Helical Supramolecular Polymer Nanotubes with Wide Lumen for Glucose Transport: Towards the Development of Functional Membrane-Spanning Channels

Chenyang Zhang,[a] Xiaoli Deng,[a] Chenxi Wang,[b] Chunyan Bao,[b] Bing Yang,[a] Houyu Zhang,[a] Shuaiwei Qi,[a] and Zeyuan Dong*[a]

[a] State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University, Qianjin Street, Changchun (P. R. China)
E-mail: zdong@jlu.edu.cn.

[b] Shanghai Key Laboratory of Functional Materials Chemistry
Institute of Fine Chemicals, East China University of Science and Technology, No. 130 Meilong Road, Shanghai, China

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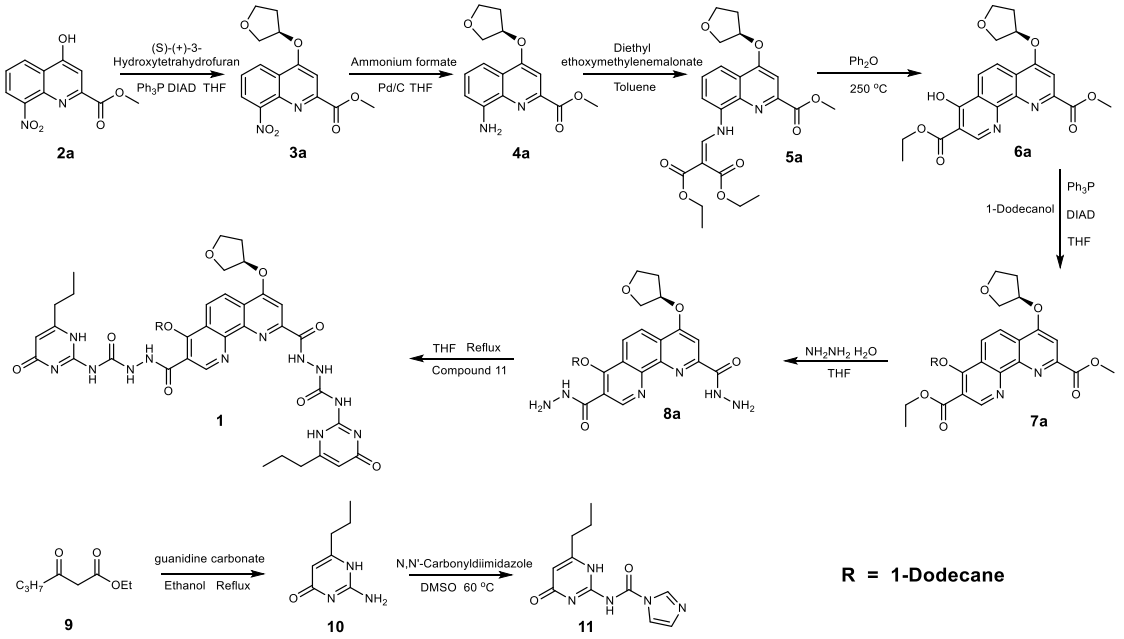
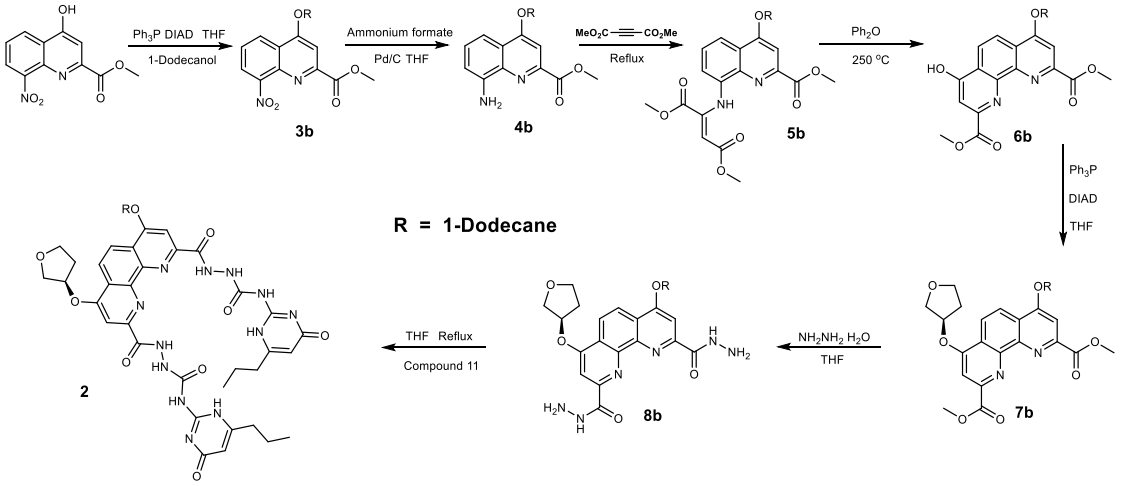
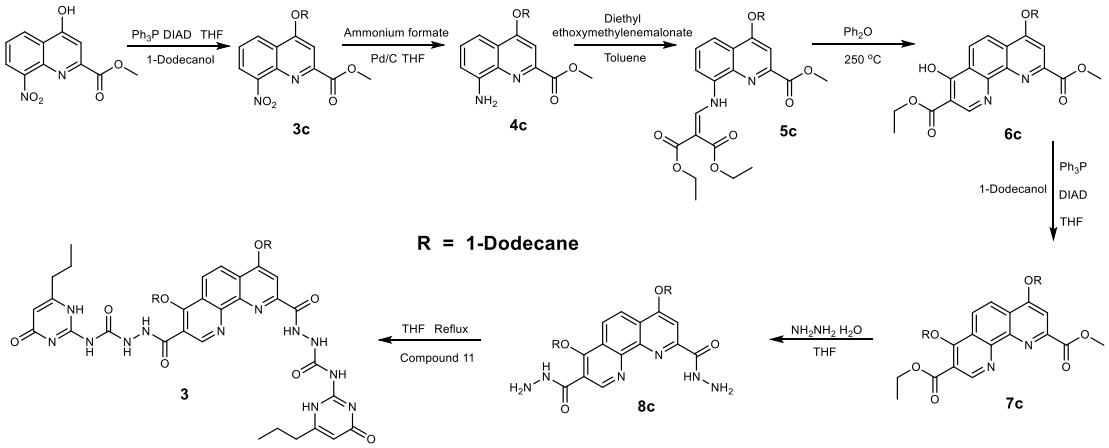


Scheme S1. Synthesis of compound **1**.



Scheme S2. Synthesis of compound **2**.

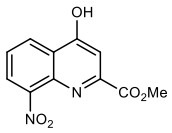


Scheme S3. Synthesis of compound **3**.

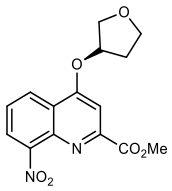
2. Synthetic procedures

General information

All reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on the Bruker AVANCEIII 500. Chemical shifts for protons and carbon are referenced to solvent residual peak in the NMR solvent ($CDCl_3$ = δ 7.26 ppm, DMSO = δ 2.5 ppm for ^{1}H NMR spectrum; $CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm for ^{13}C NMR spectrum). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Agilent1290-micrOTOF Q II and Autoflex speed TOF/TOF.

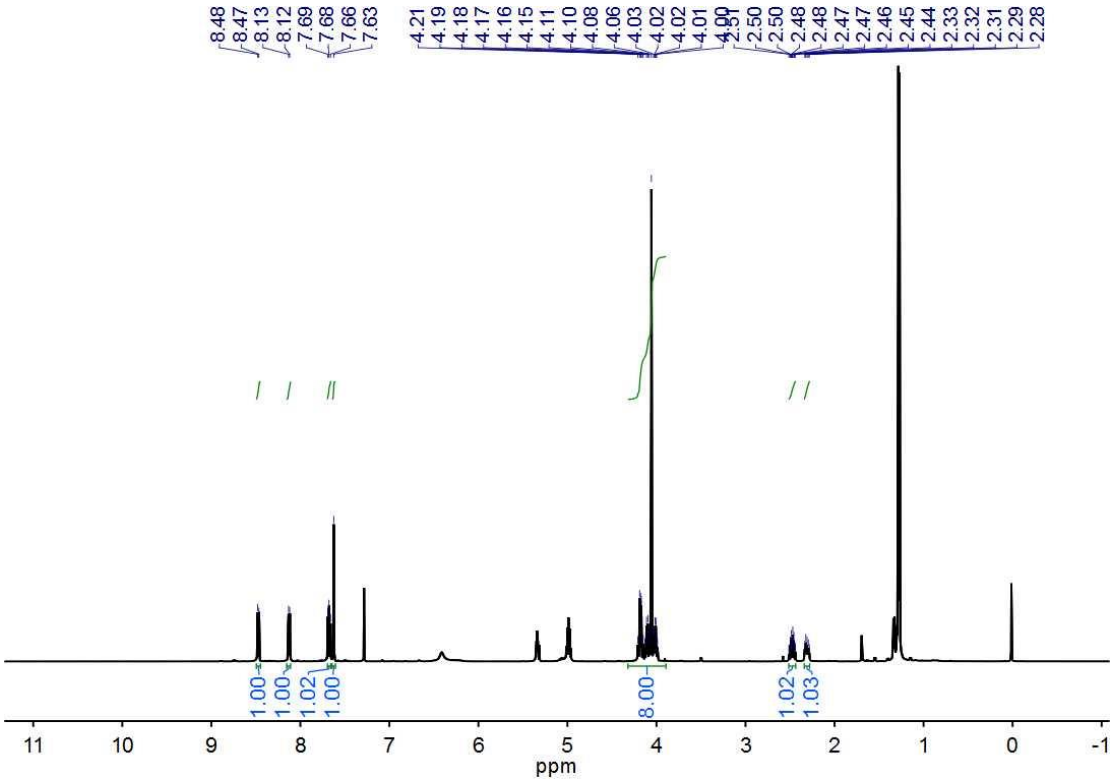


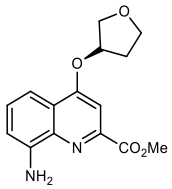
Compound 2a. Compounds **2a**.were synthesized according to the previously reported methods and fully characterized.[1]



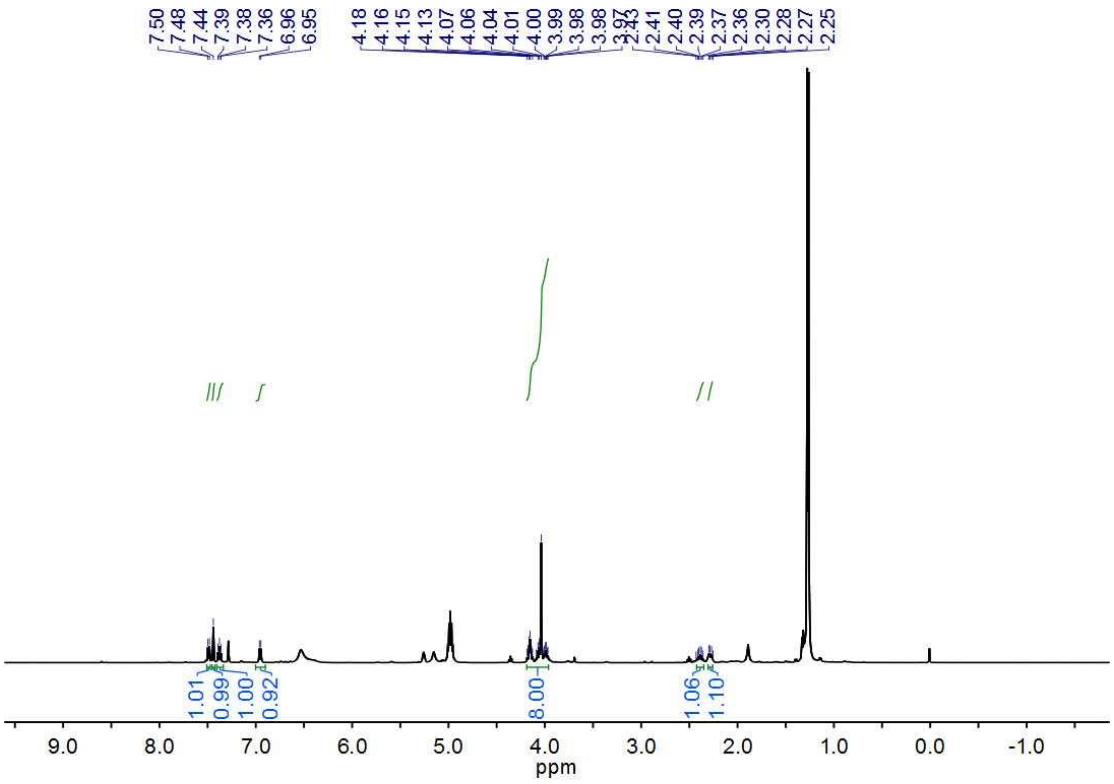
Compound 3a. A mixture of compound **2a (**1g, 4.3 mmol), triphenylphosphine (Ph_3P) (1.6g, 6.1 mmol) and (S)-(+)-3-Hydroxytetrahydrofuran (0.48mL, 6.1 mmol) was added into 10mL anhydrous THF. Diisopropyl azodicarboxylate (DIAD) (1.19mL, 6.1mmol) was added dropwise into the mixture under stirring in ice bath. The mixture was stirred for 12h. Then the reaction solution was removed under reduced pressure and the product was purified by column

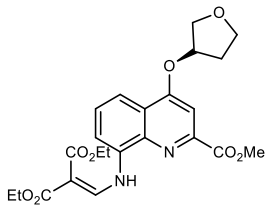
chromatography (dichloromethane / methanol = 50/1, vol / vol) to give the product as a yellow solid (1.1g, yield: 85.9%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.63 (s, 1H), 4.22 – 3.96 (m, 8H), 2.48 (m, 1H), 2.35 – 2.27 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.61, 161.21, 151.04, 148.44, 140.22, 126.41, 126.21, 125.23, 123.44, 102.74, 79.48, 72.80, 67.27, 53.44, 32.88. MS (ESI): Calculated $[M+H]^+$: 319.1, Found $[M+H]^+$:319.1.



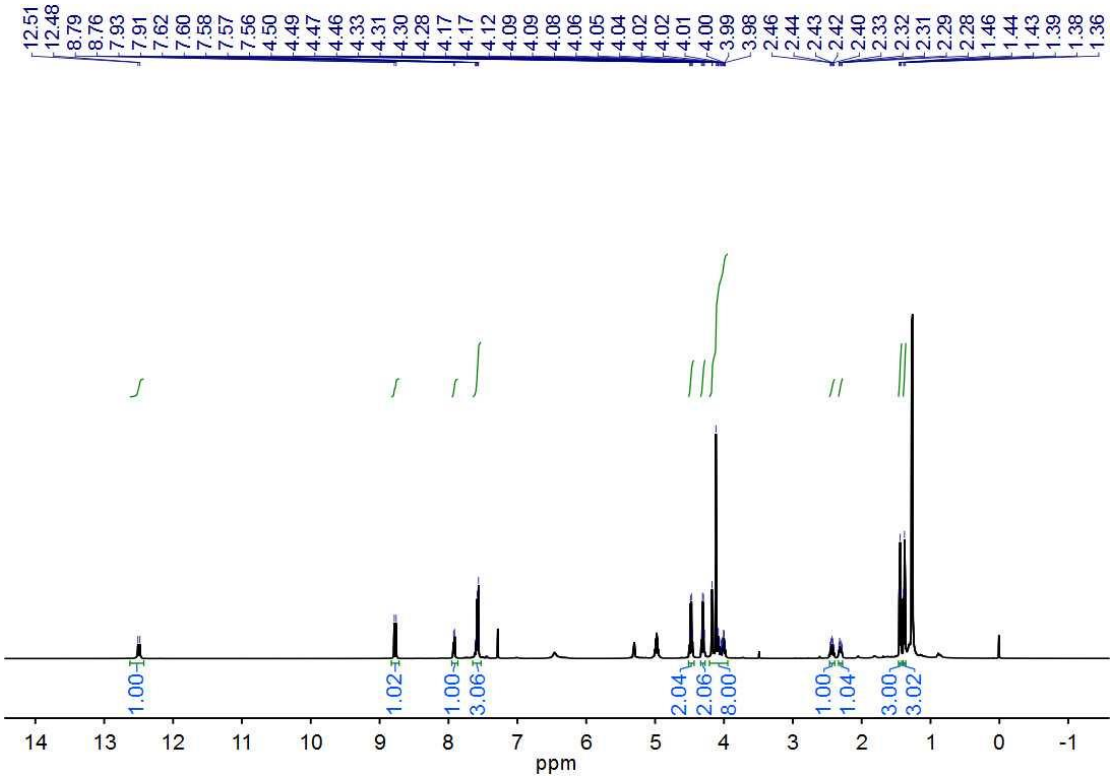


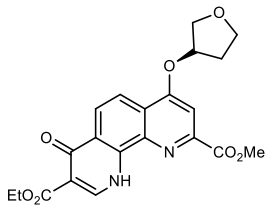
Compound 4a. Compound **3a** (1.0g, 31.4 mmol) was dissolved in the mixture of 10mL THF, 5mL methanol and 1mL distilled water. Then 10% Pd / C (0.1g), ammonium formate (1g, 15.8 mmol) and ammonium metavanadate was added into the mixture under stirring. The mixture was stirred at room temperture for 2h. Then the reaction solution was removed under reduced pressure and the residue was washed with distilled water to give a yellow oil (0.8g, yield: 91.4%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 4.05 – 3.62 (m, 8H), 2.45 – 2.36 (m, 1H), 2.36 – 2.08 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.61, 161.21, 151.04, 148.44, 140.22, 126.41, 122.81, 111.18, 109.44, 102.74, 79.27, 72.86, 67.27, 53.37, 32.86. MS (ESI): Calculated $[M+H]^+$: 289.1, Found $[M+H]^+$:289.1.



