SUPPORTING INFORMATION

Supramolecular Polymerization Couples Constitutional Adaptability and Fluorescence Response in a Dynamic Covalent Library

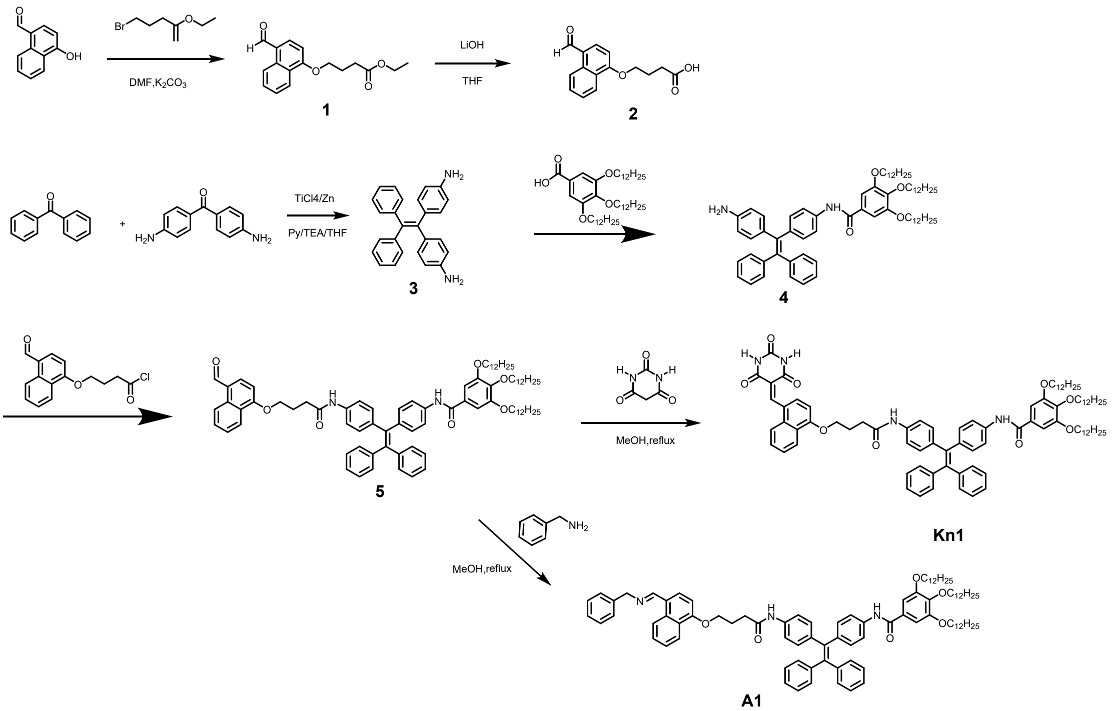
Mengying Lei, Sainan Liu, Xianhaoyan Chen, Ruirui Gu,* and Da-Hui Qu*

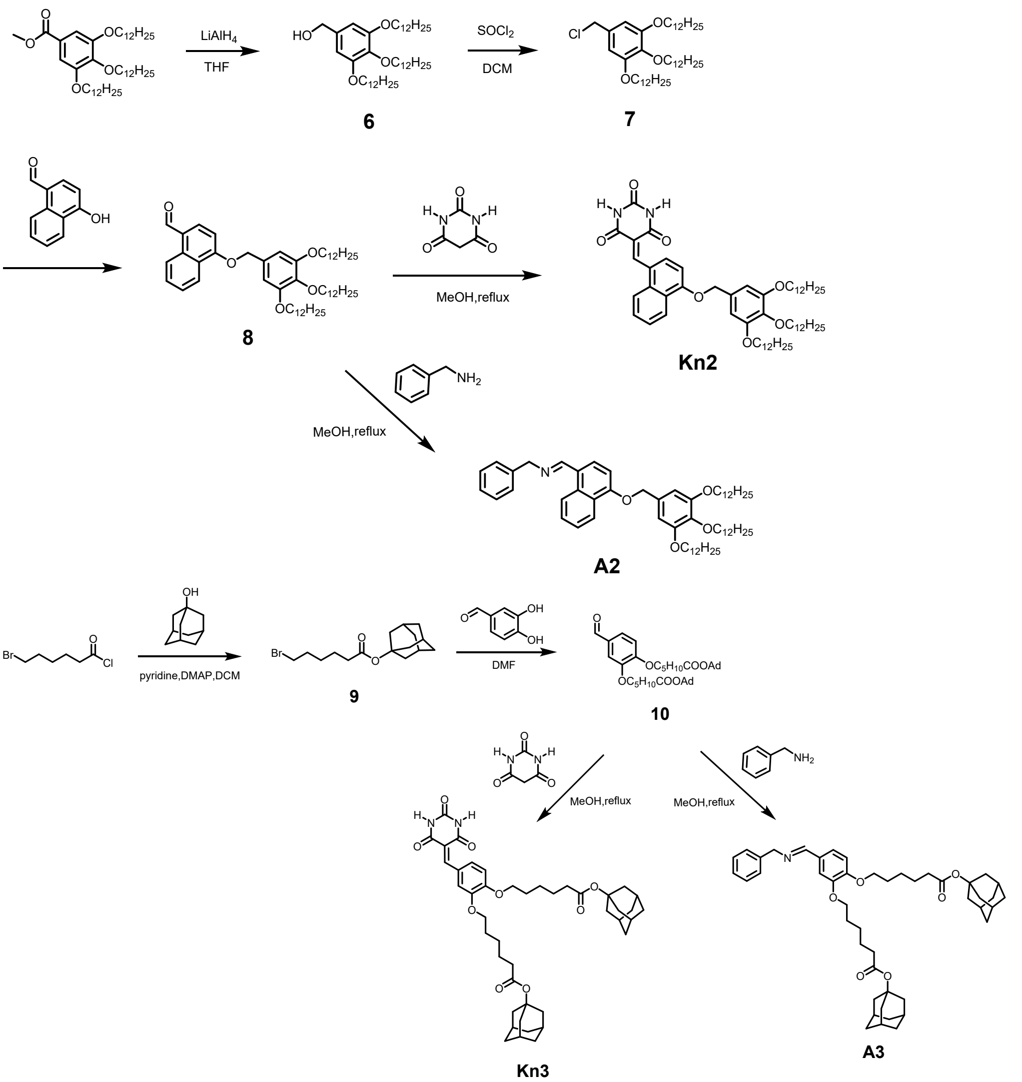
1. Instrumentation and measurement

Reagents and solvents were purchased from Aladdin, TCI, Macklin and were used without further purification. Deuterated solvents were purchased from CIL. All the $CDCl_3$ and $C_2D_2Cl_4$ used for NMR measurements were passed through basic alumina columns to remove the residual acid and water and were preserved in brown glass vials to keep out of the light. All the cyclohexane-d12 and methylcyclohexane-d14 used for NMR measurements were dried and preserved with molecular sieves in brown glass vials.

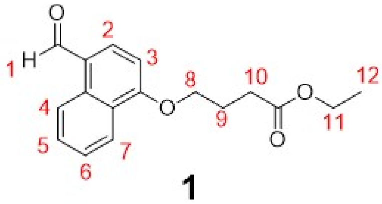
Solution nuclear magnetic resonance (NMR) was performed on a Bruker Avance 400/600 MHz spectrometer. Chemical shifts are reported in ppm relative to residual solvent signals (for 1H NMR spectra $CDCl_3$=7.283 ppm, $C_2D_2Cl_4$=6.0 ppm; for 13C NMR spectra $CDCl_3$=77.03 ppm).

2. Synthetic procedures





2.1. Synthesis of compound 1



1

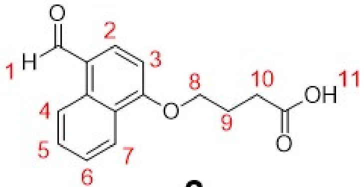
Ethyl 4-bromobutyrate (2.760 g,14.15 mmol) and 4-hydroxy-1-naphthaldehyde (1.598 g, 9.28 mmol) were added into a suspension of K_2CO_3 (3.926 g,28.41 mmol) in DMF, the mixture was then heated at 70°C for 8 h . The solution was cooled down to r.t., the solvent was removed on a rotavapor at 60°C. EtOAc and H_2O were added to dissolve the residue. The aqueous layer was extracted with EtOAc (3×30 mL). The combined organic extracts were washed with H_2O and brine (2×40 mL each) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained rude product was further purified by flash column chromatography on silica gel using EtOAc/Petroleum ether (v/v = 2/1) as eluent to give the pure product as a white solid (2.25 g, 85 %).

1H NMR (400 MHz, CDCl3, 298K): δ 10.23 (s, 1H, H1), 9.33 (d, J = 8.7 Hz, 1H, H4), 8.35 (d, J = 8.2 Hz, 1H, H7), 7.94 (d, J = 8.1 Hz, 1H, H2), 7.73 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H, H5), 7.60 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H, H6), 6.94 (d, J = 8.0 Hz, 1H, H3), 4.34 (t, J = 6.0 Hz, 2H, H8), 4.19 (q, J = 7.1 Hz, 2H, H11), 2.66 (t, J = 7.2 Hz, 2H, H10), 2.39 – 2.28 (m, 2H, H9), 1.28 (t, J = 7.2 Hz, 3H, H12).

