# Supporting Information

# Fluorescence Switching 2-D Sheet Structure Formed by Self-Assembly of Cruciform Aromatic Amphiphiles

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# 1. General methods

**Materials**

All reactions were performed in oven-dried glassware under dry argon atmosphere unless otherwise mentioned. Toluene, tetrahydrofuran (THF), dichloromethane (DCM) and acetonitrile (ACN) was dried by solvent purification system (STEEMA Scientific Research Co.Itd, PURE-3). Ultrapure water (18.2 MΩ, 25 ℃) was obtained by water purification system (ELGA, PURELAB Quest). Other solvents and reagents were purchased from commercial suppliers and used without further purification unless otherwise mentioned. Thin-layer chromatography (TLC; Merck, silica gel 60 F254 0.25 mm) was used to monitor the reaction with visualization under ultraviolet light (254 and 365 nm) or by treating the plates with iodine, KMnO4 or phosphomolybdic acid followed by heating. The products were purified by flash column chromatography on silica gel (230-400 mesh). 1H NMR, 13C NMR, and NOESY spectra were obtained on Bruker AVANCE III 400, 500 or 600 MHz NMR spectrometers. Mass spectra were conducted on Agilent 6230B LC/TOF MS. High-performance liquid chromatography (HPLC) experiments were performed on Agilent 1260 Infinity II with YMC C4, C8, C18 HPLC column (250 x 4.6 mm I.D. S-5 μm, 12 nm) or Agilent EC-C18 HPLC column (150 x 4.6 mm I.D. S-4 μm). The fluorescence spectra were obtained from JASCO FP-8500 Fluorescence Spectrophotometer. The UV-Vis spectra were obtained from JASCO V-750 Spectrophotometer. Sonication was conducted in Branson Ultra Sonic Bath (Model 2800).

**TEM**

A drop of the sample solution was placed on a carbon-coated copper grid at ambient temperature. After 2 min, the solvent was removed using filter paper. Then, the grid was stained by depositing a drop of uranyl acetate aqueous solution (1.0 wt%). The dried specimen was observed using JEOL 2100 Plus instrument operated at 120 or 200 kV and the images were acquired with a SC 1000 CCD camera (Gatan, Inc.; Warrendale, PA). The data were analyzed using Digital Micrograph software.

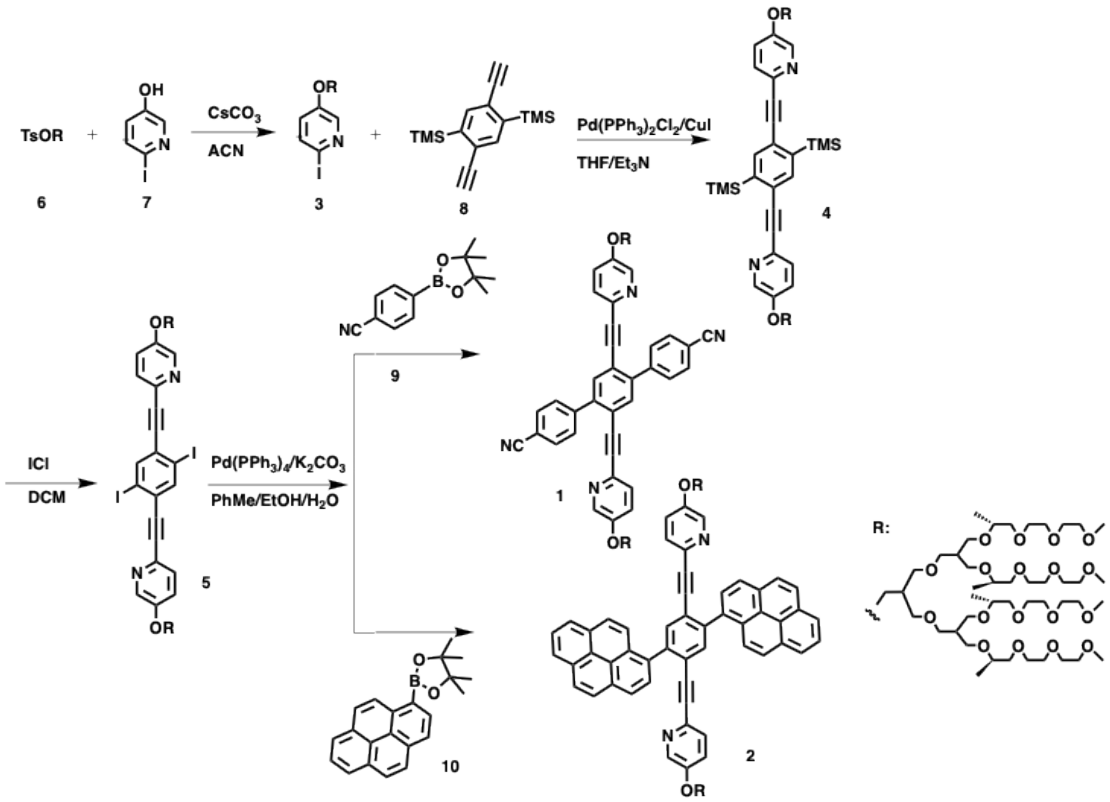
The cryogenic transmission electron microscopy (cryo-TEM) experiments were performed with a JEOL 2100 Plus instrument operated at 120 kV using a Gatan 626 cryoholder.

**Sample preparation**

**1** and **2** were first dissolved in the methanol(concentration:1mM). Then, take 10 microliters of each of the two samples and add them to two vials. Then, a certain amount of methanol and water was added gradually into the vials to form a methanol / water (60:340, v/v or 1:9 v/v) solution containing 25 μM or 50 μM **1** and **2**. The solution was subsequently conducted with sonication in ice bath for 15 min and stabilized for S1another 4 h at room temperature to form rigid **1** and **2** self-assembly before conducting the following experiments.