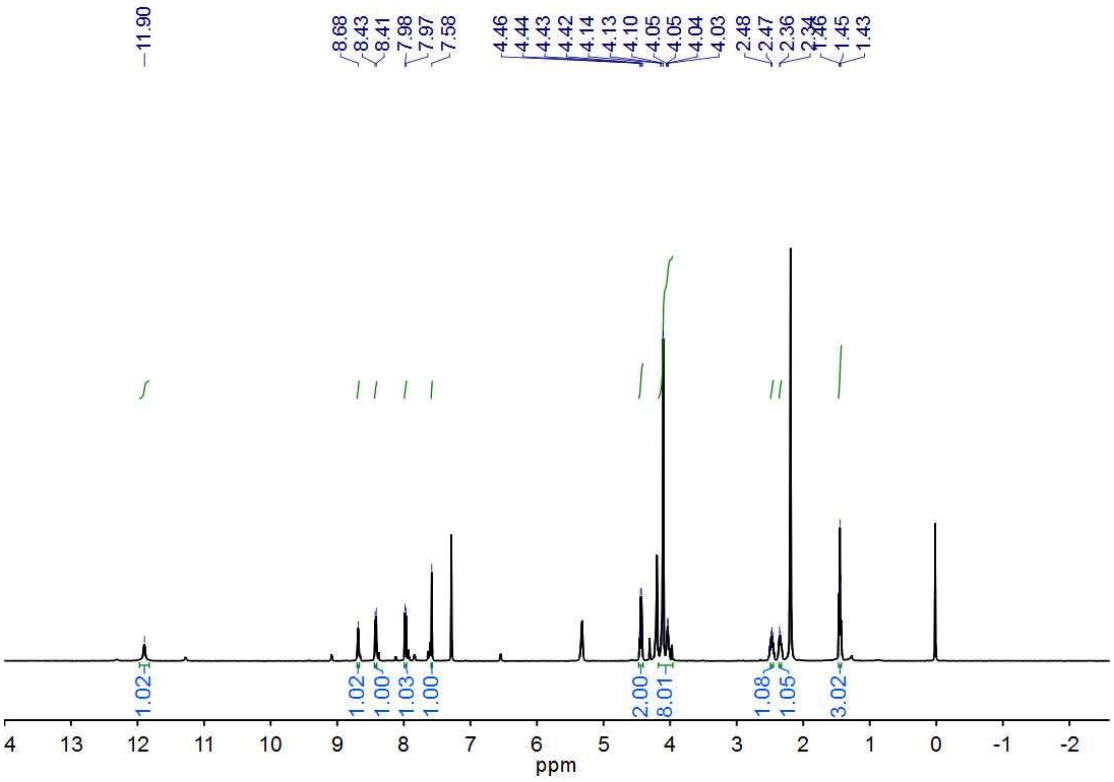


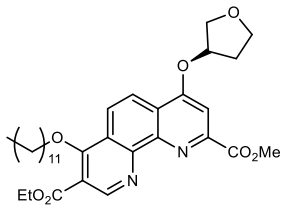
Compound 5a. Diethyl ethoxymethylenemalonate (1.5 mL) was added dropwise to a stirred solution of Compound **4a** (0.8g, 2.8 mmol) in 10 mL methylbenzene in ice bath. The mixture was stirred at r.t. for 12h. After cooling, the mixture was washed with frozen methylbenzene to give the product as a white solid (1.1g, yield: 86.7%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.50 (d, J = 14.2 Hz, 1H), 8.77 (d, J = 14.2 Hz, 1H), 7.92 (d, J = 7.3 Hz, 1H), 7.69 – 7.52 (m, 3H), 4.48 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 4.19 – 3.98 (m, 8H), 2.47 – 2.40 (m, 1H), 2.35 – 2.27 (m, 1H), 1.44 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.80, 166.08, 165.70, 148.47, 147.53, 139.11, 136.63, 127.98, 123.11, 116.42, 111.42, 102.12, 96.04, 79.00, 72.87, 67.29, 60.34, 60.29, 53.26, 32.97, 14.44. MS (ESI): Calculated $[M+H]^+$: 459.2, Found $[M+H]^+$:459.5.



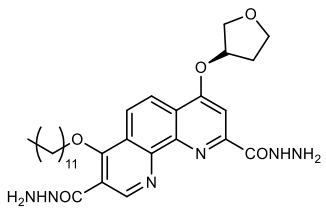


Compound 6a. Compound **5a** (1g, 2.4 mmol) was added in the boiling oxydibenzene and boiled for 15min. Then the solution was cooled to 333K, and poured into 60 mL petroleum ether, stored in 277K overnight. The crude product was obtained by filtration as a brown powder (0.6g, yield: 66.7%).^{1}H NMR (500 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.68 (s, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.58 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 4.18 – 4.00 (m, 8H), 2.51 – 2.44 (m, 1H), 2.38 – 2.31 (m, 1H), 1.45 (t, J = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 174.23, 165.28, 165.17, 161.36, 146.83, 143.59, 139.22, 136.15, 127.33, 124.34, 123.15, 117.05, 113.55, 104.04, 79.46, 72.76, 67.31, 60.78, 53.41, 32.90, 14.43. MS (ESI): Calculated $[M+H]^+$: 413.1, Found $[M+H]^+$:413.4.

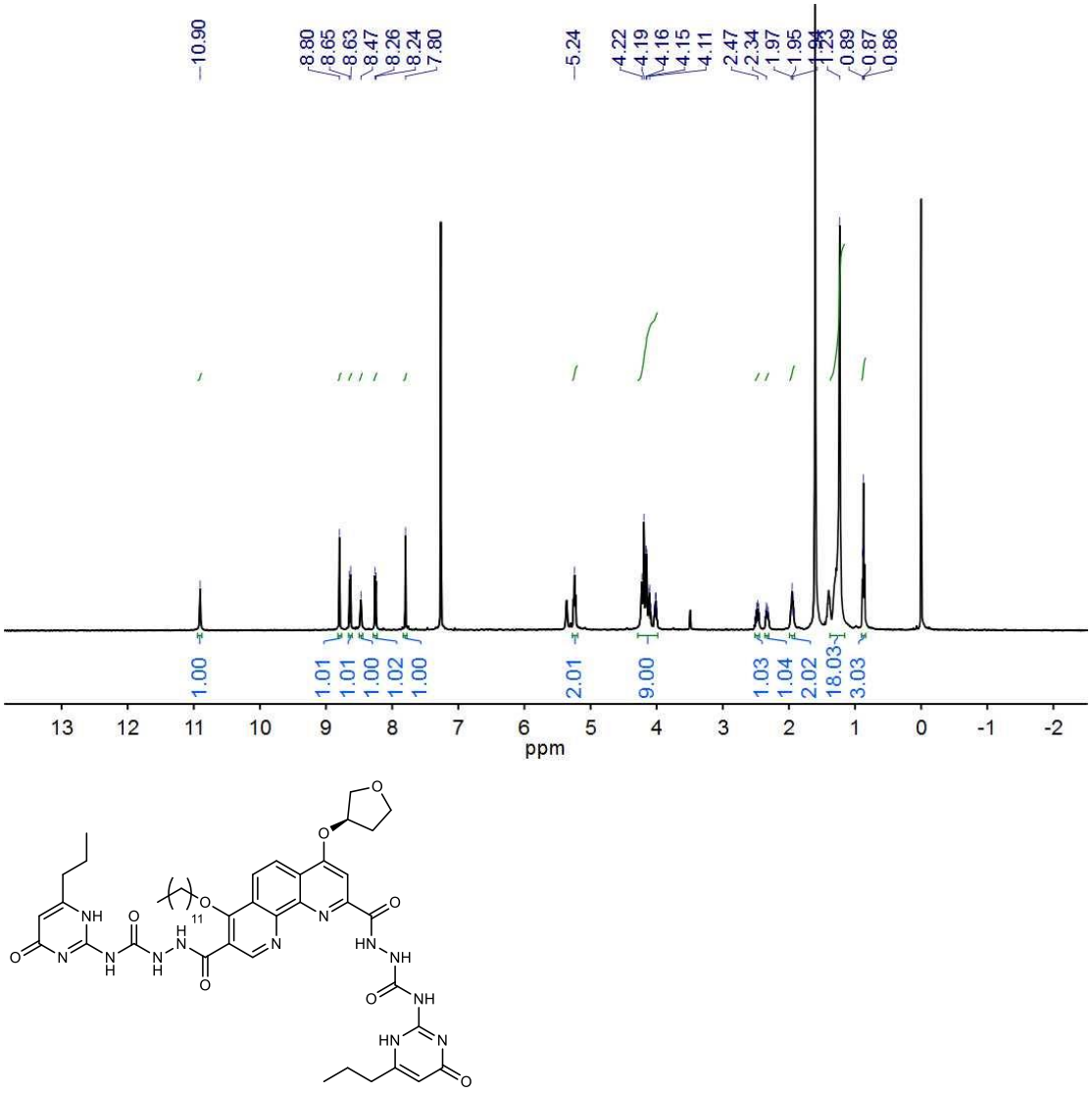




Compound 7a. A mixture of compound **6a** (1g, 2.4 mmol), triphenylphosphine (Ph_3P) (0.9g, 3.6 mmol) and lauryl alcohol (0.81 mL, 3.6 mmol) was added into 10mL anhydrous THF. Diisopropyl azodicarboxylate (DIAD) (0.7 mL, 3.6 mmol) was added dropwise into the mixture under stirring in ice bath. The mixture was stirred for 12h at rt. Then the reaction solution was removed under reduced pressure and the product was purified by column chromatography (dichloromethane / methanol = 50/1, vol / vol) to give the product as a white solid (1.2g, yield: 85.7%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.58 (d, J = 9.0 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.65 (s, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.22 – 3.97 (m, 10H), 2.51 – 2.44 (m, 1H), 2.34 – 2.30 (m, 1H), 1.91 – 1.82 (m, 2H), 1.47 – 1.18 (m, 21H), 0.885 – 0.858 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.49, 166.33, 165.61, 161.18, 151.86, 146.19, 141.02, 136.95, 131.38, 126.06, 125.27, 118.57, 118.48, 103.34, 79.17, 72.79, 67.29, 61.14, 60.73, 52.98, 32.97, 31.89, 31.34, 29.59, 29.45, 29.32, 26.36, 22.67, 14.10. MS (ESI): Calculated $[M+H]^+$:581.3, Found $[M+H]^+$: 581.3.

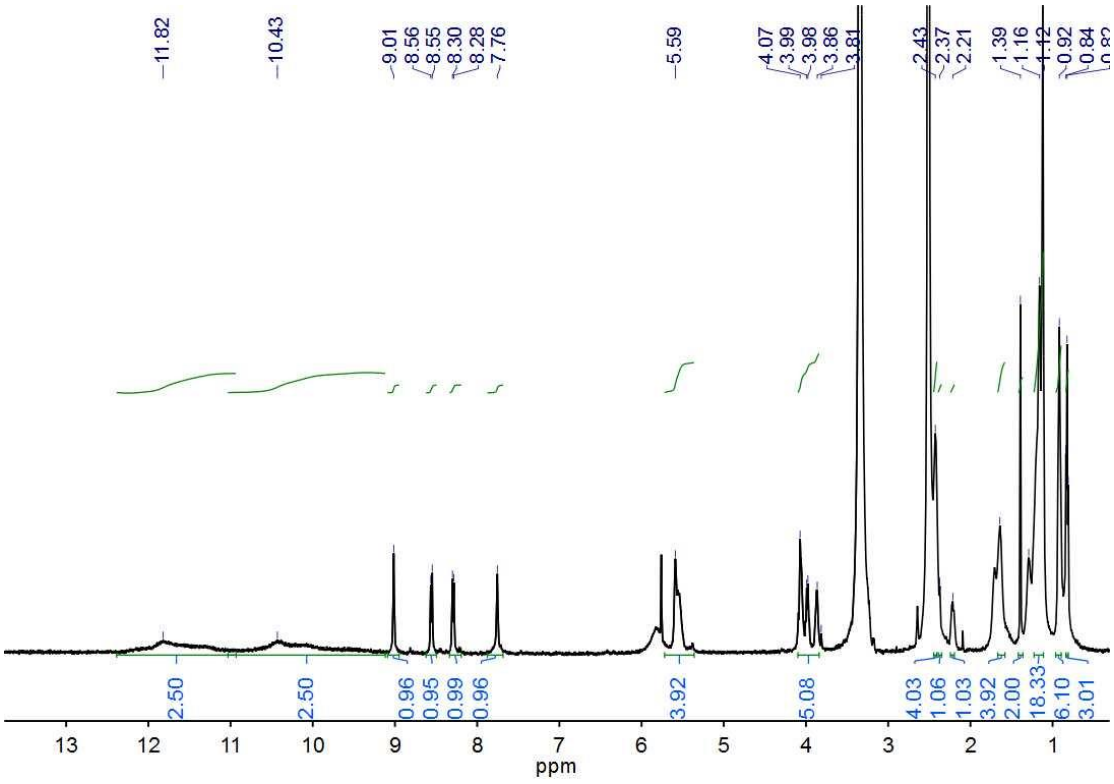


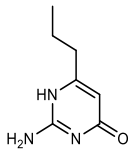
Compound 8a. Compound **7a** (1.0 g, 1.7 mmol) was dissolved in THF (10 mL), then hydrazine solution (1.0 mL, Hydrazine hydrate dissolved in the mixture of 2mL methanol and 10mL THF) was added. The mixture was stirred at room temperature for 5h. The reaction solution was removed under reduced pressure and the product was washed with methanol (0.9g, yield: 92.1%).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (m, 1H), 8.80 (s, 1H), 8.64 (d, J = 9.0 Hz, 1H), 8.47 (m, 1H), 8.25 (d, J = 9.0 Hz, 1H), 7.80 (s, 1H), 5.24 – 5.13 (m, 2H), 4.22 – 4.00 (m, 9H), 2.57 – 2.44 (m, 1H), 2.36 – 2.30 (m, 1H), 1.98 – 1.92 (m, 2H), 1.23 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.94, 165.67, 161.92, 159.23, 149.12, 148.76, 139.82, 136.52, 129.91, 125.32, 124.38, 118.98, 113.19, 101.87, 79.49, 72.82, 67.31, 61.08, 32.97, 31.89, 31.30, 29.57, 29.46, 29.31, 26.36, 22.68, 14.10. MS (ESI): Calculated $[M+H]^+$: 567.3, Found $[M+H]^+$:567.3.



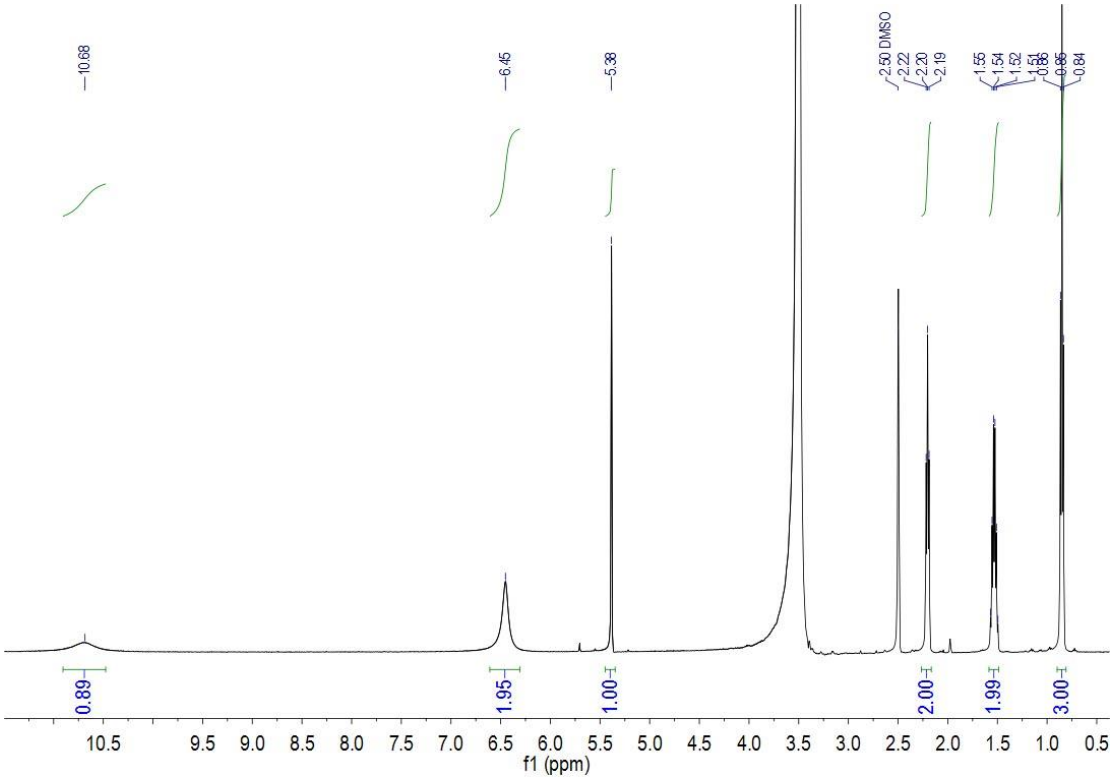
Compound 1. A suspension of **8a** (0.5 g, 0.90 mmol) and compound **8a** (0.49 g, 1.98 mmol) in 10mL tetrahydrofuran was heated under reflux overnight. Solvent was then removed at reduced pressure and the reaction mixture cooled to 4 °C. The resulting residue was washed with cold methanol, and the crude product was purified by silica gel column chromatography (dichloromethane / methanol = 20/1, vol / vol) to obtain 1 as yellow powder (0.49g, yield 60%). ^{1}H NMR (500 MHz, DMSO) δ12.23 – 9.35 (m, 6H), 9.01 (s, 1H), 8.56 (d, J = 9.0 Hz, 1H), 8.29

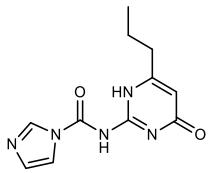
(d, J = 8.9 Hz, 1H), 7.76 (s, 1H), 5.76 – 5.59 (m, 4H), 4.13 –3.83 (m, 5H), 2.43 (m, 5H),2.24 – 2.17 (m, 1H), 1.67 (m, 4H), 1.39 (s, 2H), 1.34 – 1.05 (m, 18H), 0.92 (m, 6H), 0.82 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Pyr) δ 175.09, 163.03, 162.45, 150.15, 149.91, 149.64, 149.37, 149.09, 140.38, 136.98, 135.76, 135.51, 135.26, 135.01, 134.74, 130.16, 128.71, 125.15, 123.74, 123.50, 123.25, 123.01, 122.71, 119.02, 113.60, 102.03, 31.87, 29.71, 29.66, 29.53, 29.37, 28.78, 26.44, 26.05, 22.69, 20.97, 14.04, 13.47.(some shift were covered by solvent pyridine) MS (ESI): Calculated $[M+H]^+$: 925.4, Found $[M+H]^+$:925.5.



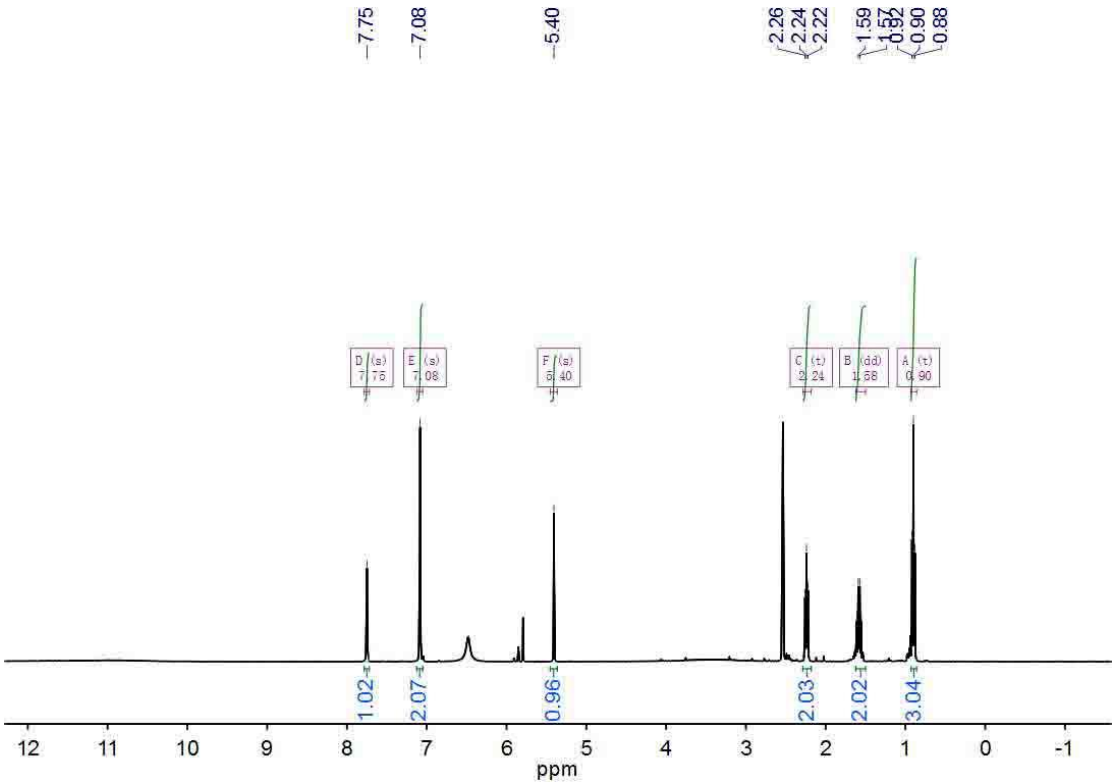


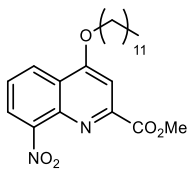
Compound 10. A suspension of the Ethyl butyrylacetate (2.5 ml, 15.8 mmol) and guanidine carbonate (2.8 g, 15.5 mmol) in ethanol (40 ml) was heated under reflux in 12 h. Solvent was then removed at reduced pressure and the reaction mixture cooled to 4 °C. The resulting residue was washed with cold acetone (2.0g, yield 84%).^{1}H NMR (500 MHz, DMSO) δ 10.69 (s, 1H), 6.49 (s, 2H), 5.38 (s, 1H), 2.21 (t, J = 7.3 Hz, 2H), 1.55 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 168.28, 165.81, 157.05, 100.17, 21.22, 14.02. MS (ESI): Calculated $[M+H]^+$: 154.1, Found $[M+H]^+$: 154.1.