13C NMR (126 MHz, CDCl3, 298K): δ 192.08, 172.88, 159.95, 139.36, 131.99, 129.50, 126.36, 125.58, 125.11, 124.88, 122.33, 103.61, 67.62, 60.56, 30.85, 24.47, 14.18, 14.18.

MS (ESI+): m/z calcd. for [12+H]+ 287.1278 found 287.1277.

2.2. Synthesis of compound 2



2

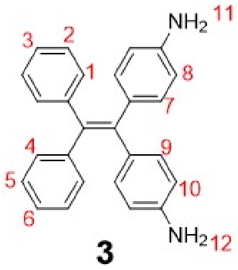
To the solution of **1** (2.25g,7.86mmol) in 80mL THF was added 1M LiOH (aqueous,25 mL). The mixture was stirred overnight at room temperature. The reaction mixture was quenched with 4M HCl and extracted with EtOAc (3×50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated on a rotavapor to give the compound **2** as a yellow solid (1.84 g, 90 %).

1H NMR (400 MHz, DMSO-d6, 298K): δ 12.22 (s, 1H, H11), 10.18 (s, 1H, H1), 9.22 (d, J = 8.5 Hz, 1H, H4), 8.31 (dd, J = 8.4, 1.4 Hz, 1H, H7), 8.15 (d, J = 8.1 Hz, 1H, H2), 7.75 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H, H5), 7.64 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H, H6), 7.21 (d, J = 8.1 Hz, 1H, H3), 4.33 (t, J = 6.2 Hz, 2H, H8), 2.57-2.50 (m, 2H, H10), 2.14 (m, 2H, H9).

13C NMR (126 MHz, DMSO-d6, 298K): δ 193.16, 174.49, 159.89, 140.64, 131.66, 129.92, 126.94, 125.32, 124.70, 124.69, 122.72, 105.15, 68.42, 30.84, 24.56.

MS (ESI+): m/z calcd. for [13+H]+ 259.0965 found 259.0965.

2.3. Synthesis of compound 3



3

To a 500 mL three-necked flask, 100 mL of THF and zinc powder (60 g, 918.13 mmol) were added to a 500 mL three-necked flask under an ice bath at 0 °C. Nitrogen was vented, titanium tetrachloride (46 mL, 418.6 mmol) was added, and after stirring for 30 min, the ice bath was removed, and the stirring refluxed for 5 hours. After stopping the heating, the system was subjected to an ice bath and triethylamine (13 mL, 94.3 mmol), pyridine (7.8 mL, 94.3 mmol) were added. After stirring for 15 min, a 100 mL THF solution of 4,4'-diaminobenzophenone (9.71 g, 45.78 mmol), benzophenone (10.00 g, 54.92 mmol) was injected into a three-necked flask using a syringe. the reaction was stirred and refluxed at 65 °C for 20 h. The pH of the reaction solution was adjusted with K_2CO_3 solution.

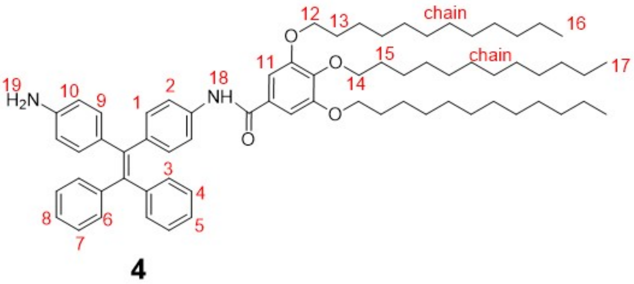
The filtrate was collected by filtration. The solvent was removed by spinning, extracted with dichloromethane (3x30mL), all the organic phase was collected and washed with water (3x20mL), followed by drying with anhydrous Na_2SO_4, filtration and spinning to remove the solvent. It was separated by column chromatography using petroleum ether/dichloromethane (v/v 3:1) as eluent. The eluate was collected and dried by spin-drying to give of compound **3** (4.89 g ,30 %).

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 7.10 (t, *J* = 7.4 Hz, 4H,H1,H4), 7.02 (t, *J* = 7.2 Hz, 2H,H3,H6), 6.91 (d, *J* = 7.1 Hz, 4H,H7,H9), 6.59 (d, *J* = 8.4 Hz, 4H,H2,H5), 6.26 (d, *J* = 8.4 Hz, 4H,H8,H10), 4.99 (s, 4H,H11,H12).

^{13}C NMR (151MHz, Chloroform-*d*) δ 144.73, 144.63, 140.93, 137.75, 134.49, 132.63, 131.45, 127.57, 125.72, 114.27.

MS (ESI+):m/z calcd for $C_{28}H_{21}N_2$ $[M+H]^+$,361.1699; found: 361.1706.

2.4. Synthesis of compound 4



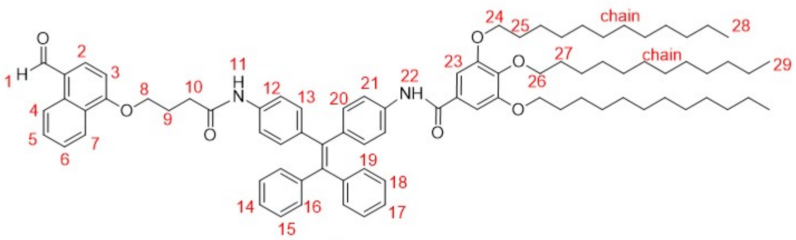
4

The 30 mL DMF solution of 3,4,5-tris(dodecyloxy)benzoic acid (1072.3 mg, 1.590 mmol), HATU (644.2 mg, 1.694 mmol) and DIPEA (785.2 mg, 6.075 mmol) was stirred for 2 h. Compound **3** (505.6 mg, 1.396 mmol) was added to 50 mL DMF to dissolve it thoroughly and stirred for 20 h at room temperature to obtain a turbid yellow solution. 50 mL of pure water was added to the reaction solution and then poured into a partition funnel, extracted with ethyl acetate (3×30 mL) and the organic phase was washed with saturated NaCl solution (3×20 mL). The organic phase was dried with anhydrous Na_2SO_4 and the solvent was spin-dried. The separation was carried out by column chromatography using petroleum ether/ethyl acetate (v/v 2:1). After drying, 443.5 mg of yellow compound **4** was obtained (31%).

^{1}H NMR (400MHz, Chloroform-*d*) δ 7.58 (s, 1H,H18), 7.36 (d, *J* = 8.6 Hz, 2H,H1), 7.15-7.07 (m, 6H,H4,H7,H9), 7.08-7.00 (m, 8H,H2,H3,H5,H6,H8), 6.99 (s, 2H,H19), 6.81 (d, *J* = 8.4 Hz, 2H, H10), 6.43 (d, *J* = 8.5 Hz, 2H, H11), 4.01 (t, *J* = 5.6 Hz, 6H,H12,H14), 1.78 (dq, *J* = 21.3, 7.9, 7.4 Hz, 6H,H13,H15), 1.26 (s, 54H,H_{chain}), 0.88(t, *J* = 6.8, 9H,H16,H17).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.47, 153.24, 144.88, 144.36, 144.29, 141.47, 140.43, 140.29, 139.27, 136.13, 133.90, 132.59, 132.27, 131.46, 131.37, 130.02, 127. 68, 126.07, 119.03, 114.35, 105.70, 73.57, 69.46, 31.94, 30.33, 30.08-28.97(m), 26.08, 22.71, 14.13.

2.5. Synthesis of compound 5



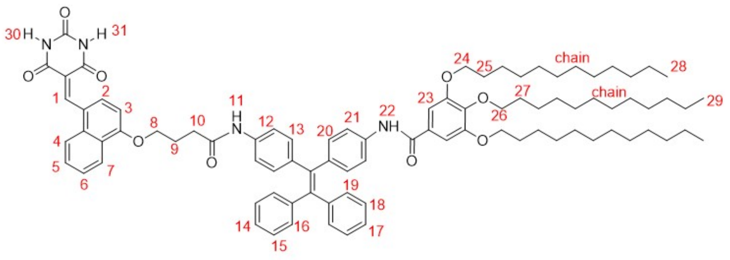
5

The 15mL DCM solution of compound**2**(106.7 mg,0.413 mmol), $C_2O_2Cl_2$ (104.8 mg,0.826 mmol) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and redissolved by adding 10 mL of DCM. Compound**4** (350.0 mg, 0.344 mmol) and DIPEA (66.7 mg, 0.516 mmol) were weighed in a three-necked flask, and 15mL of DCM was added to fully dissolve the above solution into a three-necked flask, and stirred at room temperature for 24 h. The solvent was removed by spin-distillation, and then the aqueous phase was washed with saturated NaCl (3×10 mL) and extracted with DCM (3×10 mL), all organic phase was collected and dried with anhydrous Na2SO4, and then evaporated to remove the solvent. Separation by column chromatography using petroleum ether/ethyl acetate (v/v 2:1) as the unfolding agent gave 269.4 mg (62%) of the yellow product **5**.

