Electronic Supporting Information

Fullerene-Based Liquid Crystals Acting as Acid-Sensitive Fluorescent Probes

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Synthesis of 2. A mixture of C₆₀ (130 mg, 0.18 mmol), 3 (67.8 mg, 0.12 mmol) and glycine (45 mg, 0.6 mmol) was heated under reflux for 6 h in degassed anhydrous chlorobenzene (30 mL) under inert atmosphere. After removal of the solvents, the residue was purified by column chromatography (silica gel, toluene/hexane 8:2). The product was centrifuged with CH₃OH and n-pentane to give 2 (28%) as a dark brown solid. ¹H NMR (200 MHz, CDCl₃) δ/ppm: 0.95 (t, 12H, J = 7.0 Hz), 1.23-1.44 (m, 8H), 1.49-1.67 (m, 8H), 3.28 (t, 8H, J = 7.4 Hz), 4.90 (d, 1H, J = 10.4 Hz), 5.13 (d, 1H, J = 10.4 Hz), 5.80 (s, 1H), 6.61 (d, 4H, J = 8.5 Hz), 6.90 (d, 2H, J = 16.4 Hz), 7.07 (d, 2H, J = 16.4 Hz), 7.38 (d, 4H, J = 8.5 Hz), 7.53 (s, 1H), 7.70 (s, 2H). ¹³C NMR (50 MHz, CDCl₃) δ/ppm: 156.3, 154.2, 153.9, 153.3, 151.4, 148.1, 147.4, 146.7, 146.5, 146.4, 146.1, 145.6, 145.5, 145.2, 144.8, 144.6, 144.5, 144.3, 143.3, 143.1, 142.7, 142.4, 141.9, 141.3, 140.3, 140.1, 139.9, 139.1, 138.3, 138.1, 136.6, 136.3, 136.1, 129.7, 129.1, 128.0, 124.5, 124.2, 123.6, 111.8, 73.1, 62.0, 51.0, 29.9, 20.5, 14.2. IR (KBr) ν/cm⁻¹: 525 (C₆₀). MALDI-TOF MS m/z calculated for C₁₀₀H₅₅N₃: 1297.44 (M +), found: 1297.97 (M +). UV–vis (CH₂Cl₂) λmax/nm (log ε): 257 (4.8), 325 (4.5), 374 (4.5), 431 (3.7).