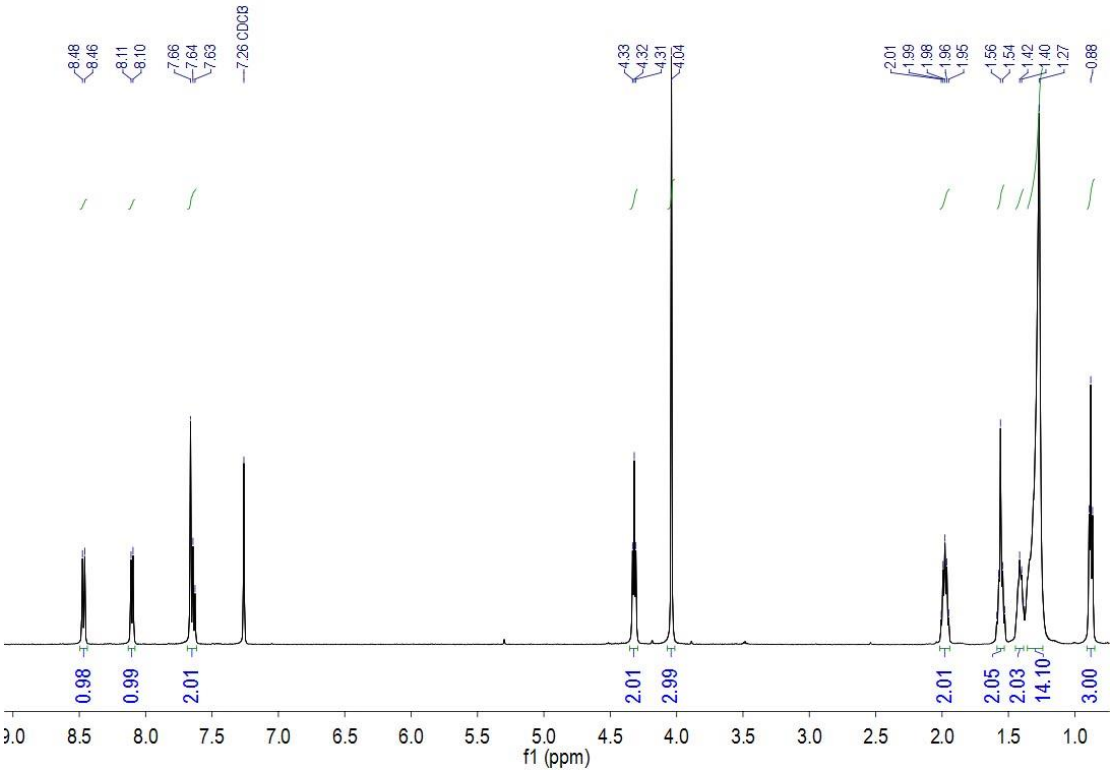


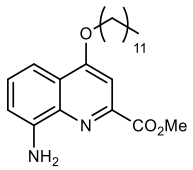
Compound 11. A suspension of the Compound 10 (1.0 g, 6.5 mmol) and N,N'-Carbonyldiimidazole (2.0g, 12.3 mmol) in 2mL DMSO was stirred at 333K for 4h. The solvent was then poured into acetone (50mL) and the residue was filtered off, washed with cold acetone as a white solid (1.3 g, 83.3%)^{1}H NMR (500 MHz, DMSO) δ 9.10 (s, 1H), 7.69 (m, 2H), 5.77 (s, 1H), 2.41 (t, J = 7.4 Hz, 2H), 1.59 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.69, 156.83, 156.67, 137.02, 129.99, 124.67, 117.49, 103.57, 39.30, 20.91, 13.71.MS (ESI): Calculated $[M+H]^{+}$:248.1 , Found $[M+H]^{+}$: 248.1.



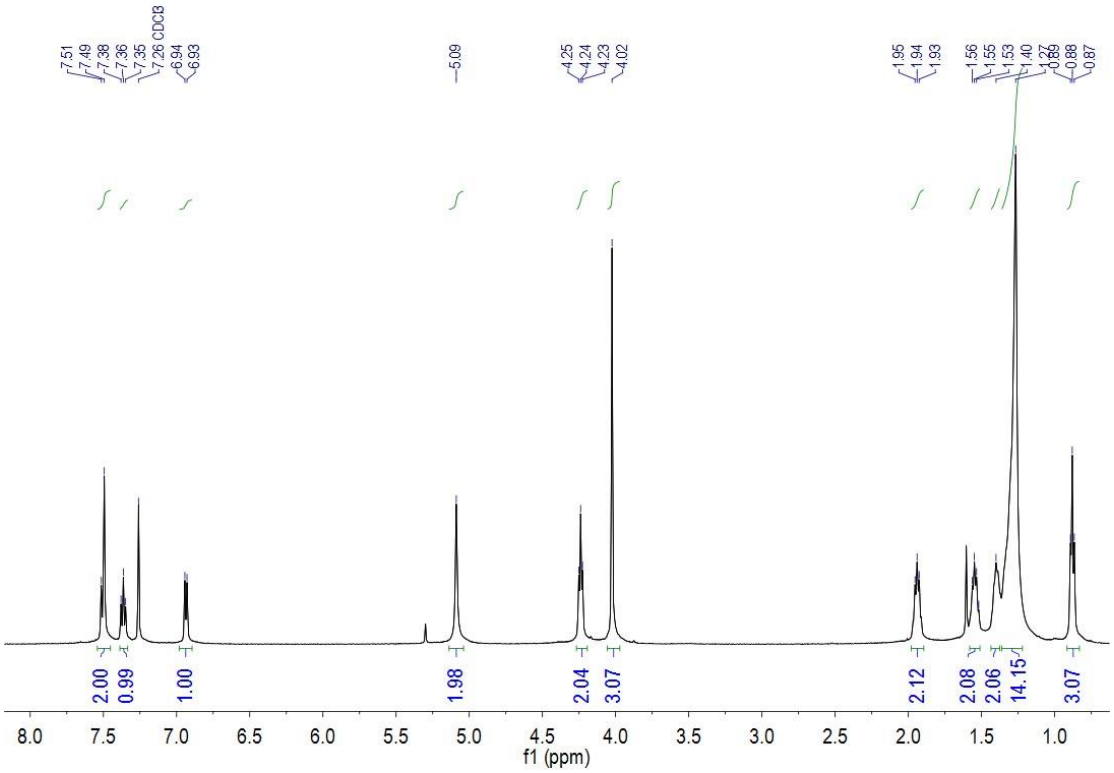


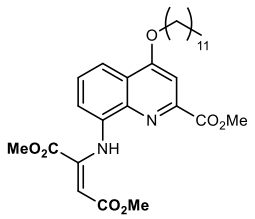
Compound 3b. A mixed solution of triphenylphosphine (7.9 g, 30.24 mmol), lauryl alcohol (6.96ml, 30.24 mmol) and compound **2a** (5.0 g, 20.16 mmol) was added into 100mL dry tetrahydrofuran under the protection of N_2 atmosphere and ice bath condition, and then diisopropyl azodiformate (6.11g, 30.24mmol) was added dropwise to it. The reaction was stirred overnight at room temperature, and the solvent was removed in vacuo. The crude mixture was purified by recrystallization in methanol to provide the desired product as yellow powder, (7.2 g, yield 86%)^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, J = 7.2 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.66-7.63 (m, 2H), 4.33 – 4.29 (m, 2H), 4.10 (s, 3H), 2.00 – 1.93 (m, 2H), 1.62 – 1.21(m,18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.72, 162.78, 151.32, 148.40, 140.04, 126.42, 125.87, 125.05, 123.32, 102.18, 69.70, 53.35, 31.91, 29.64, 29.63, 29.57, 29.53, 29.34, 29.29, 28.73, 26.01, 22.68, 14.11.MS (ESI): Calculated $[M+H]^+$: 417.2, Found $[M+H]^+$: 416.9



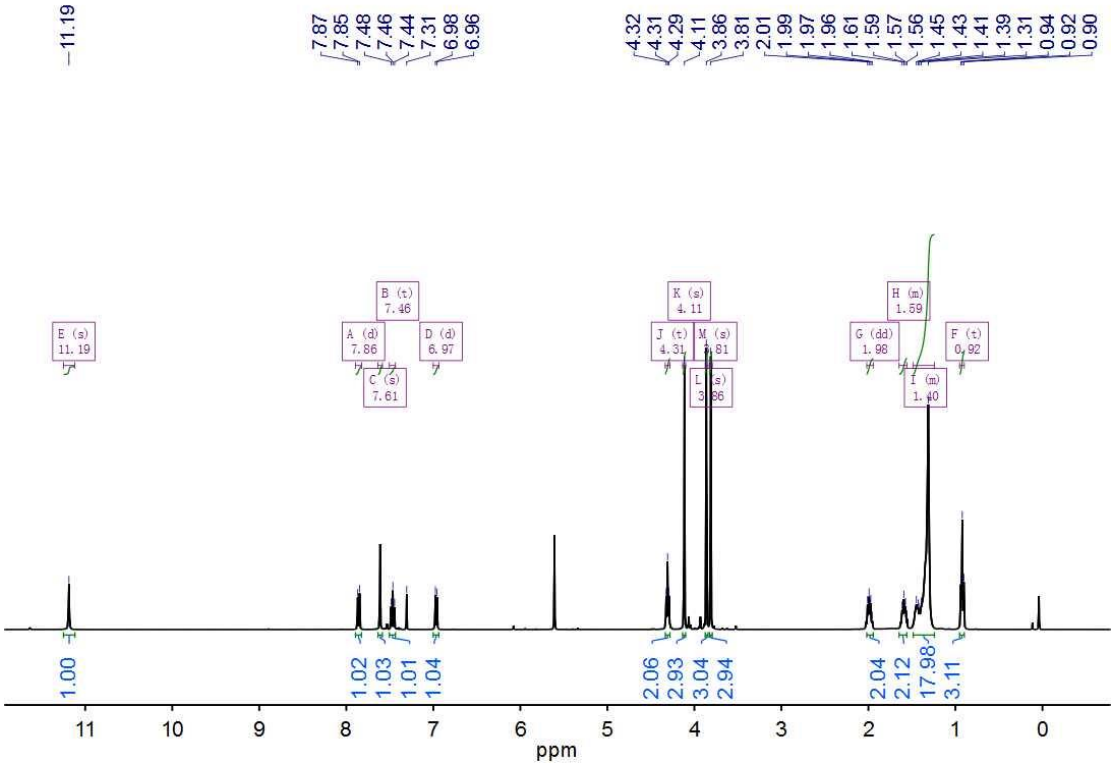


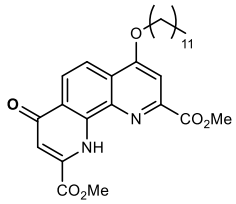
Compound 4b. Compound **3b** (5.0 g 11.6 mmol) was added to a mixed solution of methanol / water (10:1 vol / vol), and then ammonium formate (8.0 g, 60.0 mmol) and bits of ammonium metavanadate were added to the system after Pb/C (0.5 g) being added. Then the system was sealed and stirred at room temperature overnight. The precipitate was removed by the filtration, and the supernatant was concentrated under the reduced pressure. 50mL dichloromethane was added to the mixture and then washed with water to remove salts. The organic phase was collected and dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (dichloromethane / methanol = 50/1, vol / vol) to obtain **4b** as yellow powder (4.2 g, yield 90%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 5.09 (s, 2H), 4.25 – 4.23 (m, 2H), 4.02 (s, 3H), 1.97 – 1.21(m,20H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.42, 162.59, 145.83, 144.91, 138.37, 128.56, 122.98, 110.80, 109.61, 100.76, 68.82, 52.76, 31.93, 29.67, 29.65, 29.61, 29.57, 29.36, 29.35, 28.90, 26.09, 22.70, 14.13. MS (ESI): Calculated $[M+H]^+$: 387.2, Found $[M+H]^+$: 386.9.



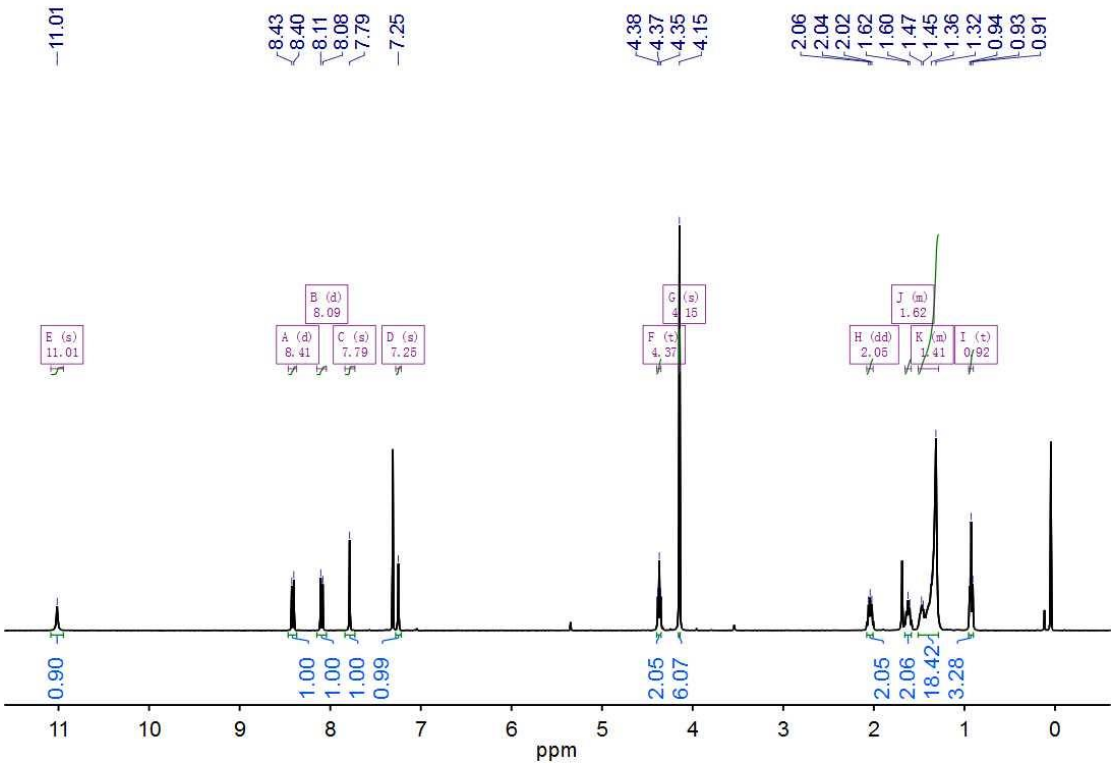


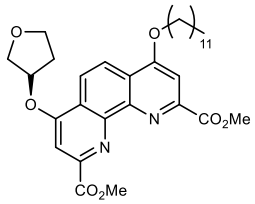
Compound 5b. Compound **4b** (400mg, 1.04mmol) was dissolved in 10 mL methanol. Dimethyl acetylenedicarboxylate (175mg, 1.24mmol) was dropwised into methanol solution. The mixture solution was reflux overnight. After reaction, the solution was cooled at -20°C and the compound 5c was obtained by filtering the solution which had precipitate and washing it with cooled methanol as yellow powder (435mg, yield 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.19 (s, 1H), 7.86 (d, *J*=8.4, 1H), 7.61 (s, 1H), 7.46 (m, 1H), 6.97 (d, *J*=7.6, 1H), 4.31 (m, *J*=6.4, 2H), 4.11 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 1.98 (m, 2H), 1.65 – 1.56 (m, 2H), 1.48 – 1.24 (m, 18H), 0.92 (t, *J*=6.8, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.01, 168.99, 166.12, 165.16, 162.85, 147.35, 145.38, 139.78, 137.37, 127.30, 122.84, 115.09, 114.50, 101.28, 101.23, 96.59, 69.12, 53.17, 53.06, 52.96, 52.67, 51.47, 51.28, 31.91, 29.63, 29.34, 28.84, 26.04, 22.69, 14.11. MS (ESI): Calculated $[M+H]^+$: 529.3, Found $[M+H]^+$:529.3.



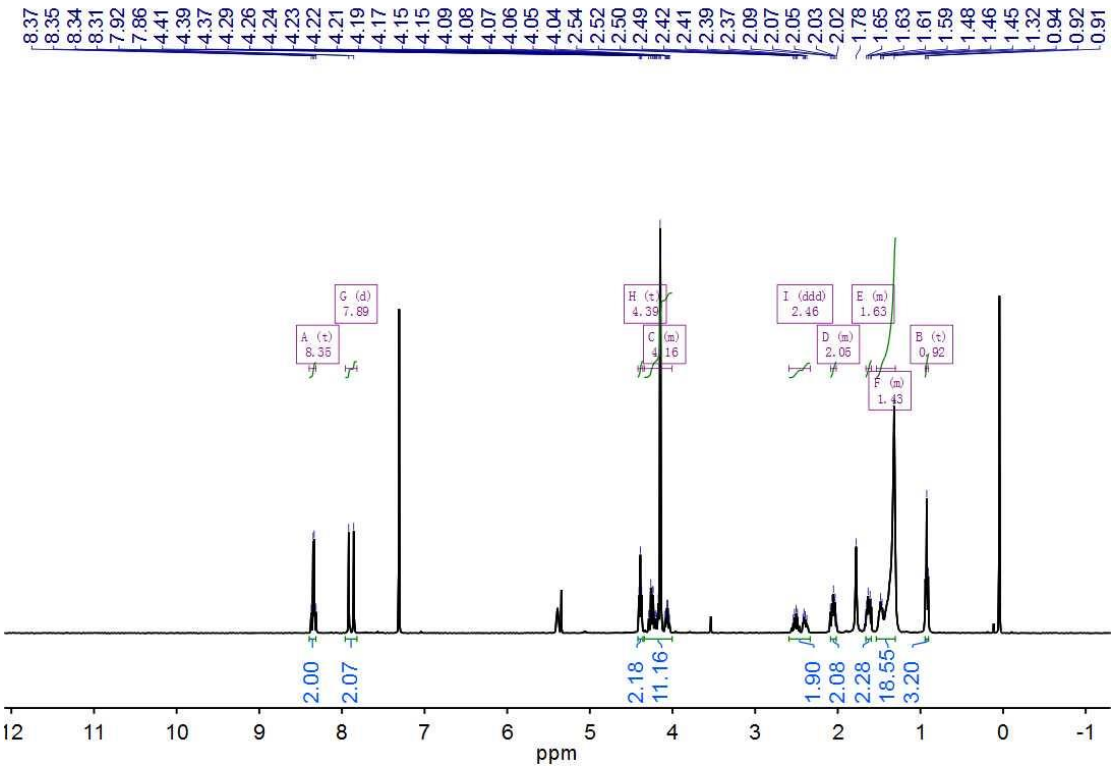


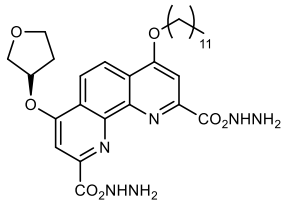
Compound 6b. Compound 5b (400mg, 0.75mmol) was suspended in 20mL diphenyl ether, and the mixed solution was boiled at 250°C for 15 minutes. The solution was cooled to 60°C and then it was added to 60 mL petroleum ether. The mixed solution was cooled at 4 °C for 12 hours, and compound 6c was obtained by filtering the solution washing with cooled petroleum ether as yellow powder (210mg, yield 59%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.01 (s, 1H), 8.41 (d, *J*=9.1, 1H), 8.09 (d, *J*=9.1, 1H), 7.79 (s, 1H), 7.25 (s, 1H), 4.37 (t, *J*=6.4, 2H), 4.15 (s, 6H), 2.05 (m, 2H), 1.66 – 1.59 (m, 2H), 1.51 – 1.29 (m, 18H), 0.92 (t, *J*=6.7, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 178.80, 165.52, 163.03, 162.81, 148.21, 139.38, 136.91, 135.71, 125.62, 123.43, 114.84, 114.70, 104.13, 31.89, 29.62, 22.68, 14.10. MS (ESI): Calculated $[M+H]^+$: 497.3, Found $[M+H]^+$:497.3.