^{1}H NMR (400 MHz, Chloroform-d) δ 10.19 (s, 1H,H1), 9.30 (d, J = 8.5 Hz, 1H,H4), 8.30 (d, J = 8.6 Hz, 1H,H7), 7.90 (d, J = 8.0 Hz, 1H,H2), 7.69 (t, J = 7.7 Hz, 1H,H5), 7.62 (s, 1H,H11), 7.49 (t, J = 8.1 Hz, 1H,H6), 7.37 (d, J = 8.5 Hz, 2H,H13), 7.24 (s, 2H,H23), 7.11-6.99 (m, 16H ,H12,H14,H15,H16,H17,H18,H19,H20,H21), 6.96 (s, 1H,H22), 6.92 (d, J = 8.1, 1H,H3), 4.34 (t, J = 5.8 Hz, 2H,H8), 4.06-3.93 (m, 6H,H24,H26), 2.65 (t, J = 6.9 Hz, 2H,H10), 2.40 (p, J = 6.9 Hz, 2H,H9), 1.81 (p, J = 6.6, 6H,H25,H27), 1.73-1.26(m, 54H,H_{chain}), 0.87(t, J = 8.0, 9H,H28,H29).

ESI-MS: m/z calcd for $C_{86}H_{113}O_7N_2$ $[M+H]^+$,1285.8542; found: 1285.8323

2.6. Synthesis of compound Kn1



Kn1

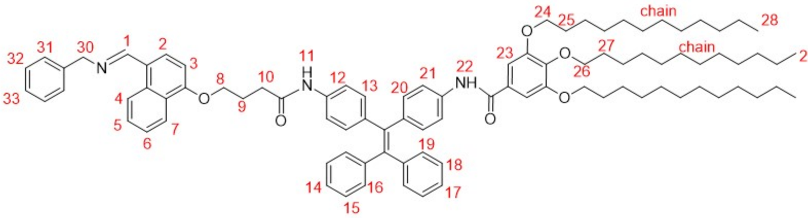
Barbituric acid (65.8 mg,0.514 mmol) and compound **5**(538.8 mg,0.428 mmol) were weighed in a 25 mL round bottom flask, 15 mL of methanol was added, and the mixture was refluxed with stirring for 16h. After recovering to room temperature, an orange-yellow solid precipitated, and the solid was collected by filtration under reduced pressure, and was dried in a vacuum drying oven overnight. 355.5mg of compound Kn1 was obtained in 60.68% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.33 (s, 1H), 8.64 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.5 Hz,1H), 8.05 (d, J = 9.6 Hz, 1H), 7.85 (s, 1H), 7.77 (s, 1H), 7.69-7.63 (m, 1H), 7.62 (s, 1H), 7.53-

7.45 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.05-6.95 (m, 14H), 6.96 (s, 1H), 6.92 (d, *J* = 9.3, 2H), 4.37 (t, *J* = 6.4 Hz, 2H), 3.75 (s, 6H), 2.68-2.61 (m, 2H), 2.45-2.37 (m, 2H), 1.87-1.69 (m, 15H), 1.52-1.41 (m, 9H), 1.26 (m, 75H), 0.88 (t, *J* = 6.4 Hz, 20H).

MS (ESI+): m/z calcd. for [**Kn1**+Na]$^+$1391.8327 found 1391.7183.

2.7. Synthesis of compound A1



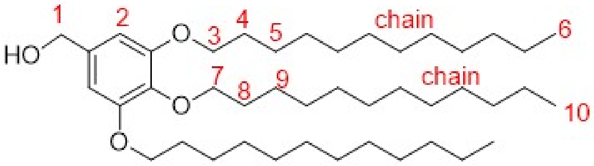
A1

Compound **5** (222.3 mg,0.177 mmol) and benzylamine (189.7 mg,1.770 mmol) were weighed into a 25 mL round-bottomed flask, 5 mL of methanol was added, and refluxed with stirring overnight. After cooling to room temperature and ice bath for 1 h, the white solid precipitated. The upper layer of white solid was collected by filtration and dried in a vacuum drying oven overnight to give 208.7 mg of compound A1 in 87.62% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.09 (d, J = 8.6 Hz, 1H), 8.91 (s, 1H), 8.29 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.60 (q, J = 7.0, 5.8 Hz, 2H), 7.49 – 7.32 (m, 8H), 7.17 – 6.94 (m, 19H), 6.84 (d, J = 7.8 Hz, 1H), 4.91 (s, 2H), 4.27 (t, J = 5.7 Hz, 2H), 4.00 (td, J = 6.5, 3.2 Hz, 7H), 2.64 (t, J = 6.9 Hz, 2H), 2.43 – 2.33 (m, 2H), 1.78 (dt, J = 26.5, 7.3 Hz, 7H), 1.57 (s, 8H), 1.47 (t, J = 8.0 Hz, 7H), 1.28 (d, J = 9.9 Hz, 54H), 0.88 (t, J = 6.6 Hz, 10H).

MS (ESI+): m/z calcd. for [**A1**+Na]$^+$ 1370.8840 found 1370.8115.

2.8. Synthesis of compound 6



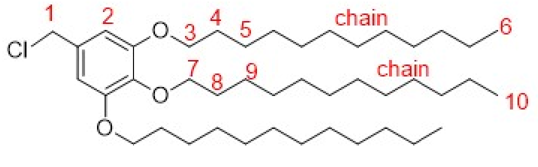
6

LiAlH$_4$ (0.6 g, 16.0 mmol) was added to 40 mL dry THF in a round-bottom flask at 0°C. To the suspension was added dropwise 20 mL THF solution of compound **5** (5.5 g, 8.0 mmol). After complete addition, the mixture was allowed to warm to r.t. and then stirred for 2 h. Quench the reaction by the addition of 1 mL H_2O, 0.6 mL 15% NaOH and 1.8 mL H_2O. The precipitated white solid was removed by filtration, the filtrate was added 100 mL H_2O and extracted with ether (3×60 mL). The combined organic extracts were washed with brine (2×60 mL), dried over anhydrous Na_2SO_4, filtered and concentrated on a rotavapor to give the product as a white solid (4.3 g, 82%)

which could be used without further purification.

^{1}H NMR (400 MHz, Chloroform-d)：δ 6.58 (s, 2H, H2), 4.61 (s, 2H, H1), 4.03-3.91 (m, 6H, H3 and H7), 1.87-1.72 (m, 6H, H4 and H8), 1.53-1.43 (m, 6H, H5 and H9), 1.41-1.18 (m, 48H, Hchain), 0.94-0.86 (m, 9H, H6 and H10).

2.9. Synthesis of compound 7

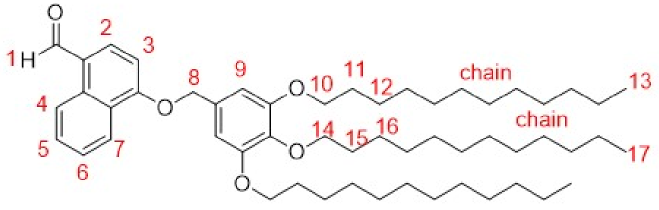


7

To the solution of **6** (5.3 g, 8.0 mmol) in 10 mL DCM was slowly added thionyl chloride (1.2 g, 10.1 mmol). The mixture was stirred at r.t. for 2 h. Then the reaction solution was concentrated on a rotavapor and residual $SOCl_2$ was removed under high vacuum for 3 h to yield compound 6 as a white solid (5.3 g, 97%).

^{1}H NMR (400 MHz, Chloroform-d)：δ 6.59 (s, 2H, H2), 4.53 (s, 2H, H1), 4.02-3.93 (m, 6H, H3 and H7), 1.86-1.71 (m, 6H, H4 and H8), 1.52-1.44 (m, 6H, H5 and H9), 1.42-1.20 (m, 48H, Hchain), 0.94-0.87 (m, 9H, H6 and H10).

2.10. Synthesis of compound 8



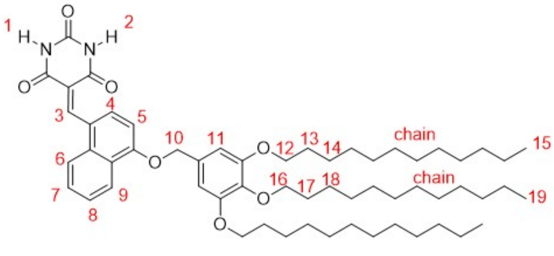
8

Compound **7** (394 mg, 0.58 mmol) and 4-hydroxy-1-naphthaldehyde (100 mg, 0.58 mmol) were added into a suspension of K_2CO_3 (481 mg, 3.48 mmol) in DMF, the mixture was then heated at 70°C for 8 h . The solution was cooled down to r.t., the solvent was removed on a rotavapor at 60°C. EtOAc and H2O were added to dissolve the residue. The aqueous layer was extracted with EtOAc (3×30 mL). The combined organic extracts were washed with H_2O and brine (2×40 mL each) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained rude product was further purified by flash column chromatography on silica gel using EtOAc/Petroleum ether (v/v = 1/4) as eluent to give the pure product as a white solid (274 mg, 58%).

