Electronic Supplementary Information

Photo-controlled order-to-order host–guest self-assembly transfer for afterglow effect with water resistance

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Materials and Methods

All reagents were purchased from Aldrich and used without additional purification. ^{1}H NMR and NOESY spectra were measured on a Bruker 400L spectrometer. MS was measured by Matrix Assisted Laser Desorption Ionization-Time of Flight/Time of Flight Mass Spectrometer (5800). X-ray diffraction measurements (XRD) were made by a PANalytical X'Pert PRO with Cu Kα radiation (λ = 0.1542 nm; operating energy, 40 kV; cathode current, 40 mA; scan rate, 20 min^{-1}). The UV-vis absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. The CD spectra were recorded on a Chirascan CD spectrophotometer (Applied Photophysics Ltd., UK). Fourier transform infrared (FTIR) spectra were obtained from a Nicolet 6700 infrared spectrophotometer by a single total reflection of diamond with a scan range of 400 − 4000 cm^{-1}. The Raman spectra were obtained from In Via Qontor/INTEGRA Spectra II. The isothermal Titration Calorimetry (ITC) experiments were performed on PeaQ-ITC (made by Malvern Instruments Ltd) with power compensation calorimetric mode. The emission spectra, decay spectra, and quantum yield were obtained from an Edinburgh FLS-1000 luminescence spectrometer equipped with a xenon lamp and a microsecond flashlamp as the excitation source. The Instrument Response Function (IRF) was collected using silica solution as the reference standard. The absolute phosphorescence photoluminescent quantum yields (QY) were collected on an FLS-1000 using the integrating sphere. The photoirradiation experiments were carried out using a hand-held UV lamp with an irradiation wavelength of 365 nm in a sealed 10 mm or 1 mm quartz cell; the distance between the sample and the lamp is ~ 10 cm; the power of the UV lamp is 5W; the light intensity on the sample is ~24 mW/cm^2). Dynamic light scattering (DLS) experiments were carried out with Nano-Zeta Potential Analyzer ZS-90. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2100 with an accelerating voltage of 200 kV, and Cryo-TEM was performed on a JEOL CryoARM 300 with an accelerating voltage of 300 kV and a Gatan K3 direct electron detector. The type of the optical microscope was DM2500P (made by Leica). GISAXS was measured on Xenocs with 8 KeV Cu Kalpha light source (area detector: Pilatus3R 200K-A, q value test range: 0.025 nm-1 ≤ q≤ 40 nm-1). The topography of HB-CyD solution before and after irradiation was analyzed with an AFM (Bruker Fastscan) in tapping mode using a silicon tip with an aluminum reflex coating (Bruker RTEASPA300).

Computational detail.

The structure of the covalently coupled complex between HB molecule and β-CD was initially optimized in the ground singlet state (S_0) by using B3LYP functional and 6-31G(d) basis set with an accounting of the empirical dispersion correction at GD3 level. Based on the optimized S_0 geometry, we have optimized the geometries of the first excited singlet state (S_1) and the first excited triplet state (T_1) by using time-dependent (TD) DFT and spin-unrestricted DFT methods, respectively. For S_1 and T_1 optimization, the B3LYP functional combined with 6-31G(d) basis set and GD3 empirical dispersion correction were employed. All the calculations were performed by using Gaussian16 software.

Preparation of co-assembly PVA films.

PVA-1795 (40 mg/mL) was added in different kinds of aqueous solution, which was stirred at 60 ℃ for 1 h. Then, the solutions were dropped on a cell culture dish plastic box and placed in the oven at 65 ℃ for 24 h.

Preparation of GISAXS sample.

The aqueous HB-CyD solutions with different irradiation periods were taken by liquid transfer gun on a clean silicon wafer substrate and dried in the oven at 65 ℃.

Preparation of Cryo-TEM sample.

3 μL of aqueous HB-CyD solution (1 mg/mL) was dropped on the copper mesh, then the filter paper was used to absorb the excess sample to obtain a skinny layer of liquid on the copper mesh, and then the resulting copper mesh was quickly put into liquid ethane to complete the rapid freezing of the sample.

Synthetic procedure

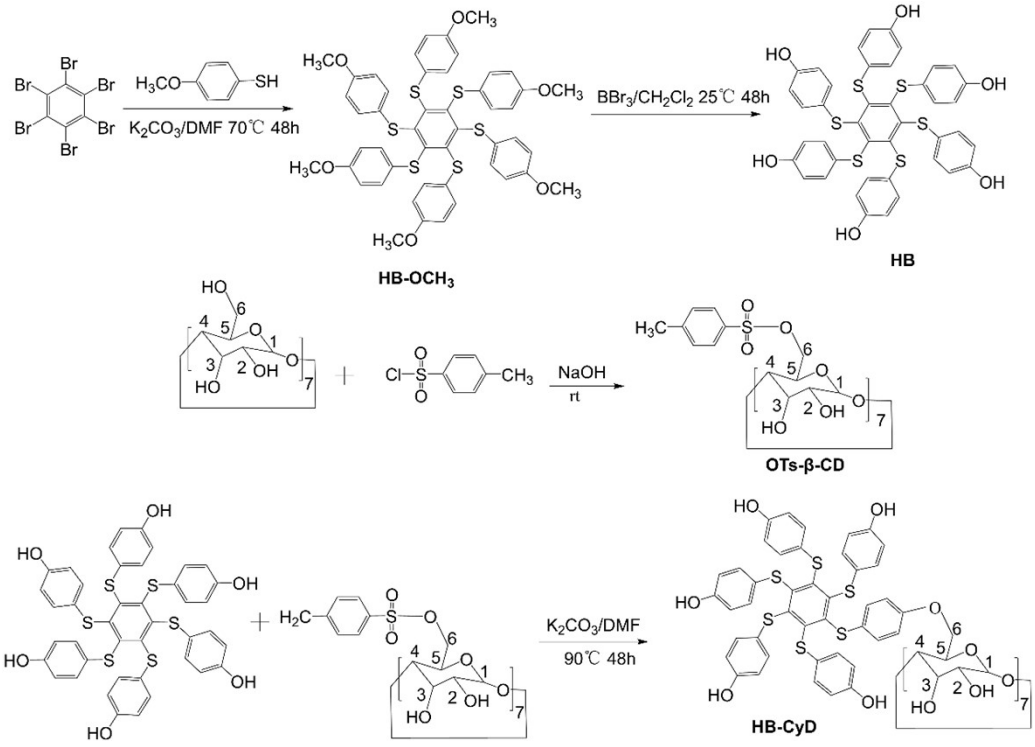
Synthesis of ***HB-OCH$_3$***. Hexabromobenzene (1 eq, 7.548 g, 13.73 mmol), 4-methoxy thiophenol (9 eq, 17.330 g, 123.6 mmol), anhydrous potassium carbonate (9 eq, 17.080 g, 123.6 mmol), and 90 mL of DMF were added to the round-bottomed flask, reacting at 75 °C for 48 h under a nitrogen atmosphere. Aqueous sodium hydroxide solution was added after the reaction is completed and the mixture stirred until the precipitate no longer formed. The precipitate was filtered and washed with ethanol and water. The resulting crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 2:1) to give the compound ***HB-OCH$_3$*** as a bright

yellow solid (7.50 g, yield 60%). The synthesis process was followed by the previous literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 8.9 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H).

Synthesis of ***HB***. The excess boron tribromide (30 eq, 3.19 mL, 33.0 mmol) was added to the anhydrous dichloromethane (80 mL) with ***HB-OCH₃*** (1 eq, 1.0 g, 1.1 mmol) under a nitrogen atmosphere, and the solution was stirred for 12 h at room temperature. The water was added dropwise until the precipitate no longer formed. The precipitate was dissolved with EA and filtered to remove a large amount of insoluble matter. The resulting filtrate was concentrated and purified by column chromatography (silica gel, petroleum ether/ethyl acetate 2:3) to give the compound ***HB*** as a yellow solid (7.56 g, yield 90%). The details of the synthesis are based on previous report.[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 6.72 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H).

Synthesis of ***OTs-β-CD***. The β-CD (1 eq, 17.220 g, 0.015 mmol) was dissolved in 200 mL of 1% aqueous sodium hydroxide solution to obtain a clear and transparent solution. Then, p-toluenesulfonyl chloride (1 eq, 2.90 g, 0.015 mmol) in acetonitrile solution (11 mL) was added dropwise in 80 min. A plenty of precipitates formed, and the mixture was further stirred for 2 h. The mixture was filtered, and the filtrate was acidified with diluted hydrochloric acid solution to pH = 2~3 and then placed at 2 °C overnight. The white precipitate was filtered and recrystallized twice with water to give the compound ***OTs-β-CD*** (1.50 g, yield 8%). The synthesis steps were carried out according to the previous literature.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 (d, J = 8.4 Hz, 2H), 7.43 (d, 2H), 5.89 – 5.61 (m, 15H), 4.93 – 4.71 (m, 7H), 4.57 – 4.43 (m, 5H), 4.41 – 4.13 (m, 3H).

Synthesis of ***HB-CyD***. ***HB*** (15 eq, 7.270 g, 8.844 mmol), ***OTs-β-CD*** (1 eq, 0.758 g, 0.59 mmol) and anhydrous potassium carbonate (30 eq, 2.370 g, 17.69 mmol) was added to 80 mL of anhydrous DMF, and stirred at 85 °C for 48 h under a nitrogen atmosphere. Then the diluted hydrochloric acid solution (20 mL, 2.83 mM) was added to obtain the neutral solution and concentrated in vacuo. The residue was diluted with 200 mL of water and 300 mL of ethyl acetate. A white suspension appeared, assigning to excess hexa(thioaryl)benzene. The aqueous phase was washed with 300 mL of ethyl acetate several times until the hexa(thioaryl)benzene in the aqueous phase was removed entirely. The aqueous phase was filtered, and the precipitate was rinsed with water several times to remove potassium chloride. Then the precipitate was dissolved in methanol and filtered. The filtrate was concentrated in vacuo, and the residue was washed with ethyl acetate. Finally, the crude product was passed through a C18 reverse-phase chromatographic column with methanol/water 8:2 to give an orange-yellow solid (0.30 g, yield 26%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 5H), 6.87 – 6.56 (m, 24H), 5.96 – 5.59 (m, 14H), 5.05 – 4.63 (m, 7H), 4.55 – 4.40 (m, 5H), 4.22 – 3.87 (m, 3H). ^{13}C NMR (151 MHz, DMSO) δ 162.79, 157.66, 156.75, 147.58, 130.89, 130.63, 126.64, 126.51, 116.64, 115.93, 102.42, 82.37, 82.00, 73.52, 72.88, 72.50, 60.36, 36.26, 31.26, 19.03.



