Supplementary Information

Crystallization and Near-Infrared Emission from Host-Guest Based Supramolecular Polymers

Wenxia Yin, Lingyi Meng, Tianjun Yu, Jinping Chen, Rui Hu, Guoqiang Yang, Yi Zeng*, and Yi Li

Contents

Material synthesis

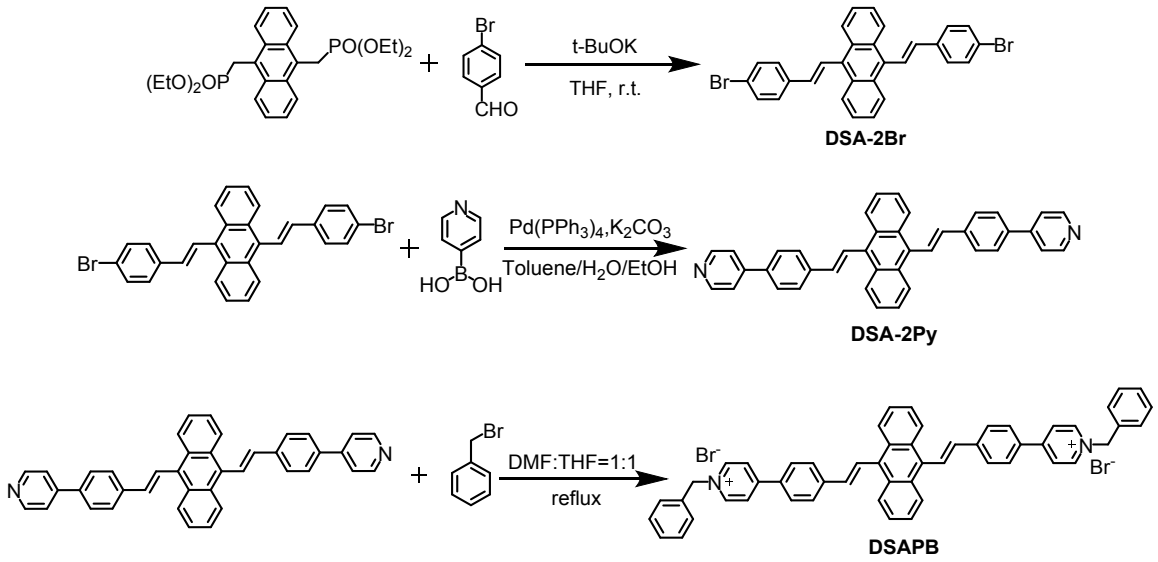
DSAPB was synthesized according to the procedure shown in Scheme S1. All chemical reagents were purchased commercially without further purification, unless otherwise noted.

9,10-bis(4-bromostyryl)anthracene (DSA-2Br). DSA-2Br was synthesized according to the method reported in the literature.[1] *p*-Bromobenzaldehyde (0.085 g, 0.46 mmol) and 9,10-bis(diethylphosphinomethyl) anthracene (0.1 g, 0.21 mmol) were dissolved in 20 mL of dry THF and potassium *t*-butoxide (0.19 g, 1.67 mmol) was added. After the reaction was completed by stirring at room temperature for 5 h, methanol was added into the mixture and the obtained solid was collected by filtration. The crude product was separated and purified by silica gel column chromatography (petroleum ether/dichloromethane = 3/1 as eluent) to obtain brown solid with a yield of 85%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (m, 4H), 7.95 (s, 1H), 7.91 (s, 1H), 7.61 – 7.53 (m, 8H), 7.49 (dd, J = 6.9, 3.2 Hz, 4H), 6.90 (s, 1H), 6.86 (s, 1H).

9,10-bis(4-(pyridin-4-yl)styryl)anthracene (DSA-2Py). The mixture of 9,10-bis(4-bromostyryl)anthracene (0.33 g, 0.6 mmol), pyridin-4-ylboronic acid (0.29 g, 2.4 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in toluene (48 mL) was stirred for 15 min in N_2 atmosphere. After that the K_2CO_3 aqueous solution (0.8 M, 6 mL) and 6 mL ethanol were added in the above solution. The reaction mixture was refluxed continuously for 6.5 h in N_2 atmosphere. The mixture was washed with deionized water for three times and the organic layer was extracted with ethyl acetate and dried with anhydrous $MgSO_4$ after cooling to the room temperature. Then the precipitate was dried in vacuo. The purer product was obtained by column chromatography using dichloromethane (CH_2Cl_2) and EtOH (9:1) as the eluent. The orange solid powder (0.27 g, yield = 81%) was obtained by recrystallization from CH_2Cl_3. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 – 8.68 (m, 4H), 8.46 – 8.38 (m, 4H), 8.08 (s, 1H), 8.04 (s, 1H), 7.84 (d, J = 7.6 Hz, 4H), 7.78 (d, J = 7.8 Hz, 4H), 7.69 – 7.61 (m, 4H), 7.55 – 7.48 (m, 4H), 7.04 (s, 1H), 7.00 (s, 1H). MS (ESI): m/z calcd. for M + H^+ 537.23; found 537.23.