^{1}H NMR (400 MHz, Chloroform-d)：δ 10.24 (s, 1H, H1), 9.34 (d, J = 8.5 Hz, 1H, H4), 8.42 (d, J

= 8.6 Hz, 1H, H7), 7.95 (d, J = 8.1 Hz, 1H, H2), 7.78-7.69 (m, 1H, H5), 7.64-7.56 (m, 1H, H6), 7.02 (d, J = 8.1 Hz, 1H, H3), 6.72 (s, 2H, H9), 5.26 (s, 2H, H8), 4.09-3.92 (m, 6H, H10 and H14), 1.88-1.64 (m, 6H, H11 and H15), 1.53-1.43 (m, 6H, H12 and H16), 1.41-1.22 (m, 48H, Hchain), 0.94-0.86 (m, 9H, H13 and H17).

2.11. Synthesis of compound Kn2



Kn2

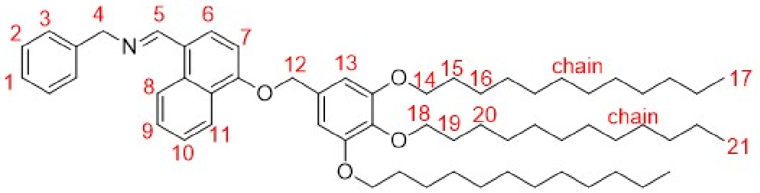
Compound **Kn2** was synthesized according to the procedure for synthesis of **Kn1**. Yield 78%.

^{1}H NMR (400 MHz, Chloroform-d)：δ 9.39 (s, 1H, H3), 8.72 (d, J = 8.5 Hz, 1H, H6), 8.47 (s, 1H, H1), 8.43 (d, J = 8.4 Hz, 1H, H9), 8.13 (s, 1H, H2), 8.10 (d, J = 8.5 Hz, 1H, H4), 7.69 (t, J = 7.1 Hz, 1H, H7), 7.58 (t, J = 7.6 Hz, 1H, H8), 7.02 (d, J = 8.5 Hz, 1H, H5), 6.72 (s, 2H, H11), 5.26 (s, 2H, H10), 4.06-3.94 (m, 6H, H12 and H16), 1.88-1.74 (m, 6H, H13 and H17), 1.56-1.41 (m, 6H, H14 and H18), 1.40-1.11 (m, 48H, Hchain), 0.93-0.88 (m, 9H, H15 and H19).

^{13}C NMR (151MHz, Chloroform-*d*): δ 160.81, 160.67, 157.11, 153.43, 138.34, 135.93, 134.58, 130.74, 128.93, 126.07, 123.52, 123.40, 121.54, 114.22, 106.31, 104.68, 73.52, 71.27, 69.25, 31.97, 31.95, 30.96, 30.39, 29.80, 29.79, 29.77, 29.73, 29.69, 29.68, 29.67, 29.66, 29.47, 29.43, 29.39, 26.17, 26.14, 22.73, 22.71, 14.14.

MS (ESI+):m/z calcd. for [Kn2-H]- 923.6519 found 923.6510.

2.12. Synthesis of compound A2



A2

To benzylamine (13 mg, 0.12 mmol) and 7 (50 mg, 0.06 mmol) were added 10 mL ethanol. The mixture was refluxed overnight and then cooled down to r.t.. The precipitated solid was collected by filtration and washed with cold ethanol as a white powder (56 mg, 50%).

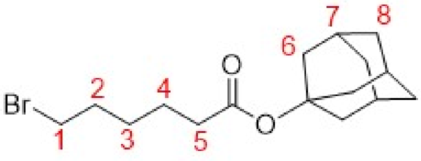
^{1}H NMR (400 MHz, Chloroform-d)：δ 9.01 (d, J = 8.5 Hz, 1H, H8), 8.86 (t, J = 1.5 Hz, 1H, H5), 8.33 (dd, J = 8.4, 1.4 Hz, 1H, H11), 7.78 (d, J = 8.1 Hz, 1H, H6), 7.54 (t, J = 7.7 Hz, 1H, H9), 7.45

(t, J = 8.3 Hz, 1H, H10), 7.36-7.26 (m, 4H, H2 and H3), 7.23-7.19 (m, 1H, H1), 6.85 (d, J = 8.1 Hz, 1H, H7), 6.63 (s, 2H, H13), 5.11 (s, 2H, H12), 4.85 (s, 2H, H4), 3.95-3.86 (m, 6H, H14 and H18), 1.77-1.64 (m, 6H, H15 and H19), 1.46-1.34 (m, 6H, H16 and H20), 1.311.13 (m, 48H, Hchain), 0.83-0.78 (m, 9H, H17 and H21).

^{13}C NMR (151MHz, Chloroform-*d*):δ 161.72, 156.71, 153.34, 139.90, 138.06, 132.47, 131.56, 130.75, 128.49, 127.91, 127.82, 126.87, 125.51, 124.56, 122.60, 106.12, 104.69, 73.49, 70.69, 69.20, 66.05, 53.45, 50.93, 31.97, 31.95, 30.96, 30.37, 29.79, 29.77, 29.73, 29.68, 29.67, 29.66, 29.65, 29.45, 29.42, 29.42, 29.39, 26.17, 26.12, 22.72, 22.71, 14.14.

MS (ESI+): m/z calcd. for [A2+H]+ 904.7177 found 904.7153.

2.13. Synthesis of compound 9



9

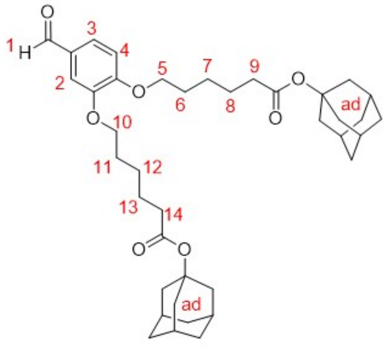
A solution of 6-bromohexanoyl chloride (4.0 g, 18.7 mmol) in DCM (10 mL) was added dropwise at 0°C to the solution of 1-adamantanol (2.2 g, 14.4 mmol), pyridine (1.8 g, 18.7 mmol), and DMAP (87 mg, 0.72 mmol) in DCM (30 mL). The mixture was stirred at room temperature for 4 h and then treated with 2 M HCl (30 mL). The layers were separated, and the aqueous layer was further extracted with DCM (3×20 mL). The combined organic extracts were washed with 2 M HCl, H_2O, sat. $NaHCO_3$, H_2O, and brine (40 mL each) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a colorless oil (5.1 g, 82%) as the product without further purification.

^{1}H NMR (400 MHz, Chloroform-d)：δ 3.43 (t, J = 6.8 Hz, 2H, H1), 2.25 (t, J = 7.4 Hz, 2H, H5), 2.20-2.15 (m, 3H, H7), 2.12 (d, J = 3.1 Hz, 6H, H6), 1.93-1.86 (m, 2H, H2), 1.73-1.58 (m, 8H, H4 and H8), 1.53-1.44 (m, 2H, H3).

^{13}C NMR (151MHz, Chloroform-*d*):δ 172.66, 80.30, 41.36, 36.20, 35.45, 33.67, 32.47, 30.80, 27.59, 24.26.

MS (ESI+): m/z calcd. for [2+H] + 329.1111 found 329.1111.

2.14. Synthesis of compound 10



10

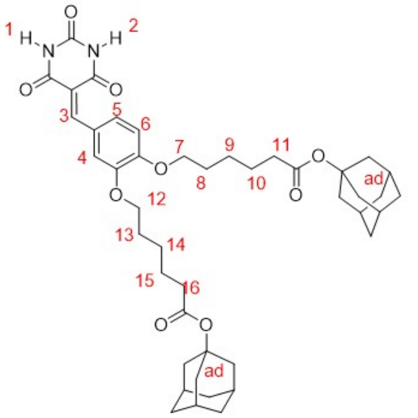
The solution of **9** (1.0 g, 3.0 mmol), 3,4-dihydroxybenzaldehyde (168 mg, 1.2 mmol), and K_2CO_3 (420 mg, 3.0 mmol) in 30 mL DMF was stirred at 80°C for 12 h. The solution was cooled down to r.t., the solvent was removed on a rotavapor at 60°C. EtOAc and H_2O were added to dissolve the residue. The aqueous layer was extracted with EtOAc (3×30 mL). The combined organic extracts were washed with H_2O and brine(2×40 mL each) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained rude product was further purified by flash column chromatography on silica gel using EtOAc/Petroleum ether (v/v = 1/4) as eluent to give the pure product as a colorless oil (579 mg, 75%).

^{1}H NMR (400 MHz, Chloroform-*d*)：δ 9.85 (s, 1H, H1), 7.44 (dd, J = 8.2, 1.9 Hz, 1H, H3), 7.40 (d, J = 1.9 Hz, 1H, H2), 6.97 (d, J = 8.2 Hz, 1H, H4), 4.08 (dt, J = 12.1, 6.6 Hz, 4H, H5 and H10), 2.27 (td, J = 7.4, 1.4 Hz, 4H, H9 and H14), 2.20-2.14 (m, 6H, Had), 2.14-2.07 (m, 12H, Had), 1.96-1.82 (m, 4H, H6 and H11), 1.75-1.61 (m, 16H, H8 and H13 and Had), 1.59-1.47 (m, 4H, H7 and H12).

