Electronic Supplementary Information for

Supramolecular nanostructures of coil–rod–coil molecules containing a 9,10-distyrylanthracene group in aqueous solution and their optical properties of assemblies

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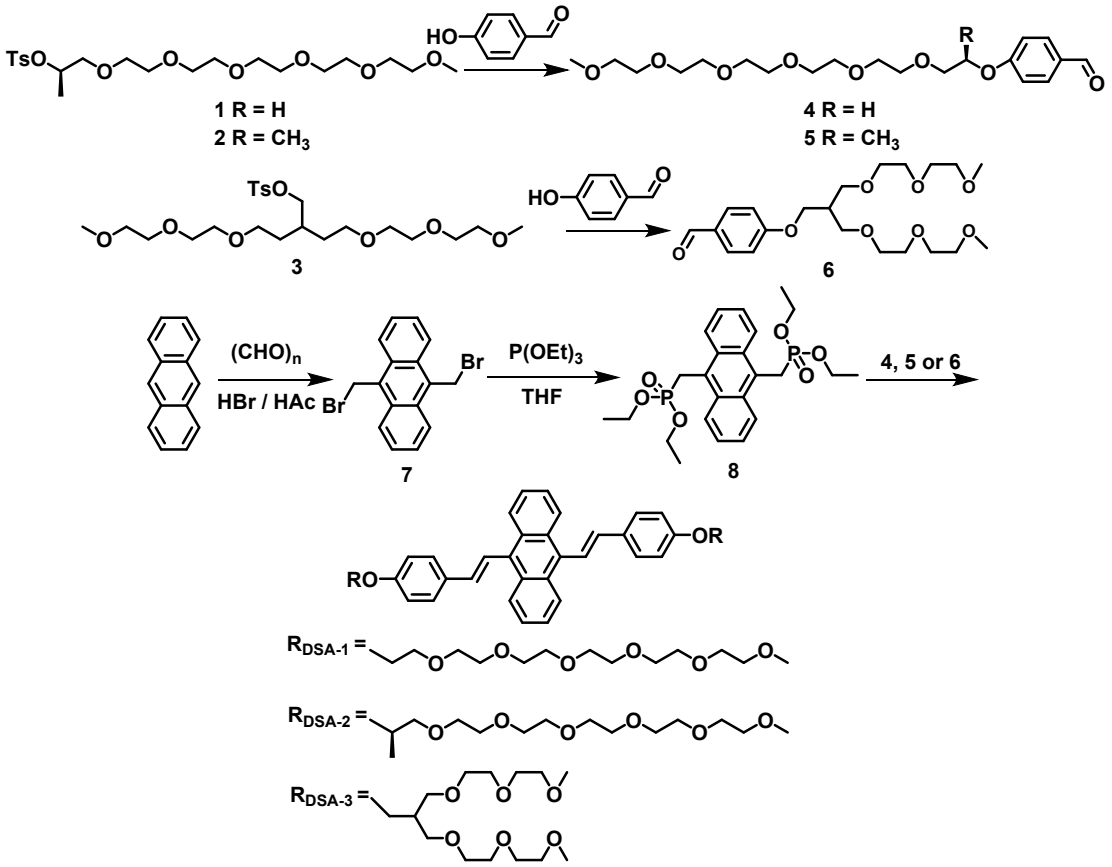
1. Techniques

Flash column chromatography was performed using silica gel (200-300 mesh). ^{1}H-NMR (300 MHz) spectra and ^{13}C-NMR (75 MHz) spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer. MALDI TOF-MS was performed on a PerSeptive Biosystems Voyager-DESTR instrument using 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as the matrix. High-resolution mass spectrometry (HRMS). Compounds were detected on an Exactive GC Orbitrap Mass Spectrometer (Thermo Fisher, USA)

equipped with a direct exposure probe (Electron impact ion source). UV-Vis and fluorescence spectra were obtained on a Shimadzu UV-1650PC spectrometer and a Hitachi F-4500 fluorescence spectrometer (fluorescence slit width: Ex. 2.5 nm, Em. 5 nm), respectively. TEM images were obtained with a Hitachi HT7700 microscope. Atomic force microscopy (AFM) measurements were performed using an Agilent 5500 SPM.

2. Experimental

Synthetic route of molecule DSA-1, DSA-2 and DSA-3



Scheme S1. Synthetic route of molecules DSA-1, DSA-2 and DSA-3.

Synthesis 3, 4 and 5. These compounds were synthesized according to the same procedure, a representation example is described for 4. 4-Hydroxybenzaldehyde (1.0 g, 8.19 mmol) was dissolved in acetone (100 mL) in a 250 mL single-neck round bottom

flask, Add compound 11 (2.9 g, 6.44 mmol) and K_2CO_3 (0.6 g). The mixture was further refluxed for 18 h. The solvent was removed by a rotary evaporator, dissolved in 15 mL of water slowly, extracted with methylene chloride, dried over anhydrous magnesium sulfate and the solvent was removed by a rotary evaporator. The crude product was purified by silica gel column chromatography on silica gel to yield 1.9 g (76 %).

Compound 3. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): 9.89 (s, 1 H), 7.85-7.83 (d, *J* = 6 Hz, 2 H), 7.05-7.03 (d, *J* = 6 Hz, 2 H), 4.24-3.88 (m, 2 H), 3.76-3.69 (m, 2 H), 3.65-3.54 (m, 20 H), 3.38 (s, 3 H).

Compound 4. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): 9.89 (s, 1 H), 7.85-7.82 (d, *J* = 9 Hz, 2 H), 7.05-7.03 (d, *J* = 6 Hz, 2 H), 4.77-4.68 (m, 1 H), 3.69-3.52 (m, 22 H), 3.39 (s, 3 H), 1.37-1.35 (d, *J* = 6 Hz, 3 H).

Compound 5. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): 9.88 (s, 1 H), 7.84-7.81 (d, *J* = 9 Hz, 2 H), 7.03-7.00 (d, *J* = 9 Hz, 2 H), 4.15-4.13 (d, *J* = 6 Hz, 2 H), 3.62-3.53 (m, 20 H), 3.36 (s, 3 H), 2.48-2.41 (m, 1 H).

Synthesis 7. Weigh 4 g of anthracene in a 500 mL flask, add 1.44 g of paraformaldehyde, 0.18 g of cetyl ammonia bromide and 14 mL of glacial acetic acid, dropwise add 35 mL of hydrobromic acid, and react at 80 °C for 5 h, the crude product was obtained by suction filtration, and the product obtained by recrystallization was a yellow solid 2.6 g (65 %).

Synthesis 8. 1g of compound 7 was dissolved in 500 mL of THF, then diethyl phosphonate was added the solvent was evaporated to dryness after refluxing for 8 h, and the purified product by column chromatography on silica gel was a yellow solid

0.35 g (35 %).

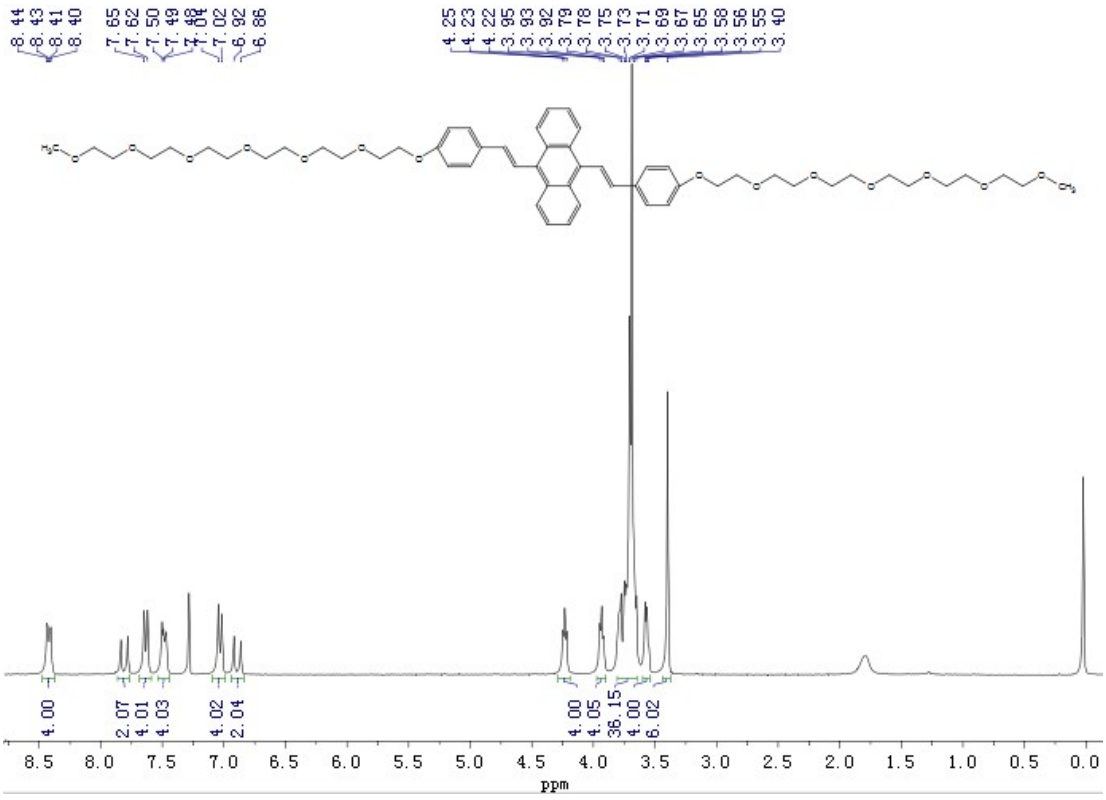
Compound 8. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): 8.42-8.39 (m, 4 H), 7.61-7.58 (m, 4 H), 4.29-4.23 (d, *J* = 18 Hz, 4 H), 3.94-3.78 (m, 8 H), 1.11-1.07 (t, *J* = 9 Hz, 12 H).

General synthetic procedure for molecules DSA-1, DSA-2 and DSA-3 were synthesized using the same synthetic procedure (Scheme 1). A representative example is described for DSA-1. Compound 8 (0.09 g, 0.19 mmol) was dissolved in THF (40 mL) in a 100 mL single-neck round bottom flask, the sodium hydride in ice water bath were added, add compound 5 (0.20 g, 0.34 mmol) after 30 min. The mixture was refluxed for 36 h. The solvent was removed using a rotary evaporator and the crude product was purified by silica gel column chromatography using CH_2Cl_2 and CH_3OH as eluent to yield 0.30 g of a chartreuse oily liquid (63.2 %). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.44-8.40 (m, 4 H), 7.84-7.78 (d, *J* = 18 Hz, 2 H), 7.65-7.62 (d, *J* = 9 Hz, 4 H), 7.50-7.47 (m, 4 H), 7.04-7.02 (d, *J* = 6 Hz ,4 H) 6.92-6.86 (d, *J* = 18 Hz, 2 H), 4.25-4.22 (t, *J* = 6 Hz, 4 H), 3.95-3.92 (t, *J* = 6 Hz, 4 H) 3.79-3.65 (m, 36 H), 3.40 (s, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 158.96, 136.85, 132.94, 130.60, 129.82, 127.73, 126.53, 125.03, 123.12, 114.98, 71.95, 70.90, 70.67, 70.62, 70.53, 69.77, 67.61, 58.97. MALDI-TOF-MS: m/z $(M)^{+}$ 971.150.

