Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Foldamer-based chiral supramolecular alternate block copolymers tuned by ion-pair binding

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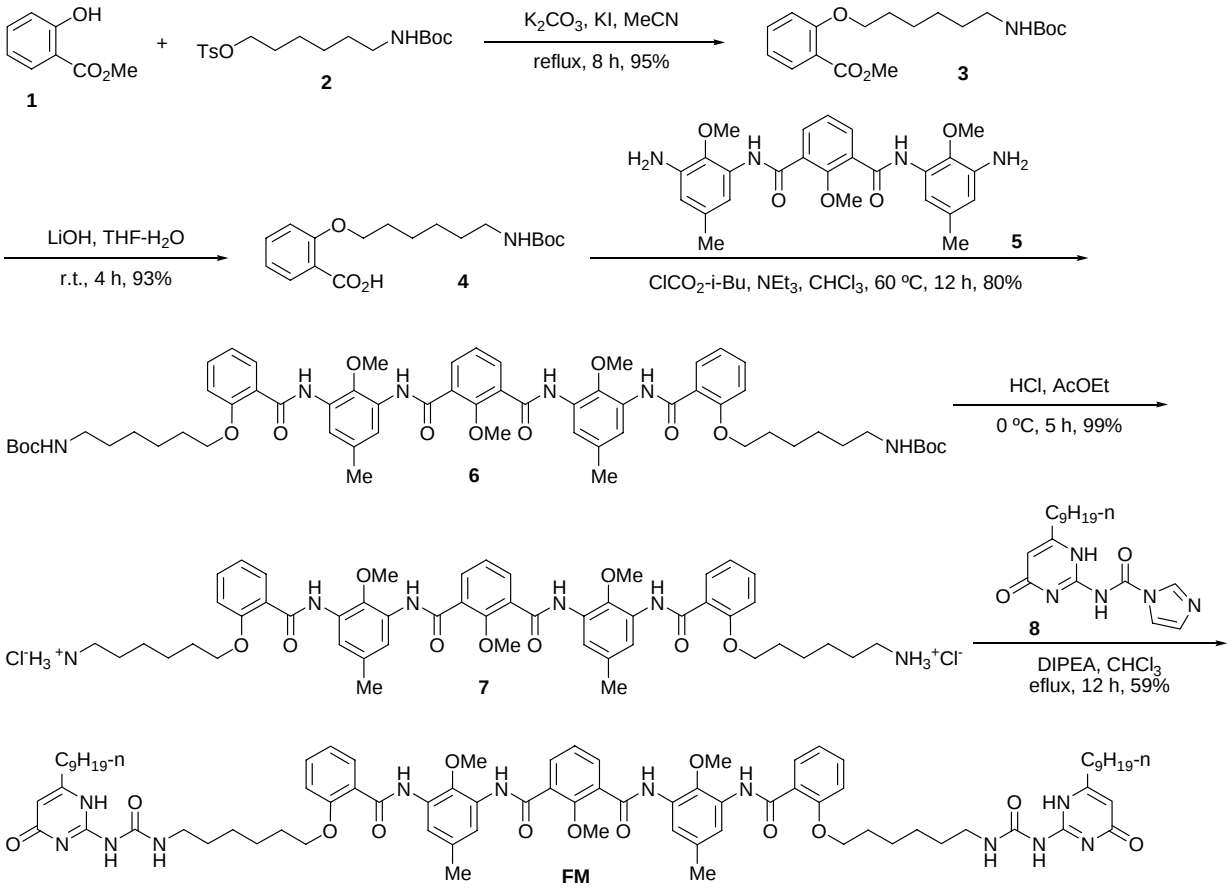
General methods. All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The solvents have been purified by standard procedures before use. Silica gel (10- 40 μ) was used for all column chromatography. The ^{1}H NMR spectra were recorded on Bruker Avance 300 or 400 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual proton resonances of the deuterated solvents as the internal standards. MS and HR-MS were carried out in Shanghai Institute of Organic Chemistry (SIOC) MS centre.



Compound 3. A suspension of compounds **1** (3.04 g, 20.0 mmol) and **2**[1] (8.16 g, 22.0 mmol) and potassium carbonate (4.14 g, 30.0 mmol) in acetonitrile (100 mL) was stirred under reflux for 8 h and then cooled to room temperature. The solid was filtrated off and the filtrate was concentrated with a rotavapor. The resulting slurry was triturated with ethyl acetate (100 mL), and the organic phase was washed with aqueous sodium carbonate (0.5 N, 50 mL), water (50 mL), and brine (50 mL), and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the resulting crude product was subjected to column chromatography (AcOEt/petroleum ether, 1:3) to give compound **3** as a colorless oil (6.67 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.6 Hz, 1 H), 7.43 (t, J = 8.0 Hz, 1 H), 6.99-6.94 (m, 2 H), 4.58 (b, 1 H), 4.03 (t, J = 6.4 Hz, 2 H), 3.88 (s, 3 H), 3.13-3.10 (m, 2 H), 1.86-1.80 (m, 2 H), 1.53-1.35 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 158.6, 156.0, 133.4, 131.6, 120.3, 120.0, 113.2, 79.0, 68.7, 51.9, 40.5, 30.0, 29.0, 28.4, 26.5, 25.7. MS (ESI) *m/z*: 352.1 $[M + H]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{19}H_{29}NO_5Na$ $[M+Na]^+$: 374.1943. Found: 374.1938.

