Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Construction of two-dimensional supramolecular nanostructure with aggregation-induced emission effect via host-guest interactions

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Supporting Information

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1. Supplementary Methods

1.1. Materials and Methods

Reagents for synthesis were purchased commercially from Adamas Reagent and used without further purification. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) and 1,1,2,2-tetrakis(4-bromophenyl)ethane were purchased from TCI. Hoechst and Lambda DNA (λDNA) (48502 base pairs) were purchased from ThermoFisher Scientific. Cucurbit[8]uril (CB[8]) and Cucurbit[7]uril (CB[7]) were purchased from Sigma. Unless otherwise specified, all aqueous solutions were prepared with Milli-Q water. Hela cells were cultured in Dulbecco's modified eagle medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% P/S in an atmosphere of 5% CO_2 and 95% air at 37 °C.[1]

All reactions were carried out under nitrogen condition unless otherwise noted. ^{1}H and ^{13}C NMR spectra were performed on 500 MHz spectrometers (Bruker AVANCE-III 500) or 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. Chemical shifts were reported in δ (ppm) relative to TMS ($\delta = 0$). High temperature and two-dimensional nuclear magnetic resonance spectroscopy (2D NMR) were recorded on Agilent NMR Spectrometer (600-54-ASC) with deuterium oxide (D_2O) as solvent. Unless otherwise indicated, column chromatography was carried out on silica gel (200-300 mesh). Thin-layer chromatography (TLC) analysis was performed on precoated silica gel plates (0.2 mm thick). Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry

(MALDI-TOF MS) analysis was performed on a Bruker Microflex-LRF mass spectrometer in positive ion, reflection mode. Dynamic Light Scattering (DLS) was performed on Malvern Zetasizer Nano ZS90. Scanning electron microscopy (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV. The UV-vis absorbance was measured by UV spectrometer (HITACHI, 3900). Fluorescence spectra were recorded on fluorescence spectrometer (HITACHI, F-2700). Atomic Force Microscope (AFM) images were recorded on Bruker Multimode 8 AFM with Nanoscope V controller. Optical microscopy (OM) and epifluorescence microscopy pictures were recorded on epifluorescence microscopy (OLYMPUS, IX73). The small-angle X-ray scattering (SAXS) experiments were performed on Small angle and wide angle X-ray scattering instrument (Xenocs, Xeuss 2.0). The scattering intensity was recorded on a Pilatus3R detector with a pixel size of 172 μm. The samples prepared by evaporating an aqueous solution of **1** and CB[8] (1:2).

Abbreviations. Dichloromethane (DCM), trichloromethane ($CHCl_3$), N,N-dimethylformamide (DMF), methanol (MeOH), Dimethylsulfoxide (DMSO), trans-dichlorobis(triphenyl-phosphine)palladium(II) ($PdCl_2(PPh_3)_2$), methyl iodide (CH_3I), Cucurbit[8]uril (CB[8]), Cucurbit[7]uril (CB[7]), Thin-layer chromatography (TLC), Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS), Dynamic Light Scattering (DLS), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic Force Microscope (AFM).

1.2 Synthesis

Compound 2.[2] To a stirred solution of 1,1,2,2-tetrakis(4-bromophenyl)ethene (0.596 g, 0.92 mmol) in DMF (20 mL) was added 4-vinylpyridine (0.483 g, 4.6 mmol), $PdCl_2(PPh_3)_2$ (0.064 g, 0.092 mmol), and potassium carbonate (0.758 g, 5.49 mmol). The reaction solution was refluxed overnight. The reaction solution was cooled down and poured over 150 mL ice water. The precipitate was collected by filtration, washed with H_2O. Silica gel column chromatography of the residue (DCM/MeOH 20:1) gave pure **2** (0.411 g, 60% yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.56 (d, J = 6.1 Hz, 8H), 7.33 (t, J = 6.8 Hz, 16H), 7.22 (d, J = 16.3 Hz, 4H), 7.09 (d, J = 8.0 Hz, 8H), 6.96 (d, J = 16.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 150.2, 144.5, 143.9, 140.9, 134.7, 132.7, 131.9, 126.7, 126.1, 120.8. MS (MALDI-TOF): 745 $[M+H]^+$.

Compound 1. A mixture of **2** (0.074 g, 0.1 mmol), CH_3I (0.709 g, 5 mmol), $CHCl_3$/MeOH (6 mL, 1/5 by vol.) was stirred at 40 ℃ for 24 h. The mixture was cooled down and the precipitate was collected by centrifugation, washed with DCM for several times to afford **1** (0.122 g, 93% yield) as an orange solid. ^{1}H NMR (500 MHz, DMSO-d_6): 8.84 (d, J = 6.4 Hz, 8H), 8.17 (d, J = 6.4 Hz, 8H), 7.93 (d, J = 16.3 Hz, 4H), 7.59 (d, J = 8.0 Hz, 8H), 7.47 (d, J = 16.3 Hz, 4H), 7.15 (d, J = 7.9 Hz, 8H), 4.24 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6): 152.8, 145.6, 145.1, 141.7, 140.5, 134.5, 132.1, 128.4, 124.1, 123.9, 47.5; MS (MALDI-TOF): 805 $[M-4I^-]^{4+}$, 932 $[M-3I^-]^{3+}$, 1059 $[M-2I^-]^{2+}$, 1186 $[M-I^-]^+$.