Molecules 2: Chartreuse oily liquid, yield (52.8 %). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.43-8.39 (m, 4 H), 7.83-7.78 (d, *J* = 15 Hz, 2 H), 7.64-7.61 (d, *J* = 9 Hz, 4 H), 7.50-7.46 (m, 4 H), 7.05-7.02 (d, *J* = 9 Hz, 4 H), 6.91-6.86 (t, *J* = 15 Hz, 2 H), 4.69-4.62 (m, 1 H), 3.79-3.64 (m, 42 H), 3.57-3.54 (m, 4 H), 3.39 (s, 6 H), 1.40-1.38 (d, *J* = 6 Hz,6 H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 157.96, 136.86, 132.78, 130.35,

129.63, 127.81, 126.54, 125.11, 122.95, 116.36, 74.47, 73.34, 71.93, 71.04, 70.61, 70.52, 59.04, 17.03. MALDI-TOF-MS: m/z (M) $^{+}$ 998.005.

Molecules 3: Chartreuse oily liquid, yield (53.6 %). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.44-8.40 (m, 4 H), 7.83-7.77 (d, *J* = 18 Hz, 2 H), 7.64-7.61 (d, *J* = 9 Hz, 4 H), 7.50-7.47 (m, 4 H), 7.03-7.01 (d, *J* = 6 Hz, 4 H), 6.92-6.86 (d, *J* = 18 Hz, 2 H), 4.15-4.13 (d, *J* = 6 Hz, 4 H), 3.76-3.66 (m, 32 H), 3.58-3.55 (m, 8 H), 3.41 (s, 12 H), 2.51-2.45 (m, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 159.18, 136.91, 132.80, 130.18, 129.77, 127.75, 126.48, 125.18, 122.93, 114.90, 71.89, 70.85, 70.69, 69.52, 66.24, 59.98, 53.49, 40.08. MA LDI-TOF-MS: m/z (M) $^{+}$ 998.031.



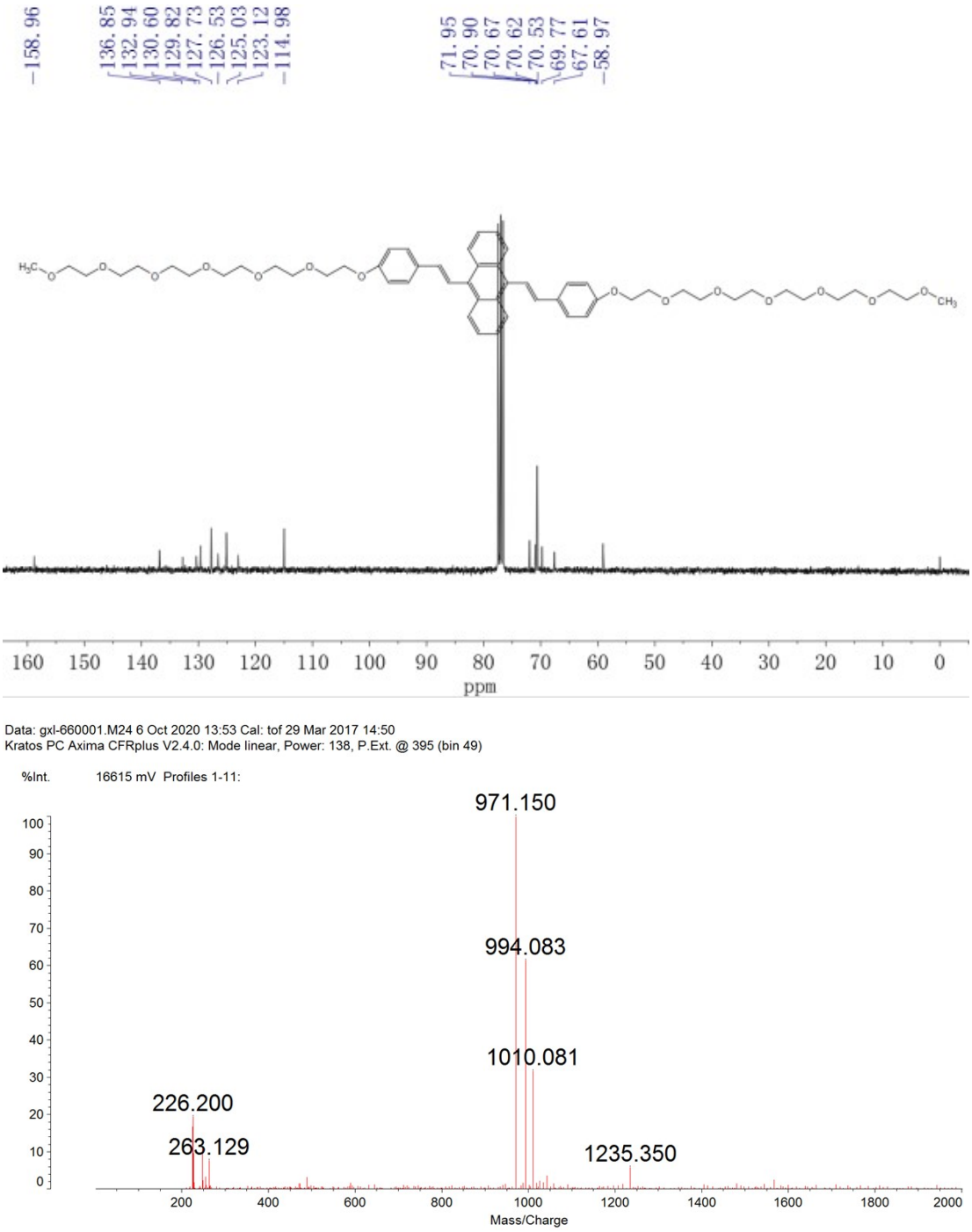
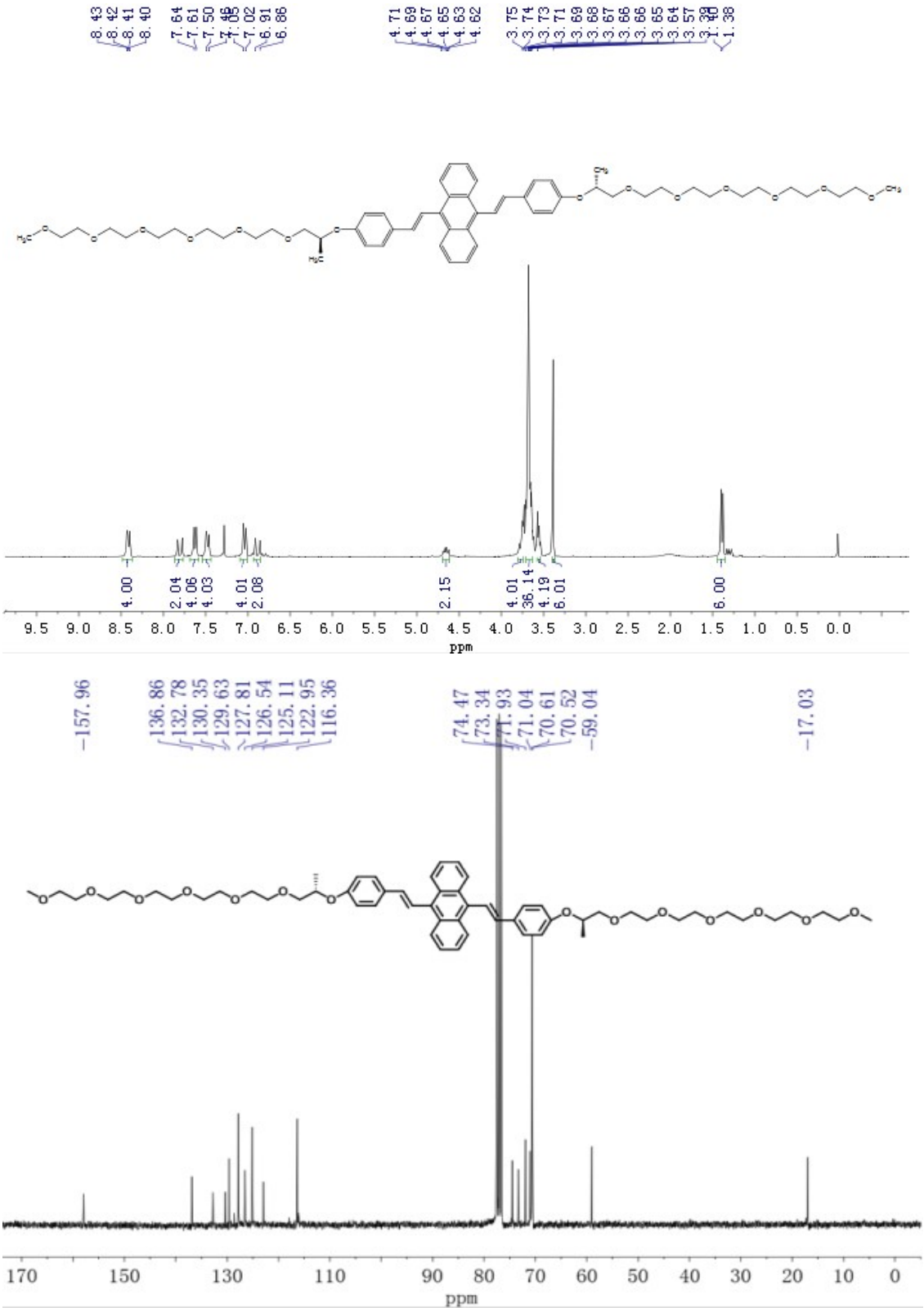


Fig. S1 ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and MALDI-TOF mass spectrum of DSA-1.


8.43
8.42
8.41
8.40
7.64
7.61
7.50
7.02
6.91
6.86
4.71
4.69
4.67
4.65
4.63
4.62
3.75
3.74
3.73
3.71
3.69
3.68
3.67
3.66
3.66
3.65
3.64
3.57
1.38
4.00
2.04
4.06
4.03
4.01
2.08
2.15
4.01
36.14
4.19
6.01
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
157.96
136.86
132.78
130.35
129.63
127.81
126.54
125.11
122.95
116.36
74.47
73.34
71.93
71.04
70.61
70.52
59.04
17.03
170 150 130 110 90 80 70 60 50 40 30 20 10 0
ppm