4,4'-((anthracene-9,10-diylbis(ethene-2,1-diyl))bis(4,1-phenylene))bis(1-benzylpyridin-1-ium) bromide (DSAPB). 9,10-bis(4-(pyridin-4-yl)styryl)anthracene (0.11 g , 0.2 mmol) was weighed into a two-necked flask, and 20 mL of DMF:THF = 1:1 mixed solvent was added. The mixture was heated to reflux, and the solution turned orange. Benzyl bromide (0.2 mL, 1.6 mmol) was added dropwise, and the solution turned red. The temperature was raised to 90 °C and reacted for 6 h, and the reaction system produces a large amount of orange precipitate. After cooling to room temperature, the orange solid powder was filtered and washing by ethanol and ether. The solid product was recrystallized in a lot of ethanol and acetone and brownish red bulk powder

DSAPB was obtained (0.14 g, yield = 81%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (d, J = 6.8 Hz, 1H), 8.64 (d, J = 6.8 Hz, 1H), 8.47 – 8.40 (m, 2H), 8.22 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.48 (q, J = 8.1, 7.2 Hz, 1H), 7.11 (d, J = 16.5 Hz, 1H), 5.86 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.07, 146.04, 141.02, 136.63, 133.11, 132.77, 129.41, 129.03, 128.43, 126.68, 126.35, 124.21, 47.51. MS (ESI): m/z calcd. for M^{2+} 359.17; found 359.17.



Scheme 1 Synthesis route of and DSAPB.

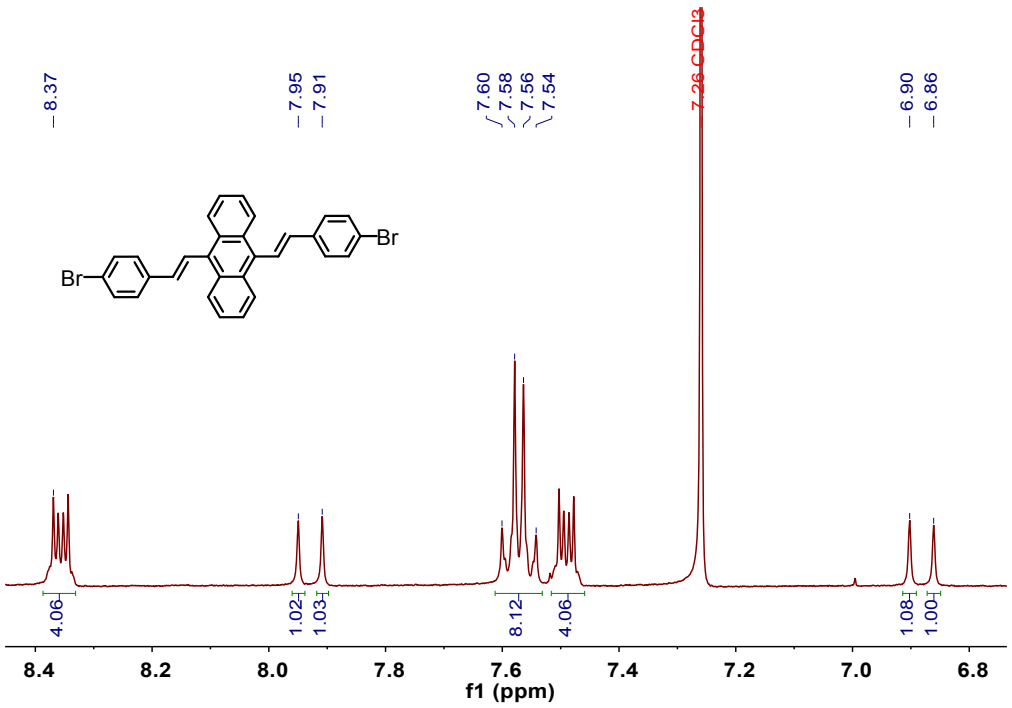


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$-d, 25℃) spectrum of compound DSA-2Br.

