# Electronic Supplementary Information (ESI)

# Self-Assembly of Propeller-Shaped Amphiphilic Molecules: Control over the Supramolecular Morphology and Photoproperties of Their Aggregates

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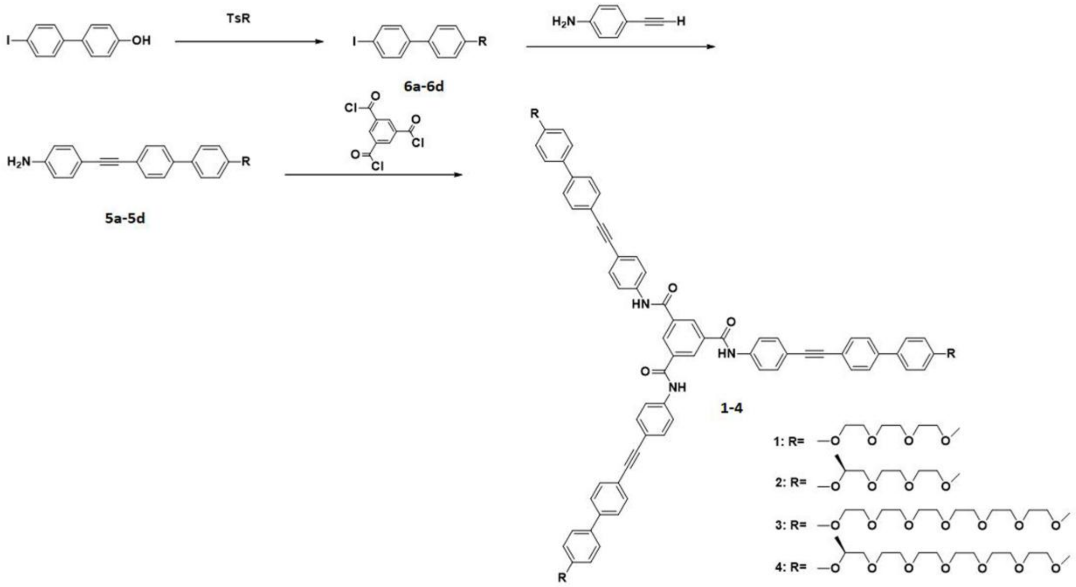
## 1. Techniques

Column chromatography filled silica gel (100-200 mesh) was used to achieve the separation of impurities. $^1$H-NMR (300 MHz) spectra were recorded in $CDCl_3$ or DMSO-d6 on a Bruker AM-300 instrument; $^{13}$C-NMR (125 MHz) spectra were recorded in $CDCl_3$ or DMSO-d6 on a Bruker AVANCE III-500M instrument; MALDI-TOF-MS was performed on a PerSeptive Biosystems Voyager-DESfTR instrument used 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as the matrix. ATR-IR spectra were obtained using a Bruker VERTEX 70 spectrometer. Under nitrogen atmosphere, a Perkin-Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions while heating and cooling rates were 5 °C min$^{-1}$. Phase transition was observed under a Zeiss polarizing microscope, which matched a Linkam heating stage. The SAXS measurements were performed at the 1W2A X-ray beamline at Beijing Synchrotron Radiation Facility (BSRF). UV-vis and FL spectra were obtained from a Shimadzu UV-1650PC spectrometer and a Hitachi F-4500 fluorescence spectrometer, respectively. CD experiments was performed by a Biologic PMS450. TEM images were collected with a JEOL 2100plus microscope.

## 2. Experimental

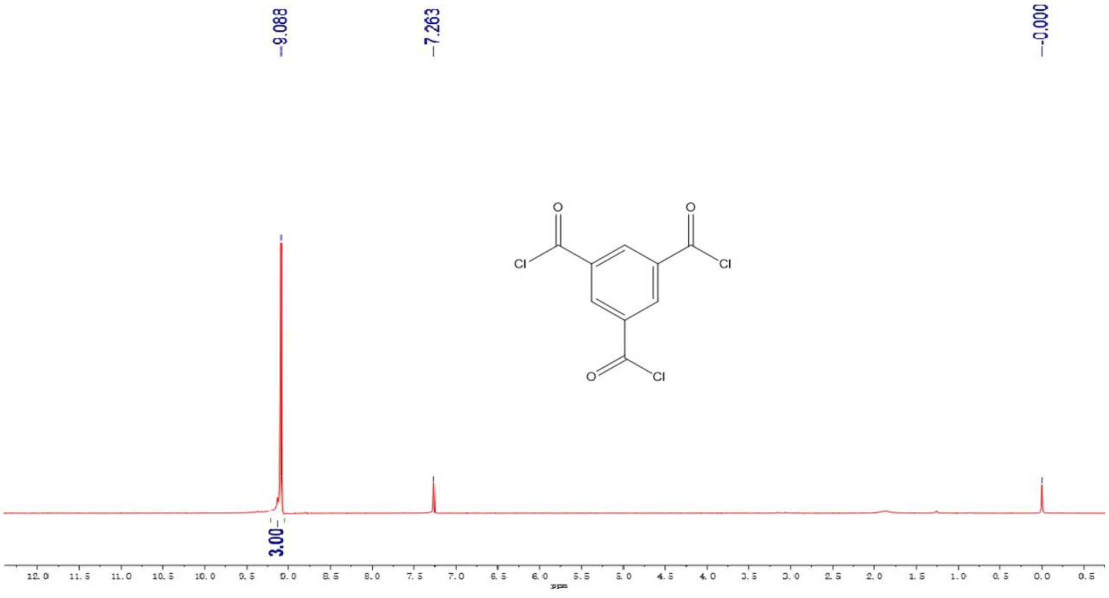


Scheme S1.Synthesis route of molecules **1-4**.

### 2.1 Synthesis of 1,3,5-benzenetricarboxylic acid chloride

Dissolved 1,3,5-Benzenetricarboxylic acid (0.15 g, 0.71 mmol) into 50 mL thionyl chloride, added 2 drops of DMF, refluxed 12 h then removed solvent, get yellow liquid (0.17g, yield 89.94%). Due to the efficiency of the reaction and the instability of product, this substance should be used immediately after generation.

$^1$H NMR (300 MHz; $CDCl_3$; $Me_4Si$) δ ppm: 9.09 (s, 3H)



### 2.2 Synthesis of compounds 1-4

All four compounds were synthesized by a similar procedure, here represent synthesis of molecule **1**.

Synthesis of compound **6a**: Compounds **6a-6d** were prepared according to the references described elsewhere.[S1] Dissolved triethylene glycol monomethyl ether (4.00 g, 24.36 mmol) and p-toluene sulfonyl chloride (10.00 g, 52.50 mmol) into 150 mL dichloromethane, added 15 mL pyridine, stired for 7.5 h at room temperature, further 20 mL water was added in the system and continue stired 1.5 h, then adjusted pH to acidic with hydrochloric acid, continue stired 1.5 h. Crude product was extracted by methylene chloride and ethyl acetate. Removed the solvent, purified the product through column chromatography, used dichloromethane as mobile phase. Concentrated the solution and obtained pale yellow oily liquid 7.08 g, yielded 91.35 %. Took 2.10 g (6.60 mmol) of it, with 4-Hydroxy-4'-iodobiphenyl (2.50 g, 8.45 mmol) and potassium carbonate (4.50 g, 32.60 mmol) dissolved into 200 mL acetonitrile, refluxed for 24 h. After cooled to room temperature, appropriate amount of water was put in the mixture, crude product was extracted by methylene chloride and ethyl acetate. Removed the solvent, purified the product through column chromatography, used dichloromethane as mobile phase. Concentrated the solution and obtained pale yellow solid (1.10 g, yield 35.00%).

