Supplementary Information

Cyclodextrin-catalyzed self-assembly of a coordinating fluorescent molecule into microflowers

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Experimental Section

Materials

1-pyrenebutyricacid (1-PBA), Thioflavin (ThT), Rhodamine 6G (Rh6G) were purchased from Tokyo Chemical Industry Co. Ltd.. α, β, γ-CD was purchased from Aladdin. Fluorescein sodium (FS), Phloxine B (Pine B) were purchased from Macklin. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. with purity above 99.0% and 98%, respectively. Eosin B was purchased from Shanghai Titan Scientific Co. Ltd.. All these chemicals were used without further purification. Water used in all experiments was purified by Milli-Q Advantage A10 ultrapure water system.

Preparation of 1-PBA/Zn^{2+} microflowers

In a typical procedure of preparation, 1-pyrenebutyricacid was neutralized by NaOH solution to achieve 30mM sodium 1-Pyrenyl butyrate solution (1-PBA). The pH was about 8~9. 1mL of 30mM 1-PBA, 1mL 30mM γ-CD, and 1mL water were added into a vessel to achieve a mixed solution and placed at room temperature to achieve equilibrium. Then 0.75mL 20mM $Zn(NO_3)_2$ solution was added into the vessel using a pipette. After the addition, the solution turned into turbid and formed white precipitation immediately. For the preparation of irregular precipitates, 1mL 30mM γ-CD solution was replaced with equal volumes of water and other steps were just the same.

Adsorption of fluorescent dyes onto the microflowers

In the typical experiment, freshly-prepared microflowers were centrifugated and washed with water three times. Then 1mL water was added to the vessel to redisperse the microflowers. 2mL dye solutions with different concentrations was then added to the above vessel. Finally, the mixed suspension was vortexed and let stand at room temperature.

Structural Characterizations

The scanning electron microscopy (SEM) was performed on a Hitachi S4800 microscope at an acceleration voltage of 3.0kV. For SEM measurements, A drop of suspension was dropped on clean silicon sheets and dried in the air. FT-IR measurements were performed on Nicolet iN10 MX microscopic infrared spectrometer (Thermo Scientific Co., UAS) in the range of 4000 to 600cm^{-1} under ambient condition. The spectrometer was equipped with an attenuated total reflection (ATR) accessory with a Smart iTR (diamond). Powder X-ray diffraction data were collected on a Rigaku Dmax-2400 diffractometer with Cu K radiation. The freeze-dried samples were placed on clean glass slides. Specific surface measurements of the samples were conducted using ASAP 2020 Plus Version 1.03. The UV-Vis spectra were taken on a Shimadzu UV-1800 spectrophotometer. Fluorescence measurements were carried out using a Hitachi F-7000 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer at room temperature with D_2O as solvent. Elemental analysis was carried out on Vario MICRO CUBE elemental analyzer. Mass spectra were carried out on a Bruker Solarix XR operating in an ESI negative mode. For CLSM measurement, a drop of the suspension was sealed between two slides. A TCS-sp inverted confocal laser scanning microscope (Leica, Germany) was used to conduct experiments in florescence and differential interference contrast (DIC) modes. The wavelength of excitation laser used are 405nm and 543nm.