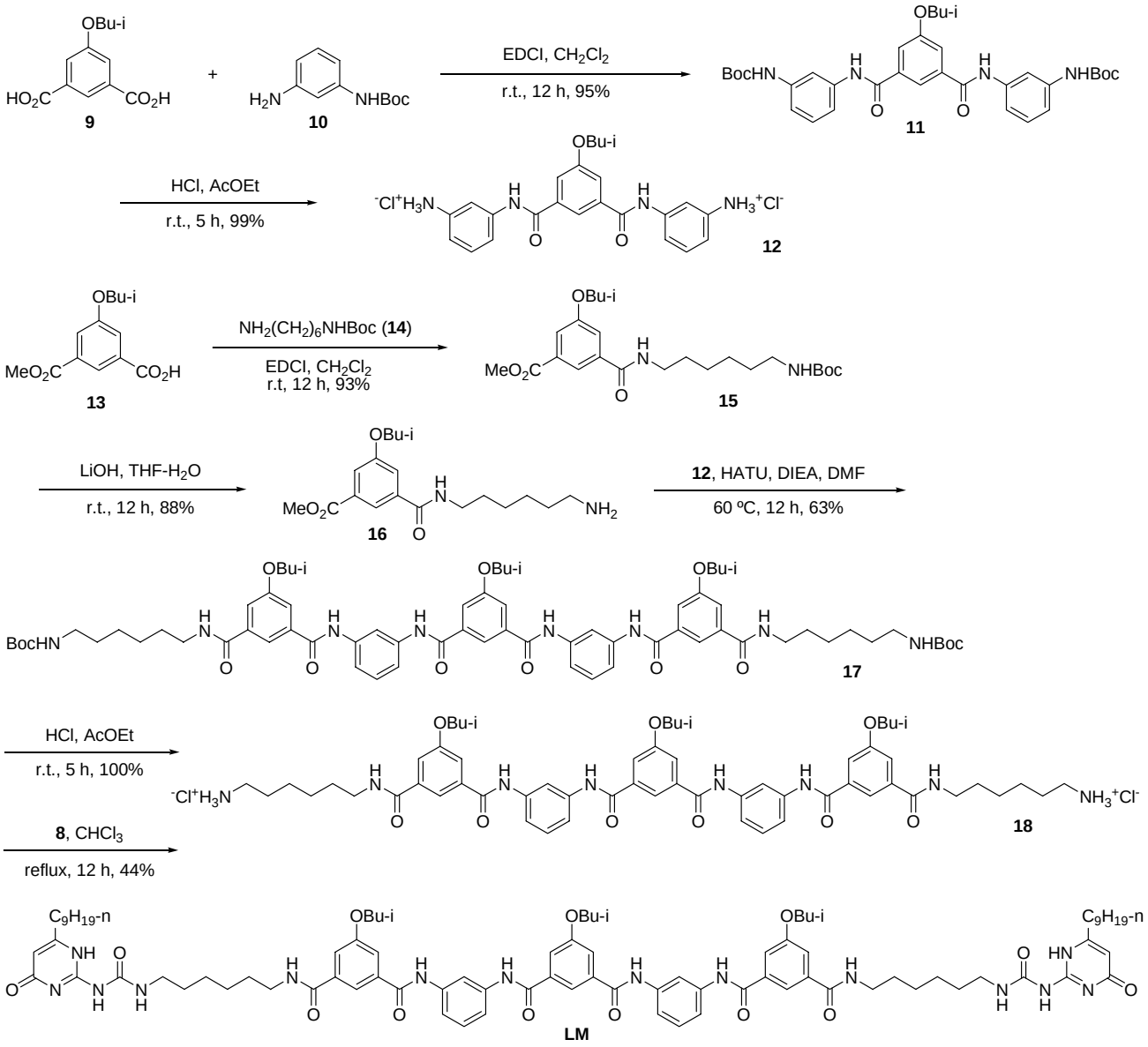
Compound 4. To a stirred solution of compound **3** (3.51 g, 10.0 mmol) in THF (50 mL) and water (50 mL) was added lithium hydroxide (2.00 g, 20.0 mmol). Stirring was continued for 4 h and then the mixture was concentrated to ca. 40 mL with a rotavapor. Dilute hydrochloric acid (1N) was added dropwise to pH = 5. The formed precipitate was filtrated and washed with water and dried in vacuo to give compound **4** as a white solid (3.12 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 7.6 Hz, 1 H), 7.54 (td, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1 H), 7.12 (t, J = 7.6 Hz, 1 H), 7.03 (d, J = 8.4 Hz, 1 H), 4.60 (b, 1 H), 4.24 (t, J = 6.4 Hz, 2 H), 3.22-3.09 (m, 2 H), 1.99-1.85 (m, 2 H), 1.56-35 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 157.6, 156.1, 134.9, 133.7, 122.1, 117.8, 112.6, 79.2, 70.0, 40.3, 29.9, 28.8, 28.4, 26.3, 25.6. MS (ESI) *m/z*: 337.2 $[M]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{18}H_{27}NO_5Na$ $[M+Na]^+$: 360.1787. Found: 360.1782.

Compound 6. A mixture of compound **4** (0.67 g, 2.00 mmol), iso-butyl chloroformate (0.25 mL, 2.00 mmol) and triethylamine (0.56 mL, 2.00 mmol) in chloroform (10 mL) was stirred for 0.5 h and then compound **5**[2] (0.46 g, 1.00 mmol) was added. The solution was stirred at 60 °C for 12 h and then concentrated with a rotavapor. The resulting residue was triturated with ethyl acetate (50 mL) and the solution was washed with dilute hydrochloric acid (1 N, 50 mL×2), water (50 mL), and brine (50 mL) and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the resulting crude product was subject to column chromatography (AcOEt/petroleum ether 2:3) to give compound **6** as a white solid (0.89 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, 2 H), 9.64 (s, 2 H), 8.32 (dd, J_1 = 7.6 Hz, J = 1.6 Hz, 2 H), 8.22 (d, J = 7.6 Hz, 2 H), 8.15 (s, 2 H), 8.07 (s, 2 H), 7.50 (td, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 2 H), 7.46 (t, J = 8.0 Hz, 1 H), 7.14 (t, J = 8.0 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 2 H), 4.48 (s, 2 H), 4.21 (t, J = 6.8 Hz, 4 H), 4.13 (s, 3 H), 3.82 (s, 6 H), 2.98-2.90 (m, 4 H), 2.42 (s, 6 H), 1.93-1.86 (m, 4 H), 1.45-1.25 (m, 30 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 163.0, 156.8, 156.0, 155.8, 137.5, 135.2, 134.6, 133.5, 132.5, 131.2, 130.9, 128.5, 125.4, 121.6, 121.5, 118.6, 117.2, 112.8, 78.8, 69.5, 64.3, 61.0, 60.9, 40.2, 29.9, 28.8, 28.3, 26.3, 25.5, 21.8 (d). MS (ESI) *m/z*: 1125.8 $[M+Na]^+$. HRMS (MALDI-FT): Calcd. for $C_{61}H_{78}N_6O_{13}Na$ $[M+Na]^+$: 1125.5525. Found: 1125.5519.

Compound 7. A solution of compound **6** (0.10 g, 0.91 mmol) in a solution of hydrochloric acid in ethyl acetate (3 N, 25 mL) was stirred at room temperature for 5 h and the then concontrated with a rotavapor to give compound **7** as white solid (0.88 g, 99%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 2 H), 10.26 (s, 2 H), 8.07 (d, J = 8.0 Hz, 2 H), 8.03 (s, 2 H), 8.00 (d, J = 8.0 Hz, 2 H), 7.80 (s, 2 H), 7.74 (b, 4 H), 7.56 (t, J = 7.6 Hz, 2 H), 7.46 (t, J = 7.2 Hz, 2 H), 8.00 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.15 (t, J = 7.6 Hz, 2 H), 4.32 (t, J = 6.4 Hz, 4 H), 4.07 (s, 3 H), 3.83 (s, 6 H), 2.70-2.62 (m, 4 H), 2.35 (s, 6 H), 1.92-1.82 (m, 4 H), 1.46-1.30 (m, 12 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 163.8, 162.8, 156.5, 156.3, 155.4, 138.8, 133.6, 133.4, 132.9 (d), 131.5, 131.4, 130.8, 128.8, 124.4, 121.4, 121.1, 118.6, 118.1, 113.6, 69.1, 63.3, 61.0, 38.4 (d), 28.0, 27.9, 26.7, 25.4, 25.3, 24.8, 24.7, 21.4. MS (ESI) *m/z*: 903.2 $[M+H]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{51}H_{63}N_6O_9$ $[M]^+$: 903.4657. Found: 903.4651.