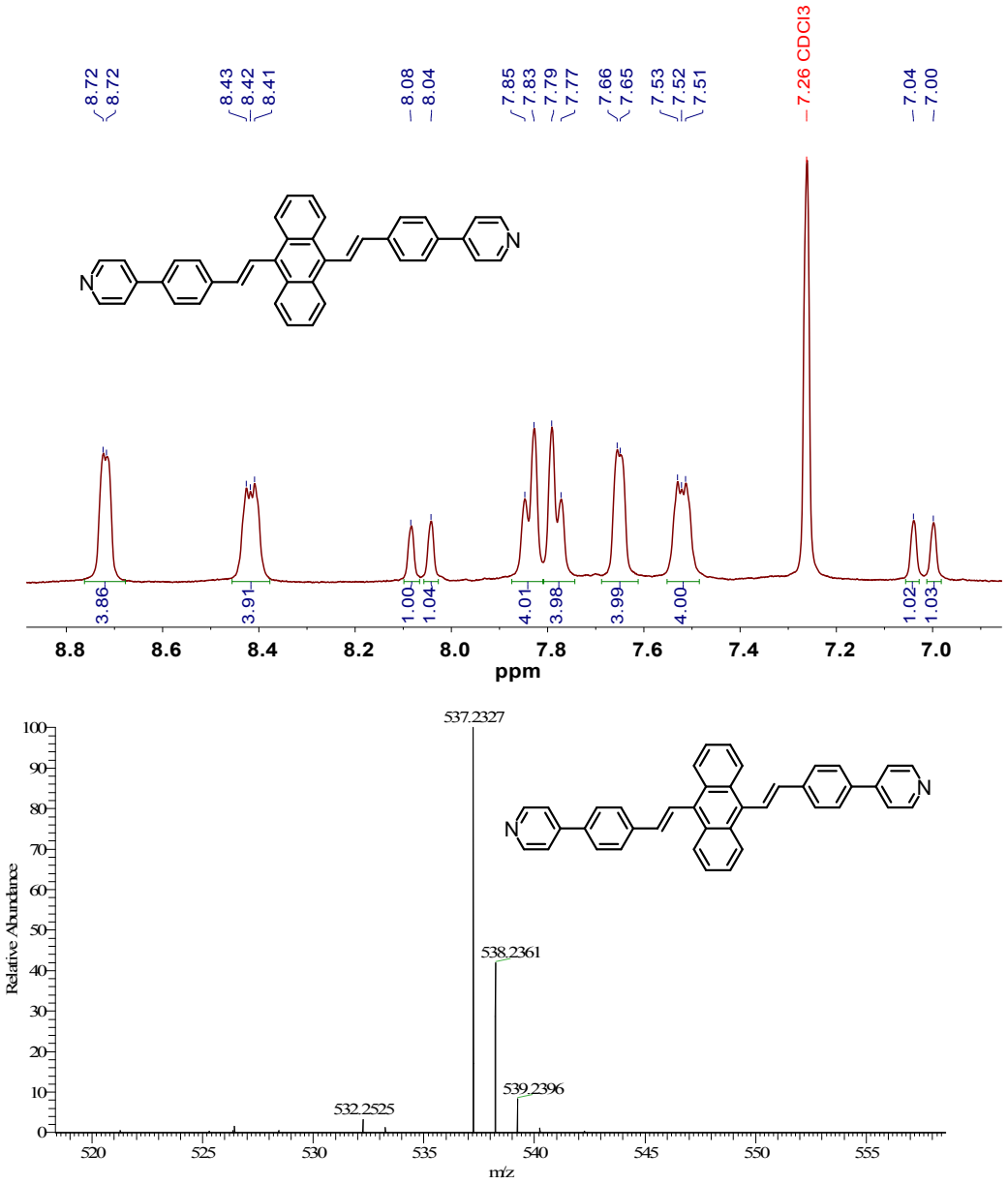


Figure S2 ^{1}H NMR (400 MHz, $CDCl_3$-*d*, 25℃) and MS (ESI) spectrum of compound DSA-2Py.

