Supporting Information

# Synthesis and Self-assembly of Unconventional $C_3$-Symmetrical Trisubstituted Triphenylenes

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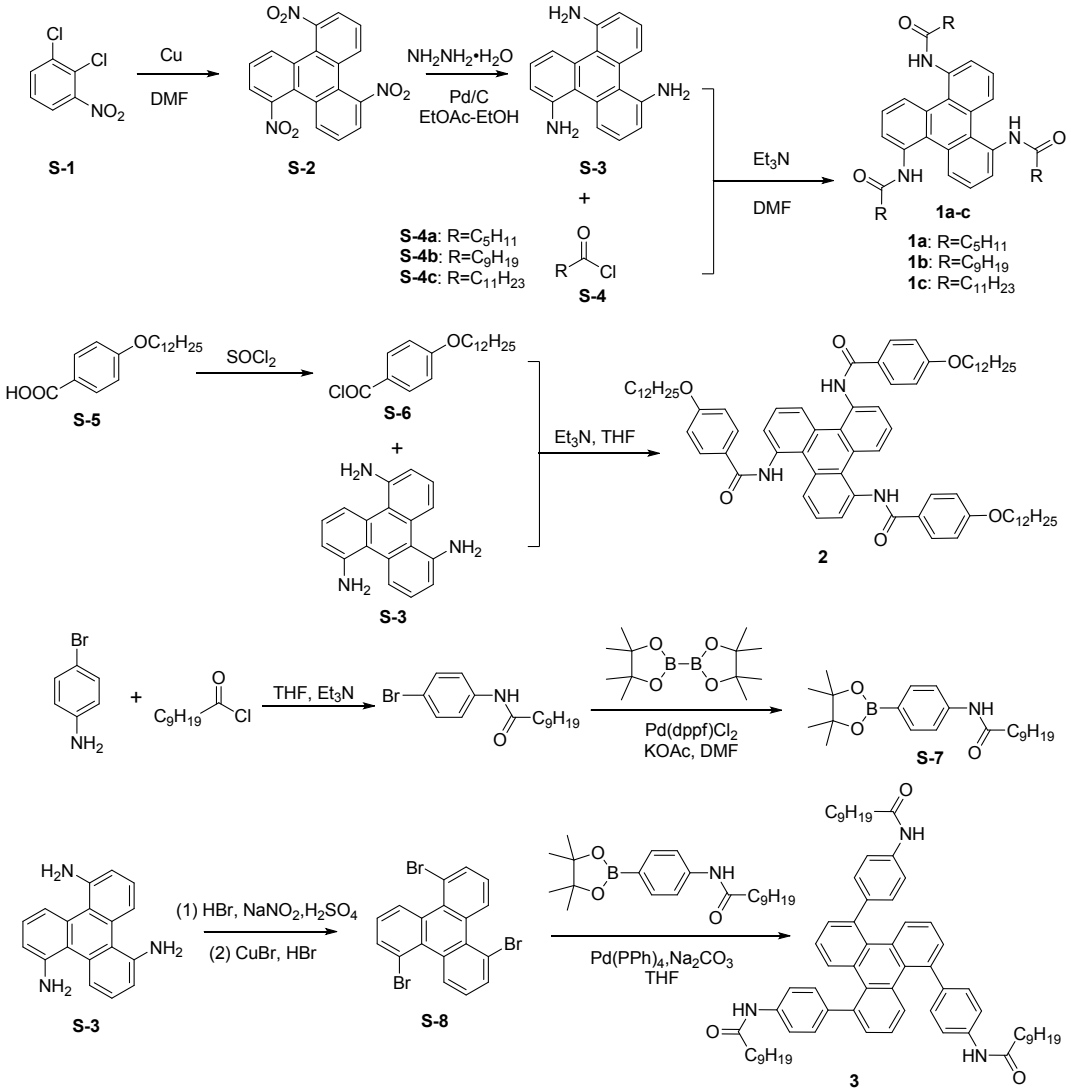
# Contents

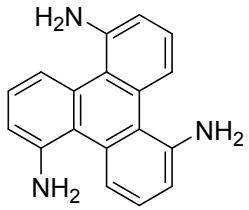
## Section 1. General Information

All starting chemical materials were directly used from commercial suppliers without further purification. Solvents were purified according to standard procedures. 1,5,9-Trinitrotriphenylene (compound **S-2**), 4-(dodecyloxy)benzoic acid (compound **S-5**) and N-(4-bromophenyl)decanamide were synthesized according to the reported procedures.[S1,S2,S3]

## Section 2. Synthesis and Characterization



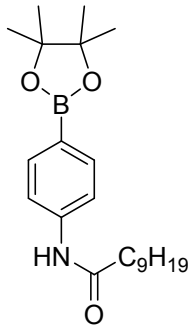

**Scheme S1.** Synthetic routes for triphenylene derivatives **1**, **2**, and **3**.



**Triphenylene-1,5,9-triamine** (**S-3**)

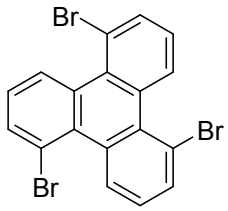
Compound **S-3** was synthesized according to the reported procedure with some modification.[S1] Activated palladium on carbon (10 % w/w, 0.60 g) was added to a solution of **S-2** (2.0 g, 5.5 mmol) in ethyl acetate (30 mL) and EtOH (25 mL) under nitrogen atmosphere, and the mixture was heated to reflux. Then $NH_2NH_2 \cdot H_2O$ (80%,

10 mL) was added dropwise to the hot solution. After refluxing for 10 h, the solution was taken off by filtration and the solids were washed with water. The filtrate was concentrated under reduced pressure to yield the amine **S-3** as a light yellow solid, which was directly used for the following reaction without further purification. Yield: 1.2 g (80%). $^1$H NMR (298K, 400 MHz, DMSO-$d_6$) δ/ppm: 8.20 (d, $J$ = 8.0 Hz, 3H), 7.15 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 6.86 (d, $J$ = 8.0 Hz, 3H), 5.33 (s, 6H).



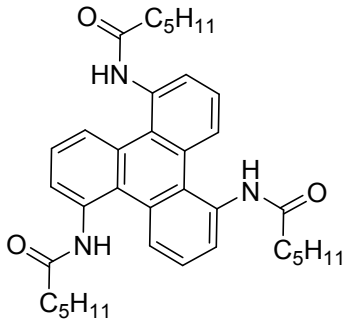

**N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)decanamide (S-7)** [S2]

A Schlenk tube was charged with N-(4-bromophenyl)decanamide (134 mg, 0.5 mmol), KOAc (246 mg, 3 mmol), bis(pinacolato)diboron (254 mg, 1 mmol), Pd(dppf)$Cl_2$ (18 mg, 0.025 mmol) and DMF (15 mL) and flushed with nitrogen atmosphere. The mixture was stirred at 80 °C for 24 h. Ethyl acetate (80 mL) was added and the mixture was washed with water to remove DMF from the organic layer. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by flash silica gel chromatography eluting with petroleum ether/ethyl acetate (4:1, v/v) to afford **S-7** as a white solid. Yield: 80 mg (51%). $^1$H NMR (298K, 400 MHz, $CDCl_3$) δ/ppm: 7.76 (d, $J$ = 8.4 Hz, 2H), 7.53 (d, $J$ = 8.0 Hz, 2H), 7.11 (s, 1H), 2.35 (t, $J$ = 7.6 Hz, 2H), 1.74–1.70 (m, 2H), 1.34 (s, 12H), 1.27–1.26 (m, 12H), 0.88 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (298K, 100 MHz, $CDCl_3$) δ/ppm: 171.69, 140.83, 136.00, 118.64, 83.92, 38.14, 32.05, 29.63, 29.58, 29.46, 25.73, 25.05, 22.87, 14.33. MALDI-TOF, m/z: calcd for $C_{22}H_{36}BNO_3$ $[M+Na]^+$ 396.269; found, 396.344.




**1,5,9-tribromotriphenylene (S-8)**

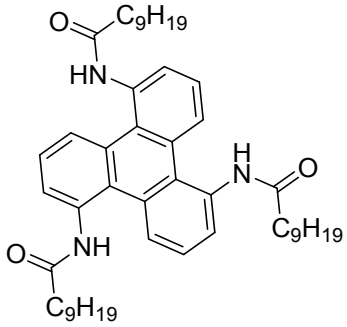
Triphenylene-1,5,9-triamine (**S-3**, 546 mg, 2 mmol) was dissolved in 40 % aqueous HBr (6 mL) and $H_2SO_4$ (6.9 M, 11 mL). After cooling to 0 °C, sodium nitrite (500 mg, 7.2 mmol) was added very slowly to the stirred solution with the temperature being kept below 0 °C. This diazonium salt solution was then poured into a flask, which contained CuBr (360 mg, 8.28 mmol) and 6 mL of 40 % aqueous HBr. The solution was heated to 80 °C for 36 h. After cooling to room temperature, the solution was extracted three times with dichloromethane. The organic layers were washed with $Na_2SO_3$ solution and dried with $MgSO_4$, and the crude product was purified by flash silica gel chromatography to afford **S-8** as a white solid. Yield: 360 mg (20%). $^1$H NMR (298K, 400 MHz, $CHCl_3$) δ/ppm: 9.21 (d, $J$ = 8.0 Hz, 3H), 7.88 (d, $J$ = 7.6 Hz, 3H), 7.34 (dd, $J_1 = J_2$ = 8.0 Hz, 3H); $^{13}$C NMR (298K, 100 MHz, $CDCl_3$) δ/ppm: δ 135.50, 132.58, 130.53, 126.96, 126.38, 119.43; HRMS (ESI), m/z: calcd. for $C_{18}H_{10}Br_3$ $[M + H]^+$ 462.8333, found: 462.8442.




***N,N′,N′′*-(Triphenylene-1,5,9-triyl)trihexanamide (1a)**

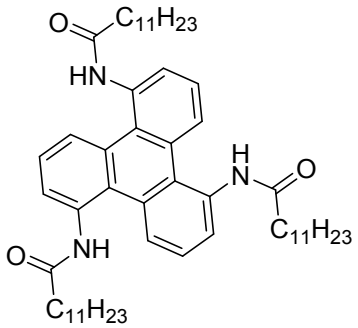
To a solution of compound **S-3** (0.3 g, 1.10 mmol) in anhydrous DMF (12 mL) with $Et_3N$ (0.662 g) was added dropwise hexanoyl chloride (0.668 g, 4.96 mmol) dissolved in anhydrous DMF (6 mL). The mixture was stirred at r.t. under nitrogen atmosphere for 24 h. Then saturated $NaHCO_3$ (aq) was added and the mixture was stirred for another 5 min. The precipitate was separated by filtration and washed with THF and

dichloromethane. After filtration, the crude product was purified by recrystallization from THF/$H_2O$ affording the pure product **1a** as a white solid. Yield: 0.36 g (57%). $^1$H NMR (298K, 400 MHz, DMSO-$d_6$) δ/ppm: 10.08 (s, 3H), 8.56 (d, $J$ = 6.8 Hz, 3H), 7.44–7.40 (m, 6H), 2.37 (t, $J$ = 7.2 Hz, 6H), 1.66–1.63 (m, 6H), 1.36–1.34 (m, 12H), 0.91 (t, $J$ = 6.8 Hz, 9H). $^{13}$C NMR (298K, 100 MHz, DMSO-$d_6$) δ/ppm: 171.28, 134.04, 130.55, 127.59, 126.48, 125.86, 123.34, 35.88, 31.08, 24.62, 21.97, 13.93. HRMS (ESI), m/z: calcd. for $C_{36}H_{46}N_3O_3$ $[M + H]^+$ 568.3539, found: 568.3542.




**N,N',N''-(Triphenylene-1,5,9-triyl)trisdecanamide (1b)**

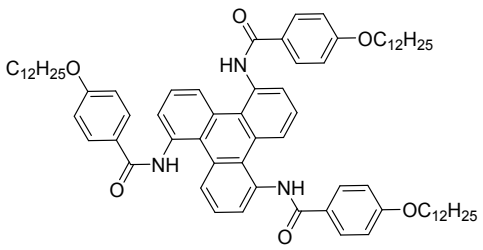
Following the procedure described for **1a**, the reaction of compound **S-3** (0.3 g, 1.10 mmol), $Et_3N$ (0.662 g), decanoyl chloride (0.943 g, 4.96 mmol) in DMF (18 mL) afforded the desired product **1b** as a white solid. Yield: 0.4 g (50%). $^1$H NMR (298K, 400 MHz, DMSO-$d_6$) δ/ppm: 10.07 (s, 3H), 8.55 (d, $J$ = 6.8 Hz, 3H), 7.43–7.41 (m, 6H), 2.37 (t, $J$ = 7.6 Hz, 6H), 1.64–1.62 (m, 6H), 1.33–1.28 (m, 36H), 0.86 (t, $J$ = 6.8 Hz, 9H). $^{13}$C NMR (343.5 K, 100 MHz, $C_2D_2Cl_4$) δ/ppm: 171.43, 133.89, 130.12, 126.47, 125.57, 125.09, 122.59, 37.26, 31.64, 29.24, 29.20, 29.17, 29.02, 25.20, 22.42, 13.86. HRMS (ESI), m/z: calcd. for $C_{48}H_{70}N_3O_3$ $[M + H]^+$ 736.5417, found: 736.5410.