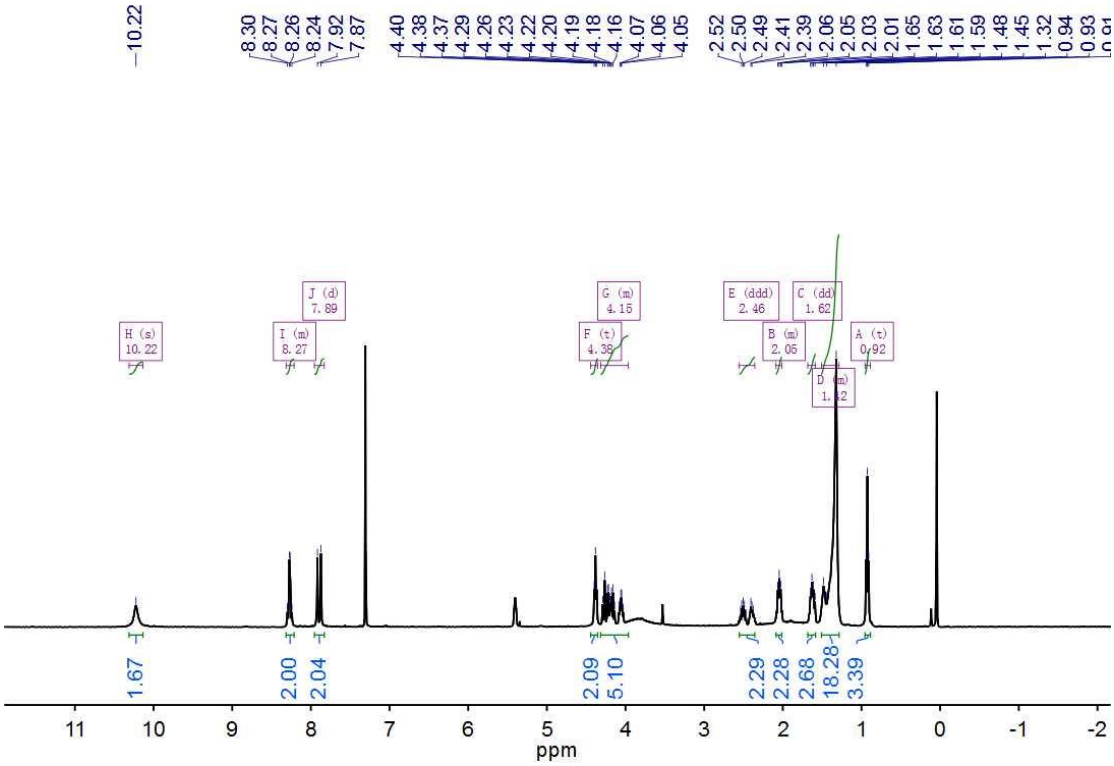


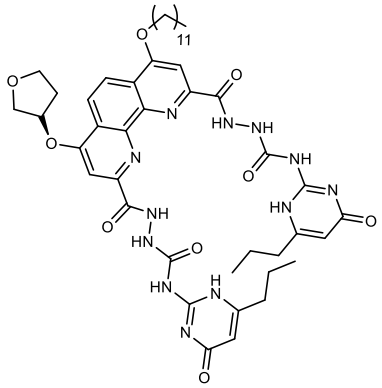
Compound 7b. A mixture of compound **6b** (200mg, 0.40 mmol), triphenylphosphine(Ph_3P) (120mg, 0.48 mmol) and lauryl alcohol (0.18mL, 0.48 mmol) was added into 5mL anhydrous THF. Diisopropyl azodicarboxylate (DIAD) (9.3μL, 0.48 mmol) was added dropwise into the mixture under stirring in ice bath. The mixture was stirred for 12h. Then the reaction solution was removed under reduced pressure and the product was purified by column chromatography (dichloromethane / methanol = 50/1, vol / vol) to give the product as a white solid (182mg, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (m, 2H), 7.89 (d, *J*=24.3, 2H), 4.39 (t, *J*=6.4, 2H), 4.34 – 4.00 (m, 11H), 2.46 (m, 2H), 2.09 – 2.02 (m, 2H), 1.66 – 1.59 (m, 2H), 1.53 – 1.30 (m, 18H), 0.92 (t, *J*=6.7, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.55, 166.48, 162.79, 161.17, 149.36, 148.98, 146.48, 146.12, 123.06, 122.90, 79.09, 53.17, 33.00, 31.90, 29.56, 22.68, 14.10. MS (ESI): Calculated $[M+H]^+$:567.3, Found $[M+H]^+$:567.3.



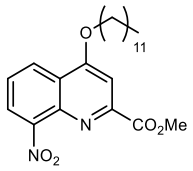


Compound 8b. Compound **7b** (100mg, 0.18 mmol) was dissolved in THF (5 mL), then hydrazine solution (0.1 mL, Hydrazine hydrate dissolved in the mixture of 0.1mL methanol and 1mL THF) was added. The mixture was stirred at room temperature for 5h. The reaction solution was removed under reduced pressure and the product was washed with cooled methanol (100g, yield: 97%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.22 (s, 2H), 8.31 – 8.21 (m, 2H), 7.89 (d, *J*=17.6, 2H), 4.38 (t, *J*=6.3, 2H), 4.32 – 3.96 (m, 5H), 2.46 (m, 2H), 2.09 – 2.01 (m, 2H), 1.62 (m, 3H), 1.51 – 1.29 (m, 18H), 0.92 (t, *J*=6.6, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.23, 164.08, 163.09, 161.49, 150.47, 150.13, 149.69, 145.74, 145.36, 123.23, 122.68, 122.51, 79.16, 75.26, 72.96, 29.71, 29.60, 22.97, 22.75, 22.69, 20.45, 15.15, 14.25, 14.20.MS (ESI): Calculated $[M+H]^+$: 567.3, Found $[M+H]^+$:566.4.

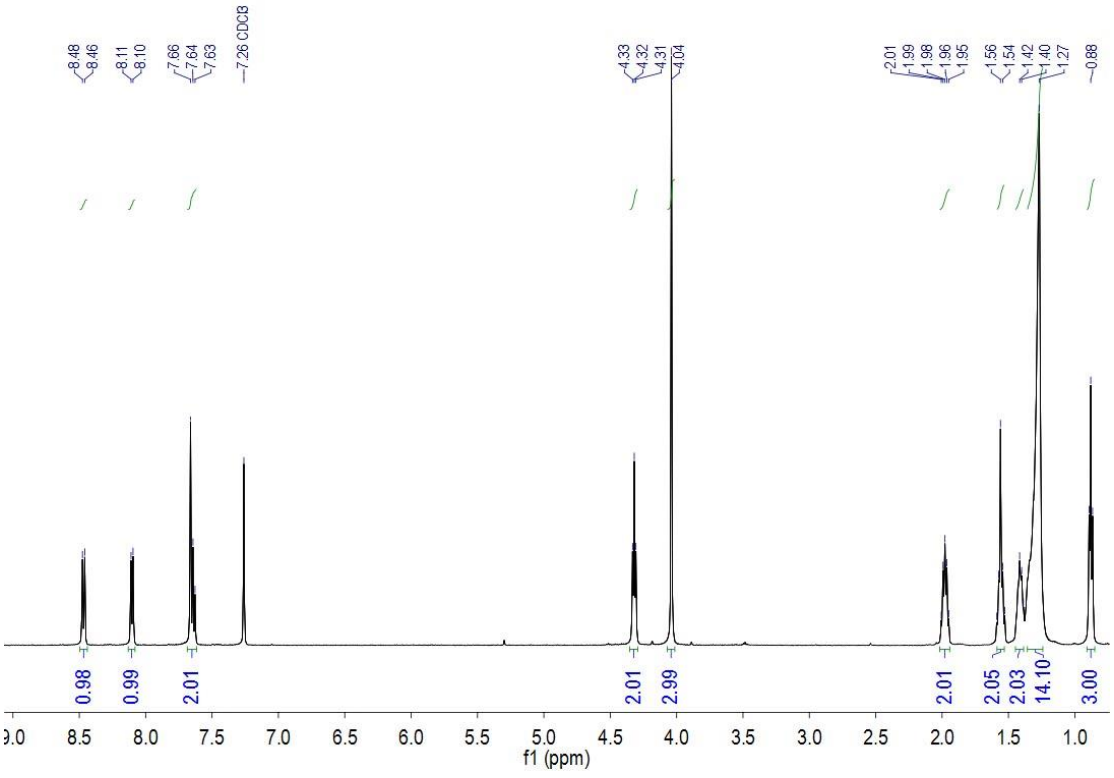


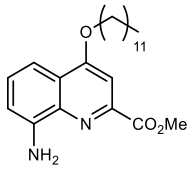


Compound 2. A suspension of **8b** (100mg, 0.18 mmol) and N-(4-oxo-6-propyl-1,4-dihydropyrimidin-2-yl)-1H-imidazole-1-carboxamide (88mg, 0.36 mmol) in 5mL tetrahydrofuran was heated under reflux overnight. Solvent was then removed at reduced pressure and the reaction mixture cooled to 4 °C. The resulting residue was washed with cold methanol, and the crude product was purified by silica gel column chromatography (dichloromethane / methanol = 20/1, vol / vol) to obtain 1 as yellow powder (87mg, yield 53%). ^{1}H NMR (400 MHz, DMSO) δ = 8.13 (s, 2H), 7.90 (s, 2H), 4.46 (s, 2H), 4.15 – 3.90 (m, 5H), 2.30 – 2.20 (m, 2H), 2.00 (m, 2H), 1.77 (m, 2H), 1.63 – 1.55 (m, 4H), 1.44 (m, 2H), 1.27 (m, 18H), 0.95 – 0.85 (m, 9H). ^{13}C NMR (101 MHz, Pyr) δ 175.09, 164.03, 162.08, 161.15, 149.91, 149.64, 149.74, 149.39, 135.76, 135.51, 135.51, 135.01, 134.94, 128.68, 125.23, 123.74, 123.25, 123.01, 122.71, 79.32, 74.78, 72.96, 31.87, 29.71, 29.66, 29.53, 26.05, 22.69, 20.97, 14.04. MS (ESI): Calculated $[M+H]^+$: 925.4, Found $[M+H]^+$:925.5.



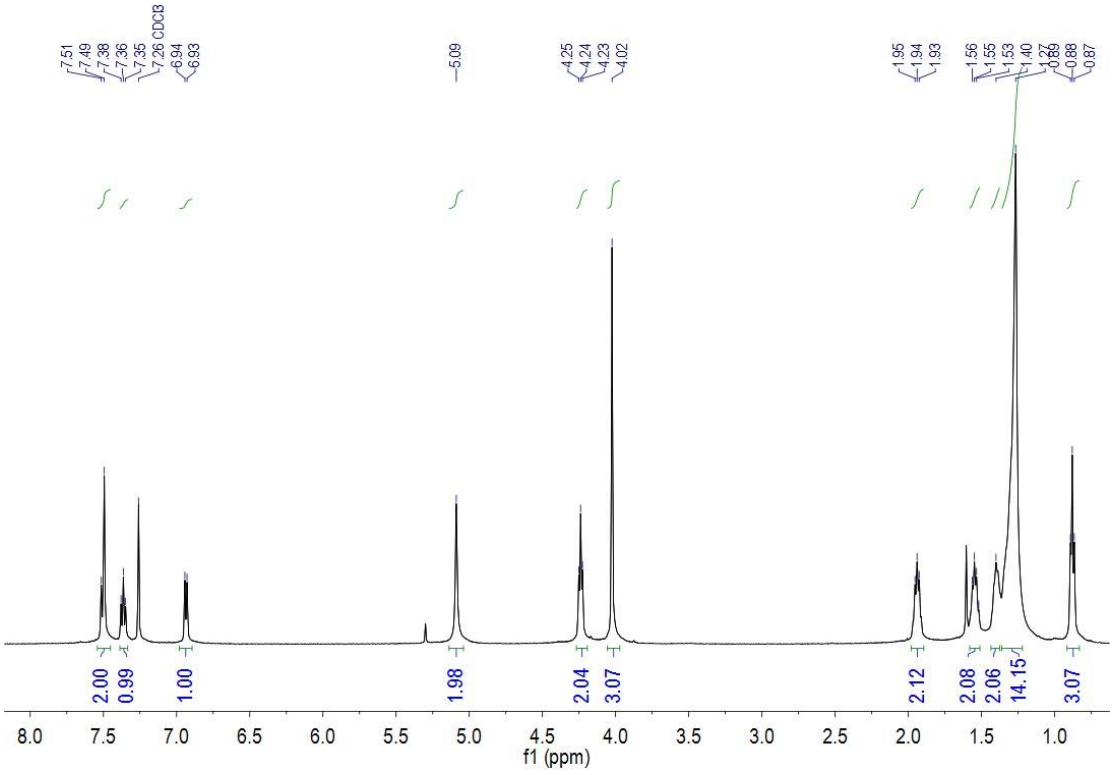
Compound 3c. A mixed solution of triphenylphosphine (7.9 g, 30.24 mmol), lauryl alcohol (6.96ml, 30.24 mmol) and compound **2a** (5.0 g, 20.16 mmol) was added into 100mL dry tetrahydrofuran under the protection of N_2 atmosphere and ice bath condition, and then diisopropyl azodiformate (6.11g, 30.24mmol) was added dropwise to it. The reaction was stirred overnight at room temperature, and the solvent was removed in vacuo. The crude mixture was purified by recrystallization in methanol to provide the desired product as yellow powder, (7.2 g, yield 86%)^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, J = 7.2 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.66-7.63 (m, 2H), 4.33 – 4.29 (m, 2H), 4.10 (s, 3H), 2.00 – 1.93 (m, 2H), 1.62 – 1.21(m,18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.72, 162.78, 151.32, 148.40, 140.04, 126.42, 125.87, 125.05, 123.32, 102.18, 69.70, 53.35, 31.91, 29.64, 29.63, 29.57, 29.53, 29.34, 29.29, 28.73, 26.01, 22.68, 14.11.MS (ESI): Calculated $[M+H]^+$: 417.2, Found $[M+H]^+$: 416.9

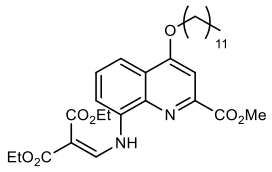




Compound 4c. Compound **3c** (5.0 g 11.6 mmol) was added to a mixed solution of methanol / water (10:1 vol / vol), and then ammonium formate (8.0 g, 60.0 mmol) and bits of ammonium metavanadate were added to the system after Pb/C (0.5 g) being added. Then the system was

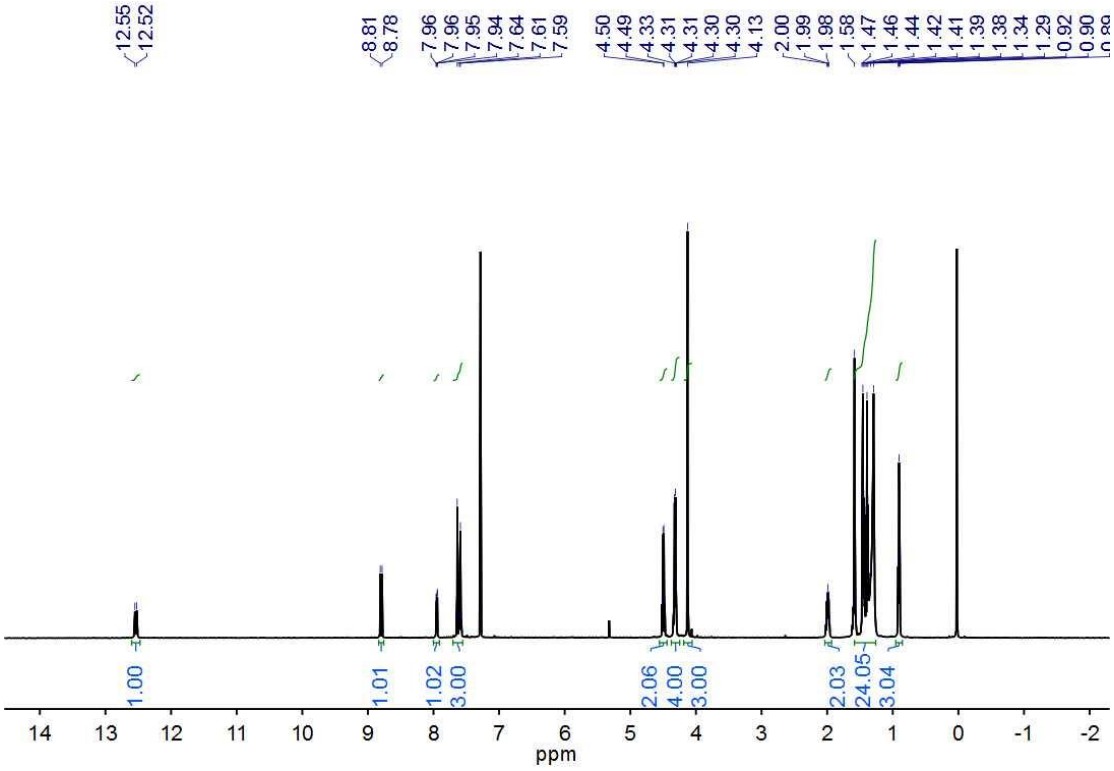
sealed and stirred at room temperature overnight. The precipitate was removed by the filtration, and the supernatant was concentrated under the reduced pressure. 50mL dichloromethane was added to the mixture and then washed with water to remove salts. The organic phase was collected and dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (dichloromethane / methanol = 50/1, vol / vol) to obtain 4a as yellow powder (4.2 g, yield 90%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.09 (s, 2H), 4.25 – 4.23 (m, 2H), 4.02 (s, 3H), 1.97 – 1.21(m,20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.42, 162.59, 145.83, 144.91, 138.37, 128.56, 122.98, 110.80, 109.61, 100.76, 68.82, 52.76, 31.93, 29.67, 29.65, 29.61, 29.57, 29.36, 29.35, 28.90, 26.09, 22.70, 14.13. MS (ESI): Calculated $[M+H]^+$: 387.2, Found $[M+H]^+$: 386.9.