Supporting Figures

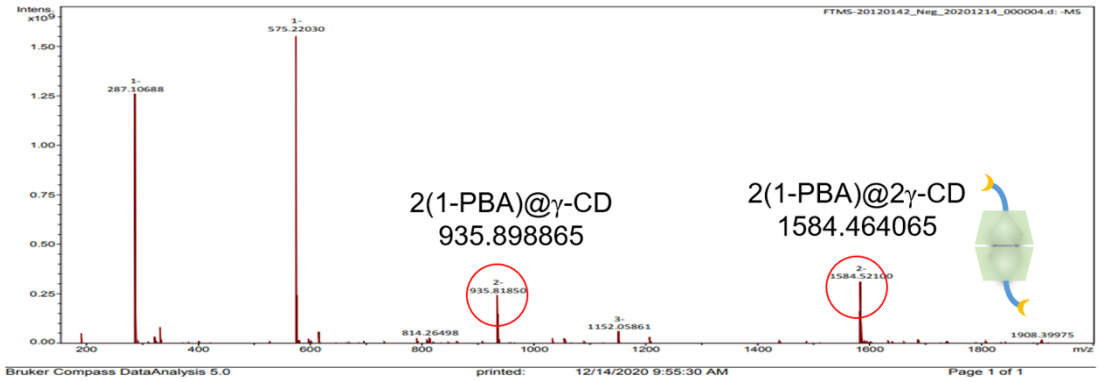


Fig. S1 High-resolution electrospray ionization mass spectrum of 1-PBA@γ-CD

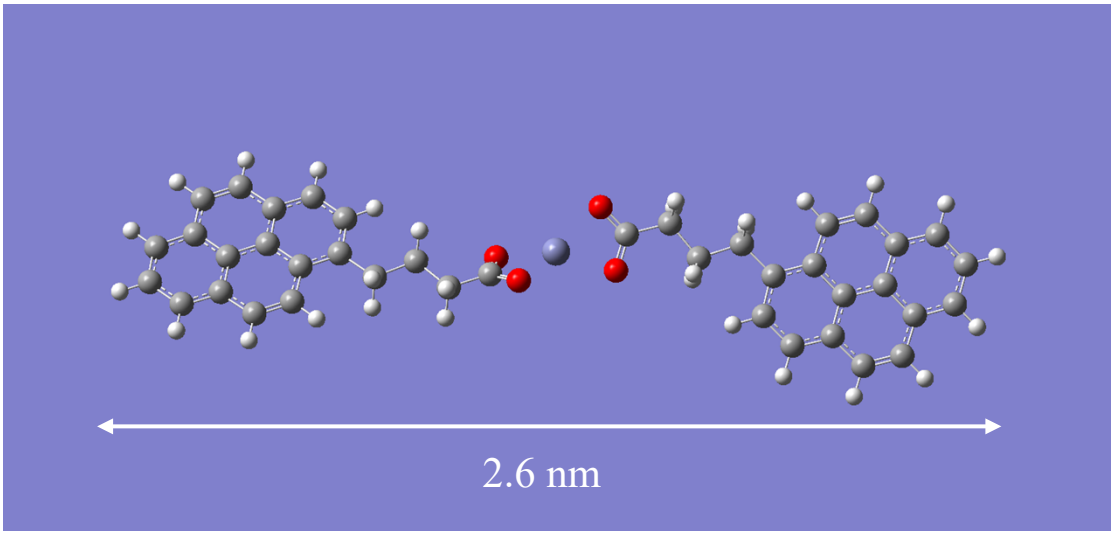


Fig. S2 Representation of a pair of 1-PBA molecules bridged by one Zn^{2+} ion

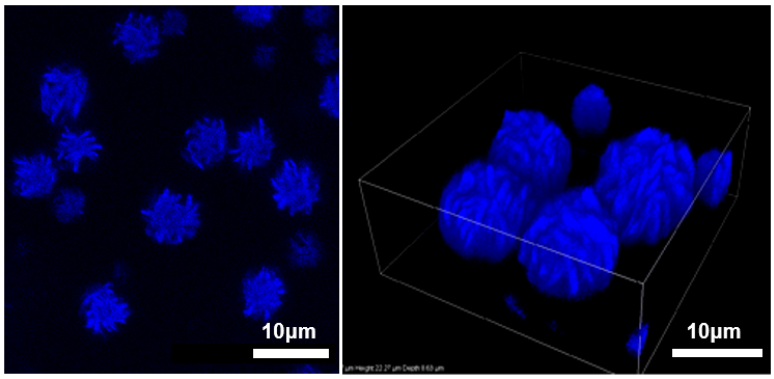
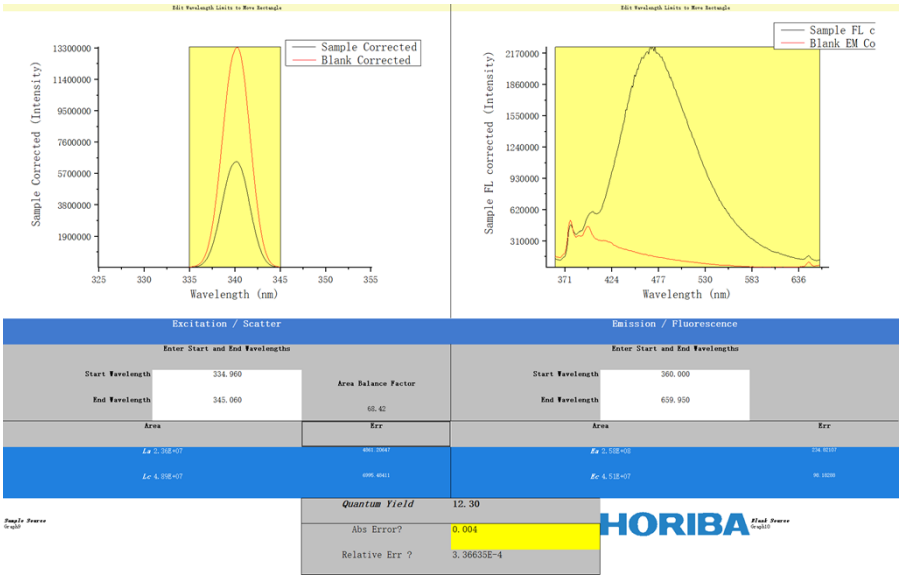