1.3 Methods for the disassociation constant (K_d) measurement[3,4]

The dissociation constant (K_d) was determined using a fluorescence titration experiment. Fluorescence intensity change at 602 nm was plotted again λDNA concentration, which was illustrated in Fig. S14a. Binding constant (K) could be determined by the fluorescence spectral change using the Benesi-Hildebrand equation (Fig. S14b). The corresponding dissociation constant (K_d) is calculated according to the binding constant (K).

1.4 References

1 X. Zhen, J. Zhang, J. Huang, C. Xie, Q. Miao and K. Pu, *Angew. Chem. Int. Ed.*, 2018, **57**, 7804-7808.

2 K. M. Hutchins, T. P. Rupasinghe, L. R. Ditzler, D. C. Swenson, J. R. G. Sander, J. Baltrusaitis, A. V. Tivanski and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2014, **136**, 6778-6781.

3 X. Zhou, F. Su, W. Gao, Y. Tian, C. Youngbull, R. H. Johnson and D. R. Meldrum, *Biomaterials*, 2011, **32**, 8574-8583.

4 A. Clémence, S. Falk, L. Rémy, B. Guillaume, F. D. Céline, C. Fabrice, T. Patrick and T. F. Marie‐Paule, *ChemBioChem*, 2007, **8**, 424-433.

2. Supporting Figures and Legends

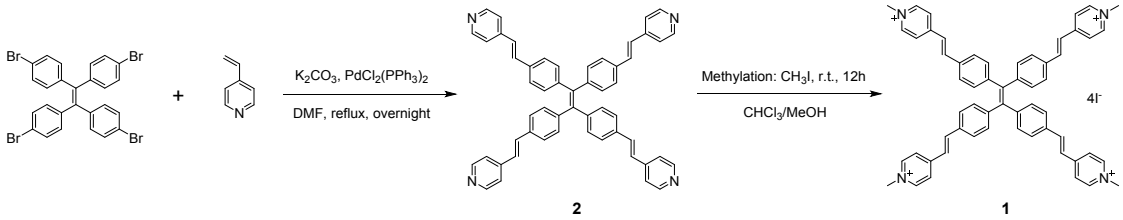

Figure S1. Synthetic scheme for the guest molecule **1**.

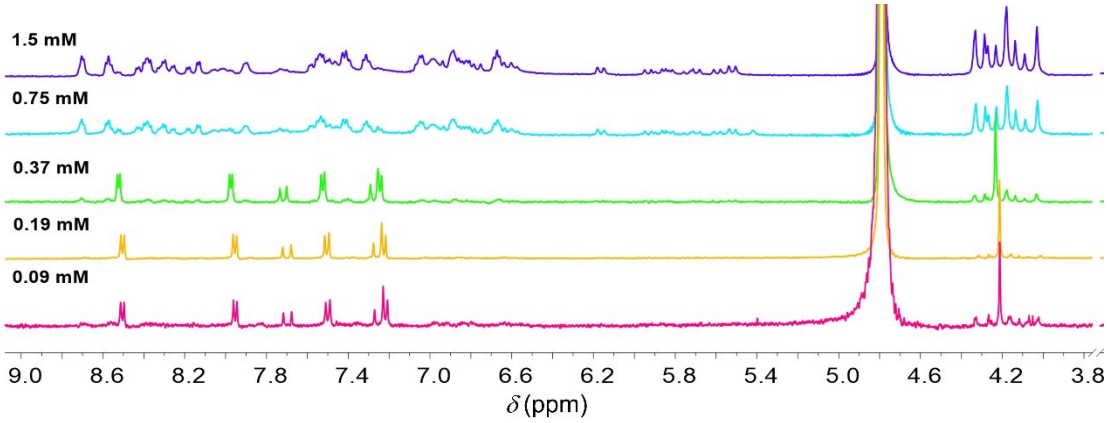

Figure S2. ^{1}H-NMR of **1** in D_2O at concentration of 0.09, 0.19, 0.37, 0.75, 1.5 mM at 25 ^oC.

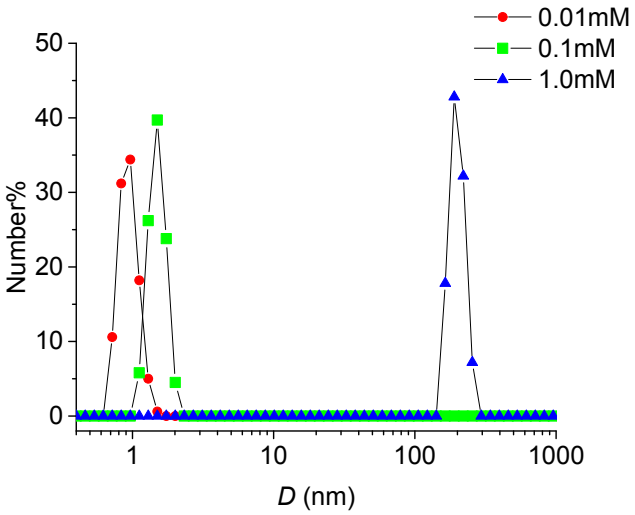

Figure S3. DLS profiles of **1** at concentration of 0.01 mM, 0.1 mM and 1.0 mM in water.