^{13}C NMR (151MHz, Chloroform-*d*): δ 191.01, 172.77, 172.74, 161.16, 154.51, 149.30, 129.90, 126.64, 111.74, 110.89, 80.22, 80.17, 68.81, 68.79, 41.37, 41.36, 36.22, 36.21, 35.62, 35.56, 30.80, 30.80, 28.78, 28.69, 25.49, 25.43, 24.86, 24.79.

MS (ESI+):m/z calcd. for [3+H]+ 635.3942 found 635.3938.

2.15. Synthesis of compound Kn3



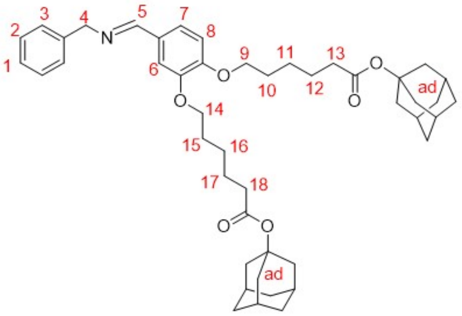
Kn3

To **10** (100 mg, 0.16 mmol) and barbituric acid (23 mg, 0.18 mmol) was added 20 mL ethanol, the mixture was heated to reflux and stirred for 2h. After cooling, the precipitate was filtered off and washed with 20 mL cold ethanol and dried under vacuum for 3 hours to give a yellow solid (92 mg, 78%) without further purification. **^{1}H NMR (400 MHz, Chloroform-d)**：δ 8.53-8.49 (m, 2H, H3 and H4), 8.28 (s, 1H, H1), 8.21 (s, 1H, H2), 7.78 (dd, J = 8.6, 2.1 Hz, 1H, H5), 6.95 (d, J = 8.6 Hz, 1H, H6), 4.18-4.08 (m, 4H, H7 and H12), 2.31-2.23 (m, 4H, H11 and H16), 2.21-2.15 (m, 6H, Had), 2.14-2.09 (m, 12H, Had), 1.96-1.85 (m, 4H, H8 and H13), 1.75-1.63 (m, 16H, H10 and H15 and Had), 1.58-1.48 (m, 4H, H9 and H14).

^{13}C NMR (151MHz, Chloroform-*d*):δ 172.93, 172.72, 163.73, 161.41, 160.41, 155.45, 148.88, 148.21, 134.05, 125.34, 118.55, 112.22, 111.66, 80.26, 80.25, 68.88, 68.79, 53.45, 50.90, 41.37, 36.21, 35.66, 35.54, 30.96, 30.81, 30.80, 28.65, 28.61, 25.51, 25.39, 24.87, 24.77.

MS (ESI+): m/z calcd. for [Kn1+H]+ 745.4059 found 745.4053.

2.16. Synthesis of compound A3



A3

Benzylamine (254 mg, 0.4 mmol) and 3 (43 mg, 0.4 mmol) were dissolved in 10 mL methanol and $MgSO_4$ was added. The mixture was refluxed overnight and the solid was filtered off. After the solvent was removed under reduced pressure, the products were isolated as a colorless oil (287 mg, 99%).

^{1}H NMR (400 MHz, Chloroform-d)：δ 8.30 (s, 1H, H5), 7.46 (d, J = 1.9 Hz, 1H, H6), 7.40-7.31

(m, 4H, H2 and H3), 7.31-7.24 (m, 1H, H1), 7.19 (dd, J = 8.2, 1.9 Hz, 1H, H7), 6.89 (d, J = 8.2 Hz, 1H, H8), 4.81 (d, J = 1.3 Hz, 2H, H4), 4.09-4.02 (m, 4H, H9 and H14), 2.30-2.22 (m, 4H, H13 and H18), 2.19-2.15 (m, 6H, Had), 2.14-2.09 (m, 12H, Had), 1.92-1.78 (m, 4H, H10 and H15), 1.73-1.57 (m, 16H, H12 and H17 and Had), 1.57-1.46 (m, 4H, H11 and H16).

^{13}C NMR (151MHz, Chloroform-*d*):δ 172.83, 172.81, 161.75, 151.42, 149.24, 139.52, 129.35, 128.47, 128.00, 126.93, 123.16, 112.44, 111.11, 80.17, 80.13, 68.84, 68.77, 64.92, 53.45, 41.38, 41.37, 41.36, 36.23, 36.22, 35.65, 35.61, 32.39, 30.96, 30.81, 28.95, 28.86, 25.53, 25.49, 25.19, 24.92, 24.86, 24.77.

MS (ESI+): m/z calcd. for [A1+H]+ 724.4572 found 724.4566.

3. Results and Discussion of the Kn1 and DCL-1 Section

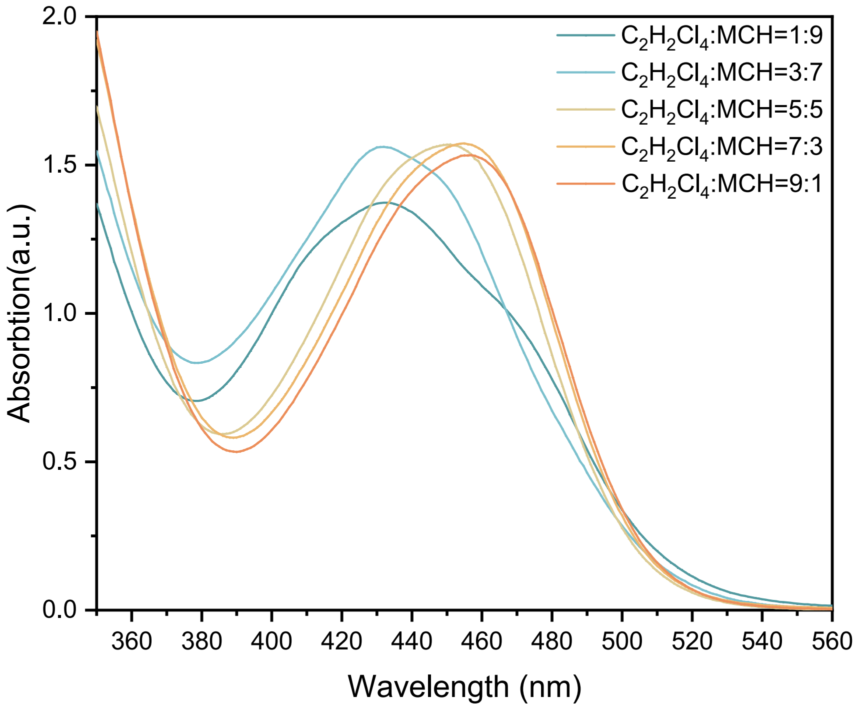


Figure S1a. UV absorption spectra of **Kn1** in different polar solvents at 293 K.

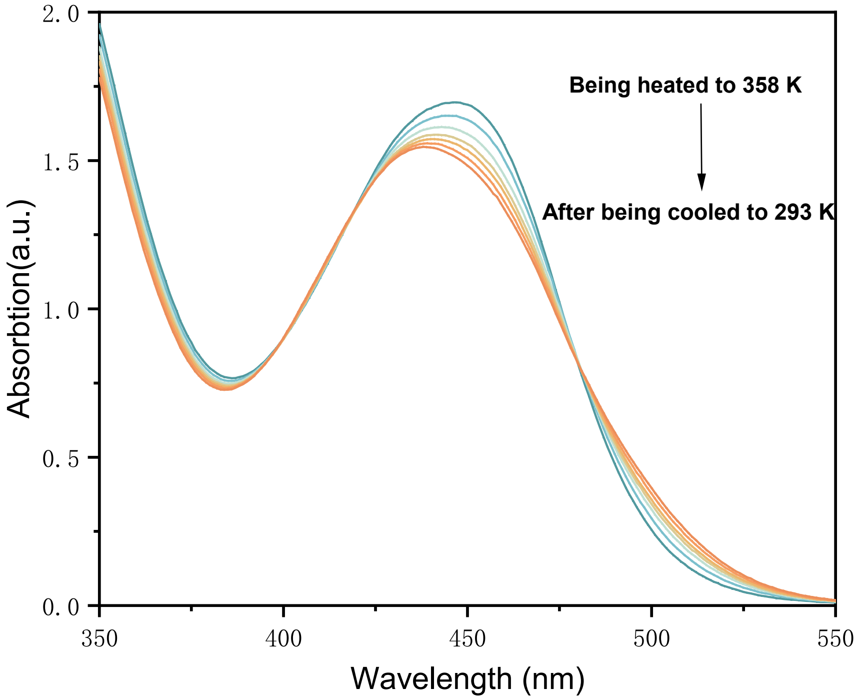


Figure S1b. UV absorption spectra of **Kn1** in 30% $C_2H_2Cl_4$ + 70% MCH at different temperatures.