Synthesis of compound **5a**: Compound **6a** (1.10 g, 2.49 mmol), tetrakis(triphenylphosphine)palladium (0) (0.10 g, 0.09 mmol), cuprous iodide (0.03 g, 0.16 mmol), triethylamine (15 mL) and tetrahydrofuran (30 mL) into a two-necked bottle, after refluxed under nitrogen atmosphere and protect from light, 2mL tetrahydrofuran solution of 4-ethynylaniline (0.32 g, 2.73 mmol) was added dropwise, then continue refluxed for 24 h. After cooled to room temperature, appropriate amount of water was put in the mixture, crude product was extracted by methylene chloride and ethyl acetate. Removed the solvent, purified the product through column chromatography, used dichloromethane, dichloromethane/ethyl acetate as mobile phase. Concentrated the solution and obtained pale yellow solid (0.80 g, yielded 81.97 %).

Synthesis of compound **1**: Compound **5a** (0.80 g, 1.85 mmol) and refined pyridine (150 μL, 1.85 mmol) were solved in 50mL tetrahydrofuran. Then the tetrahydrofuran solution of newly produced 1,3,5-benzenetricarboxylic acid chloride (0.15 g, 0.57 mmol) was slowly dropped in the mixture at 0 °C, under nitrogen atmosphere. Next kept whole system agitated at room temperature for 14 h. After added 20 mL $H_2O$, continue stirred 2 h. Evaporated THF, extracted the rough product from water by dichloromethane and ethyl acetate, collected the organic phase and remove the solvent after drying, finally purified it with silica-gel column chromatography, used dichloromethane, dichloromethane/methanol as mobile phase. Concentrated the solution and obtained yellow solid (0.35 g, yield 42.9 %).

Compound **1**：Yellow solid, $^1$H NMR (300 MHz; $CDCl_3$; $Me_4Si$) δ ppm: 8.82 (s, 3 H), 8.47 (s, 3 H), 7.66 (d, *J* = 6 Hz, 6 H), 7.57~7.47 (m, 24 H), 6.82 (d, *J* = 9 Hz, 6 H), 4.06 (t, *J* = 8.1 Hz, 6 H), 3.88 (t, *J* = 8.1 Hz, 6 H), 3.75 (t, *J* = 6 Hz, 6 H), 3.69~3.64 (m, 12 H), 3.54~3.51 (m, 6 H), 3.23 (s, 9 H). $^{13}$C NMR (125 MHz; DMSO-d6) δ ppm: 165.08, 158.98, 140.22, 139.82, 135.83, 132.53, 132.31, 131.92, 128.26, 126.78, 121.13, 120.73, 118.03, 115.51, 90.45, 89.43, 71.75, 70.43, 70.28, 70.08, 69.41, 67.73, 58.53. ATR-IR (neat, $cm^{-1}$): 3302, 2923, 2851, 1680, 1588, 1511, 1246, 1102, 821; MALDI-TOF-MS, found $[M]^+$ 1449.69, $[M+Na]^+$ 1472.63, $[M+K]^+$ 1488.85, molecular formula $C_{90}H_{87}N_3O_{15}$ requires $[M]^+$ 1449.61, $[M+Na]^+$ 1472.60, $[M+K]^+$ 1488.57 .

Compound **2**: Pale yellow solid, $^1$H NMR (300 MHz; DMSO-d6; $Me_4Si$) δ ppm: 10.81 (s, 3 H), 8.76 (s, 3 H), 7.94 (d, *J* = 6 Hz, 6 H), 7.71~7.59 (m, 24 H), 7.06 (d, *J* = 9 Hz, 6 H), 4.70~4.64 (m, 3 H), 3.64~3.56 (m, 12 H), 3.54~3.50 (m, 12 H), 3.44~3.40 (m, 6 H), 3.23 (s, 9 H), 1.25 (d, *J* = 6 Hz, 9 H). $^{13}$C NMR (125 MHz; $CDCl_3$) δ ppm: 164.18, 157.20, 140.07, 138.10, 135.40, 132.71, 132.47, 132.04, 129.82, 127.99, 127.91, 126.30, 121.64, 119.96, 119.34, 115.90, 89.83, 89.33, 74.67, 72.76, 71.74, 70.94, 70.53, 58.81, 16.54. ATR-IR (neat, $cm^{-1}$): 3302, 2923, 2862, 1680, 1588, 1511, 1240, 1087, 821; MALDI-TOF-MS, found $[M]^+$ 1491.06, $[M+Na]^+$ 1514.20, molecular formula $C_{93}H_{93}N_3O_{15}$ requires $[M]^+$ 1491.66, $[M+Na]^+$ 1514.65.

Compound **3**: Pale yellow slightly sticky solid, $^1$H NMR (300 MHz; $CDCl_3$; $Me_4Si$) δppm: 9.10 (s, 3 H), 8.61 (s, 3 H), 7.74 (d, J = 9 Hz, 6 H), 7.54~7.49 (m, 24 H), 6.86 (d, J = 9 Hz, 6 H), 4.05

(t,J = 9 Hz, 6 H), 3.84 (t, J = 9 Hz, 6 H), 3.71 (t, J = 6 Hz, 6 H), 3.66~3.63 (m, 18 H), 3.59~3.49 (m, 36 H), 3.33 (s, 9 H). $^{13}$C NMR (125 MHz; $CDCl_3$) δ ppm: 164.47, 158.37, 140.16, 138.31, 135.63, 132.86, 132.41, 131.99, 127.91, 126.38, 121.55, 120.01, 119.23, 114.84, 89.76, 89.34, 71.82, 70.77, 70.57, 70.52, 70.49, 70.44, 69.77, 67.31, 58.95. ATR-IR (neat, cm$^{-1}$): 3312, 2918, 2867, 1675, 1588, 1511, 1240, 1092, 821; MALDI-TOF-MS, found $[M+Na]^+$ 1870.23, molecular formula $C_{108}H_{123}N_3O_{24}$ requires $[M+Na]^+$ 1870.13.

Compound **4**: Brownish yellow transparent sticky solid, $^1$H NMR (300 MHz; $CDCl_3$; $Me_4Si$) δ ppm: 9.13 (s, 3 H), 8.64 (s, 3 H), 7.76 (d, *J* = 9 Hz, 6 H), 7.56~7.46 (m, 24 H), 7.86 (d, *J* = 9 Hz, 6 H), 4.59~4.51 (m, 3 H), 3.76~3.65 (m, 14 H), 3.64~3.54 (m, 44 H), 3.52~3.50 (m, 8 H), 3.34 (s, 9 H), 1.28(d, *J* = 6 Hz, 9 H). $^{13}$C NMR (125 MHz; $CDCl_3$) δ ppm: 164.39, 157.43, 140.26, 138.32, 135.67, 132.78, 132.44, 132.00, 129.59, 127.97, 126.39, 121.53, 119.98, 119.24, 116.06, 89.75, 89.34, 71.84, 70.51, 70.49, 70.46, 58.96, 16.72. ATR-IR (neat, cm$^{-1}$): 3317, 2923, 2867, 1675, 1588, 1511, 1240, 1087, 821; MALDI-TOF-MS, found $[M+Na]^+$ 1912.20, molecular formula $C_{111}H_{129}N_3O_{24}$ requires $[M+Na]^+$ 1912.21.