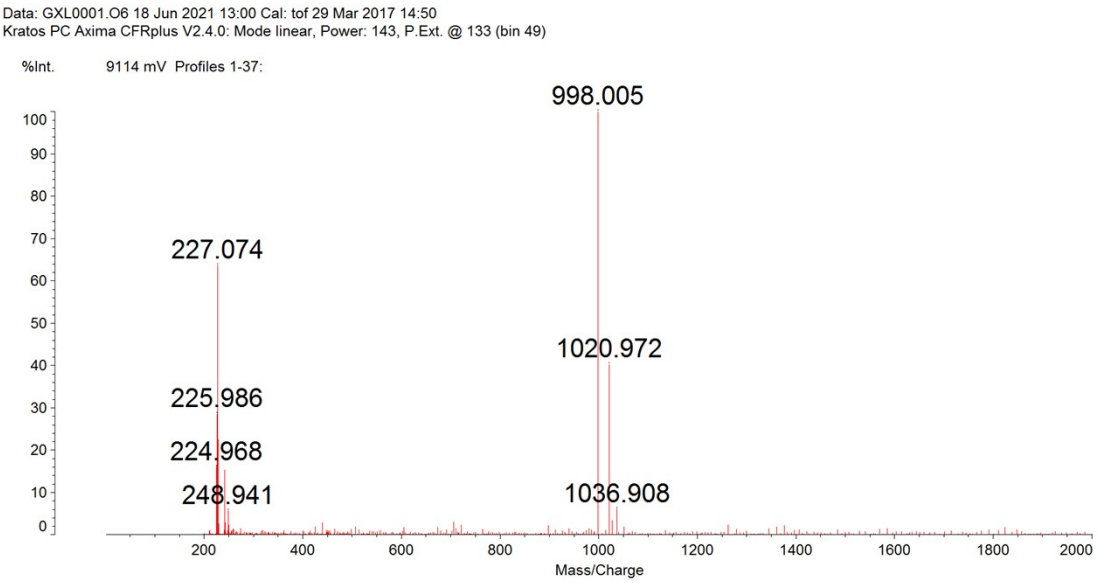
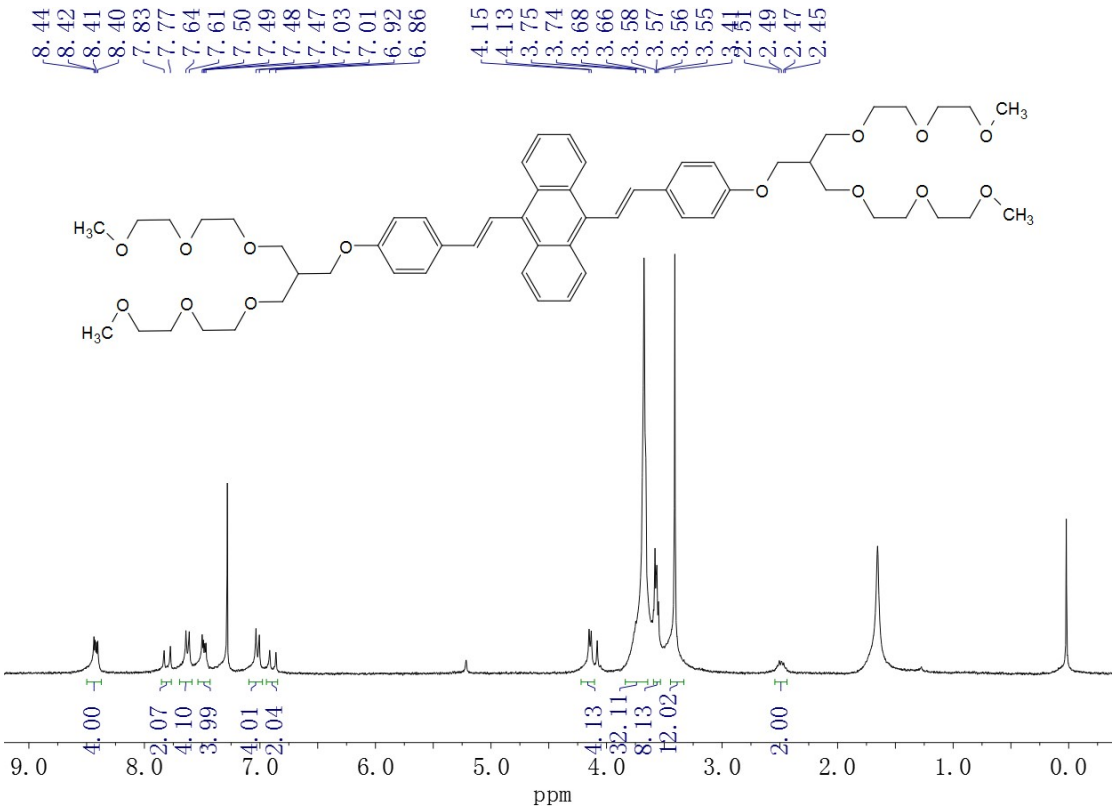
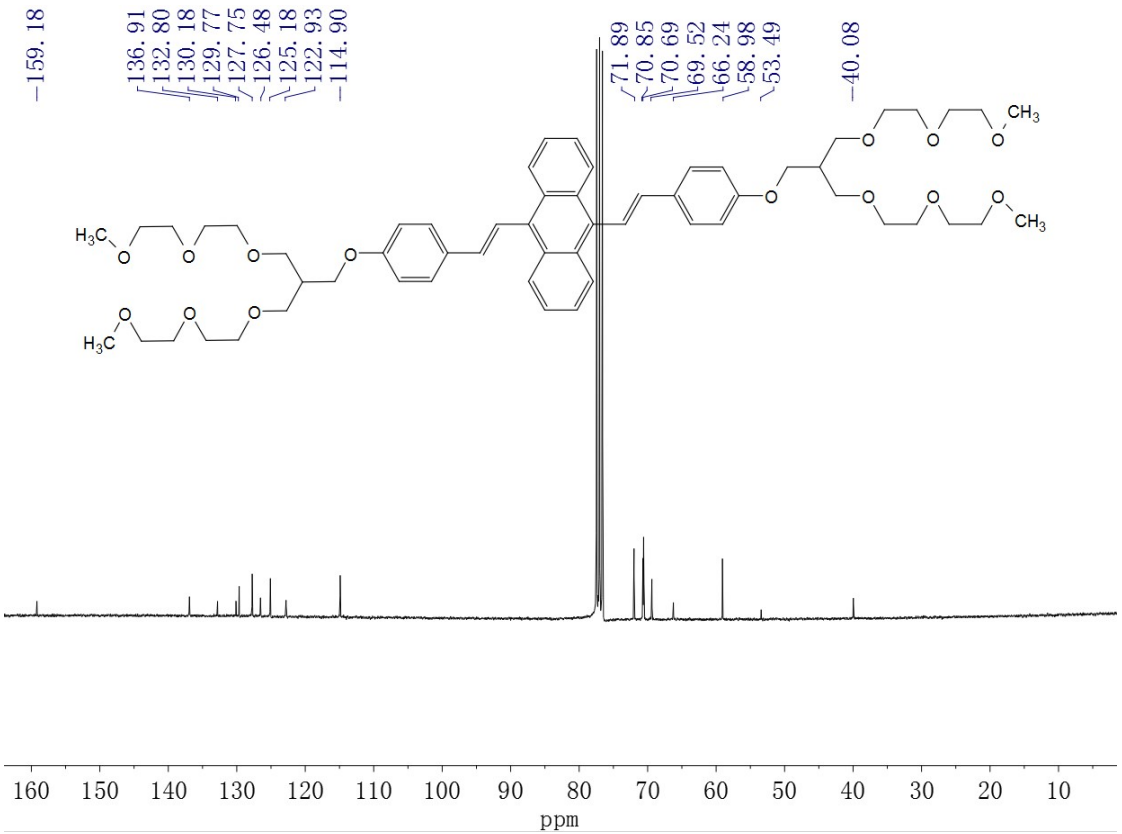


Fig. S2 ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and MALDI-TOF mass spectrum of DSA-2.





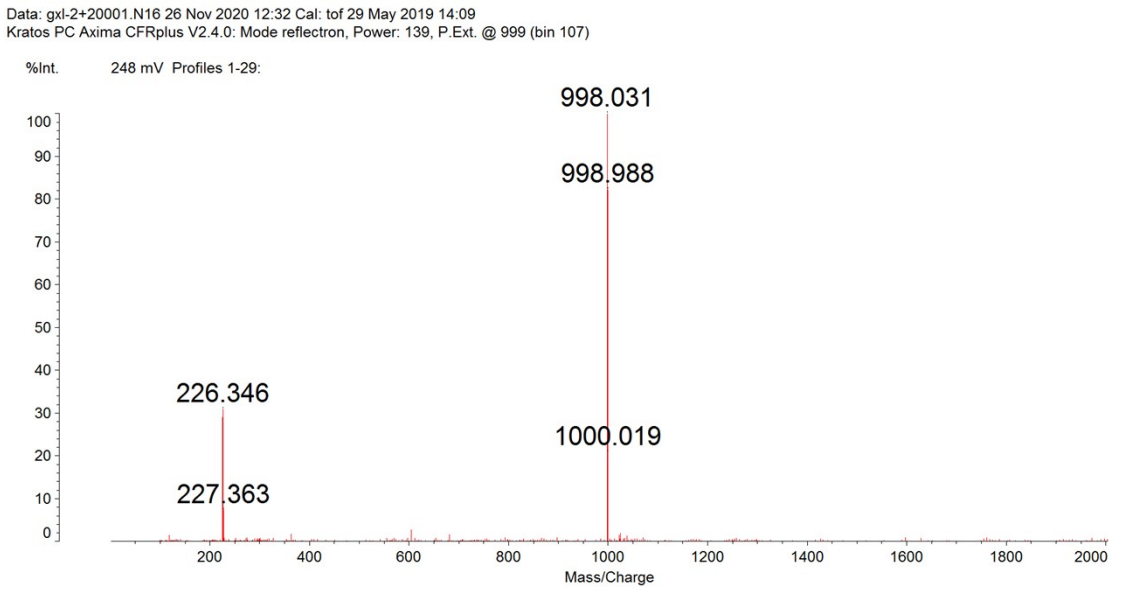


Fig. S3 ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and MALDI-TOF mass spectrum of DSA-3.

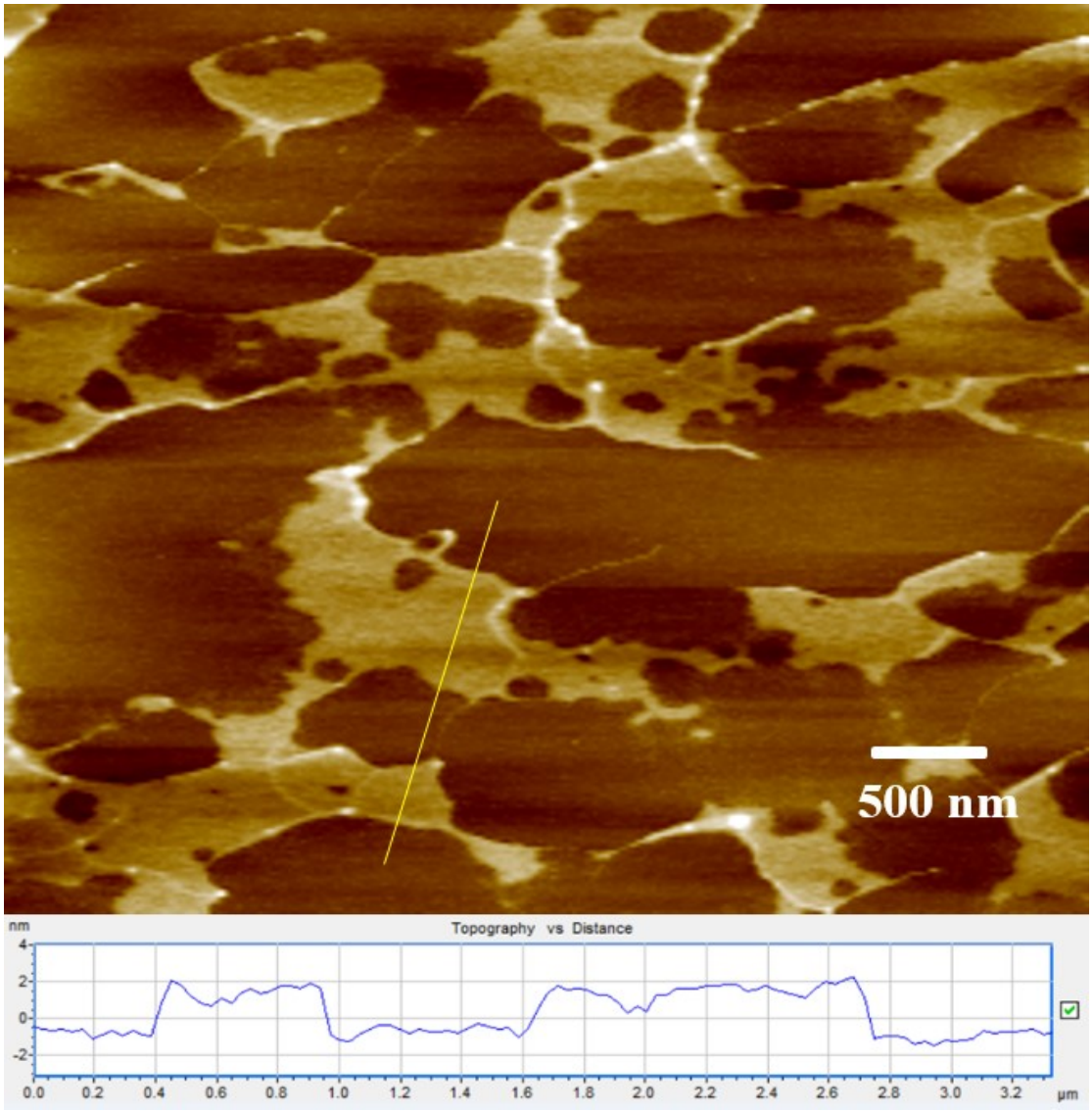


Fig. S4 Height image of the assembled structures of DSA-3 (0.004 wt%) in the mixed solution of THF and water (1:49).