Fig. S3 2D and 3D CLSM images of the obtained microflowers, laser wavelength is 405 nm



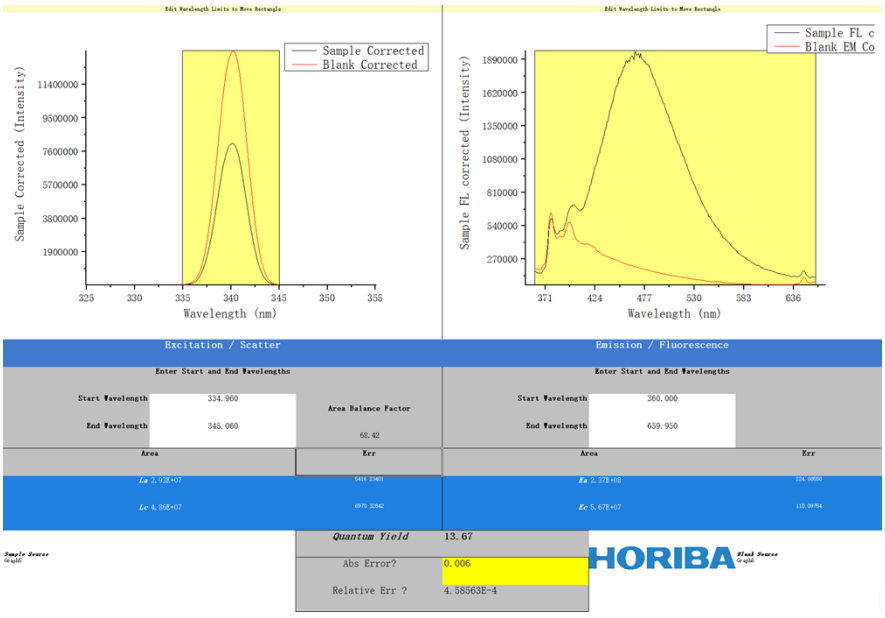


Fig. S4 Fluorescence quantum yield results of microflowers (up) and amorphous precipitates (down).