Substances and solvents mentioned in the synthesis method were used as received. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen.

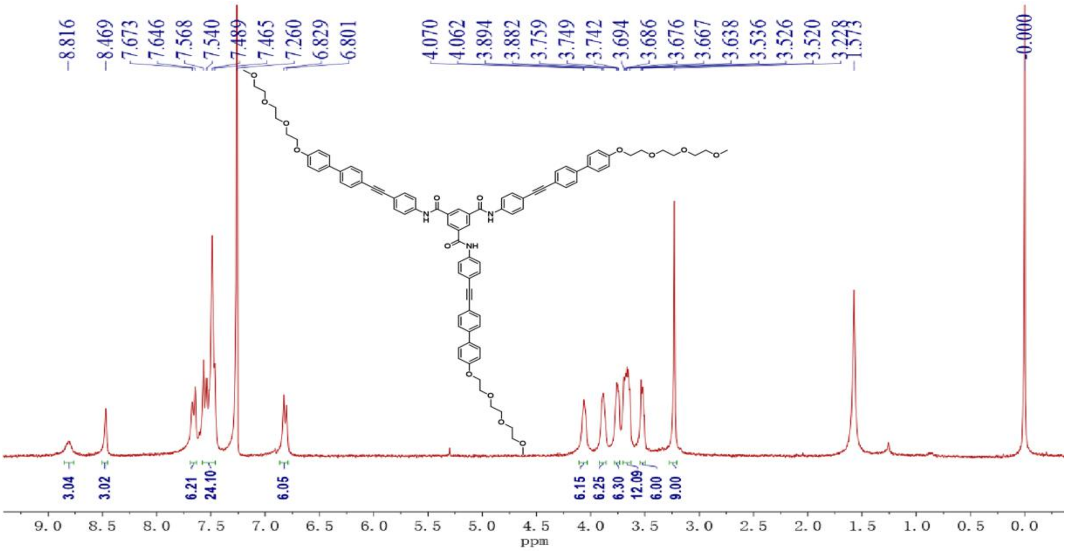


Figure S1. $^1$H-NMR spectrum of molecule **1** in $CDCl_3$.

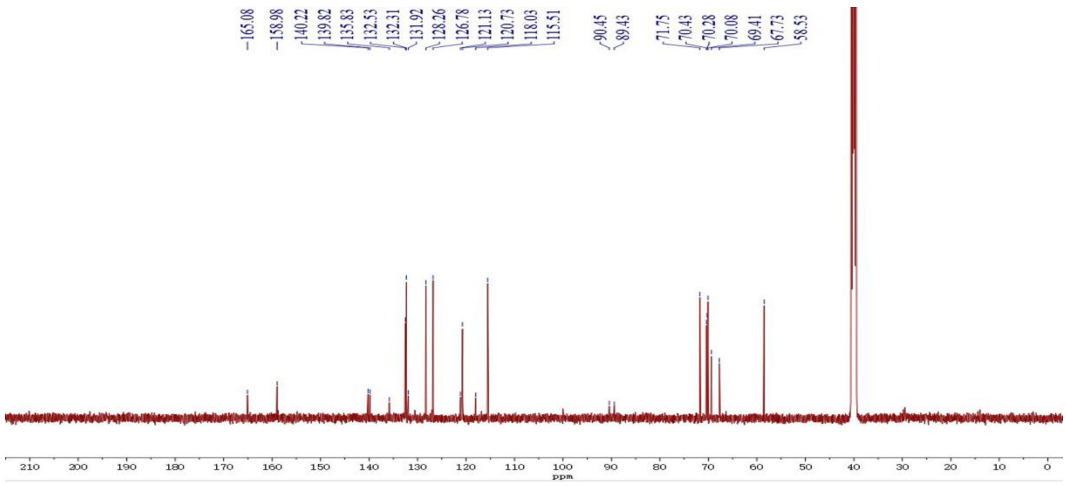


Figure S2. $^{13}$C-NMR spectrum of molecule **1** in DMSO-d6.

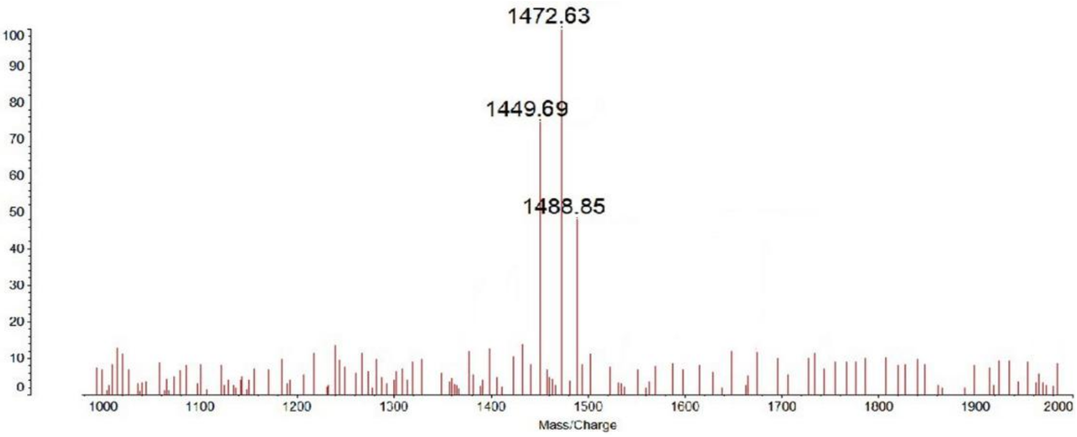


Figure S3. MALDI-TOF mass spectrum of molecule **1**.

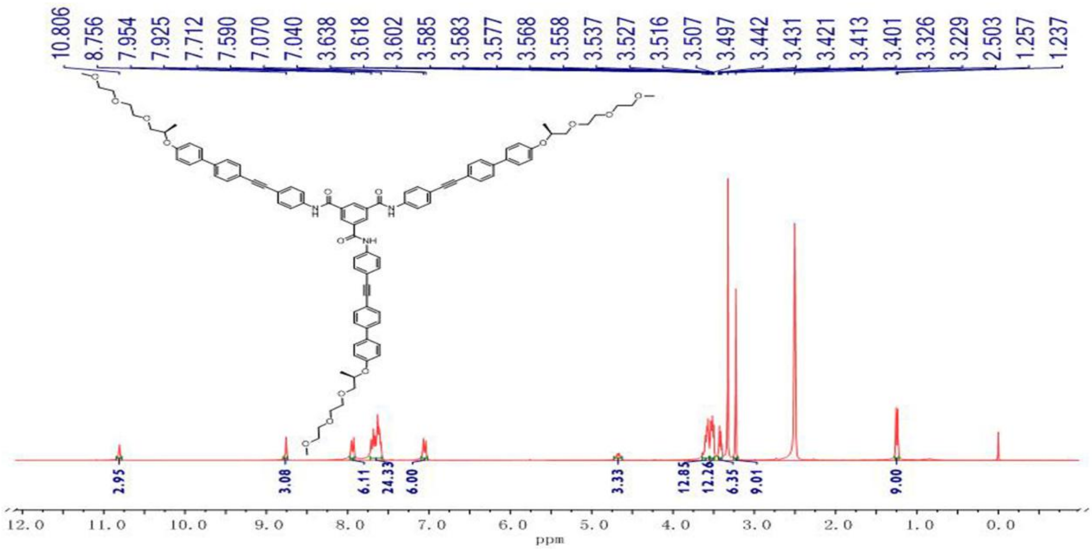


Figure S4. $^1$H-NMR spectrum of molecule **2** in DMSO-d6.

