Supporting Information for

# Calixarene-Induced Aggregation of Perylene Bisimides

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**Synthesis**

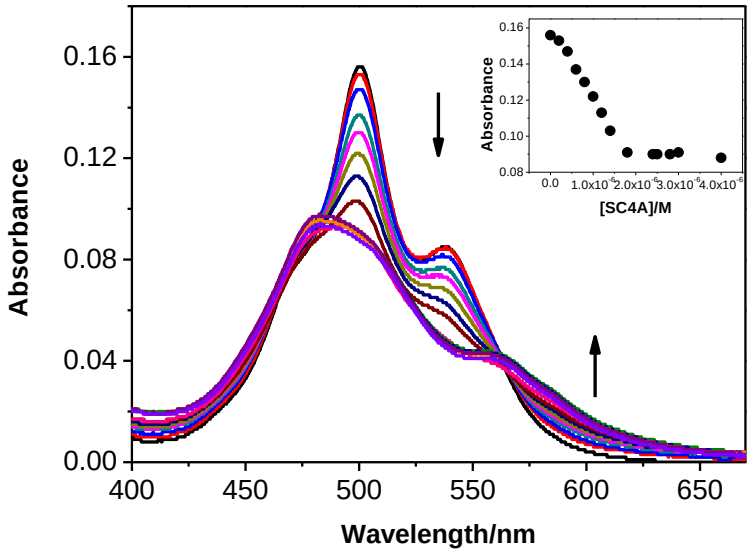
*p*-Sulfonatocalix[n]arenes (SCnAs, n = 4–8): SCnA was synthesized referring to the literature process.[1] Briefly, (*p*-tert-Butyl- or H-)calix[n]arenes were reacted in conc. $H_2SO_4$, followed by treating with inorganic salts.

*N*, *N*´-bis(propylenetrimethylammonium)-3,4,9,10-perylene bidimide (BPTA-PBI): Briefly, BPTA-PBI was prepared according to the literature method[2] through two reactive steps as follows: first, *N*, *N*´-bis(propylenedimethylamine)-3,4,9,10-perylene diimide was synthesized according to condensation reaction between 3-dimethylaminopropylamine and perylene tetracarboxylic bisanhydride. Finally, the condensation of *N*, *N*´-bis(propylenedimethylamine)-3,4,9,10-perylene diimide with methyl iodide in the toluene afforded the target compound BPTA-PBI.

**Measurements**

UV–Vis absorption spectra were recorded in a conventional quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C. All solutions were prepared in water.

a

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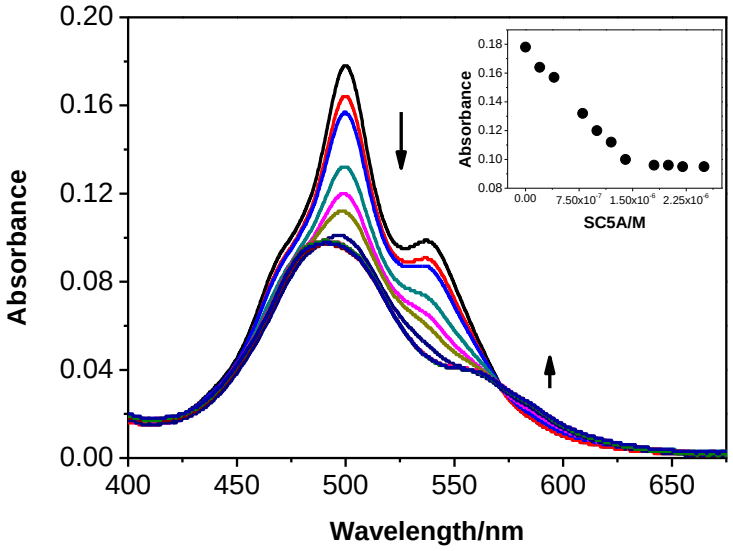