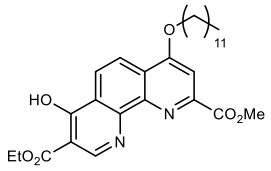




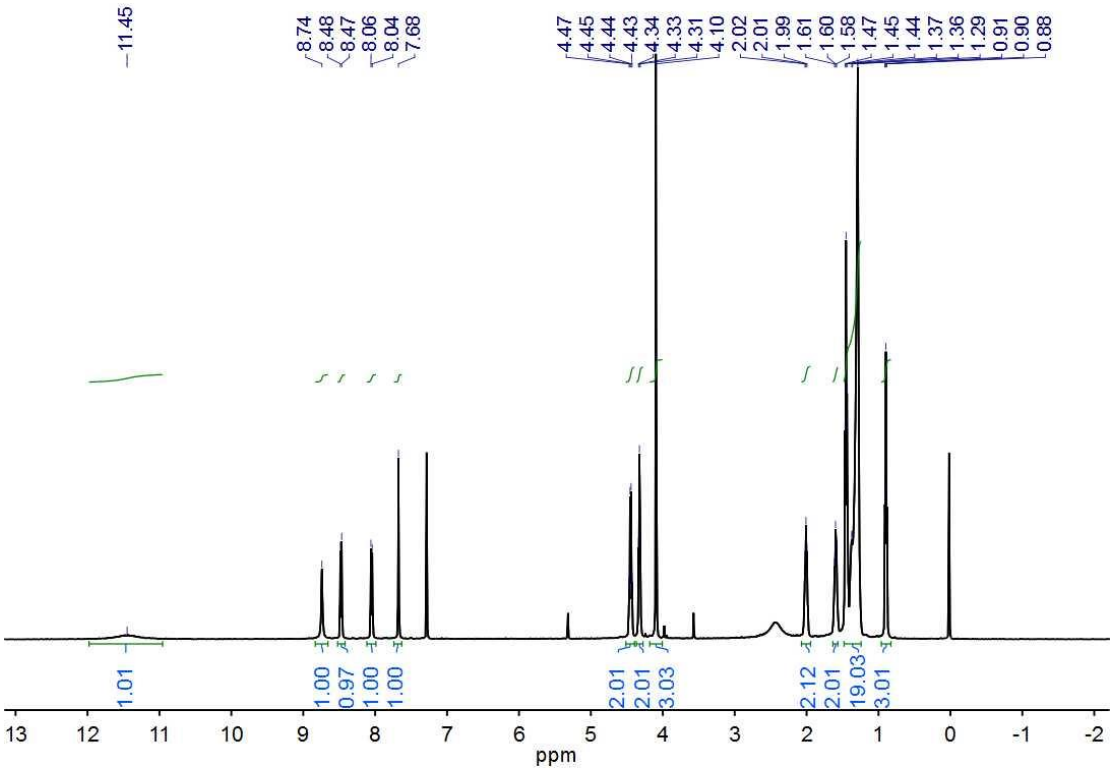
Compound 5c. Compoung 4c (4.0 g, 10.0 mmol) was added to a mixed solution of methylbenzene (25 mL) and diethyl ethoxymethylenemalonate (4.8 mL), and the solution was stirred at room temperature overnight. After reaction, the solution was cooled at -20°C for 12 hours, and then the compound 5a was obtained by filtering the solution which had precipitate and washing it with cooled methylbenzene as yellow powder (5.1 g, yield 90%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.54 (d, *J* = 14.2 Hz, 1H), 8.80 (d, *J* = 14.2 Hz, 1H), 7.95 (d, *J* = 14.2 Hz, 1H), 7.70 – 7.51 (m, 3H), 4.50 (m, 2H), 4.35 – 4.29 (m, 4H), 4.13 (s, 3H), 2.04 – 1.95 (m, 2H), 1.56 – 1.23 (m, 24H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.80, 166.12, 165.84, 162.98, 148.49, 147.84, 138.96, 136.54, 127.64, 122.96, 116.45,

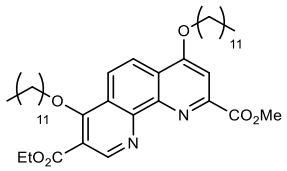
111.15, 101.57, 95.88, 69.30, 60.31, 60.25, 53.18, 31.91, 29.65, 29.63, 29.58, 29.54, 29.34, 29.31, 28.83, 26.06, 22.68, 14.45, 14.11. MS (ESI): Calculated $[M+H]^+$: 557.3, Found $[M+H]^+$: 556.9.



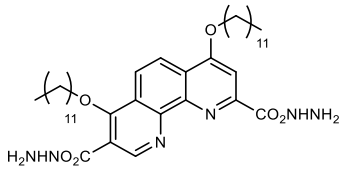


Compound 6c. Compound 5c (1.5g, 2.70 mmol) was suspended in diphenyl ether, and the mixed solution was boiled at 250°C for 15 minutes. The solution was cooled to 60°C and then it was added to 100 mL petroleum ether. The mixed solution was cooled at 4 °C for 12 hours, and compound 6a was obtained by filtering the solution washing with cooled petroleum ether as yellow powder(0.82 g , yield 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.74 (s, 1H), 8.47 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.68 (s, 1H), 4.45 (q, J = 7.0 Hz, 2H), 4.40 – 4.16 (m, 2H), 4.10 (s, 3H), 2.07 – 1.94 (m, 2H), 1.69 – 1.16 (m, 21H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.42, 165.57, 165.39, 163.09, 147.69, 143.38, 139.16, 136.17, 127.53, 124.45, 123.19, 117.29, 114.12, 103.67, 69.64, 60.87, 53.24, 31.90, 29.66, 29.63, 29.60, 29.55, 29.34, 28.80, 26.05, 22.68, 14.42, 14.11. MS (ESI): Calculated $[M+H]^+$: 511.2, Found $[M+H]^+$: 511.2.



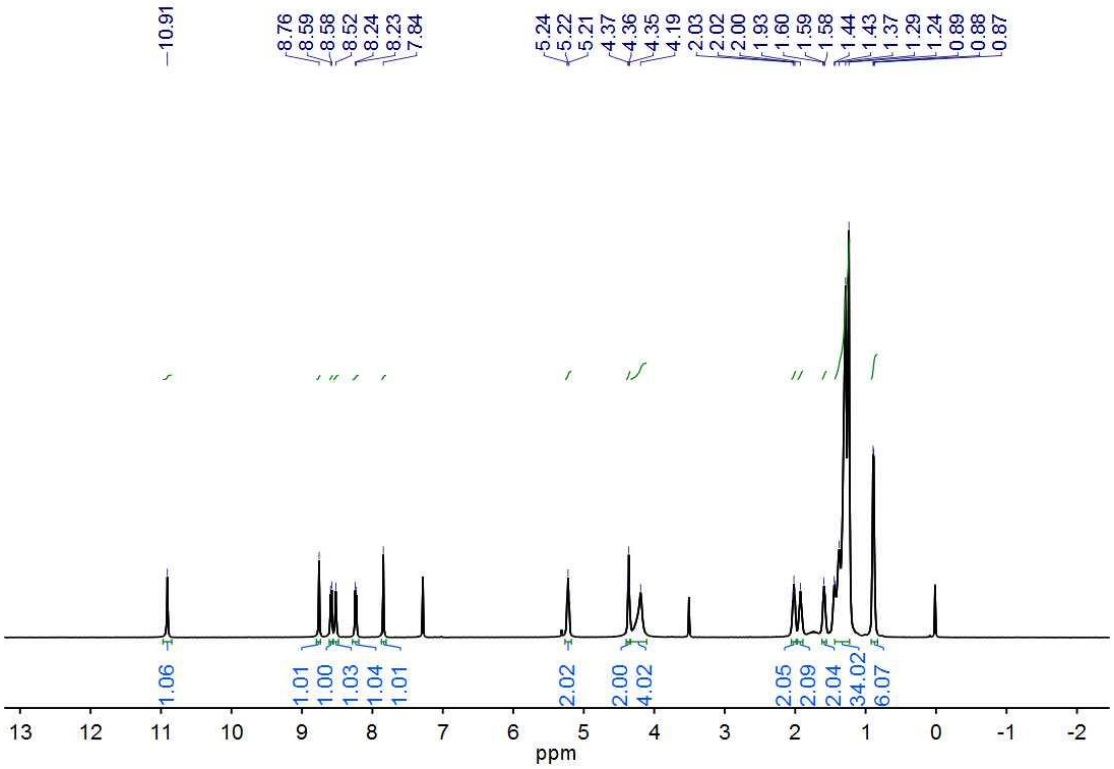


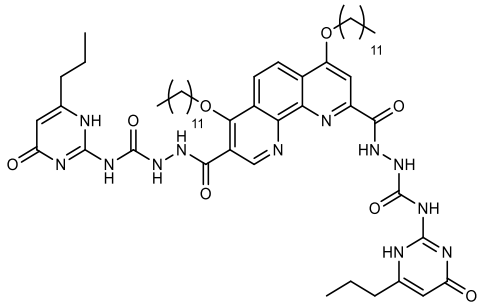
Compound 7c. To a mixed solution of triphenylphosphine (0.7 g, 2.94mmol), lauryl alcohol (0.67 mL,2.94 mmol) and compound 6c (1.0 g, 1.96 mmol) in dry tetrahydrofuran (15 ml) under N_2 atmosphere and ice bath condition was added diisopropyl azodiformate (0.49mL, 2.94mmol). The reaction was stirred overnight at room temperature, and the solvent was removed in vacuo. The crude mixture was purified by recrystallization in methanol to provide the desired product 7a as yellow powder (1.0 g, yield 75.2%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.0 Hz, 1H), 8.59 (s, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 7.73 (s, 1H), 5.43 – 5.34 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 4.07 (s, 3H), 2.05 – 1.97 (m, 2H), 1.93 – 1.83 (m, 2H), 1.63 – 1.21 (m, 39H), 0.94 – 0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.53, 165.90, 165.78, 162.78, 151.83, 146.48, 140.86, 136.99, 131.35, 125.78, 125.10, 118.52, 113.31, 102.77, 69.48, 61.11, 60.70, 52.89, 31.90, 31.35, 29.65, 29.63, 29.59, 29.57, 29.54, 29.45, 29.34, 29.32, 28.82, 26.36, 26.07, 22.69, 14.47, 14.11. MS (ESI): Calculated $[M+H]^+$: 679.5, Found $[M+H]^+$: 680.1



Compound 8c. 1mL Hydrazine hydrate added to a solution of compound 7c (1.0 g, 1.47 mmol) in a mixture of tetrahydrofuran (3 mL), the solution was stirred at room temperature overnight,

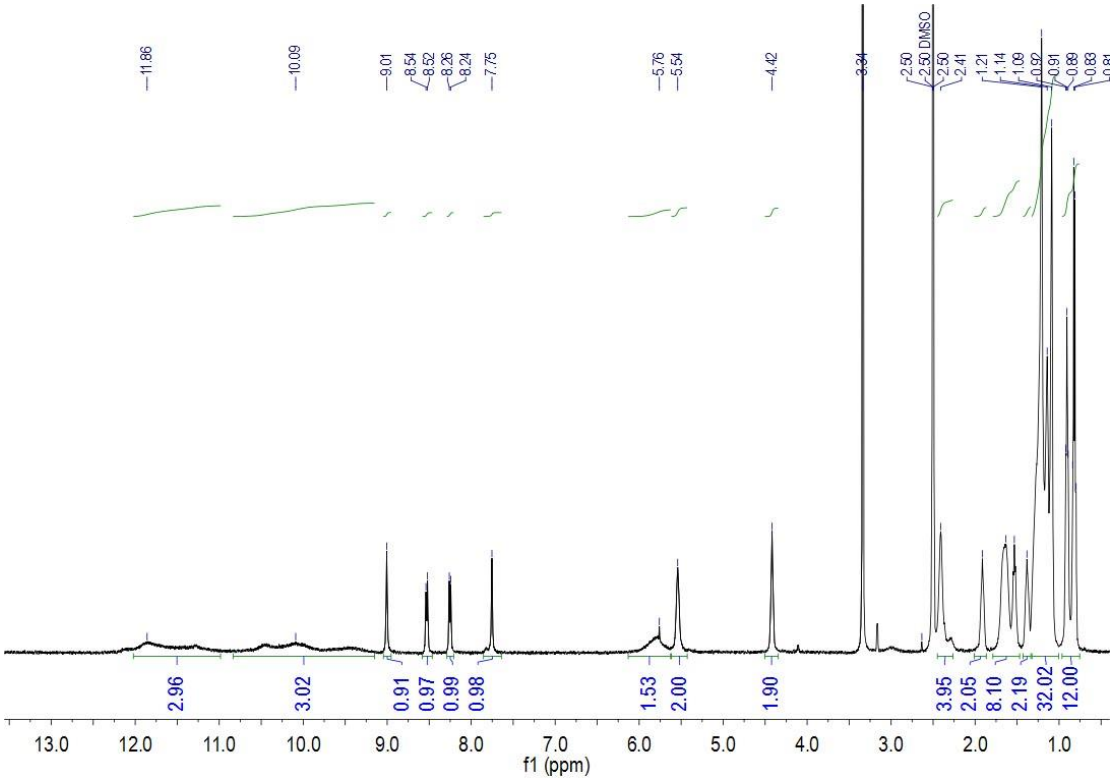
Then the solvents were removed in vacuo, the residue was washed with methanol and the pure product was obtained by filtration as white powder (0.96 g, yield 99%).[1]H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.76 (s, 1H), 8.59 (d, *J* = 9.0 Hz, 1H), 8.52 (s, 1H), 8.24 (d, *J* = 9.0 Hz, 1H), 7.84 (s, 1H), 5.22 (t, *J* = 7.1 Hz, 2H), 4.36 (t, *J* = 6.2 Hz, 2H), 4.19 (s, 4H), 2.09 –1.93 (m, 4H), 1.65 – 1.18 (m, 36H), 0.95 – 0.82 (m, 6H). [13]C NMR (126 MHz, $CDCl_3$) δ 174.94, 165.17, 164.92, 163.23, 149.62, 148.86, 140.08, 136.52, 129.91, 125.32, 124.38, 118.98, 113.19, 101.34, 69.82, 60.28, 31.91, 31.88, 31.10, 29.65, 29.63, 29.59, 29.56, 29.54, 29.49, 29.42, 29.40, 29.34, 29.32, 29.31, 28.80, 26.44, 26.05, 22.68, 22.67, 14.11, 14.11. MS (ESI): Calculated $[M+H]^+$: 665.5, Found $[M+H]^+$: 665.8





Compound 3. A suspension of 8c (0.5 g, 0.75 mmol) and compound 11(0.45 g,1.8 mmol) in 10mL tetrahydrofuran was heated under reflux overnight. Solvent was then removed at reduced pressure and the reaction mixture cooled to 4 °C. The resulting residue was washed with cold methanol, and the crude product was purified by silica gel column chromatography (dichloromethane / methanol = 20/1, vol / vol) to obtain 1a as yellow powder (0.41g, yield 53%). [1]H NMR (500 MHz, DMSO) δ 12.13 – 9.25 (m, 6H), 9.01 (s, 1H), 8.53 (d, *J* = 9.1 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 5.76 (m, 2H), 5.54 (m, 2H), 4.42 (m, 2H), 2.41 (m,

4H), 1.97 – 1.01 (m, 44H), 0.96 – 0.75 (m, 12H). MS (ESI): Calculated $[M+H]^+$: 1023.6, Found $[M+H]^+$: 1023.6.



3. Supplementary Figures

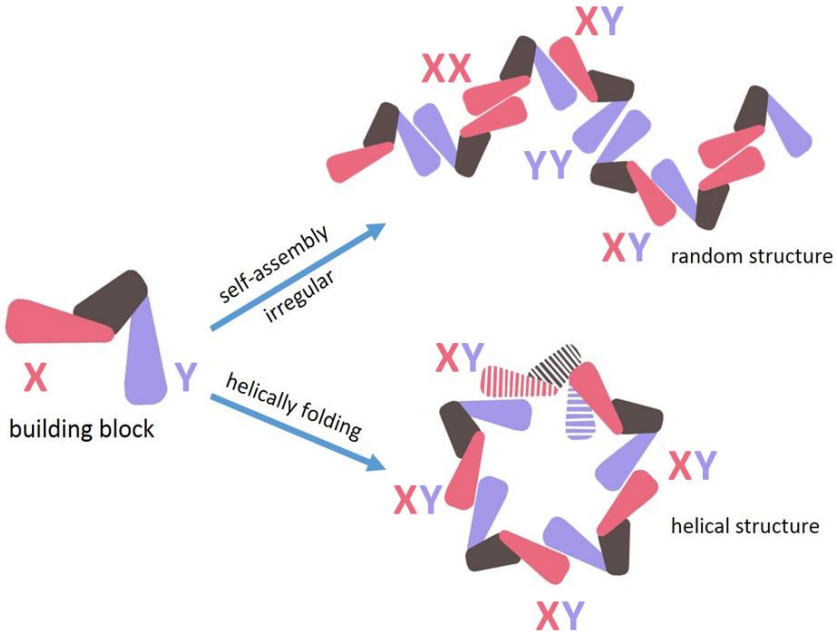


Figure S1. Schematic representation of structure modes from the self-assembly of building block. Molecular self-assembly at equilibrium is prone to form boundary-defined supramolecular structures owing to the symmetry in the geometry of self-assembly.[2] Therefore, self-assembling helical structure will always dominate with alternating XY sequences in this case, whereas the random linear structures of supramolecular polymers with irregular sequences (binding mode XX, YY, and XY) is kinetically difficult to form due to the lack of symmetry.

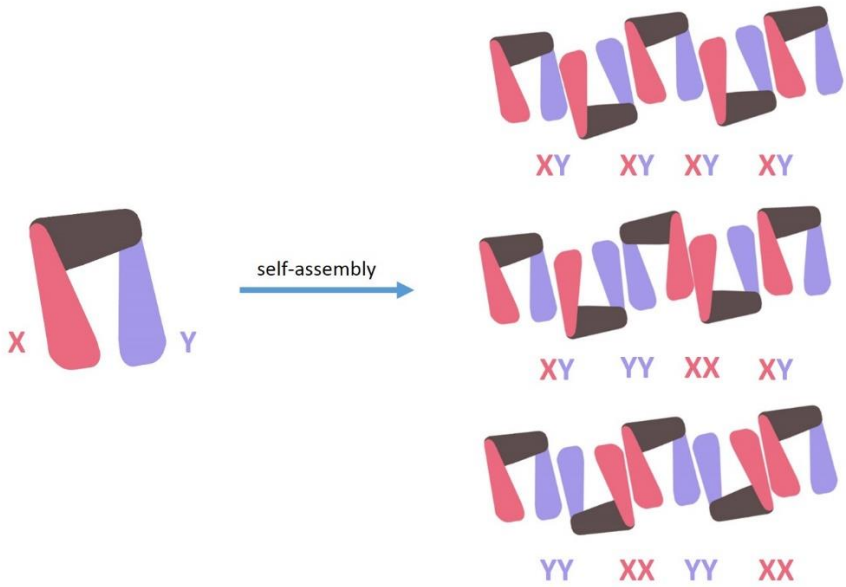


Figure S2. The liner self-assembly structure of **2** is difficult to form pore-containing helical supramolecular polymers.