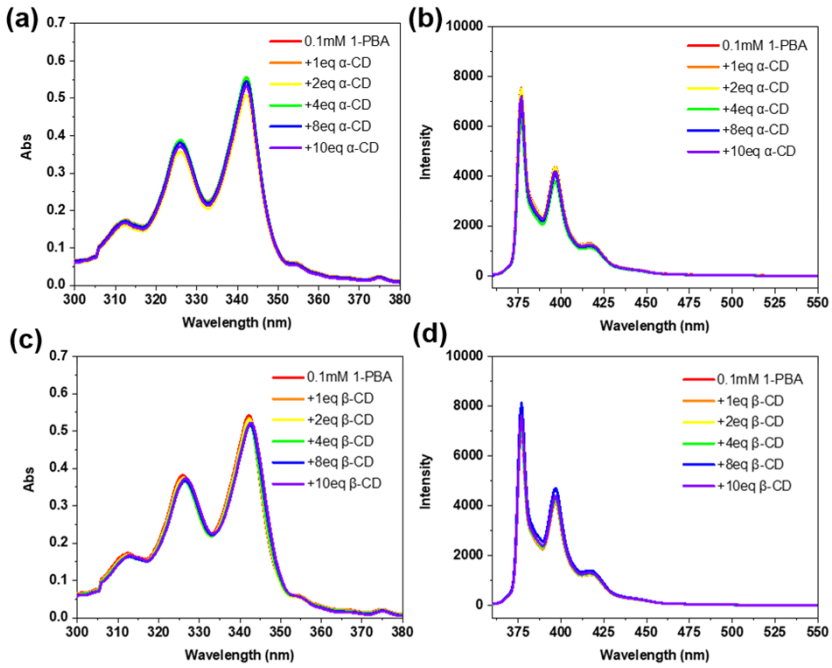


Fig. S5 UV-Vis spectra and fluorescence spectra (λ_{ex}=340 nm) of 1-PBA (0.1 mM) at different concentration of α-CD (a,b) and β-CD (c,d)

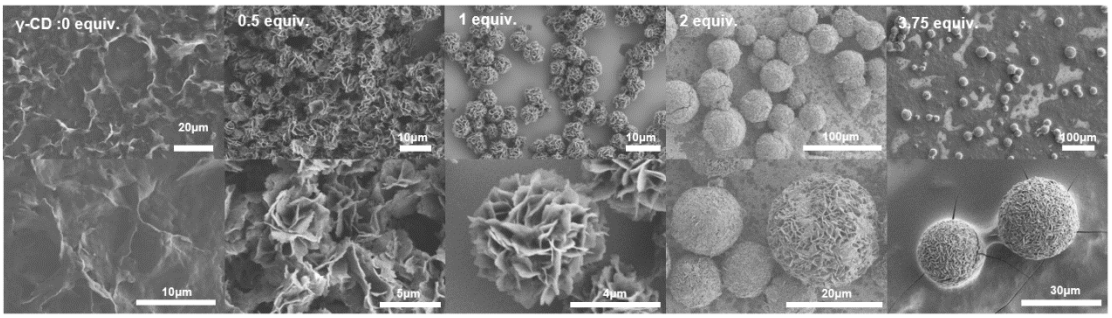


Fig. S6 SEM images of precipitates obtained under different γ-CD concentrations. [1-PBA] and [Zn^{2+}] are fixed at 8 mM and 4 mM, respectively.

