# From Vesicles to Solid Spheres: Terminal Group Induced Morphology Modification

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## Electronic supplementary information

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**General procedure for preparation of compound 1a and 1b.**

**Synthesis of 2a and 2b.** 11-bromoundecanoic acid (5.0 g, 18.8 mmol) was dissolved in 30 mL $SOCl_2$. The solution was refluxed at 75 °C for 4 hours. Then the $SOCl_2$ was evaporated and the resulted brown liquid was dried under vacuum. The brown liquid in 20 mL dry THF was then slowly added to the 30 mL THF solution of 4-amino-pyridine (2.13 g, 22.6 mmol, 1.2 eq) in argon. The mixture was stirred at room temperature for 4 h and was purified by washing with hydrochloride acid (2 mol/L, 30 mL), followed by saturated $NaHCO_3$ solution. **2a** was obtained as a light yellow solid (5.8 g, 91%). $^1$H NMR ($CDCl_3$), 400 MHz: 8.48 (dd, $J$ = 4.9, 1.5 Hz, 2H); 7.92 (s, 1H); 7.52 (dd, $J$ = 4.9, 1.5 Hz, 2H); 3.42 (t, $J$ = 6.8 Hz, 2H); 2.41 (t, $J$ = 7.5 Hz, 2H); 1.91 – 1.81 (m, 2H), 1.78 – 1.68 (m, 2H), 1.30 (m, 12H). $^{13}$C NMR ($CDCl_3$), 100 MHz: 172.6; 155.3; 149.4; 109.0; 36.1; 33.7; 32.6; 29.6; 28.0; 25.6. MS (ESI) calcd for $C_{16}H_{25}BrN_2O$: 340.12, Found: 341.1 $[M+H]^+$. Elemental analysis calcd (%) for $C_{16}H_{25}BrN_2O$: C, 66.57; H, 7.12; N, 10.66; Found: C, 66.23; H,7.59; N, 10.90.

**2b** was synthesized using a similar process with **2a** by 11-bromoundecanoic acid (5.0 g, 18.8 mmol) and *p*-methylaniline (2.13 g, 22.6 mmol, 1.2 eq) as a light yellow solid (4.5 g, 68%). $^1$H NMR ($CD_3OD$), 400 MHz: 7.39 (d, $J$ = 6.3 Hz, 2H), 7.09 (d, $J$ = 8.3 Hz, 2H), 3.40 (t, $J$ = 6.8 Hz, 2H), 2.32 (t, $J$ = 7.5 Hz, 2H), 2.27(s, 3H), 1.84 – 1.80 (m, 2H), 1.69 – 1.65 (m, 2H), 1.34 (m, 12H). $^{13}$C NMR ($CDCl_3$), 100 MHz: 171.2; 135.4; 132.0; 127.3; 121.5; 36.1; 33.7; 32.6; 29.6; 28.1; 25.6; 24.3. MS (ESI) calcd for $C_{18}H_{28}BrNO$: 353.14, Found: 354.3 $[M+H]^+$. Elemental analysis calcd (%) for $C_{18}H_{28}BrNO$: C, 61.02; H, 7.97; N, 3.95; Found: C, 60.80; H,7.87; N, 3.83.

**Synthesis of compound 3.** In ice bar, $SOCl_2$ (16.41 g, 137.8 mmol) was slowly added to a suspension of L-Tyrosine (10 g, 55.2 mmol) in 150 mL MeOH. The mixture was stirred at 0 °C for 3 h and then warmed to room temperature. The solvent was evaporated under vacuum. The chloride salt of **3** was obtained as a white solid (12.78 g, 99%). $^1$H NMR ($CDCl_3$), 400 MHz: 7.08 (d, $J$ = 8.5 Hz, 2H); 6.79 (dd, $J$ = 6.7, 4.8 Hz, 2H); 4.25 (dd, $J$ = 7.2, 6.1 Hz, 1H); 3.82 (s, 3H); 3.13 (ddd, $J$ = 21.9, 14.5, 6.6 Hz, 2H). $^{13}$C NMR ($CDCl_3$), 100 MHz: 169.2; 157.0; 130.1; 124.2; 115.5; 54.0; 52.2; 35.3. MS (ESI) calcd for $C_{10}H_{13}NO_3$: 195.09, Found: 196.1 $[M+H]^+$.

Elemental analysis calcd (%) for $C_{10}H_{14}ClNO_3.H_2O$: C, 48.10; H, 6.46; N, 5.61; Found: C, 48.24; H,6.36; N, 5.41.

**Synthesis of compound 4.** $Boc_2O$ (13.92 g, 63.7 mmol), $NEt_3$ (18.6 mL, 133 mmol) were added to a suspension of compound **3** (12.78 g, 55.2 mmol) in 50 mL of distillated THF. The mixture was stirred at room temperature for 12 h and was purified by chromatography to give **4** as a white solid (7.62 g, 25.8 mmol, 47%). Melting point: 98 °C. $^1$H NMR ($CDCl_3$), 400 MHz: 6.97 (d, $J$ = 8.4 Hz, 2H), 6.73 (d, $J$ = 8.1 Hz, 2H), 5.01 (d, $J$ = 7.7 Hz, 1H), 4.64 – 4.45 (m, 1H), 3.72 (s, 3H), 3.00 (qd, $J$ = 14.1, 6.0 Hz, 2H), 1.43 (s, 9H). $^{13}$C NMR ($CDCl_3$), 100 MHz: 172.6; 155.3; 130.4; 127.6; 115.5; 80.2; 54.6; 52.3; 37.6; 28.3. MS (ESI) calcd for $C_{15}H_{21}NO_5$: 295.14, Found: 296.0$[M+H]^+$. Elemental analysis calcd (%) for $C_{15}H_{21}NO_5$: C, 61.00; H, 7.71; N, 4.74; Found: C, 60.37; H,7.75; N, 4.64.