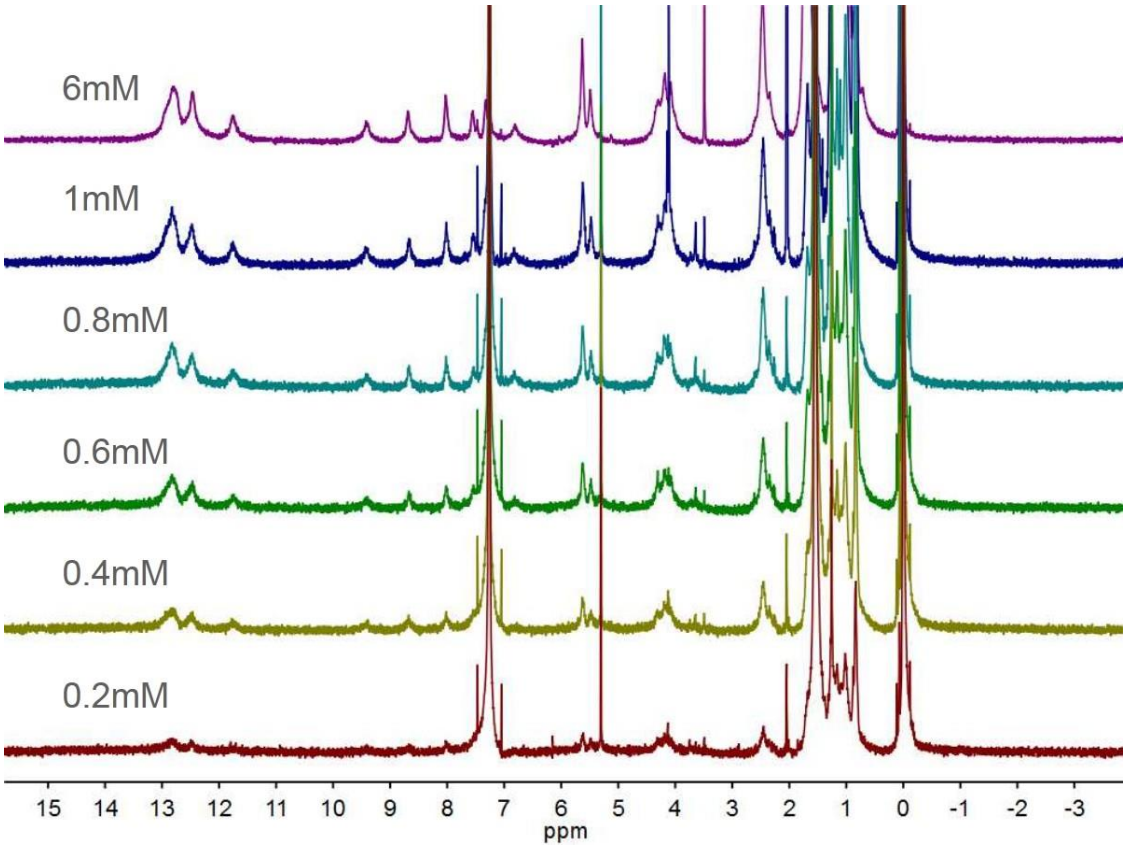
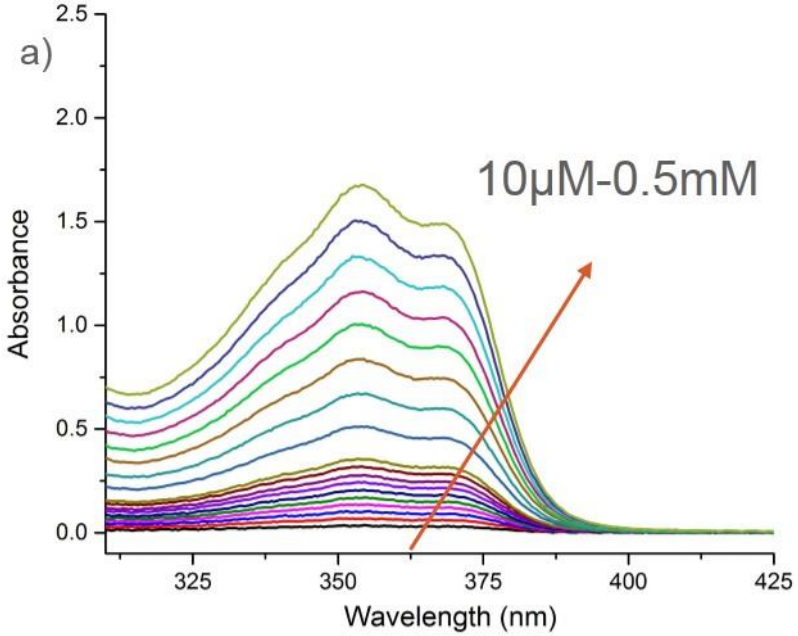


Figure S3. ^{1}H-NMR spectra of **1** in $CDCl_3$ from 0.2 mmol·L^{-1} to 6 mmol·L^{-1}.



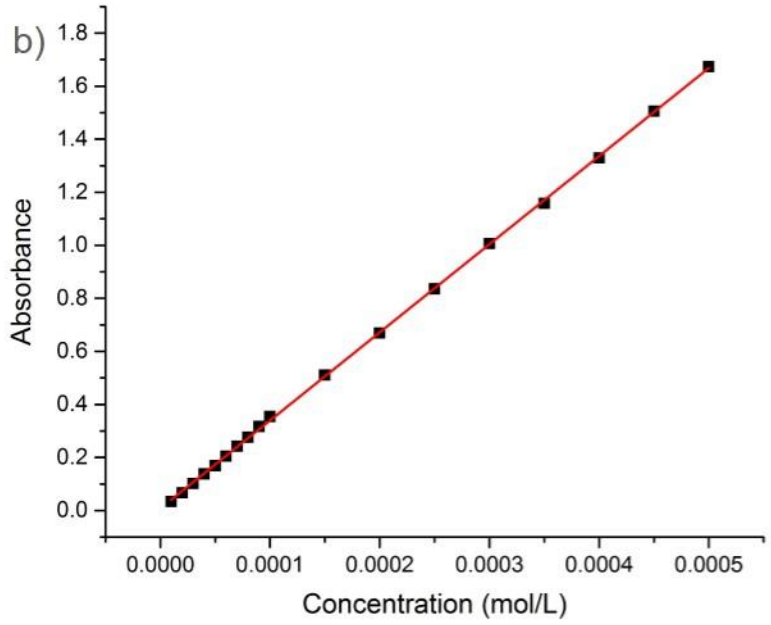


Figure S4. (a)UV-Vis titrations of **1** in chloroform from 10 μmol·L^{-1} to 0.5mmol·L^{-1}. (b) Variations in the absorbance at 353nm versus the concentration of **1** in chloroform

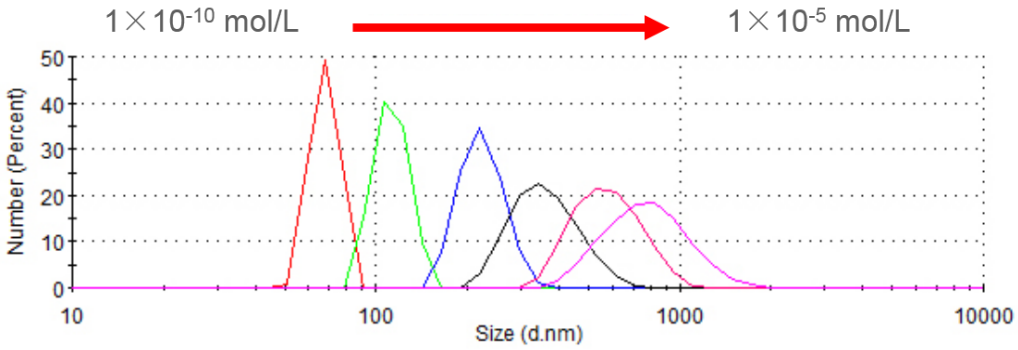


Figure S5. DLS profiles of **1** at different concentrations from 1.0 × 10^{-10} mol·L^{-1} to 1.0 × 10^{-5} mol·L^{-1} in chloroform

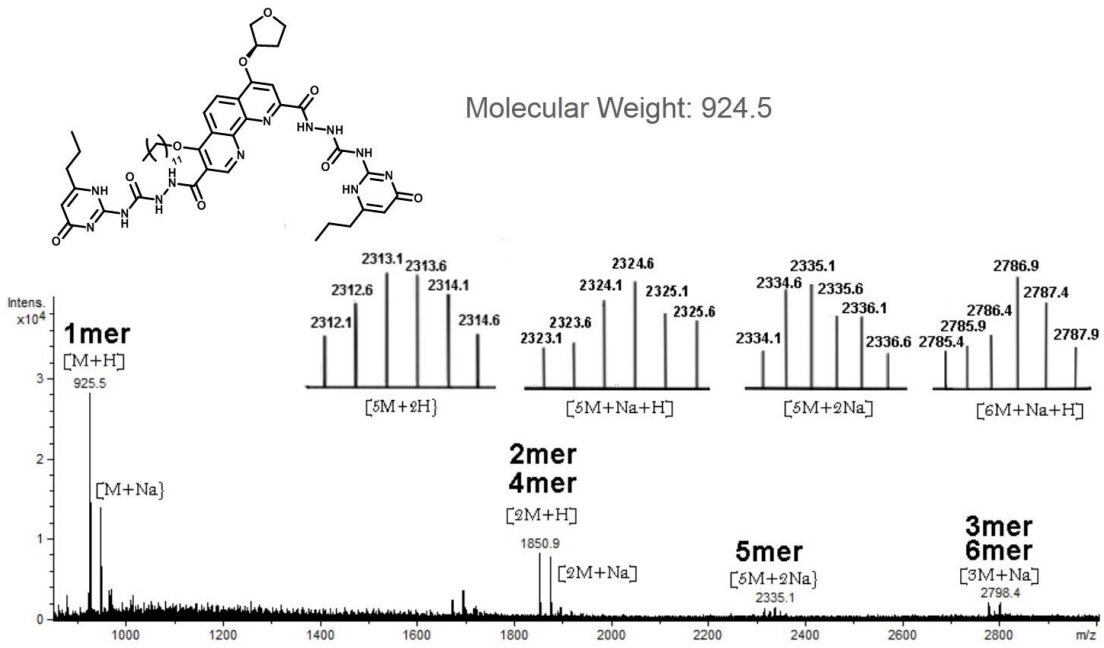


Figure S6. MS spectrum of **1**.

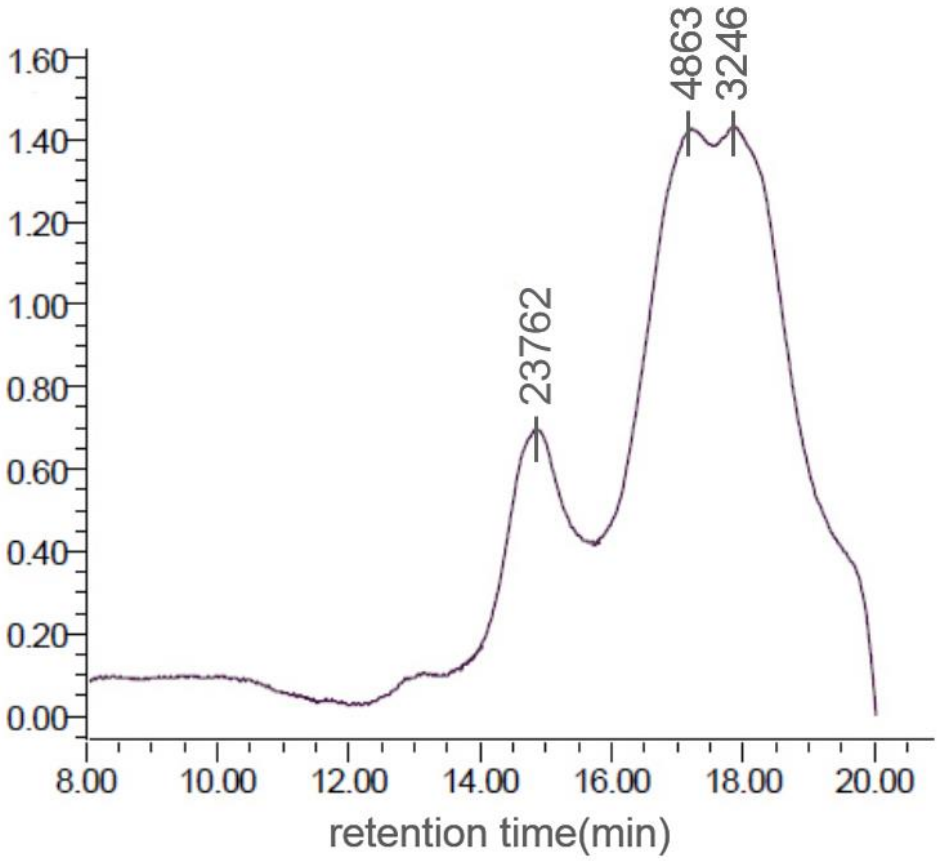


Figure S7. GPC trace of **1** in tetrahydrofuran (2.0×10^{-3} mol·L^{-1}) at 37 °C. The molecular weight is indicated in the figure.

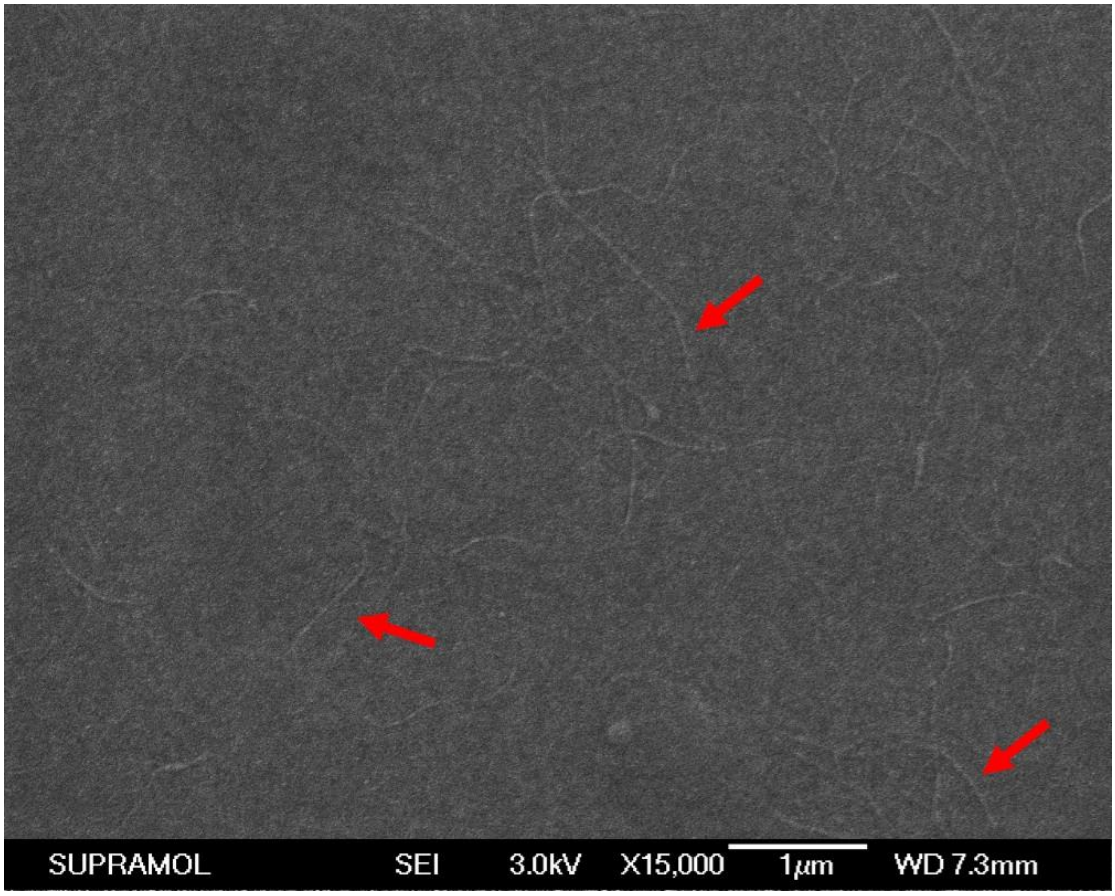


Figure S8. SEM image of **1** on silicon surface with a concentration of 10μmol·L^{-1} in chloroform.

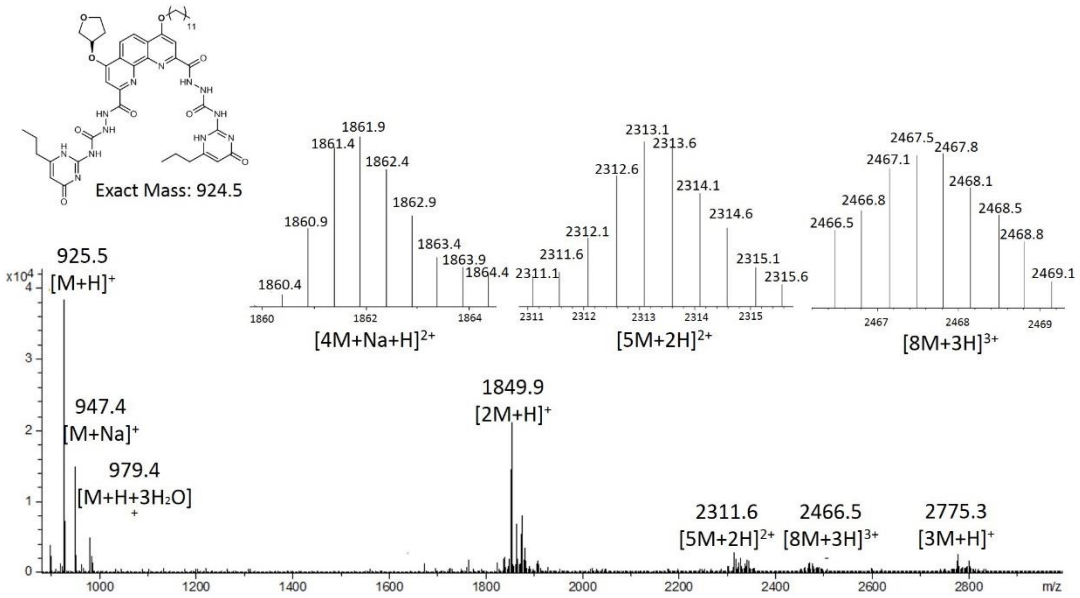


Figure S9. MS spectrum of **2** in which several supramolecular oligomers were detected.