# 2. Synthesis of target molecule

### 2.1 Synthesis of amphiphilic 1 and 2

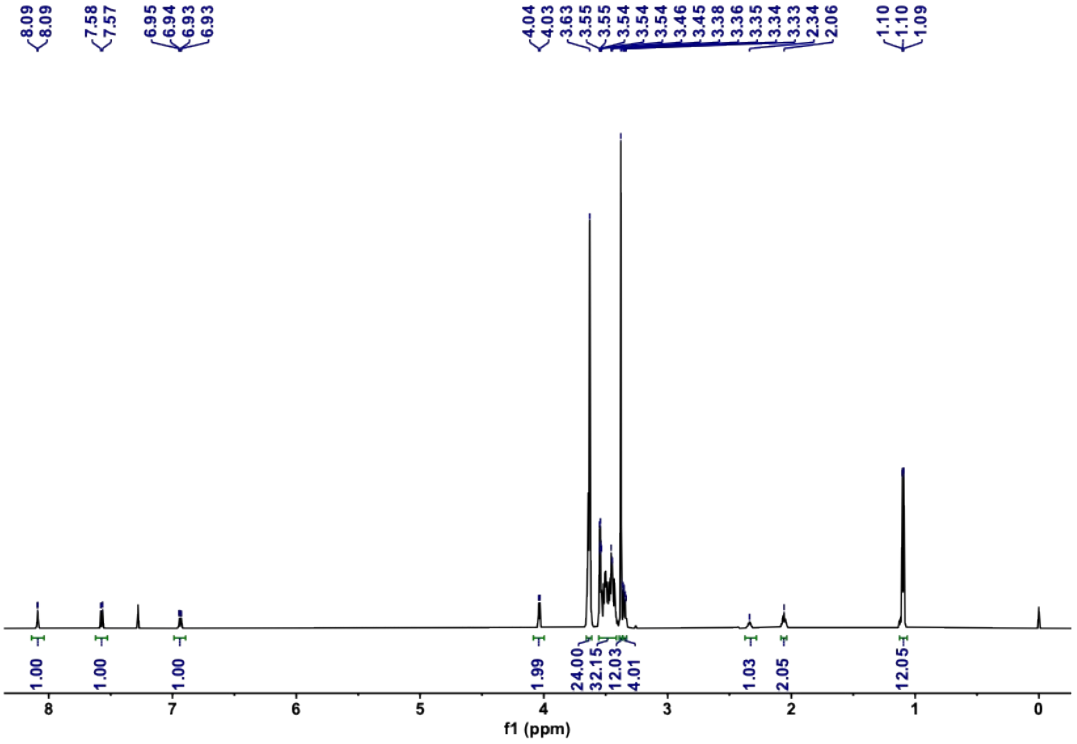



**Scheme S1.** Synthetic route for amphiphilic **1** and **2**.

**Compound 3.** Compound **6**[1] (2.0 mg, 1.86 mmol) and compound **7** (411 mg, 1.86 mmol) were dissolved in acetonitrile (80 mL) with cesium carbonate (3 g, 9.3 mmol). The mixture was stirred at 70 °C overnight under Ar atmosphere. After completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature and was extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtrated. The mixture was condensed under reduced pressure and the crude product was purified by silica gel flash column chromatography using ethyl acetate / methanol (97:3, v/v) as eluent to provide 95% yield as a light-yellow oil.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, J = 3.1 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 6.94 (dd, J = 8.6, 3.2 Hz, 1H), 4.04 (d, J = 5.6 Hz, 2H), 3.63 (m, 24H), 3.57 – 3.41 (m, 32fH), 3.39 – 3.33 (m, 16H), 2.37 – 2.30 (m, 1H), 2.09 – 2.03 (m, 2H), 1.15 – 1.01 (d, 12H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 155.60, 138.96, 134.64, 123.96, 105.56, 75.00, 74.76, 74.74, 71.90, 70.71, 70.58, 70.50, 69.56, 69.53, 68.90, 67.31, 66.65, 58.99, 40.72, 39.85, 17.07, 17.06. **MS** (ESI-TOF, m/z): $[M+Na]^+$ calcd. for $C_{49}H_{92}NaO_{19}$: 1148.5200, found 1148.5262.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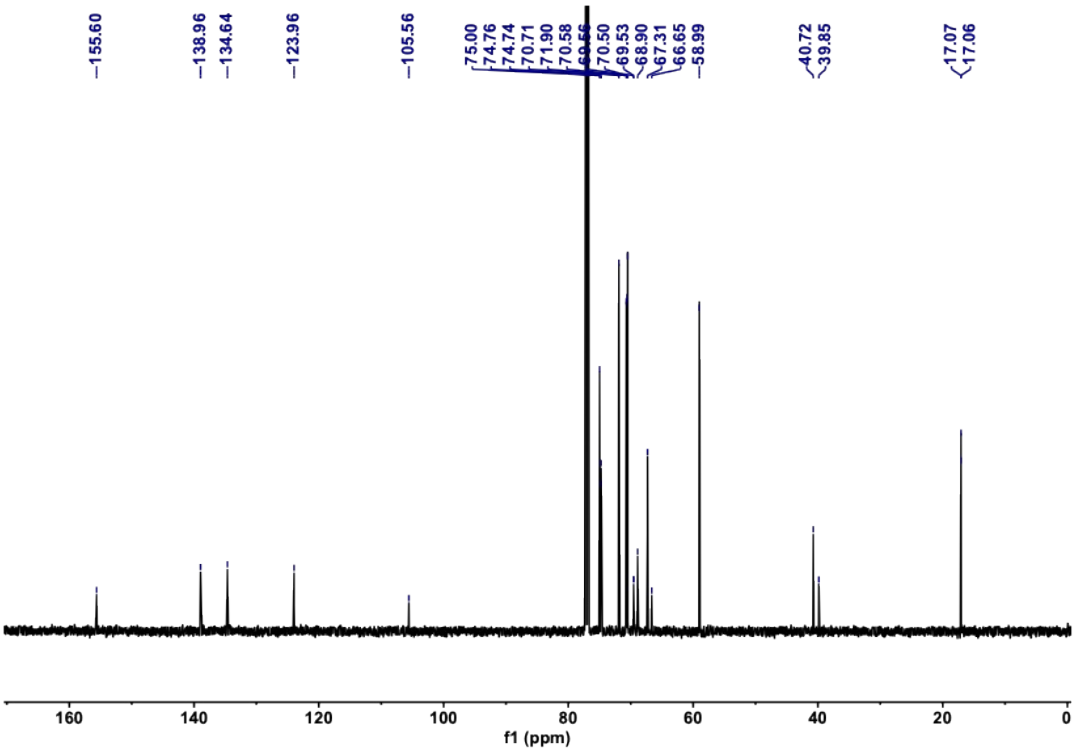
f1 (ppm)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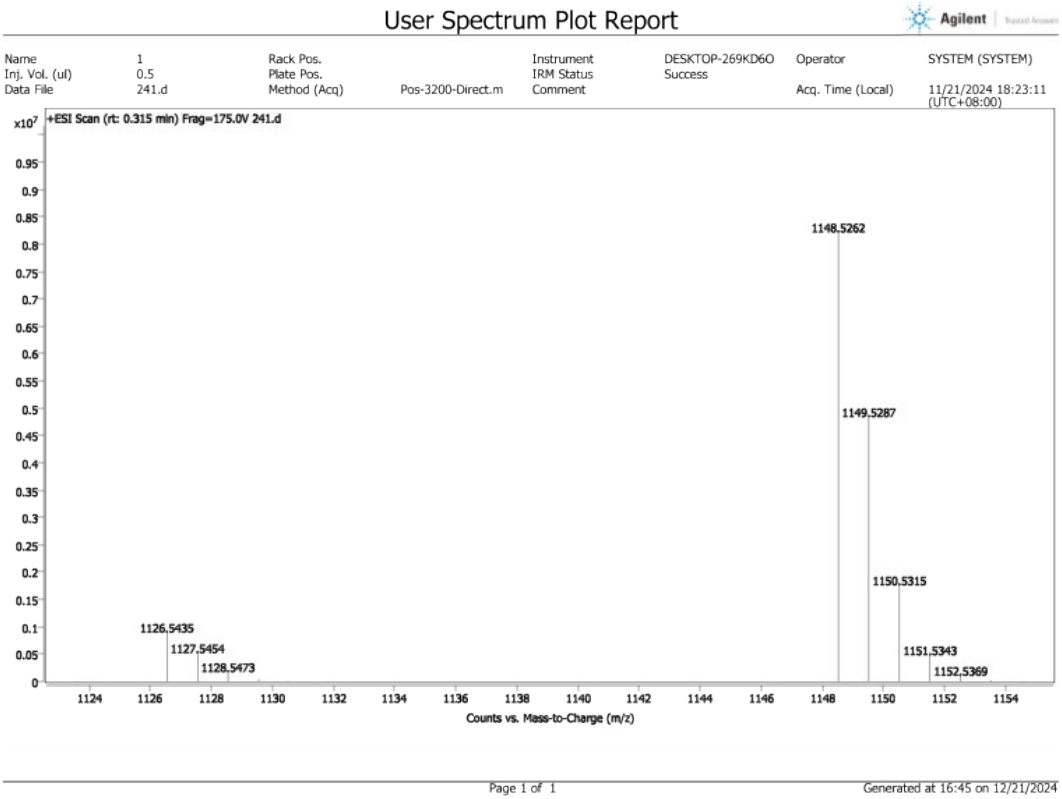