**N,N',N''-(Triphenylene-1,5,9-triyl)tridodecanamide (1c)**

Following the procedure described for **1a** with some modification, the reaction of

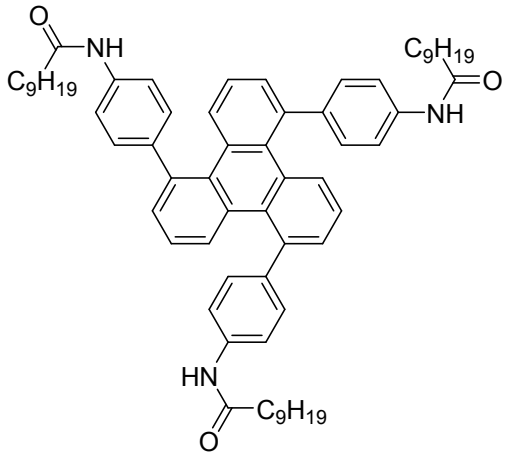
compound **S-3** (136 mg, 0.5 mmol), $Et_3N$ (300 mg), dodecanoyl chloride (492 mg, 2.25 mmol) in DMF (6 mL) afforded cure product. And the product was purified by flash silica gel chromatography and recrystallization from THF/$H_2O$ to afford **1c** as a white solid. Yield: 120 mg (29%). $^1$H NMR (298K, 400 MHz, DMSO-$d_6$) δ/ppm: 10.07 (s, 3H), 8.56 (d, $J$ = 6.8 Hz, 3H), 7.42–7.40 (m, 6H), 2.37 (t, $J$ = 7.2 Hz, 6H), 1.64–1.62 (m, 6H), 1.32–1.24 (m, 48H), 0.85 (t, $J$ = 7.2 Hz, 9H). $^{13}$C NMR (343.5 K, 100 MHz, $C_2D_2Cl_4$) δ/ppm: 171.50, 133.90, 130.17, 126.52, 125.66, 125.15, 122.66, 37.29, 31.67, 29.39, 29.38, 29.28, 29.20, 29.15, 29.06, 25.20, 22.42, 13.84. HRMS (ESI), m/z: calcd. for $C_{54}H_{82}N_3O_3$ $[M + H]^+$ 820.6356, found: 820.6328.




**N,N',N''-(triphenylene-1,5,9-triyl)tris(4-(dodecyloxy)benzamide) (2)**

A suspension of compound **S-5** (612 mg, 2 mmol) in thionyl chloride (20 mL) was stirred and refluxed overnight. Then thionyl chloride was evaporated under reduced pressure, and the resulting product was dried under vaccum to give compound **S-6**. To a solution of **S-3** (120 mg, 0.44 mmol) in anhydrous THF (6 mL) with $Et_3N$ (600 mg) was added compound **S-6** dissolved in anhydrous THF (6 mL). The mixture was stirred at r.t. under nitrogen atmosphere for 48 h. Dichloromethane and saturated $NaHCO_3$ (aq) was added, and the mixture was stirred for 5 min. The organic layer was separated and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was evaporated in vacuum to give the crude product which was purified by silica gel column eluting with dichloromethane/ethyl acetate (4:1, v/v) to afford a yellowish solid. Yield: 225 mg (45%). $^1$H NMR (298K, 400 MHz, $CDCl_3$) δ/ppm: 8.38 (s, 3H), 8.32–8.30 (d, $J$ = 7.6 Hz, 3H), 8.00 (d, $J$ = 7.6 Hz, 3H), 7.87 (d, $J$ = 8.0 Hz, 6H), 7.34 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 6.97 (d, $J$ = 8.4 Hz, 6H), 4.02 (t, $J$ = 6.4 Hz, 6H), 1.85–1.77 (m, 6H), 1.50–1.43 (m, 6H) 1.35–1.22 (m, 48H), 0.88 (t, $J$ =

6.8 Hz, 9H). $^{13}$C NMR (298K, 100 MHz, $CDCl_3$) δ/ppm: 165.43, 162.46, 134.01, 130.26, 129.51, 126.67, 125.88, 125.49, 122.75, 117.49, 114.62, 68.50, 32.14, 29.90, 29.87, 29.66, 29.58, 29.39, 26.25, 22.91, 14.35. HRMS (ESI), m/z: calcd. for $C_{75}H_{100}N_3O_6$ $[M + H]^+$ 1138.7612, found: 1138.7694.




**N,N',N''-(triphenylene-1,5,9-triyltris(benzene-1,4-diyl))trisdecanamide (3)**

The general procedure for Suzuki cross-coupling was followed. Compound **S-7** (290 mg, 0.78 mmol), compound **S-8** (60 mg, 0.13 mmol), Pd $(PPh_3)_4$ (15 mg, 0.013 mmol), 2M $Na_2CO_3$ (3 mL), and THF (10 mL) were charged sequentially in a 50 mL flask under a nitrogen atmosphere and heated to reflux for 36 h. After cooling to room temperature, the solution was poured into water and extracted with dichloromethane and ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated in vacuum to give the crude product. The residue was purified by silica gel column eluting with petroleum ether/ethyl acetate (4:1, v/v) to afford a yellowish solid. Yield: 40 mg (31%). $^1$H NMR (298K, 400 MHz, DMSO-$d_6$) δ/ppm: 10.01 (s, 3H), 7.67 (d, $J$ = 8.0 Hz, 6H), 7.58 (d, $J$ = 8.0 Hz, 3H), 7.28–7.24 (m, 9H), 7.10 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 2.35–2.31 (m, 6H), 1.63–1.59 (m, 6H), 1.30–1.25 (m, 36H), 0.86 (t, $J$ = 6.0 Hz, 9H). $^{13}$C NMR (298K, 100 MHz, $CDCl_3$) δ/ppm: 171.77, 141.19, 139.35, 137.01, 131.57, 131.01, 130.10, 130.01, 128.64, 124.69, 120.35, 38.15, 32.08, 29.68, 29.64, 29.56, 29.51, 25.90, 22.89, 14.33. HRMS (ESI), m/z: calcd. for $C_{66}H_{82}N_3O_3$ $[M + H]^+$ 964.6356, found: 964.6327.

## Section 3. Photographs of Gels

**Gelation method:** A suspension of compound **1** in appropriate organic solvent was heated until all solids were completely dissolved to form a clear solution. The solution was allowed to cool gradually to room temperature.

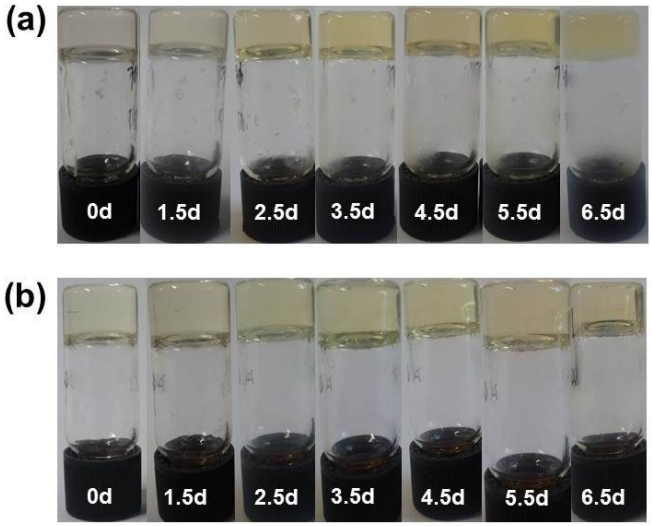



**Figure S1.** Photographs taken under natural light of (a) **1b** and (b) **1c** gels in chlorobenzene after cooling at room temperature over one week.

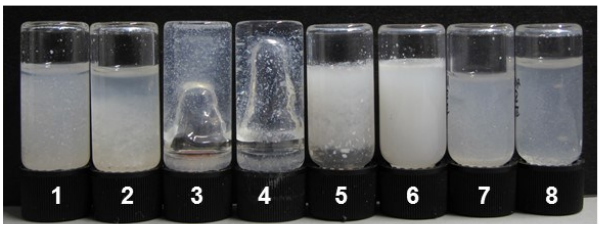



**Figure S2.** Photographs taken under natural light of **1a** (4.3 mM) sols in various solvents after cooling at room temperature (from left to right: toluene, xylene, chlorobenzene, dichlorobenzene, tetrachloromethane, dichloromethane, n-hexane and cyclohexane).

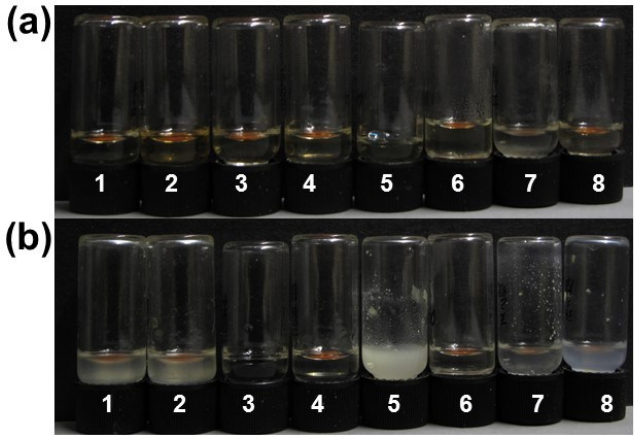
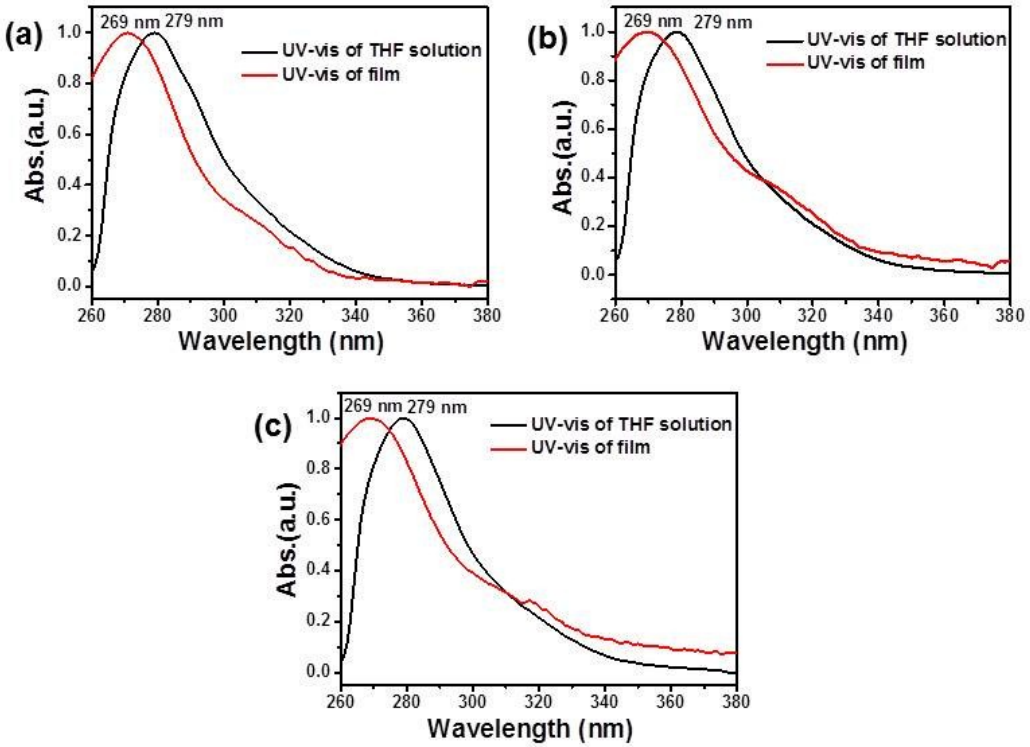



**Figure S3.** Photographs taken under natural light of (a) **2** and (b) **3** sols in various solvents after cooling at room temperature (from left to right: toluene, xylene, chlorobenzene, dichlorobenzene, tetrachloromethane, dichloromethane, n-hexane and cyclohexane).

## Section 4. Photophysical Properties



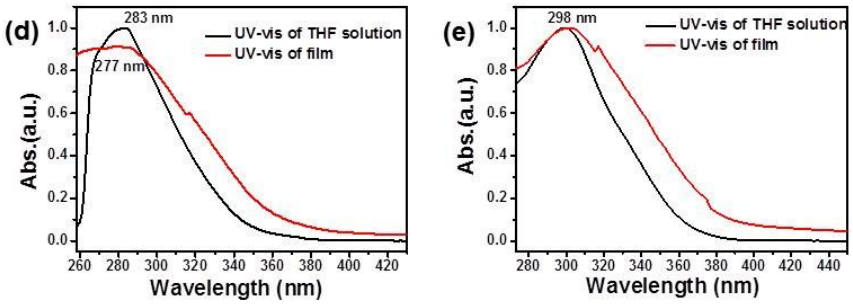



**Figure S4.** Normalized UV–Vis spectra of compounds (a) **1a**, (b) **1b**, (c) **1c**, (d) **2**, and (e) **3** in tetrahydrofuran ($10^{-5}$ M, black line) and in the film-state (red line).

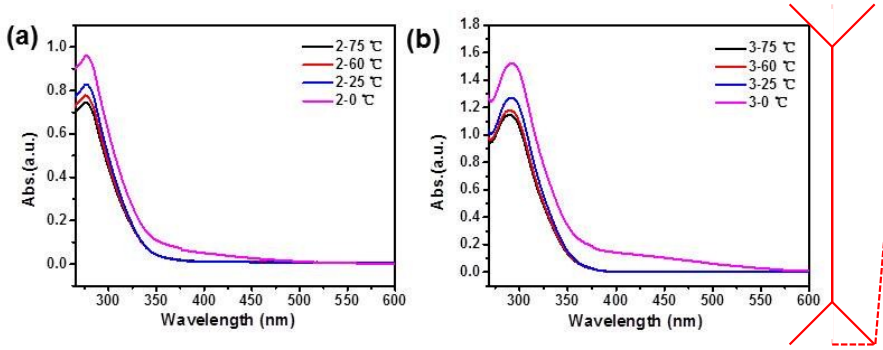



**Figure S5.** UV–Vis spectra of (a) **2** and (b) **3** in acetonitrile ($10^{-5}$ M) at different temperatures.

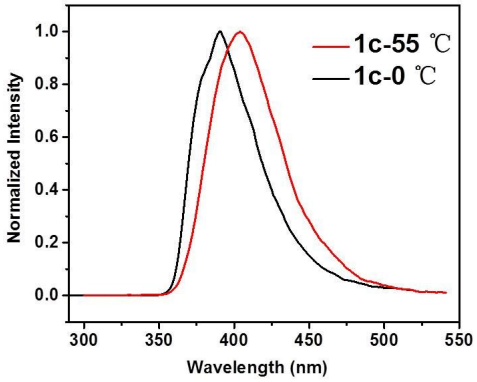



**Figure S6.** Normalized photoluminescence spectra of **1c** in $CCl_4$ ($10^{-5}$ M) at 55 °C (red line, excited at 282 nm) and 0 °C (black line, excited at 271 nm).