Scheme S1. Synthetic route for the HB-CyD.

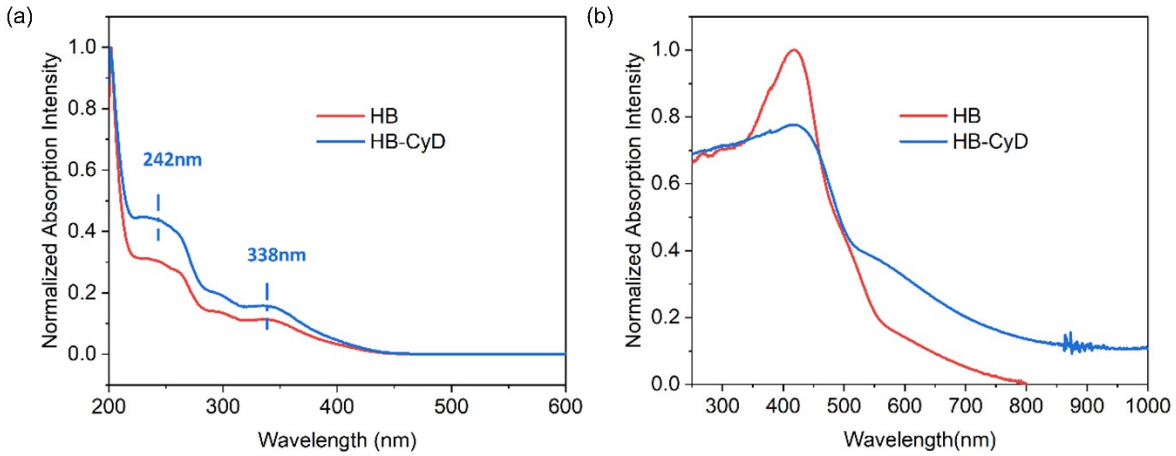


Fig. S1. (a) Normalized absorbance spectra of HB and HB-CyD in ethanol solution (concentration: 10 μM). (b) Normalized absorbance spectra of HB and HB-CyD in powder state.

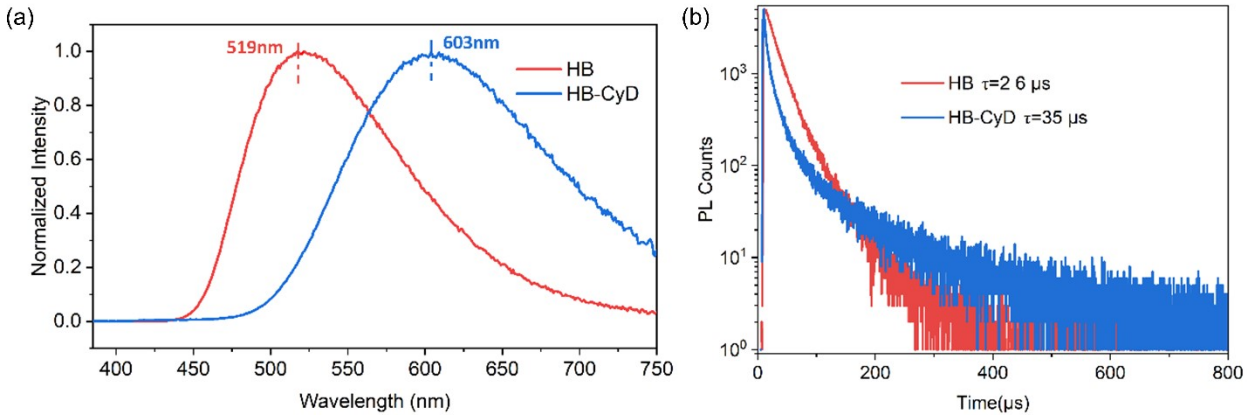


Fig. S2. (a) Normalized emission spectra and (b) PL lifetime curves of HB and HB-CyD in powder state.

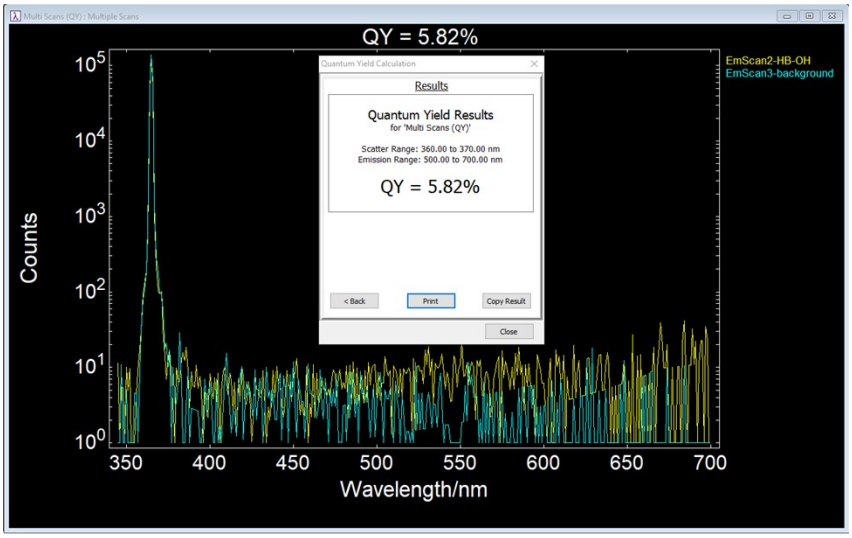


Fig. S3. PL quantum yield of HB-OH in the powder state.

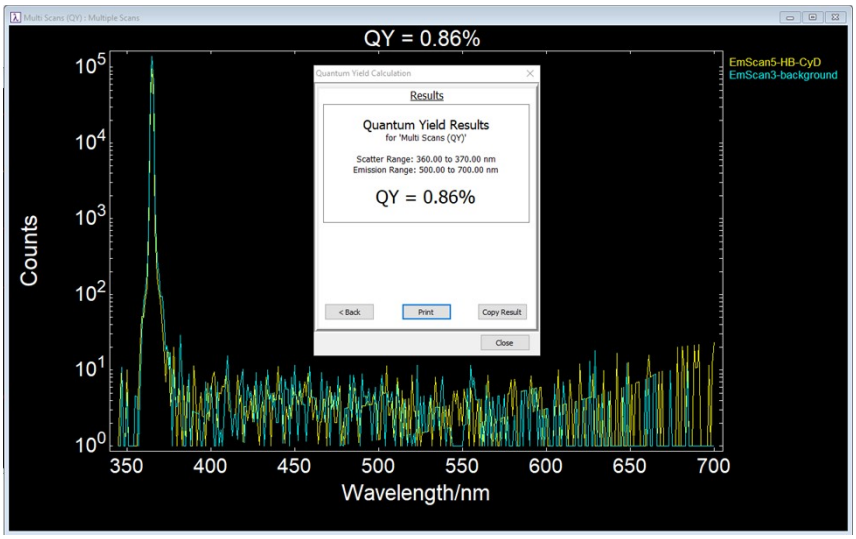


Fig. S4. PL quantum yield of HB-CyD in the powder state.

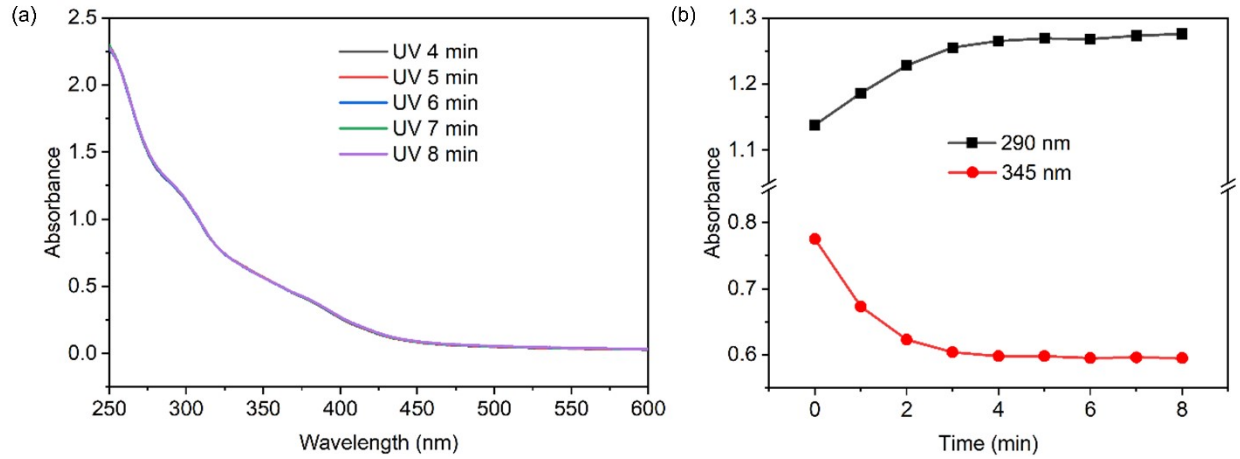


Fig. S5. (a) UV–vis absorbance spectra of aqueous HB-CyD solution upon UV irradiation for 4~8 min at 298 K (concentration: 0.05 mg/mL). (b) The absorbance at 290 nm and 345 nm as irradiation time.

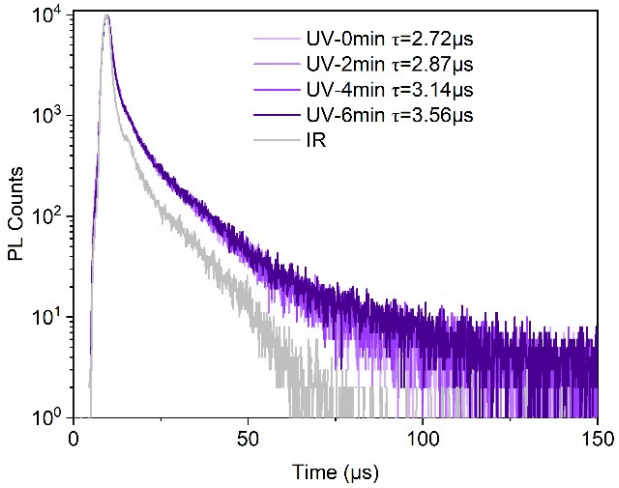


Fig. S6. The phosphorescence lifetime of aqueous HB-CyD solution as irradiation time.