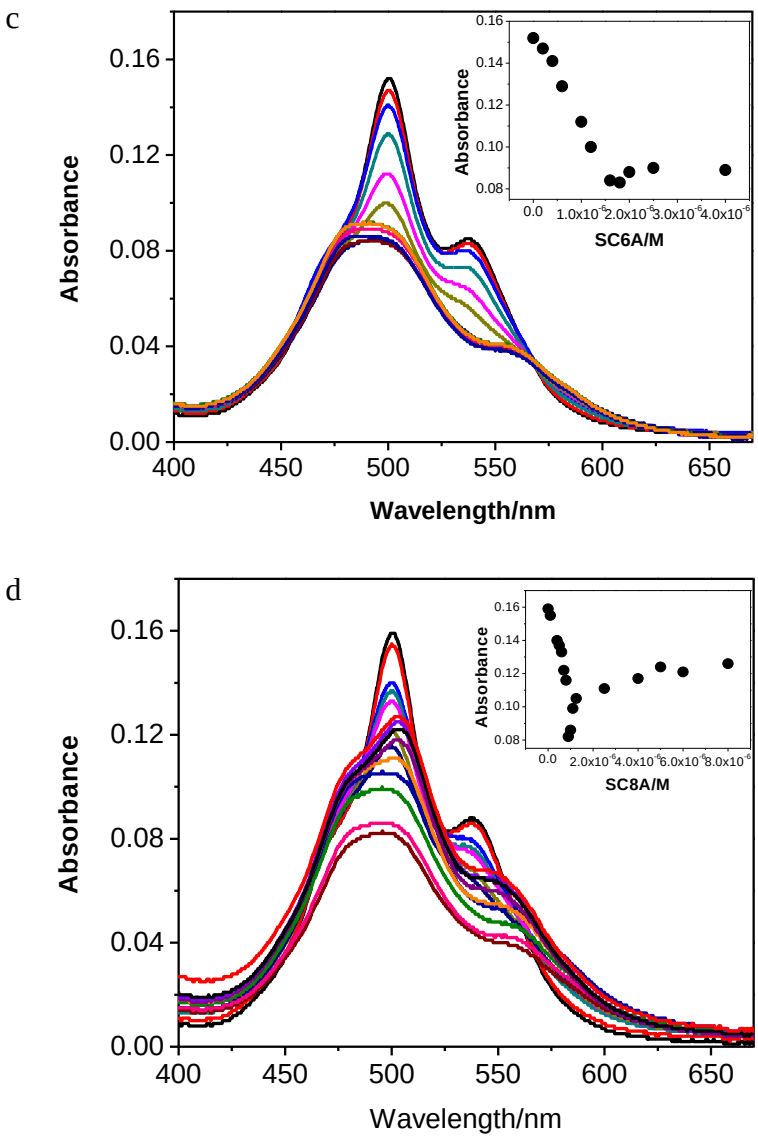
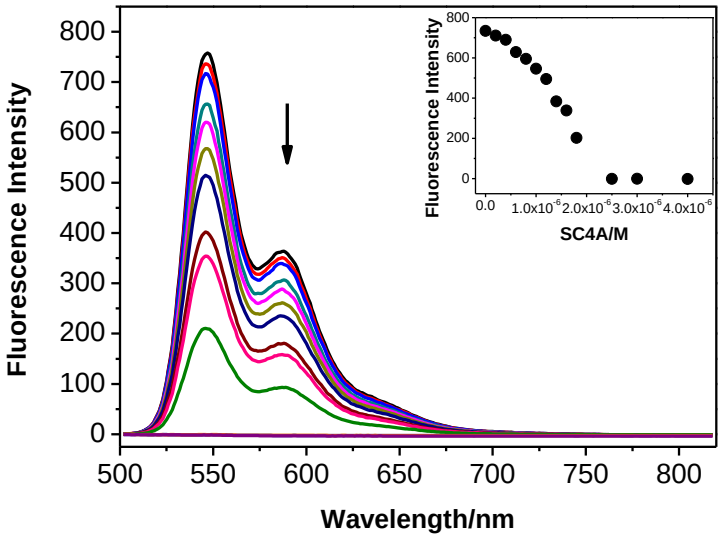



**Fig. S1** UV–Vis titration spectra of BPTA-PBI upon addition of SC*n*As in water: (a) BPTA-PBI ($5.0\times10^{-6}$ M), SC4A ($0–4.0\times10^{-6}$ M); (b) BPTA-PBI ($5.7\times10^{-6}$ M), SC5A ($0–2.5\times10^{-6}$ M); (c) BPTA-PBI ($5.0\times10^{-6}$ M), SC6A ($0–4.0\times10^{-6}$ M); (d) BPTA-PBI ($5.0\times10^{-6}$ M), SC8A ($0–8.0\times10^{-6}$ M).