Preparation of DSA morphology samples:

The mixture of the 0.1mg of DSA and 0.1 mL THF was added to 10 mL distilled water. The flask was sonicated for 3~5 minutes at 25 ℃ in KQ-250E ultrasonicator (250W), until the molecule was dissolved in water. Then, the flask was further sonicated for 40 minutes at 25 ℃ in KQ-100KDE ultrasonicator (60 W). Finally, the solution is allowed to stand for 30 minutes to prepare samples of AFM (sample solution dripped onto mica sheets for testing) or TEM (sample solution dripped onto glow treated copper mesh and performed negative staining before testing).

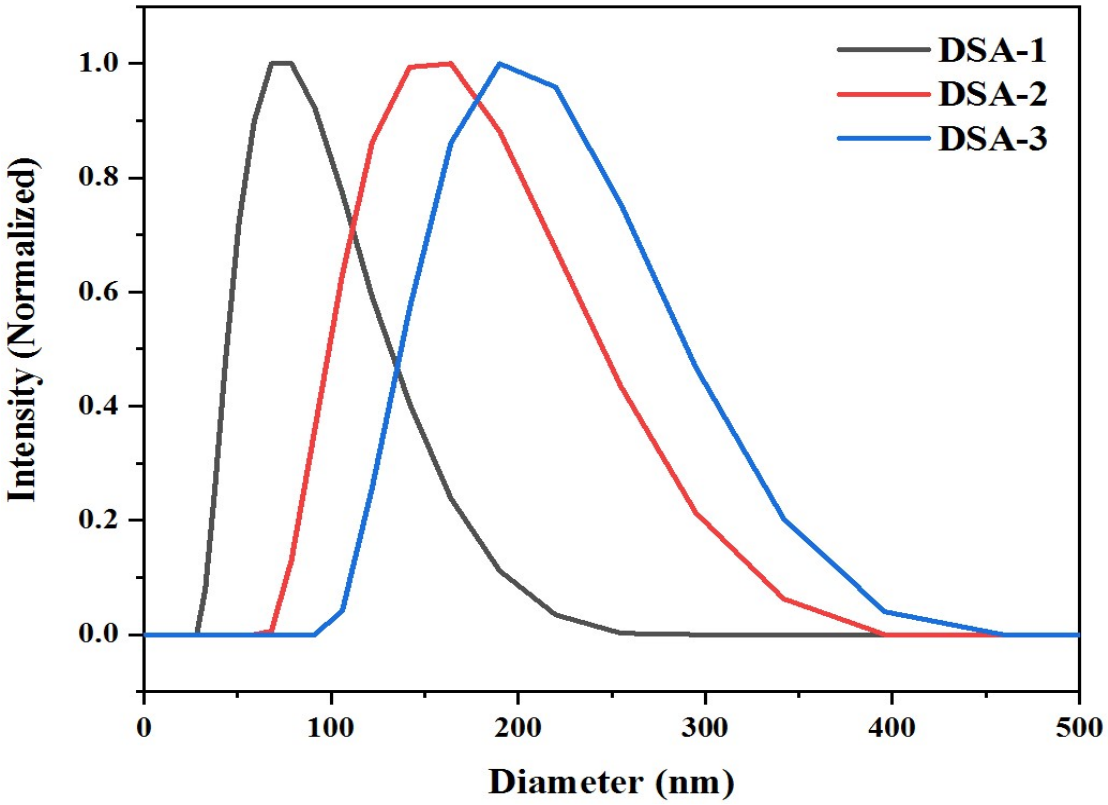


Fig. S5 Size distribution image of the in 98 % aqueous solutions of DSA-1, DSA-2 and DSA-3 (0.004 wt%) in the mixed solution of THF and water (1:49) from DLS.

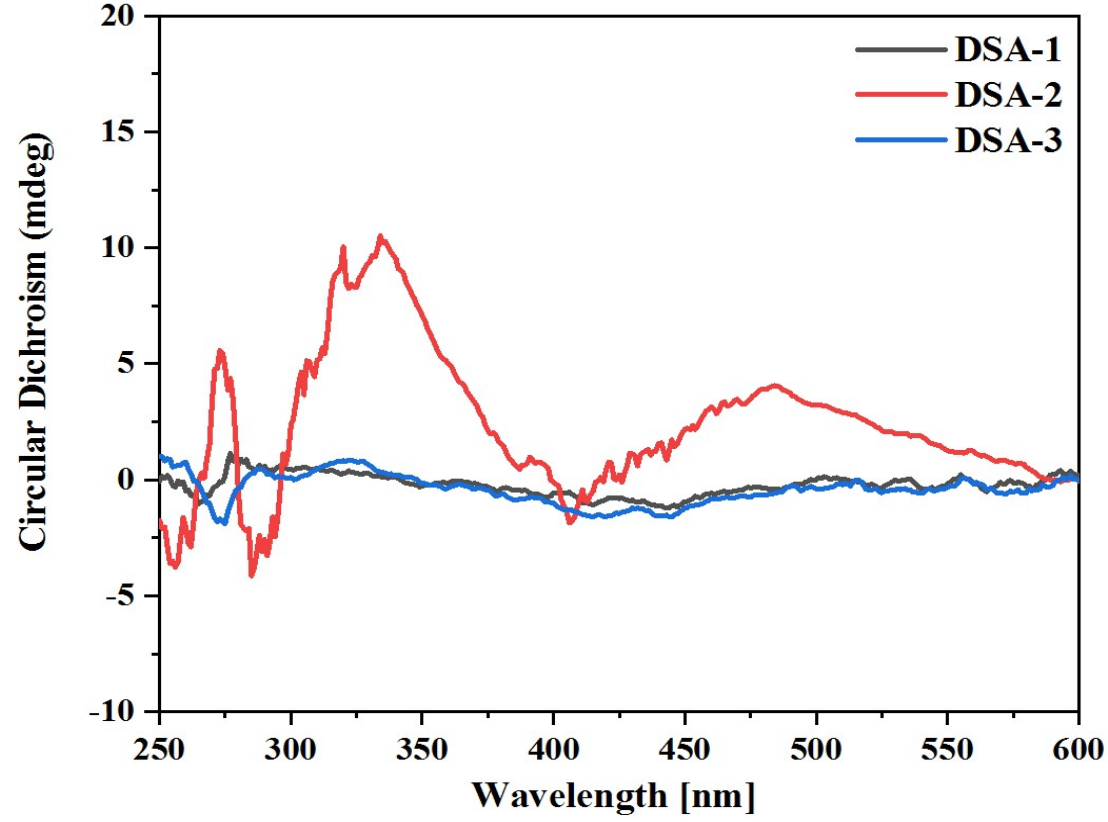
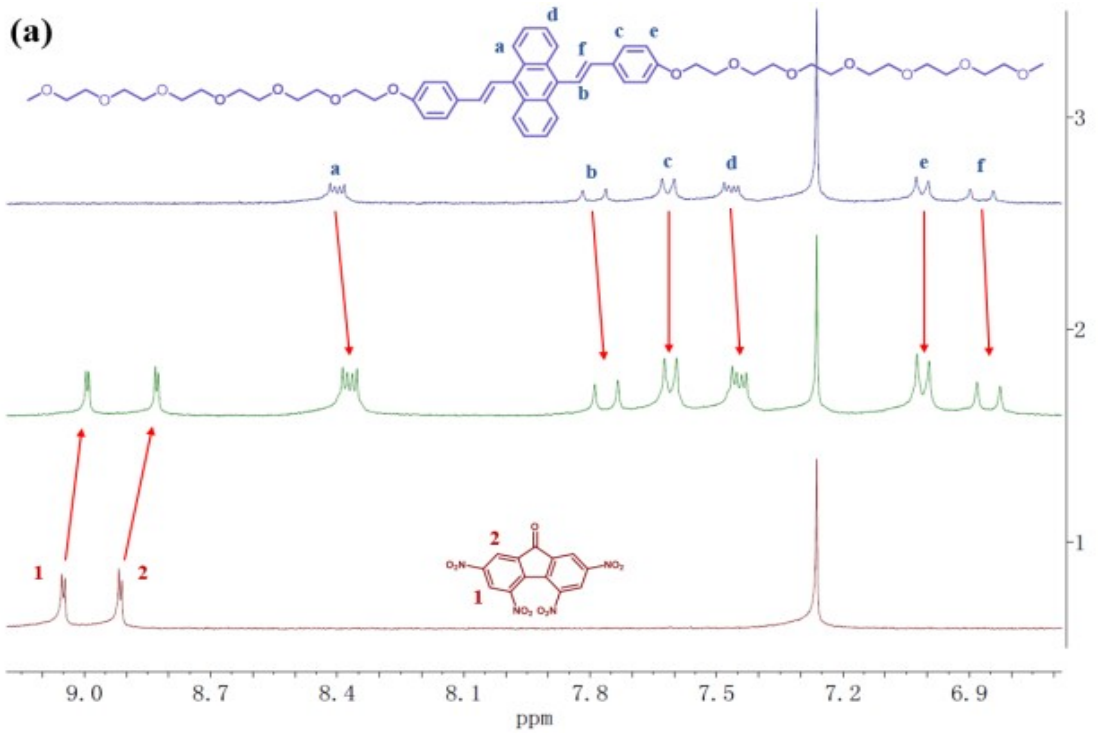
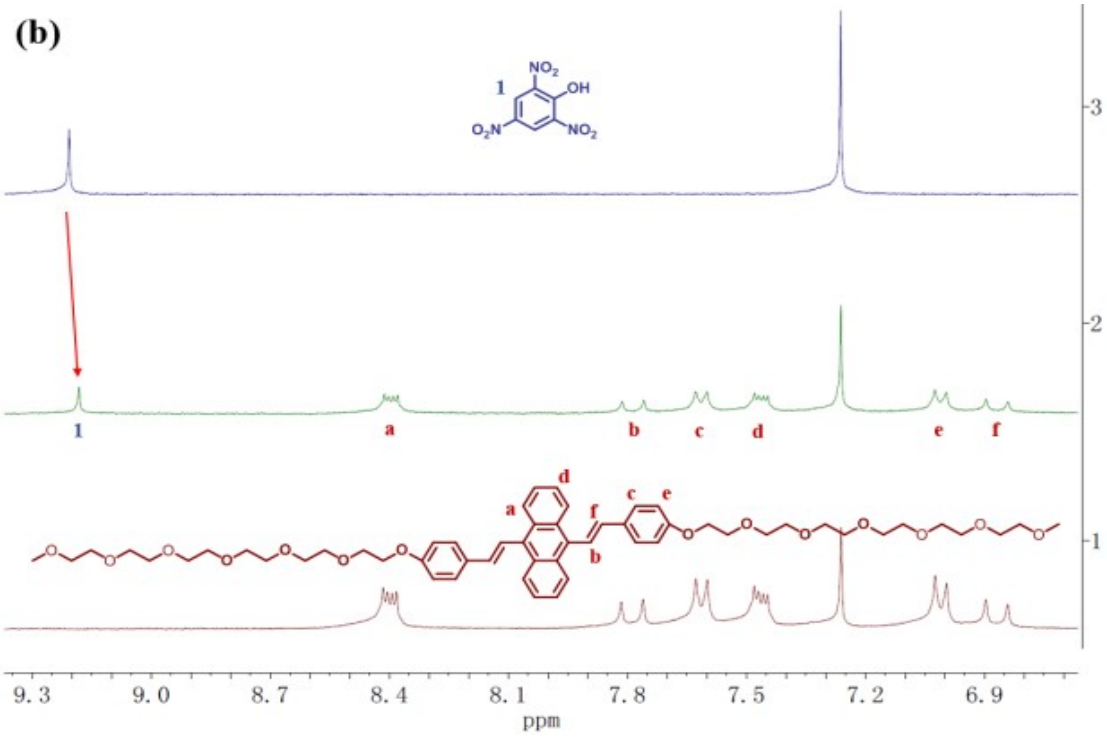
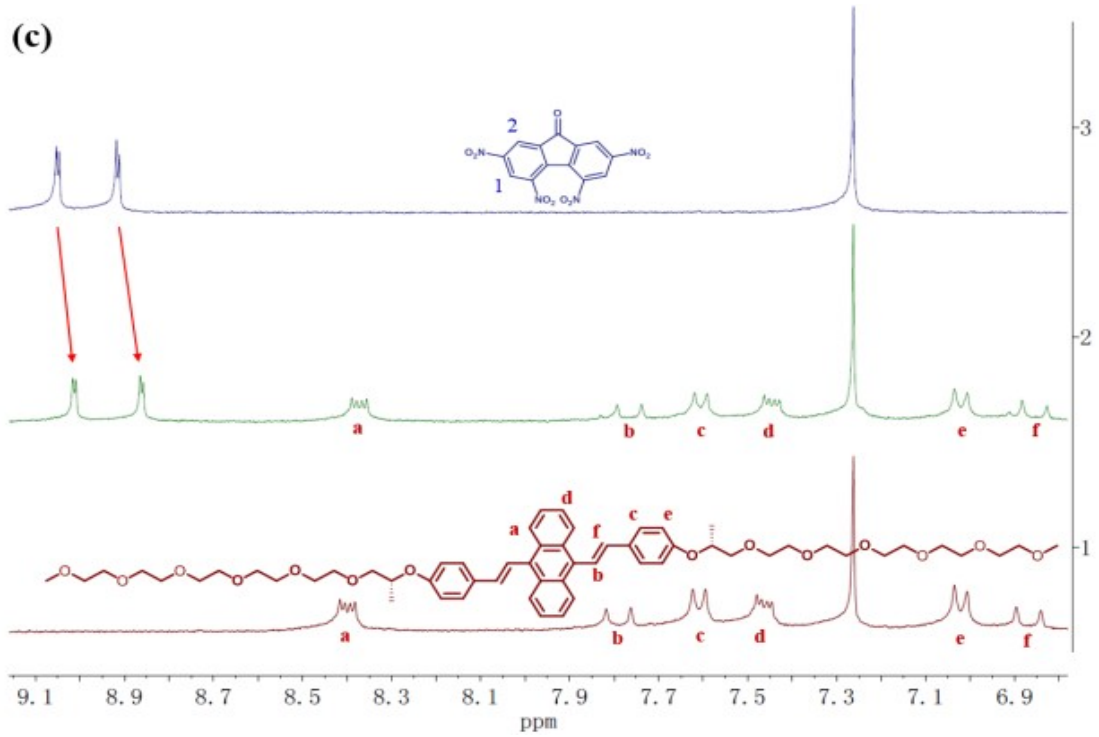


