

Supporting Information

Cucurbiturils-based supramolecular host-guest complexes: single-crystal structures and dual-state fluorescence enhancement

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1. Supplementary Methods

1.1 General Materials and Methods

Unless otherwise specified, all reactions were performed in dried glassware under ambient atmosphere. All other reagents were purchased commercially and used without further purification. Organic solvents including methanol, ethanol, acetic anhydride, diphenyl ether, dichloromethane (DCM), N, N-dimethylformamide (DMF), and were purchased from Tansoole. Benzil, pentan-3-one, potassium hydroxide pellets (KOH), diphenylacetylene, 4-vinylpyridine, potassium carbonate, bis(triphenylphosphine)palladium(II) chloride ($\text{PdCl}_2(\text{PPh}_3)_2$), Iodomethane were purchased from Energy Chemical. All aqueous solutions were prepared with Milli-Q water.

^1H and ^{13}C NMR spectra were performed on 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 ($\delta = 0$).

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. Scanning electron microscope (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV.

Transmission electron microscope (TEM) imaging was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV. Low-dose selected-area electron diffraction was conducted on an aberration-corrected FEI Titan 80-300 operated at 300 kV.

Atomic Force Microscope (AFM) images were recorded on Bruker Multimode 8 AFM with Nanoscope V controller. HQ:NSC19/AI BS silicon tips were used for imaging with a resonance frequency about 65 kHz and a spring constant of about 0.5 N/m.

The liquid UV-Vis absorbance was measured by UV spectrophotometer (HITACHI, U-2910).

Time-dependent fluorescence decay spectra were measured at room temperature using FLS 1000 spectrometer (Edinburgh Instruments, UK). The data was fit with the exponential reconvolution function and the non-linear least square method.

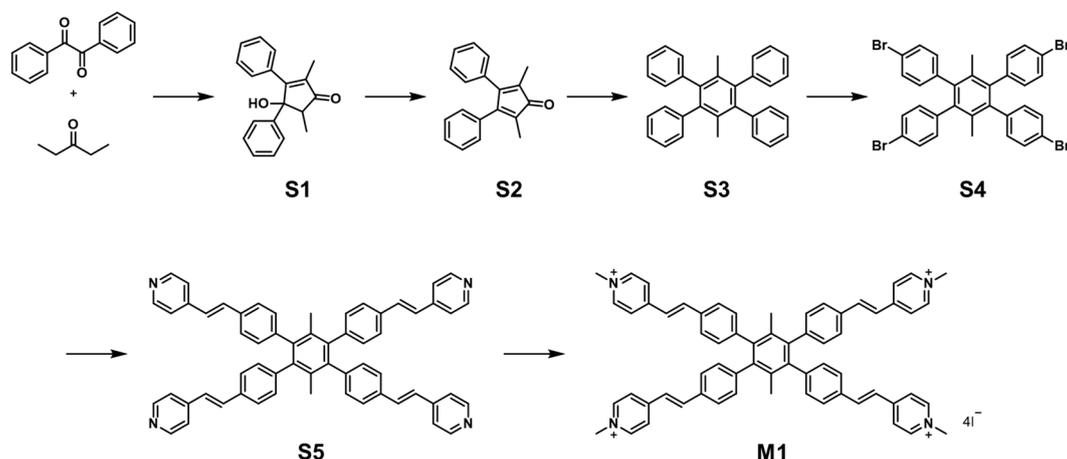
The absolute fluorescence quantum yield was determined on the C11347-11 absolute quantum yield spectrometer (HAMAMATSU, Japan).

Epifluorescence microscopy pictures were recorded on epifluorescence microscopy (OLYMPUS, IX73).

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).

Optical microscope was performed on Nikon ECLIPSE LV100ND POL.

1.2 Synthesis and compound characterization



Scheme S1. Synthetic scheme for the guest molecule **M1**.