**Synthesis of compound 6a.** Compound **2a** (5.0 g, 14.7 mmol), compound **4** (4.34 g, 14.7 mmol), $CsCO_3$ (0.5 g, 2.6 mmol) and KI (trace) were dissolved in 100 mL dried acetone. The solution was refluxed at 75 °C for 48 hours. After the solution was filtered and concentrated. The residue was purified by chromatography (EtOAc), and gave **5a** as a colorless oil (1.3 g, 16%).

Compound **5a** (1 g, 1.8 mmol) and LiOH (0.5 g, 20.8 mmol) were dissolved in 80 mL THF/$H_2O$ (3: 2, V/V). The solution was stirred at RT for 24 hours. TLC shows completely conversion of the starting compound. After the solvent was evaporated, 40 mL $CH_2Cl_2$ was added. The solution was neutralized to pH = 7.0 and was stirred at RT for 30 minutes. The organic phase was separated and dried under vacuum to give **6a** which was used in the next reaction without further purification.

$^1$H NMR ($CD_3OD$), 400 MHz: 8.39 (d, $J$ = 5.8 Hz, 2H), 7.71 (d, $J$ = 6.4 Hz, 2H), 7.11 (d, $J$ = 8.3 Hz, 2H), 6.80 (d, $J$ = 8.2 Hz, 2H), 4.26 (m, 1H), 3.92 (t, $J$ = 6.4 Hz, 2H), 3.17 – 2.70 (m, 2H), 2.42 (t, $J$ = 7.4 Hz, 2H), 1.84 – 1.59 (m, 4H), 1.52 – 1.18 (m, 21H). $^{13}$C NMR ($CD_3OD$), 100 MHz: 174.2; 158.0; 156.3; 148.2; 147.8; 129.9; 129.2; 114.0; 113.7; 79.0; 55.5; 36.7; 29.2; 29.1; 29.0; 28.9; 28.8; 27.3; 25.7; 24.9. MS (EI) calcd for $C_{30}H_{43}N_3O_6$: 541.32, Found: 541.3. Elemental analysis calcd (%) for $C_{30}H_{43}N_3O_6$ $3H_2O$: C, 60.48; H, 8.29; N, 7.05; Found: C, 60.35; H, 7.84;

N, 7.04.

**Synthesis of compound 6b.** Compound **2b** (5.0 g, 14.2 mmol), compound **4** (4.18 g, 14.2 mmol), $CsCO_3$ (0.5 g, 2.6 mmol) and KI (trace) were dissolved in 100 mL dried acetone. The solution was refluxed at 75 °C for 48 hours. After the solution was filtered and concentrated. The residue was purified by chromatography (EtOAc), and gave a colorless oil **5b** (2.8 g, 35%). Compound **6b** was obtained in a similar process with **6a** and used without any further purification. $^1$H NMR ($CDCl_3$), 400 MHz: 7.39 (d, *J* = 8.2 Hz, 2H), 7.32 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.96 (d, *J* = 7.8 Hz, 1H), 4.52 (d, *J* = 7.1 Hz, 1H), 3.91 (t, *J* = 6.5 Hz, 2H), 3.00 (d, *J* = 7.1 Hz, 2H), 2.34 – 2.29 (m, 5H), 1.74 – 1.70 (m, 4H), 1.42 – 1.21 (m, 22H). $^{13}$C NMR ($CD_3OD$), 100 MHz: 172.5; 171.4; 158.2; 135.4; 133.8; 130.2; 129.5; 127.7; 119.9; 114.6; 79.9; 69.6; 67.9; 54.7; 54.6; 37.7; 31.8; 29.5; 29.4; 29.3; 28.3; 26.0; 25.7; 20.9. MS (EI) calcd for $C_{32}H_{46}N_2O_6$: 554.34, Found: 554.34. Elemental analysis calcd (%) for $C_{32}H_{46}N_2O_6$: C, 69.29; H, 8.30; N, 5.05; Found: C, 68.96; H, 8.41; N, 4.98.