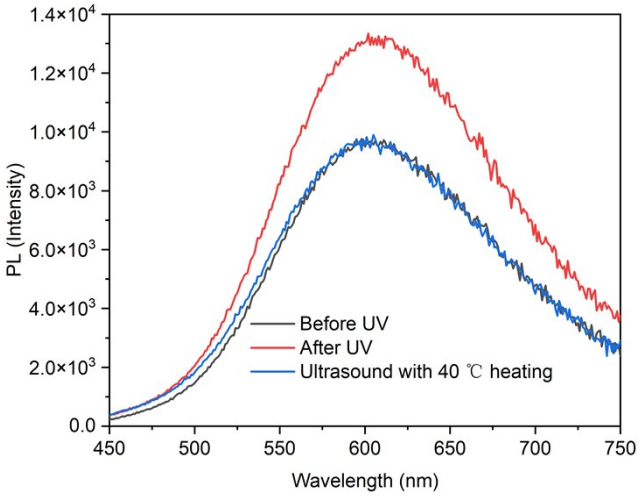


Fig. S7. Emission spectra of HB-CyD before irradiation, after irradiation, and followed by ultrasonic treatment at 40 °C for 5 min.

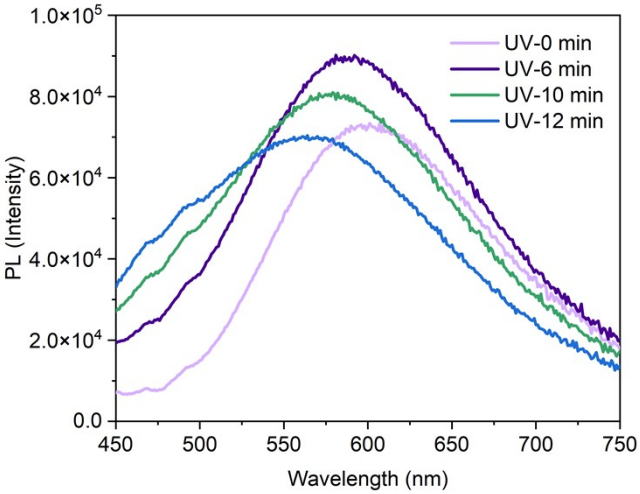


Fig. S8. Emission spectra of HB-CyD (concentration: 1 mg/mL, λ_{ex} = 365 nm, 298 K) upon irradiation for 6~12 min with UV light.

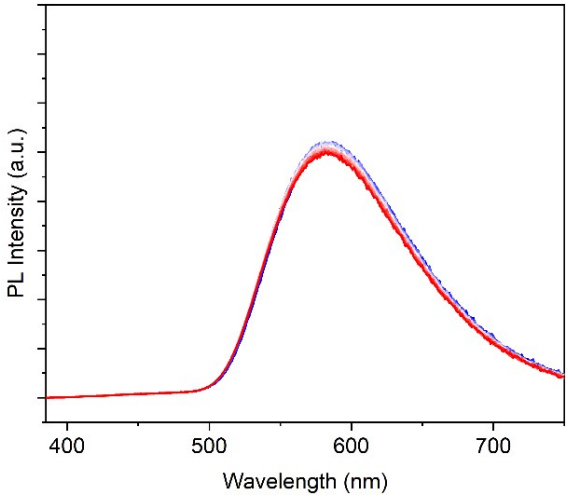


Fig S9. Emission spectra of HB-CyD (concentration: 1 mg/mL, λ_{ex} = 365 nm, 77 K) upon irradiation.

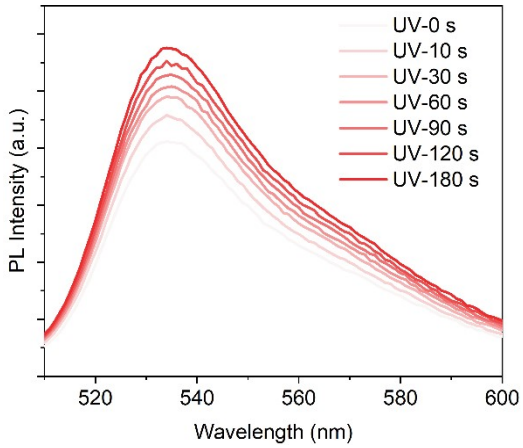


Fig S10. Emission changes of a mixed aqueous solution of HB-CyD (0.02 mg/mL) and SOSG (5 μM) as irradiation time.

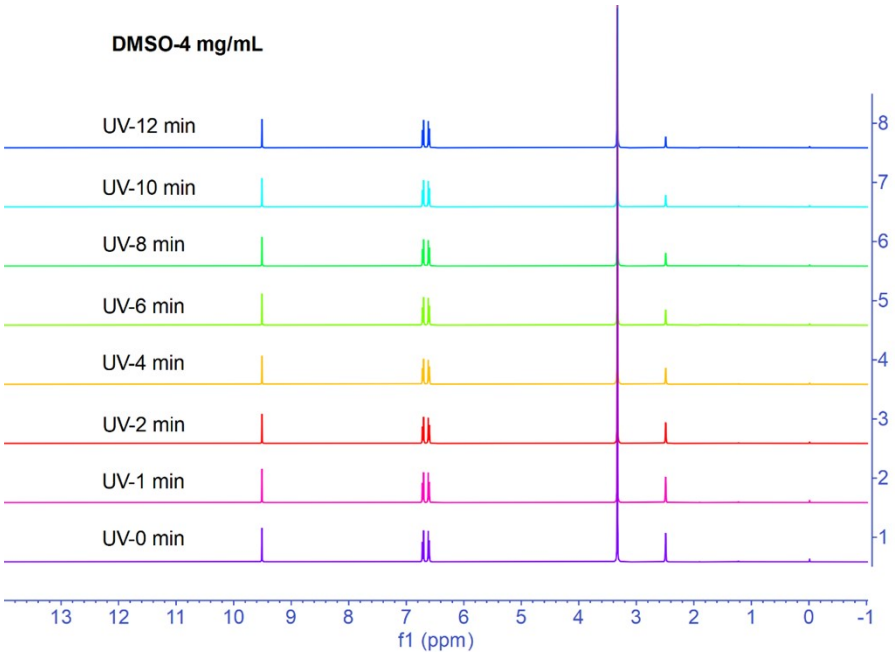


Fig S11. ^{1}H NMR spectra of HB in deuterated DMSO upon UV irradiation (concentration: 4 mg/mL).

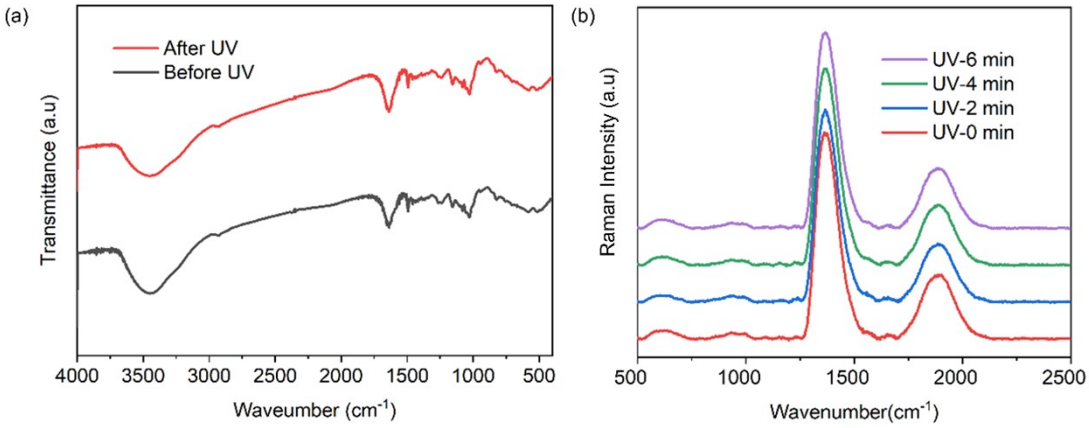


Fig S12. (a) FTIR and (b) Raman spectra of aqueous HB-CyD solution before and after UV irradiation.

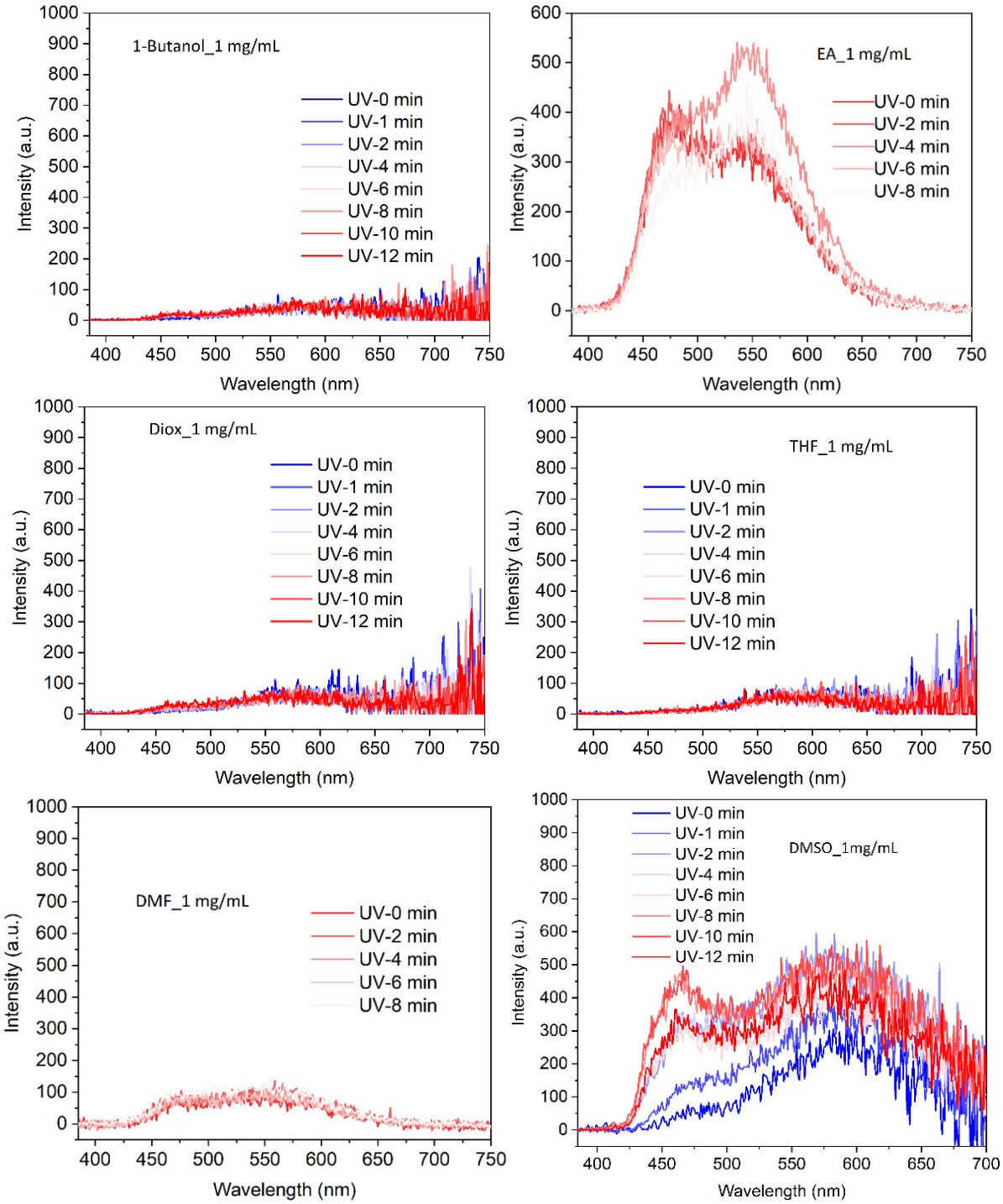


Fig S13. Emission spectra of HB in different organic solvents upon UV irradiation (concentration:1 mg/mL), respectively.