Fig. S6 CD spectra of DSA-1, DSA-2 and DSA-3 in aqueous solution (0.008 wt%).


(a)
a
b
c
d
e
f
1
2
9.0
8.7
8.4
8.1
7.8
7.5
7.2
6.9
ppm


(b)
1
a
b
c
d
e
f
9.3
9.0
8.7
8.4
8.1
7.8
7.5
7.2
6.9
ppm


(c)
2
1
3
2
1
a
b
c
d
e
f
9.1
8.9
8.7
8.5
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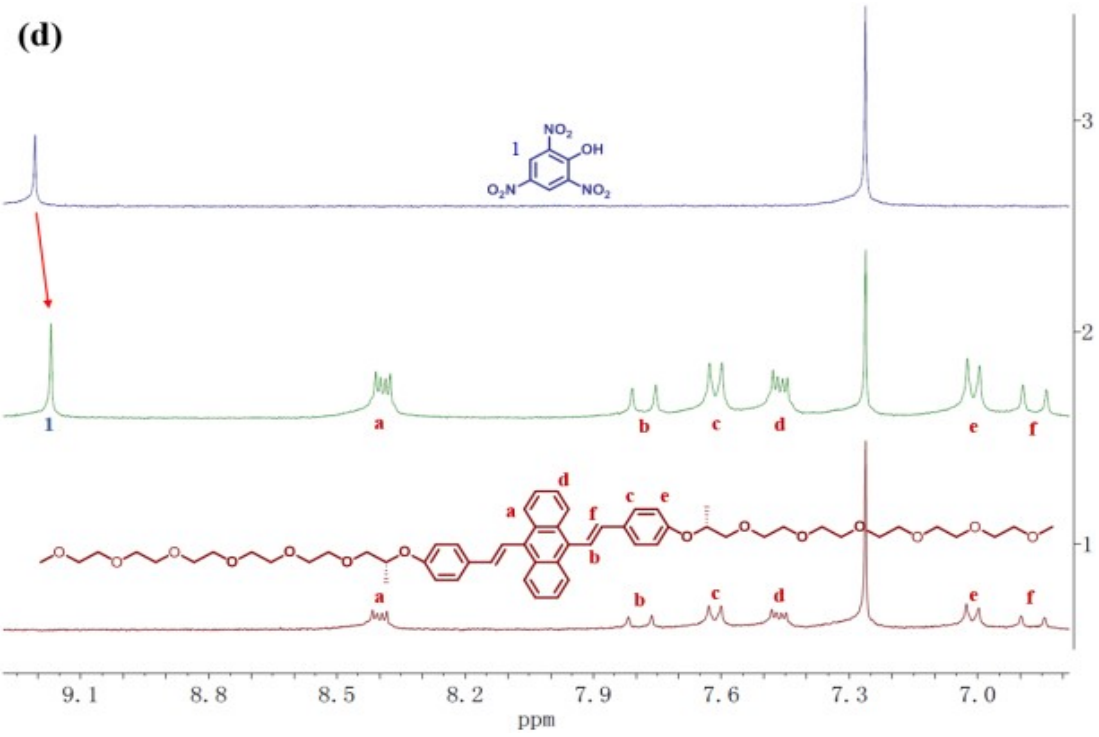
7.7
7.5
7.3
7.1
6.9
ppm


(d)
1
OH
3
2
1
a
b
c
d
e
f
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8.8
8.5
8.2
7.9
7.6
7.3
7.0
ppm

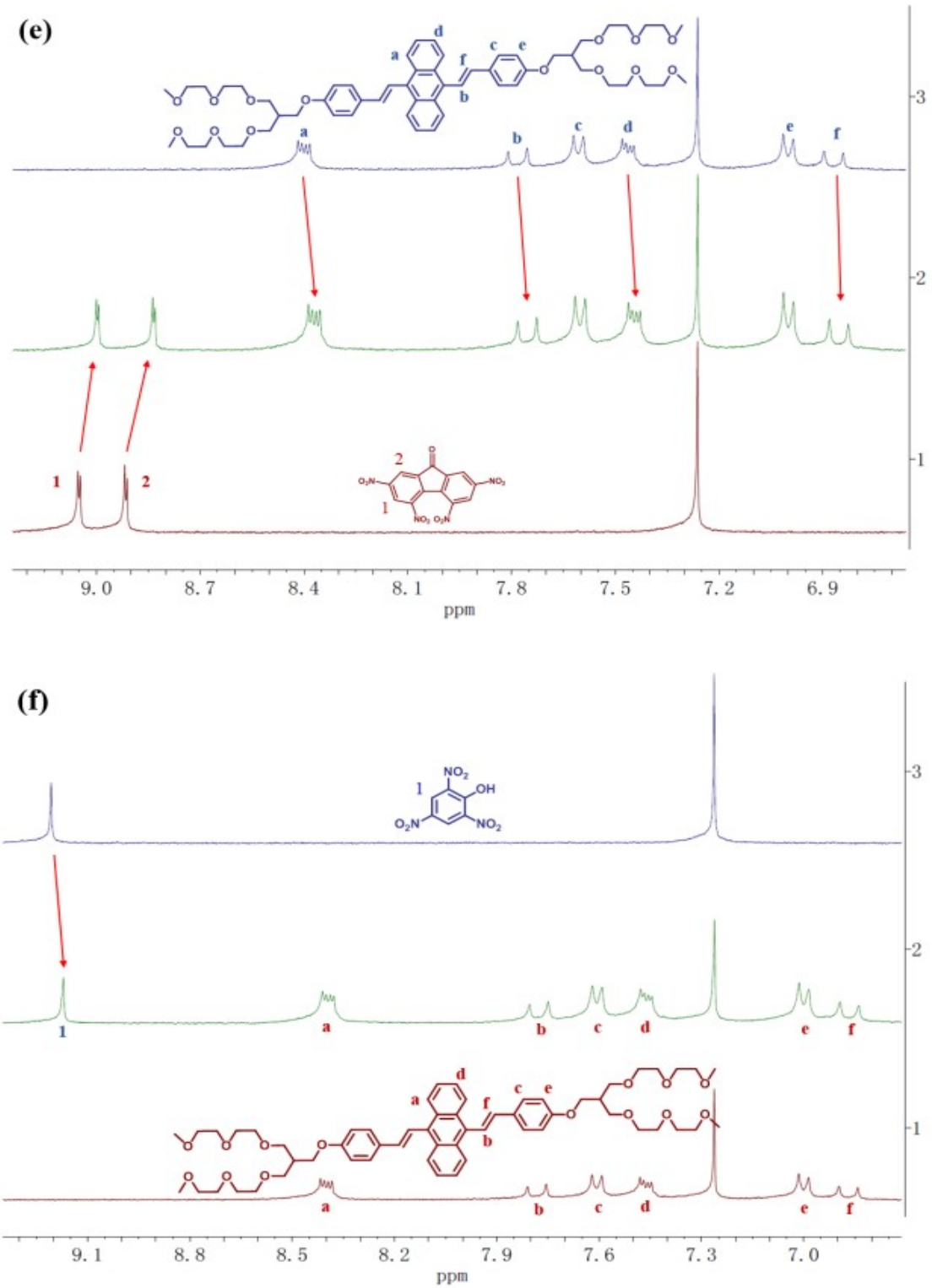


Fig. S7 ^{1}H-NMR experiments of DSA-1 (a and b), DSA-2 (c and d) and DSA-3 (e and f) with the TNF and TNP in $CDCl_3$.