Compound FM. A solution of compounds **7** (97.4 mg, 0.10 mmol), **8**[3] (70.0 mg, 0.21 mmol) and DIPEA (0.2 mL) in chloroform (5 mL) was stirred under reflux for 12 h and then concentrated with a rotavapor. The resulting residue was dissolved in choroform (5 mL) and the solution was washed with dilute hydrochloric acid (0.2 N, 3 mL×2), water (3 mL) and brine (3 mL), and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the resulting residue was subject to column chromatography (dichloromethane/MeOH 20:1) to give compound **FM-1** as a white solid (84 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.56 (s, 2 H), 10.47 (s, 2 H), 10.32 (s, 2 H), 8.36 (d, J = 11.2 Hz, 2 H), 8.35 (s, 2 H), 8.03 (b, 4 H), 7.53 (t, J = 7.6 Hz, 3 H), 7.18-7.98 (m, 7 H), 5.54 (s, 2 H), 4.29 (m, 7 H), 3.80 (s, 6 H), 3.36-3.18 (m, 4 H), 2.45 (s, 6 H), 2.39-2.30 (m, 4 H), 2.27-2.14 (m, 4 H), 1.90-1.30 (m, 20 H), 0.90-0.80 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 172.9, 163.4, 163.3, 162.9, 157.2, 156.8, 156.5, 156.3, 155.8, 154.5, 154.2, 152.6, 152.5, 138.6, 137.4, 135.2, 134.8, 134.6, 133.4,

133.1, 132.7, 131.4, 131.2, 130.9, 130.5, 128.5, 128.2, 125.4, 121.8, 121.7, 121.5, 118.9, 118.7, 117.1, 112.7, 105.6, 105.5, 69.6, 60.9 (d), 39.9, 39.7, 32.6, 32.5, 31.8, 29.4, 29.2 (d), 29.1, 28.9, 28.8, 28.6, 26.9, 26.7 (d), 26.4, 25.9, 25.6, 25.5, 22.6, 21.9, 14.1. MS (ESI) *m/z*: 1429.8 $[M+H]^+$. HR-MS (MALDI-FT): Calcd. for $C_{79}H_{104}N_{12}O_{13}Na$: 1451.7744. Found: 1451.7735.



Compound 11. A solution of compounds **9** (2.37 g, 10.0 mmol), **10** (4.16 g, 20.0 mmol) and EDCI (3.23 g, 25.0 mmol) in dichloromethane (25 mL) was stirred for 12 h and then washed with saturated ammonium chloride solution (15 mL×2), water (15 mL) and brine (20 mL), and dried over sodium solfate. Upon removal of the solvent with a rotavapor, the resulting crude product was subjected to column chromatography (AcOEt/petroleum ether 1:1) to give compound **11** as a waxy solid (5.86 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 2 H), 7.82 (s, 2 H), 7.80 (s, 1 H), 7.49 (s, 2 H), 7.37 (t, *J* = 4.4 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 6.09 (s, 2 H), 3.78 (d, *J* = 6.4 Hz, 2 H), 2.10-2.03 (m, 1 H), 1.51 (s, 18 H), 1.03 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 165.9, 159.4, 153.1, 138.8, 138.4, 136.2, 129.3, 117.1, 116.9, 115.3, 115.0, 111.1, 80.6, 74.7, 28.3, 28.1, 19.1. MS (ESI)

m/z: 641.2 $[M+Na]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{34}H_{42}N_4O_7Na$ $[M+Na]^+$: 641.2951. Found: 641.2946.

Compound 12. A solution of compound **11** (0.20 g, 0.30 mmol) in a solution of hydrochloric acid (3 N, 10 mL) was stirred for 5 h and then concentrated with a rotavapor to give compound **12** a white solid (0.16 g, 99%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 2 H), 9.85 (s, 4 H), 8.26 (s, 1 H), 7.97 (s, 2 H), 7.70 (s, 4 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 7.04 (s, 2 H), 3.94 (d, *J* = 6.4 Hz, 2 H), 2.10-2.05 (m, 1 H), 1.03 (d, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.9, 158.8, 140.2, 135.8, 131.9, 129.8, 119.8, 119.5, 118.4, 117.0, 114.9, 74.3, 27.7, 19.0. MS (ESI) *m/z*: 419.3 $[M+H]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{24}H_{27}N_4O_3$ $[M]^+$: 419.2083. Found: 419.2078.

Compound 15. A solution of compounds **13** (2.50 g, 10.0 mmol), **14** (2.20 g, 10.0 mmol) and EDCI (1.50 g, 12.0 mmol) in dichloromethane (200 mL) was stirred for 12 h and then washed with saturated ammonium chloride solution (200 mL), water (200 mL) and brine (200 mL), and dried over sodium sulfate. Upon removal of the solvent, the resulting residue was subject to column chromatography (AcOEt/petroleum ether 1:1) to give compound **15** as a waxy solid (0.43 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1 H), 7.66 (s, 1 H), 7.61 (s, 1 H), 6.37 (b, 1 H), 4.54 (b, 1 H), 3.93 (s, 3 H), 3.80 (d, *J* = 6.8 Hz, 2 H), 3.47-3.43 (m, 2 H), 3.13-3.10 (m, 2 H), 2.15-2.07 (m, 1 H), 1.67-1.60 (m, 2 H), 1.53-1.50 (m, 2 H), 1.49 (s, 9 H), 1.30-1.20 (m, 4 H), 1.03 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (d), 159.6, 156.1, 136.3, 131.5, 119.2, 118.3, 118.2, 79.1, 74.9, 52.4, 40.1, 39.8, 30.1, 29.4, 28.4, 28.2, 26.2, 26.0, 19.2. MS (ESI) *m/z*: 473.2 $[M+Na]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{24}H_{38}N_2O_6Na$ $[M]^+$: 473.2628. Found: 473.2622.

Compound 16. A solution of compound **15** (0.40 g, 0.88 mmol), lithium hydroxide monohydrate (67.0 mg, 1.60 mmol) in THF (40 mL) and water (20 mL) was stirred for 12 h and the concentrated to ~15 mL. Dilute hydrochloric acid (1N) was then added dropwise to pH = 5 and the formed precipitate was filtrated and washed with water and dried in vacuo to give compound **16** as a white solid (0.34 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.12 (b, 1 H), 8.60 (t, *J* = 1.2 Hz, 1 H), 8.00 (s, 1 H), 7.61 (s, 1 H), 7.53 (s, 1 H), 6.75 (b, 1 H), 3.84 (d, *J* = 6.4 Hz, 2 H), 3.27-3.20 (m, 2 H), 2.93-2.85 (m, 2 H), 2.05-2.00 (m, 1 H), 1.55-1.45 (m, 2 H), 1.36 (s, 9 H), 1.28-1.20 (m, 6 H), 1.03 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 164.9, 158.7, 155.5, 136.3, 132.3, 120.3, 117.6, 117.0, 77.2, 74.1, 29.4, 29.0, 28.2, 27.7, 26.2, 26.0, 18.9. MS (ESI) *m/z*: 436.2 $[M]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{23}H_{36}N_2O_6Na$ $[M+Na]^+$: 459.2471. Found: 459.2466.