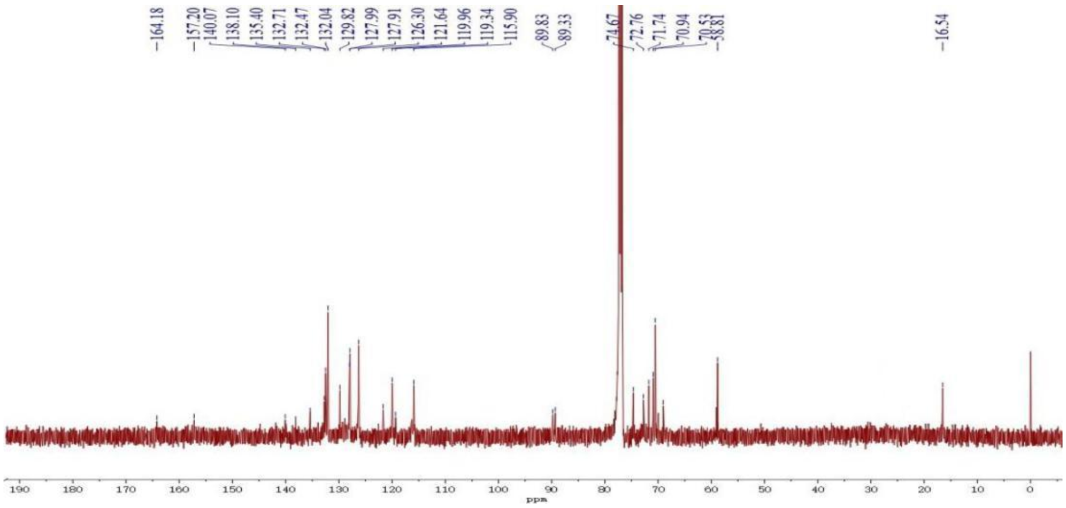


Figure S5. $^{13}$C-NMR spectrum of molecule **2** in CDCl$_3$.

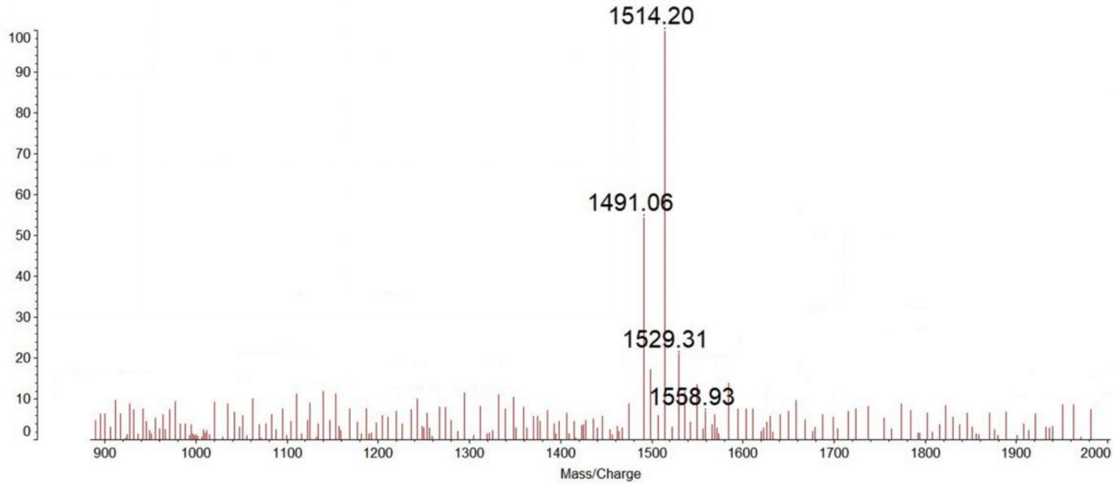


Figure S6. MALDI-TOF mass spectrum of molecule **2**.

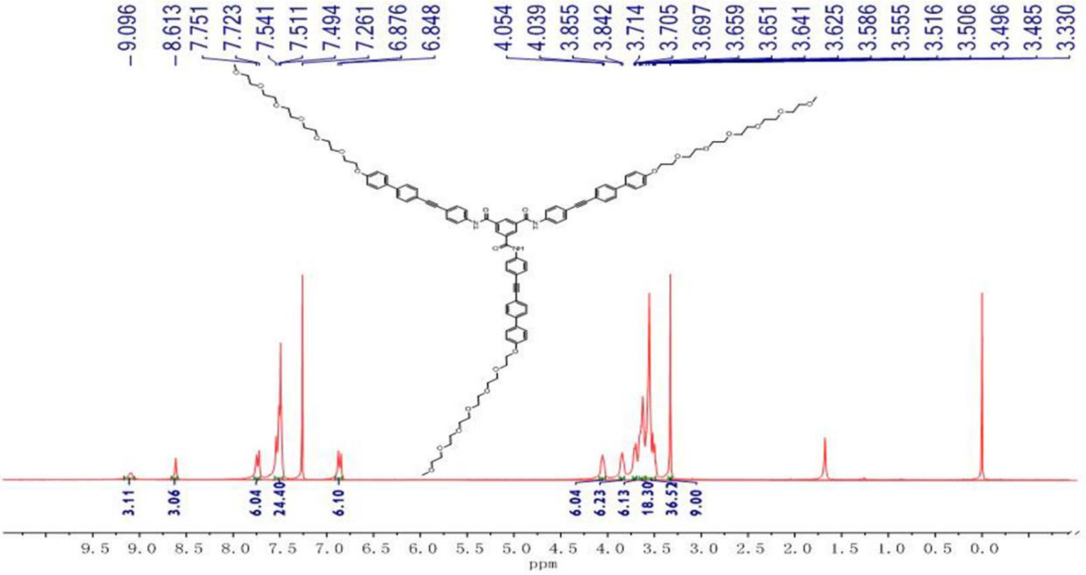


Figure S7. $^{1}$H-NMR spectrum of molecule **3** in $CDCl_3$.