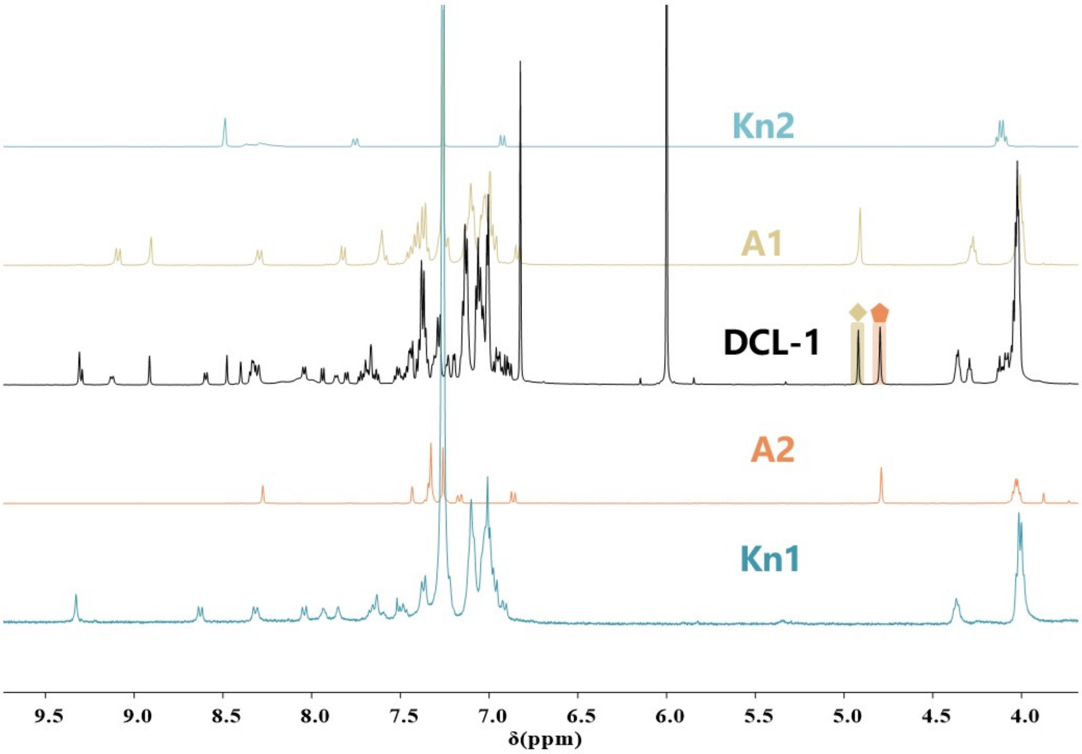


Figure S2a. NMR spectrum of single-component and DCL-1 (293 K, 90% $C_2H_2Cl_4$ + 10% MCH).

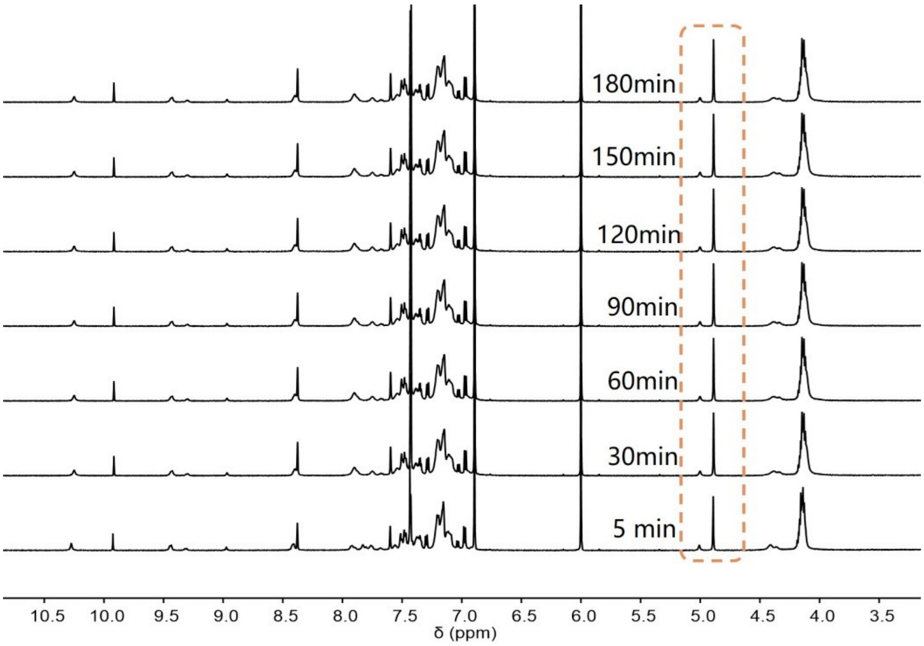


Figure S2b. NMR kinetic spectrum obtained from a Kn1+A2 sample (293 K, 30% $C_2H_2Cl_4$ + 70% MCH).

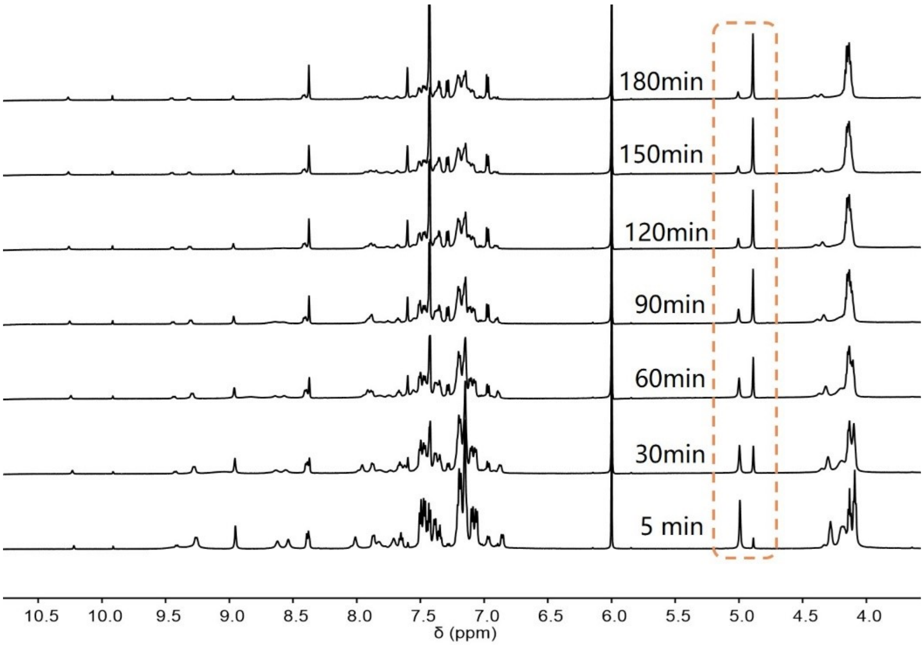


Figure S2c. NMR kinetic spectrum obtained from a Kn2+A1 sample (293 K, 30% $C_2H_2Cl_4$ + 70% MCH).

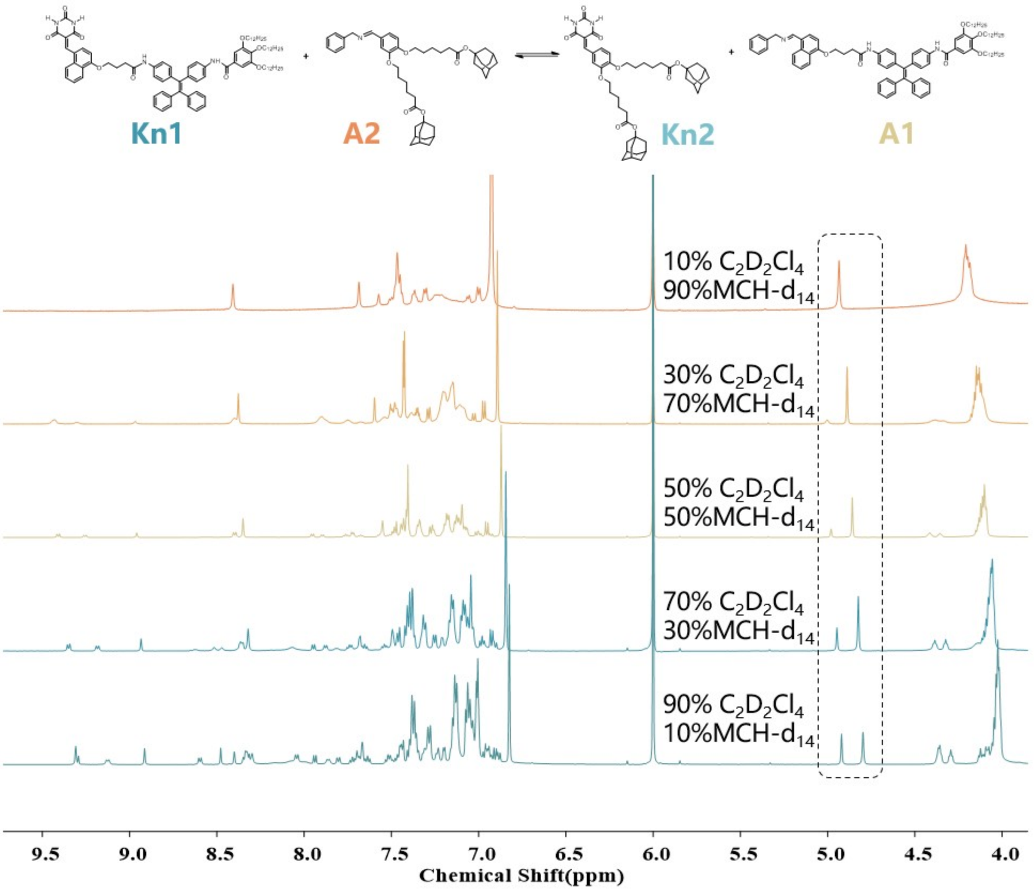


Figure S3. 1H NMR of **DCL-1** in different polar solvents at 293 K.