Comment [M]: ?

## Section 5. Investigation on Driving Forces for Assembly

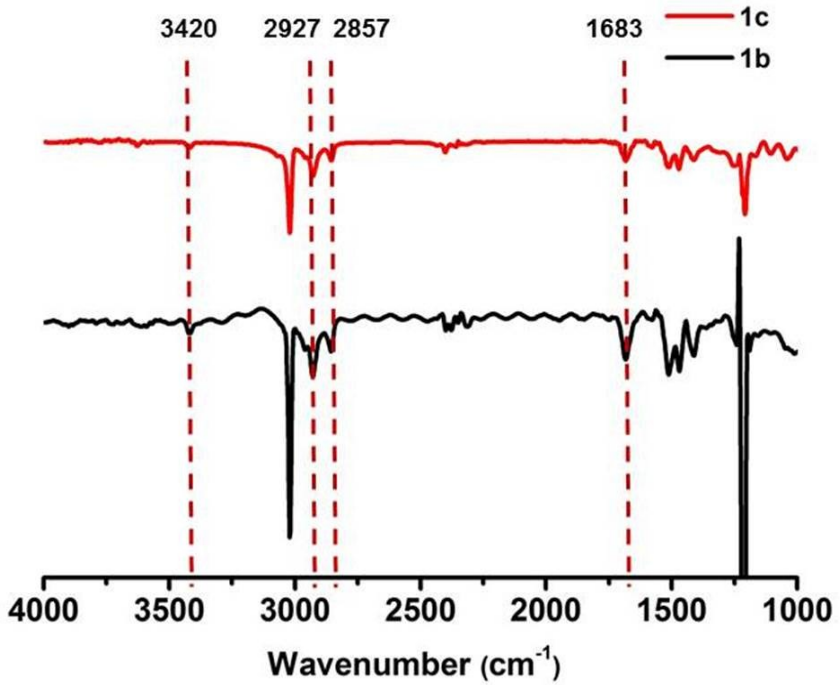



**Figure S7.** FT-IR spectra of **1b** and **1c** in dilute $CHCl_3$ solutions.

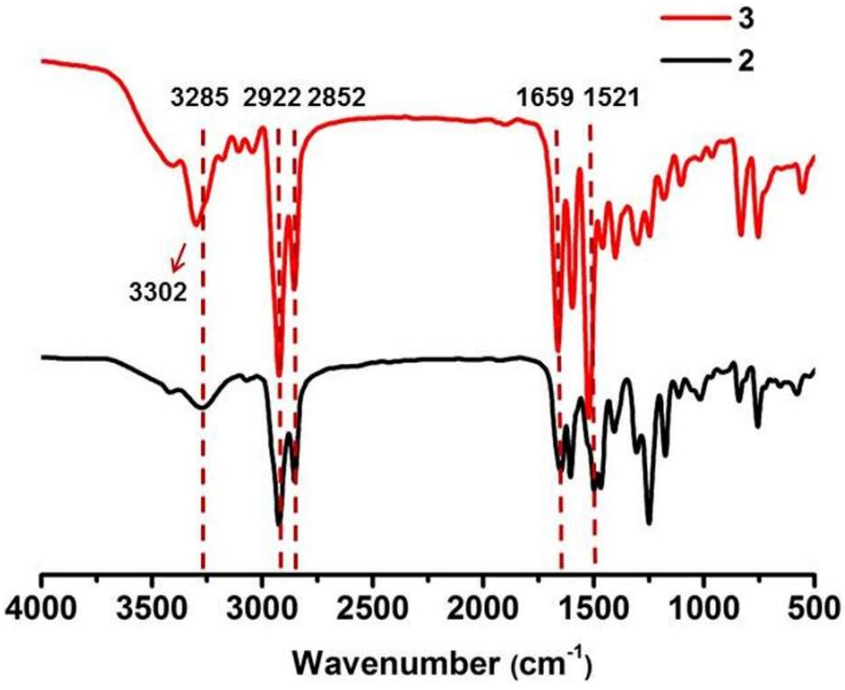



**Figure S8.** FT-IR spectra of **2** and **3** aggregates obtained from acetonitrile by the heating-cooling protocols.

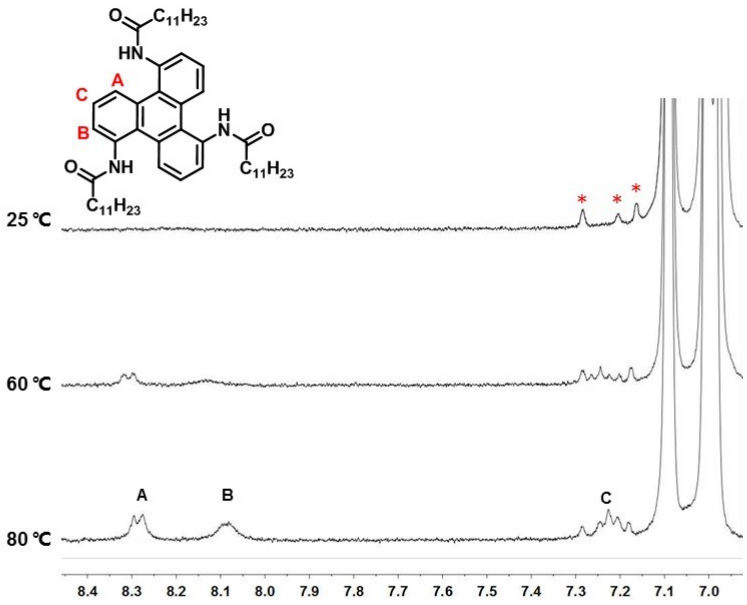



**Figure S9.** $^1$H NMR spectra of **1c** in toluene-$d_8$ for the aromatic protons at different temperatures. The solvent peaks are denoted as star symbols.