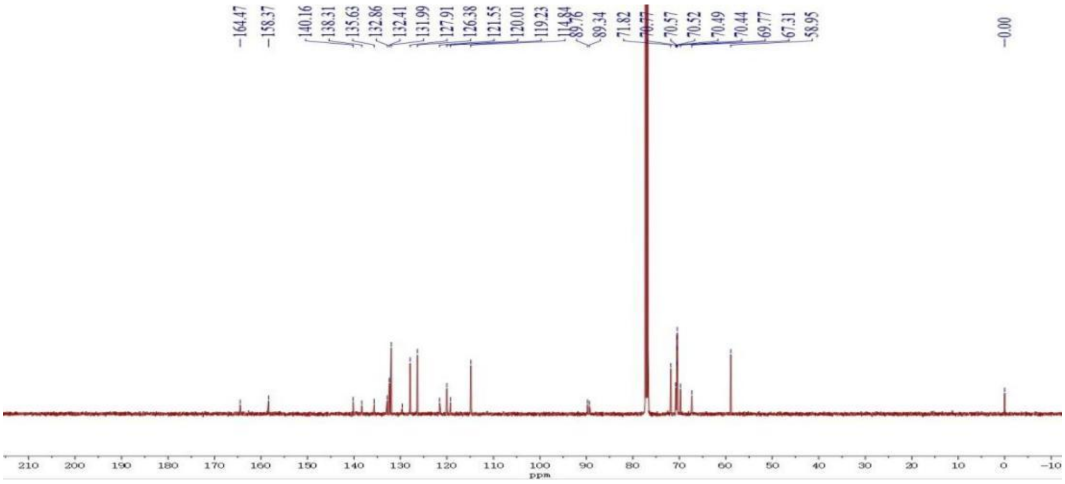


Figure S8. $^{13}$C-NMR spectrum of molecule **3** in $CDCl_3$.

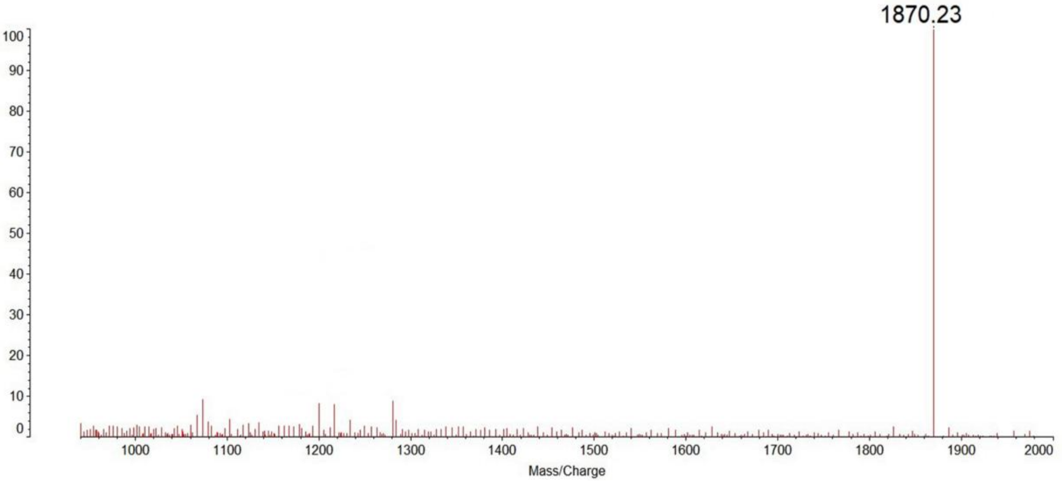


Figure S9. MALDI-TOF mass spectrum of molecule **3**.

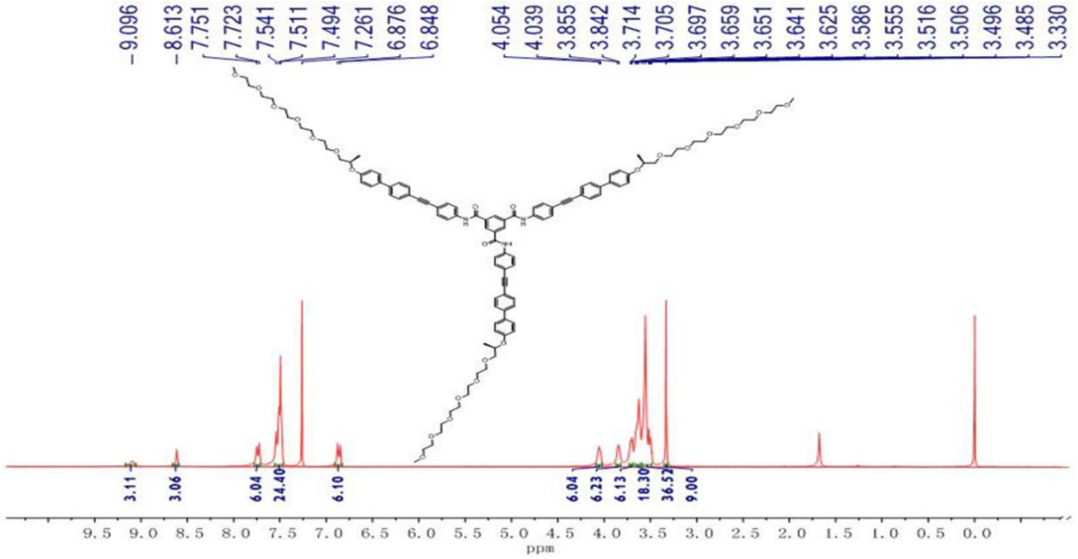


Figure S10. $^1$H-NMR spectrum of molecule **4** in CDCl$_3$.

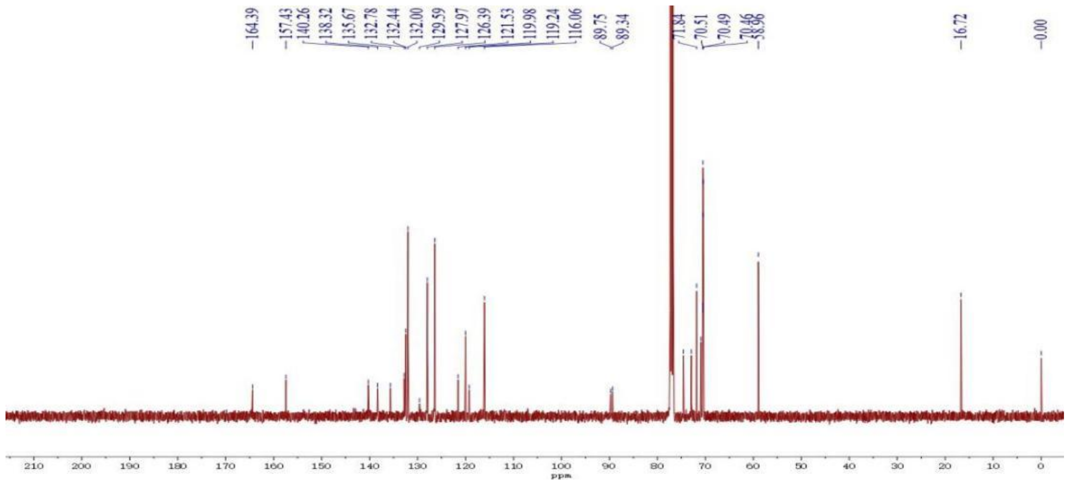


Figure S11. $^{13}$C-NMR spectrum of molecule **4** in CDCl$_3$.