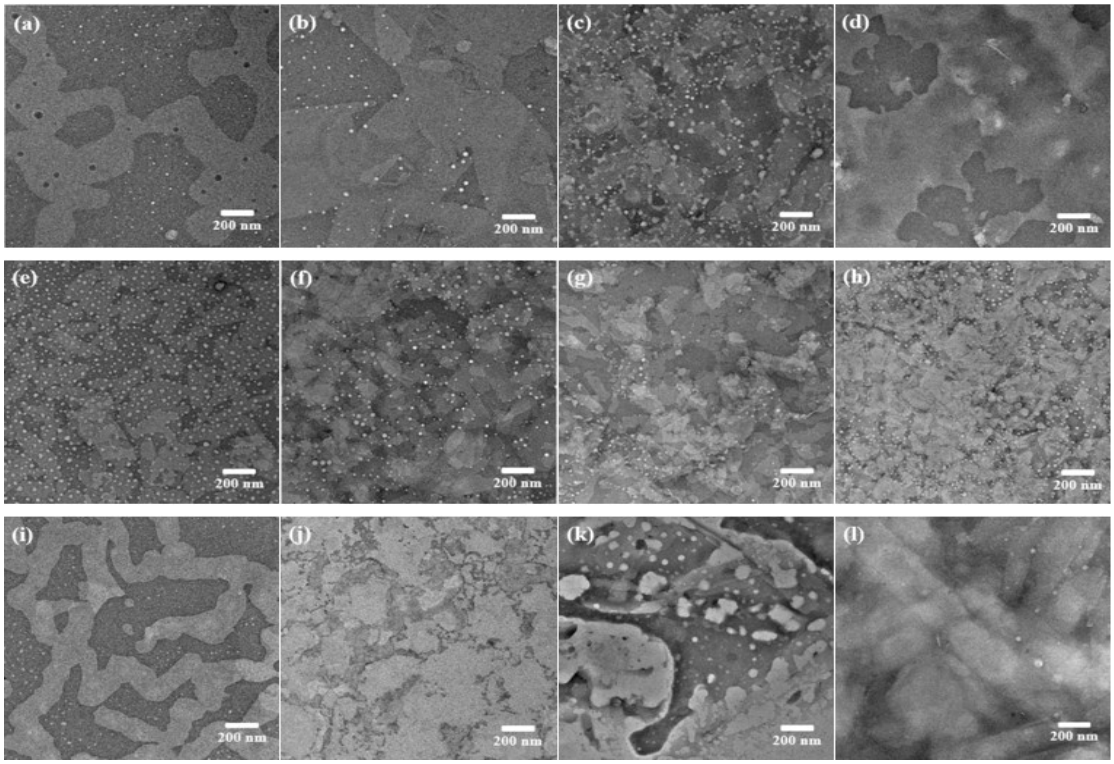
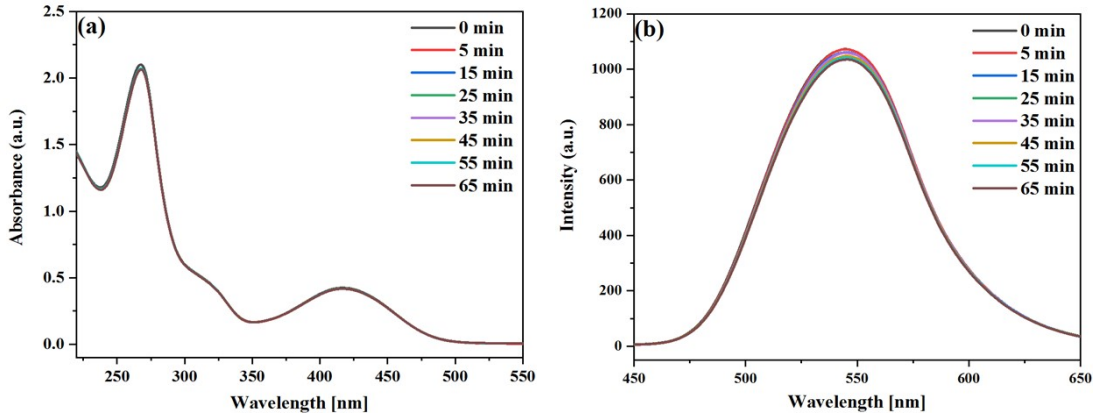


Fig. S8 TEM images of the assembly structures of DSA-1 (a 0.05 eq., b 0.10 eq., c 0.20 eq., and d 0.30 eq.), DSA-2 (e 0.05 eq., f 0.10 eq., g 0.20 eq., and h 0.30 eq.), and DSA-3 (i 0.05 eq., j 0.10 eq., k 0.20 eq., and l 0.30 eq.) (0.004 wt%) at different equivalence ratios of TNF in the 98 % aqueous fraction.



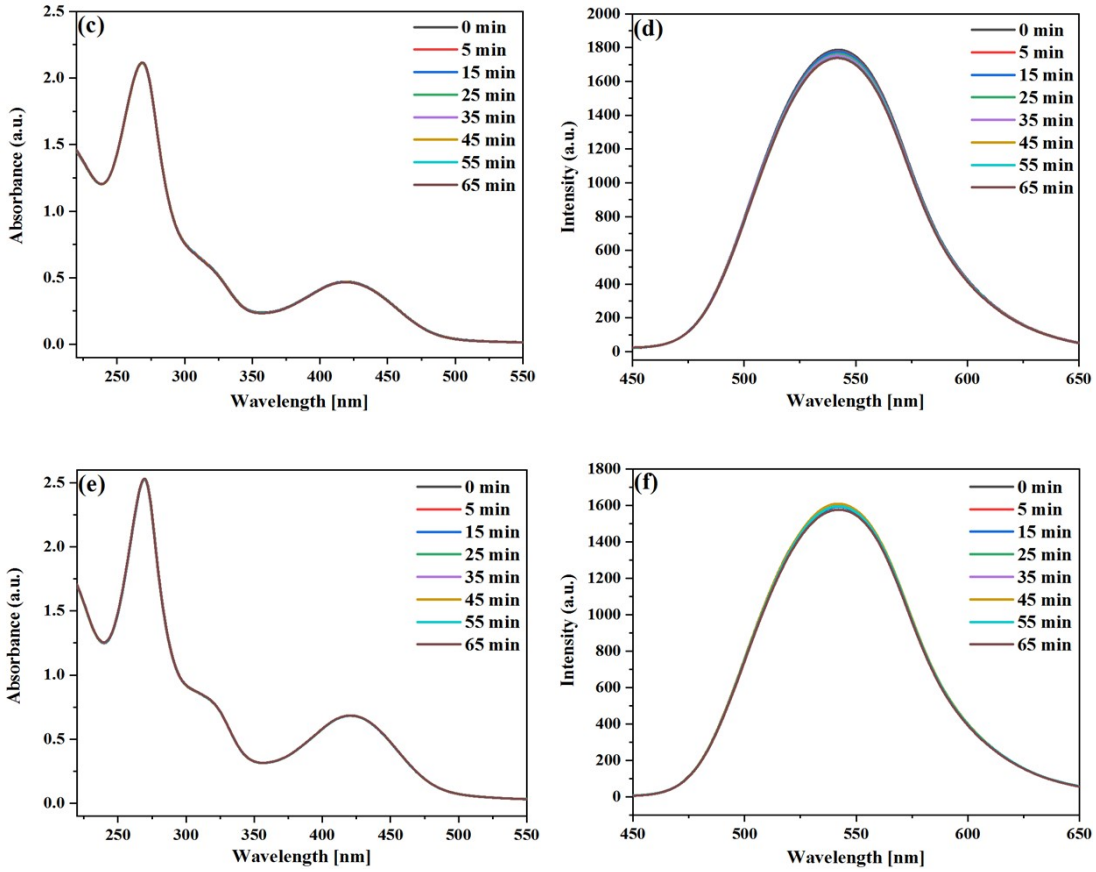
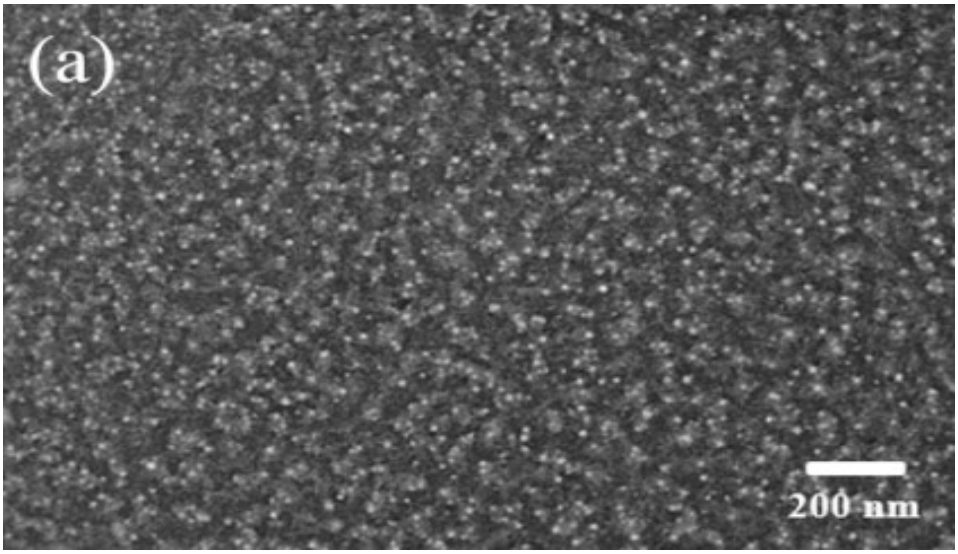


Fig. S9 Absorption and emission spectra of DSA-1 (a and b), DSA-2 (c and d) and DSA-3 (e and f) (0.004 wt %) after natural light different times in 98 % aqueous fraction.