**Synthesis of compound 1a.**

Compound **6a** (300 mg, 0.55 mmol), naphthalimide compound [1] (0.26 g, 0.66 mmol), HOBt (trace) and DCC (0.23 g, 1.1 mmol) was dissolved in 30 mL $CHCl_3$. The solution was stirred at RT for 12 hours. TLC shows completely conversion of the starting compounds. Then the solvent was evaporated and the resulting solid was purified by chromatography (EtOAc/ $CH_2Cl_2$: 4/1). **1a** was obtained as a yellow solid (415 mg, 95%). Melting point: 135 °C. $^1$H NMR (DMSO $D_6$), 500 MHz: 10.21 (s, 1H); 8.48 (d, *J* = 7.0 Hz, 2H); 8.40 (dd, *J* = 9.6, 7.2 Hz, 3H); 7.96 (s, 1H); 7.80 (dd, *J* = 8.3, 7.5 Hz, 2H); 7.55 (d, *J* = 6.3 Hz, 2H); 7.35 (d, *J* = 8.1 Hz, 1H); 7.09 (d, *J* = 8.1 Hz, 2H); 6.78 (d, *J* = 8.3 Hz, 2H); 6.73 (d, *J* = 8.5 Hz, 1H); 4.13 (t, *J* = 6.1 Hz, 2H); 4.02 (m, 1H); 3.91 (t, *J* = 4.3 Hz, 4H); 3.85 (t, *J* = 6.5 Hz, 2H); 3.38 (m, 2H); 3.25 (t, *J* = 6.5 Hz, 2H); 3.20 (t, *J* = 4.3 Hz, 4H); 2.83 (m, *J* = 4.6Hz, 2H); 2.30 (t, *J* = 8.5 Hz, 2H); 2.16 (m, 2H); 1.63 (m, 4H); 1.33 (t, *J* = 7.6 Hz, 2H); 1.25 (m, 19H). $^{13}$C NMR (DMSO $d_6$), 125 MHz: 173.0; 171.9; 170.9; 164.3; 163.8; 157.6; 155.8; 155.6; 150.6; 146.4; 132.5 131.0; 130.9; 130.6; 130.3; 129.7;126.5; 125.7; 123.3; 116.6; 115.5; 114.5; 113.5; 78.4; 67.7; 66.67; 56.5; 53.5; 37.3; 37.0; 36.9; 35.8; 35.7; 29.4; 29.3;

29.2; 29.0; 28.6; 26.0; 25.2. MALDI-TOF calcd for $C_{51}H_{65}N_7O_9$: 919.49, Found: 920.61 $[M+H]^+$. Elemental analysis calcd (%) for $C_{51}H_{65}N_7O_9$: C, 66.57; H, 7.12; N, 10.66; Found: C, 66.23; H,7.59; N, 10.90.

**Synthesis of compound 1b.** Compound **6b** (0.30 g, 0.53 mmol), naphthalimide compound (0.25 g, 0.64 mmol), HOBt (trace) and DCC (0.22 g, 1.08 mmol) was dissolved in 30 mL $CHCl_3$. The solution was stirred at RT for 12 hours. Then the solvent was evaporated and the resulting solid was purified by chromatography (EtOAc/ $CH_2Cl_2$: 4/1). **1b** was obtained as a yellow solid (385 mg, 89%). Melting point: 156 °C. $^1$H NMR (DMSO $d_6$), 500 MHz: 9.72 (s, 1H); 8.49 (d, *J* = 8.1 Hz, 1H); 8.45 (d, *J* = 8.5 Hz, 1H); 8.40 (d, *J* = 8.0 Hz, 1H); 7.96 (s, 1H); 7.80 (t, *J* = 7.8 Hz, 2H); 7. 44 (d, *J* = 8.3 Hz, 2H); 7.34 (d, *J* = 8.1 Hz, 1H); 7.07 (t, *J* = 9.0 Hz, 2H); 7.05 (t, *J* = 8.2 Hz, 2H); 6.77 (d, *J* = 8.1 Hz, 2H); 6.75 (s, 1H); 4.13 (s, 2H); 4.03 (m, 1H); 3.90 (t, *J* = 4.3 Hz, 4H); 3.87 (t, *J* = 6.5 Hz, 2H); 3.25 (m, 6H); 2.88 – 2.57 (m, 2H); 2.30 (t, *J* = 8.5 Hz, 5H); 2.11 (m, 2H); 1.74 (m, 4H); 1.36 (t, *J* = 7.6 Hz, 2H); 1.27 (m, 19H). $^{13}$C NMR (DMSO $d_6$), 125 MHz: 171.9; 171.5; 171.0; 164.3; 163.8; 157.6; 155.8; 137.3; 132.6; 132.2; 131.0; 130.9; 130.6; 129.8; 129.5; 126.5; 125.8; 123.3; 119.5; 116.6; 115.5; 114.5; 78.5; 67.7; 66.6; 53.5; 48.0; 37.0; 36.8; 35.7; 33.8; 32.7; 29.4; 29.1; 28.6; 25.9; 25.6; 25.1; 24.9. MS (EI) calcd for $C_{53}H_{68}N_6O_9$: 923.50, Found: 923.60. Elemental analysis calcd (%) for $C_{53}H_{68}N_6O_9$: C, 68.22; H, 7.35; N, 9.01; Found: C, 68.67; H, 7.09; N, 9.20.

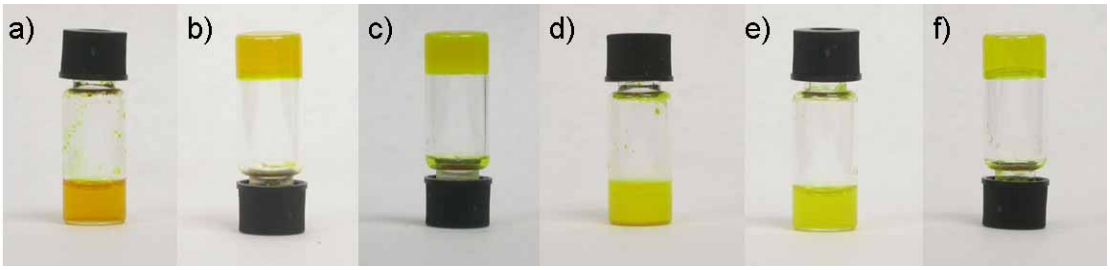


**Figure S1.** Pictures of gel formation. (a) **1a** sol in ethanol; (b) **1a** gel in ethanol (20 ºC, 25 mg $mL^{-1}$); (c) **1a** gel in isopropanol (20 ºC, 25 mg $mL^{-1}$); (d) **1a** gel in acetonitrile (20 ºC, 25 mg $mL^{-1}$); (e) **1b** sol in acetonitrile (20 ºC, 5 mg $mL^{-1}$); (f) **1b** gel in acetonitrile (20 ºC, 5 mg $mL^{-1}$).