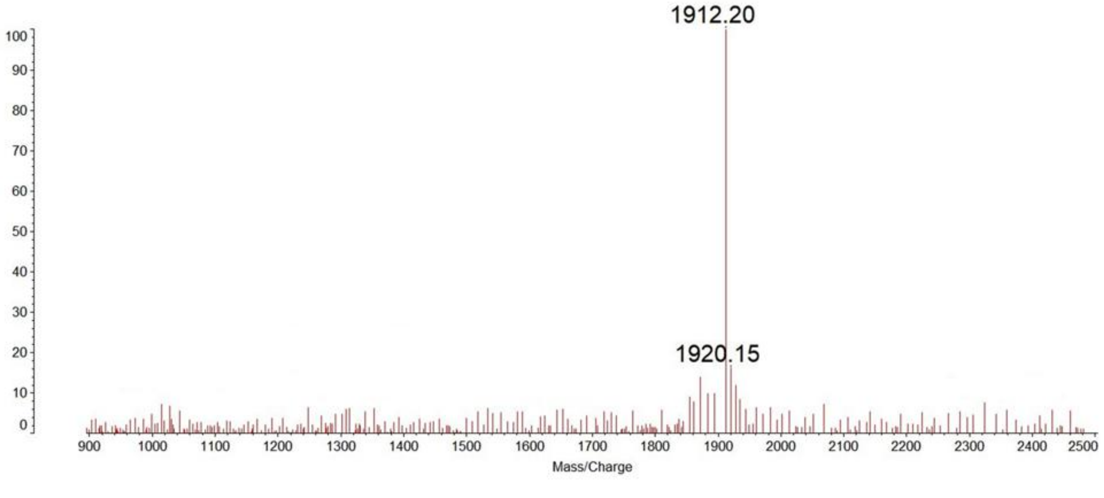


Figure S12. MALDI-TOF mass spectrum of molecule **4**.

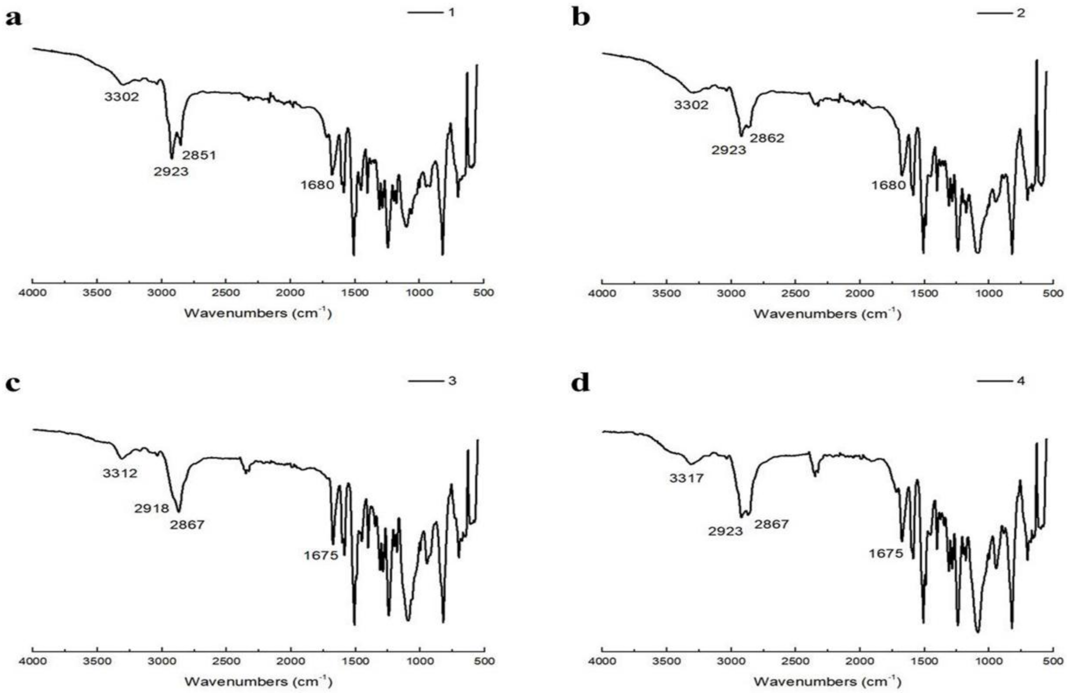


Figure S13. ATR-IR spectra of (a) **1**, (b) **2**, (c) **3** and (d) **4**.

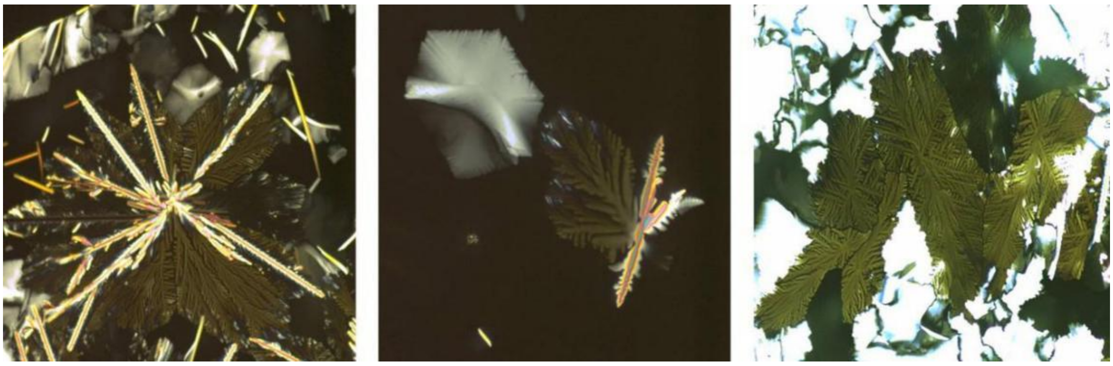


Figure S14. POM textures (×50) of molecule **3**, showed fern leaf textures, which may means typical body-centered tetragonal micellar phase.

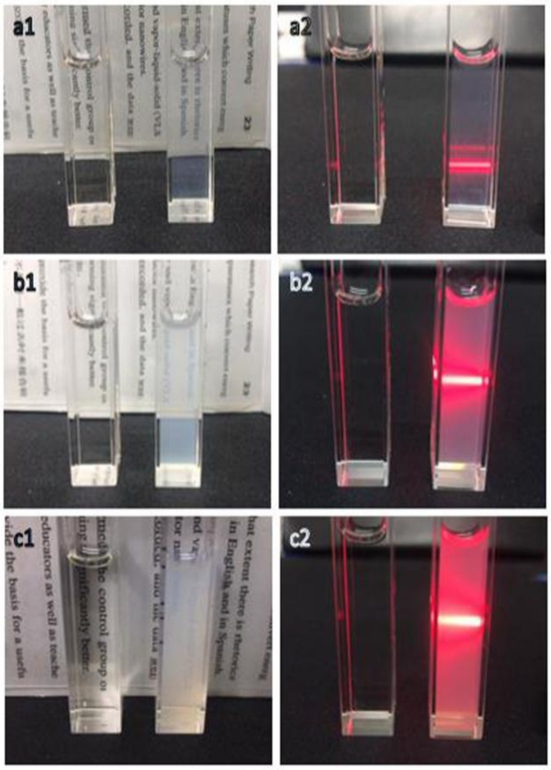


Figure S15. Comparison of (a1, b1 and c1) the turbidity and (a2, b2 and c2) Tyndall effect between different concentration of molecule **4**'s THF solution (the left sample slot in every picture) and THF/$H_2O$=1/9 solution (the right sample slot in every picture). ($[c]_a$=10 μM; $[c]_b$=50 μM; $[c]_c$=100 μM)