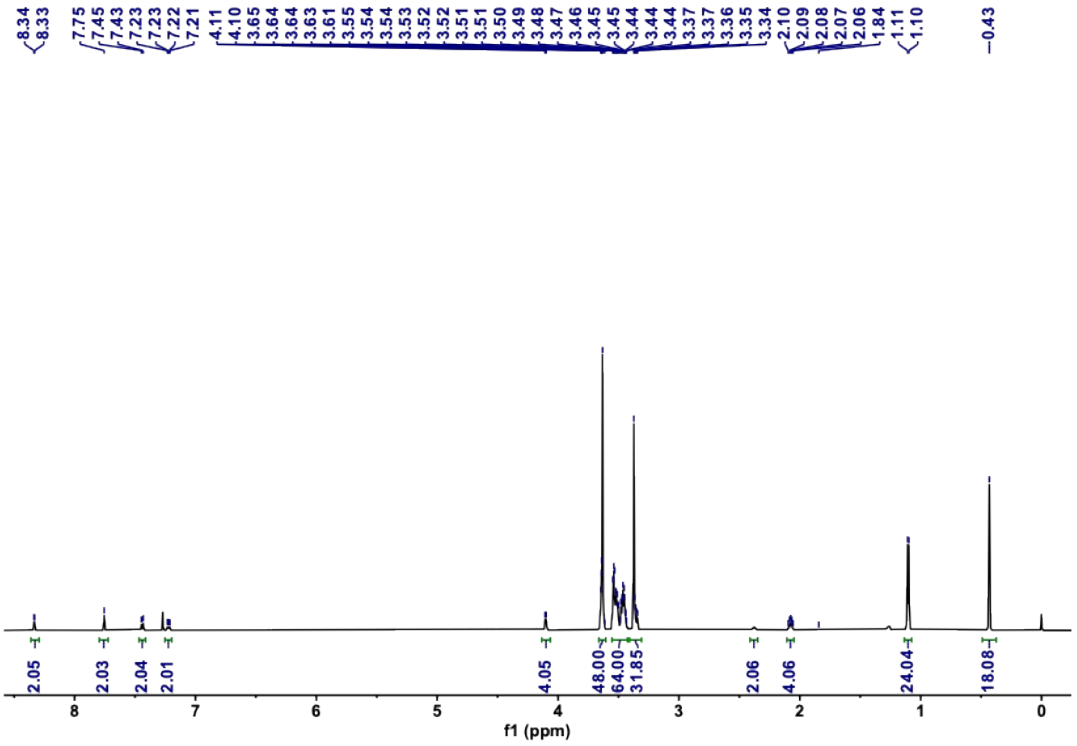

**Figure S1.** $^{1}H$ / $^{13}C$ NMR/ MS spectra of compound **3** in $CDCl_3$.

**Compound 4.** Compound **3** (1.0g, 0.89 mmol), compound **8**[2](122 mg, 0.45 mmol), $PdCl_2(PPh_3)_2$ (16 mg, 0.022 mmol), CuI (5 mg, 0.022 mmol) were dissolved in the mixture solution of 15 mL anhydrous TEA and 30 mL anhydrous toluene under Ar atmosphere. Then the solution was stirred and heated to 80 ℃ overnight. The completion of reaction was monitored by TLC. After cooling to room temperature, and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtrated. The mixture was condensed under reduced pressure and the crude product was purified by silica gel flash column chromatography using ethyl acetate / methanol (95:5, v/v) as eluent to provide 70% yield as a light-yellow oil.

**$^{1}H$ NMR** (600 MHz, $CDCl_3$) δ 8.33 (d, J = 2.9 Hz, 2H), 7.75 (s, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.22 (dd, J = 8.7, 2.9 Hz, 2H), 4.10 (d, J = 5.6 Hz, 4H), 3.66 – 3.62 (m, 48H), 3.56 – 3.42 (m, 64H), 3.38 – 3.33 (m, 32H), 2.38 (p, J = 5.9 Hz, 2H), 2.08 (p, J = 5.9 Hz, 4H), 1.10 (d, J = 6.2 Hz, 24H), 0.43 (s, 18H).

**$^{13}C$ NMR** (151 MHz, $CDCl_3$) δ 154.68, 142.98, 138.78, 138.09, 135.28, 127.38, 126.87, 120.84, 75.03, 74.80, 74.78, 71.93, 70.73, 70.61, 70.52, 69.60, 69.58, 68.98, 67.34, 66.60, 59.00, 40.76, 39.91, 31.87, 29.74, 29.28, 27.18, 17.08, -0.04, -1.07.

**MS** (ESI-TOF, m/z): $[M+2Na]^{2+}/2$ calcd. for $C_{114}H_{204}N_2NaO_{38}Si_2$: 1156.1723, found 1156.1756.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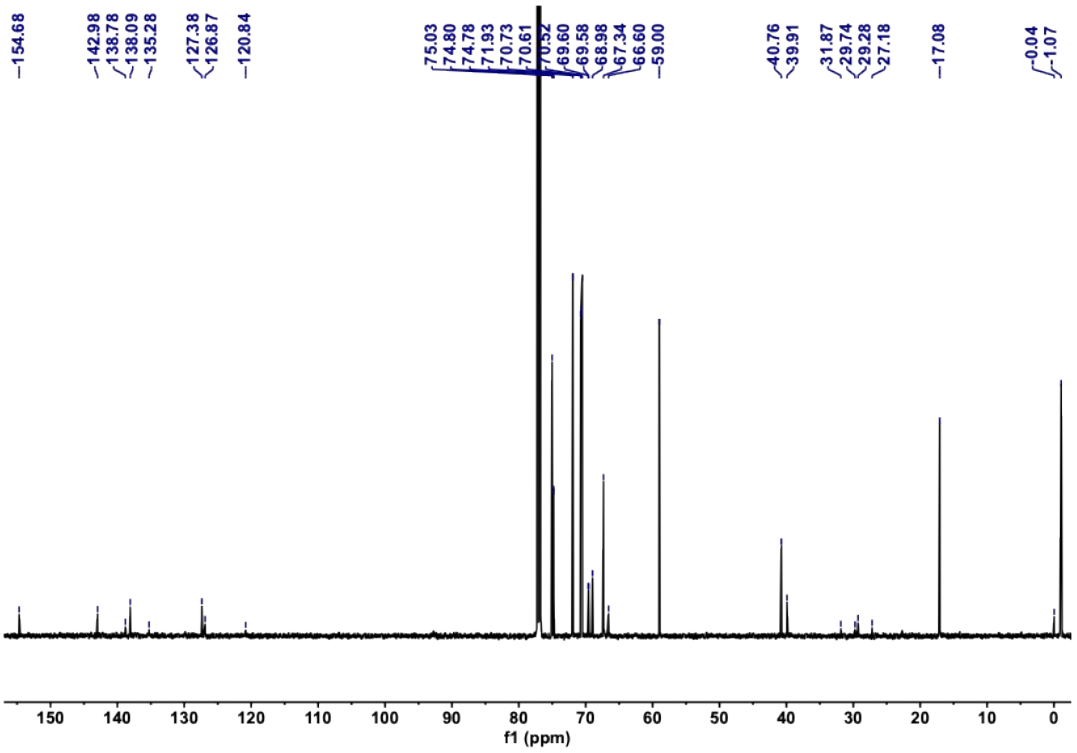
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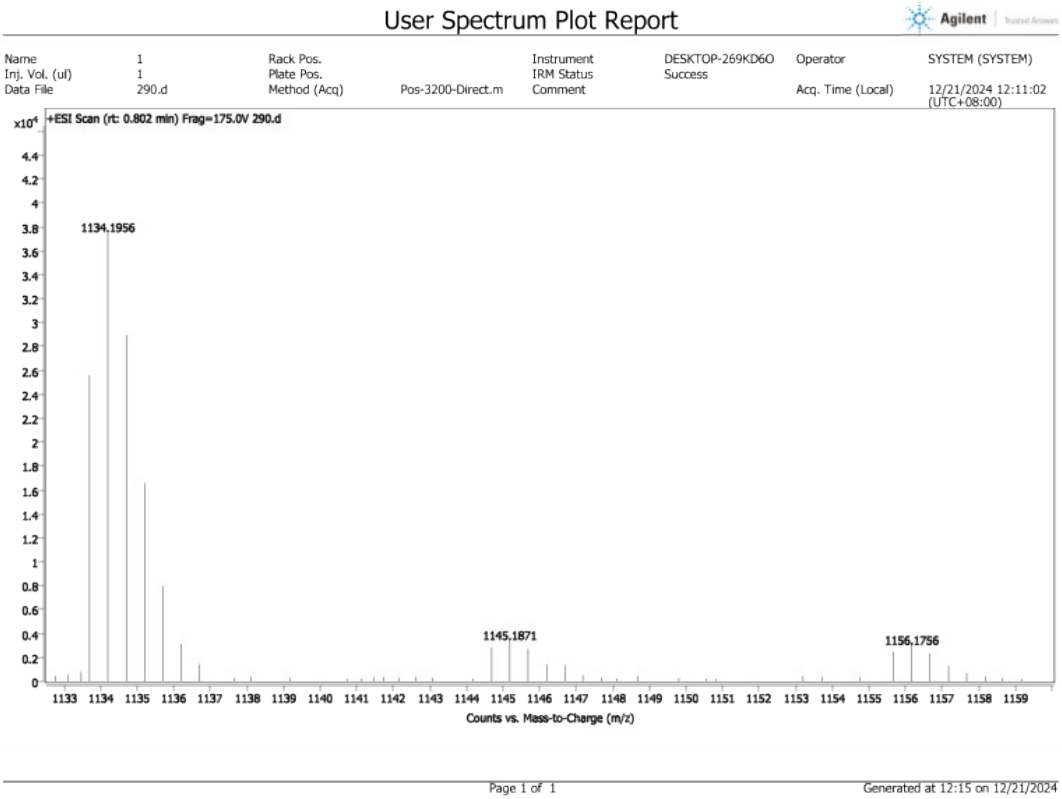