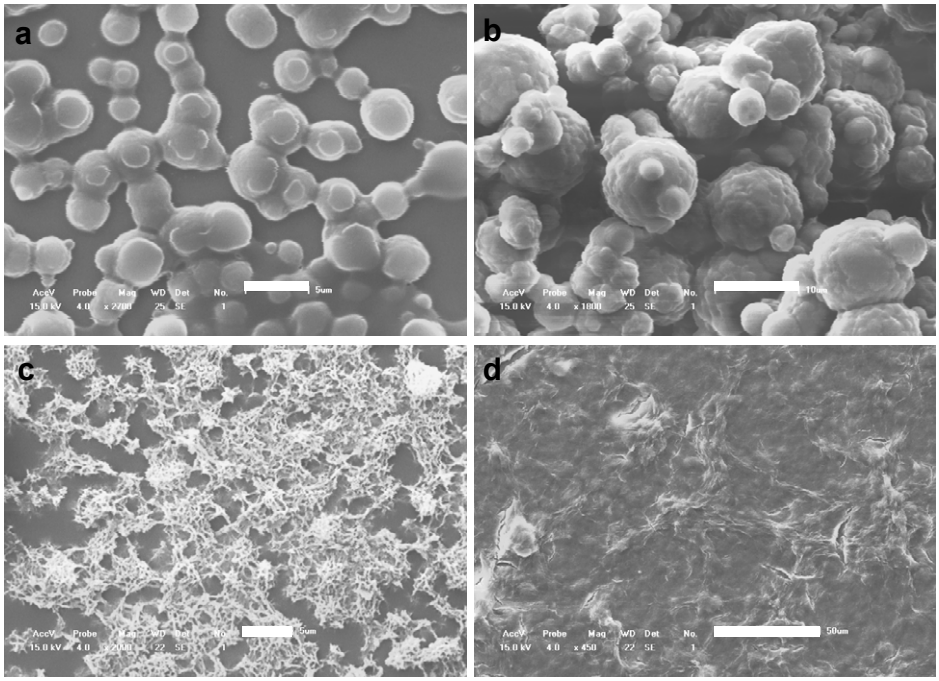


**Figure S2.** SEM images of the **1a**, **1b** after the solutions evaporated at room temperature (18 ºC). a) **1a** in ethyl acetate, b) **1a** in acetone, c) **1b** in ethanol, d) **1b** in acetone. Scale bar: a) 5 µm; b) 10 µm; c) 5 µm; d) 50 µm.