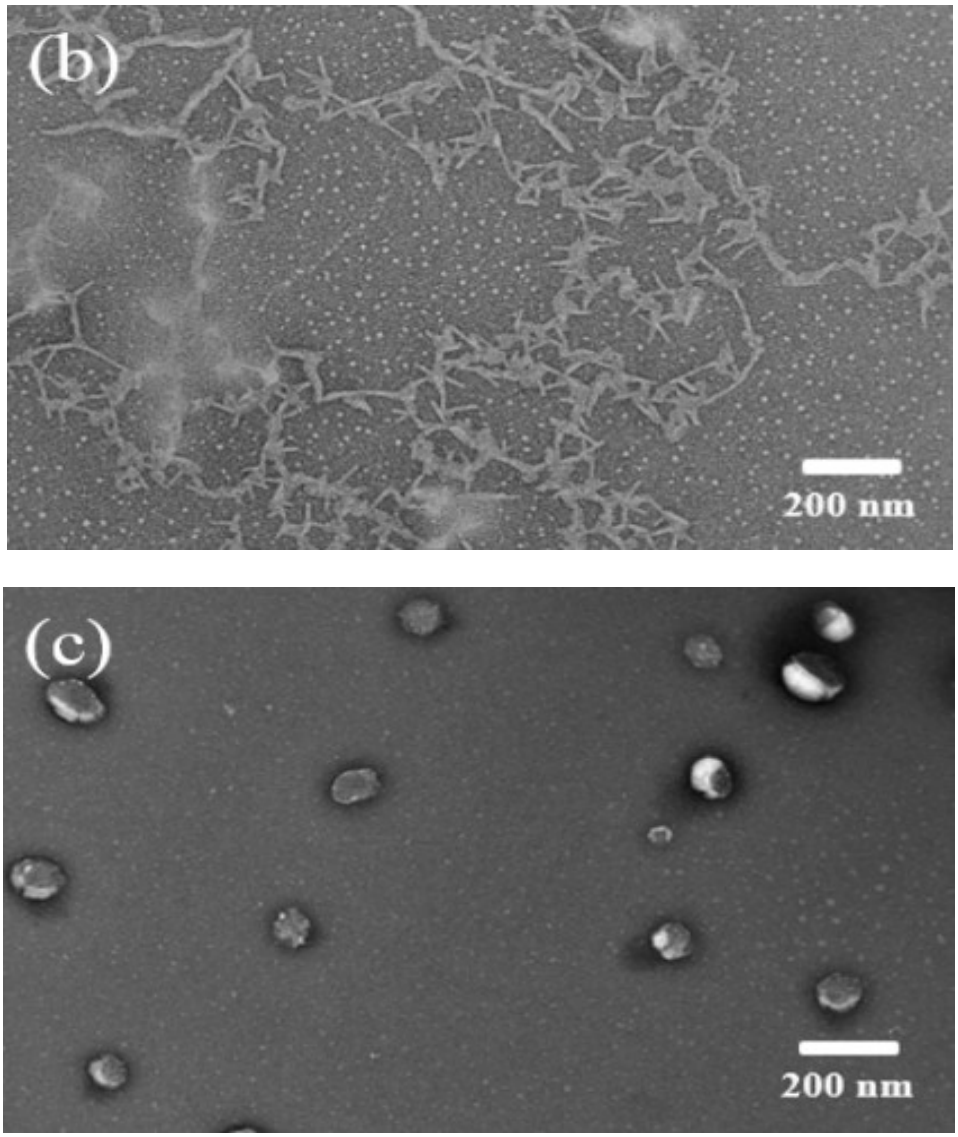
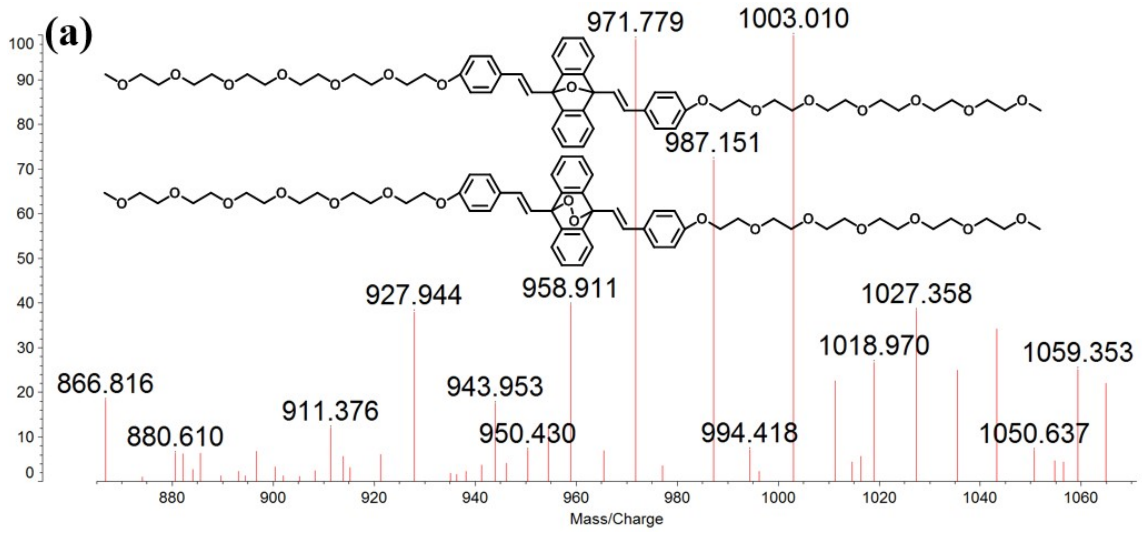
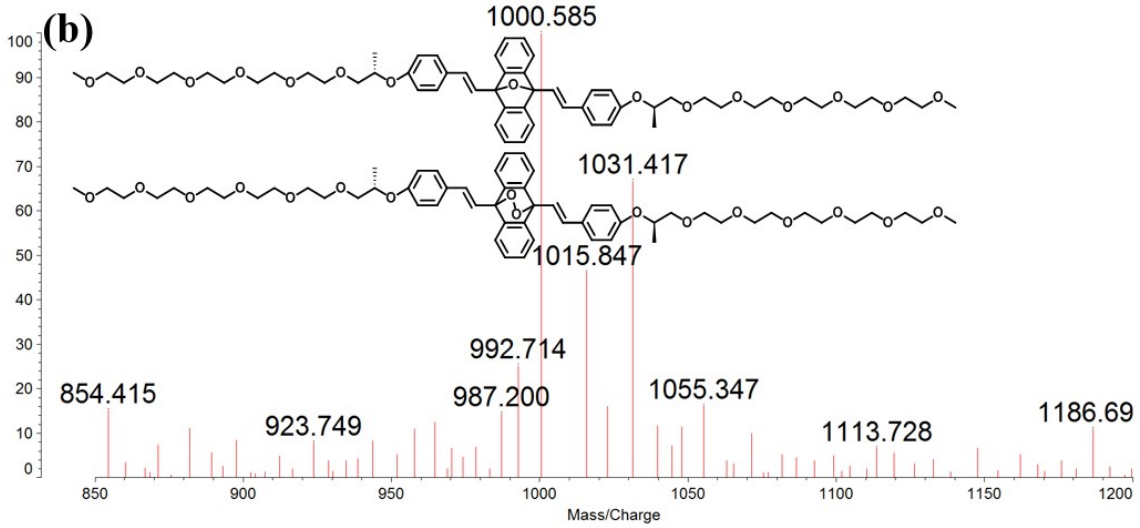
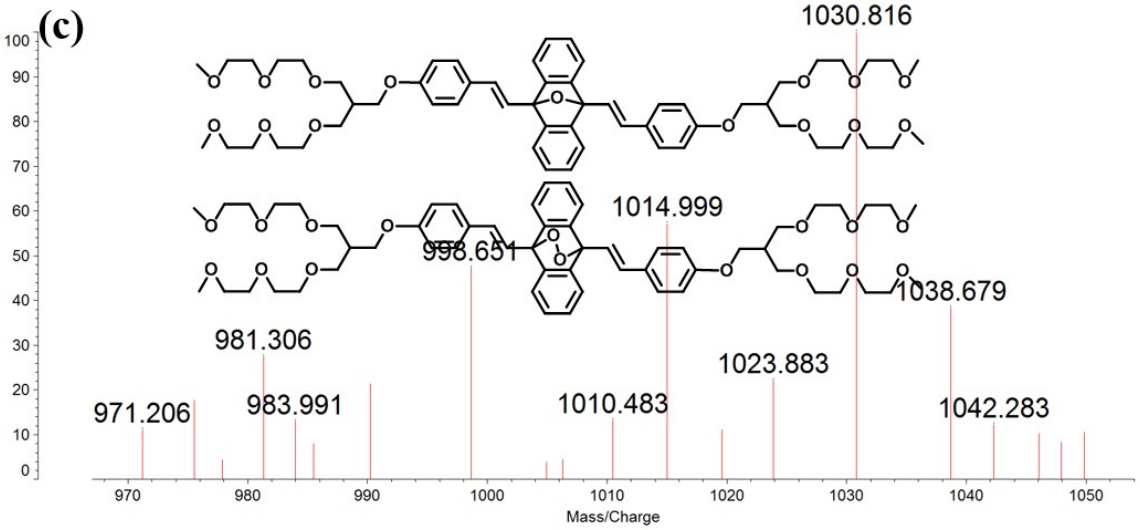
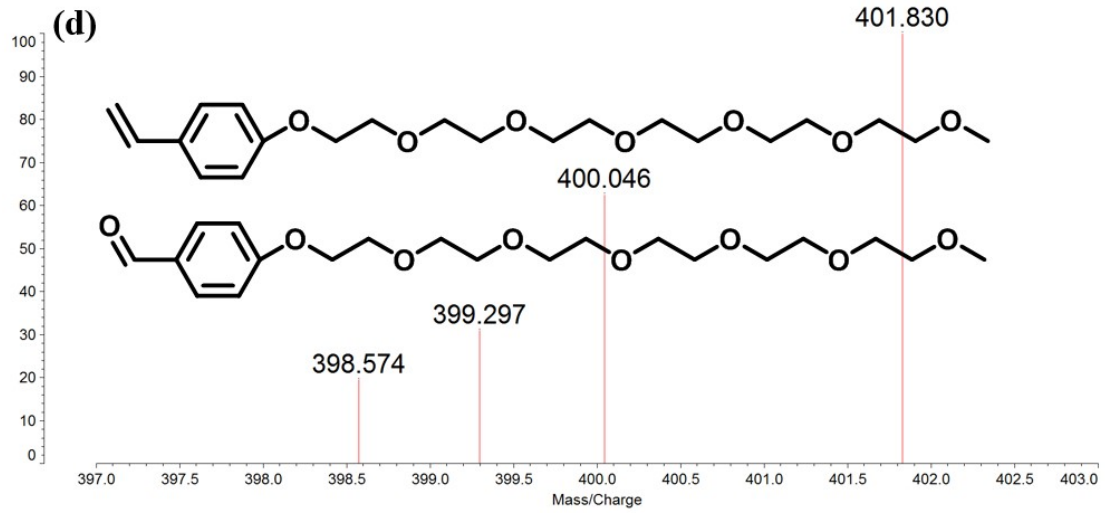


Fig. S10 TEM image of the assembly structures (a) of DSA-1, (b) of DSA-2 and (c) of DSA-3 (0.004 wt %) after 365 nm UV irradiation 2 h in 98 % aqueous fraction.




(b)
1000.585
1031.417
1015.847
992.714
854.415
987.200
1055.347
923.749
1113.728
1186.69
Mass/Charge


(c)
1030.816
1014.999
998.651
1038.679
981.306
1023.883
971.206
983.991
1010.483
1042.283
Mass/Charge


(d)
401.830
400.046
399.297
398.574
Mass/Charge

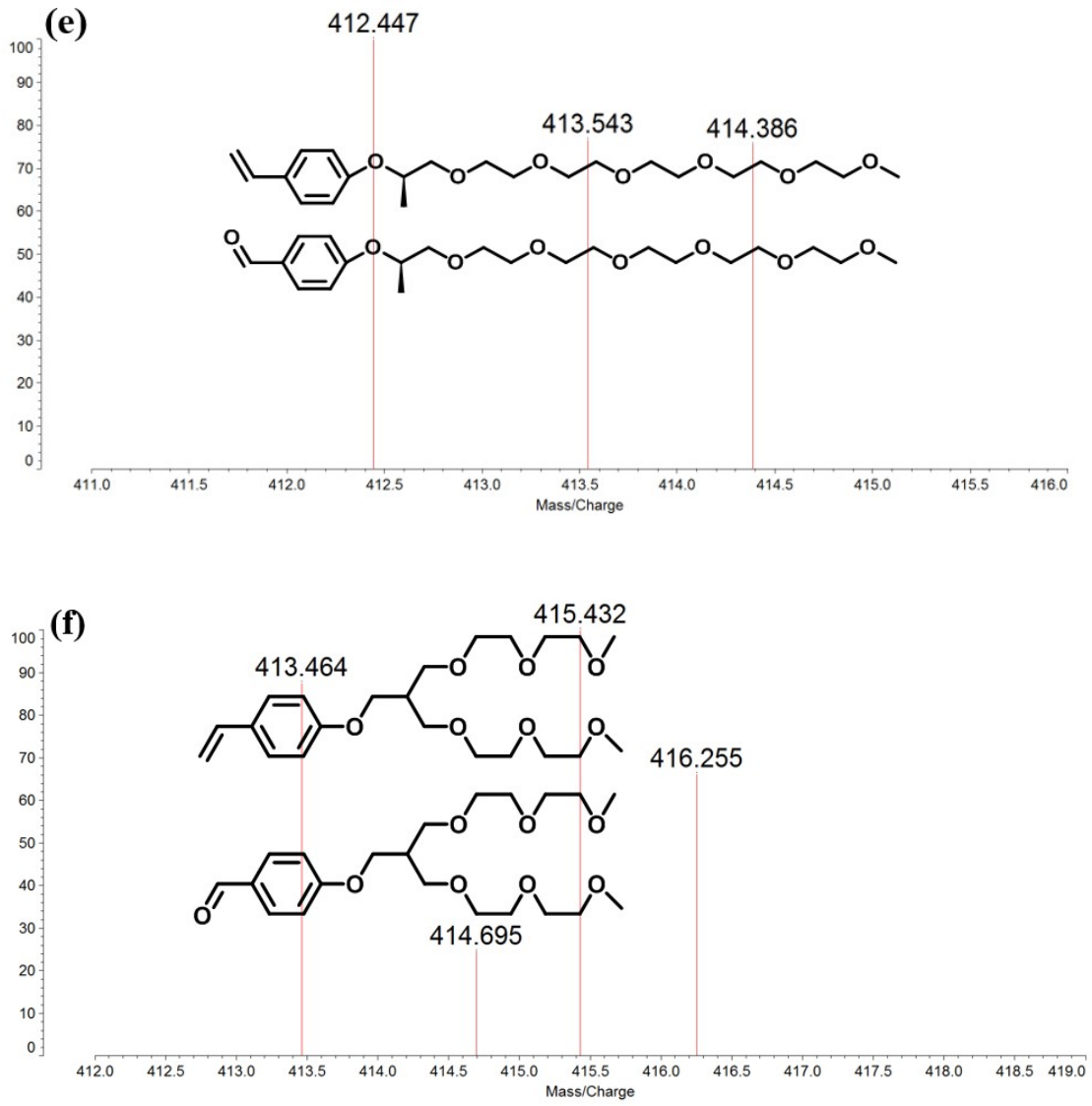


Fig. S11 MALDI-TOF mass spectra a and d of DSA-1, b and e of DSA-2 and c and f of DSA-3 in 98 % aqueous fraction after 2 hours of 365 nm UV light irradiation.