Compound 17. A solution of compound **16** (0.20 g, 0.46 mmol) and HATU (0.17 g, 0.46 mmol) in DMF (50 mL) was stirred for 1 h and then compound **12** (98 mg, 0.20 mmol) and DIEA (0.17 mL, 1.0 mmol) were added. The solution was stirred at 60 °C for 12 h and then concentrated with a rotavapor. The resulting residue was triturated with ethyl acetate (50 mL) and the solution washed with saturated ammonium chloride (20 mL), water (25 mL) and brine (25 mL), and dried over sodium sulfate. After the solvent was removed under reduced pressure, the resulting crude product was subjected to column chromatography (dichloromethane/MeOH 20:1) to give compound **17** as a white solid (158 mg, 63%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.43 (s, 2 H), 10.38 (s, 2 H), 8.57 (t, *J* = 4.2 Hz, 2 H), 8.33 (s, 2 H), 8.14 (s, 1 H), 8.00 (s, 2 H), 7.70 (s, 2 H), 7.62 (s, 2 H), 7.57 (s, 2 H), 7.53 (b, 4 H), 7.35 (t, *J* = 8.4 Hz, 2 H), 6.75 (t, *J* = 6.4 Hz, 2 H), 3.94 (d, *J* = 6.0 Hz, 2 H), 3.88 (d, *J* = 6.0 Hz, 4 H), 3.29-3.24 (m, 4 H), 2.95-2.91 (m, 4 H), 2.13-2.04 (m, 2 H), 2.02-1.98 (m, 1 H), 1.56-1.48 (m, 4 H), 1.38-1.35 (m, 23 H), 1.37-1.25 (m, 8 H), 1.05 (d, *J* = 6.4 Hz, 6 H), 1.02 (d, *J* = 6.4 Hz, 12 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.3, 164.9, 164.8, 158.7, 158.6, 155.6, 139.2 (d), 136.4, 136.3, 136.2, 128.6, 119.5, 119.0, 116.6, 116.5, 116.3, 116.1, 115.9, 113.2, 77.2, 74.2, 29.4, 29.0, 28.2, 28.0, 27.8, 26.2, 26.0, 19.0. MS (ESI) *m/z*: 1277.7 $[M+Na]^+$. HRMS (MALDI-FT) *m/z*: Calcd. for $C_{70}H_{94}N_8O_{13}Na$ $[M+Na]^+$: 1277.6838. Found: 1277.6833.

Compound 18. A solution of compound **17** (0.13 g, 0.10 mmol) in a solution of hydrochloric acid (3N) in ethyl acetate (10 mL) was stirred for 5 h. TLC showed that the starting material was completely converted into the dichloride salt. Upon removal of the solvent with a rotavapor, the resulting product **18** (99 mg, 100%) was used for the next step without further purification.

Compound LM. The above compound **18** (99 mg, 0.10 mmol) was dissolved in chloroform (25 mL) and compound **8** (80 mg, 0.24 mmol) and triethylamine (0.30 mL, 0.30 mmol) was then added. The solution was heated under reflux for 12 h and then washed with water (15 mL×2) and brine, and dried over sodium sulfate. Upon removal of the solvent, the resulting residue was subjected to column chromatography (dichloromethane/MeOH 20:1) to give **LM-1** as a white solid (70 mL, 44%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.44 (b, 2 H), 10.42 (s, 2 H), 10.38 (s, 2 H), 9.58 (b, 2 H), 8.58 (t, J = 6.0 Hz, 2 H), 8.33 (s, 2 H), 8.14 (s, 1 H), 8.00 (s, 2 H), 7.70 (s, 2 H), 7.62 (s, 2 H), 7.57 (b, 5 H), 7.34 (t, J = 8.4 Hz, 2 H), 6.87 (s, 1 H), 5.74 (s, 2 H), 3.94 (d, J = 6.8 Hz, 2 H), 3.88 (d, J = 6.8 Hz, 2 H), 3.30 (m, 4 H), 3.15 (m, 4 H), 2.34 (m, 4 H), 2.10 (m, 3 H), 1.54 (m, 8 H), 1.46 (m, 4 H), 1.35 (m, 8 H), 1.20 (m, 20 H), 1.04 (d, J = 6.4 Hz, 6 H), 1.02 (d, J = 6.4 Hz, 12 H), 0.83 (t, J = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.3, 164.9, 164.7, 158.6, 151.5, 139.2 (d), 136.5, 136.4, 136.2, 128.6, 124.9, 119.5, 119.0, 116.5, 116.2, 116.0 (d), 115.8, 113.1, 104.1, 74.2, 54.6, 36.5, 34.3, 31.3, 30.4, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.4, 27.8, 27.7, 27.2 (d), 26.2, 26.0, 22.0, 14.0. IR (KBr/cm^{-1}): 3272, 2956, 2957, 2856, 1657, 1591, 1539, 1484, 1437, 1336, 1315, 1250, 1048. MS (ESI): *m/z* 1581.8 $[M+H]^+$. HR-MS (MALDI-FT): $C_{88}H_{120}N_{14}O_{13}Na$ $[M+Na]^+$: 1603.9057. Found: 1603.9043.

References:

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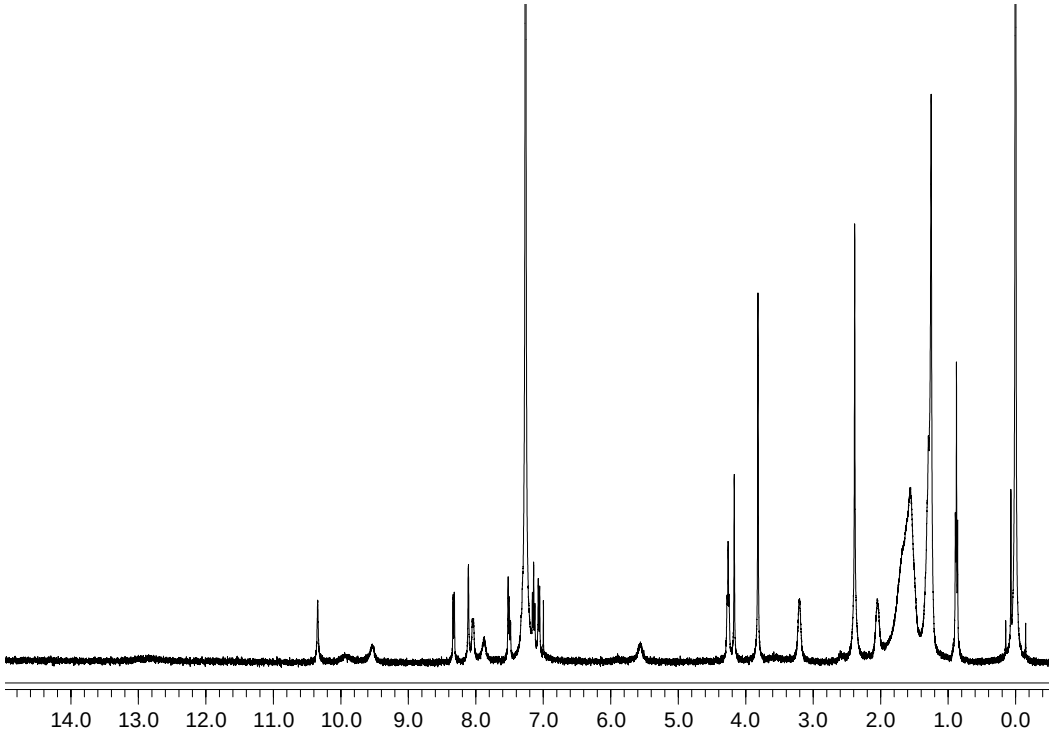

Figure S1. ^{1}H NMR of **FM** in $CDCl_3$ (5 mM).