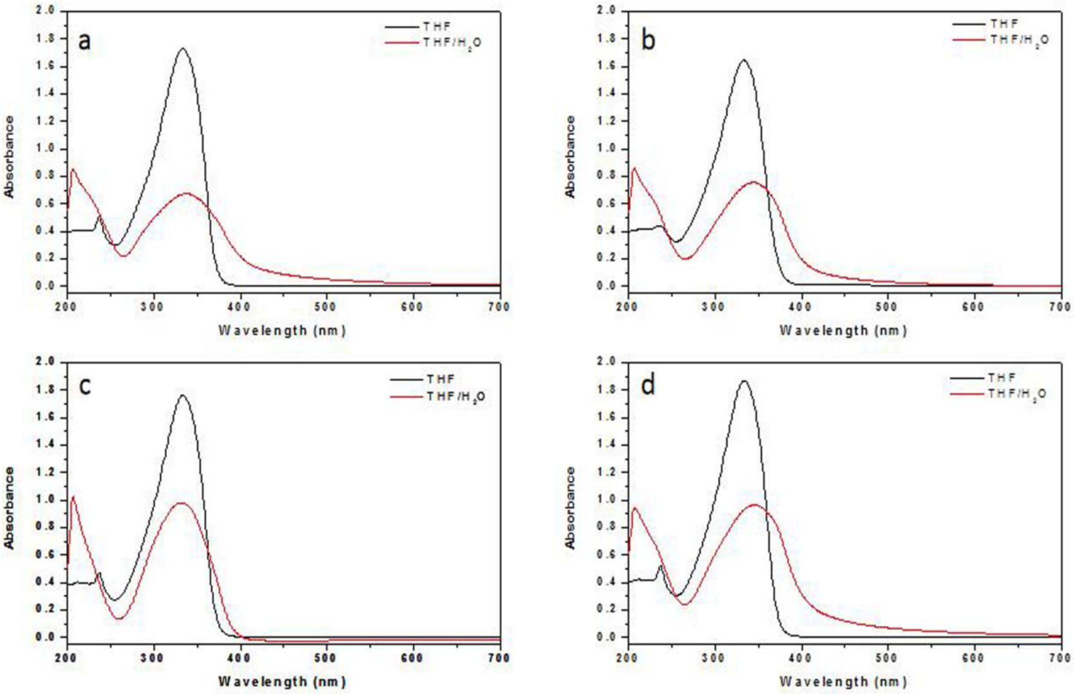


Figure S16. Absorption spectra in THF and THF/$H_2O$=1/9 solution of (a) molecule **1**, (b) molecule **2**, (c) molecule **3** and (d) molecule **4** ([c]=10 μM) .

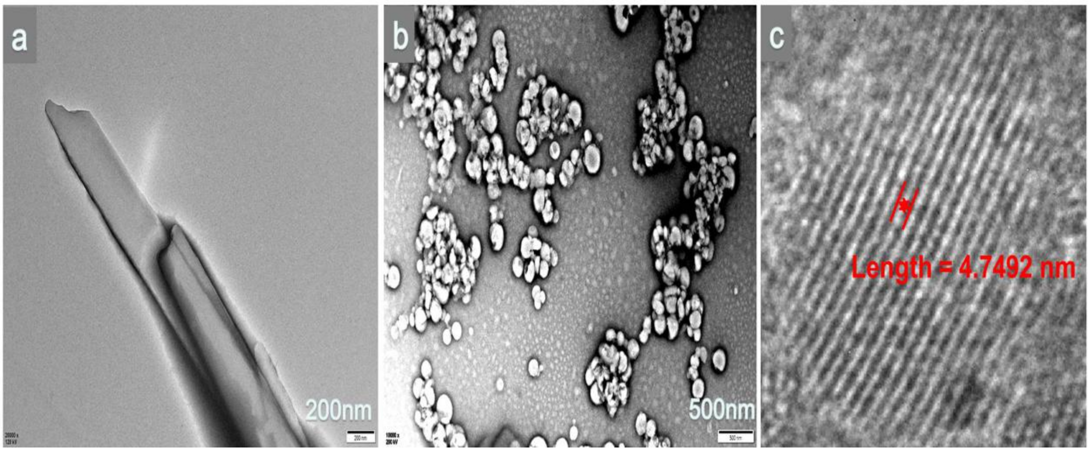


Figure S17. (a) TEM image of molecule **1**, [c]=50 μM, (b) TEM image of molecule **2**, [c]=50 μM, (c) Distance between the center of two dark stripes of molecule **4** is about 4.7 nm.

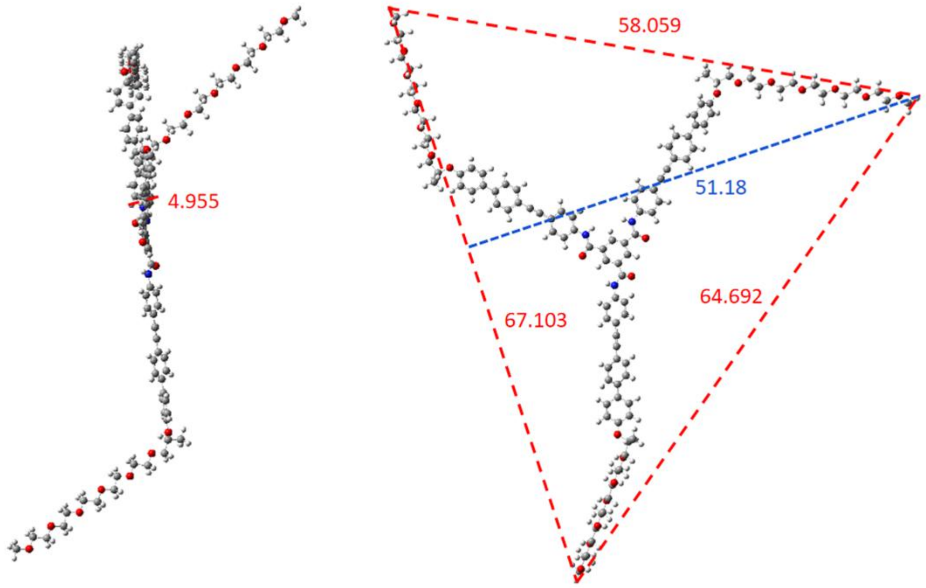


Figure S18. Model of molecule **4**, side view (left) and front view (right). (Unit of measurement: Å)