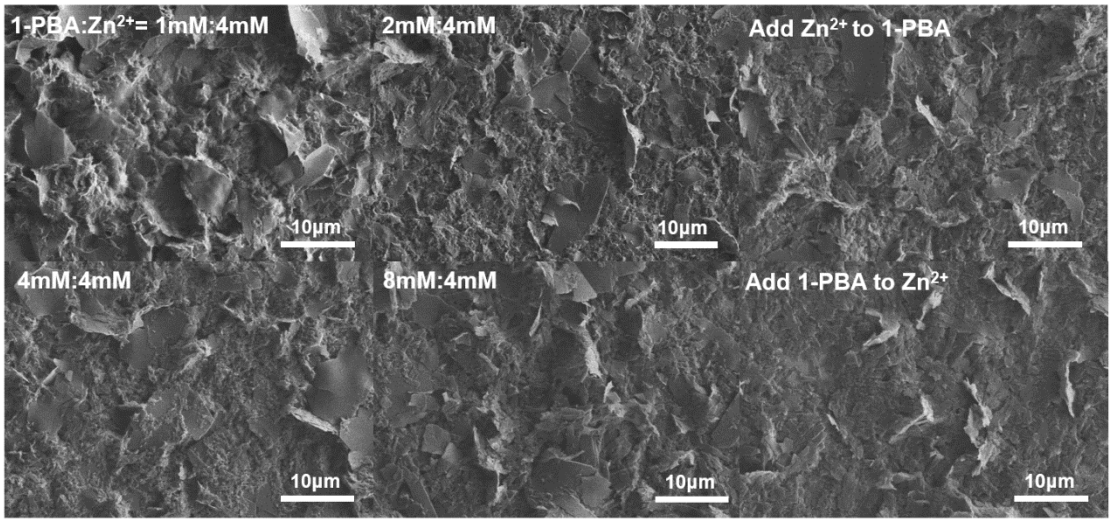


Fig. S7 SEM images of the precipitates obtained under different 1-PBA/Zn^{2+} ratio by adding equal amount of Zn^{2+} to 1-PBA solution with different concentrations, and of the precipitates obtained by changing adding sequence.

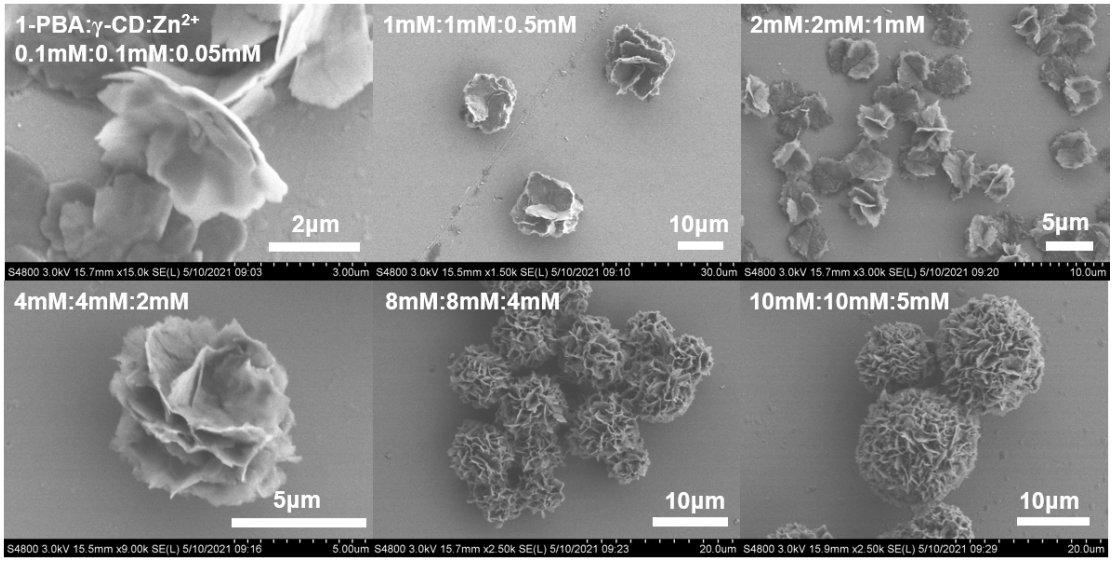


Fig. S8 SEM images of the precipitates obtained at different concentration.

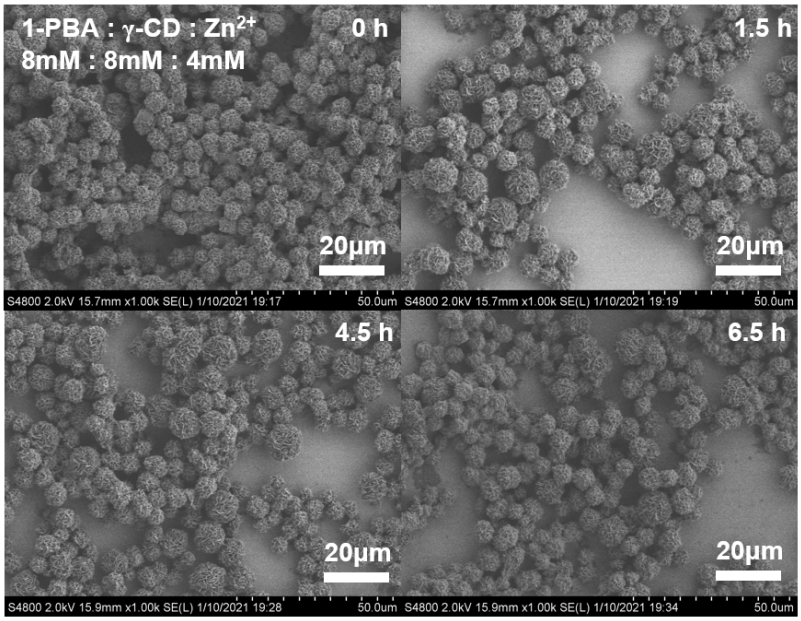


Fig. S9 SEM images of the microflowers with different aging time.