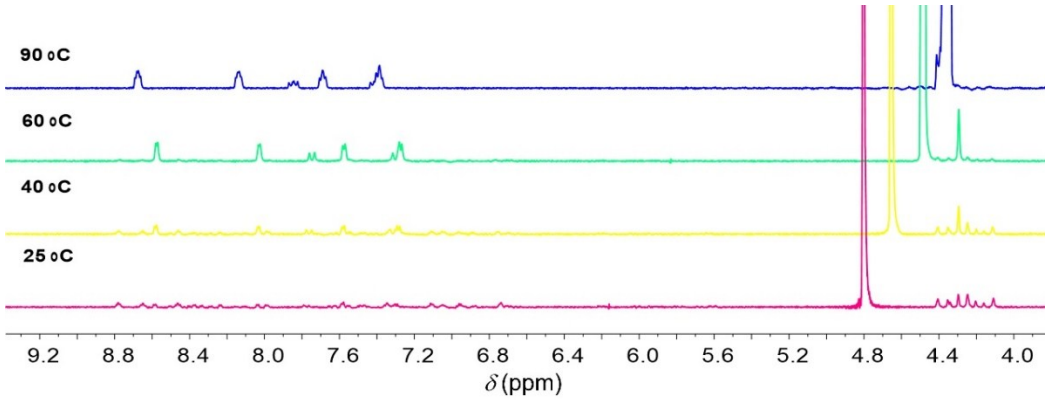

Figure S4. ^{1}H-NMR of **1** in D_2O at concentration of 0.75 mM at 25 ^{o}C, 40 ^{o}C, 60 ^{o}C and 90 ^{o}C.

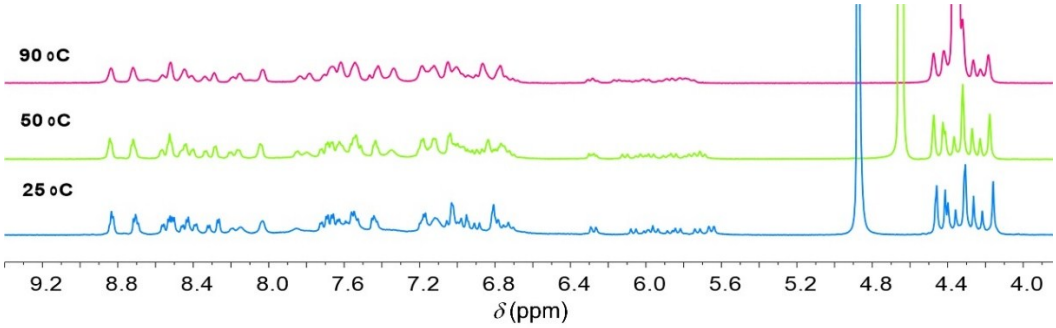

Figure S5. ^{1}H-NMR of **1** in D_2O at concentration of 1.5 mM at 25 ^{o}C, 50 ^{o}C and 90 ^{o}C.

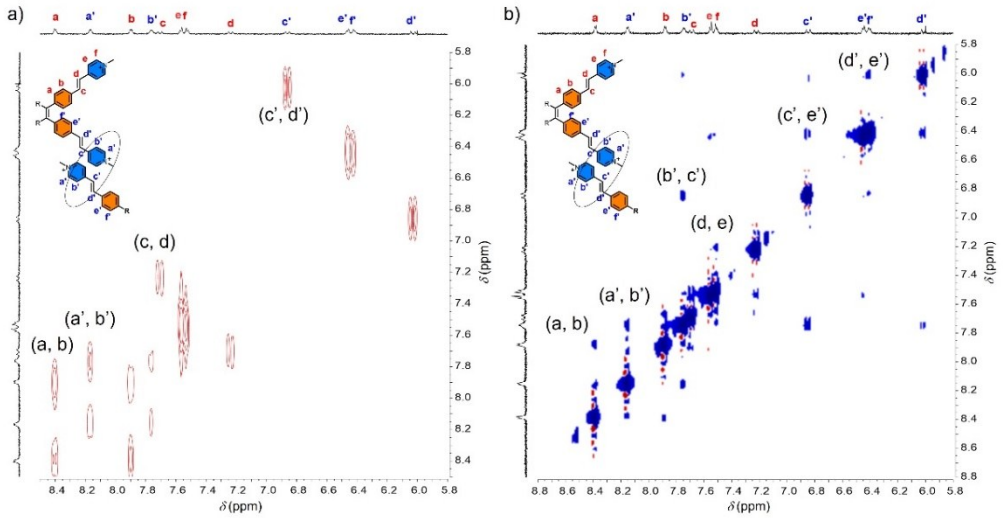

Figure S6. 2D ^{1}H NMR. (a) correlation spectroscopy (COSY) and (b) nuclear Overhauser effect spectroscopy (NOESY) spectrum (600 MHz) of **1**_CB[8] in D_2O at 25 ^{o}C. (The ratio between guests and CB[8] is 1:1; the concentration of **1**_CB[8] is 0.37 mM).

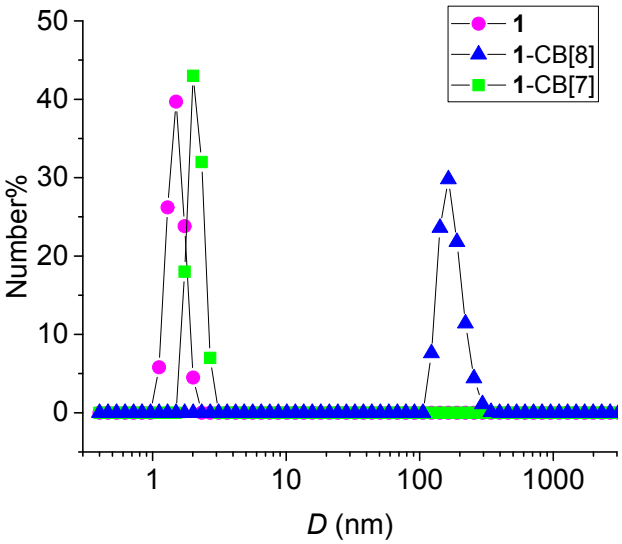

Figure S7. DLS profiles of **1** solution (0.1 mM) and the mixture with CB[8] (the ratio is 1:1) and CB[7] (the ratio is 1:4) in water.