Compound **S1-S4**: These compounds were prepared following the literature procedure.¹⁻³

Compound **S5**: To a stirred solution of **S4** (1.038 g, 1.43 mmol) in DMF (80 mL) was added 4-vinylpyridine (1.5 mL, 14.30 mmol), PdCl₂(PPh₃)₂ (0.101 g, 0.14 mmol), and potassium carbonate (1.180 g, 8.54 mmol). The reaction was gradually warmed to 154°C in a nitrogen atmosphere for 18 h. The reaction solution was cooled down and poured over 200 mL ice water. The precipitate was collected by filtration, and washed with H₂O. Silica gel column chromatography of the residue (DCM/MeOH, 30:1) gave pure **S5** (0.871 g, 74% yield) as a yellow solid. CCDC: 2285495. ¹H NMR (400 MHz, CDCl₃): 8.54 (d, *J* = 6.2 Hz, 8H), 7.37 (d, *J* = 8.3 Hz, 8H), 7.31 (d, *J* = 6.3 Hz, 8H), 7.21 (d, *J* = 16.3 Hz, 4H), 7.12 (d, *J* = 8.2 Hz, 8H), 6.94 (d, *J* = 16.3 Hz, 4H), 1.85 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): 149.6, 145.2, 142.0, 140.5, 133.8, 133.4, 130.7, 126.5, 125.4, 120.8, 19.6. MALDI-TOF-MS *m/z* for C₆₀H₄₆N₄ 823.83 (calc. 823.06).

Compound **M1**: A mixture of **S5** (82 mg, 0.1 mmol), CH₃I (0.3 mL, 5.0 mmol), CHCl₃/MeOH (6.0 mL, 1/5 by vol.) was stirred at 25°C for 12 h. The mixture was cooled down and the precipitate was collected by centrifugation, and washed with DCM for several times to afford **M1** (129 mg, 93% yield) as an orange solid. ¹H NMR (400 MHz, DMSO-*d*₆): 8.85 (d, *J* = 6.9 Hz, 8H), 8.18 (d, *J* = 6.9 Hz, 8H), 7.93 (d, *J* = 16.3 Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 8H), 7.47 (d, *J* = 16.3 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 8H), 4.25 (s,

12H), 1.77 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$): 152.9, 145.6, 143.3, 140.7, 140.5, 133.6, 131.3, 131.2, 128.1, 123.9, 123.7, 49.1, 19.7. MALDI-TOF-MS m/z for $\text{C}_{64}\text{H}_{58}\text{N}_4\text{I}_4$ 1390.98 (calc. 1391.2).