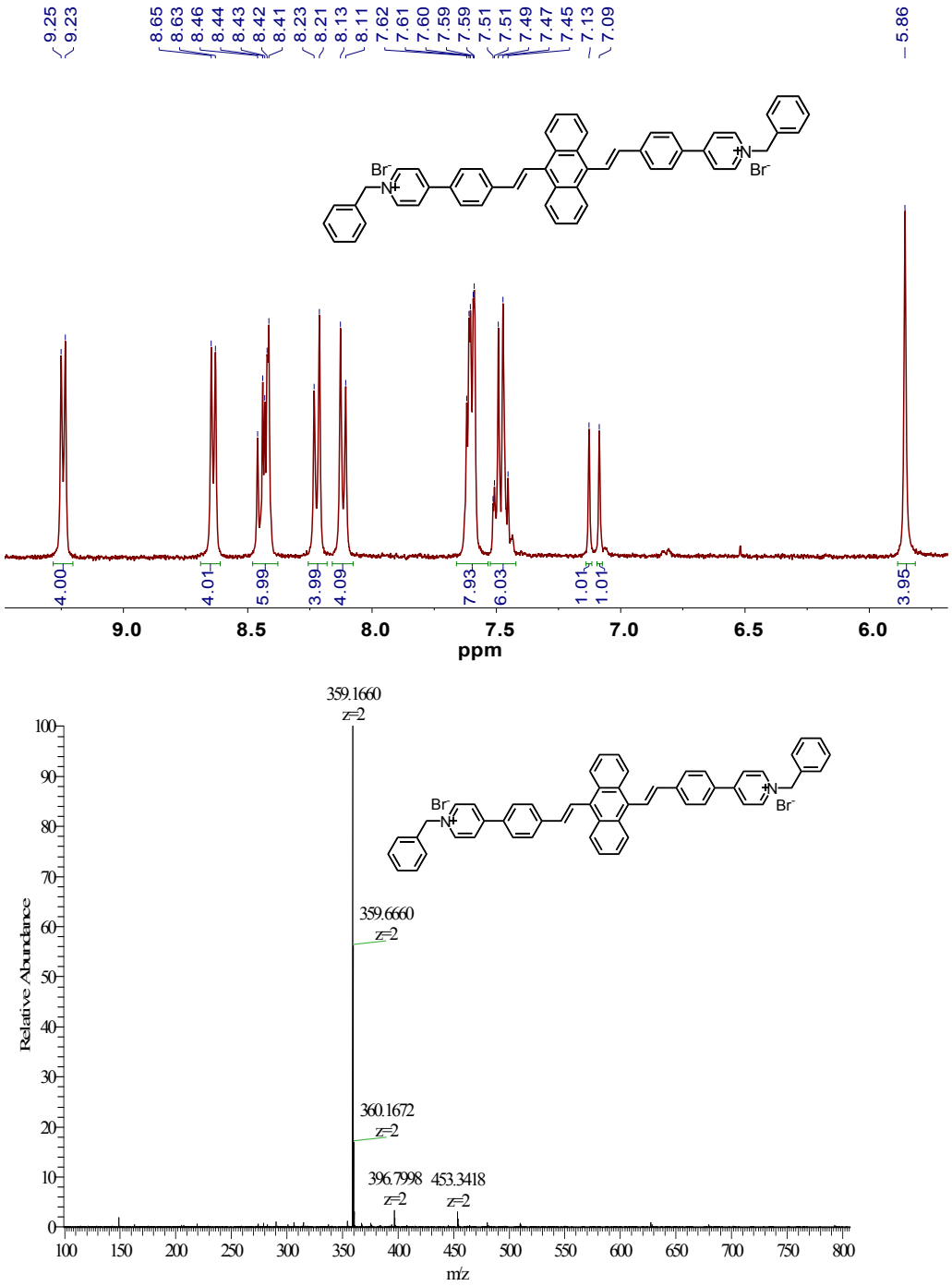


Figure S3 ^{1}H NMR (400 MHz, DMSO-d_6, 25℃) and MS (ESI) spectrum of compound DSAPB.

Sample Preparation

Assembly samples preparation for XRD

DSAPB (2.2 mg) was weighed into a round bottom flask and dissolved in methanol and deionized water was added. 2 equiv of CB[7] was added into the above solution to assemble with DSAPB, and then 1 equiv of CB[8] solution was added. After 12 h, the mixture was concentrated by rotary evaporation and dried in a vacuum oven.

Instrumentation.

^{1}H NMR spectra were recorded with a Bruker Avance-400 (400 MHz) in DMSO-d_6 and D_2O solutions with tetramethylsilane as an internal standard. Scanning electron microscopy (SEM) was performed on the HITACHI S-4800 with silicon substrate and transmission electron microscope (TEM) was performed using JEM-2100 with samples on holey copper grids. X-ray powder diffraction (XRD) patterns were obtained with a Bruker D8 Focus X-ray diffractometer equipped with CuKα radiation (λ=1.54050 Å) at a scanning rate of 5° min^{-1} in the 2θ range from 5° to 50°. Polarized microscope pictures were taken with Transflective polarizing microscope LWT300LPT and Data acquisition CCD MV-VS142FC. UV-visible absorption spectra were recorded using a Shimadzu UV-2550PC spectrometer and photoluminescence emission spectra were measured by using a Hitachi F-4600 spectrometer. The absolute photoluminescence quantum efficiency was measured by using an integrating sphere (Labsphere) combining to a Princeton Instrument Acton SP2500 spectrograph and a SPEC-10 liquid nitrogen-cooled CCD. Time-resolved fluorescence lifetime experiments were carried out by the time-correlated single photon counting (TCSPC) technique with an Edinburgh FLS920 spectrometer excited with a ns flash lamp (ca. 2 ns FWHM).