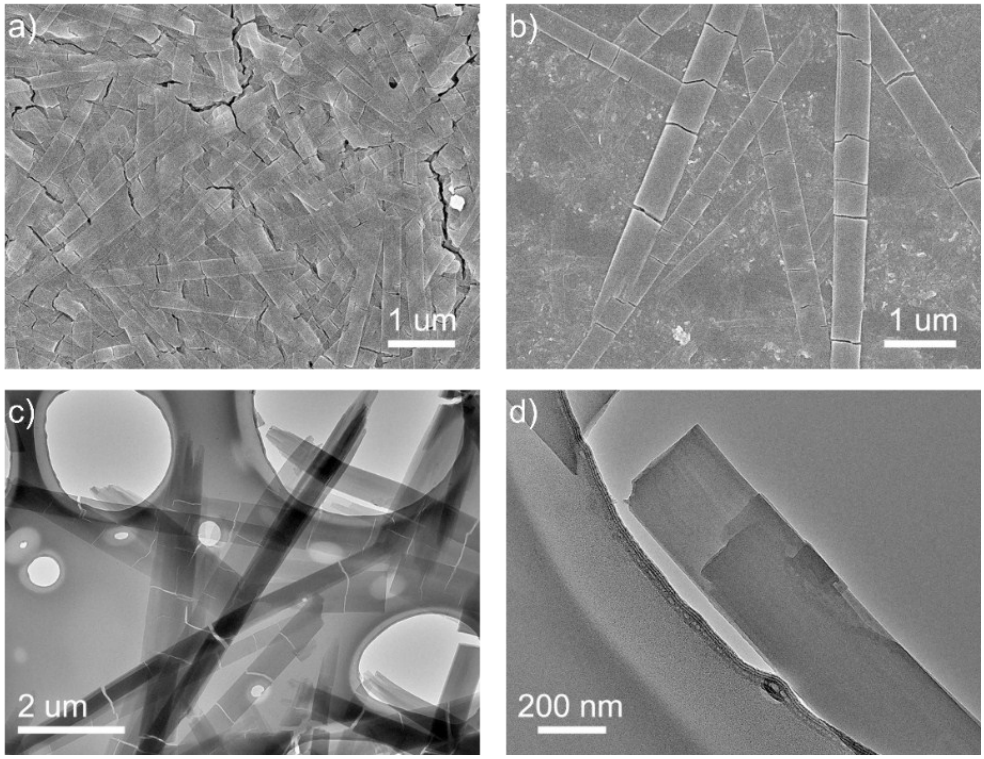

Figure S8. (a) and (b) SEM; (c) and (d) TEM images of self-assembled structures for **1**_CB[8] (The ratio between guests and CB[8] is 1:1; the concentration of **1**_CB[8] is 0.37 mM).

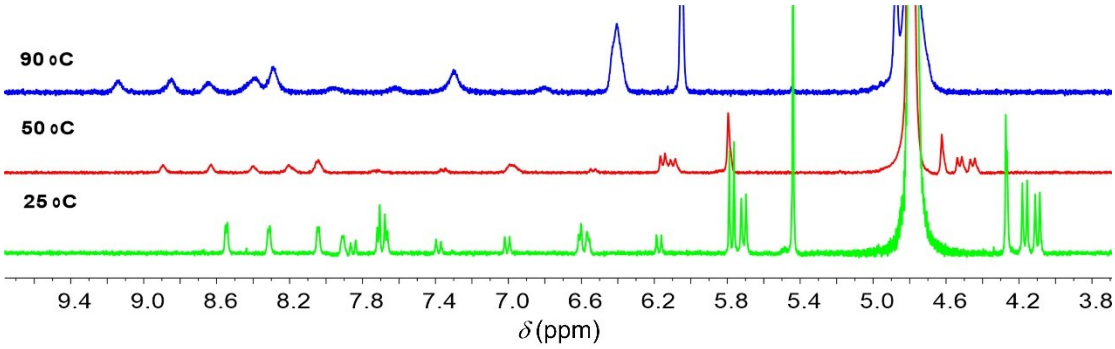

Figure S9. ^{1}H-NMR of **1**_CB[8] complex (1:1) in D_2O at concentration of 0.37 mM at 25 ^{o}C, 50 ^{o}C and 90 ^{o}C.

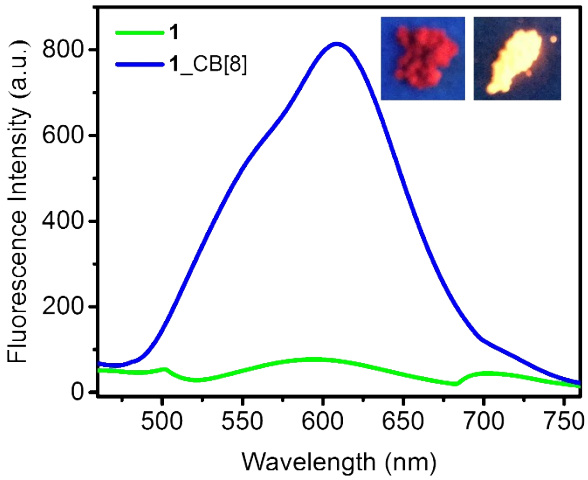

Figure S10. Solid state fluorescence spectra of **1** (in green) and **1**_CB[8] complex (1:2) (in blue). The inset is the photographs of **1** and **1**_CB[8] complex under 375 nm UV lamp.