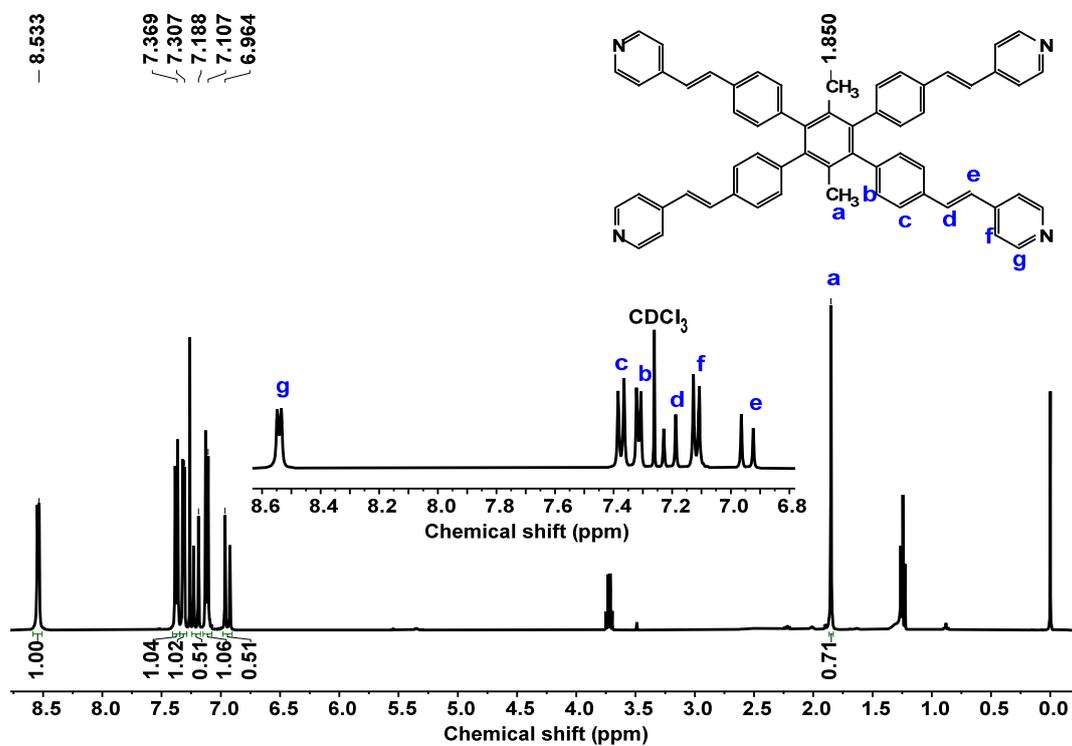


Fig. S1. ^1H NMR (400 MHz) spectrum of compound S5 in CDCl_3 .

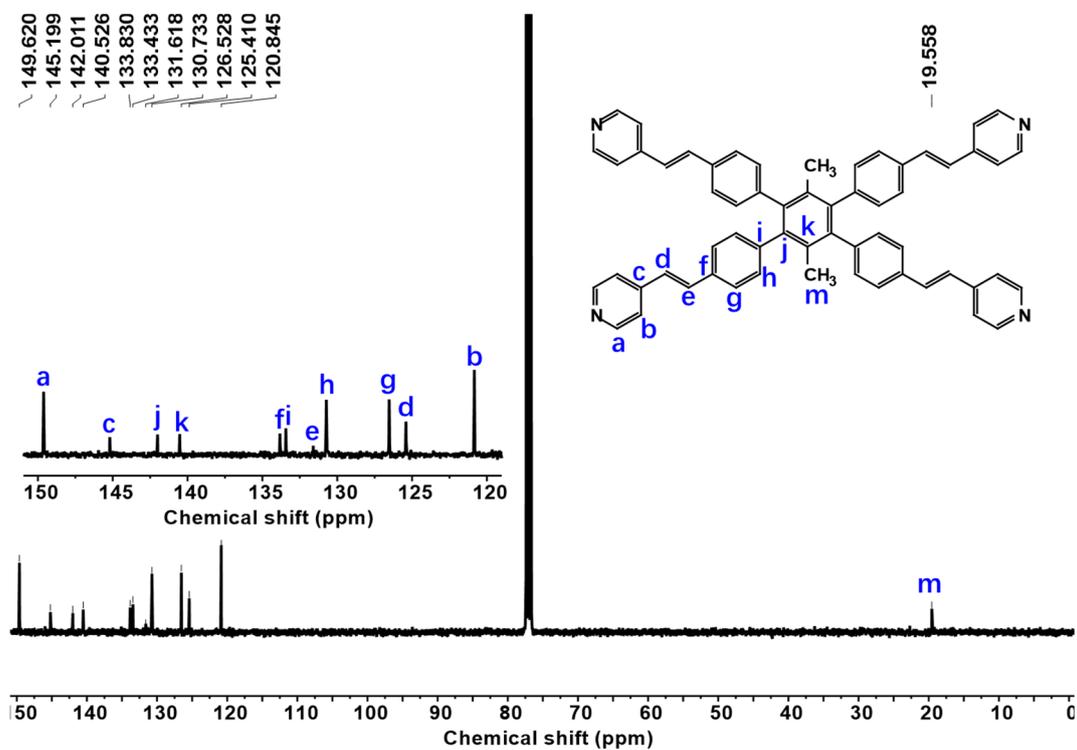


Fig. S2. ^{13}C NMR (100 MHz) spectrum of compound S5 in CDCl_3 .

