

New Fluorescent Amide-Functionalized Phenylethynyl-Thiophene Low-Molecular-Weight Gelator

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Supporting Information

Materials and General Procedures. All solvents used in synthesis were distilled under nitrogen and saturated with nitrogen prior to use. All chemical reagents were commercially available and used without further purification unless otherwise noted. Flash column chromatography was carried out with 230-400 mesh silica gel from Merck using the wet-packing method. NMR spectra were recorded on either a Bruker AMX400 (400.168 MHz for ^1H and 100.622 MHz for ^{13}C) or a Bruker AV500 spectrometer (499.773 MHz for ^1H , 125.669 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. Electrospray mass spectra were obtained using a Thermo Finnigan mass spectrometer equipped with an electrospray interface. TEM and SEM images were obtained using JEOL JEM-2011 and JEOL JSM-5400, respectively. Power X-ray diffractions were measured using Philips X'Pert PRO instrument.

Emission spectra were recorded in air-equilibrated CH₂Cl₂ solution at 293 K with a Fluorolog II photoluminescence spectrometer. The emission spectra were collected on samples with OD ~ 0.1 at the excitation wavelength. UV-visible spectra were checked before and after irradiation to monitor possible sample degradation. Luminescence quantum yields were calculated relative to 9,10-diphenylanthracene in cyclohexane solution ($\Phi_{\text{em}} = 0.95$). Corrected emission spectra were used for the quantum yield measurements. Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%.

Synthesis

Compound 2: Under an atmosphere of nitrogen, a 100-mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with phenylacetylene (1.6 g, 15.4 mmol), 2,3,4,5-tetrabromothiophene (3 g, 7.5 mmol), Pd(PPh₃)₂Cl₂ (530 mg, 0.75 mmol), CuI (145 mg, 0.75 mmol), MeOH (30 mL), and *i*Pr₂NH (30 mL). The mixture was refluxed for 24 h. After the reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the brown suspension was extracted with CH₂Cl₂ (100 mL x 3). The organic layer was collected, dried over MgSO₄, filtered through a short neutral alumina column, and then evaporated to dryness. The resulting brown residue was washed with MeOH to yield a pale brown solid (3 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.45 (m, 4 H), 7.45-7.28 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 131.7, 129.2, 128.5, 121.9, 121.4, 119.0, 98.7, 81.0. HREIMS: $m/z = 439.8866$ (Calcd. $m/z = 439.8870$ for M⁺). Anal. Calcd. for C₂₀H₁₀Br₂S: C, 54.33; H, 2.28. Found: C, 54.33; H, 2.56.

Compound 3: Under an atmosphere of nitrogen, a 100-mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with **2** (1.5 g, 3.4 mmol), Pd(PPh₃)₄ (390 mg, 0.34 mmol), CuI (60 mg, 0.34 mmol), MeOH (30 mL), and *i*Pr₂NH (15 mL). To this mixture was added ethynyltrimethylsilane (4.9 g, 7.0 mmol) and the solution was stirred at room temperature for 2 days followed by heating at 50 °C for 7 days. After the reaction, the volatile solvent was removed under reduced pressure. The resulting brown residue was subjected to column chromatography with hexanes/ethyl acetate (100/1) eluent. The desired product eluted as a yellow band. The solvent was evaporated on a rotary evaporator to yield a yellow solid (0.8 g, 50%). ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.45 (m, 4 H), 7.40-7.28 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 131.4, 128.7, 128.2, 125.7, 122.2, 101.3, 98.3, 97.1, 81.3, -0.253. HREIMS: *m/z* = 476.1445 (Calcd. *m/z* = 476.1450 for M⁺). Anal. Calcd. for C₃₀H₂₈SSi₂: C, 57.57; H, 5.92. Found: C, 75.66; H, 5.62.

Compound 4: A 100-mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with **3** (200 mg, 0.4 mmol), KF (35 mg, 1.7 mmol), MeOH (30 mL), and THF (30 mL). The mixture was stirred at room temperature for 8 h. The resulting brown residue was washed with MeOH to yield a pale yellow solid (150 mg, 99%). ¹H NMR (500 MHz, CDCl₃): δ 7.62-7.45 (m, 4 H), 7.45-7.25 (m, 6 H), 3.48 (s, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ 131.8, 129.2, 128.4, 127.0, 122.1, 98.8, 83.5, 80.8, 76.3. HREIMS: *m/z* = 332.0665 (Calcd. *m/z* = 332.0660 for M⁺). Anal. Calcd. for C₂₄H₁₂S: C, 86.70; H, 3.64. Found: C, 86.56; H, 3.62.