Steady-state fluorescence spectra were recorded in a conventional quartz cell (10×10×45 mm) on a Varian Cary Eclipse equipped with a Varian Cary single cell peltier accessory to maintain the temperature at 25 °C. All solutions were prepared in water. The chromophores were excited at 490 nm.

a

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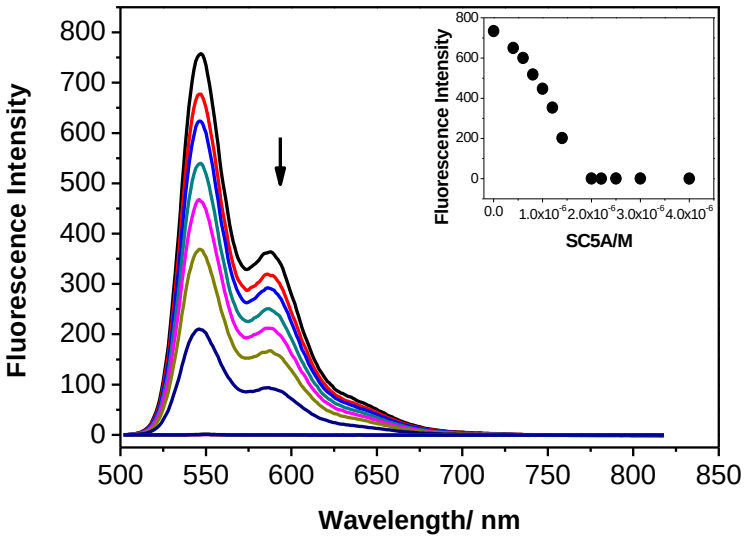