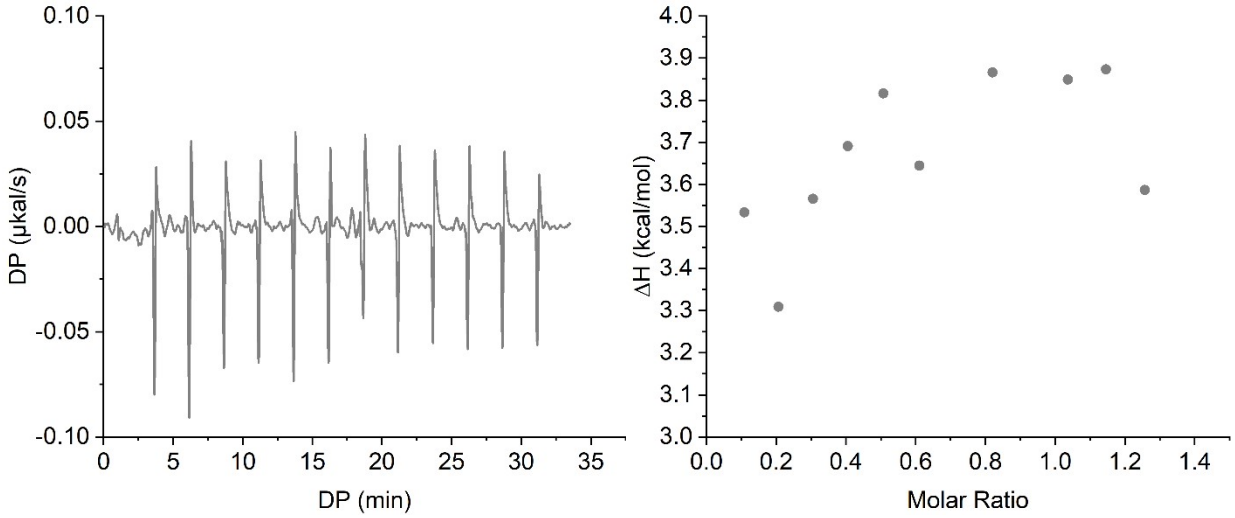


Fig S14. Isothermal titration calorimetry curve of the interaction between HB (0.25 mg/mL) and β-CyD (0.025 mg/mL). The solution is formed by 10% DMSO and 90% H2O.

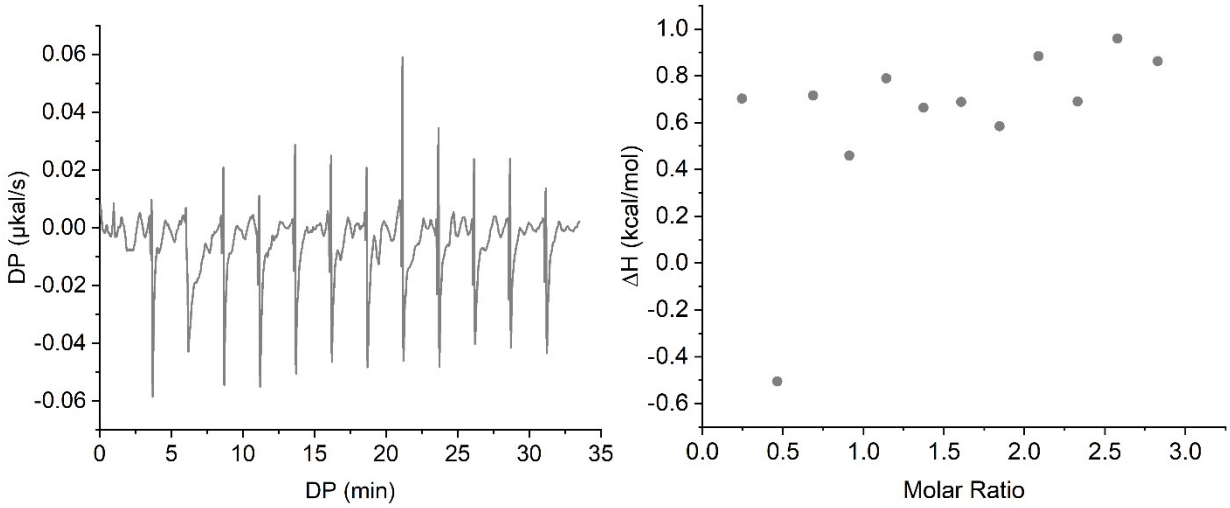


Fig S15. Isothermal titration calorimetry curve of the interaction between HB-ONa (0.25 mg/mL) and β-CyD (0.025 mg/mL). The solvent is aqueous sodium hydroxide solution with pH = 10.

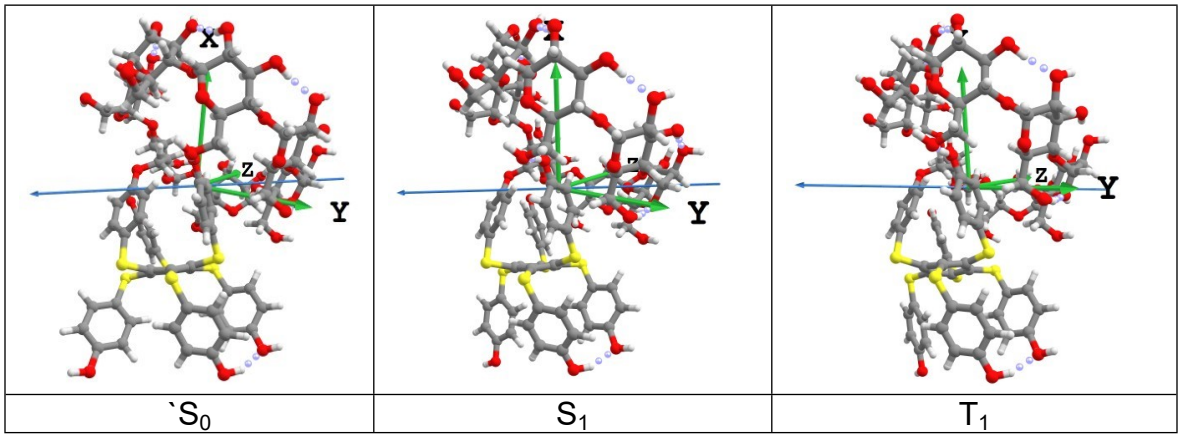


Fig S16. The orientation of the dipole moment (blue vector) corresponds to the principal axes' orientation.

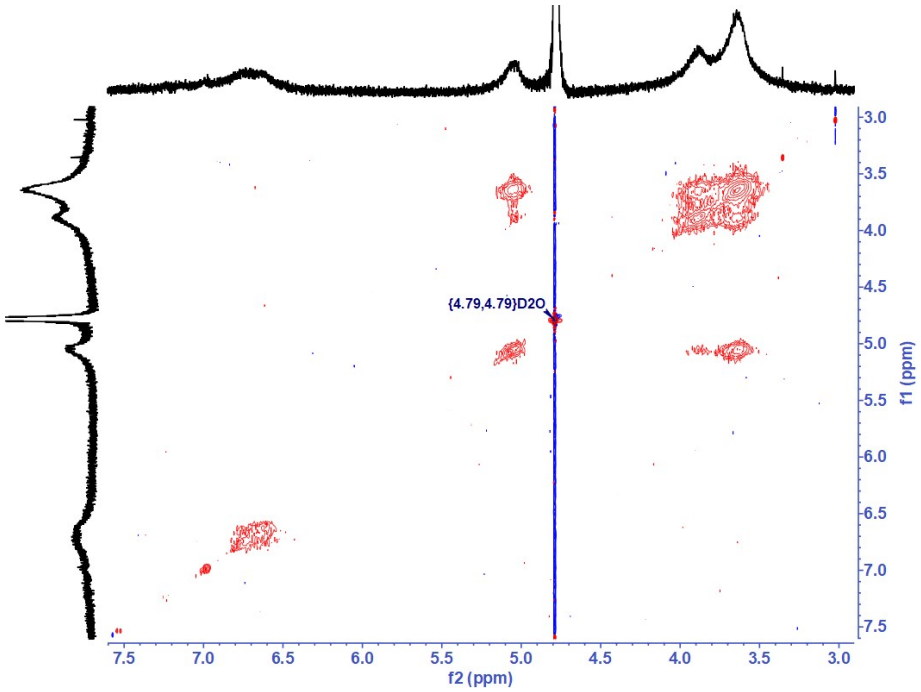


Fig S17. 2D NOESY spectra of HB-CyD in the solution of 10% deuterated DMSO and 90% deuterated H_2O after irradiation.

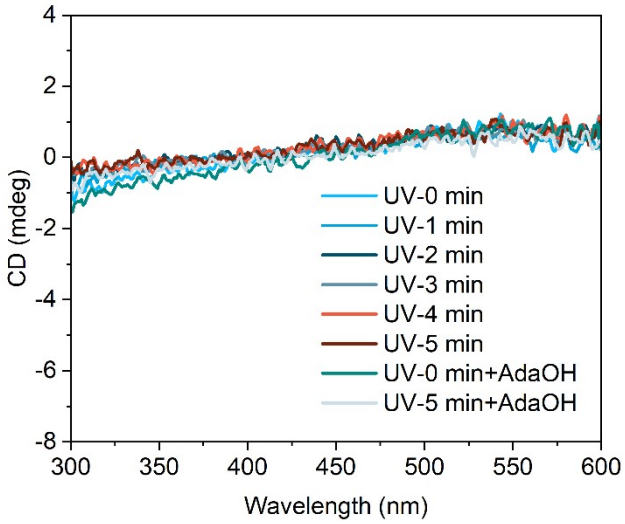


Fig S18. The circular dichroism spectra of the aqueous mixture of HB and β-CyD (concentration: 0.42 mg/mL and 0.58 mg/mL, respectively) in a sealed 1 mm quartz cell as UV irradiation time and with the addition of 1-adamantanol after irradiation.