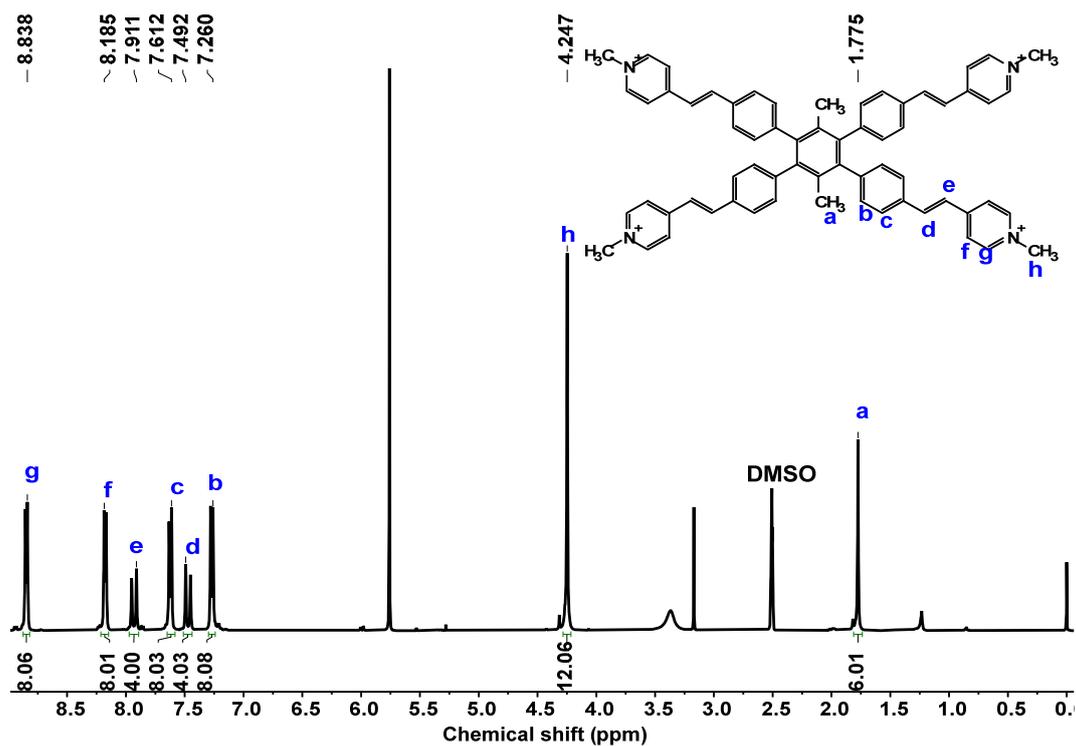


Fig. S3. ^1H NMR (400 MHz) spectrum of compound **M1** in $\text{DMSO-}d_6$.