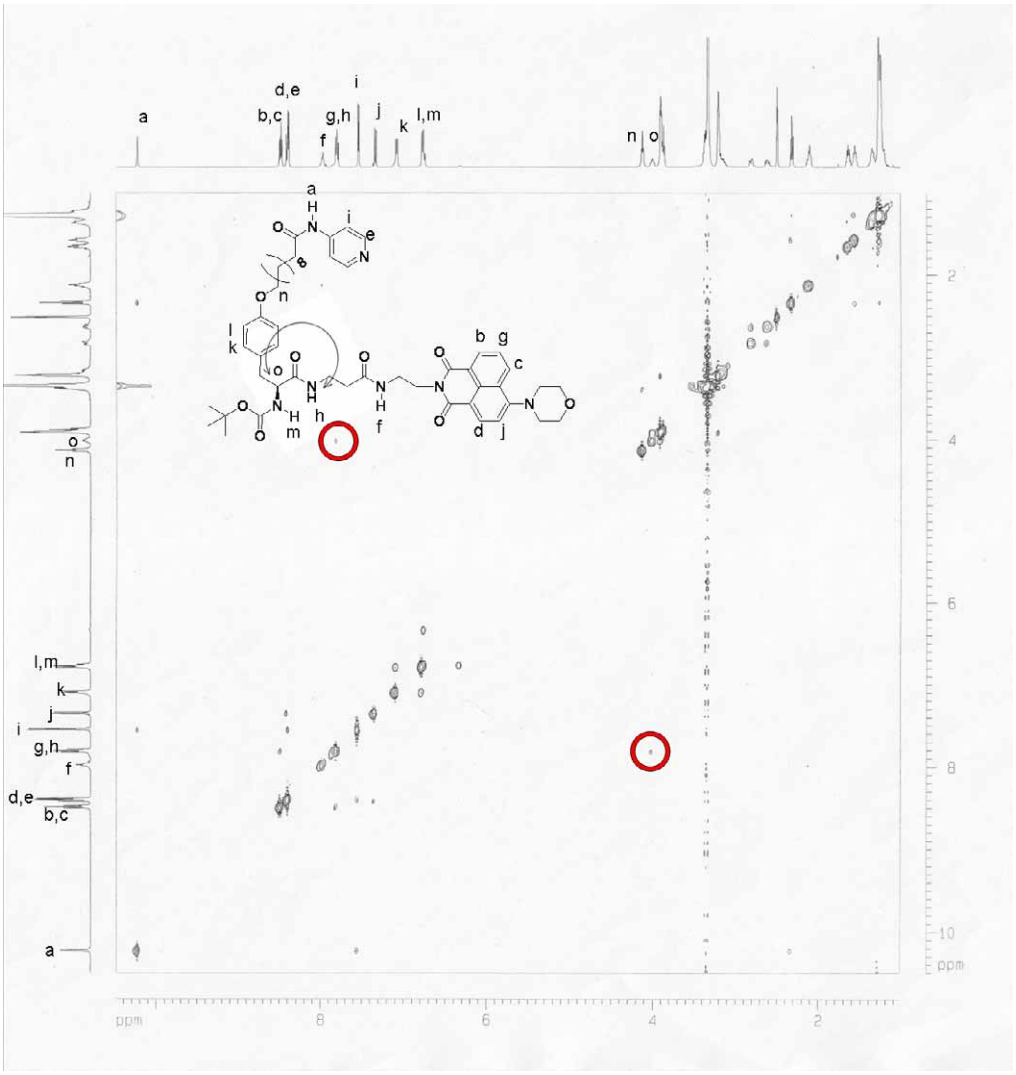


**Figure S3.** 2D-NOESY experiment performed on a $d_6$-DMSO solution of peptide **1a** (10 mg, 2 mM) at 0 ºC.

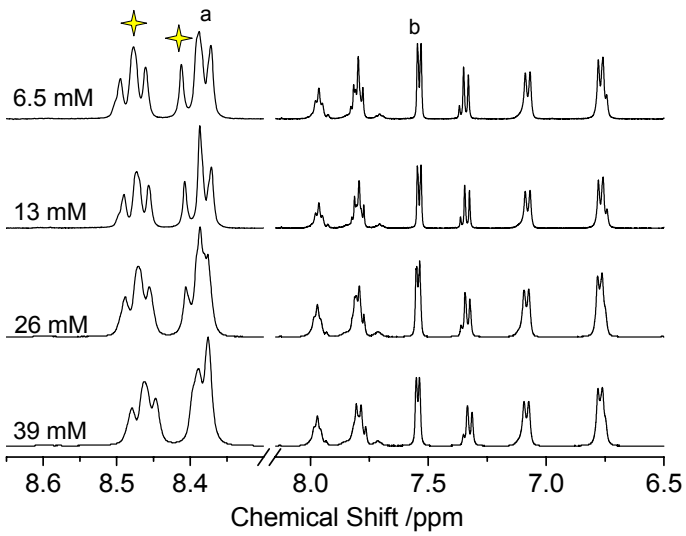


**Figure S4**. Concentration-dependent $^{1}$H NMR of **1a** in DMSO (6.5 – 39 mM) (**star**, protons in naphthalimide; a and b, protons in pyridine).

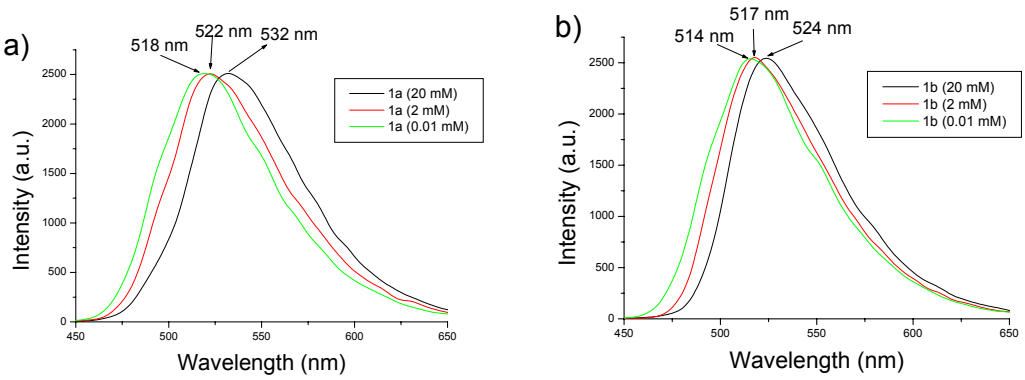


**Figure S5.** Concentration dependent fluorescent emission of (a) **1a** and (b) **1b** in dichloromethane at 25 °C (0.01 – 20 mM, $\lambda_{ex}$ = 400 nm).