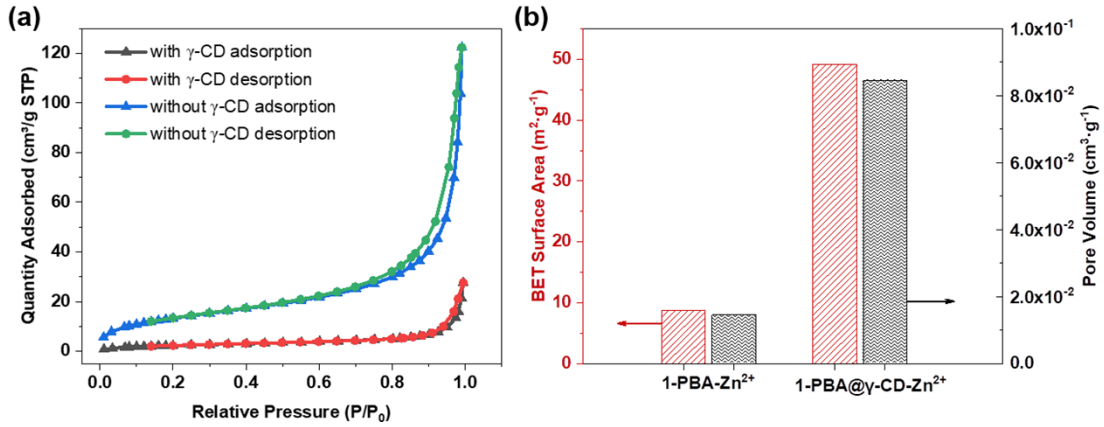


Fig. S10 N_2 adsorption-desorption isotherms (a), BET surface area and pore volume histograms (b) of the microflowers and irregular aggregates.

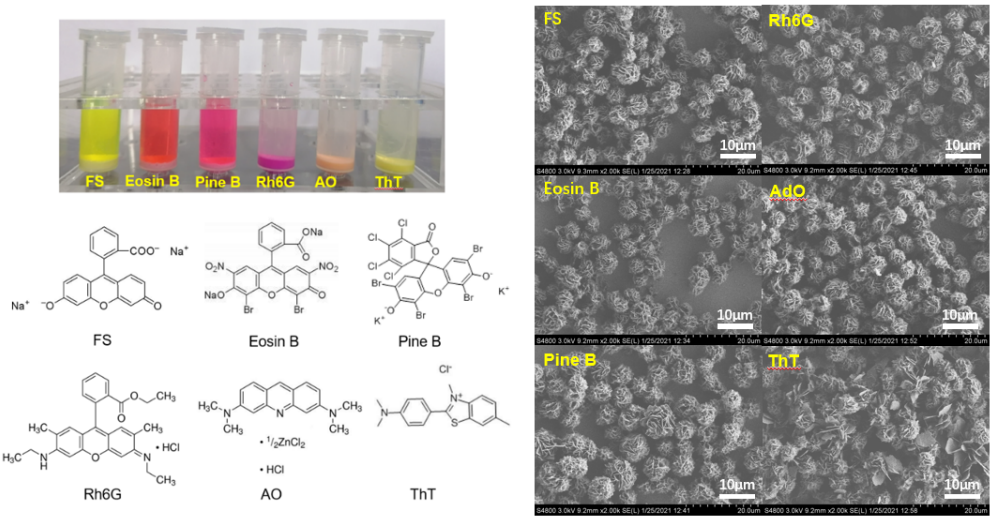


Fig. S11 Structures of dyes and photos of solution after adsorption (left), SEM images of samples after adsorption (right).