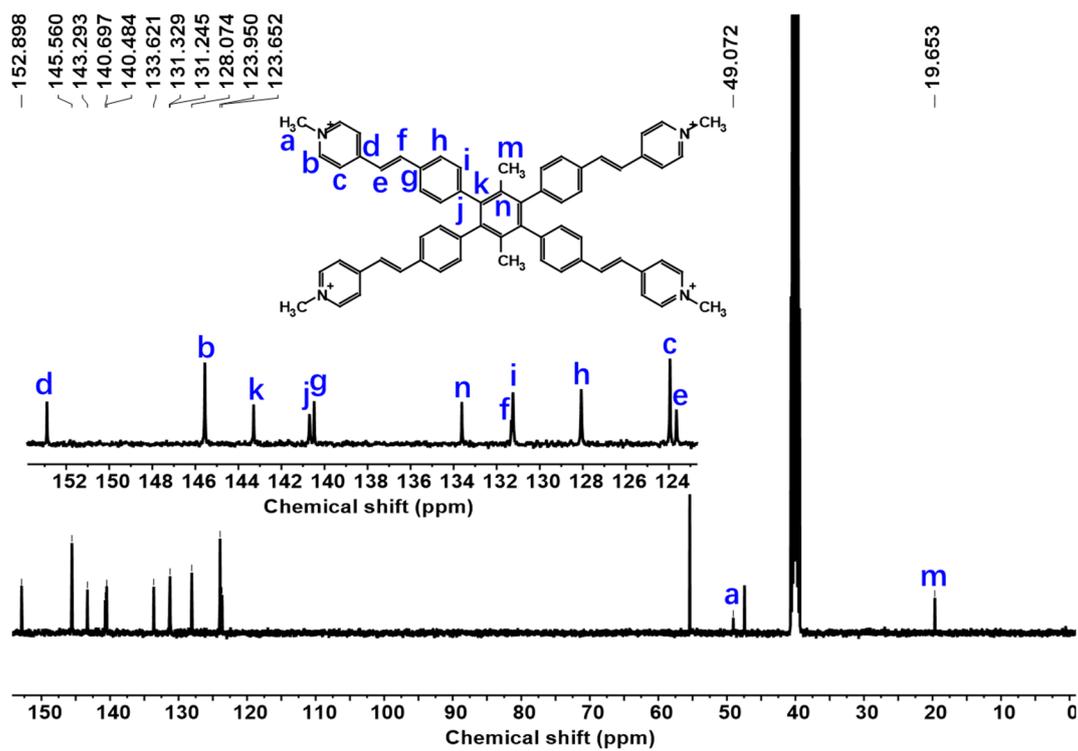


Fig. S4. ^{13}C NMR (100 MHz) spectrum of compound **M1** in $\text{DMSO-}d_6$.

1.3 Crystal growth of M1_CB[7] and M1_CB[8] and characterization

A screw cap vial (2 mL) charged with M1 (1 mg, 1.0 eq.), CB[7] (2.0 eq.)/ CB[8] (2.0 eq.) and H₂O (300-450 μ L) was mounted in a thermo-block placed onto Heidolph MR Hei-Connect which could control precisely the rate of heating or cooling. The vials were heated up to 115°C within 25 min and maintained 30 min at this temperature to ensure that the monomer had completely dissolved. Then, the temperature was slowly cooled down from 115°C to 29°C within 48 h to give crystals with 50-300 μ m edge length. The crystal structure was performed by an X-ray diffractometer (XRD, X-Pert, PANalytic, Netherlands) with Cu K α radiation (40 kV, 30 mA). CCDC 2285496 and 2285497 contain supplementary crystallographic data for this paper. Using Olex2, the structures were solved by direct methods (SHELXT 2018/2) and refined by full-matrix leastsquares by using SHELXL 2018/3. Crystallographic data and parameters for M1_CB[7] and M1_CB[8] can be seen in Table S1.