The XRD patterns of CB[7] and CB[8] was obtained from simulating the X-ray single crystal data.[2]

Supporting spectra and image data

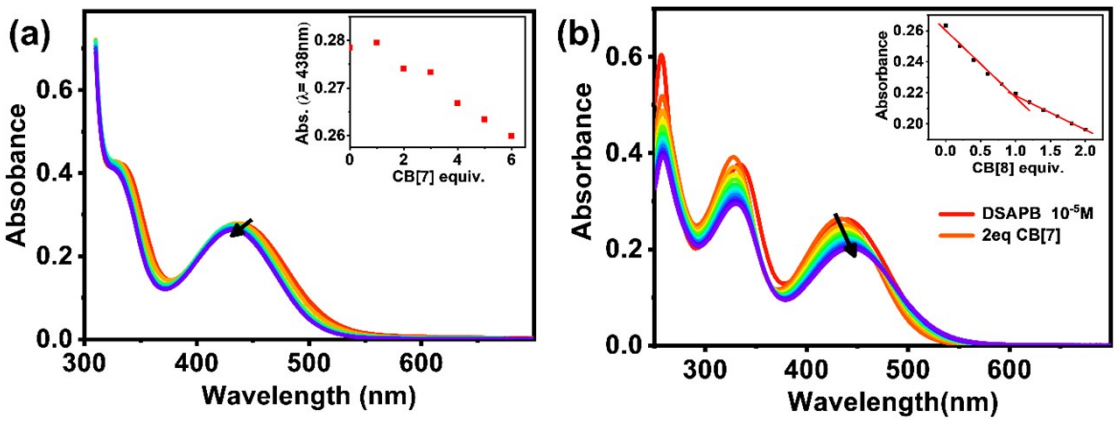


Figure S4 (a) UV/Vis absorption spectra for DSAPB (0.01 mM) upon addition of CB[7] (1 mM) in water/methanol 9/1 mixture. The inset shows the change of absorption at 438 nm upon increasing CB[7] concentration. (b) UV-vis absorption spectra for DSAPB (0.01 mM) and 2 equiv of CB[7] upon addition of CB[8] (0.1 mM) in water with methanol of 10%. The inset shows the absorption change as a function of CB[8] concentration.

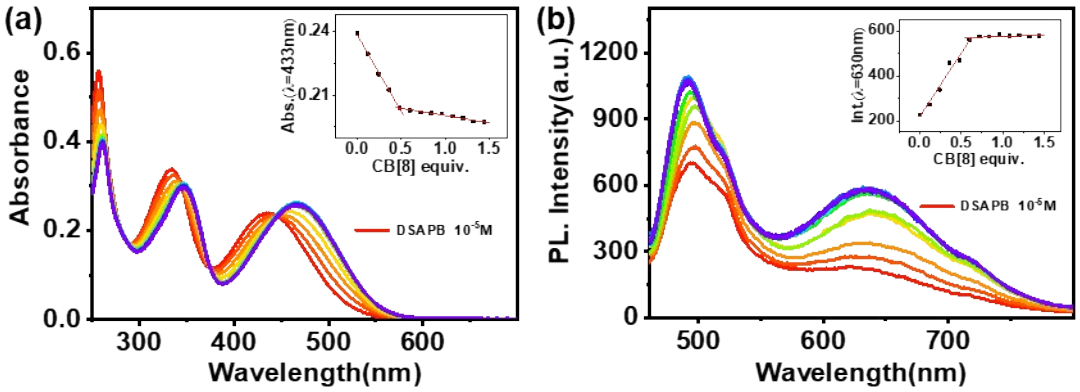


Figure S5 (a) UV/Vis absorption spectra and (b) fluorescence spectra for DSAPB (0.01 mM) upon addition of CB[8] (0.091 mM) in water/methanol 9/1 mixture. The inset shows the change of absorption at 433 nm and emission intensity at 630 nm upon increasing CB[8].