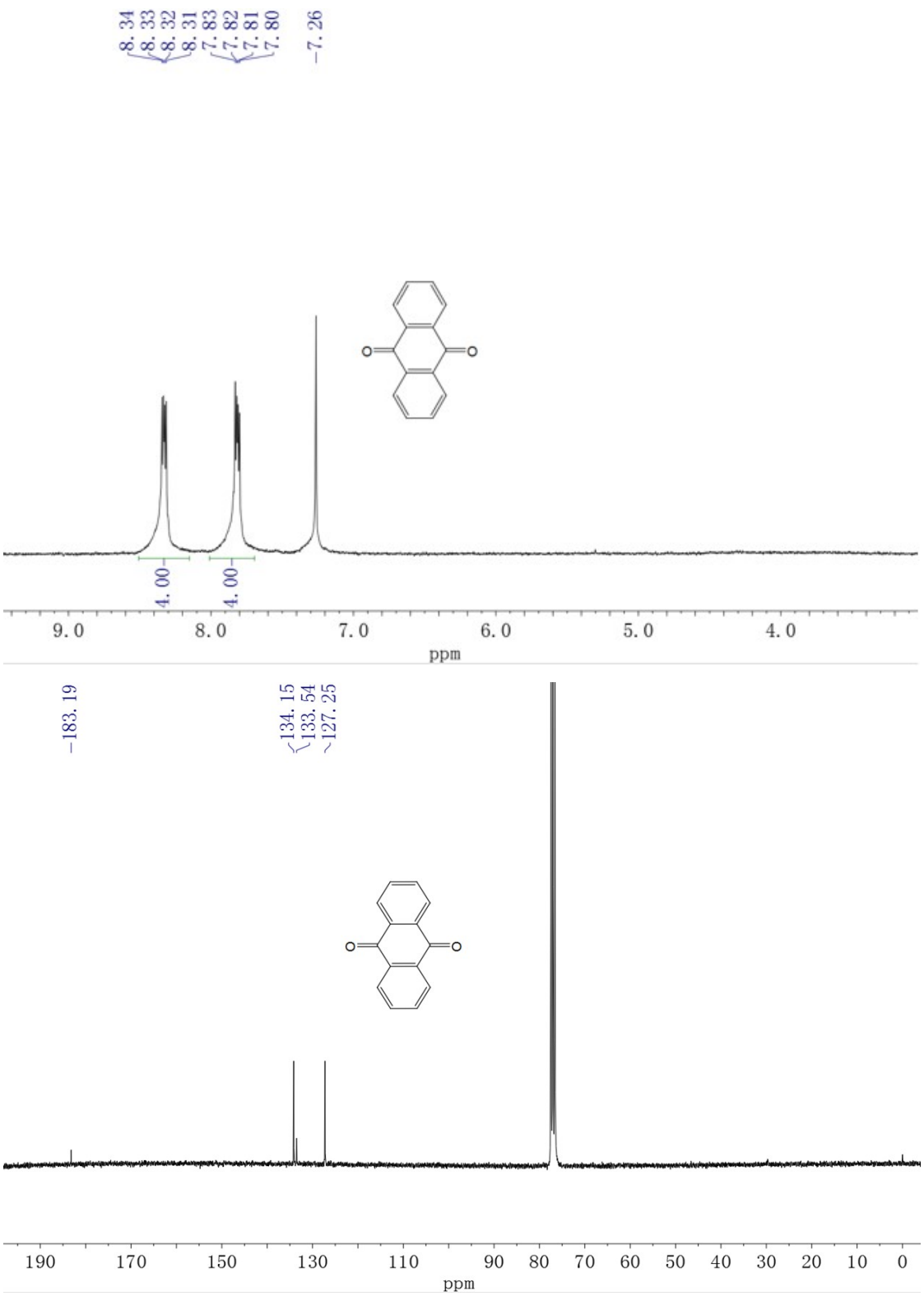


Fig. S12 After irradiation with 365nm UV light for 2 h, the ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra in $CDCl_3$ of the purified sample were obtained from the DSA aqueous solution.

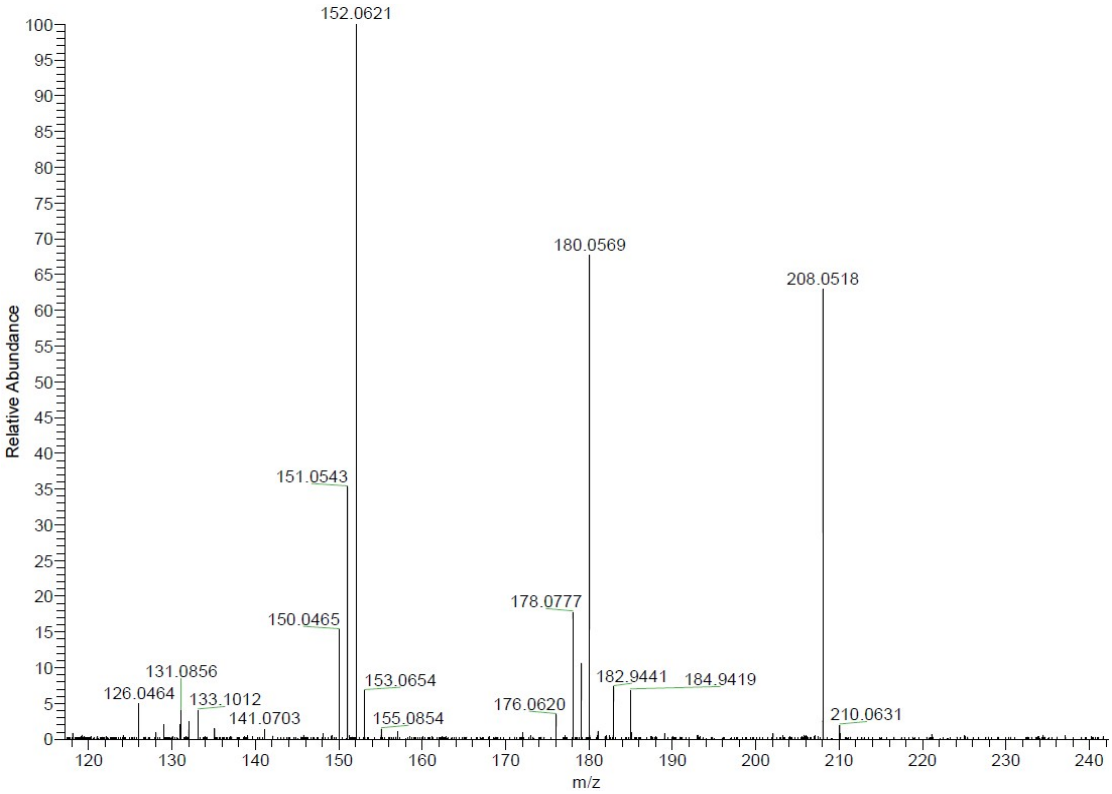


Fig. S13 High-resolution mass spectrum of separating and purifying DSA aqueous solution after 2 h of 365 nm UV light irradiation.

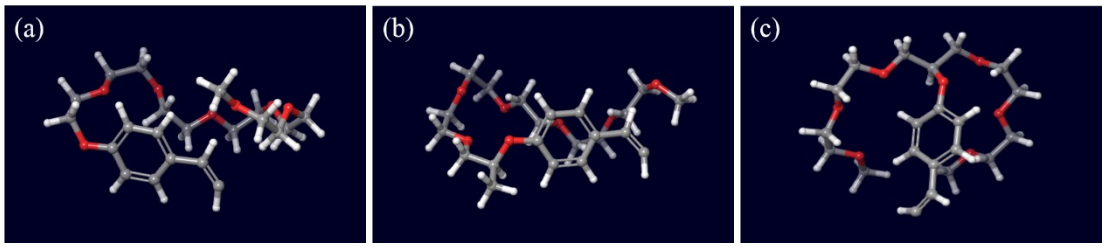


Fig. S14 Theoretical calculation obtains the corresponding fragment structure through the BDE module of Schrodinger Simulation Software by B3LYP/LACV3P** basis set, a of DSA-1, b of DSA-2, and c of DSA-3 were styrene structures connected to relevant ethylene oxide chains, respectively.

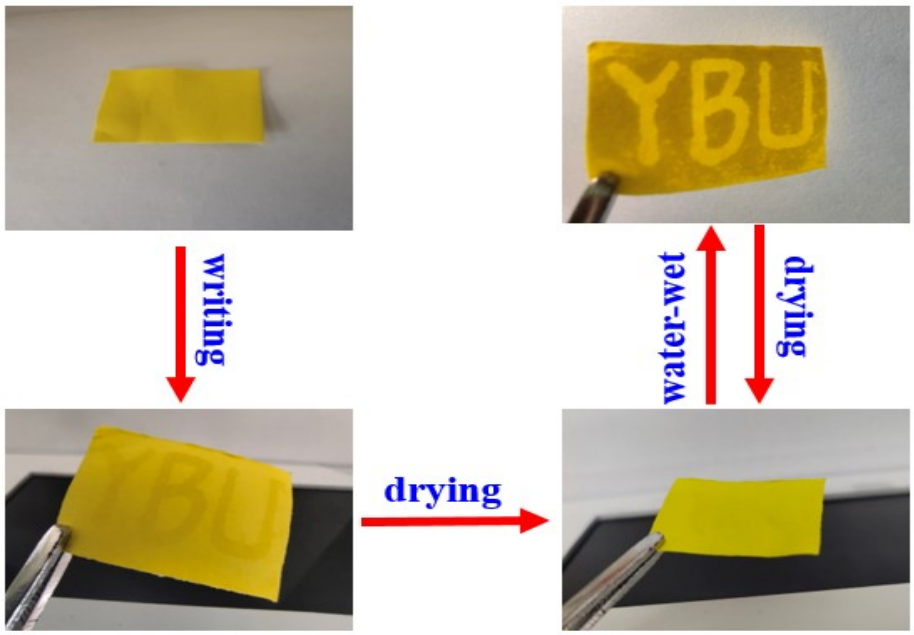


Fig. S15 Flowchart of compound DSA-1 as a supramolecular ink for information encryption and anti–counterfeiting applications.

References

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