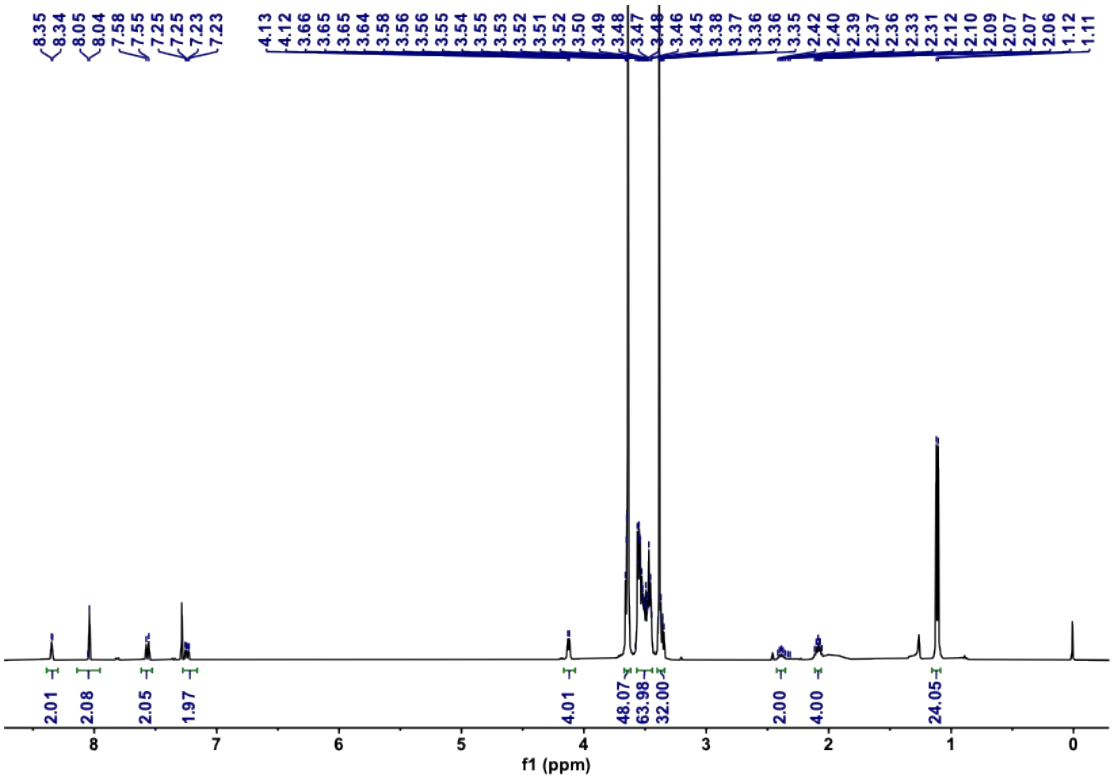

**Figure S2.** $^{1}H$ / $^{13}C$ NMR/ MS spectra of compound **4** in $CDCl_3$.

**Compound 5.** Compound **4** (200mg, 0.088 mmol) and ICl (72mg, 0.44 mmol) were dissolved in the dichloromethane under Ar atmosphere. Then the solution was stirred at -10 ℃ for 2 h. The completion of reaction was monitored by TLC. the resulting mixture was quenched by sodium sulfite, and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtrated. The mixture was condensed under reduced pressure and the crude product was purified by silica gel flash column chromatography using ethyl acetate / methanol (92:8, v/v) as eluent to provide 50% yield as a light-brown oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.9 Hz, 2H), 8.04 (s, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.24 (dd, J = 8.7, 2.9 Hz, 2H), 4.12 (d, J = 5.6 Hz, 4H), 3.68 – 3.60 (m, 48H), 3.59 – 3.43 (m, 64H), 3.40 – 3.33 (m, 32H), 2.42 – 2.34 (m, 2H), 2.13 – 2.04 (m, 4H), 1.11 (d, J = 6.1 Hz, 13H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 154.69, 142.99, 138.80, 138.10, 135.29, 127.39, 126.88, 120.86, 75.05, 74.81, 74.79, 71.94, 70.75, 70.62, 70.53, 69.62, 69.60, 68.99, 67.36, 66.62, 59.02, 40.77, 39.92, 31.89, 29.76, 29.30, 27.19, 17.09.

**MS** (ESI-TOF, m/z): $[M+2Na]^{2+}/2$ calcd. for $C_{108}H_{186}I_2N_2NaO_{38}$: 1210.0296, found 1210.0341.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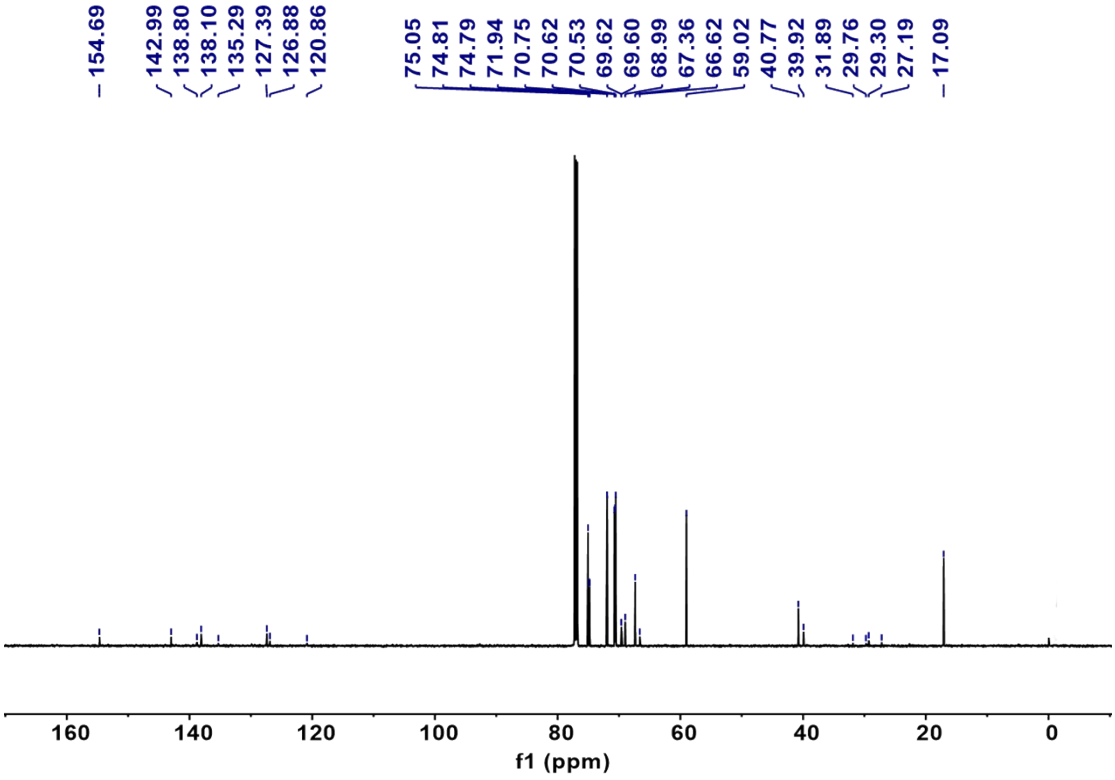
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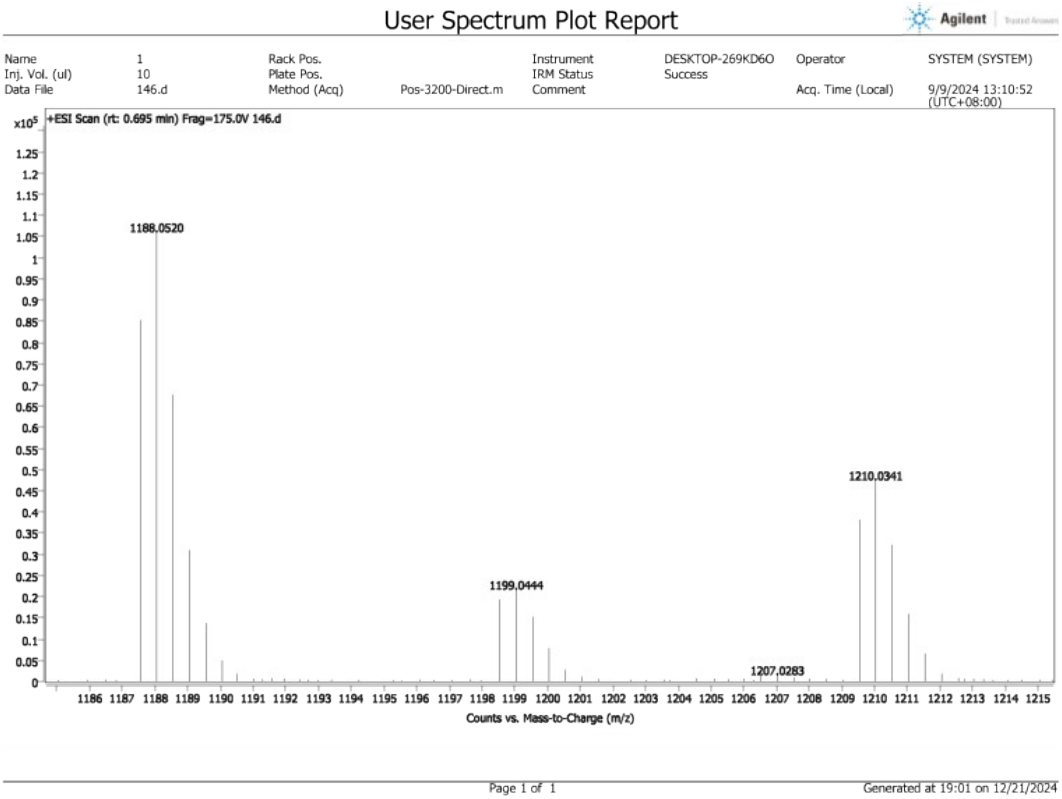