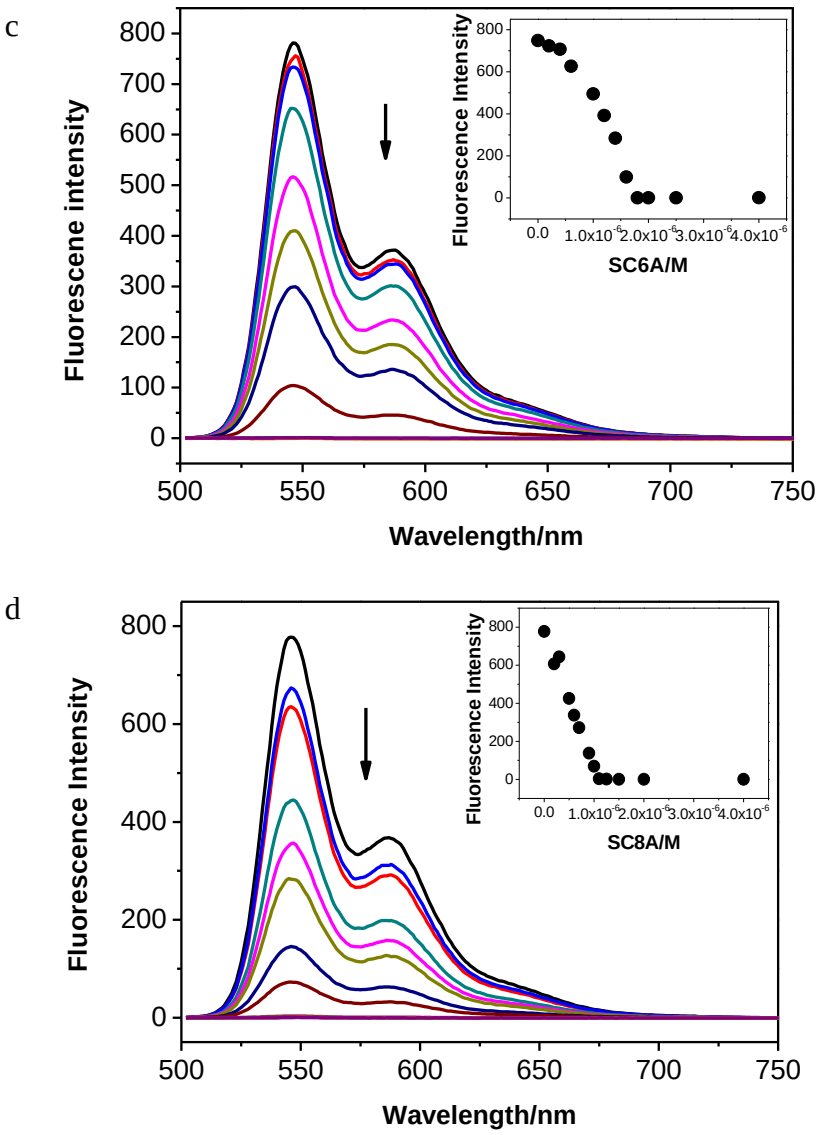


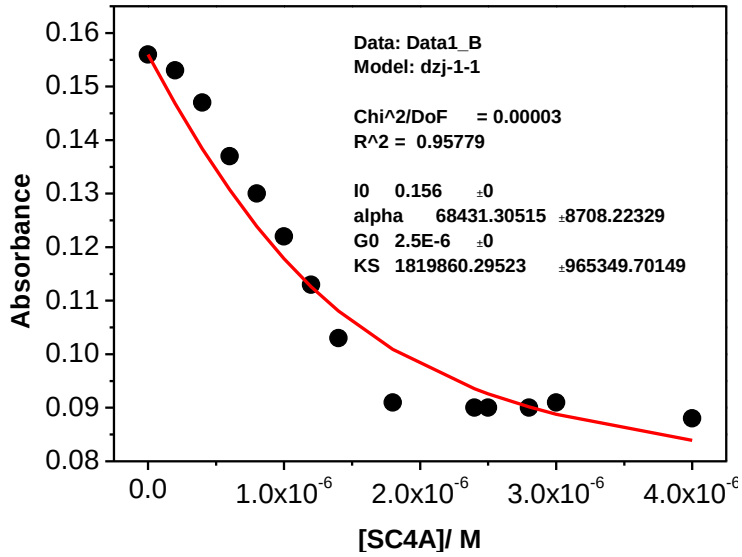

**Fig. S2** Fluorescent titration spectra of BPTA-PBI ($5.0\times10^{-6}$ M) upon addition of SC4A ($0–4.0\times10^{-6}$ M) (a), SC5A ($0–4.0\times10^{-6}$ M) (b), SC6A ($0–4.0\times10^{-6}$ M) (c), and SC8A ($0–4.0\times10^{-6}$ M) (d) in water, excited at 490 nm.

The obvious binding stability constant ($K_S$) was calculated, utilizing nonlinear least-squares analysis of the UV–Vis spectral titration data by the isodesmic or equal-K model (eq 1). To SC4A and SC5A, two as well as two and a half BPTA-PBI molecules are assumed as one binding unit for simplify, respectively.

$$\Delta A = \frac{\alpha([H]+[G]_0+1/K_S) \pm \sqrt{\alpha^2([H]+[G]_0+1/K_S)^2 - 4\alpha^2[H][G]_0}}{2} \qquad (1)$$

where $[G]_0$ is the initial concentration of BPTA-PBI ($2.5\times10^{-6}$ M for SC4A and $2.3\times10^{-6}$ M for SC5A) and is an invariable value, and [H] is the concentration of SCnA while $\Delta A$ is the change of absorbance of BPTA-PBI when [H] is increased compared with the absorbance in absence of SCnA, and $\alpha$ is a sensitive factor of absorbance, also a constant value.

a



b

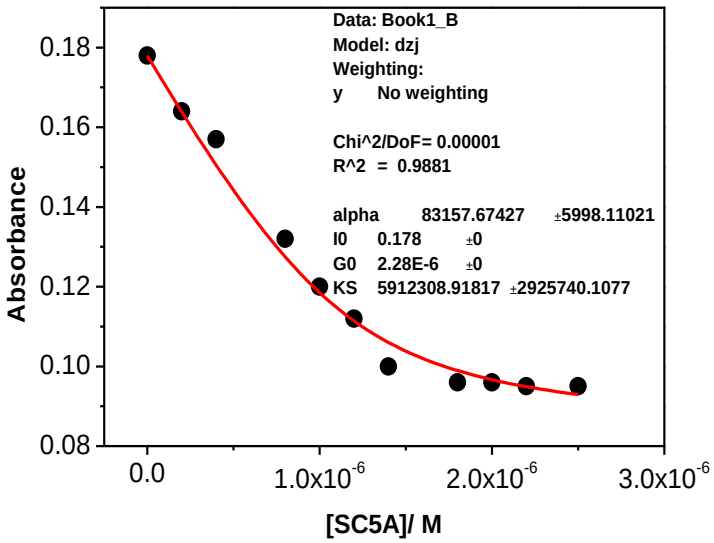



**Fig. S3** Plots of the absorbance of BPTA-PBI at 500 nm against the concentration of SC4A (a) and SC5A **(**b**)**, together with the fitted curve determined by using the nonlinear least-squares curve-fitting on the basis of eq 1, done in Origin 6.1 program.

The dynamic light scattering (DLS) was performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 636 nm at a scattering angle of 90° at 25 °C. Sample solutions were prepared by filtering solutions (BPTA-PBI, about 1 mL) through 0.45 μm filters into clean vials at the concentrations of $1.0\times10^{-5}$ M, and then equivalent volume of pure water, SC4A ($5.0\times10^{-6}$ M) or SC5A ($4.0\times10^{-6}$ M) was filtered into corresponding vials through 0.45 μm filters, respectively.

Transmission electron microscopy (TEM) experiments were performed using a Philips Tacnai G2 20 S-TWIN microscope operating at 200 kV. TEM samples (free BPTA-PBI ($5.0\times10^{-6}$ M) and the SC5A+BPTA-PBI complex ($2.0\times10^{-6}$ M for SC5A and $5.0\times10^{-6}$ M for BPTA-PBI) ) were prepared by placing a drop of the solution onto a carbon coated copper grid.