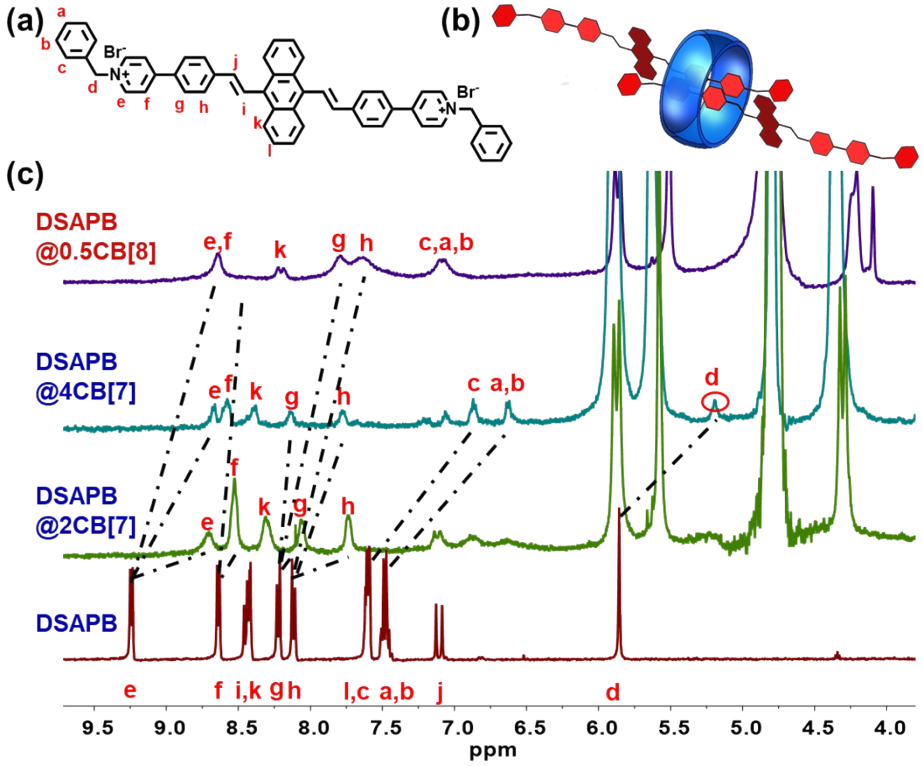


Figure S6 (a) The structure of distyrylanthracene derivative monomer DSAPB. (b) Schematic diagram of the assembly model of 2DSAPB@CB[8]. (c) Partial ^{1}H NMR spectra (400 MHz, D_2O/DMSO-d_6 7/3) of DSAPB with addition of 2 equiv of CB[7], 4 equiv of CB[7], and 0.5 equiv of CB[8], respectively.

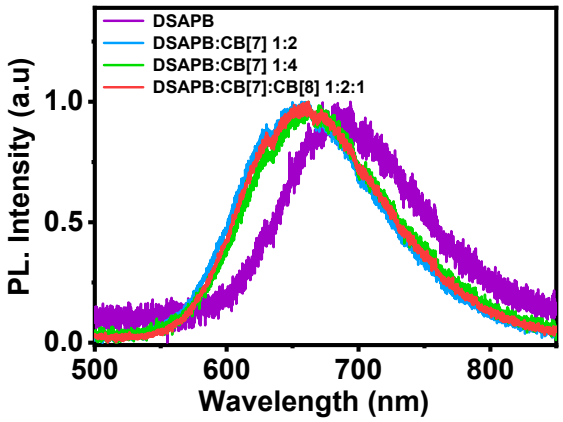


Figure S7 Fluorescence spectra of DSAPB and corresponding supramolecular assemblies in solid state (λ_{ex} = 470 nm).