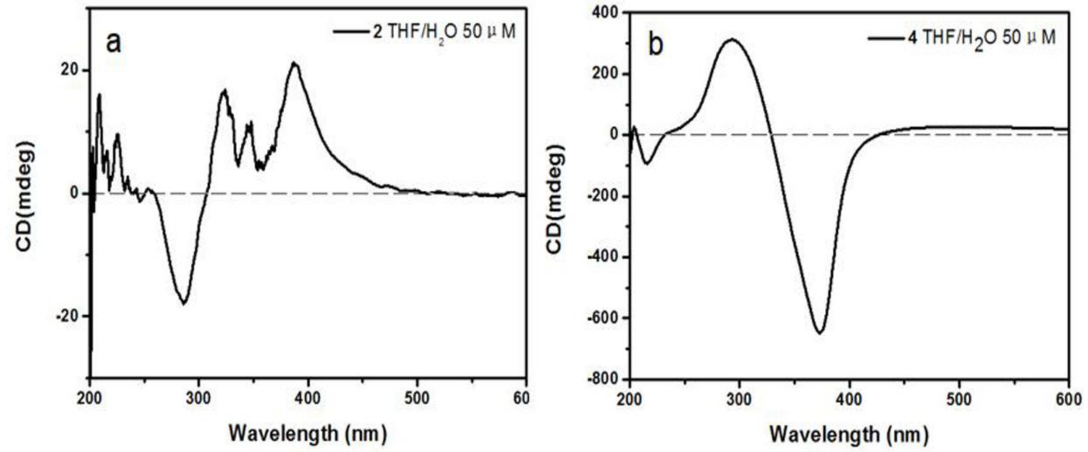


Figure S19. CD spectra of (a) molecule **2** and (b) molecule **4**. (Solvent: THF/$H_2O$=1/9, [c]=50 μM) Drop lines represent 0 scale horizontal lines.

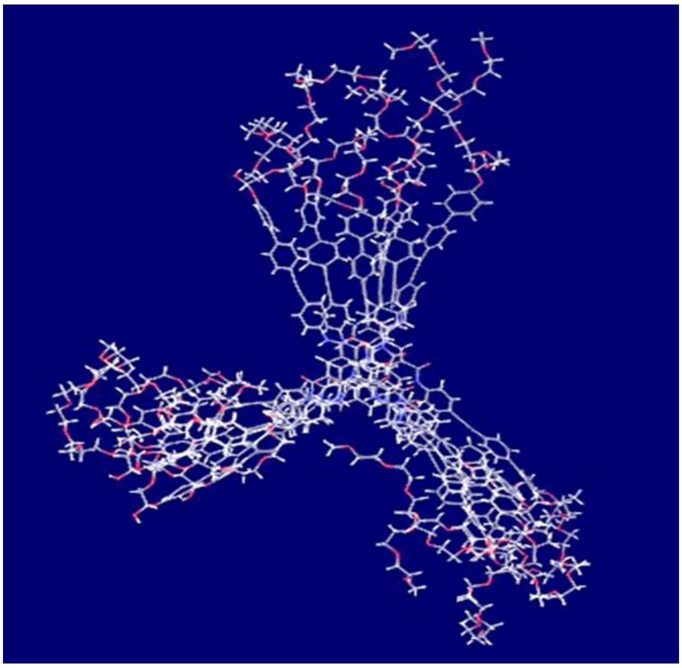


Figure S20. Five molecules group dynamics simulation photo of molecule **4**.

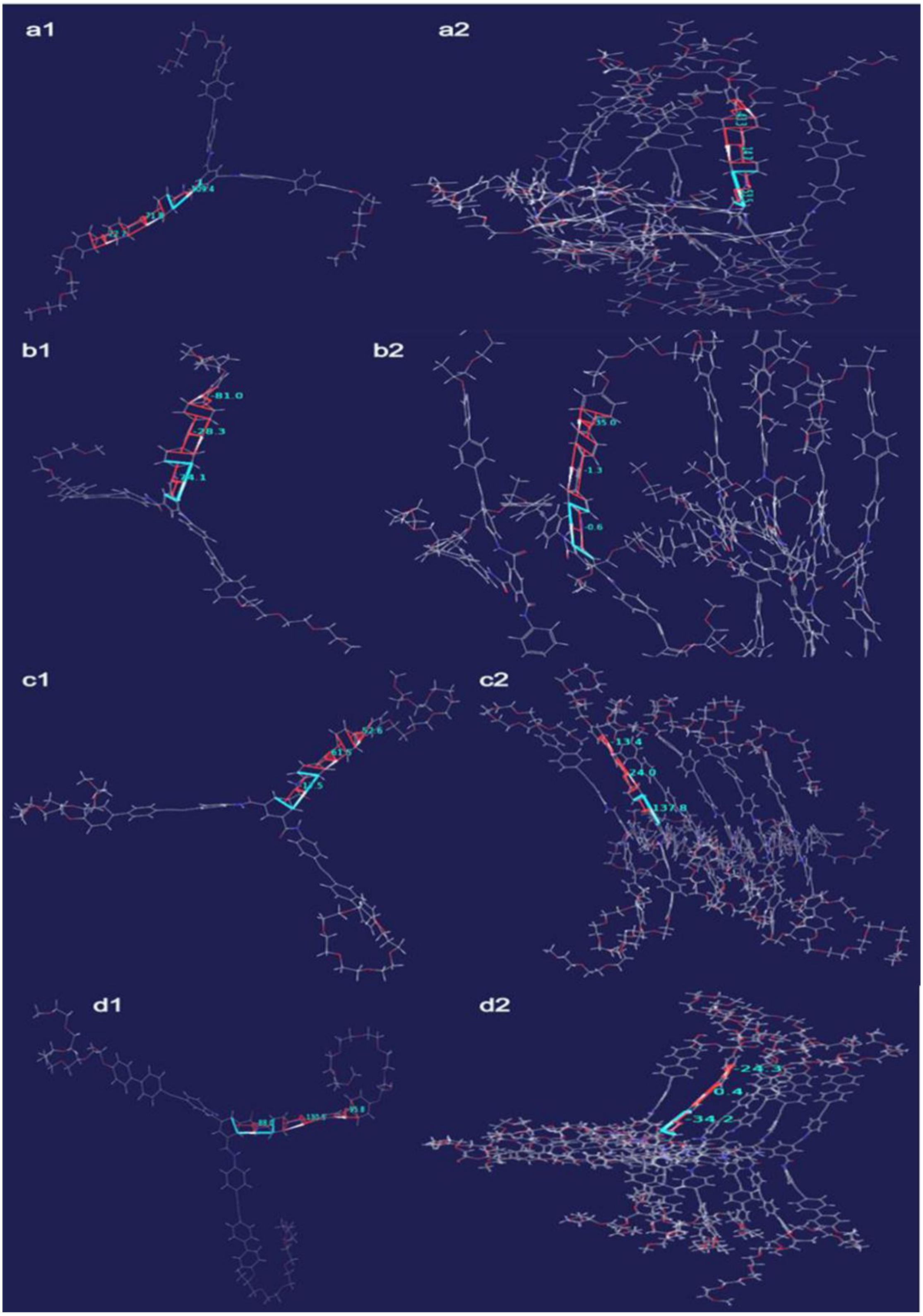


Figure S21. Images of molecular dynamics simulation, (a1) single molecule **1**, (a2) gathered molecule **1**, (b1) single molecule **2**, (b2) gathered molecule **2**, (c1) single molecule **3**, (c2) gathered molecule **3**, (d1) single molecule **4** and (d2) gathered molecule **4**.

# References

S1. S. Yu, Y. Yang, T. Chen, J. Xu and L. Y. Jin, *Nanoscale*, 2017, **9**, 17975-17982.