## Section 6. Morphology Features and PXRD Profiles

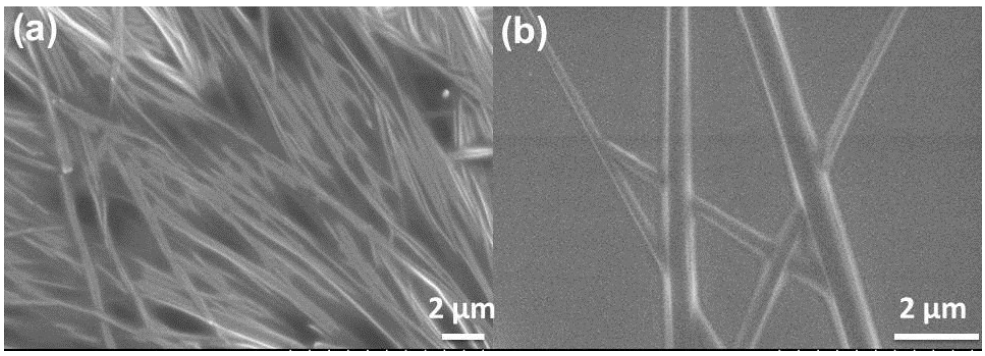



**Figure S10.** SEM images of **1a** partial gel.

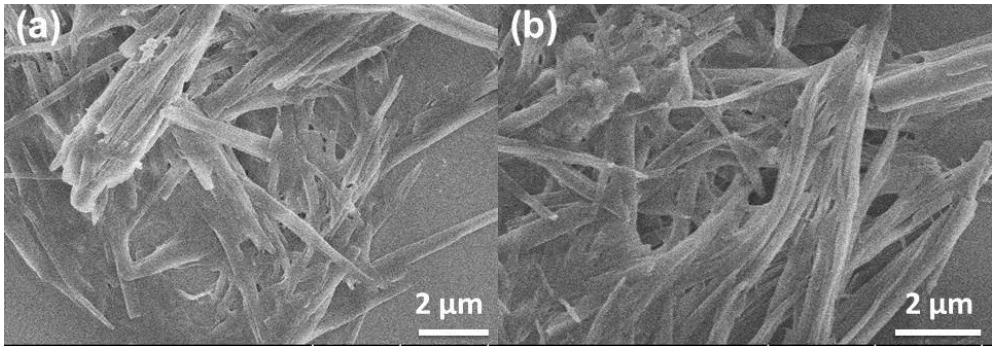



**Figure S11.** SEM images of **1b** gel.

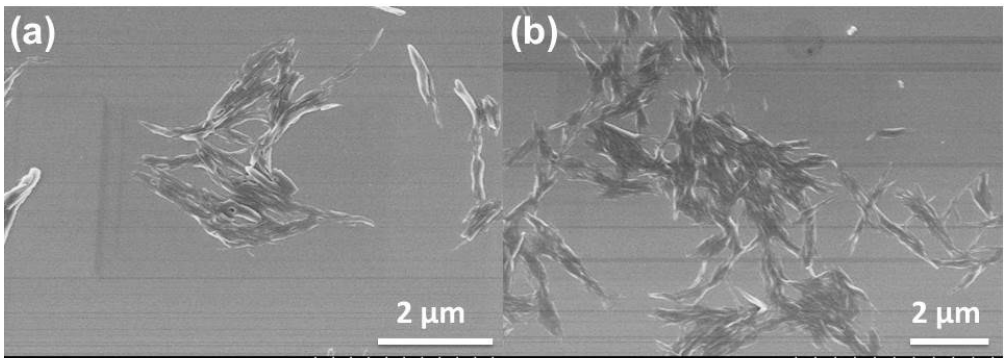



**Figure S12.** SEM images of **1c** gel.

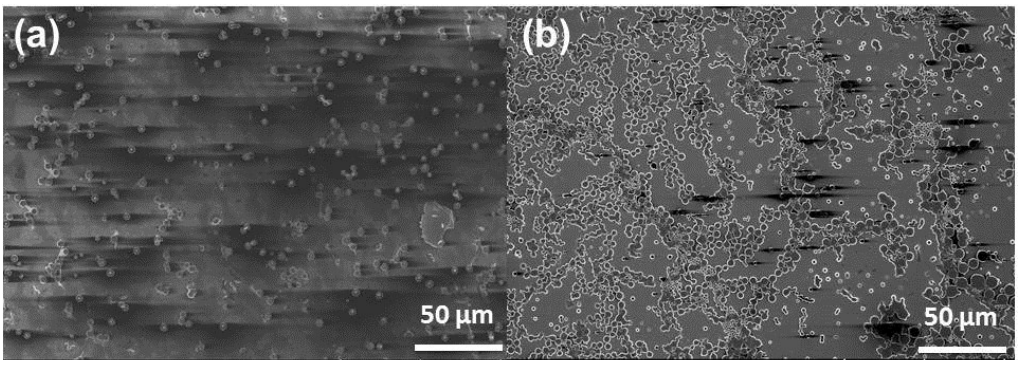



**Figure S13.** SEM images of (a) **2** and (b) **3** (assemblies from acetonitrile).

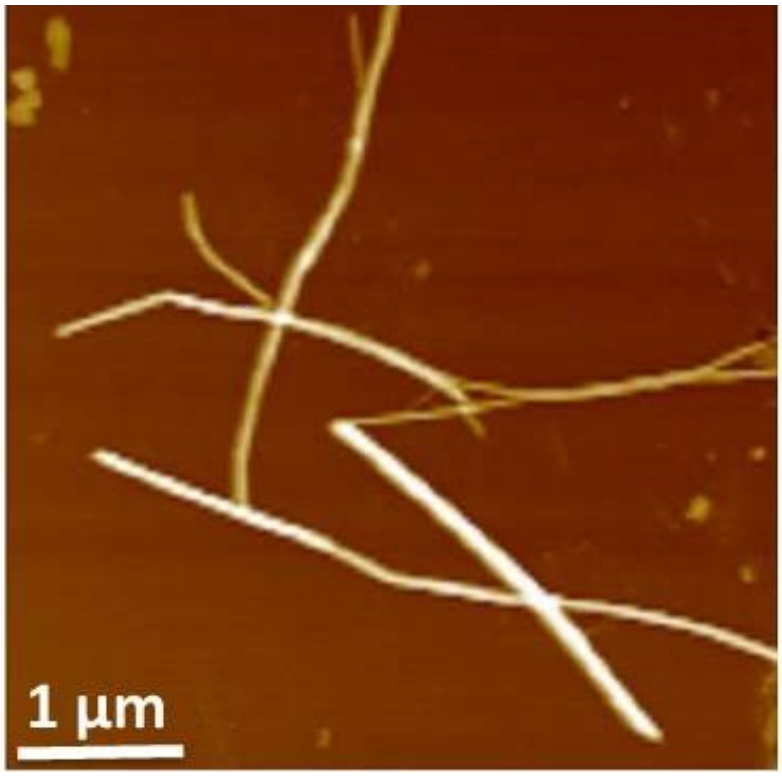



**Figure S14.** AFM image of **1a** partial gel.

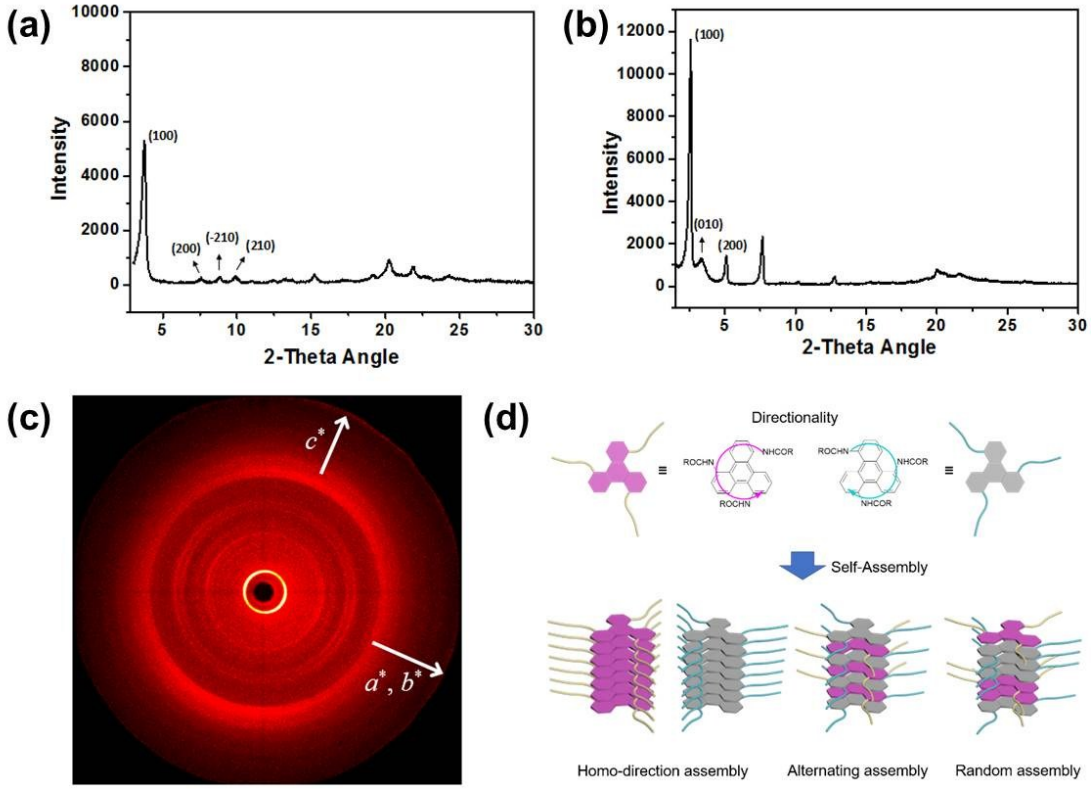



**Figure S15.** XRD spectra of (a) **1b** and (b) **1c** assemblies from THF/$H_2O$, (c) 2D-WAXD pattern of sheared **1b**, (d) schematic illustration of the rotational directionalities of C3 symmetric triphenylenes. (In Figure S15c, the *a**- and *b**- axes are assigned to the equator, and the *c**- axis is along the meridian. it can be seen that the *d*-spacing of strongest low-angle equatorial diffraction arc accords with the molecular diameter calculated by DFT calculation (Figure S16), indicating that the axes of column are aligned along the shear direction. On the meridian, there are no extinct diffraction spots and low-angle diffraction arcs which correspond to large *c* parameter can be detected. Based on these results, it is speculated that the directionalities of triphenylene molecules are aligned randomly in the supramolecular column.)

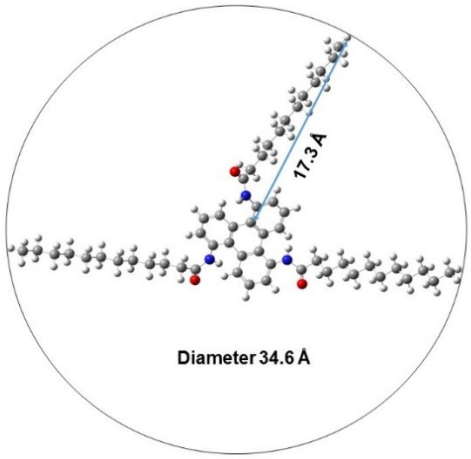



**Figure S16.** Computing model of molecule **1c** calculated by DFT calculation.

## Section 7. Thermal Stability

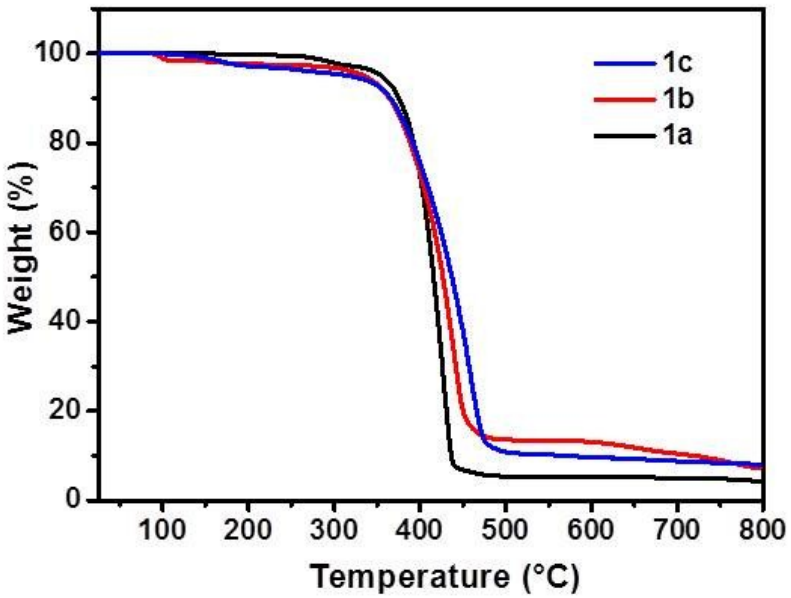



**Figure S17.** TGA curves of **1a** (black line), **1b** (red line) and **1c** (blue line).

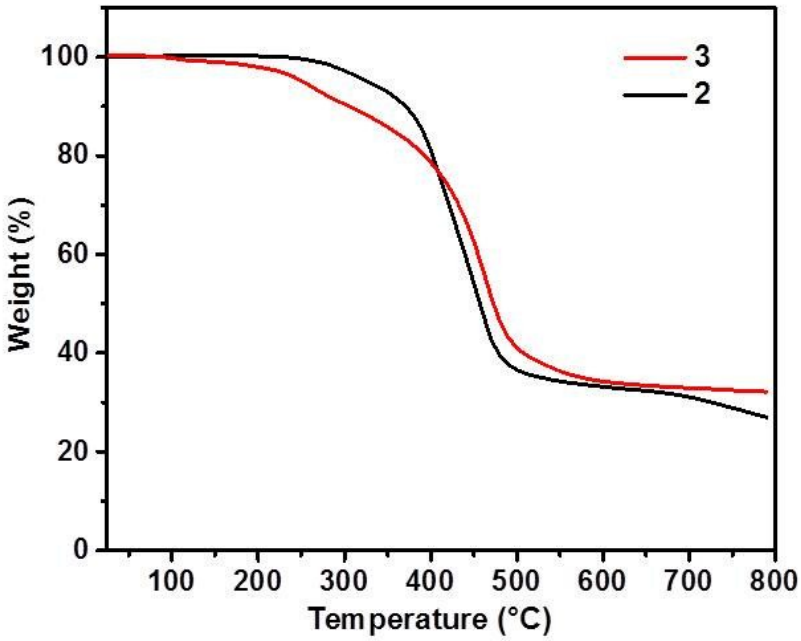
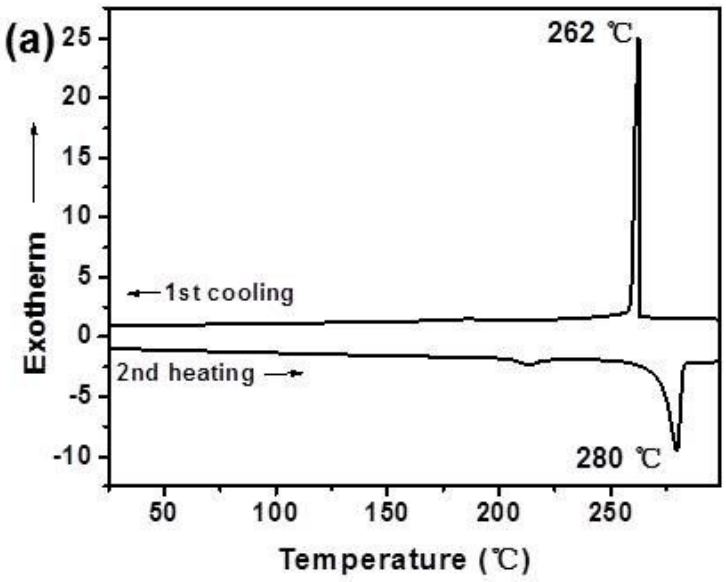
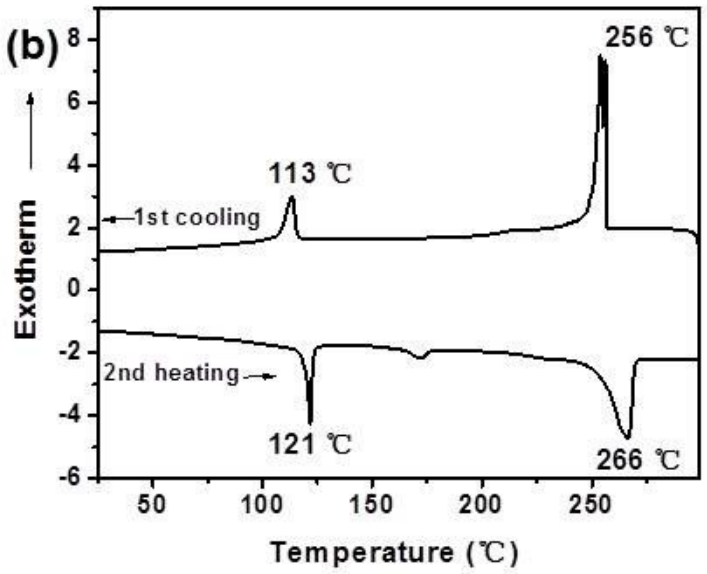



**Figure S18.** TGA curves of **2** (black line) and **3** (red line).

## Section 8. Phase Transitions and Characterization


(a)
262 ℃
Exotherm
1st cooling
2nd heating
280 ℃
Temperature (℃)


(b)
256 ℃
113 ℃
Exotherm
1st cooling
2nd heating
121 ℃
266 ℃
Temperature (℃)

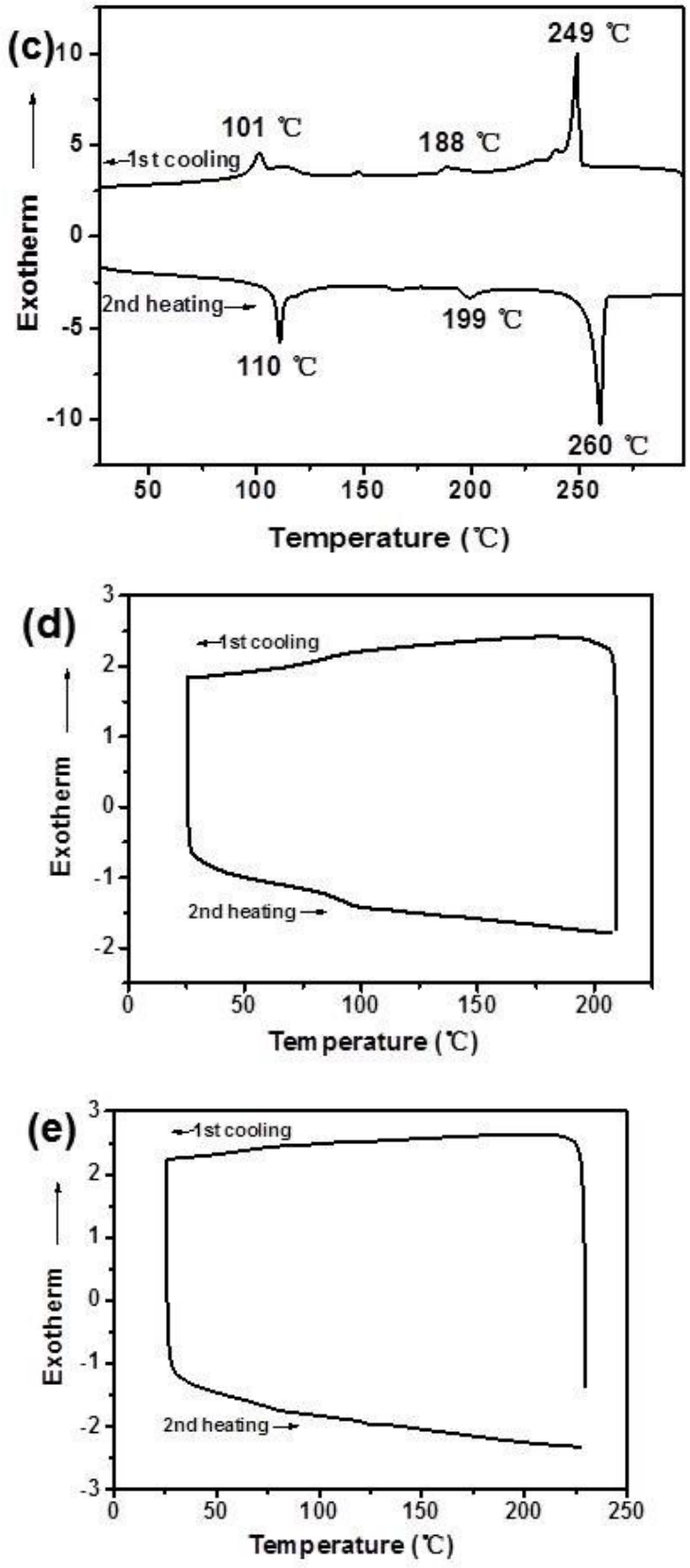



**Figure S19.** DSC data of (a) **1a**, (b) **1b**, (c) **1c** (d) **2** and (e) **3** in the first cooling scan and the second heating scan). Heating and cooling rates were 10 °C/min.

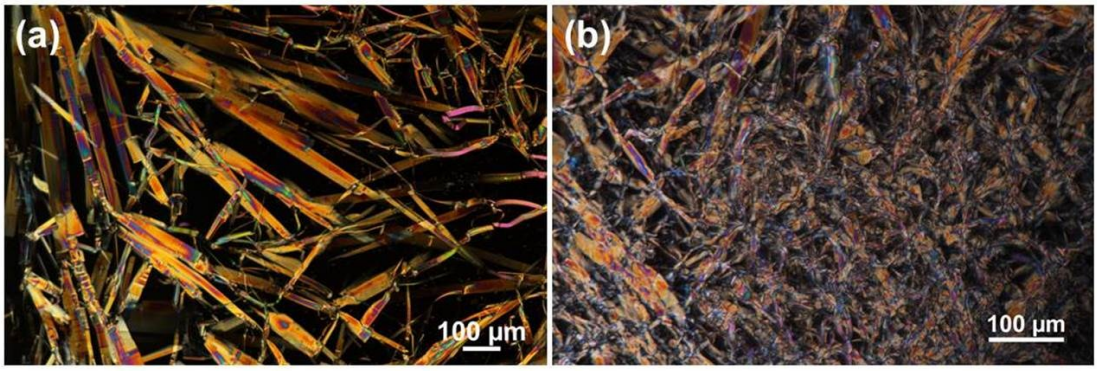



**Figure S20.** Polarizing optical micrographs of (a) **1b** (recorded at 260 °C), and (b) **1c** (recorded at 255 °C), respectively, on the first cooling cycle.