Synthesis of 1a. A mixture of 4a (100 mg, 0.036 mmol) and thionyl chloride (0.1 mL, 1.3 mmol) was heated under reflux for 7 h in anhydrous CH₂Cl₂. The solvent was evaporated under reduced pressure and a solution of 2 (35 mg, 0.025 mmol) in CH₂Cl₂ (30 mL) and anhydrous pyridine (3.7 mg, 0.05 mmol) was added. The mixture was stirred at room temperature for 30 minutes. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/ethyl acetate 3:2). A further purification by centrifugation with CH₃OH afforded 1a in quantitative yield as a green solid. ¹H NMR (200 MHz, CDCl₃) δ/ppm 0.98 (t, 12H, J = 7.0 Hz), 1.23-1.44 (m, 8H), 1.82 (broad m, 28H), 3.31 (t, 8H, J = 7.4 Hz), 4.04 (t, 10H, J = 6.4 Hz), 4.39 (t, 10H, J = 6.4 Hz), 5.75 (d, 1H, J = 10.4 Hz), 5.82 (d, 1H, J = 10.4 Hz), 6.00 (s, 1H), 6.65 (d, 4H, J = 8.6 Hz), 6.99 (m, 10H), 7.11 (d, 2H, J = 16.2 Hz), 7.15-7.35 (m, 10H), 7.43 (d, 4H, J = 8.6 Hz), 7.62-7.77 (m, 24H), 7.88 (s, 1H), 7.92 (s, 2H), 8.12-8.24 (m, 18H), 8.38 (t, 2H, J = 1.6 Hz), 8.67 (t, 2H, J = 1.6 Hz), 8.98 (t, 1H, J = 1.6 Hz). ¹³C NMR (125 MHz, CDCl₃) δ/ppm: 164.8, 164.72, 164.7, 164.6, 164.4, 164.1, 163.6, 163.0, 155.5, 152.8, 151.8, 151.6, 151.5, 150.5, 148.0, 147.9, 147.4, 146.3, 146.2, 146.0, 145.6, 145.4, 145.3, 144.8, 144.5, 144.3, 143.0, 142.7, 142.4, 141.9, 141.6, 141.3, 140.3, 140.1, 139.9, 139.1, 138.3, 138.1, 136.6, 136.3, 136.1, 129.7, 129.1, 128.0, 124.5, 124.2, 123.6, 111.8, 73.1, 62.0, 51.0, 29.9, 20.5, 14.2. IR (KBr) ν/cm⁻¹: 525 (C₆₀). MALDI-TOF MS m/z calculated for C₁₀₀H₅₅N₃: 1297.44 (M⁺), found: 1297.97 (M⁺). UV–vis (CH₂Cl₂) λmax/nm (log ε): 257 (4.8), 325 (4.5), 374 (4.5), 431 (3.7).
Synthesis of 1b. A mixture of 4b (75 mg, 0.014 mmol) and thionyl chloride (0.04 mL, 0.5 mmol) was heated under reflux for 40 h in anhydrous CH₂Cl₂. The solvent was evaporated under reduced pressure and a solution of 2 (18 mg, 0.014 mmol) in CH₂Cl₂ (30 mL) and anhydrous pyridine (2.3 mg, 0.03 mmol) was added. The mixture was stirred at room temperature for 30 minutes. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/ethyl acetate 7:3). A further purification by centrifugation with CH₃OH afforded 1b in quantitative yield as a green solid. ¹H NMR (200 MHz, CDCl₃) δ/ppm 0.95 (m, 12H, J = 13.5 Hz), 1.25-1.57 (m, 116H), 1.57-1.76 (broad m, 44H), 3.28 (t, 8H, J = 7.4 Hz), 4.03 (t, 18H, J = 6.3 Hz), 4.36 (t, 18H, J = 6.6 Hz), 5.71 (d, 1H, J = 10.4 Hz), 5.77 (d, 1H, J = 10.4 Hz), 6.21 (s, 1H), 6.62 (d, 4H, J = 8.8 Hz), 6.88-7.17 (m, 20H), 7.27-7.42 (m, 22H), 7.60-7.81 (m, 49H), 7.86 (d, 2H, J = 8.8 Hz), 8.12 (m, 30H), 8.35 (t, 6H, J = 1.4 Hz), 8.63 (t, 4H, J = 1.4 Hz), 8.92 (t, 3H, J = 1.5 Hz). ¹³C NMR (125 MHz, CDCl₃) δ/ppm: 166.0, 165.0, 164.9, 163.8, 163.0, 151.7, 151.2, 150.7, 148.2, 146.3, 145.5, 145.0, 142.8, 142.3, 139.9, 139.7, 136.8, 132.8, 132.5, 131.6, 131.0, 130.4, 130.2, 128.5, 128.2, 127.8, 127.1, 124.3, 122.7, 121.4, 119.0, 114.7, 114.5, 111.8, 111.5, 111.2, 68.5, 66.0, 50.9, 41.5, 34.8, 31.7, 29.6, 29.4, 29.2, 28.8, 26.1, 25.5, 22.8, 20.8, 20.5, 18.9, 14.5, 14.3, 14.2, 11.6. IR (KBr) ν/cm⁻¹: 528 (C₆₀). MALDI-TOF MS m/z calculated for C₁₂₆H₁₁₀N₁₇O₃₀: 4026.583 (M⁺), found: 4026.93 (M⁺).
Figure S1. $^{1}$H NMR spectrum of compound 2
Figure S2. $^{13}$C NMR spectrum of compound 2
Figure S3. MALDI-TOF MS spectrum of compound 2
Figure S4. $^1$H NMR spectrum of compound 1a
Figure S5. $^{13}$C NMR spectrum of compound 1a
Figure S6. MALDI-TOF MS spectrum of compound 1a
Figure S7. $^1$H NMR spectrum of compound 1b
Figure S8. $^{13}$C NMR spectrum of compound 1b
Figure S9. MALDI-TOF MS spectrum of compound 1b
**Figure S10.** CV plot of compound 1a in ODCB/CH$_3$CN 4:1 at room temperature

**Figure S11.** CV plot of compound 2 in ODCB/CH$_3$CN 4:1 at room temperature
**Figure S12.** Absorption spectra of non-protonated (---) and protonated (---) 1a.

**Figure S13.** Emission spectra of fulleropyrrolidine 1a in dichloromethane upon addition of Et₃N ($\lambda_{exc} = 336$ nm).
Figure S14. Small-angle diffraction pattern of compound 1a in the smectic A phase

Figure S15. Small-angle diffraction pattern of compound 1b in the smectic A phase. The sample adopts some preferential orientation