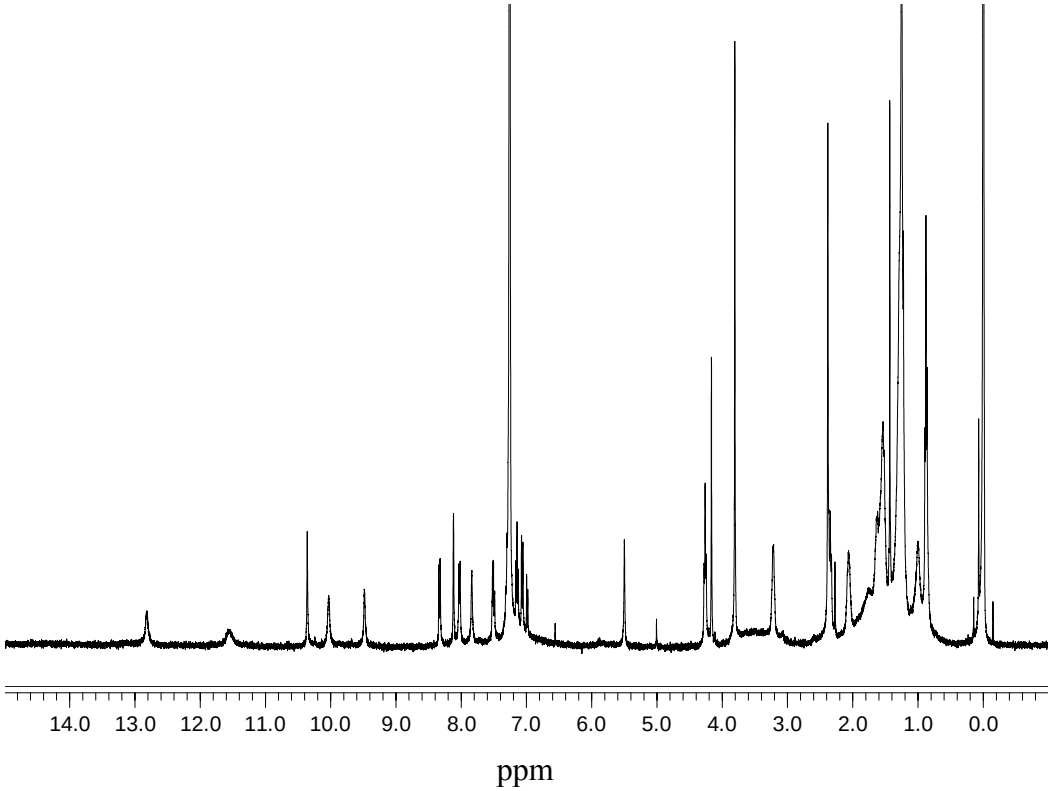

Figure S2. ^{1}H NMR of the 1:1 mixture of **FM** and **LM** in $CDCl_3$ (5 mM).

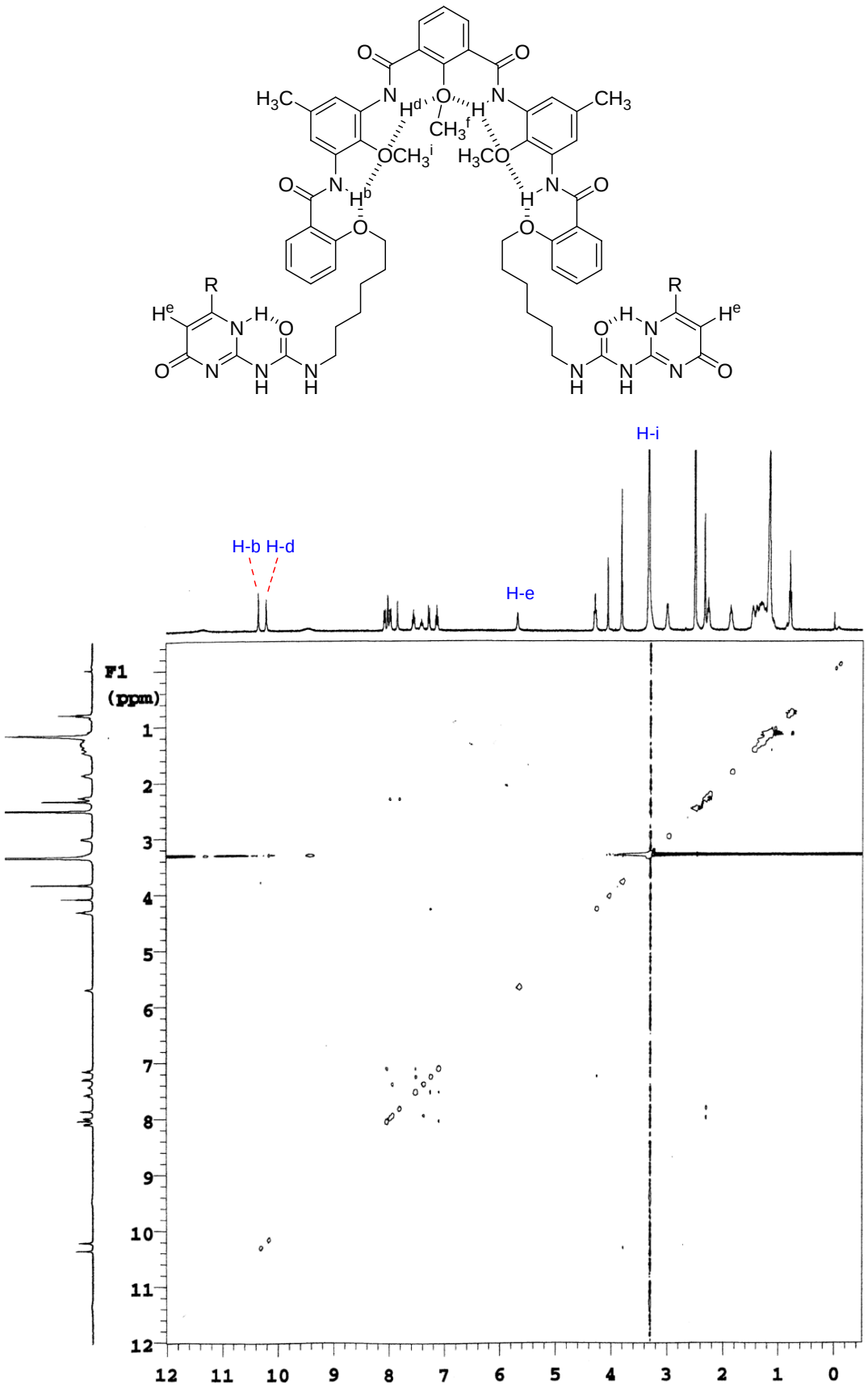

Figure S3. NOESY spectrum of **FM** (5 mM) in DMSO-d_6.