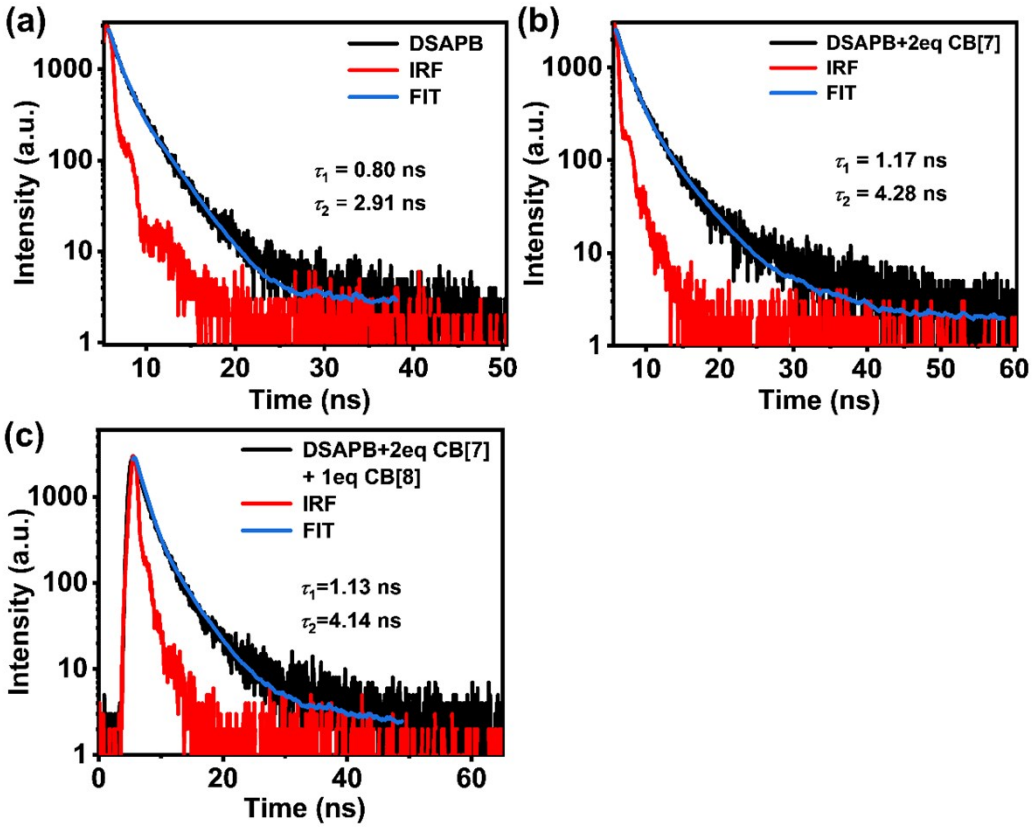


Figure S8 Photoluminescence decays at 610 nm of DSAPB (a), the supramolecular assemblies DSAPB@2CB[7] (b) and DSAPB@2CB[7]/CB[8] (c) (black line) in solid state under pulsed laser excitation at 485 nm. The solid blue lines are the exponential fits of the decay trace.

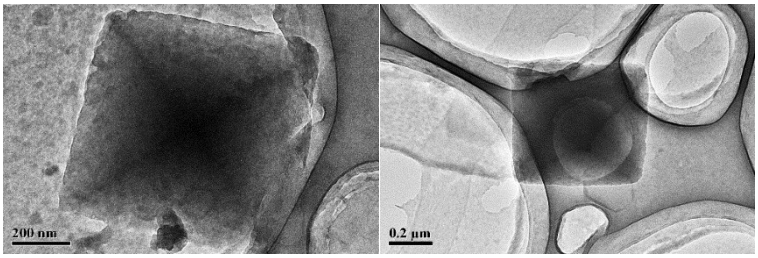


Figure S9 TEM image of the aggregate from DSAPB@2CB[7]/CB[8].