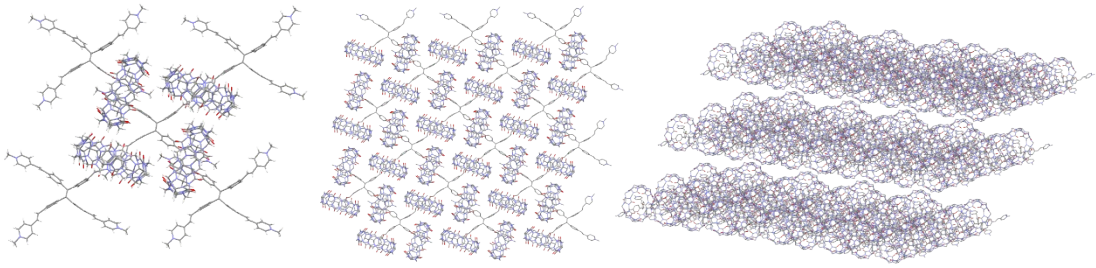

Figure S11. Optimized structure of the 2D complex of guest **1** and host CB[8] molecule in a ratio of 1:2.

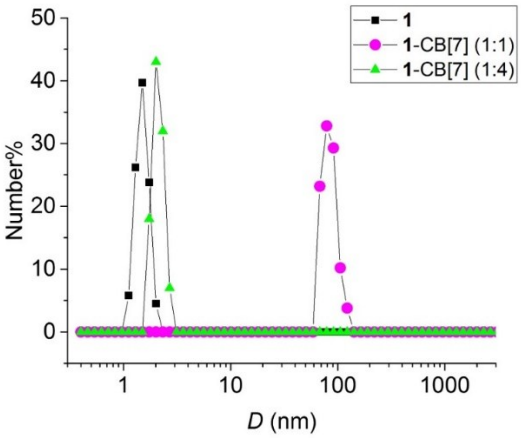

Figure S12. DLS profiles of **1** solution (0.1 mM) and the mixture with CB[7] (the ratio is 1:1 and 1:4) in water.

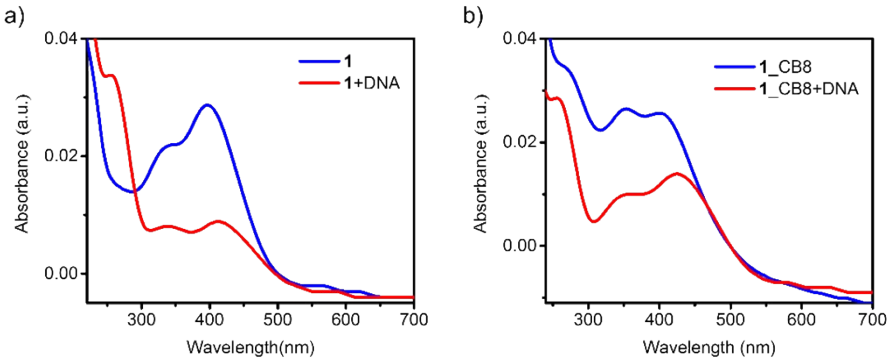

Figure S13. (a) UV-vis spectrum of the **1** (3 μM) and in the presence of λDNA (9 equiv.) in H_2O at room temperature; (b) UV-vis spectrum of the **1**_CB[8] (1:2) (3 μM) and in the presence of λDNA (9 equiv.) in H_2O at room temperature.

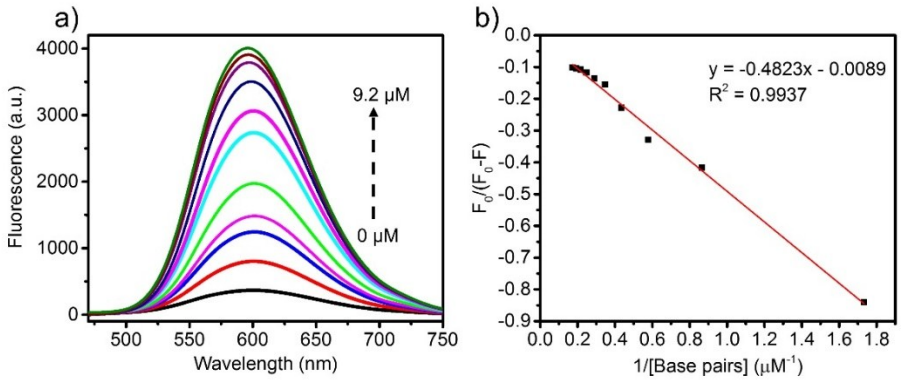

Figure S14. (a) Fluorescence intensity of compound **1** (5 μM) in the presence of an increasing amounts of λDNA in H_2O; (b) Benesi-Hildebrand plot of **1** with λDNA (F_0 is the integrated fluorescence intensity of free **1**, F is the observed integrated fluorescence intensity, the binding constant is given by the ratio intercept/slope).