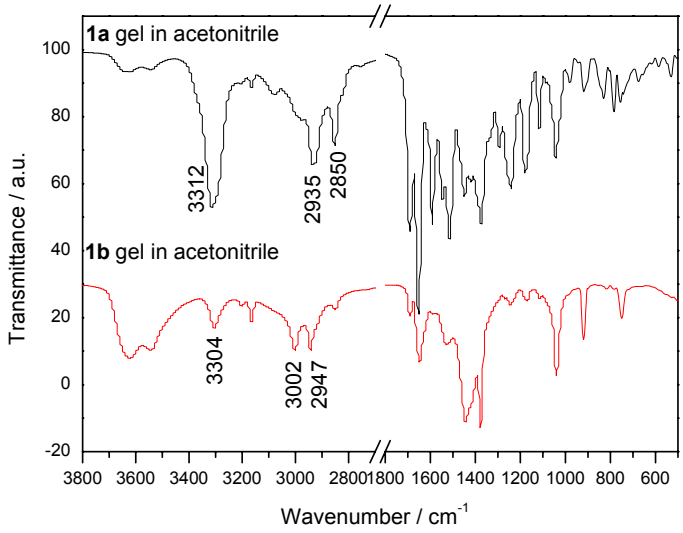


**Figure S6.** IR spectra of **1a** (25 mg $mL^{-1}$) and **1b** (10 mg $mL^{-1}$) wet gels in acetonitrile.

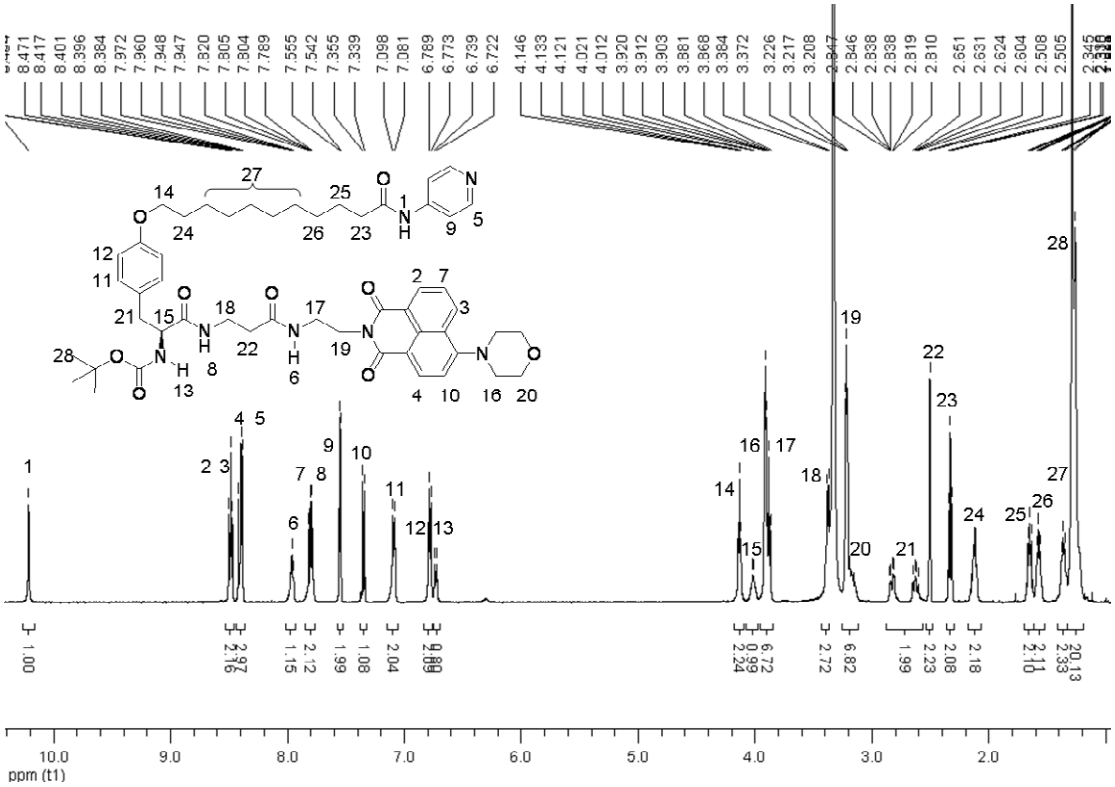


**Figure S7.** $^{1}H$ NMR spectrum of **1a** in $d_6$-DMSO solution at 20 °C (10 mg, 2 mM)

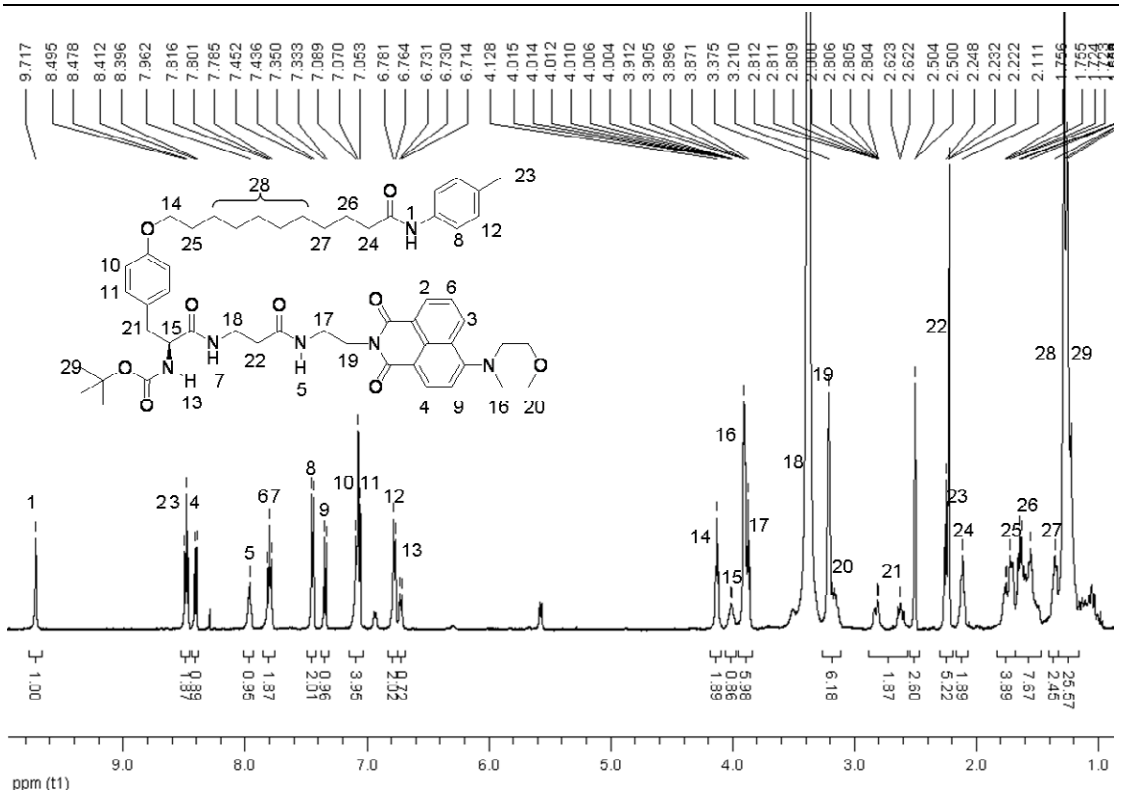