**Table S1.** Transition temperatures of **1a**, **1b** and **1c**.

| Compound | Phase transition[a] | Temperature (°C) |
|---|---|---|
| **1a** | Iso→Cryst | 262 |
| **1b** | Iso→Cryst | 256 |
| **1c** | Iso→Liquid crystal | 249 |

[a] Cryst: crystal, Iso: isotoropic liquid.

## Section 9. NMR Spectra and High-resolution Mass Spectrometry

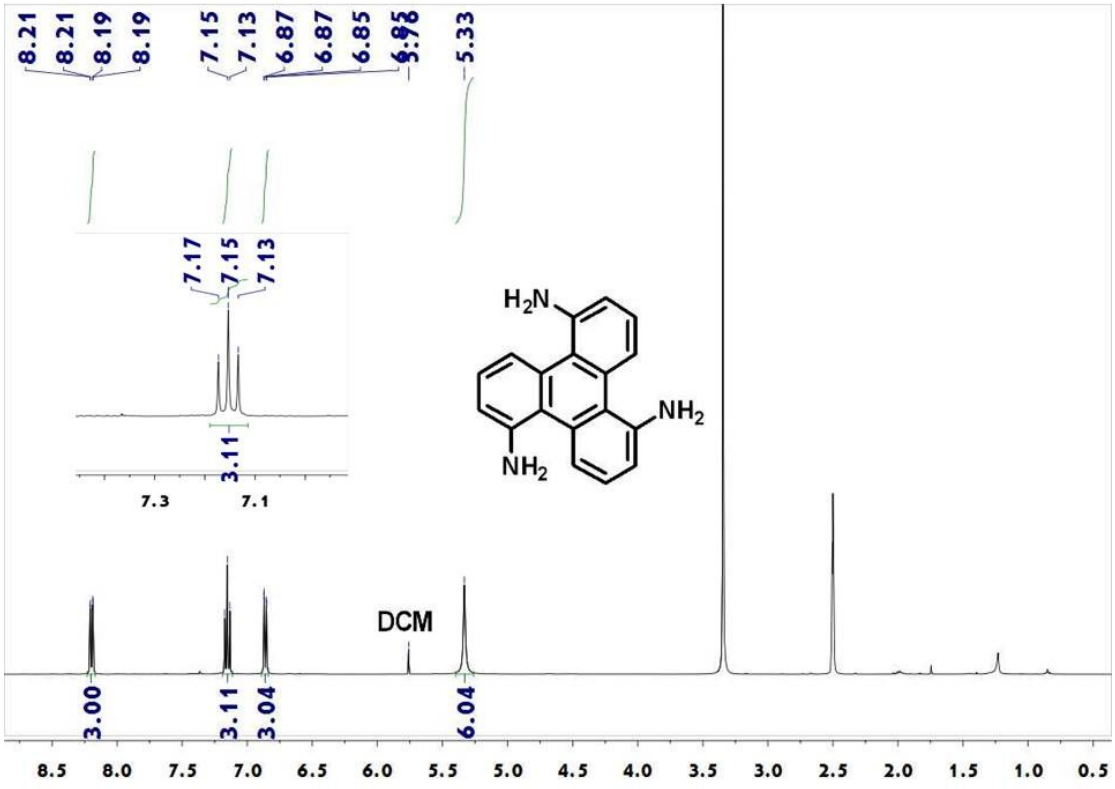



**Figure S21.** $^{1}$H NMR spectrum of compound **S-3** (298K, 400 MHz, DMSO-$d_6$).

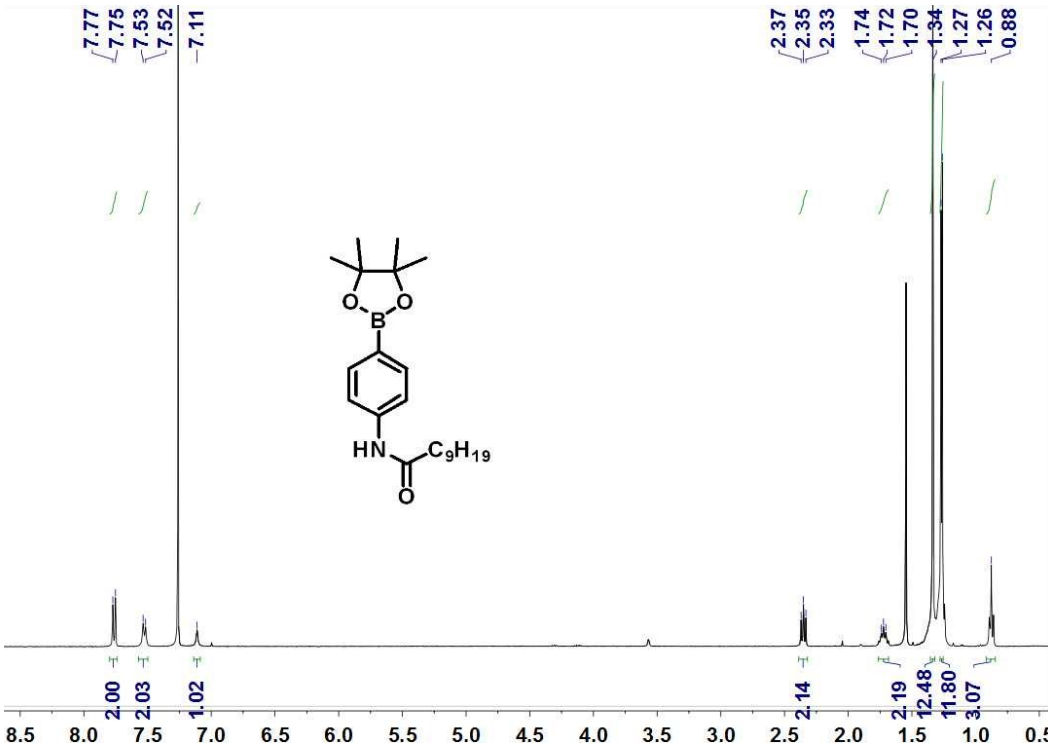



**Figure S22.** $^{1}$H NMR spectrum of compound **S-7** (298K, 400 MHz, $CDCl_3$).

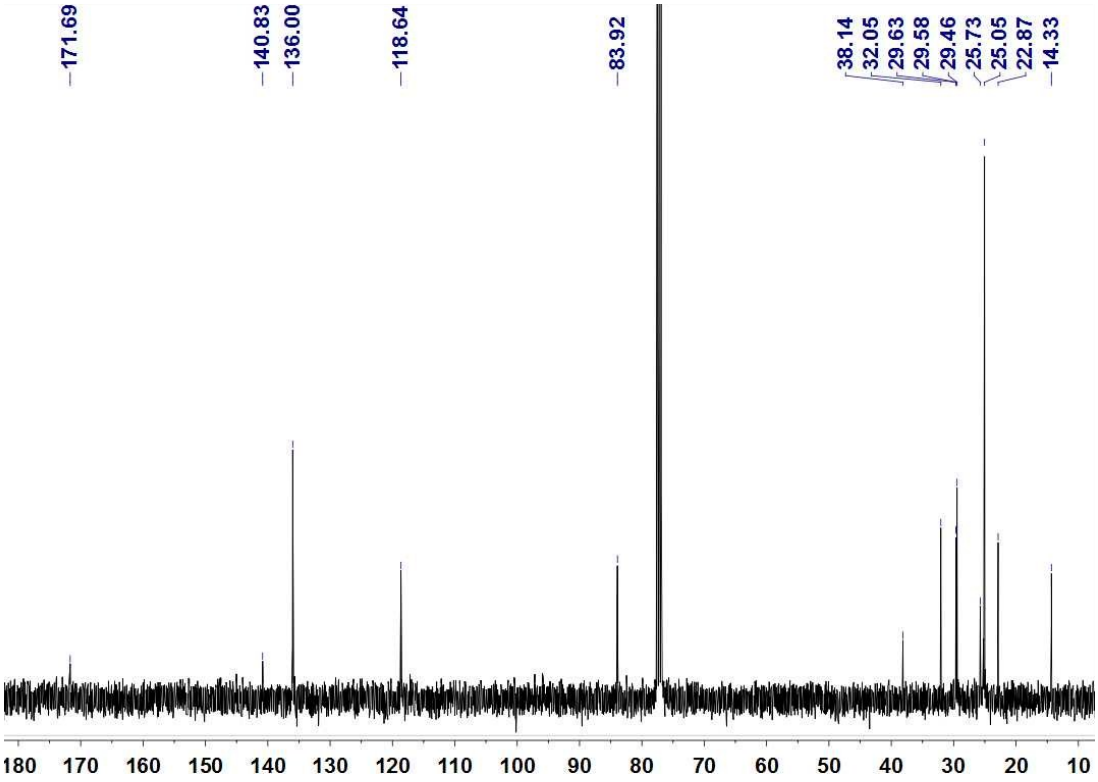



**Figure S23.** $^{13}C$ NMR spectrum of compound **S-7** (298K, 100 MHz, $CDCl_3$).

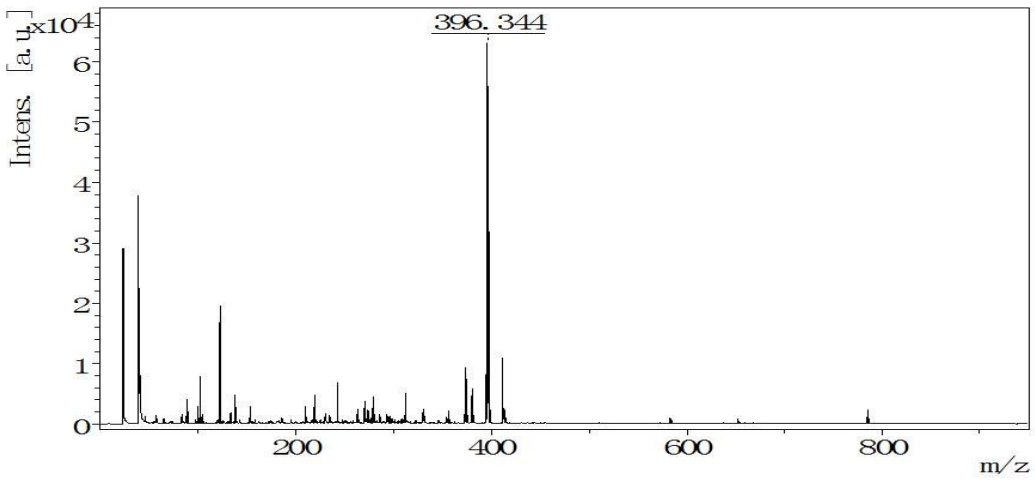