Compound 5: To a 500-mL flask containing 3,4,5-tris-dodecyloxyphenylamine (13.1 g, 19.5 mmol) and 4-bromo-pyridine-2,6-dicarbonyl dichloride (2.6 g, 9.3 mmol) was added CH₂Cl₂ (200 mL) and NEt₃ (2.8 mL) and the resulting mixture was stirred at room temperature for 12 h. The solution was washed with

water (100 mL x 3). The organic layer was collected and dried over MgSO₄. After evaporating the solvent, the residue was subjected to column chromatography eluting with hexanes. The obtained crude product was recrystallized with ethyl acetate to afford white powder of **5** (11.5 g, 83%). The product was not further purified and adequately pure to next reaction. ¹H NMR (400 MHz, CDCl₃): δ 9.23 (s, 2 H), 8.55 (s, 2 H), 6.94 (s, 4 H), 3.94 (m, 12 H), 1.85-1.65 (m, 12 H), 1.55-1.35 (m, 12 H), 1.35-1.15 (m, 96 H), 0.86 (t, 18 H, ³J = 6.7 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 160.0, 153.4, 150.1, 137.0, 135.8, 132.2, 128.8, 99.6, 73.6, 69.3, 31.9, 30.4, 29.8, 29.72, 29.70, 29.67, 29.5, 29.43, 29.39, 29.37, 26.2, 26.1, 22.7, 14.1. HRFABMS: m/z = 1500.1262 (Calcd. m/z = 1500.1232 for M⁺).

Compound 6: Essentially the same procedure as above was employed to synthesize this compound. Yield: 83%. The product was not further purified and adequately pure to next reaction. ¹H NMR (400 MHz, CDCl₃): δ 9.39 (s, 2 H), 8.48 (s, 2 H), 7.53 (d, 4 H, ³J = 8.4 Hz), 6.81 (d, 4 H, ³J = 8.3 Hz), 3.89 (t, 4 H, ³J = 6.5 Hz), 1.85-1.55 (m, 4 H), 1.50-1.35 (m, 4 H), 1.35-1.15 (m, 32 H), 0.86 (t, 6 H, ³J = 6.3 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 160.0, 156.6, 150.0, 136.6, 129.6, 128.5, 122.1, 114.76, 68.3, 31.9, 29.7, 29.63, 29.61, 29.59, 29.4, 29.34, 29.27, 26.0, 22.7, 14.1. HRFABMS: m/z = 764.3985 (Calcd. m/z = 764.4002 for M⁺).

Compound 7: Under an atmosphere of nitrogen, a 100-mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with **4** (150 mg, 0.44 mmol), **5** (1.4 g, 0.91 mmol), Pd(PPh₃)₄ (50 mg, 0.04 mmol), CuI (10 mg, 0.04 mmol), and *i*Pr₂NH (10 mL). The mixture was stirred at room temperature for 24 h. After the reaction, the volatile solvent was removed under reduced pressure. The resulting brown residue was subjected to column chromatography. The undesired side products were eluted with hexanes. The desired product eluted with CH₂Cl₂ as a

yellow band, which was collected. The solvent was evaporated on a rotary evaporator to yield a yellow solid (0.66 g, 47%). ^1H NMR (400 MHz, CDCl_3 , 333K): δ 9.24 (s, 4 H), 8.50 (s, 4 H), 7.70-7.60 (m, 4 H), 7.50-7.30 (m, 6 H), 7.0 (s, 8 H), 4.0-3.8 (m, 24 H), 1.85-1.60 (m, 24 H), 1.55-1.35 (m, 24 H), 1.35-1.12 (m, 96 H), 0.93-0.75 (m, 18 H). ^{13}C NMR (100 MHz, CDCl_3) (333K): 160.8, 153.2, 150.2, 136.0, 134.2, 133.0, 132.8, 132.0, 129.6, 128.8, 128.4, 126.4, 126.2, 121.9, 101.0, 100.2, 92.9, 89.5, 80.6, 73.7, 69.6, 69.5, 32.0, 30.7, 30.5, 29.82, 29.79, 29.74, 29.68, 29.4, 26.32, 26.26, 22.7, 14.0. MALDIMS: m/z = 3173.6 (Calcd. m/z = 3172.5 for $[\text{M}+\text{H}]^+$). Anal. Calcd. for $\text{C}_{206}\text{H}_{326}\text{N}_6\text{O}_{16}\text{S}\cdot 8\text{H}_2\text{O}$: C, 74.55; H, 10.39; N, 2.53. Found: C, 74.64; H, 10.15; N, 2.48.