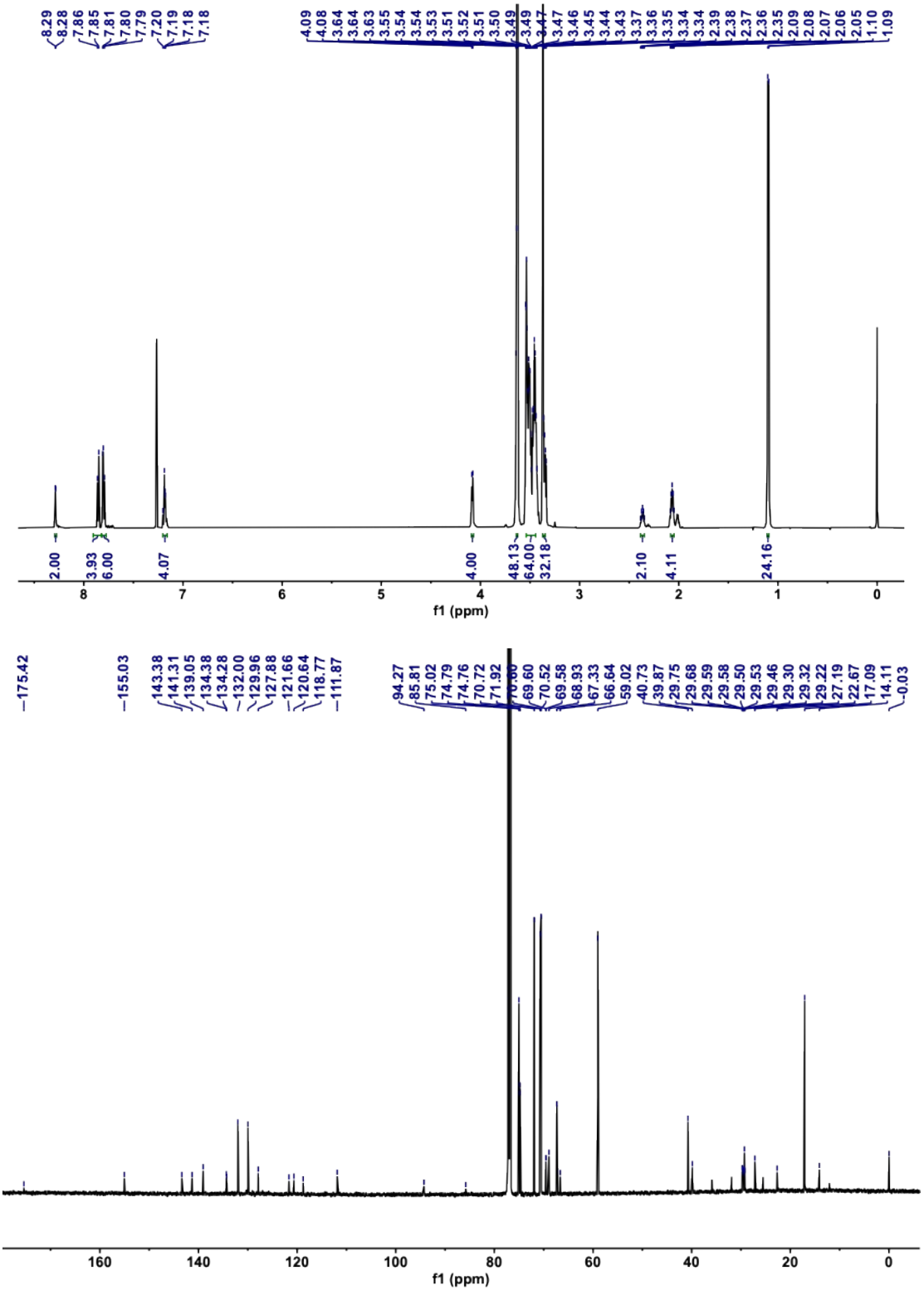

**Figure S3.** $^{1}H$ / $^{13}C$ NMR/ MS spectra of compound **5** in $CDCl_3$.

**Compound 1.** Compound **5** (30 mg, 0.012 mmol), compound **9** (11 mg, 0.048 mmol), $Pd(PPh_3)_4$ (2 mg, 0.0012 mmol), $K_2CO_3$ (2 M, 1 mL) were dissolved in 2mL tetrahydrofuran under Ar atmosphere. Then the solution was stirred at 80 ℃ overnight. The completion of reaction was monitored by TLC. and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtrated. The mixture was condensed under reduced pressure and the crude product was purified by silica gel flash column chromatography using ethyl acetate / methanol (92:8, v/v) as eluent to provide 90% yield as a light-yellow oil. The final purification was accomplished by reverse phase prep-HPLC (C8 column, ACN / H2O=75:25 v/v, 14.0 mL/min, retention time at around 17 min) to yield 60% as a light-yellow oil.

**$^{1}H$ NMR** (600 MHz, $CDCl_3$) δ 8.29 (d, J = 2.6 Hz, 2H), 7.86 (d, J = 8.1 Hz, 4H), 7.83 – 7.77 (m, 6H), 7.20 – 7.17 (m, 4H), 4.08 (d, J = 5.6 Hz, 4H), 3.56 – 3.60 (m, J = 5.1 Hz, 48H), 3.55 – 3.42 (m, 64H), 3.38 – 3.32 (m, 32H), 2.39 – 2.33 (m, 2H), 2.10 – 2.03 (m, 4H), 1.10 (d, J = 6.1 Hz, 24H).

**$^{13}C$ NMR** (151 MHz, $CDCl_3$) δ 175.42, 155.03, 143.38, 141.31, 139.05, 134.38, 134.28, 132.00, 129.96, 127.88, 121.66, 120.64, 118.77, 111.87, 94.27, 85.81, 75.02, 74.79, 74.76, 71.92, 70.72, 70.60, 70.52, 69.60, 69.58, 68.93, 67.33, 66.64, 59.02, 40.73, 39.87, 29.75, 29.68, 29.59, 29.58, 29.53, 29.50, 29.46, 29.32, 29.30, 29.22, 27.19, 22.67, 17.09, 14.11, -0.03.