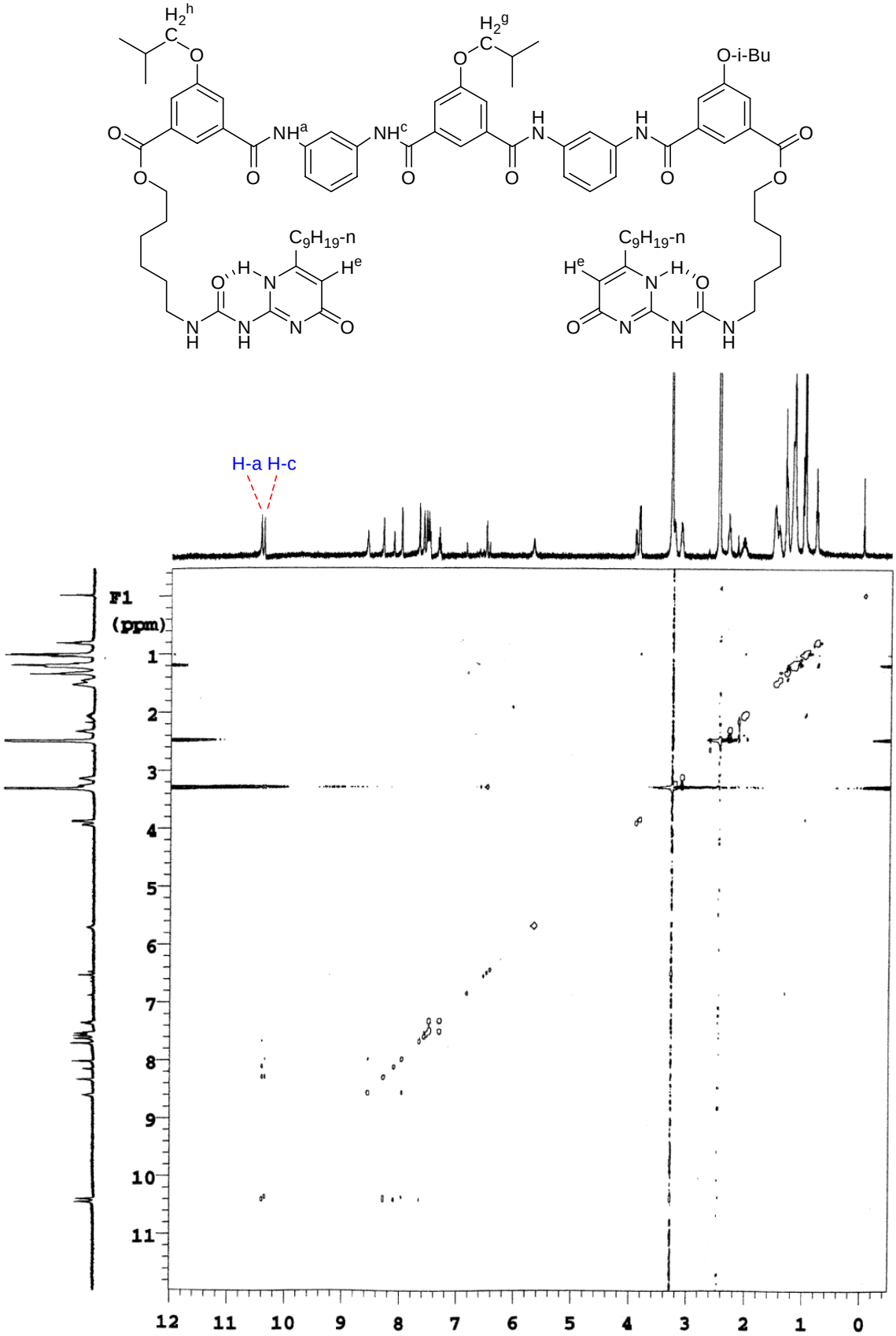

Figure S4. NOESY spectrum of **LM** (5 mM) in DMSO-d_6.

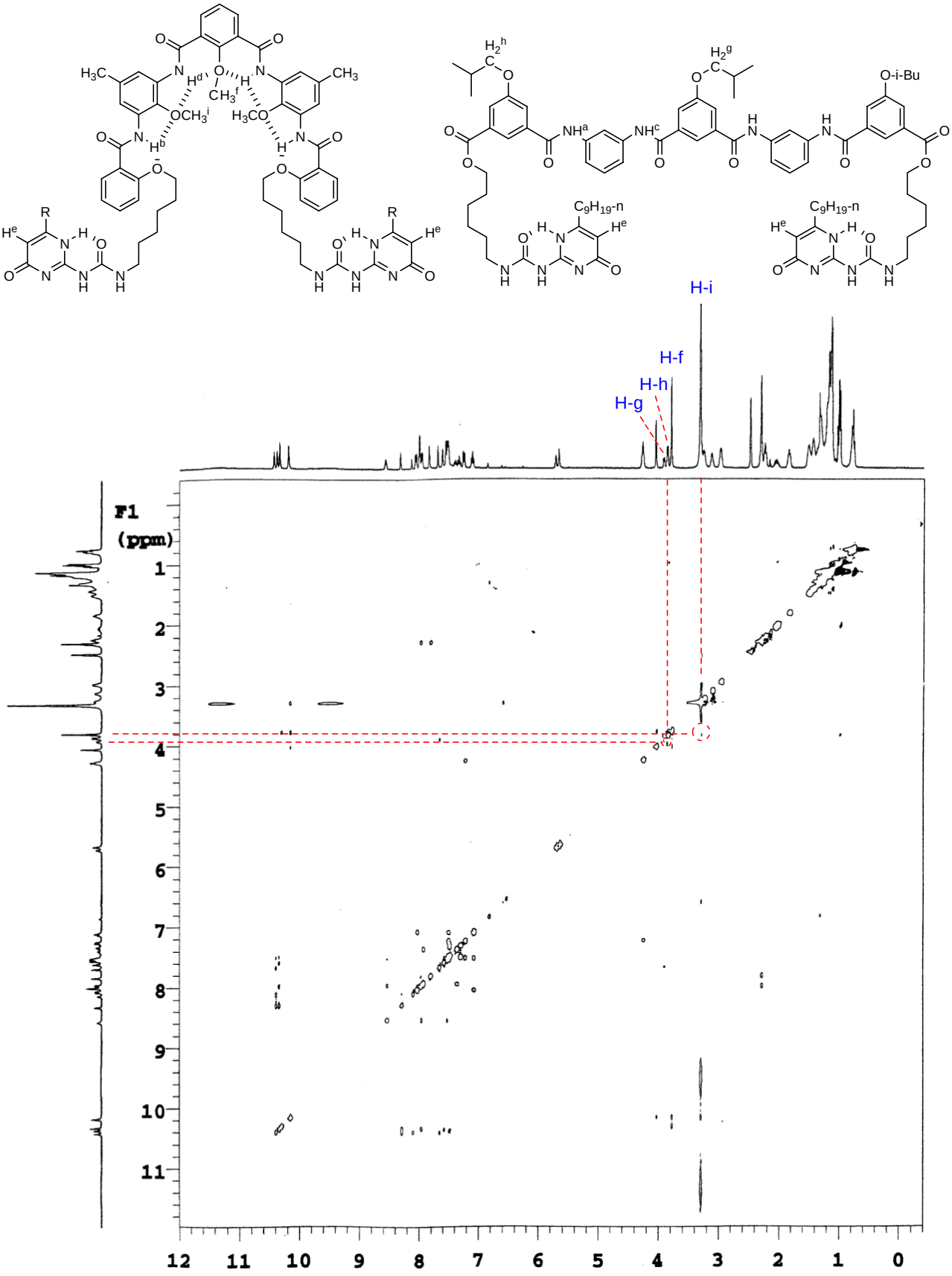

Figure S5. NOESY of the 1:1 mixture of **FM** and **LM** (5 mM) in DMSO-d_6.