**Figure S24.** MALDI-TOF spectrum of compound **S-7**.

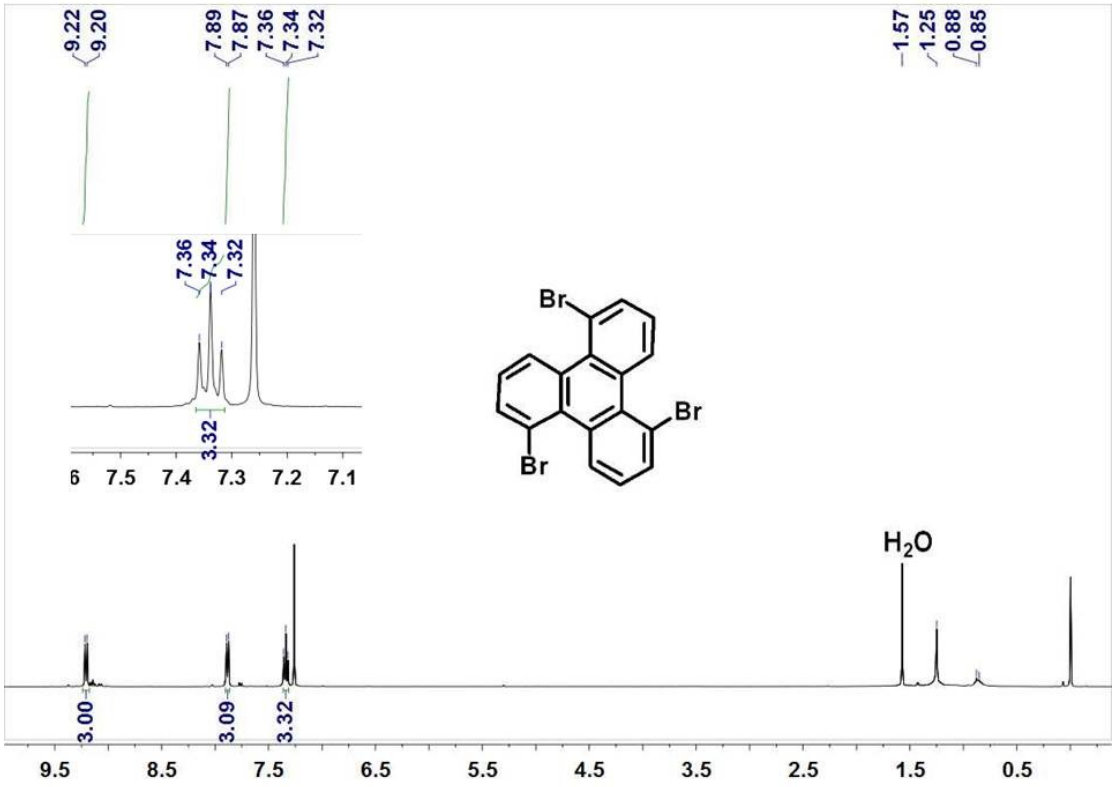



**Figure S25.** $^{1}$H NMR spectrum of compound **S-8** (298K, 400 MHz, $CDCl_3$).

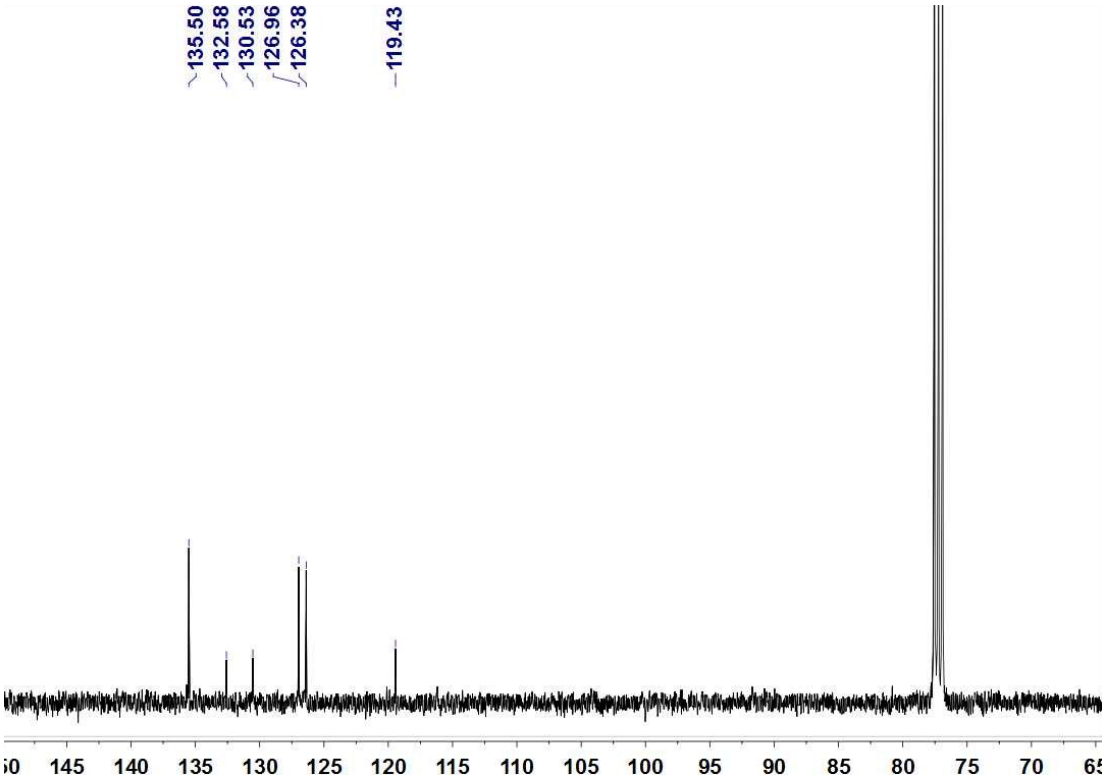



**Figure S26.** $^{13}$C NMR spectrum of compound **S-8** (298K, 100 MHz, $CDCl_3$).

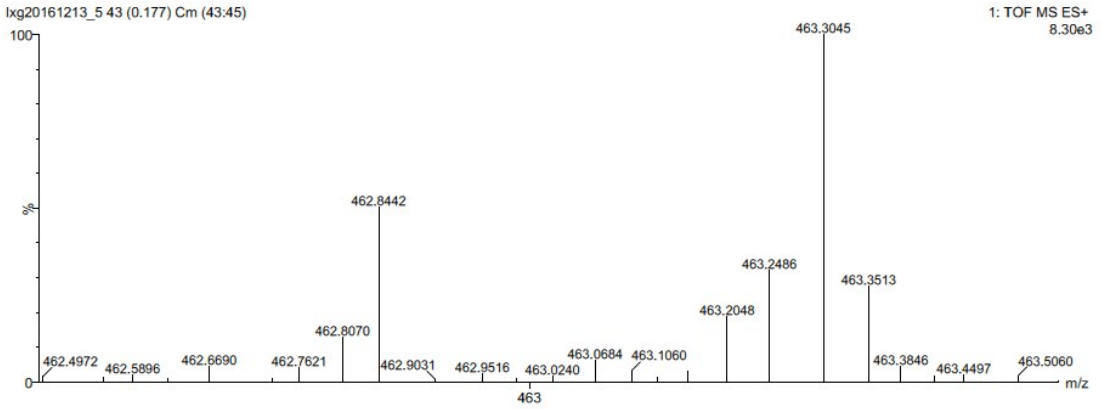



**Figure S27.** HRMS spectrum of compound **S-8**.

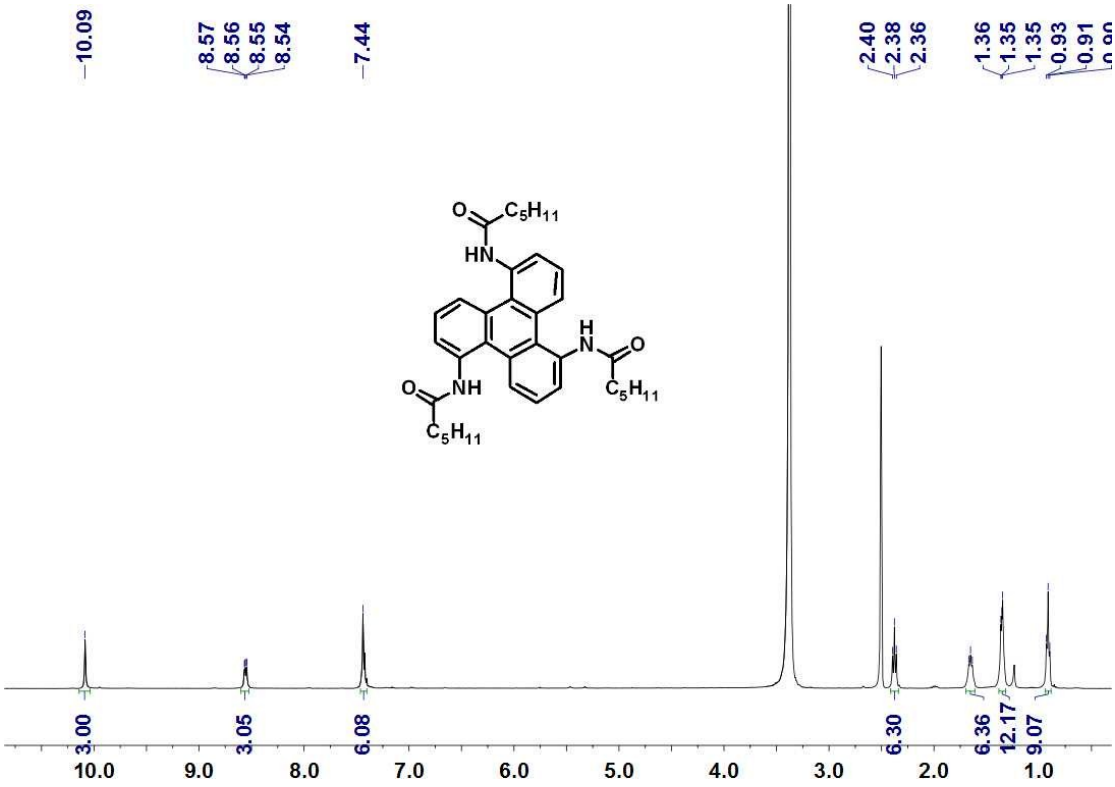



**Figure S28.** $^{1}$H NMR spectrum of compound **1a** (298K, 400 MHz, DMSO-$d_6$).

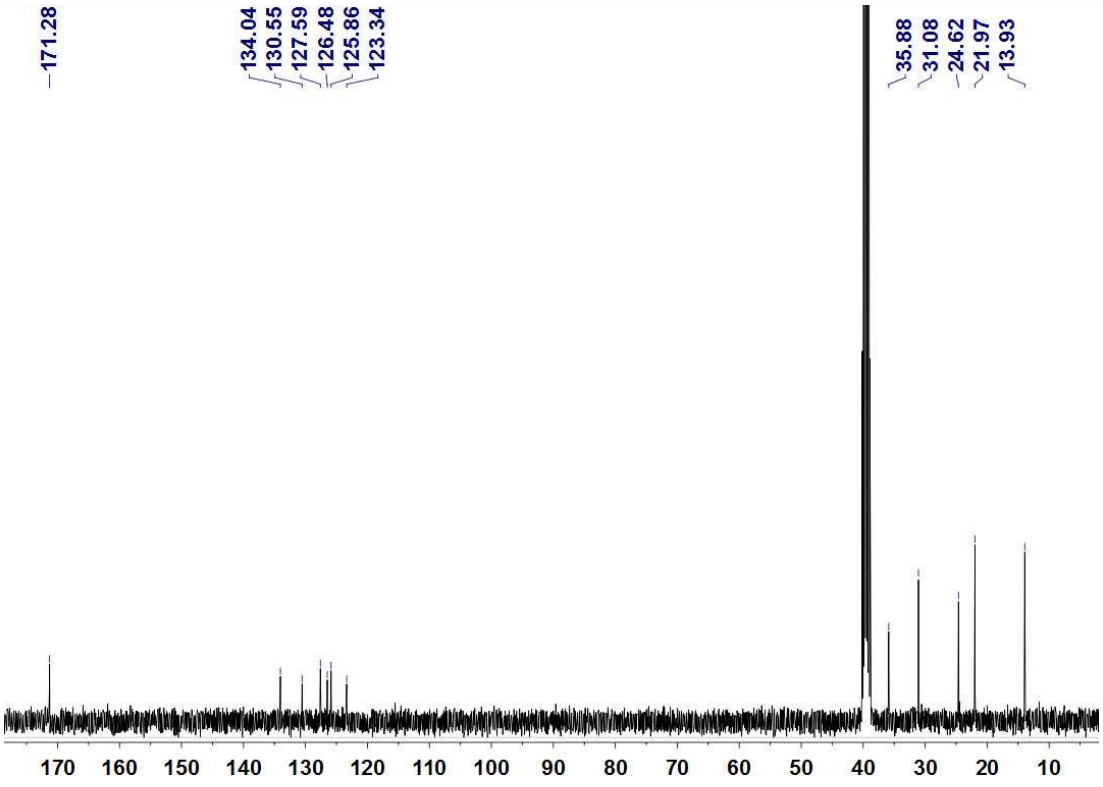



**Figure S29.** $^{13}$C NMR spectrum of compound **1a** (298K, 100 MHz, DMSO-$d_6$).

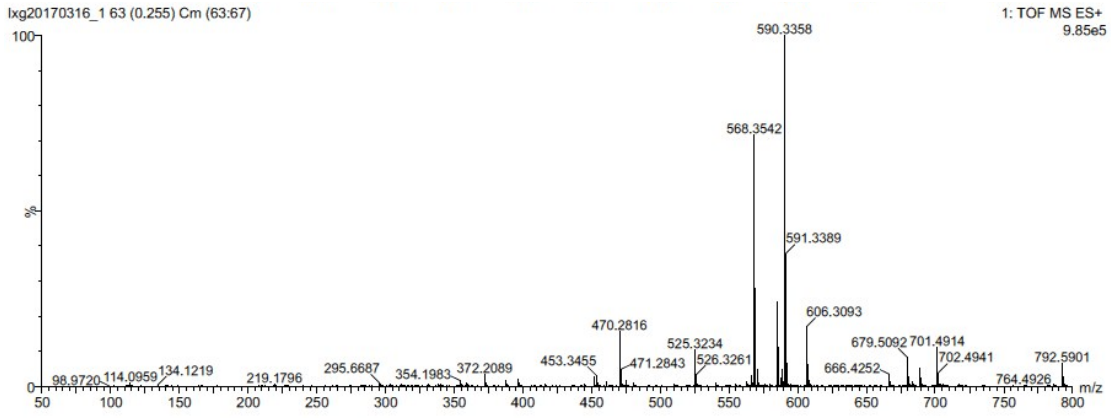



**Figure S30.** HRMS spectrum of compound **1a**.

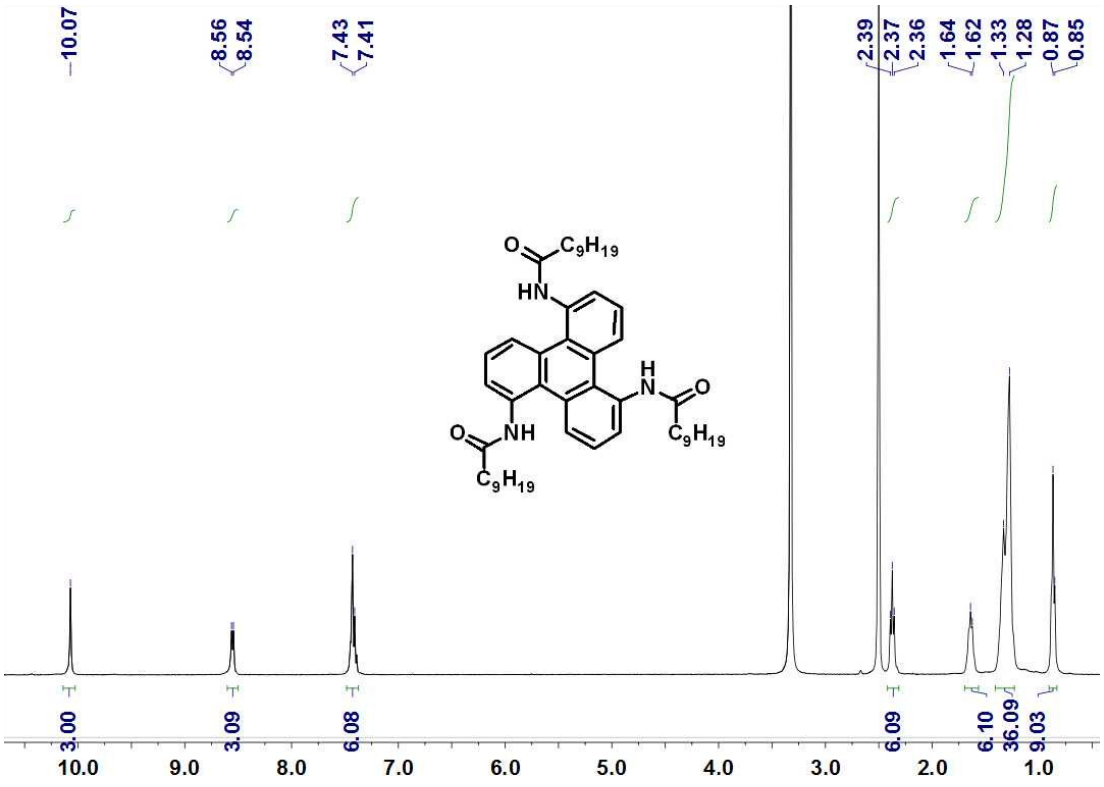



**Figure S31.** $^{1}$H NMR spectrum of compound **1b** (298K, 400 MHz, DMSO-$d_6$).

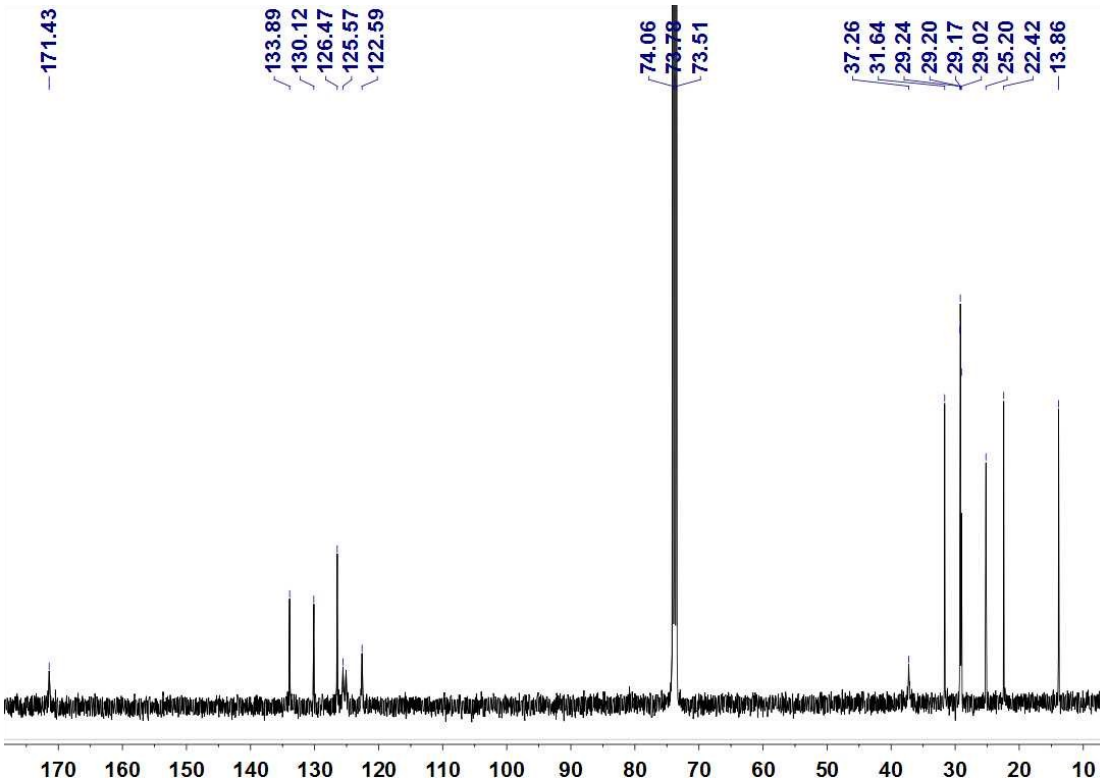