**MS** (ESI-TOF, m/z): $[M+2Na]^{2+}/2$ calcd. for $C_{122}H_{194}N_4NaO_{38}$: 1185.1594, found 1185.1564.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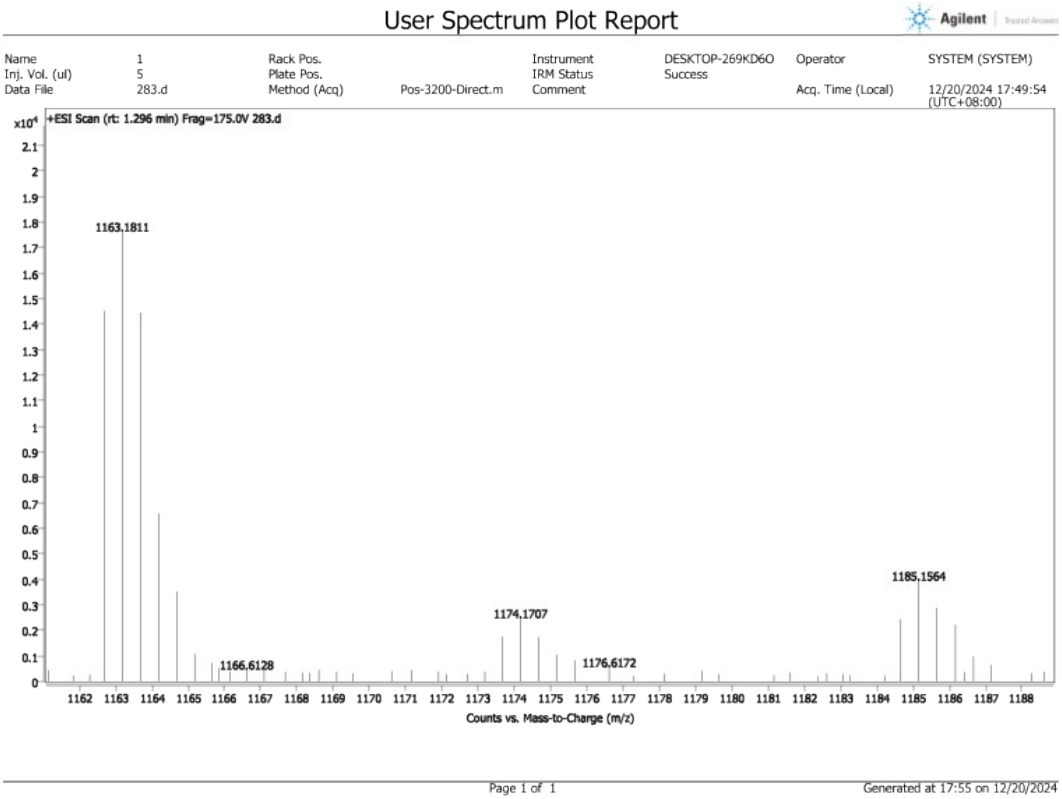



**Figure S4.** $^{1}H$ / $^{13}C$ NMR/ MS spectra of compound **1** in $CDCl_3$.

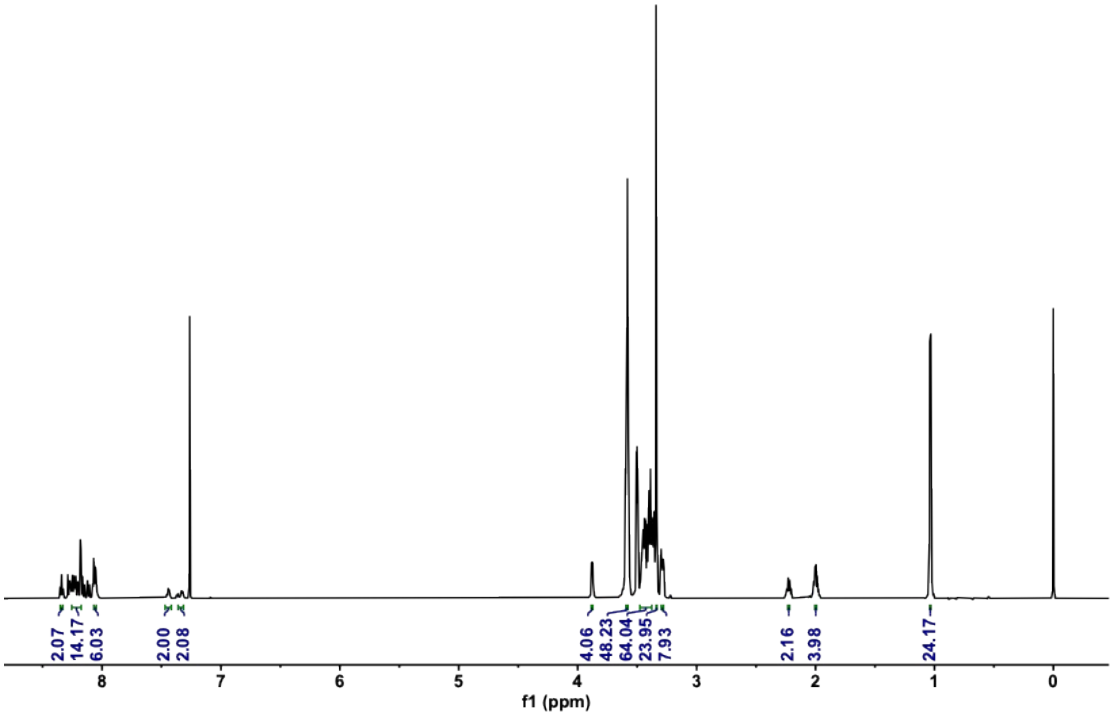
**Compound 2.** Compound **5** (30 mg, 0.012 mmol), compound **10**[3] (16 mg, 0.048 mmol), $Pd(PPh_3)_4$ (2 mg, 0.0012 mmol), $K_2CO_3$ (2 M, 1 mL) were dissolved in 2mL tetrahydrofuran under Ar atmosphere. Then the solution was stirred at 80 ℃ overnight. The completion of reaction was monitored by TLC. and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtrated. The mixture was condensed under reduced pressure and the crude product was purified by silica gel flash column chromatography using ethyl acetate / methanol (92:8, v/v) as eluent to provide 90% yield as a light-yellow oil. The final purification was accomplished by reverse phase prep-HPLC (C8 column, ACN / H2O=85:15 v/v, 14.0 mL/min, retention time at around 40 min) to yield 60% as a light-yellow oil.

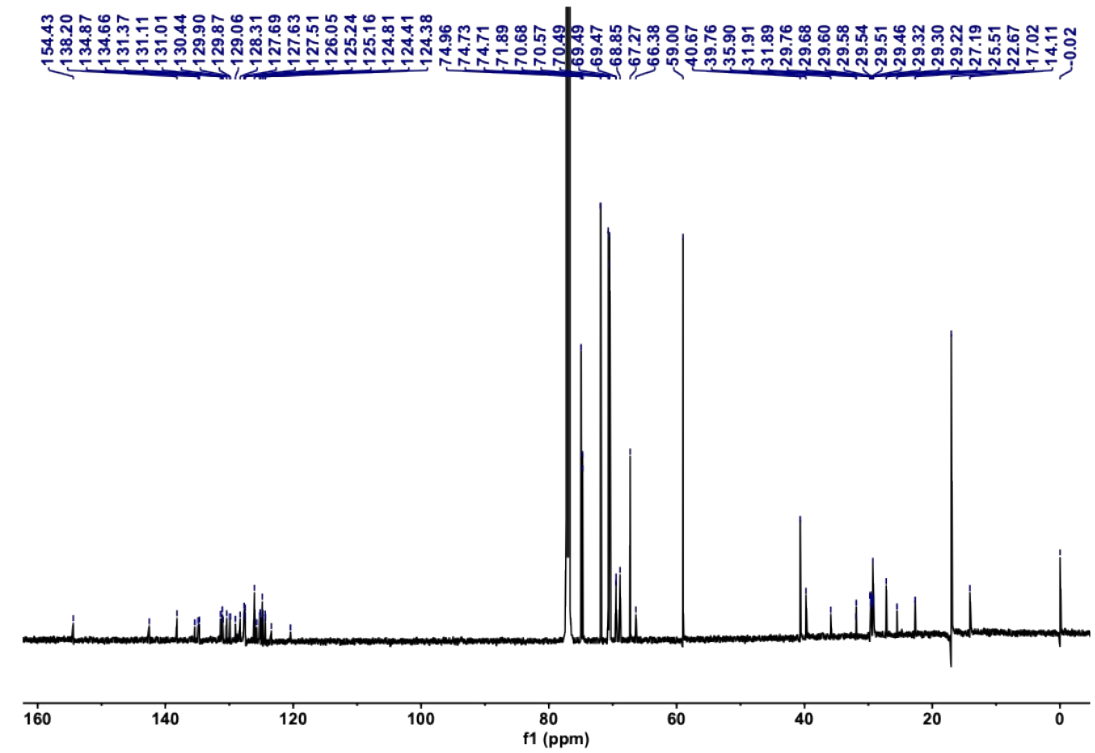
**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.34 (t, J = 7.4 Hz, 2H), 8.31 – 8.14 (m, 14H), 8.08–8.03 (m, 6H), 7.44 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 3.88 (d, J = 5.7 Hz, 4H), 3.61 – 3.55 (m, 48H), 3.52 – 3.48 (m, 16H), 3.47 – 3.32 (m, 48H), 3.30 – 3.26 (m, 6H), 2.26 – 2.19 (m, 2H), 2.03 – 1.95 (m, 4H), 1.06 – 1.01 (m, 24H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 154.43, 142.54, 138.20, 135.41, 134.87, 134.66, 131.37, 131.11, 131.01, 130.44, 129.90, 129.87, 129.06, 128.31, 127.69, 127.63, 127.51, 126.05, 125.73, 125.24, 125.16, 124.81, 124.41, 124.38, 123.40, 120.44, 74.96, 74.73, 74.71, 71.89, 70.68, 70.57, 70.49, 69.49, 69.47, 68.85, 67.27, 66.38, 59.00,

40.67, 39.76, 35.90, 31.91, 31.89, 29.76, 29.68, 29.60, 29.58, 29.54, 29.51, 29.46, 29.32, 29.30, 29.22, 27.19, 25.51, 22.67, 17.02, 14.11, -0.02.