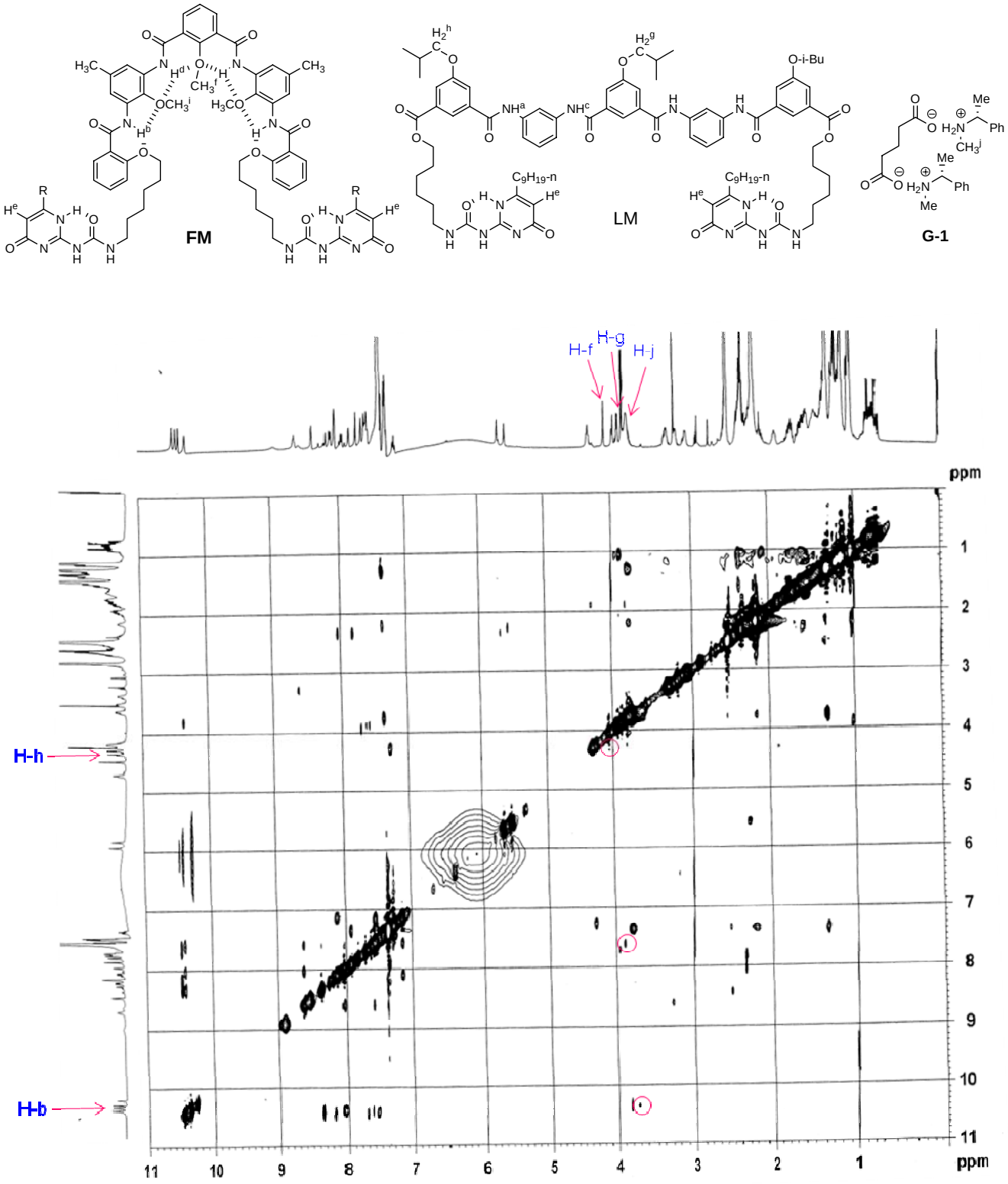

Figure S6. NOESY of the 1:1 mixture of **FM** and **LM** (5 mM) in the presence of **G-1** (20 mM) in DMSO-d_6.

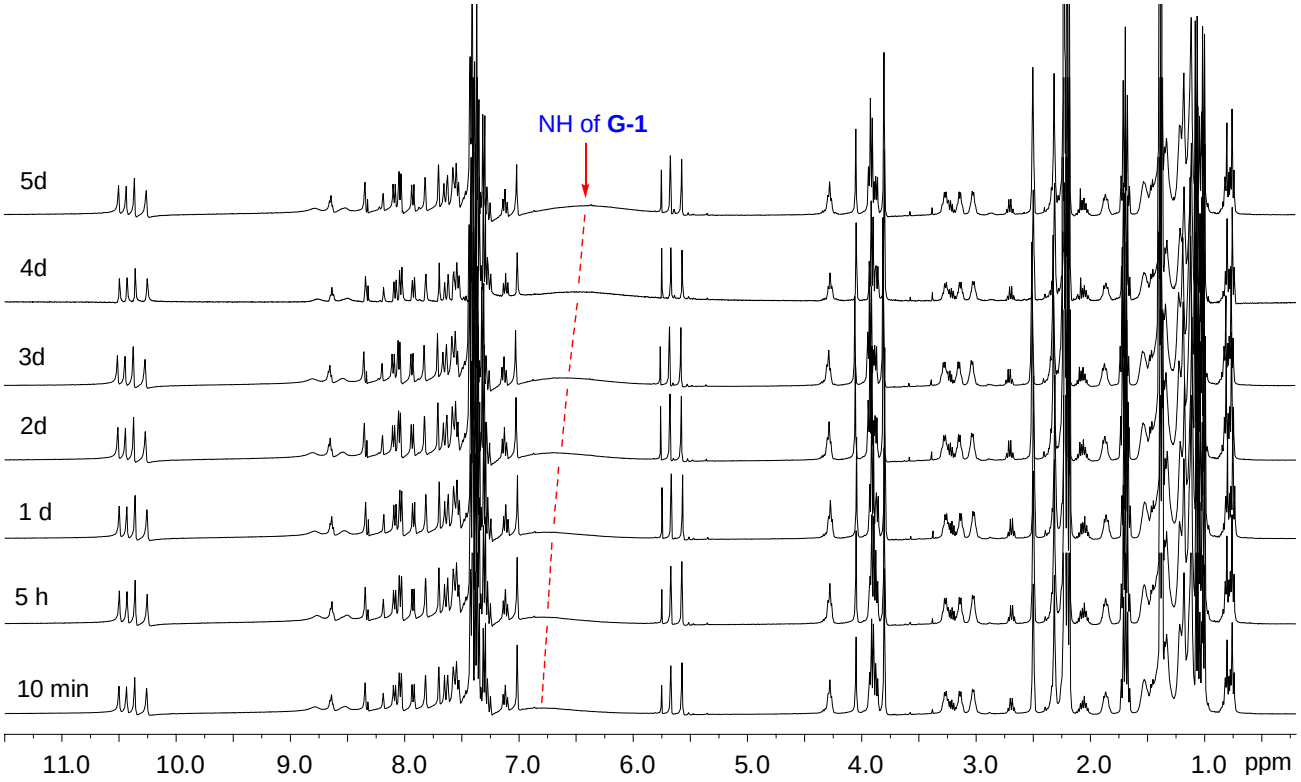

Figure S7. ^{1}H NMR of **FM** (2 mM), **LM** (2 mM) and **G-1** (5 mM) in DMSO-d_6 recorded after mixing for different time.