Compound 8: Under an atmosphere of nitrogen, a 100-mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with **4** (230 mg, 0.7 mmol), **6** (1.1 g, 0.91 mmol), $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 0.07 mmol), CuI (13 mg, 0.07 mmol), toluene (40 mL), and $i\text{Pr}_2\text{NH}$ (20 mL). The mixture was stirred at room temperature for 24 h followed by heating at 50 $^\circ\text{C}$ for another 24 h. After the reaction, the volatile solvent was removed under reduced pressure. The resulting residue was redissolved in THF and slowly precipitated with CH_2Cl_2 in freezer to afford a yellow solid (0.62 g, 52%). ^1H NMR (500 MHz, CDCl_3 , 298K): 9.40 (s, 4 H), 8.37 (s, 4 H), 7.57 (s, 8 H), 7.36 (s, 4 H), 7.24 (s, 6 H), 6.71 (s, 8 H), 3.83 (s, 8 H), 1.73 (s, 8 H), 1.5-1.15 (m, 72 H), 0.87 (s, 12 H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): 160.5, 156.1, 149.5, 134.2, 131.9, 130.3, 129.4, 128.6, 127.8, 126.7, 126.4, 121.6, 114.6, 100.6, 92.7, 89.11, 80.7, 68.3, 31.9, 29.7, 29.5, 29.4, 26.1, 22.7, 14.10. ^1H NMR (400 MHz, CDCl_3 , 333K): δ 10.63 (s, 4 H), 8.38 (s, 4 H), 7.72 (d, 8 H, 3J = 8.4 Hz), 7.59 (s, 4 H), 7.38 (s, 6 H), 6.80 (d, 8 H, 3J = 4.25 Hz), 3.89 (t, 8 H, 3J = 6.2 Hz), 1.83-1.63 (m, 8 H), 1.5-1.1 (m, 72 H), 0.95-0.70 (m, 12 H). ^{13}C NMR (100 MHz,

CDCl₃, 333K): 160.0, 155.3, 149.4, 132.4, 131.1, 130.7, 129.1, 128.2, 126.9, 125.7, 125.5, 122.2, 120.7, 131.9, 99.9, 92.7, 87.5, 80.1, 67.5, 30.9, 28.7, 28.6, 28.54, 28.51, 28.31, 25.2, 21.7, 13.3. HRFABMS: $m/z = 1698.9994$ (Calcd. $m/z = 1698.9984$ for $[M+H]^+$). Anal. Calcd. for C₁₁₀H₁₃₄N₆O₈S•H₂O: C, 76.89; H, 7.98; N, 4.89. Found: C, 76.62; H, 7.94; N, 4.80.

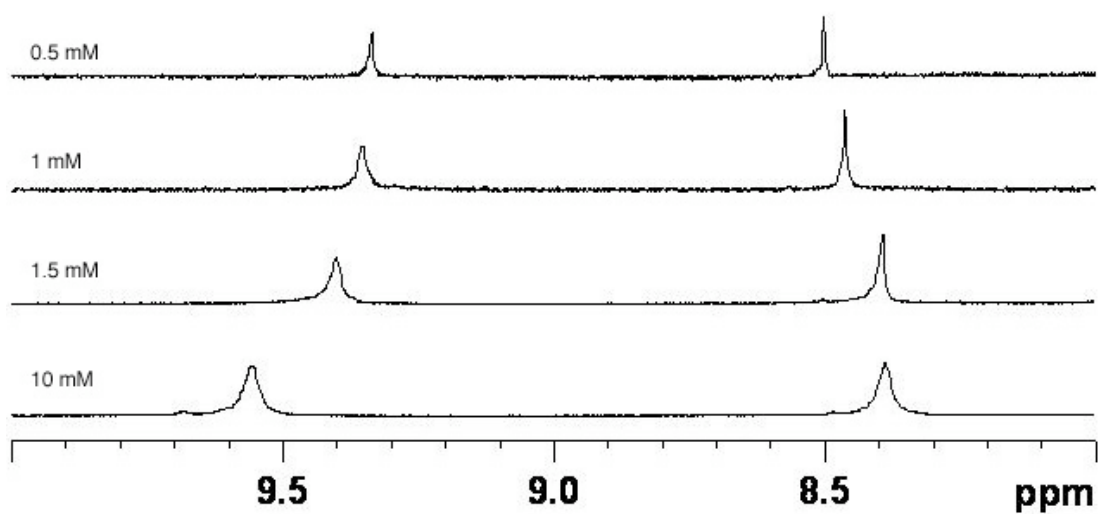


Figure S1. The ¹H NMR spectra of dilution experiments of **8** in CDCl₃.