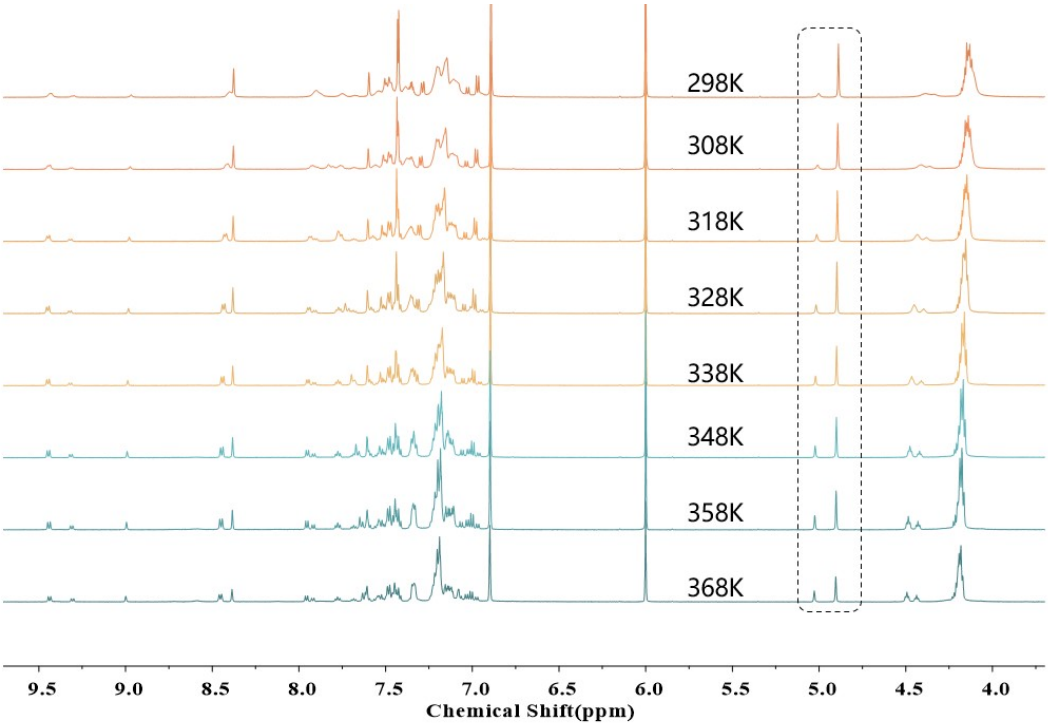


Figure S4. DCL-1 in 30% $C_2H_2Cl_4$ + 70% MCH at different temperatures.

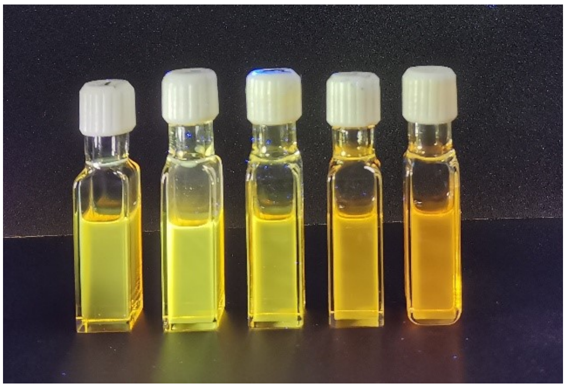


Figure S5. Fluorescence color charts for different solvent polarities, from left to right: 10% $C_2H_2Cl_4$ + 90% MCH; 30% $C_2H_2Cl_4$ + 70% MCH; 50% $C_2H_2Cl_4$ + 50% MCH; 70% $C_2H_2Cl_4$ + 10% MCH; 90% $C_2H_2Cl_4$ + 10% MCH.

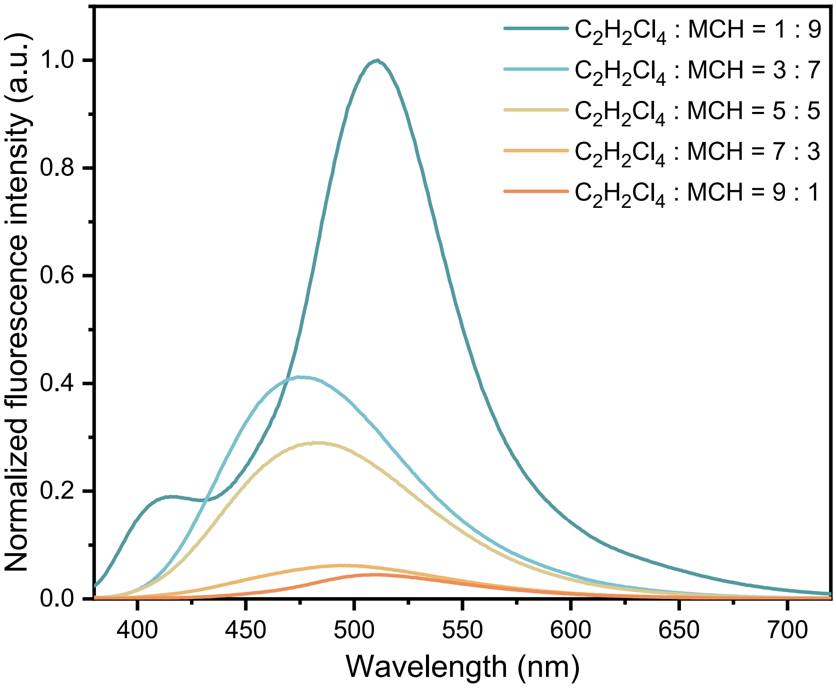


Figure S6. Fluorescence emission spectra of **DCL-1** in different solvents at 293 K (c = 100μM; λ_{ex} = 365 nm).

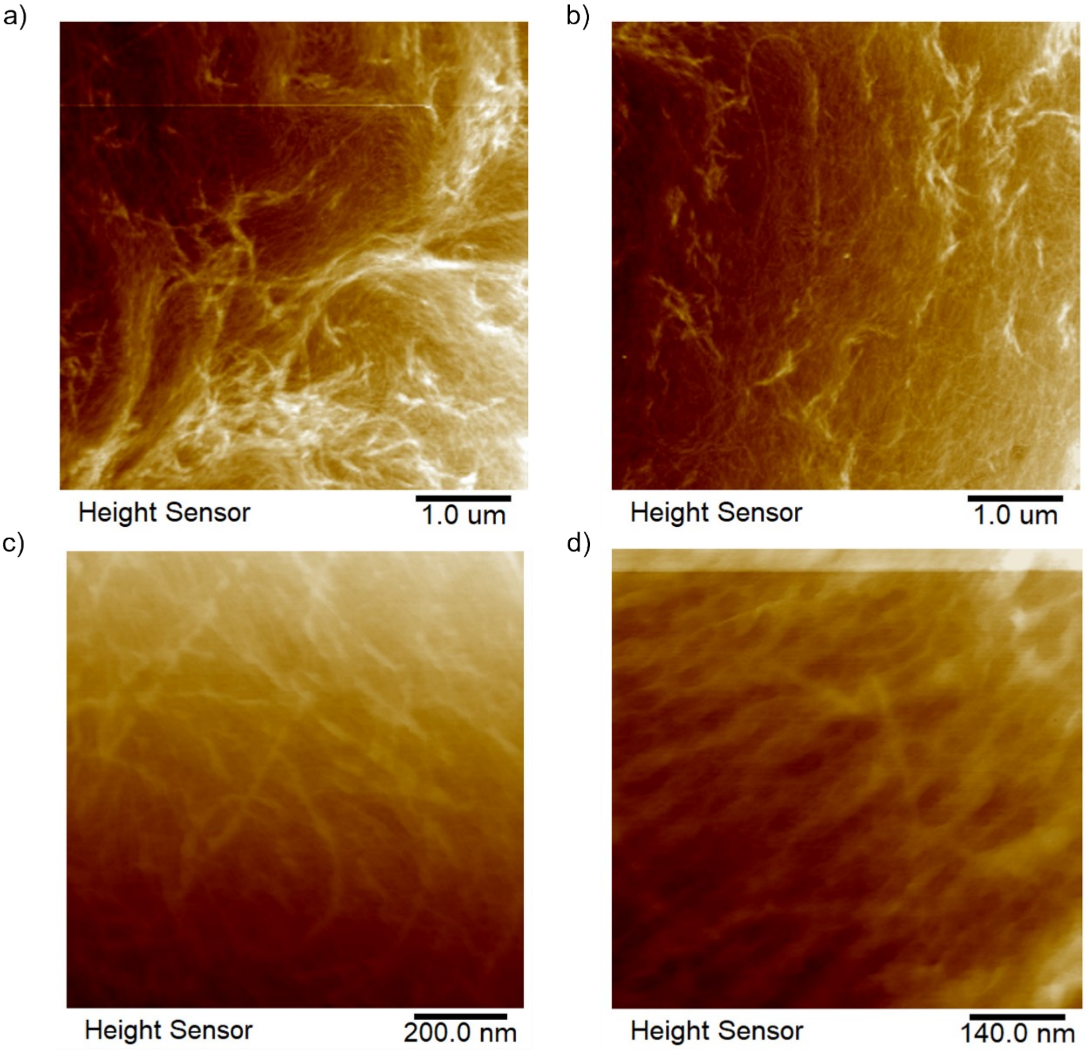


Figure S7. The AFM images of **Kn1** (c = 200μM) in 30% $C_2H_2Cl_4$ + 70% MCH at 293 K

