): 0.88 (m, 27H,  $\text{CH}_3$ ), 1.30–1.83 (m, 216H,  $\text{CH}_2$ ), 3.99–4.07 (m, 18H,  $-\text{CH}_2-\text{O}-$ ), 7.49 (s, 6H, H-aryl), 7.88 (m, 6H, H-aryl), 8.92 (m, 6H, H-aryl), 9.20 (m, 6H, H-aryl). IR (KBr-pellet,  $\text{cm}^{-1}$ ): 3530 (m,  $\nu(\text{N-H})$ ), 2920, 2850 (s, C–H and C–F stretch), 1242, 1028 (s, S–O stretch), 918 (s,  $\nu(\text{U=O})$ ), 636, 517 (s,  $\nu(\text{S-O})$ ). Calcd for  $\text{C}_{185}\text{H}_{288}\text{F}_6\text{N}_{12}\text{O}_{17}\text{S}_2\text{U}$ : C 65.96, H 8.62, N 4.99. Found: C 65.59, H 8.87, N 4.74. The compound is a liquid crystal:  $\text{Cr} \cdot 95 \cdot \text{Col}_h \cdot 181 \cdot \text{I}$ .