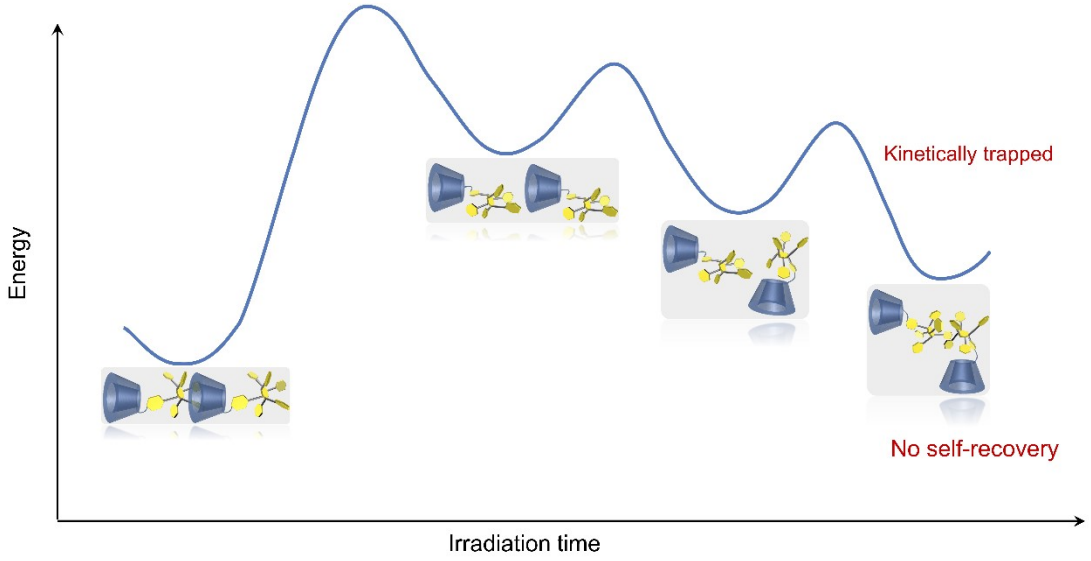


Fig S19. Proposed thermodynamic energy diagram showing the process by the excited-state conformation-driven self-assembly.

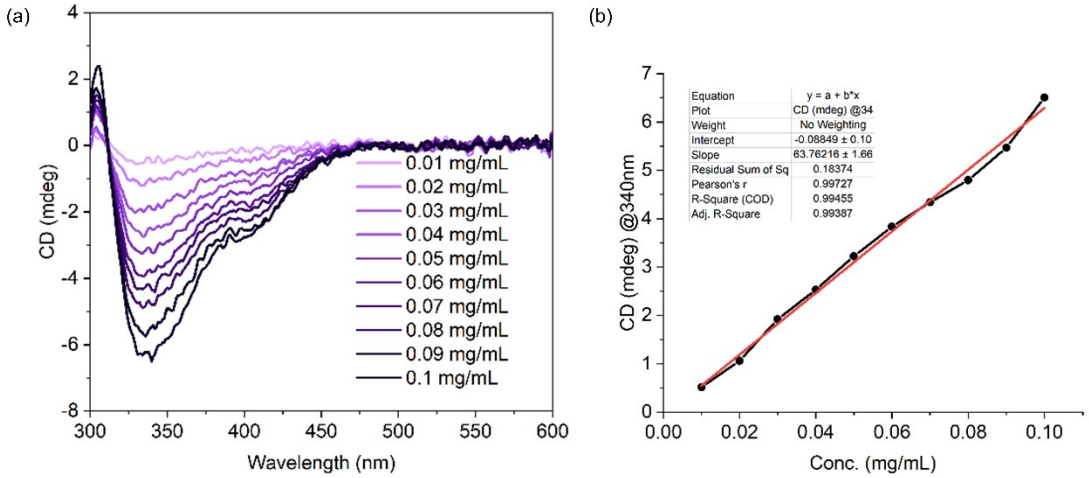


Fig S20. (a) The circular dichroism spectra of HB-CyD and (b) the changes of signal intensity at 340 nm with different concentrations of HB-CyD in a mixed solvent of 10% DMSO and 90% water in a sealed 10 mm quartz cell. The concentration range is between 0.01 mg/mL and 0.1 mg/mL.

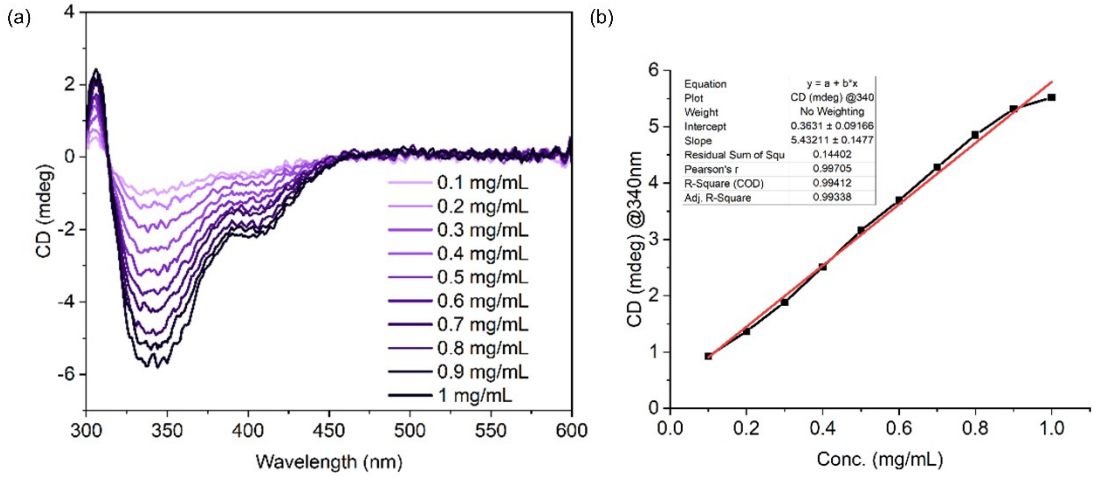


Fig S21. (a) The circular dichroism spectra of HB-CyD and (b) the changes of signal intensity at 340 nm with different concentrations of HB-CyD in a mixed solvent of 10% DMSO and 90% water in a sealed 1 mm quartz cell. The concentration range is between 0.1 mg/mL and 1 mg/mL.

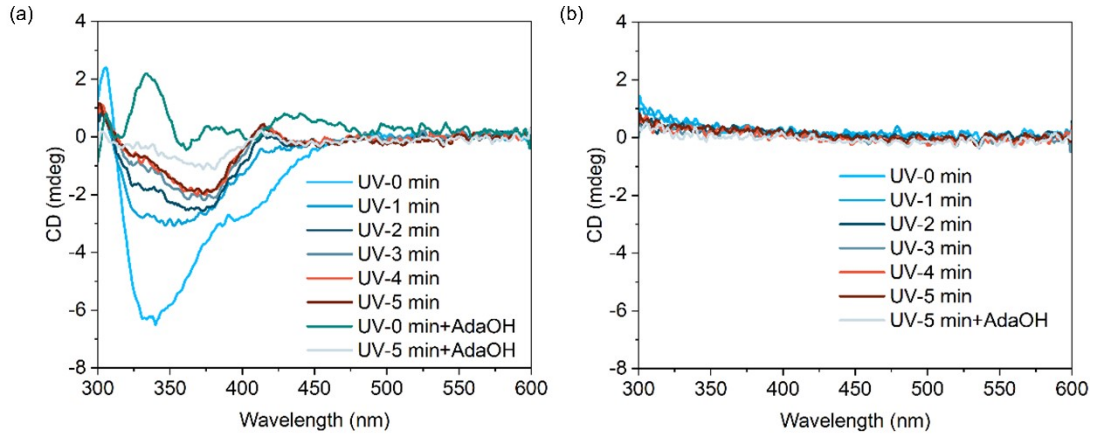


Fig S22. The circular dichroism spectra of (a) aqueous HB-CyD solution (concentration: 0.1mg/mL) and (b) the aqueous mixture of HB and β-CyD (concentration: 0.042 mg/mL and 0.058 mg/mL, respectively) in a sealed 10 mm quartz cell during UV irradiation with different periods and with the addition of 1-adamantanol after UV irradiation.

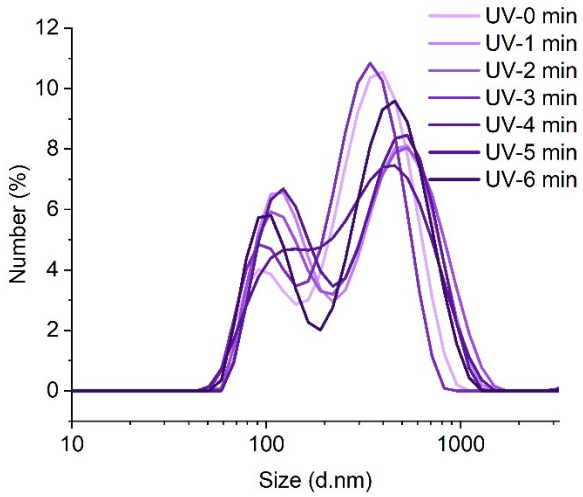


Fig S23. Dynamic Light Scattering Spectra of HB-CyD in a mixed solvent of 10% DMSO and 90% water upon irradiation with different periods. The concentration is 1 mg/mL.