**Figure S32.** $^{13}$C NMR spectrum of compound **1b** (343.5 K, 100 MHz, $C_2D_2Cl_4$).

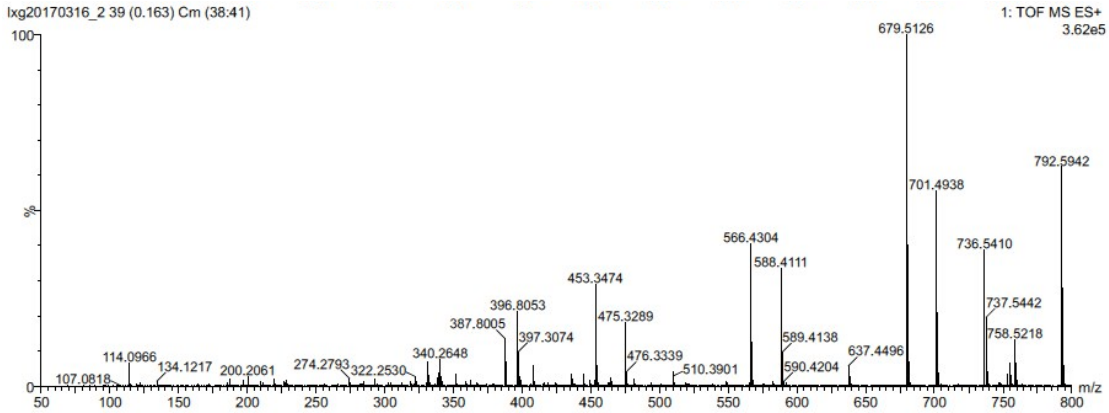



**Figure S33.** HRMS spectrum of compound **1b**.

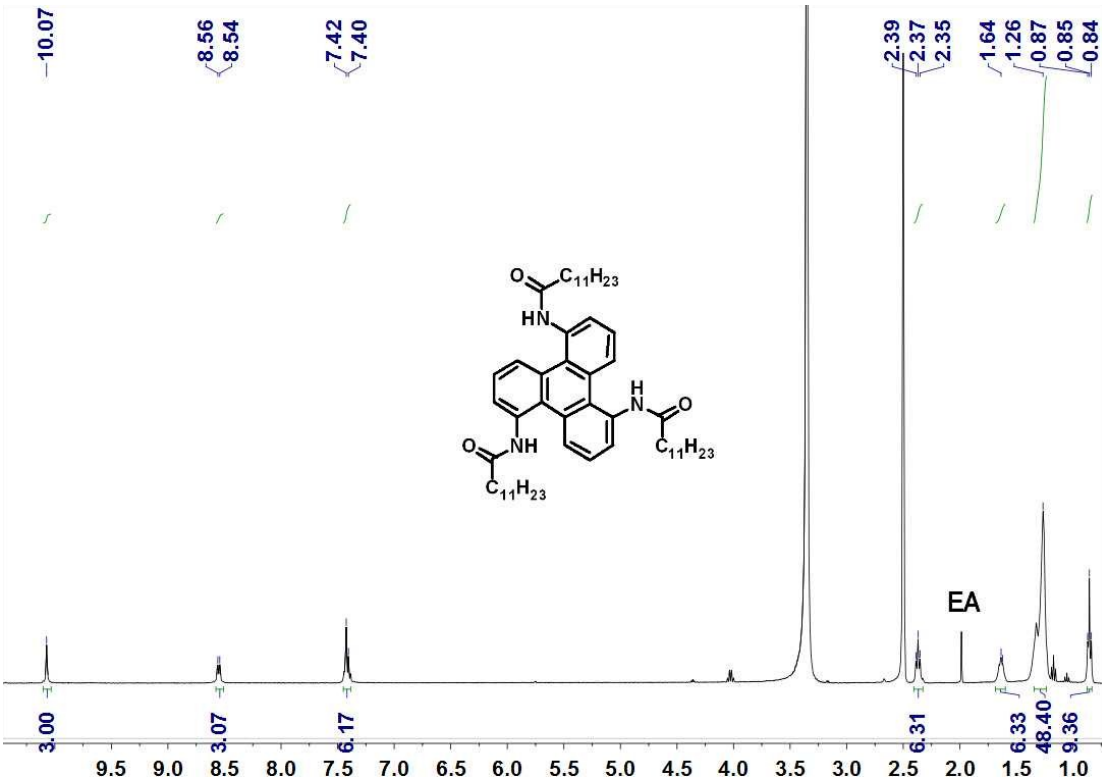



**Figure S34.** $^{1}$H NMR spectrum of compound **1c** (298K, 400 MHz, DMSO-$d_6$).

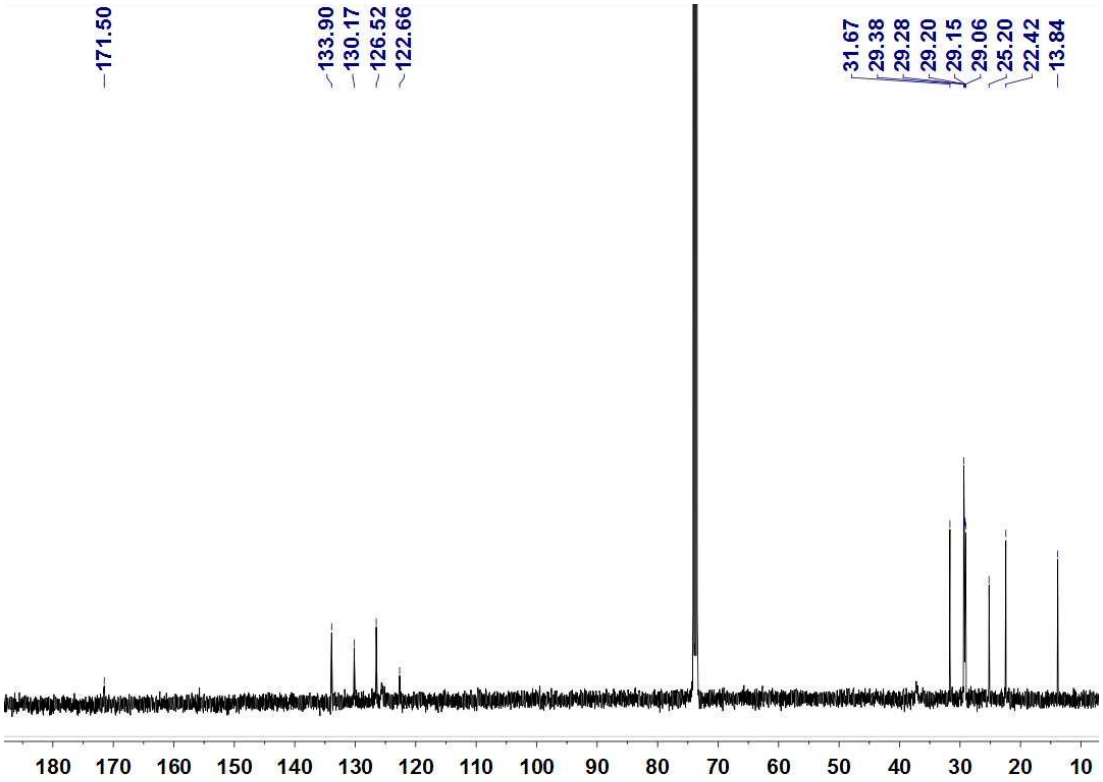



**Figure S35.** $^{13}C$ NMR spectrum of compound **1c** (343.5 K, 100 MHz, $C_2D_2Cl_4$).

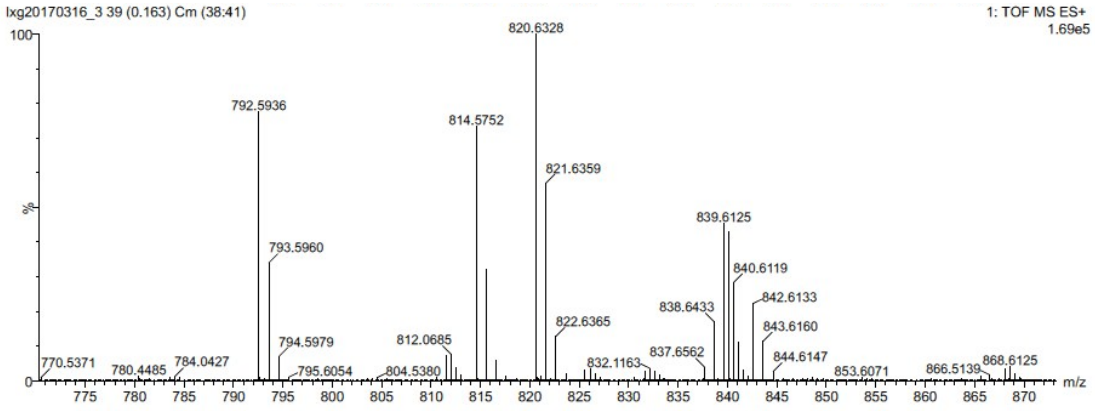



**Figure S36.** HRMS spectrum of compound **1c**.

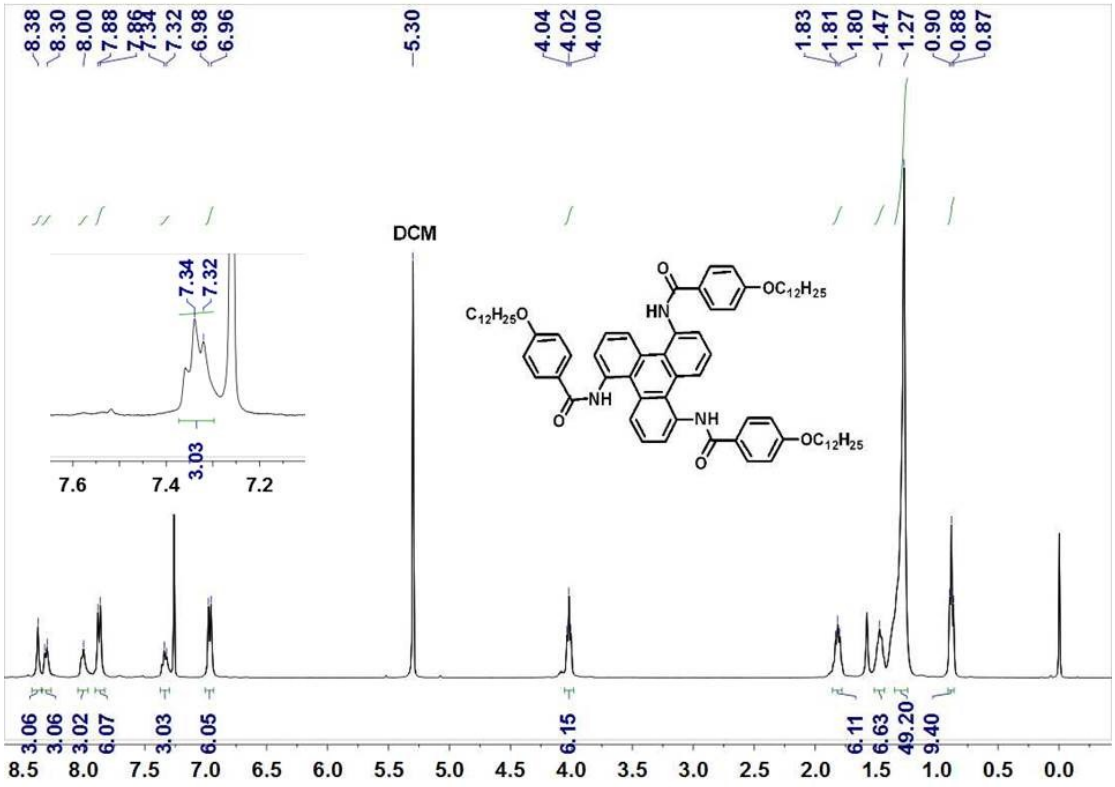



**Figure S37.** $^{1}H$ NMR spectrum of compound **2** (298K, 400 MHz, $CDCl_3$).

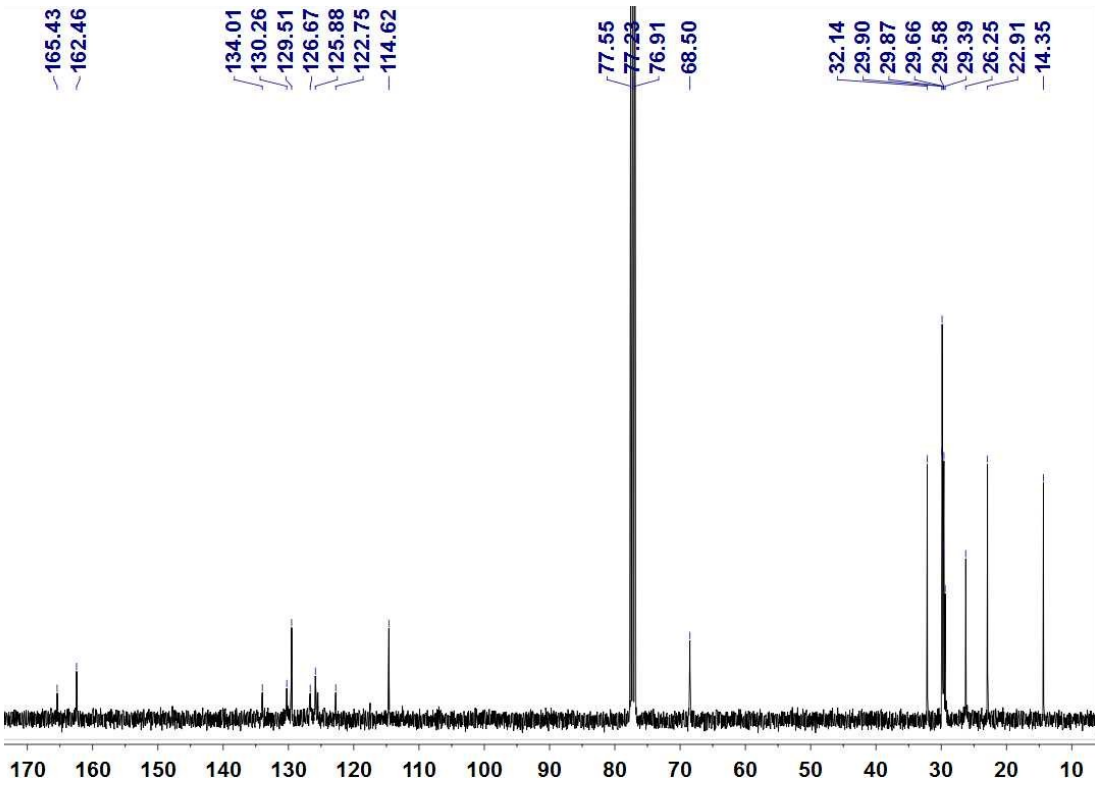