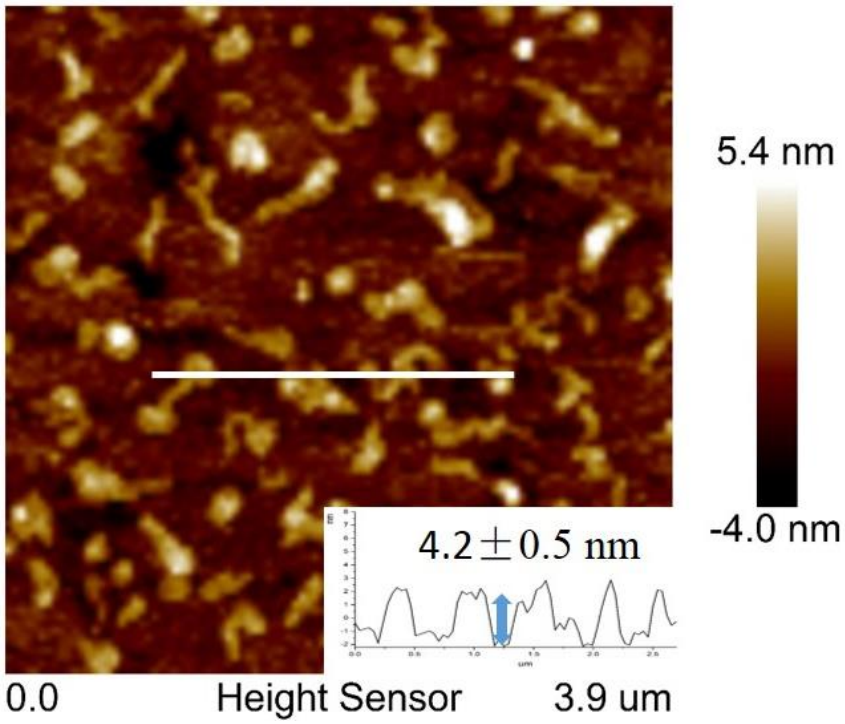


Figure S10. AFM image of variant **2** on the silicon surface with a concentration of 0.1 μM in chloroform. The height profile was shown at the bottom right.

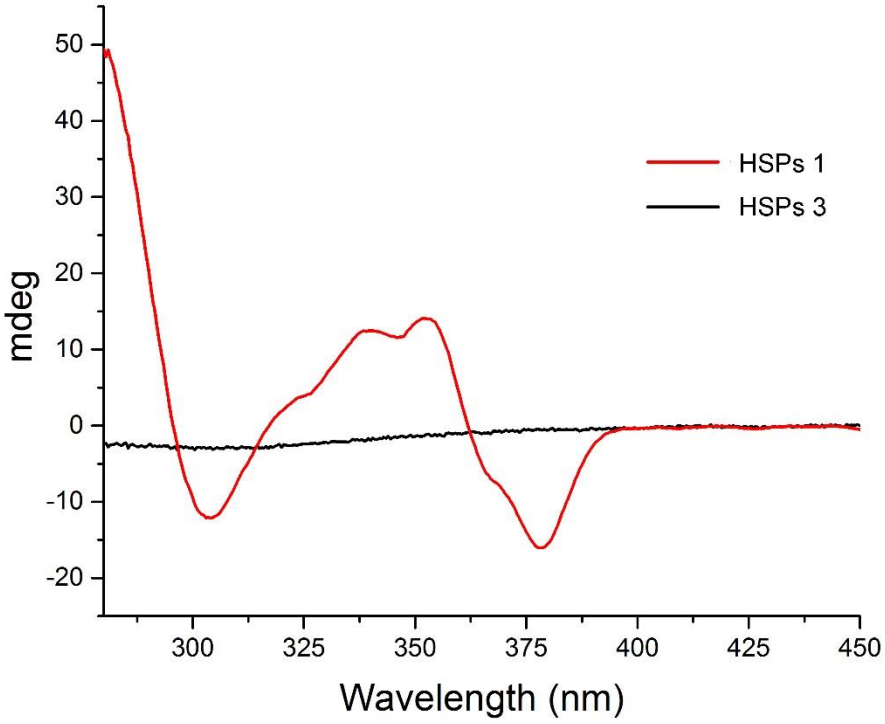


Figure S11. CD spectra of **1** (red) and **3** (black) with a concentration of 1 mM in chloroform.

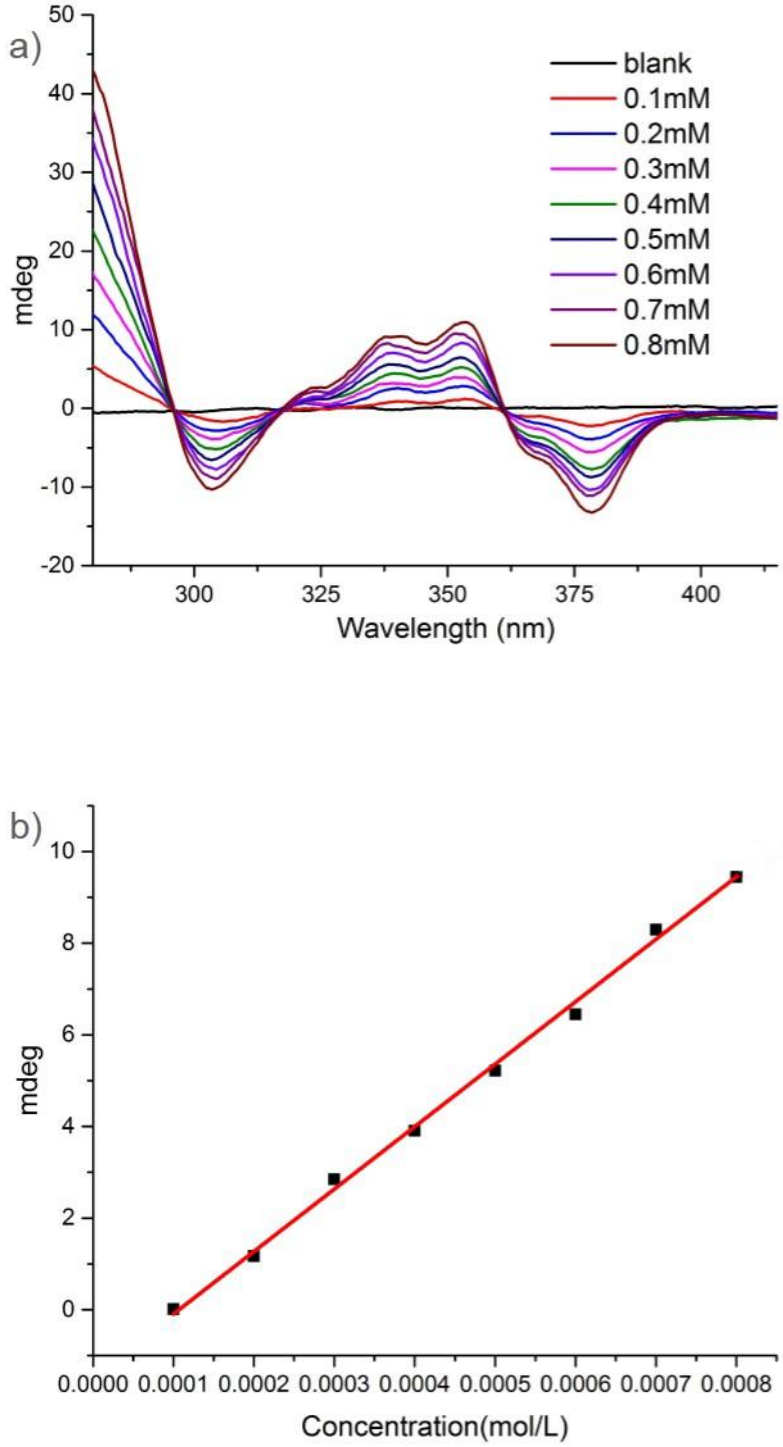


Figure S12. (a)Concentration-dependent CD spectra of **1** in chloroform from 0.01 mmol·L^{-1} to 0.8mmol·L^{-1}. (b) Variations at 353nm versus the concentration of 1 in chloroform.

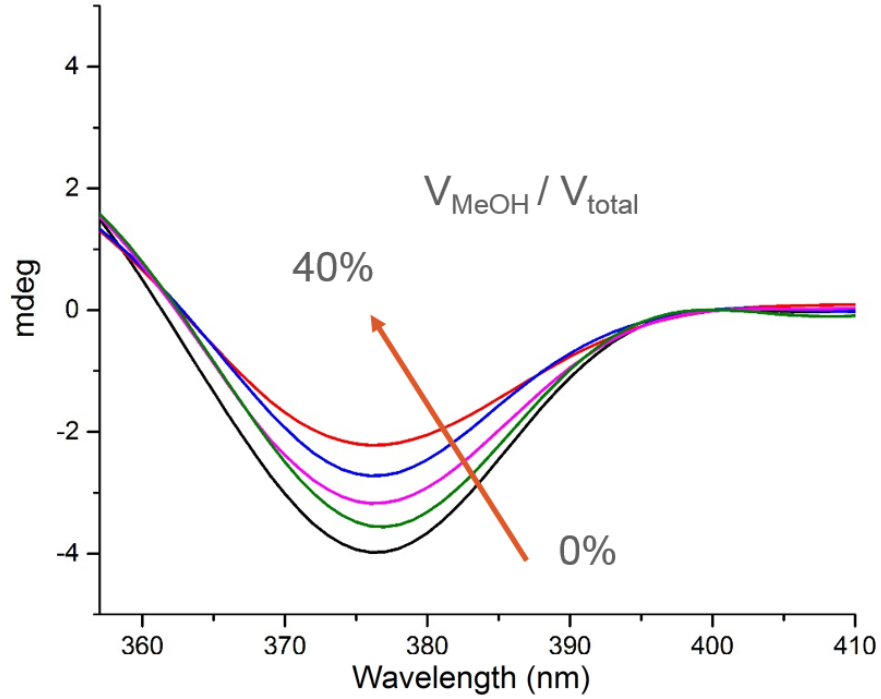


Figure S13. CD spectra titrations of **1** by increasing proportion of methanol in chloroform.

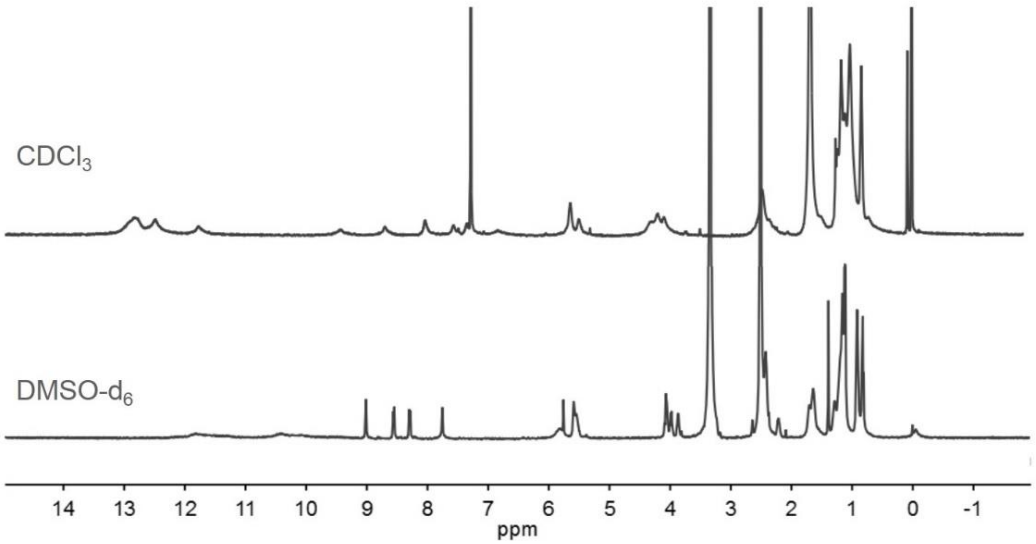


Figure S14. ^{1}H-NMR spectra of 1 (2 mmol·L^{-1}) in $CDCl_3$ and DMSO-d_6.

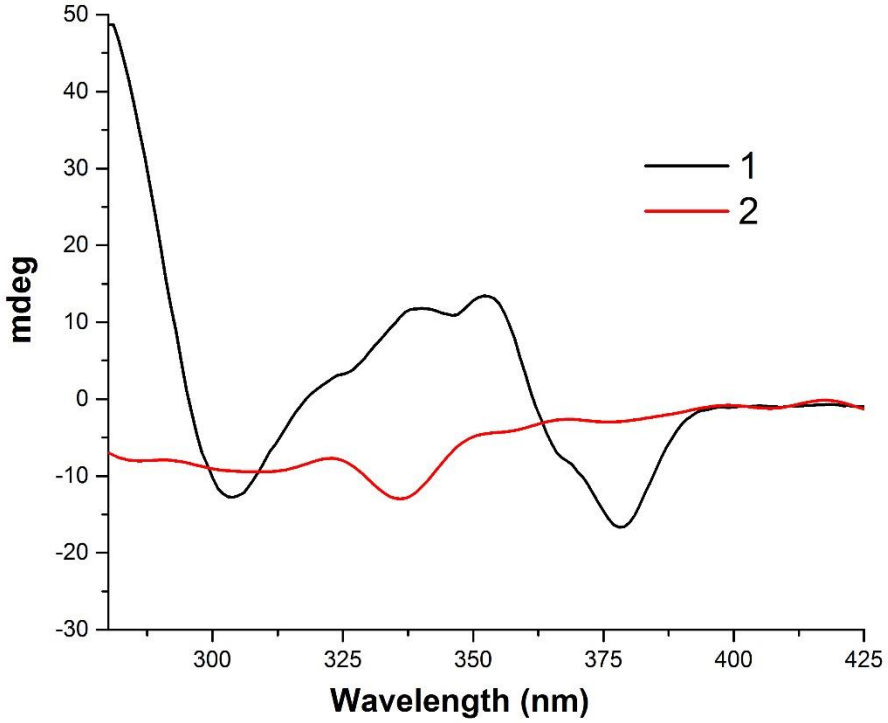


Figure S15. CD spectra of **1** (black) and **2** (red) with a concentration of 1 mM in chloroform.

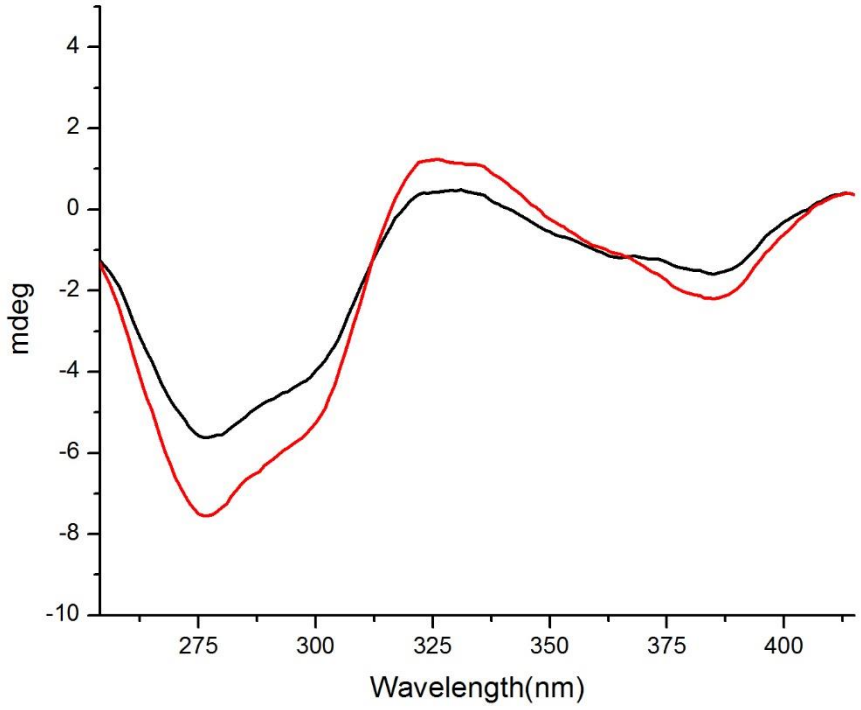


Figure S16. CD spectra of **1** added to buffer (black) or EYPC-LUVs (red).

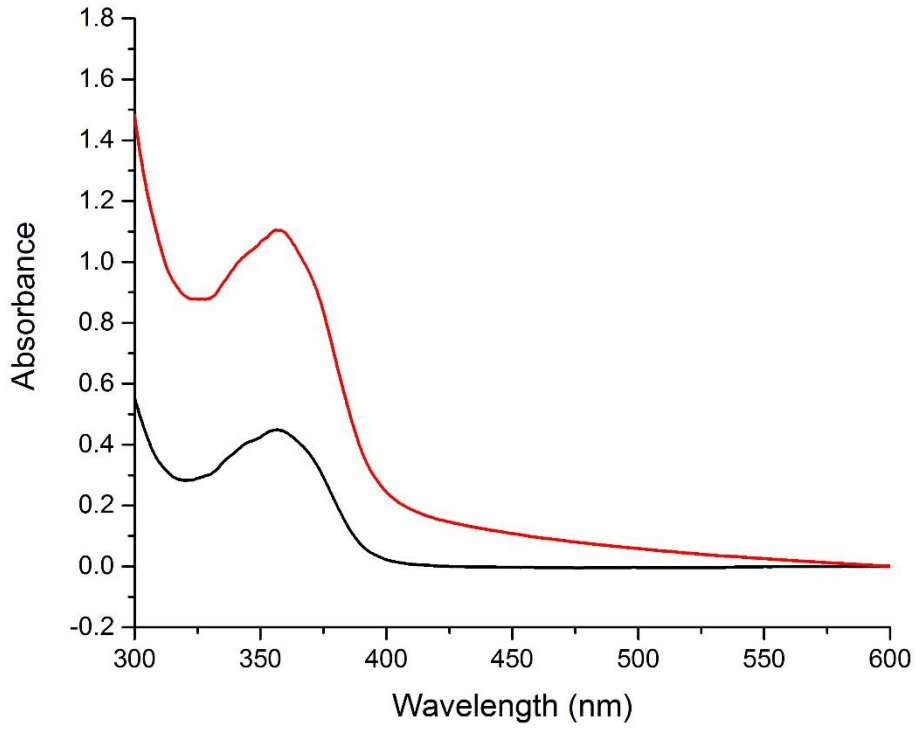


Figure S17. UV-visible spectra of **1** added to buffer (black) or EYPC-LUVs (red).

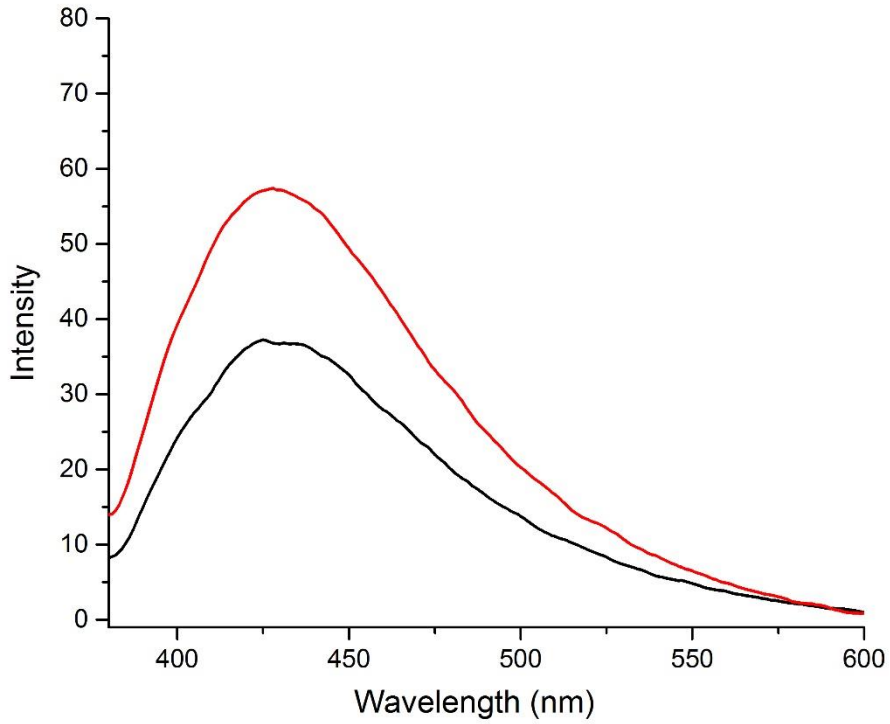


Figure S18. Fluorescence spectra of **1** added to buffer (black) or EYPC-LUVs (red).