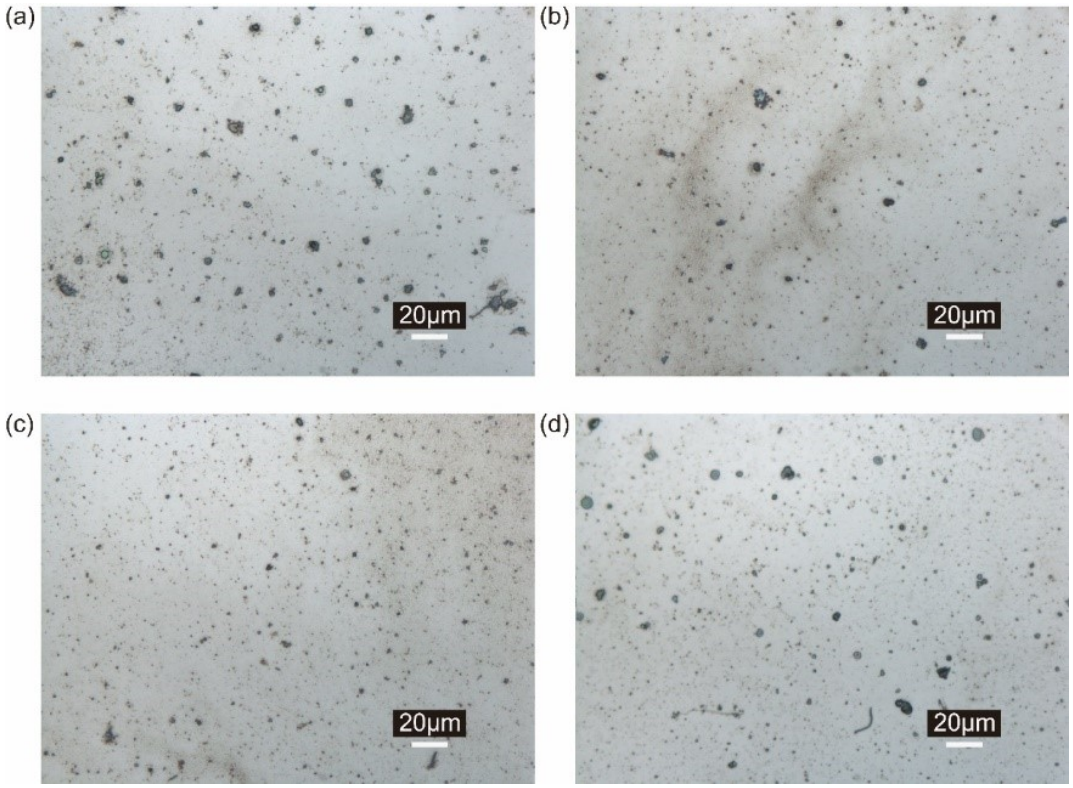


Fig S24. Morphology for aqueous HB-CyD solution with a lower concentration (0.1 mg/mL) under optical microscope observation (a) before and after irradiation for (b) 2 minutes, (c) 4 minutes, and (d) 6 minutes, respectively.

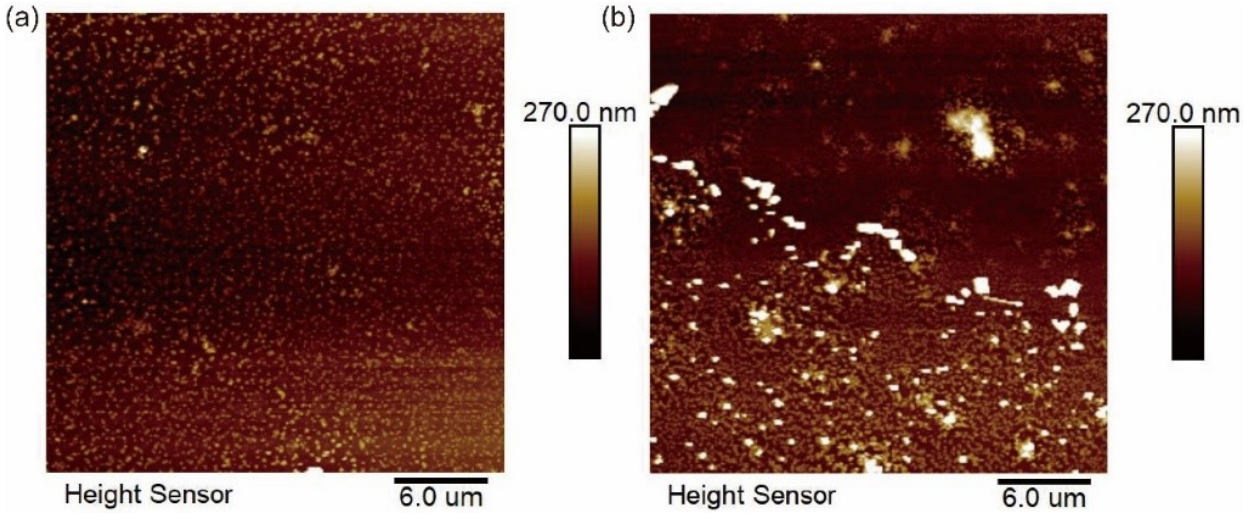


Fig S25. AFM images (height mode) of HB-CyD prepared from the aqueous solution (a) before and (b) after UV irradiation, respectively.

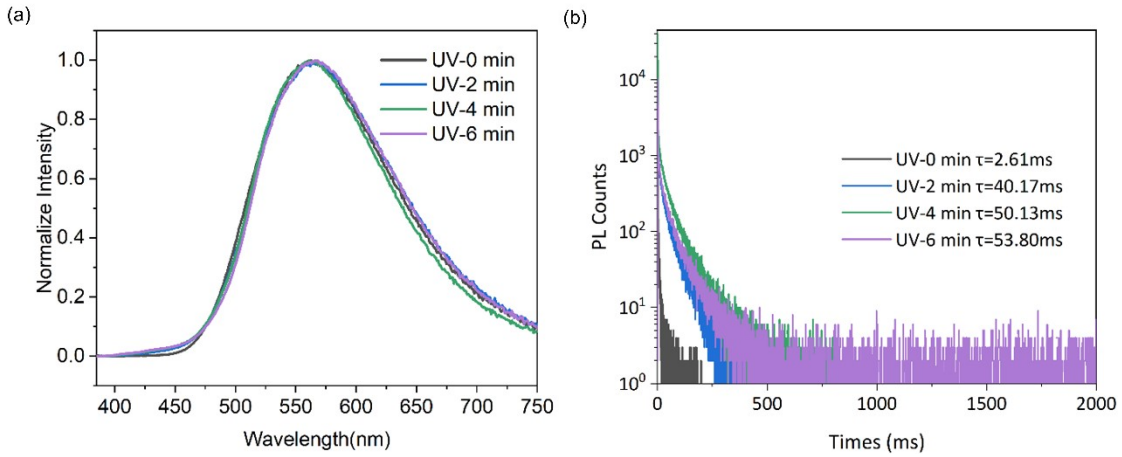


Fig S26. (a) Normalized emission spectra and (b) phosphorescence lifetime curves of the PVA film doped with HB-CyD before and after irradiation with different periods. The concentration of the original solution is 0.5 mg/ mL.

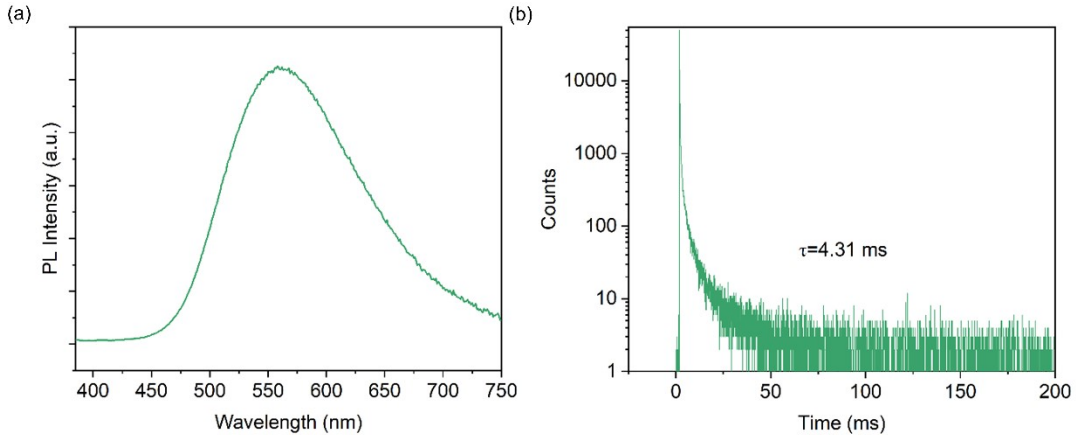


Fig S27. (a) The emission spectrum and (b) PL lifetime curve of the HB-CyD@PVA film after in situ UV irradiation.

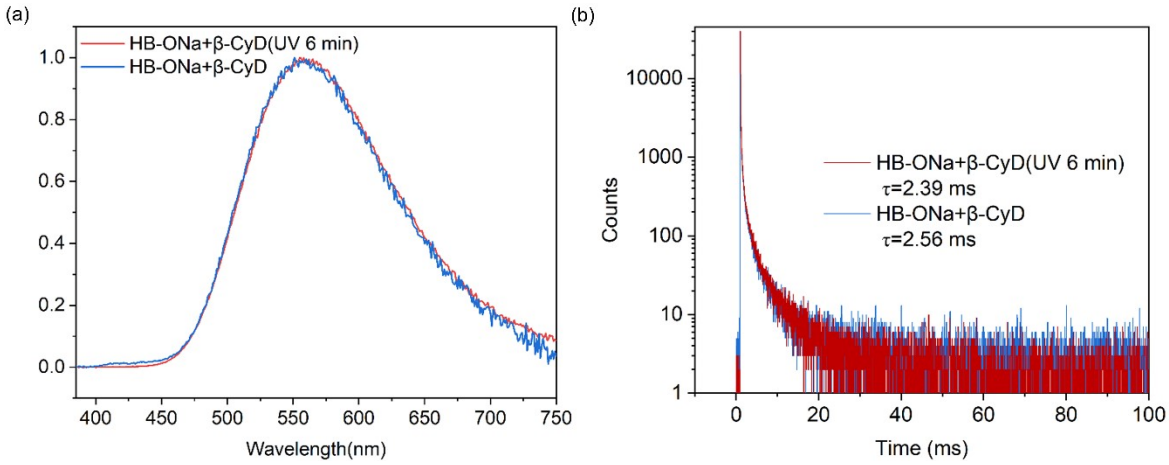


Fig S28. (a) Normalized emission spectra and (b) phosphorescence lifetime curves of the PVA film doped with the mixture of HB-ONa (concentration: 0.21 mg/mL) and β-CyD (concentration: 0.29 mg/mL) before and after irradiation, respectively.