Atomic Force Microscope (AFM) measurements were performed using an AFM (Veeco Company, Multimode, Nano IIIa). AFM samples (the SC5A+BPTA-PBI complex ($4.0 \times 10^{-7}$ M for SC5A and $1.0 \times 10^{-6}$ M for BPTA-PBI) ) were prepared by dropping onto newly clipped mica and then air-dried.

Scanning Electron Microscopy (SEM) images were recorded on a HITACHI S-3500N SEM. SEM samples were solid-state crystal, which were prepared by evaporating aqueous solution of the SC5A+BPTA-PBI complex.

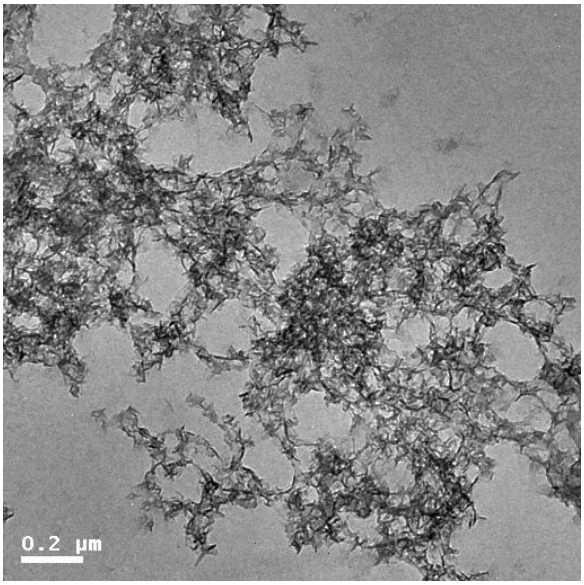



**Fig. S4** TEM image of free BPTA-PBI.

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku D/max 2500 diffractometer with Cu Kα radiation (40 kV,100 mA). Samples were prepared by addition of SC4A and SC5A into BPTA-PBI solutions, filtered to obtain precipitates, and dried.

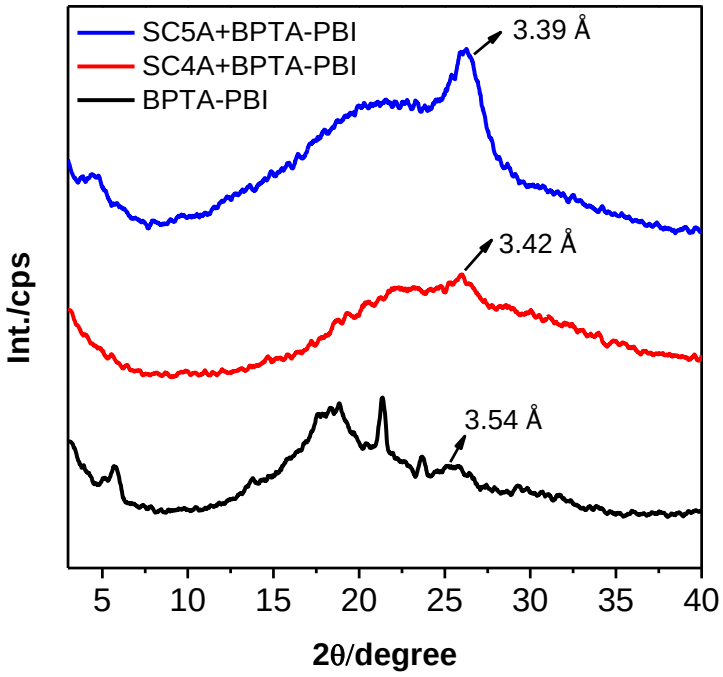



**Fig. S5** XRD patterns of BPTA-PBI in the absence (black curve) and the presence of SC4A (red curve) and SC5A (blue curve), respectively.

## References

(1) (a) S. Shinkai, S. Mori, T. Tsubaki, T. Sone and O. Manabe, *Tetrahedron Lett.* 1984, **25**, 5315–5318; (b) R. Lamartine, J.-B. Regnouf-de-Vains, P. Choquar and A. Marcillac, *World Patent* 1997, WO 97/49677; (c) S. Shinkai, K. Araki, T. Tsubaki, T. Arimura and O. Manabe, *J. Chem. Soc. Perkin Trans.* 1987, **1**, 2297–2299.

(2) T. Ma, C. Li and G. Shi, *Langmuir* 2008, **24**, 43–48.