**Figure S8.** $^{1}$H NMR spectrum of **1b** in $d_6$-DMSO at 20 ºC (10 mg, 2 mM)

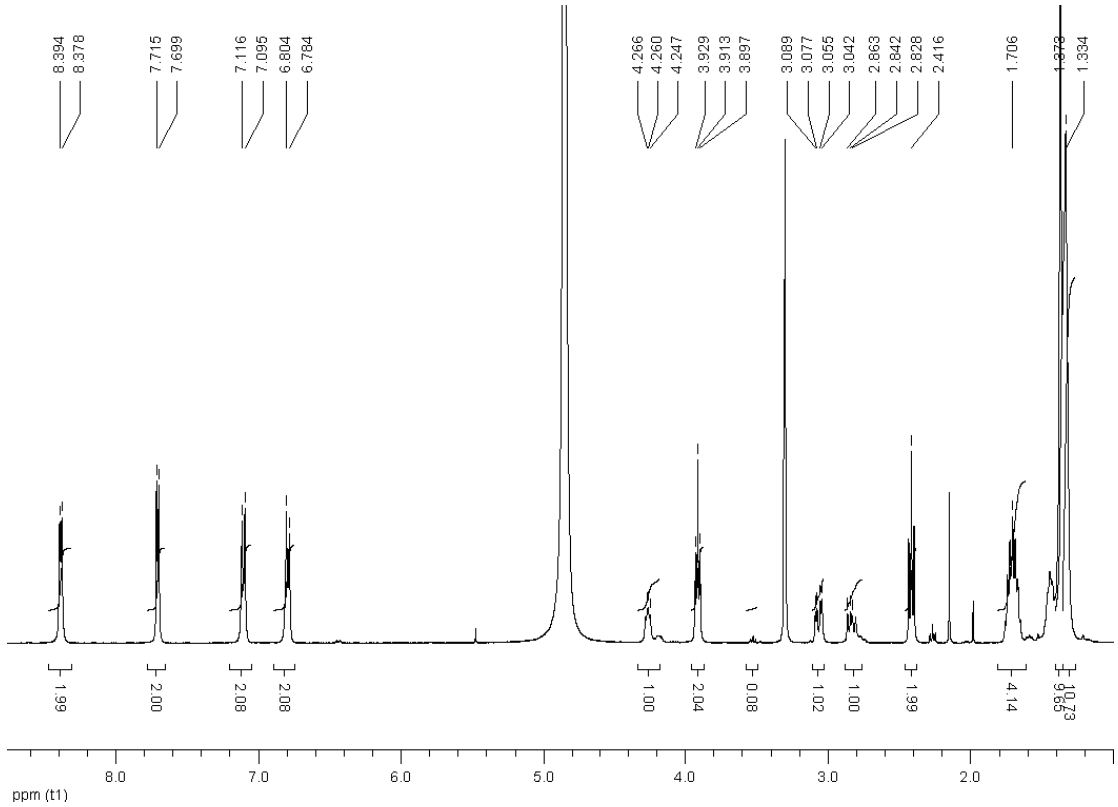

**Figure S9.** $^{1}$H NMR spectrum of **6a** in $d_4$-$CD_3OD$ at 20 ºC (10 mg, 2 mM)

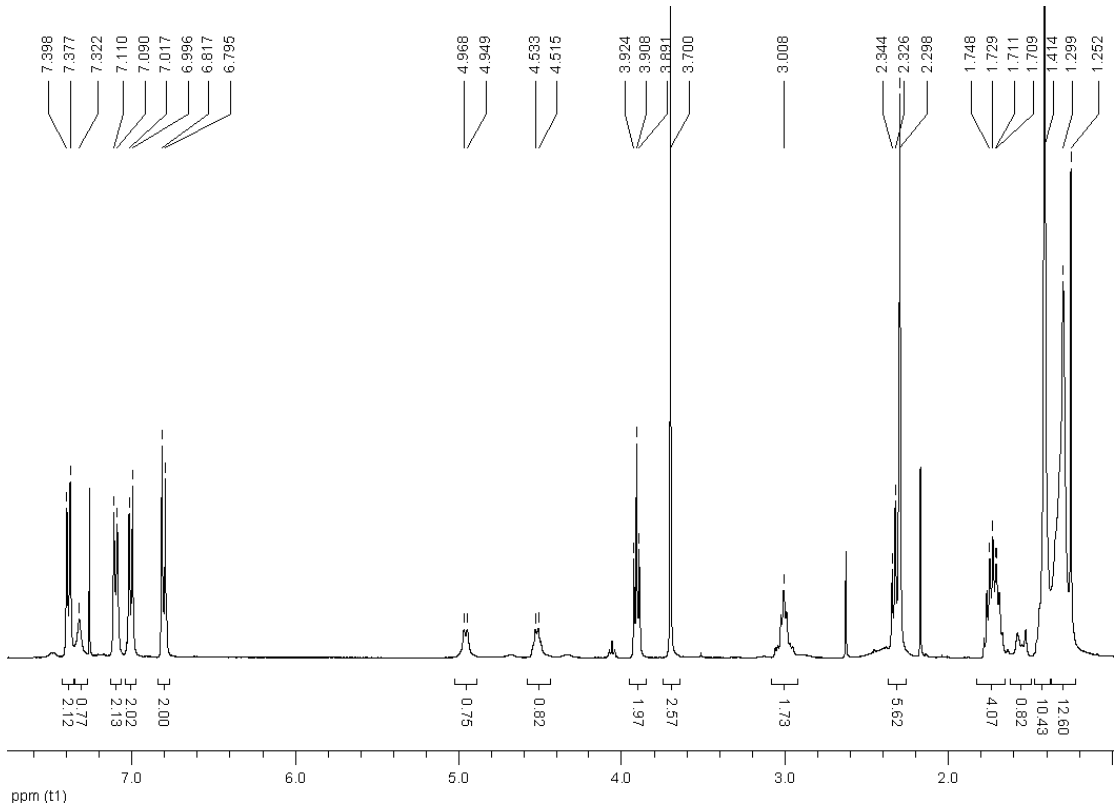