**MS** (ESI-TOF, m/z): $[M+2Na]^{2+}/2$ calcd. for $C_{140}H_{204}N_2NaO_{38}$: 1284.1955, found 1284.1985.



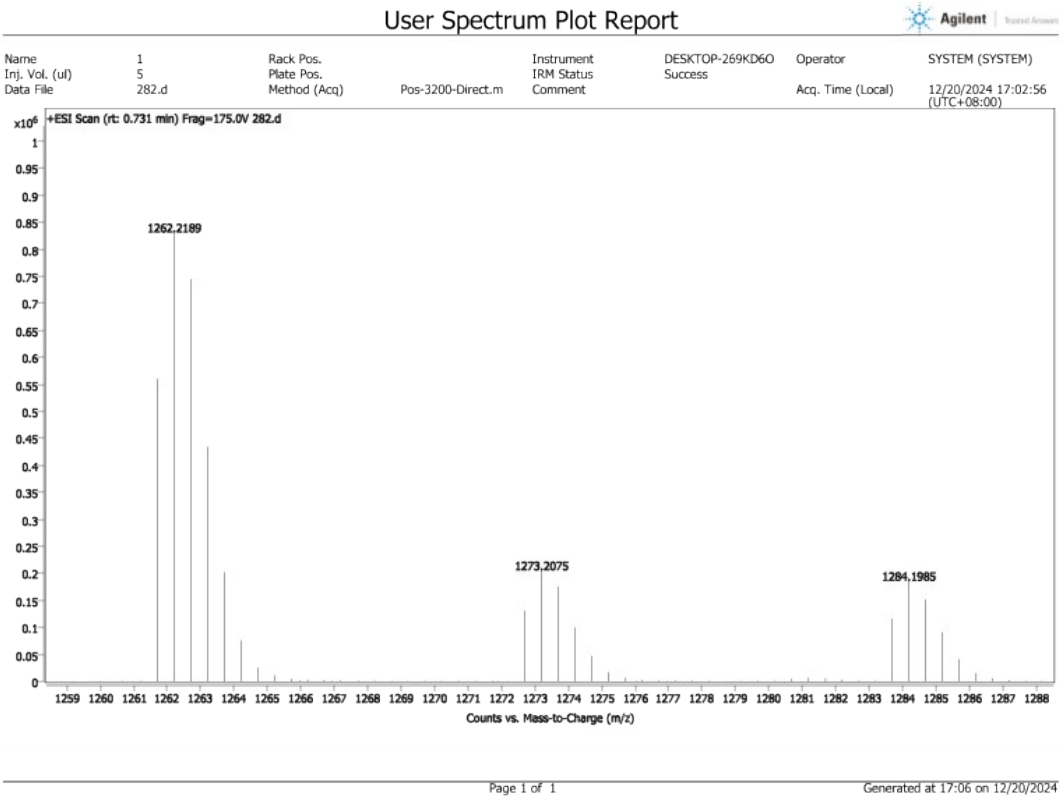



**Figure S5.** $^{1}H$ / $^{13}C$ NMR/ MS spectra of compound **2** in $CDCl_3$.

## 3. Morphology investigation

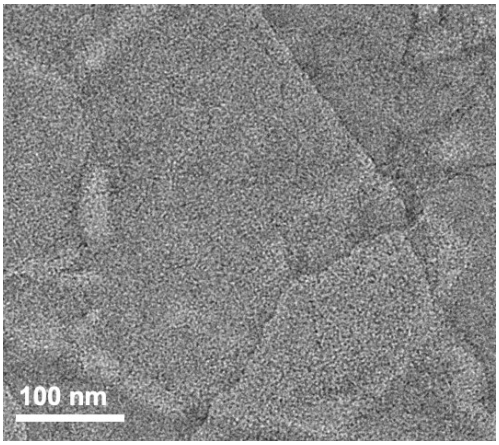



**Figure S6.** TEM image of **2** (25 μM) in MeOH/$H_2O$=3:17 v/v pH = 5.

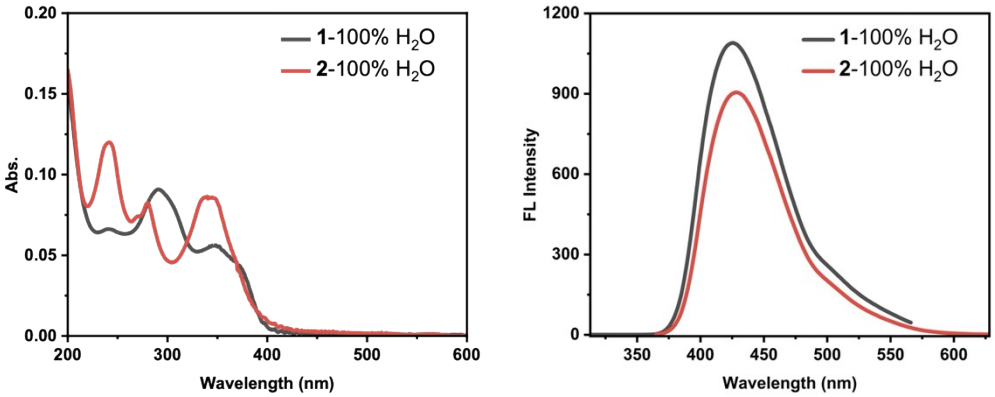



**Figure S7.** Fluorescence and UV-Vis of **1** and **2** (50 μM) in water.

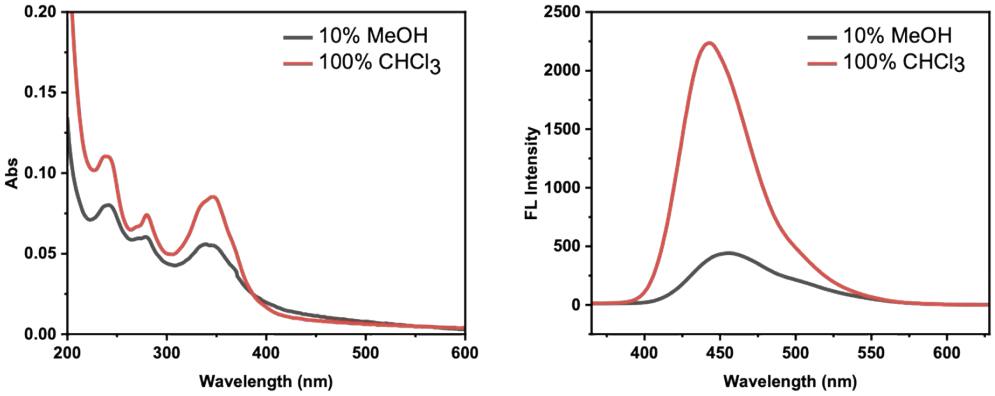



**Figure S8.** UV-Vis and Fluorescence spectrum of 1 (50 μM) in MeOH/$H_2O$=1:9 v/v and 100%$CHCl_3$.

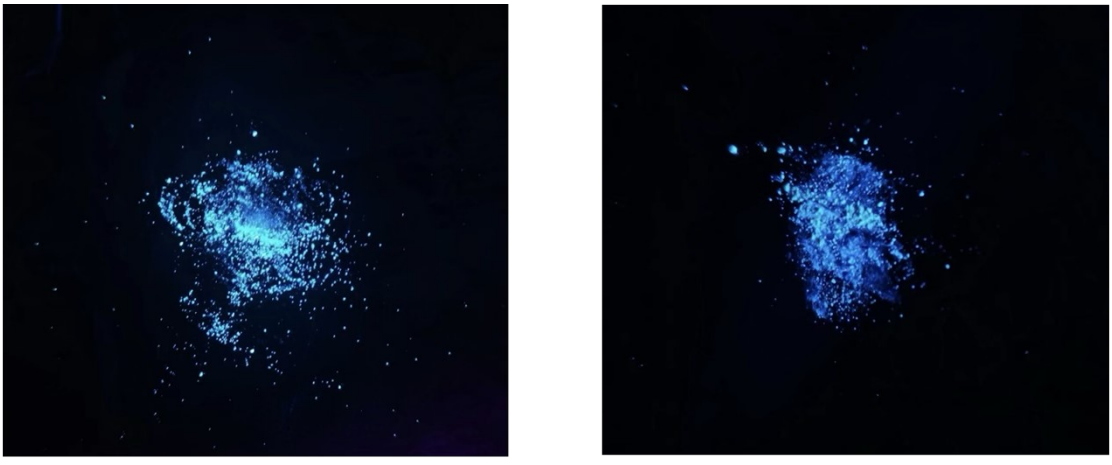
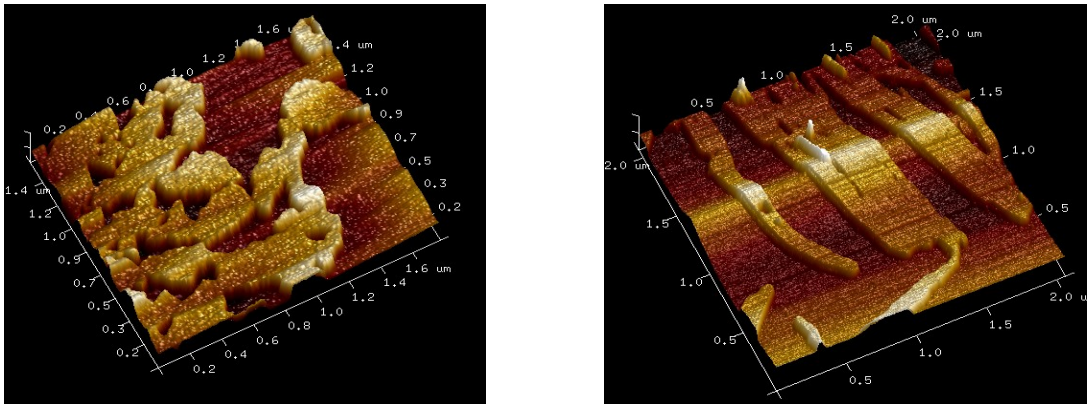



**Figure S9.** Fluorescence images of **1** and **2** (solid nano sheet) at neutral condition.



**1** **2**

**Figure S10.** 3-D AFM images of **1** and **2**.

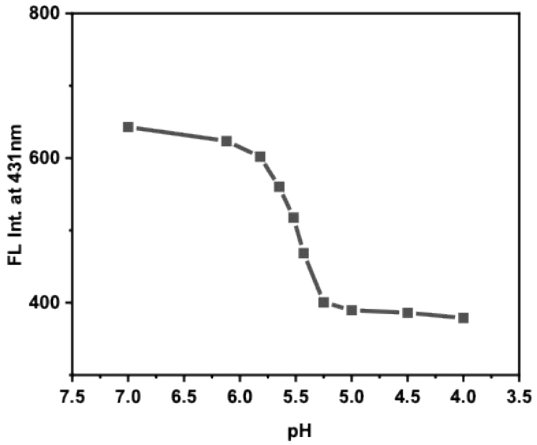