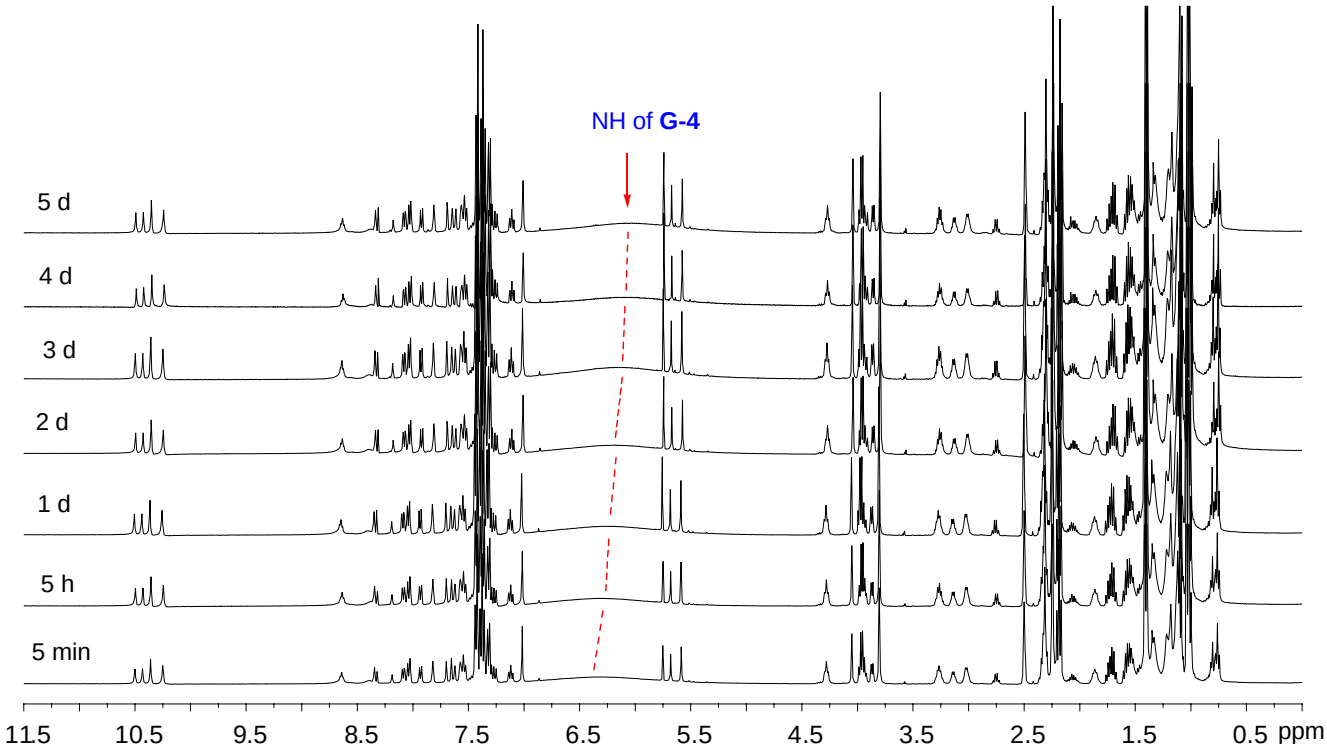

Figure S8. ^{1}H NMR of **FM** (2 mM), **LM** (2 mM) and **G-4** (5 mM) in DMSO-d_6 recorded after mixing for different time.

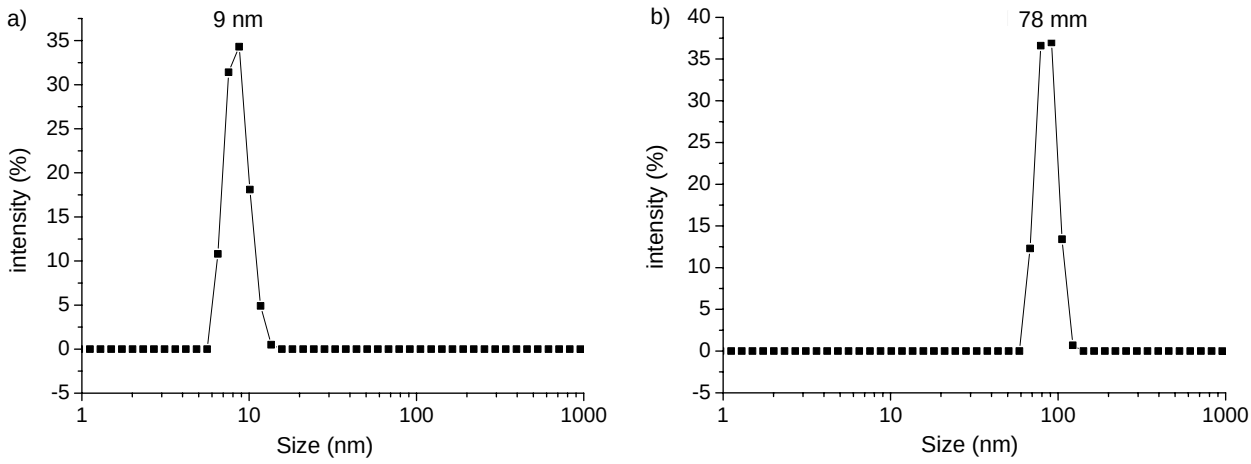

Figure S9. The DLS intensity-weighted distribution of aggregates of a) the **FM-LM** (1:1, 0.2 mM) and b) the **FM-LM-G-1** (1:1:1, 0.2 mM) in DMSO (0.4 mM).

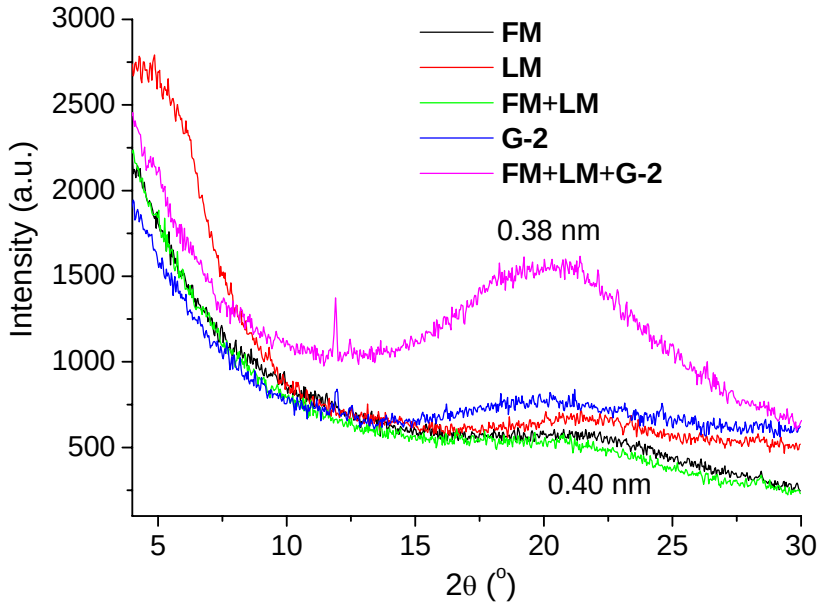

Figure S10. The XRD profiles of **FM**, **LM**, **FM + LM** (1:1), **G-2** and **FM + LM + G-2** (1:1:2). The samples were prepared by evaporating the solution of DMSO ([**FM**] = [**LM**] = 0.2 mM, [**G-2**] = 0.4 mM) under reduced pressure after the solutions were set for 7 days.