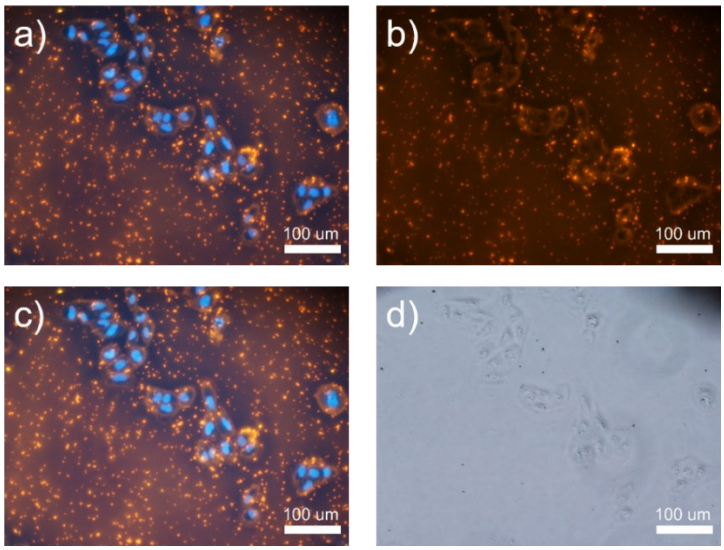

Figure S15. Epifluorescence microscopy pictures of Hela cells treated with Hoechst (5 μM) and with **1**_CB[8] (1:2) (1 μM). (a) fluorescence of Hoechst, (b) fluorescence of **1**_CB[8], (c) the merged picture (d) Bright-field image.

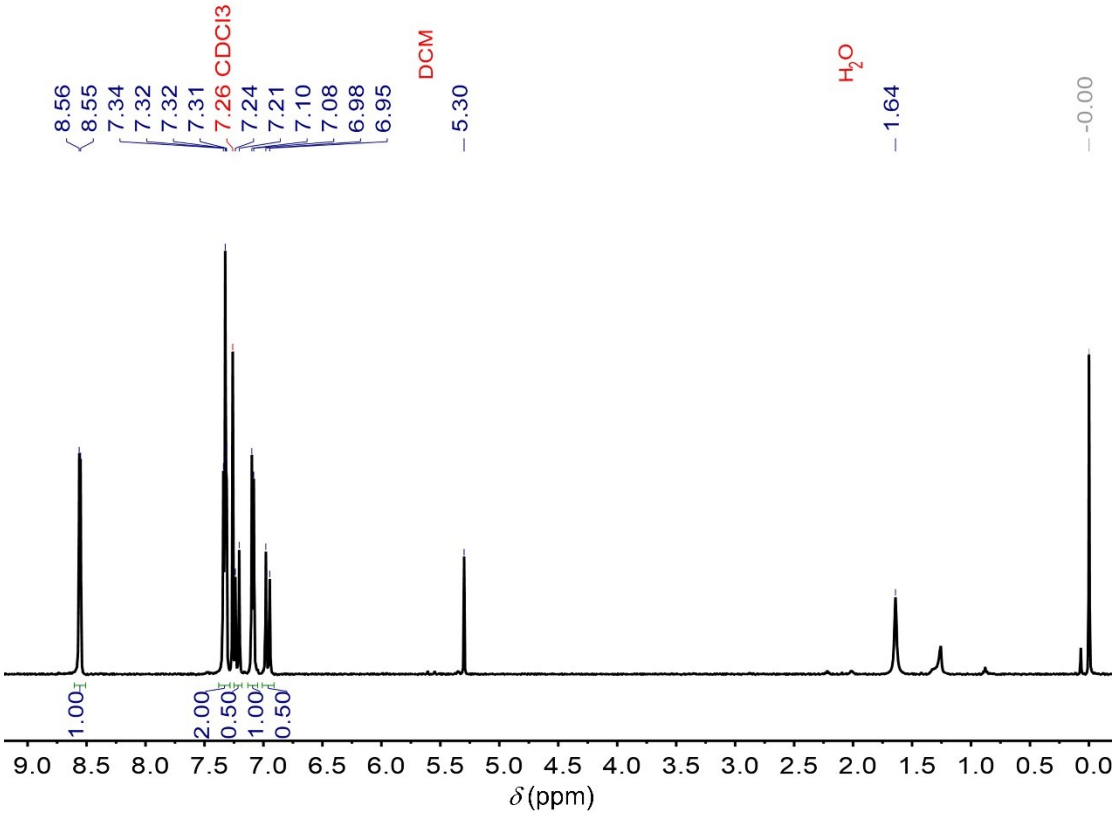

Figure S16. ^{1}H-NMR (500 MHz) spectrum of compound **2** in $CDCl_3$.