**Figure S38.** $^{13}C$ NMR spectrum of compound **2** (298K, 100 MHz, $CDCl_3$).

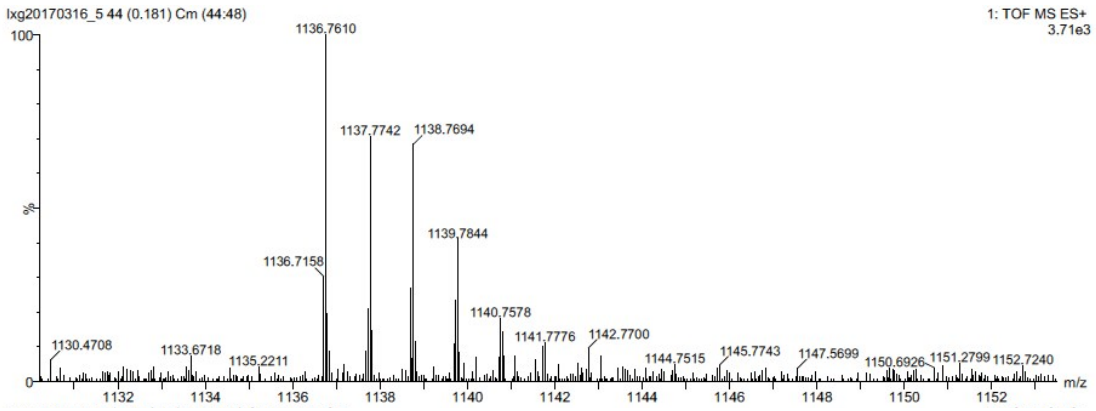



**Figure S39.** HRMS spectrum of compound **2**.

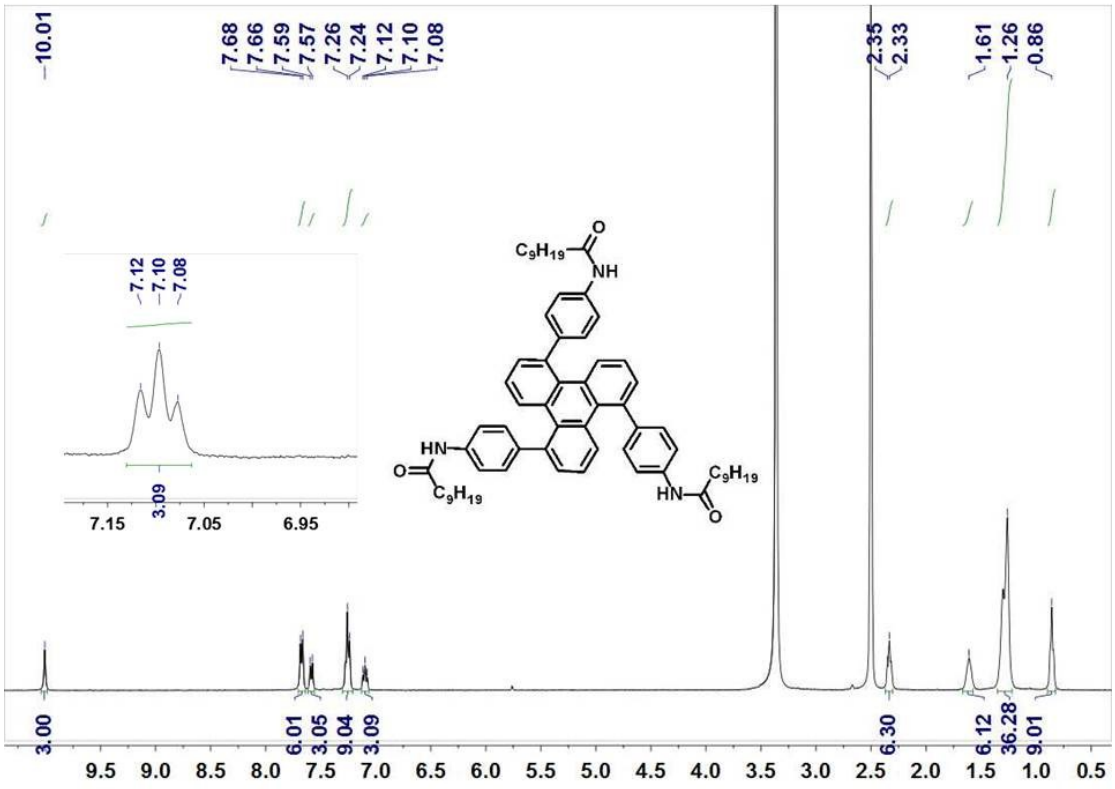



**Figure S40.** $^{1}$H NMR spectrum of compound **3** (298K, 400 MHz, DMSO-$d_6$).

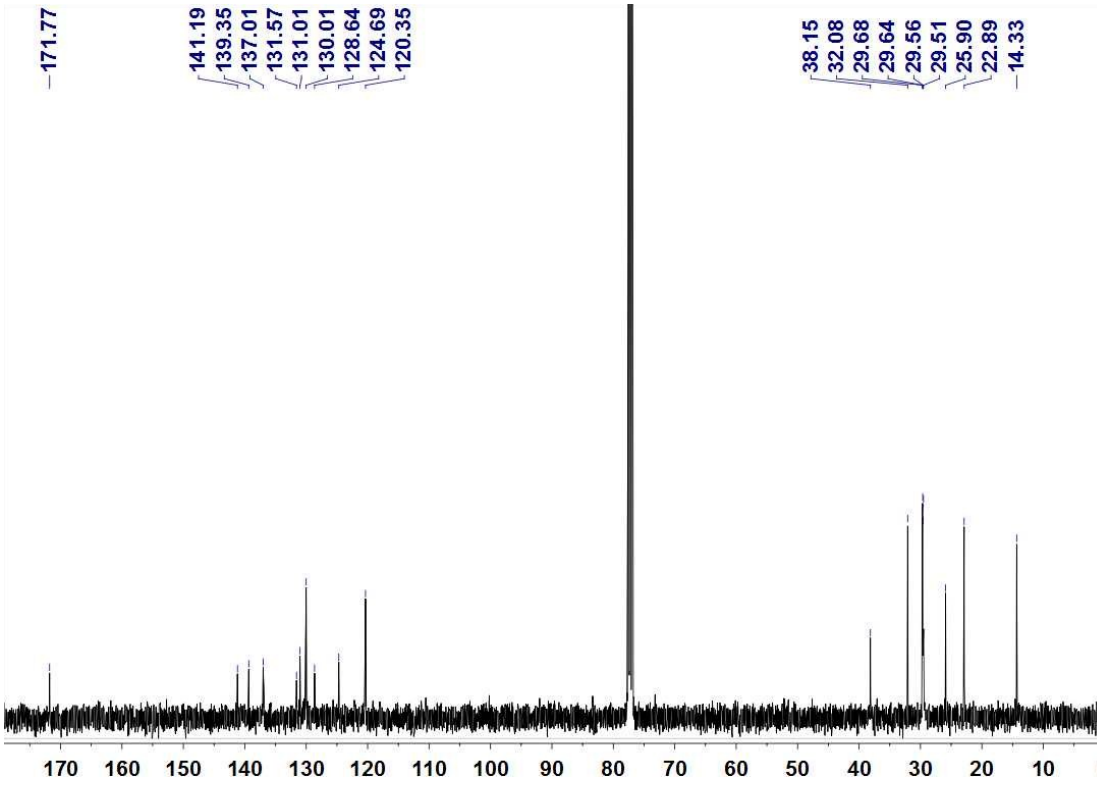



**Figure S41.** $^{13}C$ NMR spectrum of compound **3** (298K, 100 MHz, $CDCl_3$).

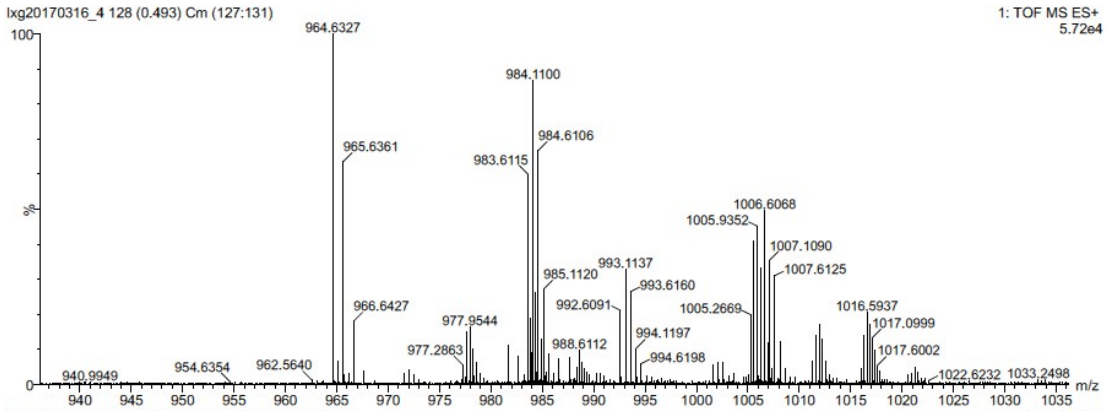



**Figure S42.** HRMS spectrum of compound **3**.

## Section 10. Supporting References

[S1] Q. Tan, H. Chen, H. Xia, B. Liu and B. Xu, *Chem. Commun.*, 2016, **52**, 537–540.

[S2] Y. Chen, F. Zhang, B. Zhu, Y. Han and Z. Bo, *Chem.–Asian J.*, 2011, **6**, 226–233.

[S3] K. R. Reddy, E. Varathan, N. Lobo, S. Easwaramoorthi and T. Narasimhaswamy, *J. Phys. Chem. C*, 2016, **120**, 22257–22269.