4. Giant unilamellar vesicles assays

As reported before[3], 0.3mg EYPC added to 3 ml $CHCl_3$ with or without 0.01mg building block **1**. The solvent was dried by N_2 flow and under vacuum for three hours. Before the giant unilarmellar vesicles fluorescence assays, the lipid was mixed with sorbitol (1M, 1mL) and incubated at 37℃ overnight. Fluorescent imaging was carried out on OLYMPUS BX61 microscope. The bright field images were performed by the monochromatic mode and fluorescence images were excited at 365 nm. The outline of the **1**•GUV appears significant fluorescence, indicating that HSPs were effectively embedded in the membrane.

5. Ion transport experiment with HPTS assay

Preparation of LUVs: 9mg EYPC and 1mg cholesterol was first dissolved in 3 mL $CHCl_3$, the solvent was dried by N_2 flow and under vacuum for three hours. Then the lipid was placed in 1 mL buffer solution (100 mM NaCl solution, 10 mM HEPES and 1mM pH sensitive dye HPTS) at pH 7. The suspension was incubated at 37 ℃ for 2 hours and subjected to 10 freeze-thaw cycles by using liquid nitrogen and warm water bath at 40 ℃. Then the suspension was filtered through 0.22 μm polycarbonate membrane and purified by Sephadex G-50 to remove un-entrapped HTPS against the same buffer solution without the dye. The LUVs suspension was kept under 4 ℃ and used within 48 hours (the vesicles can maintain 60% entrapped rate over one week, but for accuracy and repeatability, the experiment was recommended to be performed within 48 hours).

Fluorescent experiments: All the experiments were carried out by Shimadzu RF-5301PC fluorescence spectrophotometer under time course mode in 1.5mL cuvette. 50 μL LUVs suspension and 950 μL buffer solution (100 mM NaCl solution, 10 mM HEPES, pH at 7.0) were placed in fluorescent cuvette. 10 μL NaOH solution was added to the suspension, resulting a pH gradient for HPTS assay.

The fluorescence intensity (E_t) was continuously monitored at 510 nm (excited at 460nm) and 10 μL channel solution in DMSO was added to the cuvette with stirring. After 300s, 10 μL 50% Triton X-100 aqueous solution was added with stirring to break the vesicles. The data collection will not be terminated until the fluorescence intensity (E_∞) is no longer changed. The collected data were normalized according to the equation:

$$R_f = (E_0 - E_t) / (E_0 - E_\infty)$$

R_f: relative fluorescence.

E_0: the initial emission intensity.

R_f was defined as transmembrane transport activity Y. The effective concentration EC_{50} (concentration needed to reach 50% transport activity) and Hill coefficient *n* can be calculated by the Hill equation:

$$Y = Y_\infty + (Y_0 - Y_\infty)/(1 + (c/EC_{50})^n)$$

Y_0 is the transport activity without channels, Y_∞ is the transport activity mixed with excess channels (in most cases, this value defaults to 1). Value c is the monomers/channels concentration.

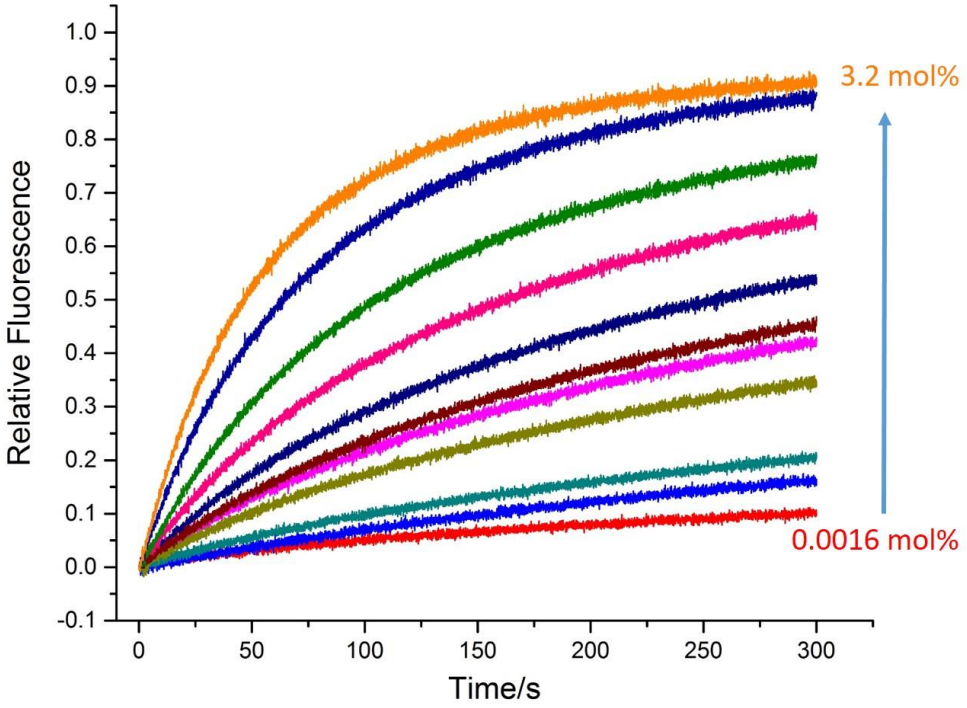


Figure S19. Normalized ion transport activities of **1** from 0.0016 mol% to 3.2 mol%.

6. Planer Lipid Bilayer Conductance Experiment

Preparation of phospholipid: 1,2-diphytanoyl-sn-glycero-3-phosphocholine (diPhyPC, 10mg/mL) was dissolved in 0.5 mL $CHCl_3$ and divided into 10 vials. The solvent was evaporated with N_2, under vacuum for three hours and the lipid was stored at -20℃. Before BLM experiments, the phospholipid was thawed to room temperature and re-suspended in 20 μL n-decane(25mg/mL).

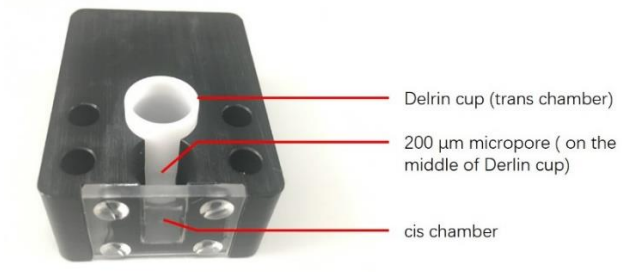


Figure S20. The illustration of BLM experiments apparatus.

Conductance Measurements: 0.3 μL decane solution was applied to precoat on the Delrin® cup (Warner Instruments) and was blown dry by N_2 flow for 3 min. Delrin cup was held in the cis chamber and both of two side were filled with KCl solution (1 mL, 1M). Ag/AgCl electrodes were set in each chamber to record membrane currents and stirring bar was added to cis chamber. The input electrode was inserted into cis chamber and the reference electrode into trans chamber. 0.5 μl phospholipid solution was dropped on a thin round glass rod and brush a lipid film over the micropore in the Delrin cup. The capacitance shown as 80-120 pF proved that good lipid bilayers were formed. The channels dissolved in DMSO was added to cis chambers under stirring over 2 minutes. If channel opened in lipid bilayer, the current signal can be recorded by computer. Changing the clamping voltage on both sides of the membrane from -200 mV to +200 mV, I-V curve was generated. The whole experiment was done on the Axon patch clamp station. The current signal was collected by Warner BC-535 amplifier （Axon Instruments）and data stored by Clampex software（version 10.0；Axon Instruments，Foster City，CA）

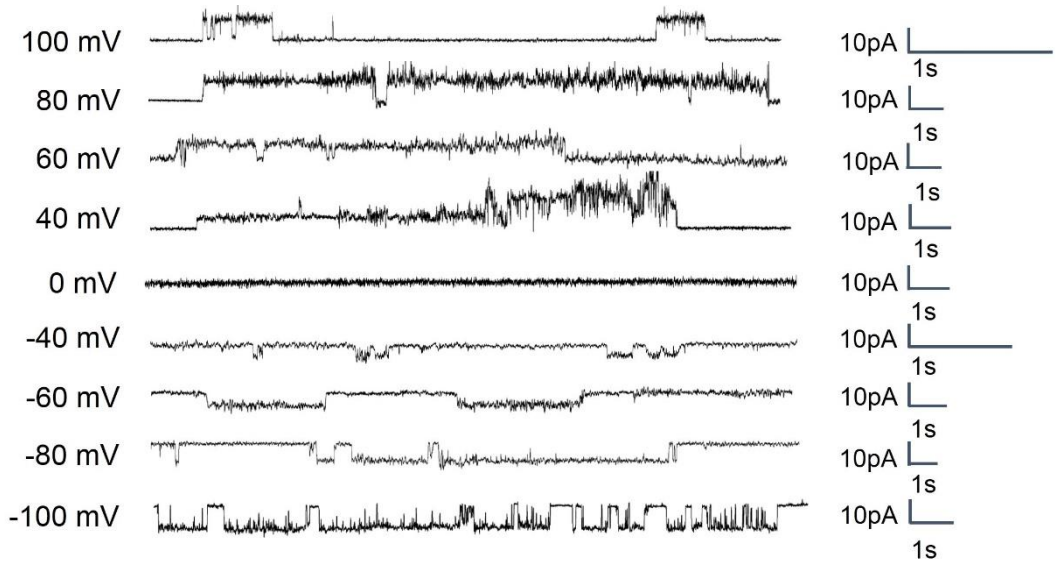


Figure S21. Electrophysiology channel recordings of **1** from +100 mV to -100mV.

Diameter of the channel under BLM data: It is a common method to estimate the inner diameter of channels by Hille equation. Unfortunately, for our system, the value calculated by this formula cannot match the actual situation. This is not an isolated case, and has occurred in many systems.[4]

$$1/g = l\rho/[\pi(d/2)^2] + \rho/d$$

According to the work we have reported previously,[3, 5] the helical-shaped nanoscale channels did not match the equations, but maintained a certain regularity of their own (Figure S22). We found that the current signal increased with the increase of channel diameter. Therefore, we believed that the current signal from BLM experiments was reliable.

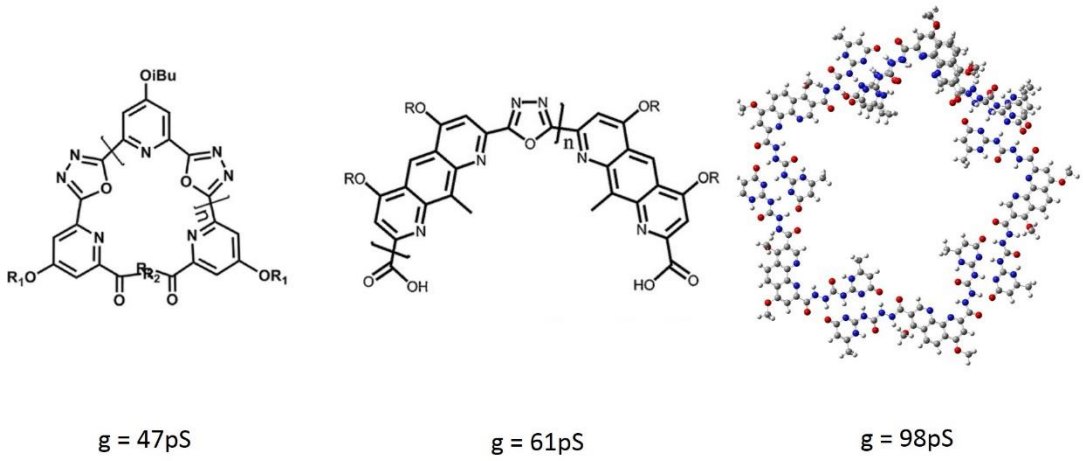


Figure S22. The conductance of helical channels increased with the increase of channel diameter.

Generally, it is appropriate to estimate the channel diameter by combining the data of BLMs, LUVs, and molecular models. [6] For our helical supramolecular polymer channels, we think that the channel structure was dynamic in the embedded membrane state. The helical channel can be squeezed or expanded like a spring, causing a change in the diameter of the inner cavity, which is no longer a standard cylindrical structure. Therefore, the current signal was interfered by the change of the cavity, which results in the deviation of the Hille equation. In this regard, the effect of mechanical stress on supramolecular channel have been reported.[7]

However, this squeezing state does not last forever. According to the glucose transport experiment, the helical channel can transfer larger glucose molecules, indicating that helical channels still have a large inner diameter enough to transfer glucose molecules.

Sansom and his co-workers reported that empirical correction factors were available to correct for conductance at 1997. Because of the absence of more similar structure data, we did not get an appropriate empirical correction factor at present.

7. Glucose leakage enzyme-coupled assay

Preparation of LUVs containing glucose: 9mg EYPC and 1mg cholesterol was first dissolved in 1 mL $CHCl_3$, the solvent was dried by N_2 and under vacuum for three hours. Then the lipid was placed in 1 mL PBS buffer solution (100mM, pH=6.5) with glucose (200mM). The suspension was incubated at 37 ℃ for 3 hours and subjected to 10 freeze-thaw cycles by using liquid nitrogen and warm water bath. Then the suspension was filtered through 0.22 μm polycarbonate membrane and purified by Sephadex G-50 twice to remove un-entrapped glucose against the same buffer solution. The LUVs suspension was kept under 4 ℃

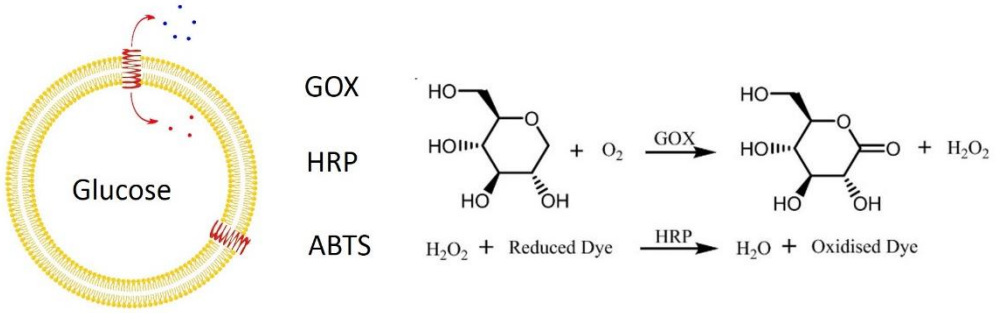


Figure S23. The illustration of glucose transport experiment by enzyme-coupled assay

Enzyme-Coupled Assay: All the reaction was placed in 1.5mL cuvette at 37℃ under SHIMADZU UV-2450 spectrophotometer. In the cuvette: 100μL LUVs suspension, 100μL Horseradish Peroxidase (HRP) solution (200 units/mL, PBS buffer solution, pH=6.5) and 400μL 2, 2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) solution (5mM, PBS buffer solution, pH=6.5) were mixed with 300μL PBS buffer solution (100mM, pH=6.5). The cuvette was placed in water bath at 37℃ for 3 minutes. Then, 100μL Glucose Oxidase (GOX) solution (100 units/mL, PBS buffer solution, pH=6.5) and 10μL channel solution in DMSO were added with gentle stirring to start the reaction. The production of ABTS•+ was monitored at 405 nm for 40 minutes at 120s time intervals. Triton X-100 was added at 42 minutes and wait 3min to determine the total glucose content (to catalyze the substrate thoroughly). In order to measure the background, pure DMSO was added to instead channel solution. The absorbance after adding triton X-100 was measured as the total glucose content. The absorbance of 405 nm corresponds to the proportion of the glucose leakage and calculated every 2 minutes.
The leakage percent was calculated under this equation:

$$R = (A_0 - A_t) / (A_0 - A_{45})$$

R: leakage percent
A_0: the initial absorbance under 405 nm.
A_t: the absorbance under 405 nm at time = t.
A_{45}: the absorbance under 405 nm at time = 45 min (X-100 was added).

PS: Glucose - entrapped vesicles just need to be purified twice with Sephadex G50 to effectively remove unembedded glucose (neither dialysis nor ultrafiltration membranes can remove glucose quickly and efficiently).

8. Molecular Simulation

The molecular structures were simulated by the density functional theory (DFT) calculation. The optimization of the monomer structure was carried out at M062X/6-31G* level in a chloroform solution using a polarizable continuum model. We found that building block of monomer **1** was a flat structure.

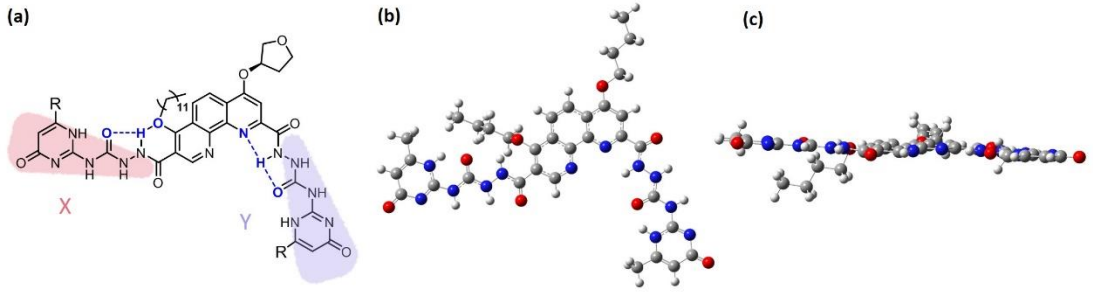


Figure S24. a) Molecular structure of 1 and molecular model of buiding block 1 in top view and c) front view, side chain was simplified to short alkyl chain.

For the oligomer simulation, X3LYP was employed for the better description of the hydrogen bonding interaction, and the basis set of 3-21G* was adopted for the sake of saving computational cost. The optimized hexamer and its helical structure were shown in Figure R2. We found that the most stable structure of the complex was still in the XY ordered helical structure, which was consistent with the electron microscope and spectrum data.

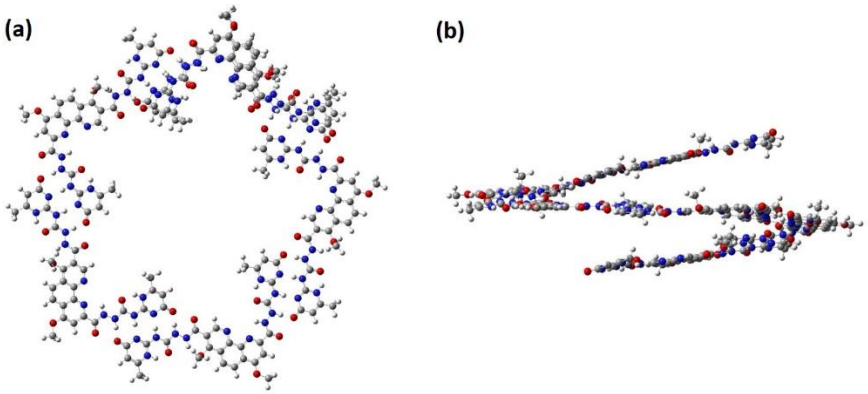


Figure S25. a) Molecular model of hexamer in top view and b) front view, side chain was simplified to methoxyl.

9. Reference

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