**Figure S10.** $^{1}$H NMR spectrum of **6b** in $CDCl_3$ at 20 ºC (10 mg, 2 mM)

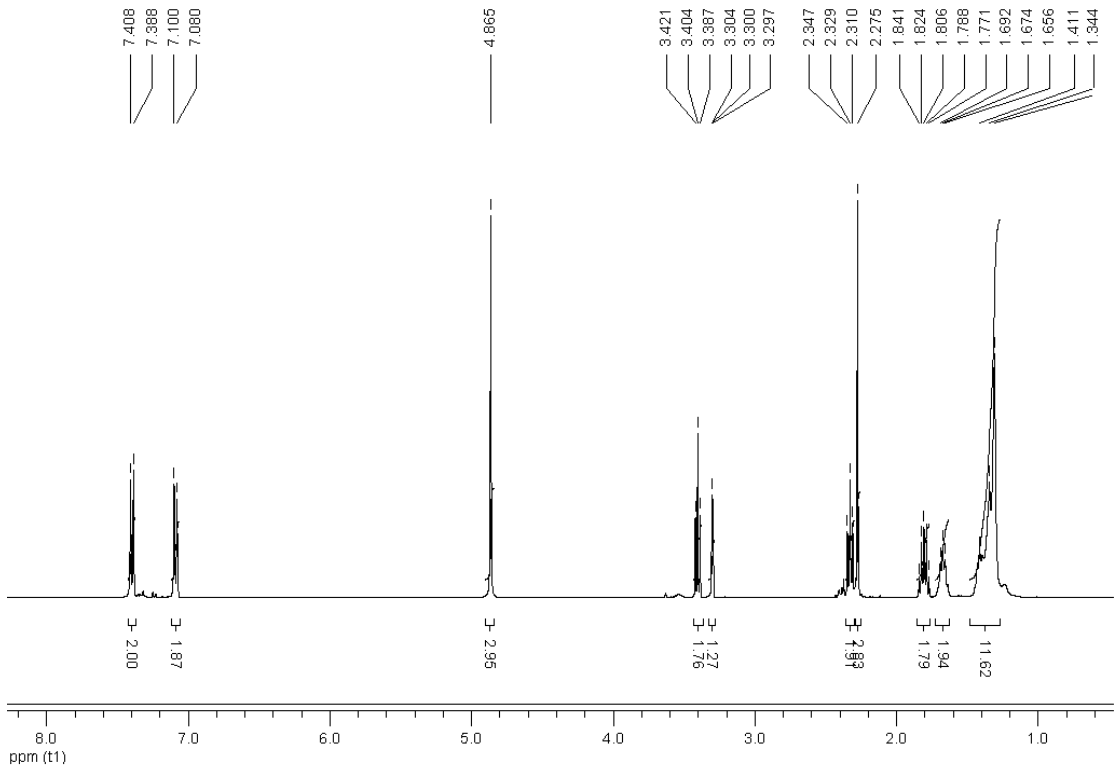

**Figure S11.** $^{1}$H NMR spectrum of **2b** in $d_4$-$CD_3OD$ at 20 ºC (10 mg, 2 mM)

## Reference

1. J. Wu, T. Yi, T. Shu, M, Yu, Z. Zhou, M. Xu, Y. Zhou, H. Zhang, J. Han, F. Li, C. Huang, *Angew. Chem. Int. Ed.,* 2008, **47**, 1063