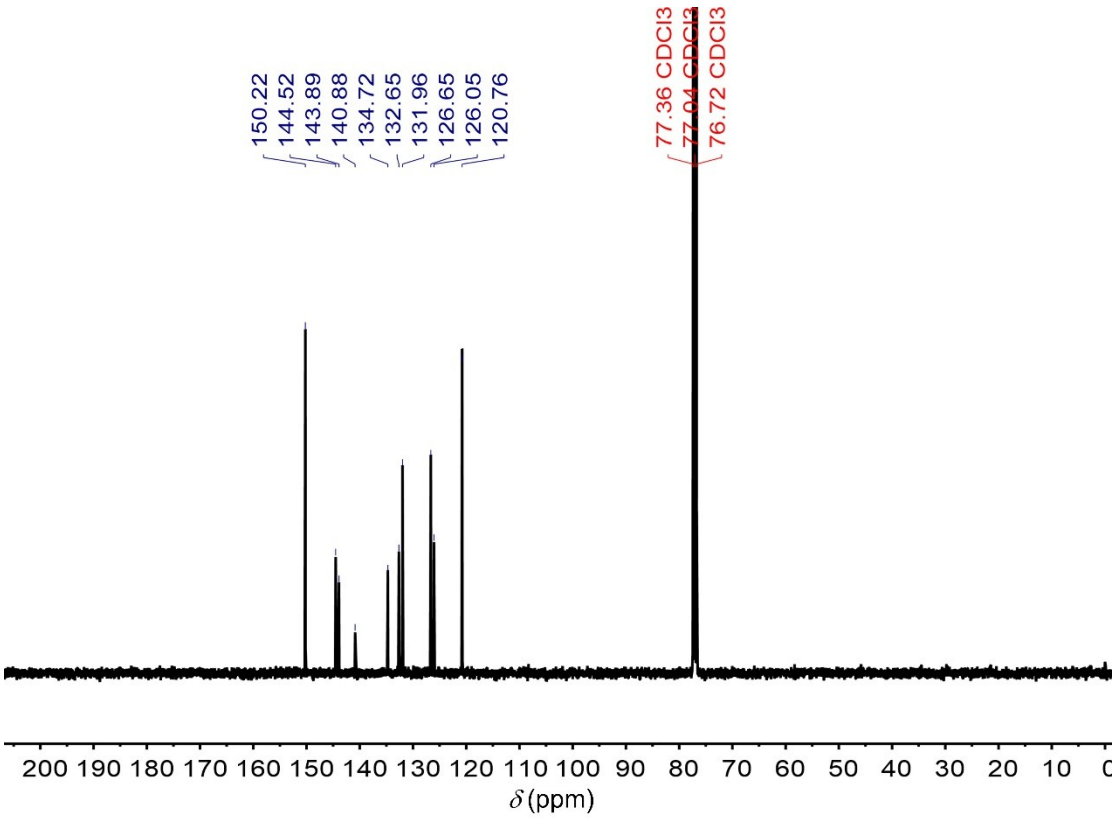

Figure S17. ^{13}C-NMR (101 MHz) spectrum of compound **2** in $CDCl_3$.

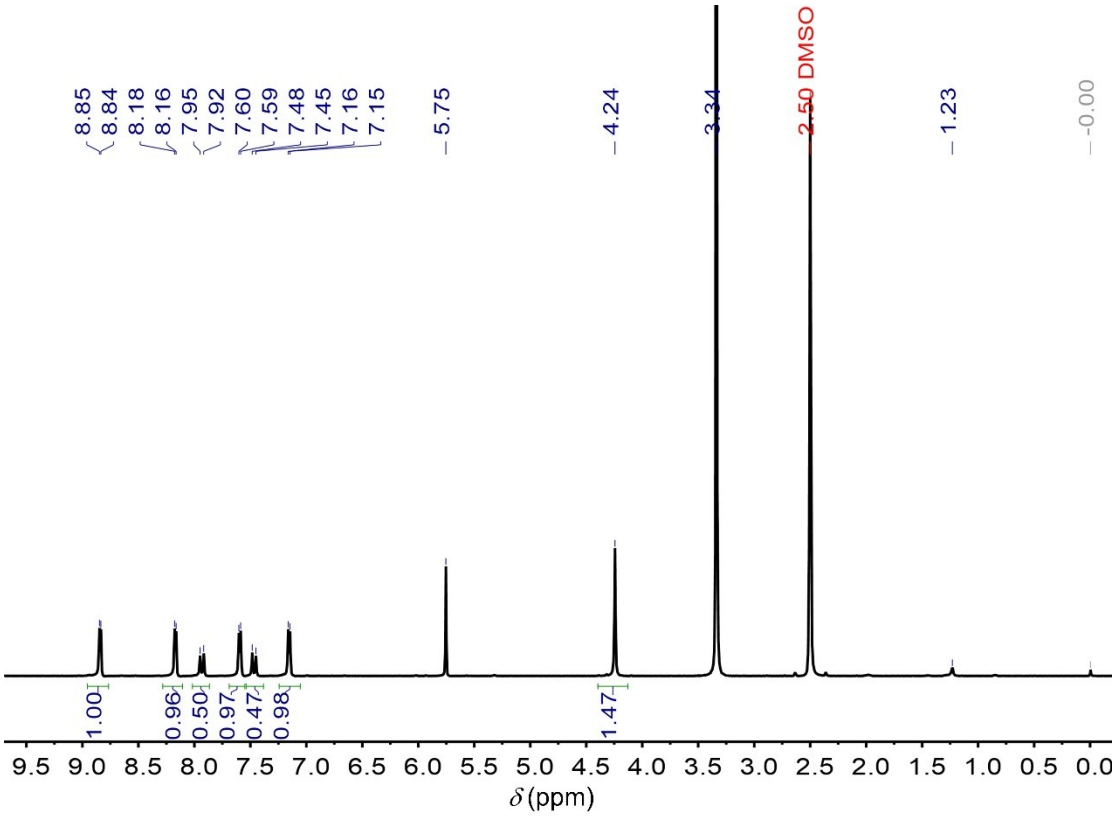

Figure S18. ^{1}H-NMR (500 MHz) spectrum of compound **1** in DMSO-d_6.