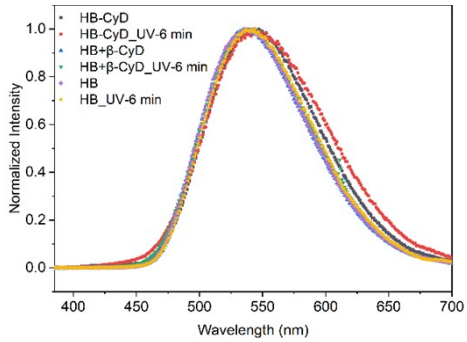


Fig S29. Normalized emission spectra of the PVA film doped with HB (concentration: 0.021 mg/mL), the mixture of HB (concentration: 0.21 mg/mL) and β-CyD (concentration: 0.29 mg/mL), the HB-CyD (concentration: 0.5 mg/mL) before and after irradiation, respectively.

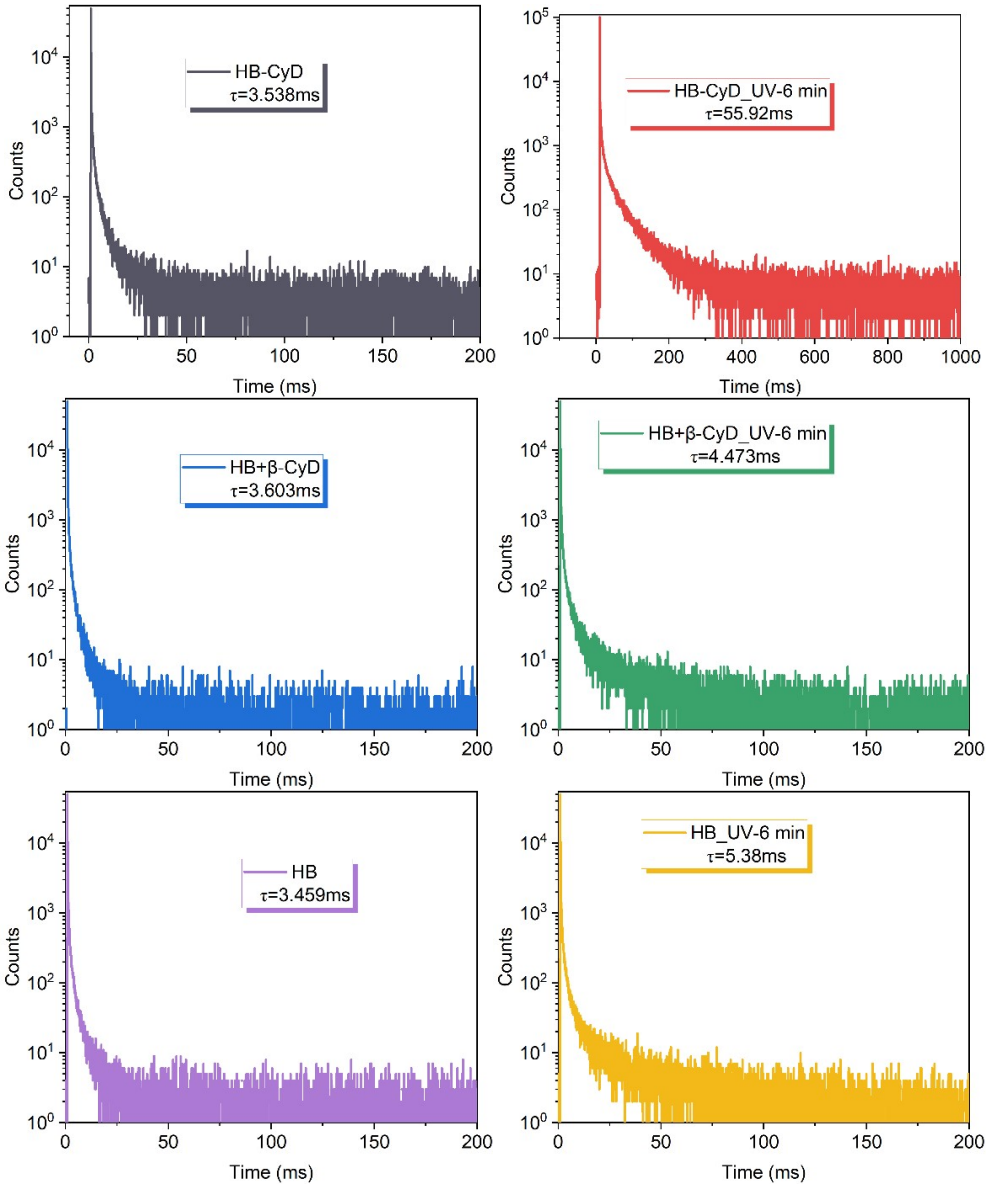


Fig S30. The phosphorescence lifetime curves of the PVA film doped with HB (concentration: 0.21 mg/mL), the mixture of HB (concentration: 0.21 mg/mL) and β-CyD (concentration: 0.29 mg/mL), the HB-CyD (concentration: 0.5 mg/mL) before and after irradiation, respectively.

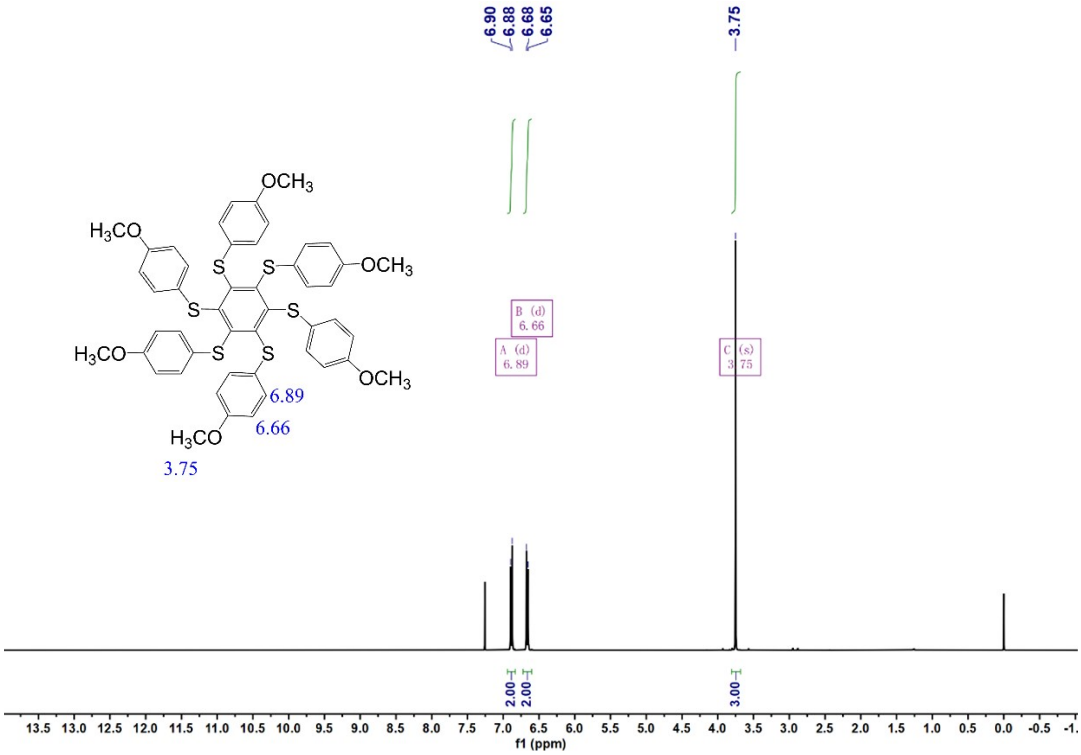


Fig S31. [1]H NMR spectrum of ***HB-OCH$_3$***.

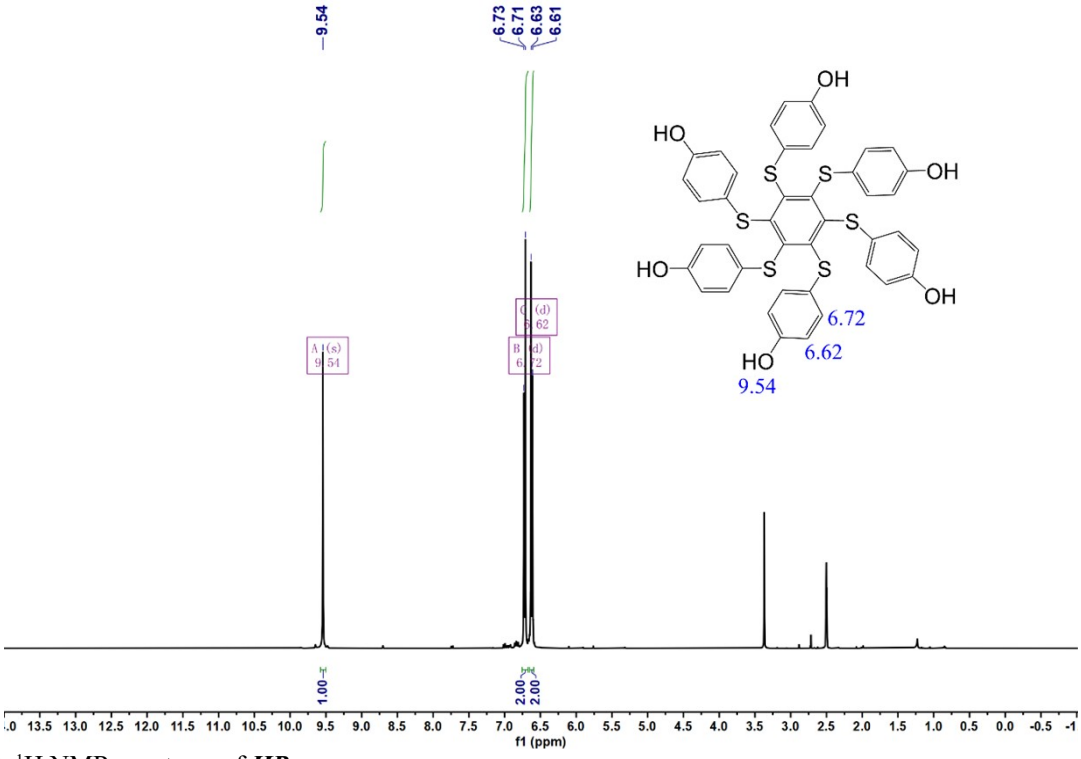


Fig S32. [1]H NMR spectrum of ***HB***.