1.4 References

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2. Supporting Figures

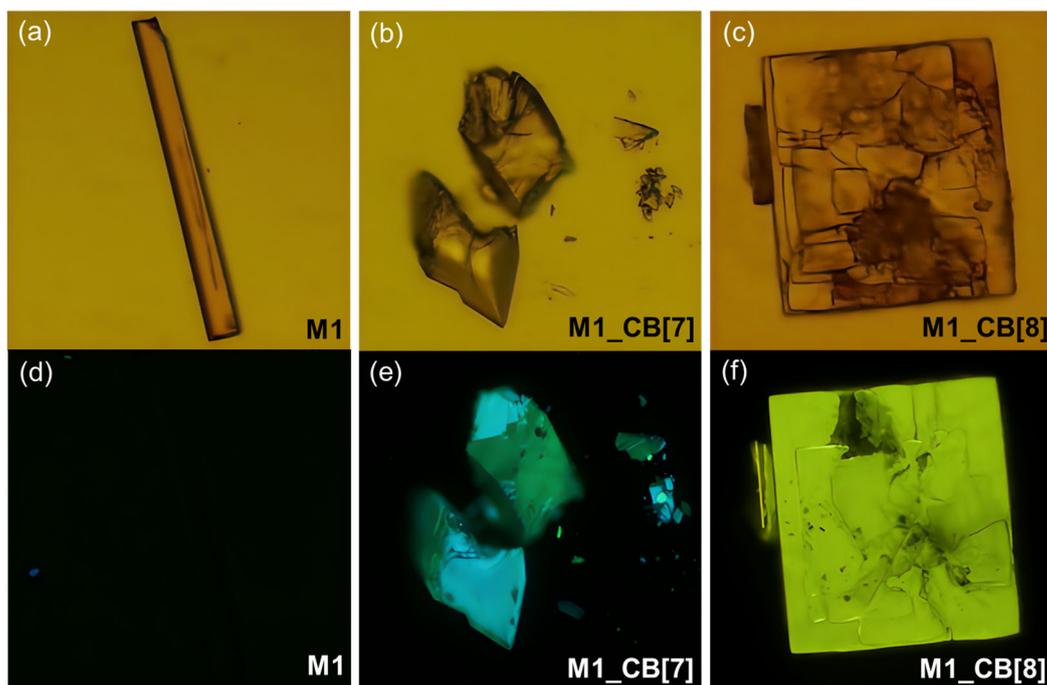


Fig. S5. Fluorescence optical microscope image of M1 (a), M1_CB[7] (b) and M1_CB[8] (c) crystal by visible light. Fluorescence optical microscope image of M1 (d), M1_CB[7] (e) and M1_CB[8] (f) crystal, excited with UV light (BP 340–390 nm, U-FUW).

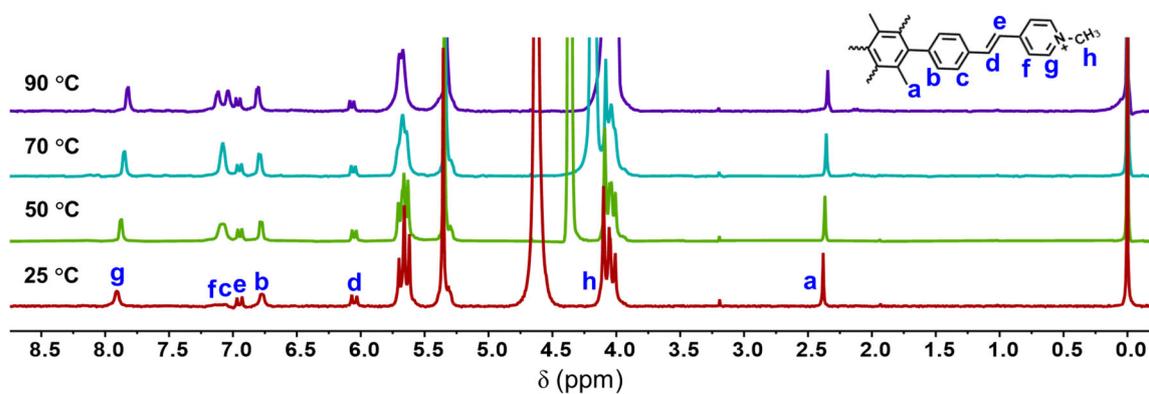


Fig. S6. $^1\text{H-NMR}$ of M1_CB[8] complex (1:2) in D_2O at concentration of 1.40 mM at 25 °C, 50 °C, 70 °C and 90 °C.

Table S1. Crystallographic data and parameters for **S5**, **M1_CB[7]** and **M1_CB[8]**.

Compound	S5	M1_CB[7]	M1_CB[8]
Identification code	data_4N_0m_sq	data_TX13207_auto_sq_sq	data_S6_CCF_SA_0m_sq_sq
CCDC	2285495	2285496	2285497
Empirical formula	C ₆₀ H ₄₆ N ₄	C ₇₄ H ₇₁ O ₁₄ N ₃₀ I ₂	C ₁₆₀ H ₁₅₀ O ₃₂ N ₆₈ I ₄
Formula weight	823.01	1858.41	4044.95
Temperature/K	296 K	170 K	220 K
Space group	<i>P</i> 21/n	<i>P</i> -1	<i>P</i> -42 <i>c</i>
a/Å	15.447	13.1070	18.6227
b/Å	5.8857	17.0258	18.6227
c/Å	29.629	25.9476	90.614
α/°	90	75.072	90
β/°	91.258	85.004	90
γ/°	90	77.546	90
Volume/Å³	2693.1	5460.3	31425.4
Z	2	2	4
Data completeness	0.995	0.998	0.998
R(reflections)	0.0714	0.1841	0.0880
wR2(reflections)	0.2350	0.3531	0.2812