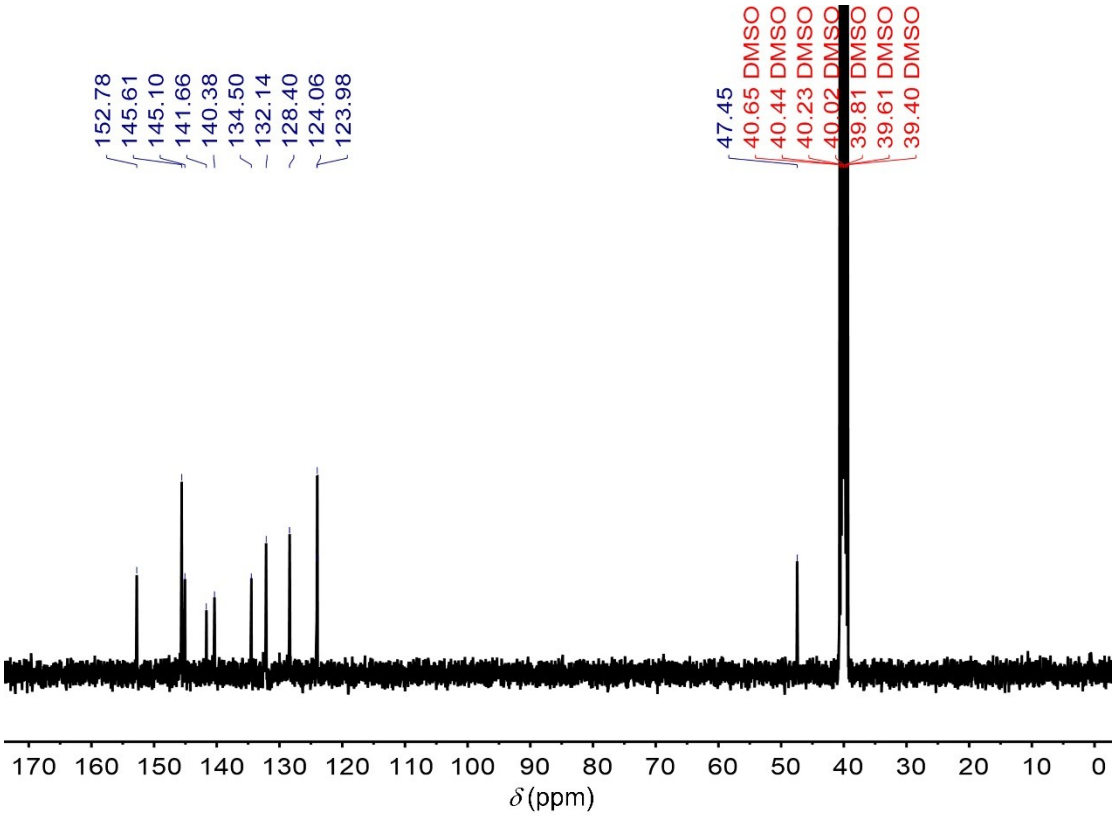

Figure S19. ^{13}C NMR (101 MHz) spectrum of compound **1** in DMSO-d_6

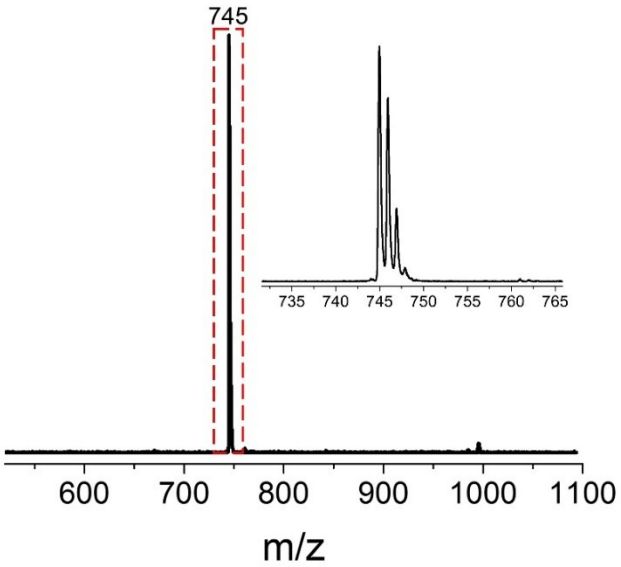

Figure S20. MALDI-TOF mass spectrum of compound **2**. The sample solutions (2 mg/mL in DCM) and DCTB solution (20 mg/mL in THF) were mixed in a volume ratio of 1:1, 2μL of which was then deposited on the target plate and dried before measurement.

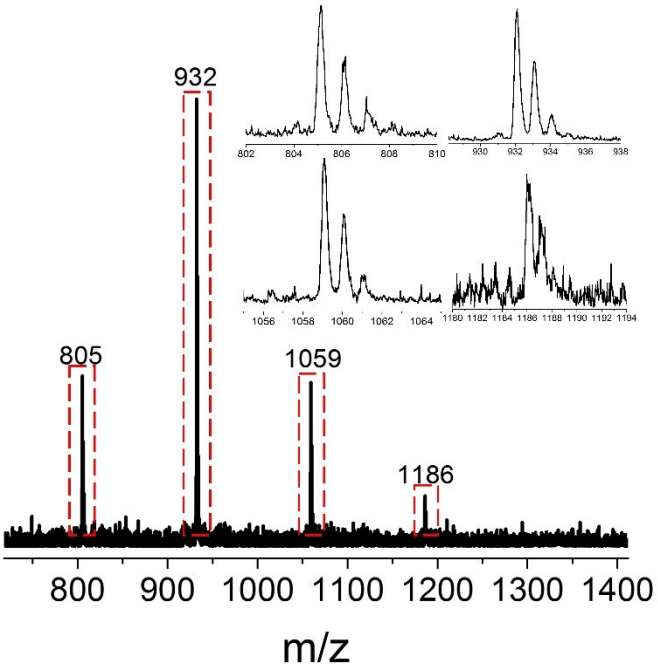

Figure S21. MALDI-TOF mass spectrum of compound **1**. The sample solutions (2 mg/mL in H_2O) and DCTB solution (20 mg/mL in THF) were mixed in a volume ratio of 1:1, 2μL of which was then deposited on the target plate and dried before measurement.