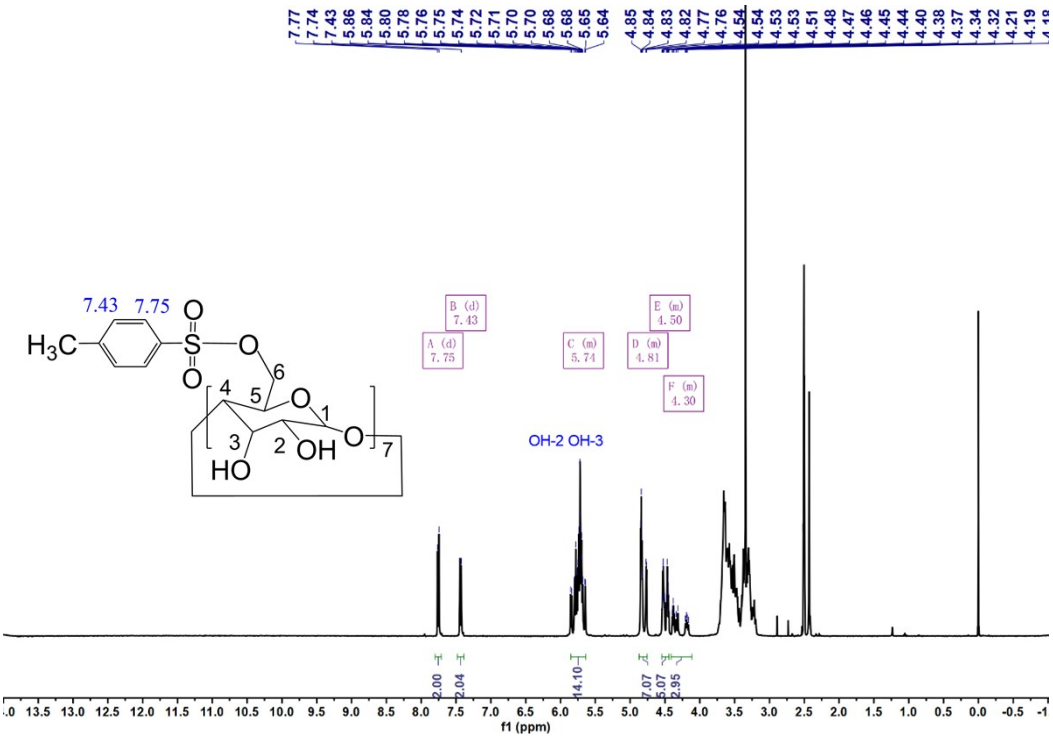


Fig S33. [1]H NMR spectrum of ***OTs-β-CD***.

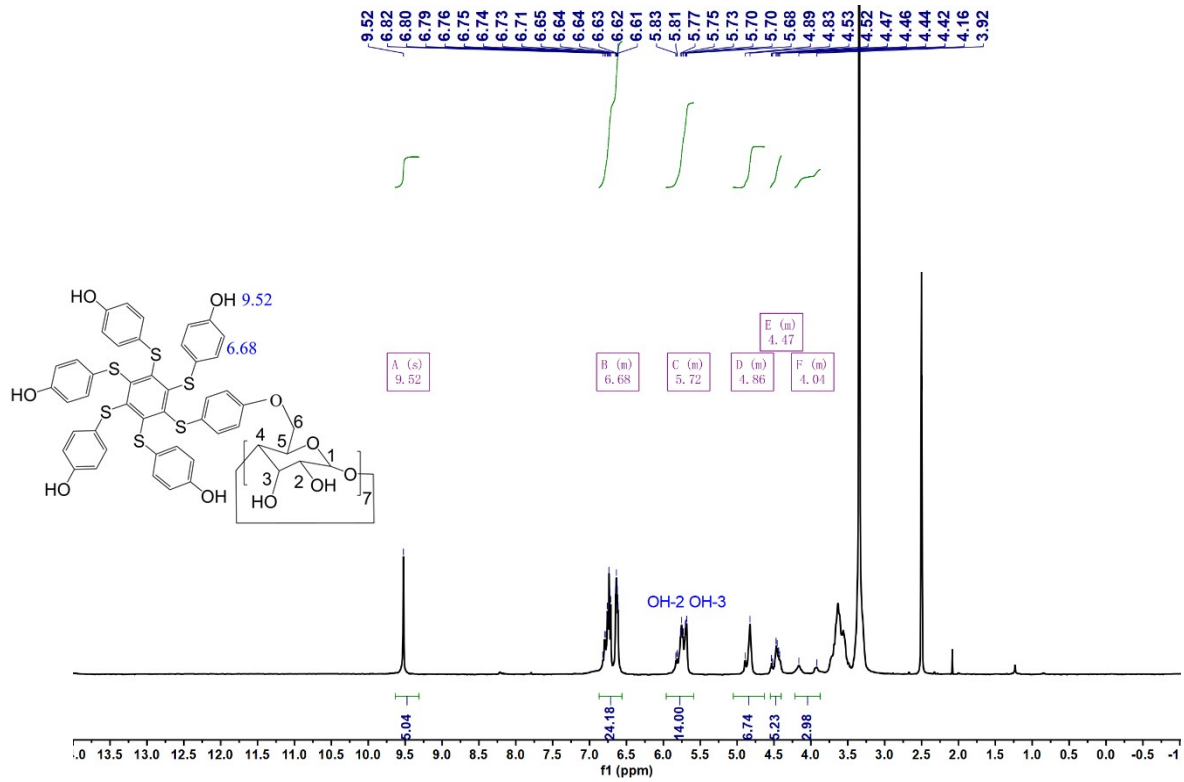


Fig S34. [1]H NMR spectrum of ***HB-CyD***.

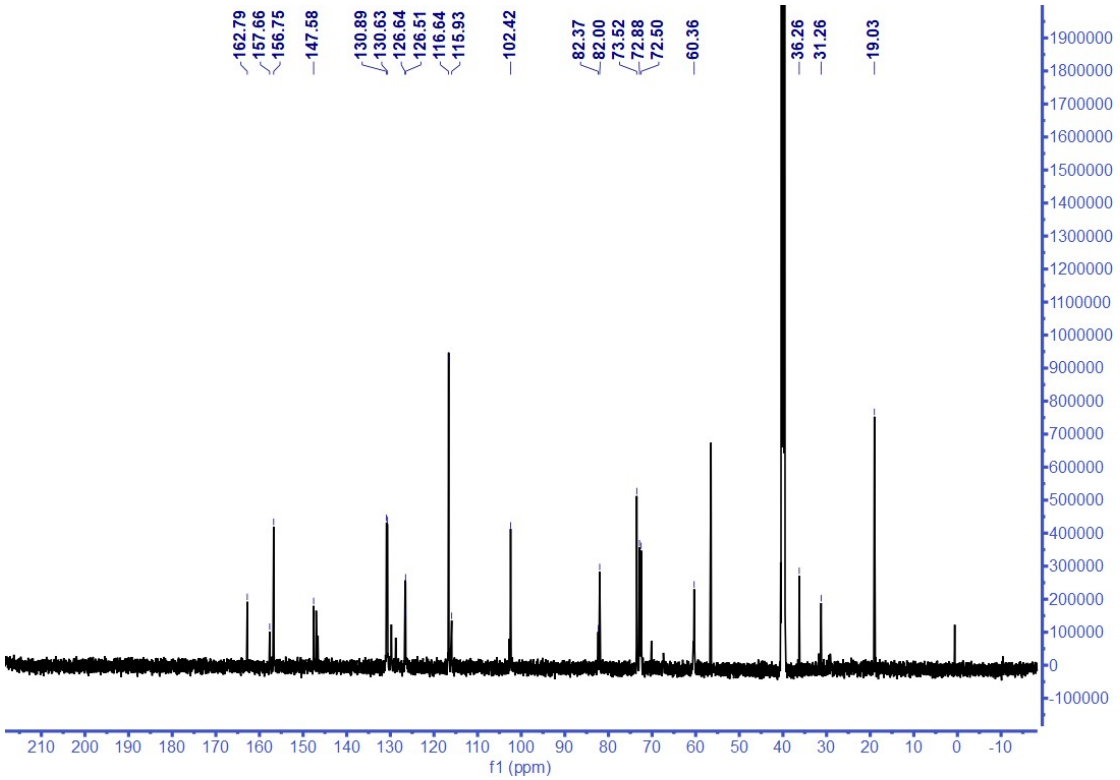


Fig S35. ^{13}C NMR spectrum of ***HB-CyD***.

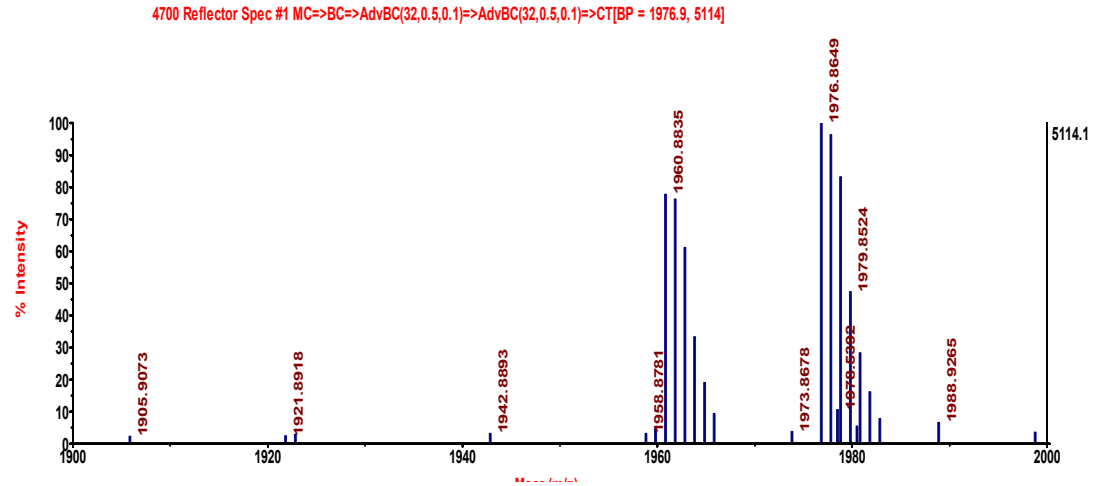


Fig S36. MALDI-TOF of ***HB-CyD***.

References and Notes

1. J. Xu, H. Feng, H. Teng, G. Chen, S. Pan, J. Chen and Z. Qian, Reversible Switching between Phosphorescence and Fluorescence in a Unimolecular System Controlled by External Stimuli, *Chemistry – A European Journal*, 2018, **24**, 12773-12778.
2. R. C. Petter, J. S. Salek, C. T. Sikorski, G. Kumaravel and F. T. Lin, Cooperative binding by aggregated mono-6-(alkylamino)-.beta.-cyclodextrins, *J. Am. Chem. Soc.*, 1990, **112**, 3860-3868.