**Figure S11.** Fluorescence intensity of **1** decrease with acid increase.

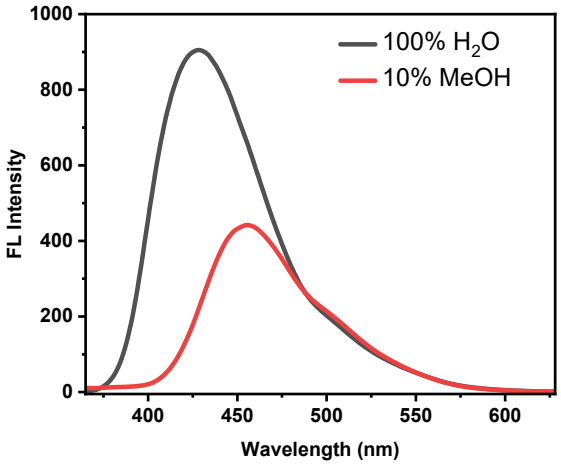



**Figure S12.** Fluorescence of **2** (50 μM) in MeOH/$H_2O$=9/1 v/v and water.

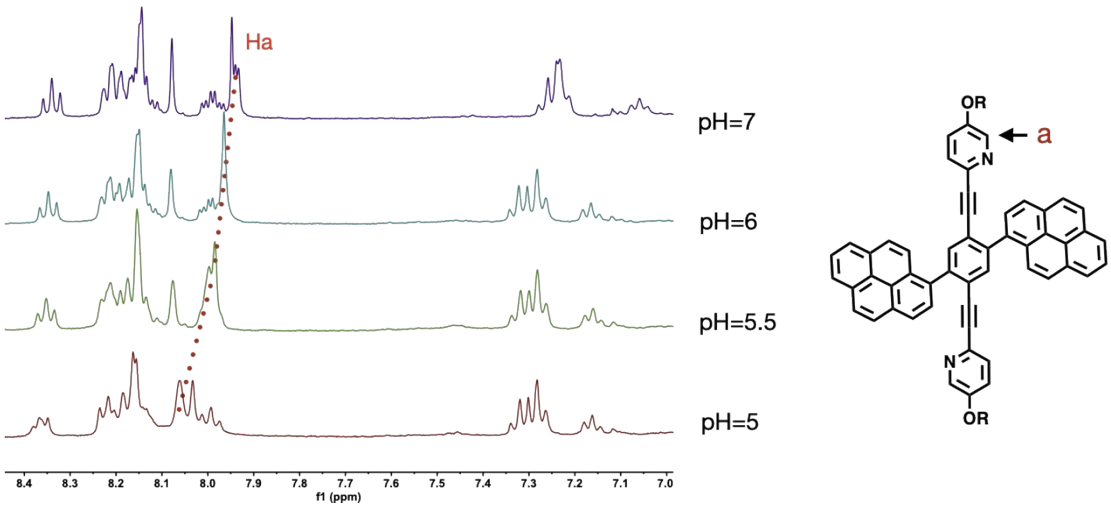



**Figure S13.** $^{1}$H NMR spectra of compound **2** in tetrahydrofuran-$d_8$ with different pH.

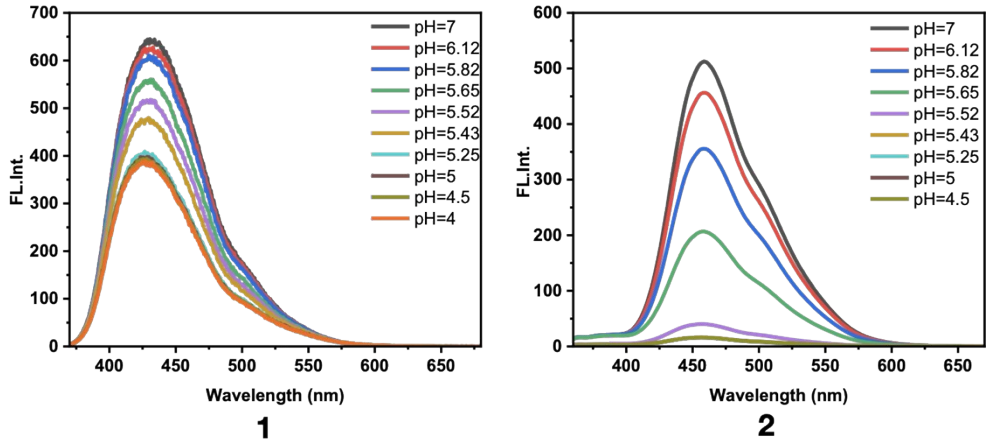



**Figure S14.** Fluorescence of **1** and **2** (50 μM) in MeOH/$H_2O$=9/1 v/v with pH decrease.

## References


1. Y. Wang, Y. Kim and M. Lee, *Angew. Chem. Int. Ed.*, 2016, **55**, 13122-13126.
2. D. Lehnherr, J. Gao, F. A. Hegmann and R. R. Tykwinski, *Org. Lett.*, 2008, **10**, 4779-4782.
3. S. Seifert, D. Schmidt, K. Shoyama and F. Wurthner, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 7595-7600.