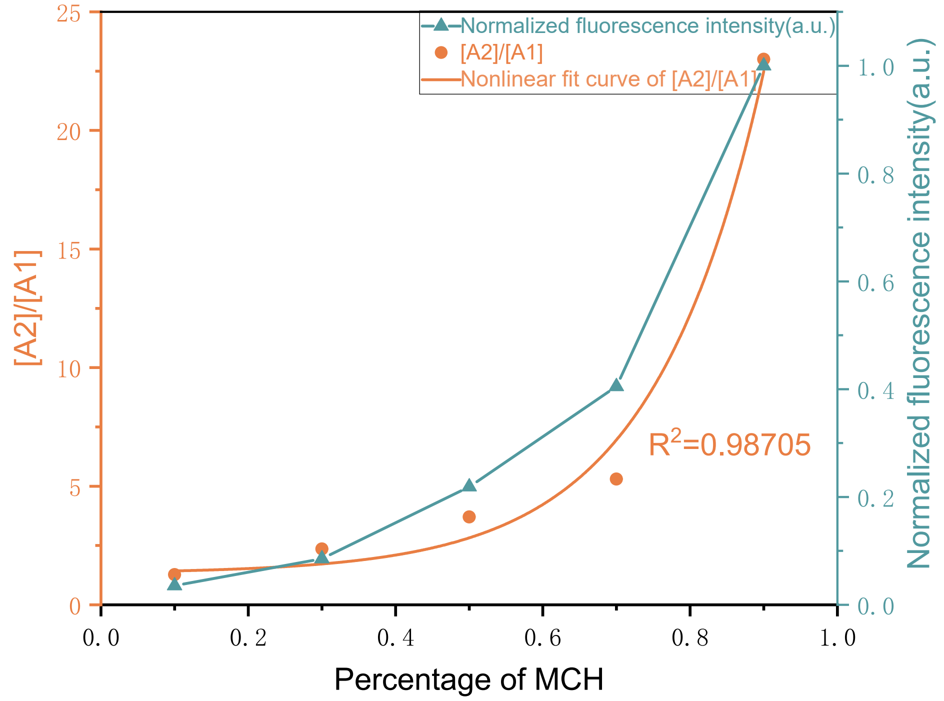


Figure S8. Plot of the relationship between the composition of DCL-1 and fluorescence emission intensity at different polarities of the $C_2H_2Cl_4$ + MCH solvent.

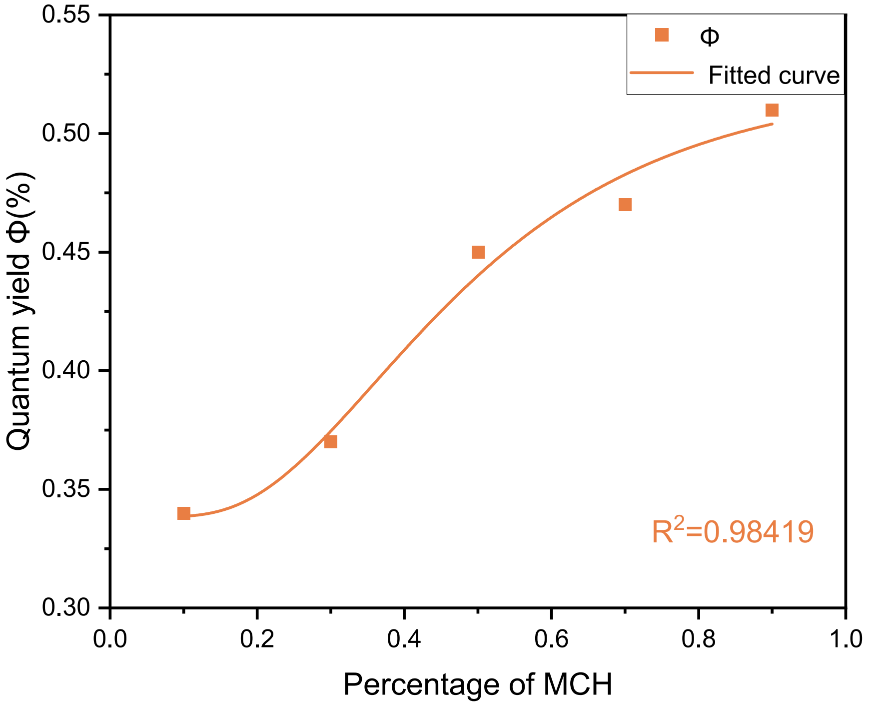


Figure S9. Absolute fluorescence quantum yields of Kn1 in various $C_2H_2Cl_4$/MCH mixed solvents and S-type fitting curves

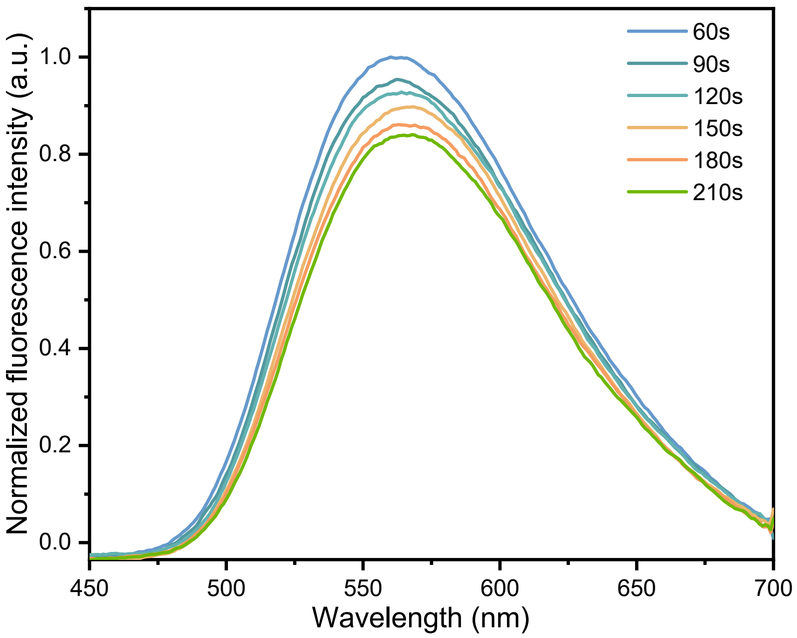


Figure S10a. Fluorescence kinetics measured using a Kn1+A2 mixture (Concentration = 1 mM)

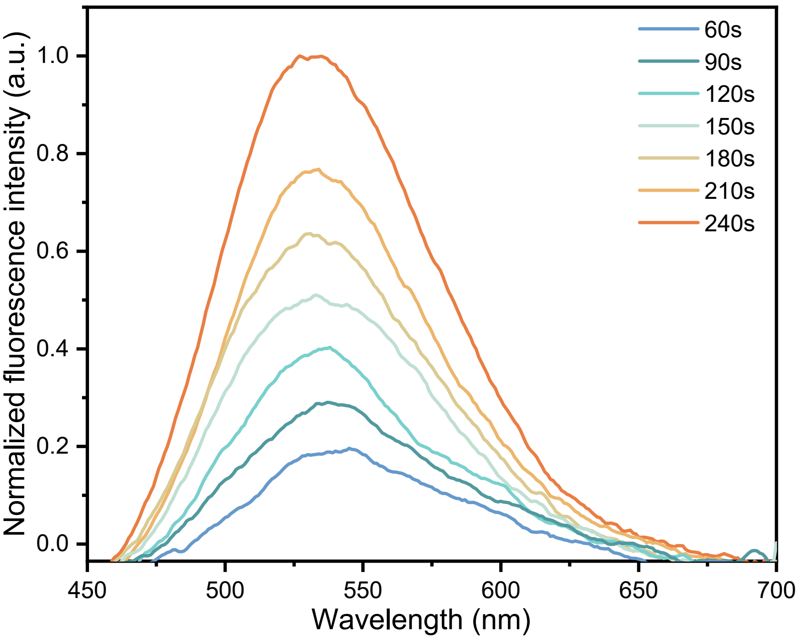


Figure S10b. Fluorescence kinetics measured using a Kn2+A1 mixture (Concentration = 1 mM)