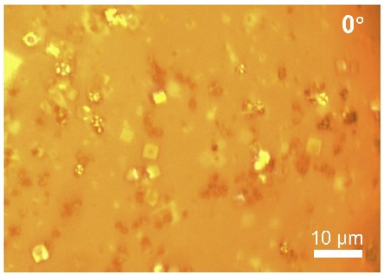
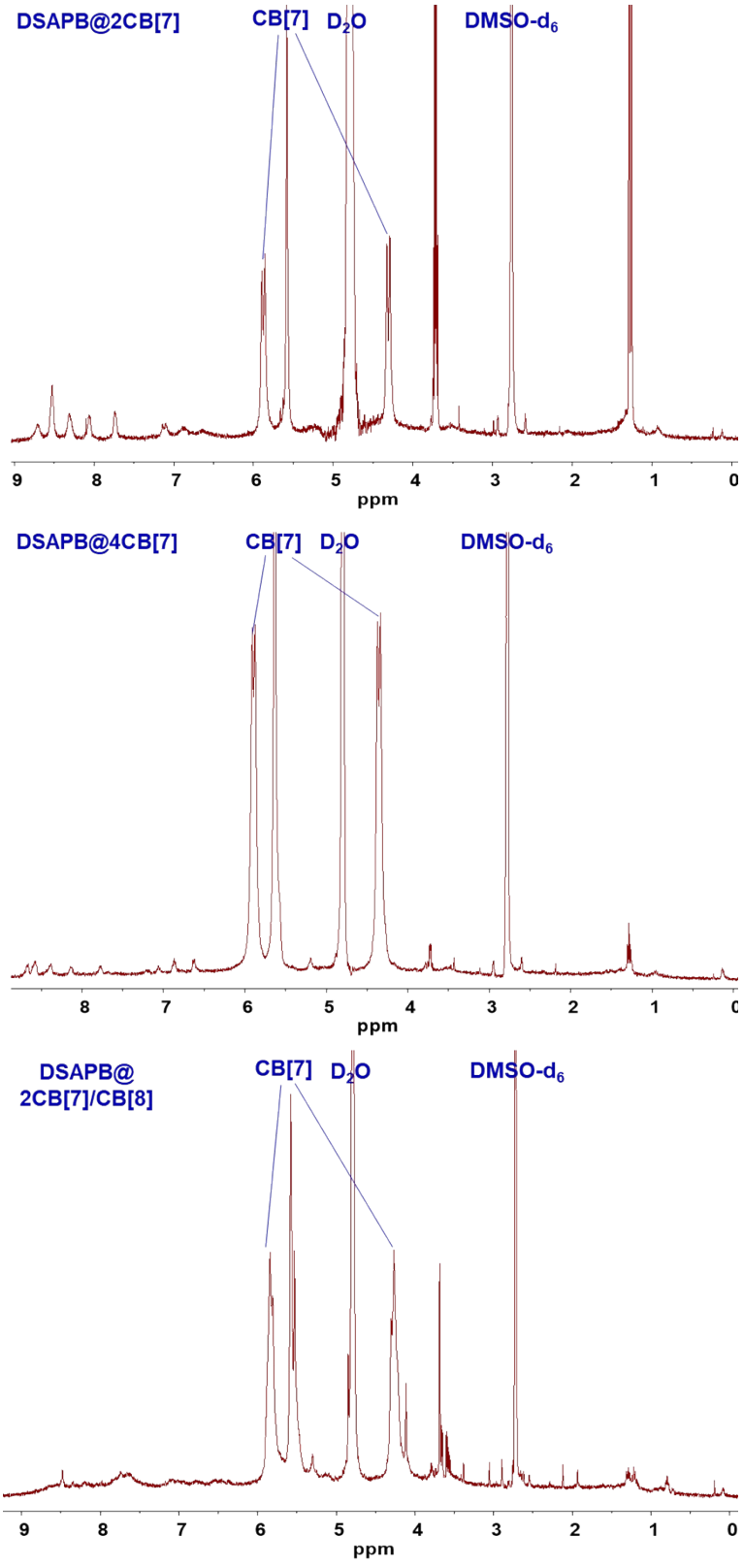


Figure S10 Photograph of the supramolecular pyramidal crystal under a polarized light microscope with parallel polarizers.


DSAPB@2CB[7]
CB[7]
D2O
DMSO-d6
9 8 7 6 5 4 3 2 1 0
ppm
DSAPB@4CB[7]
CB[7]
D2O
DMSO-d6
8 7 6 5 4 3 2 1 0
ppm
DSAPB@
2CB[7]/CB[8]
CB[7]
D2O
DMSO-d6
9 8 7 6 5 4 3 2 1 0
ppm

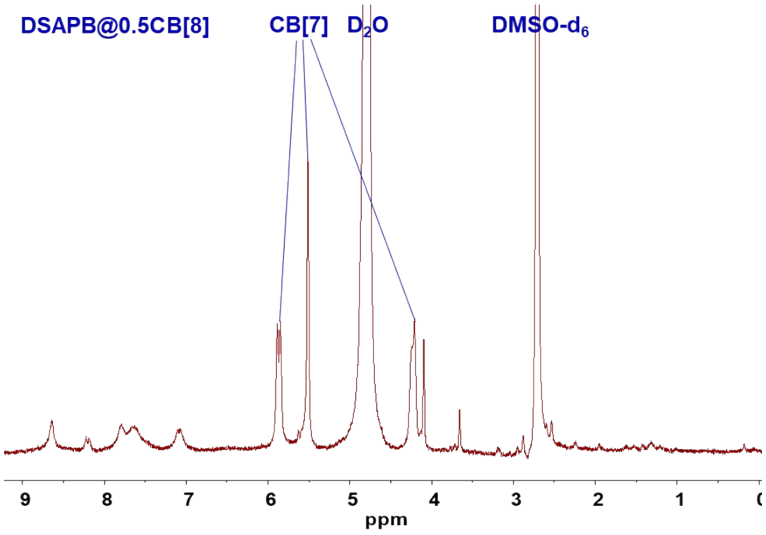


Figure S11 Full 1H NMR spectra (400 MHz, D2O/DMSO-d6 7/3) of DSAPB with addition of 2 equiv of CB[7], 4 equiv of CB[7], 2 equiv of CB[7] plus 2 equiv of CB[8] and 0.5 equiv of CB[8], respectively.

References

[1] D. E. Wu, M. N. Wang, Y. H. Luo, G. J. Wen, B. W. Sun, *CrystEngComm*, **2015**, *17*, 9228-9239.

[2] J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.*, **2000**, *122*, 540-541.