# Supporting Information

# A Time-Resolved and Visualized Host–Guest Self-assembly Behavior Controlled through Kinetic Trapping

Ying Zhang,<sup>‡a</sup> Zhuoran Xu,<sup>‡a</sup> Tao Jiang\*<sup>a</sup>, Yanyan Fu\*<sup>b</sup> and Xiang Ma\*<sup>a</sup>

### \*Corresponding Author

<sup>a</sup> Key Laboratory for Advanced Materials, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237 (China).

<sup>b</sup> State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050 (China).

E-mail: 1048768259@qq.com (Tao Jiang);

fuyy@mail.sim.ac.cn (Yanyan Fu);

maxiang@ecust.edu.cn (Xiang Ma)

#### 1. Materials, general procedures and syntheses

**1.1 Materials.** Unless stated otherwise, all reagents were purchased from Sigma-Aldrich or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR and high-resolution ESI mass spectroscopy.

**1.2. General.** *p*-sulfonated calixarenes (SC4) was synthesized according to our previous work.<sup>1</sup> Other reagents used for the synthesis or measurements were commercially available without further purification. Water used in tests was ultrapure. <sup>1</sup>H NMR spectra were measured on a Brüker AV-400 spectrometer. The UV-vis absorption spectra and PL spectra were performed on a Varian Cary 500 spectrophotometer and a Horiba Fluoromax-4 at 25 °C, respectively. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 25°C. FESEM images were obtained by using a GeminiSEM 500 (droplets of the sample solution (5× 10<sup>-5</sup> M) were applied to a silicon slice and dried in air at room temperature, and then coated with nano Au in a vacuum). TEM images were record on a JEOL JEM-1400 apparatus. The samples (5 × 10<sup>-5</sup> M) were dropped on a perforated copper grid (400 mesh) covered with a carbon film (additional 1% wt PEG300 as stabilizer).

1.3 Synthesis and characterization of Py-TMA



**1-((6-bromohexyl)oxy)pyrene (Py-Br)** 1-Pyrenol 1.09 g (5 mmol) and cesium carbonate 3.25 g (10 mmol) were stirred at 82 °C under the protection of nitrogen. After 30 minutes, acetonitrile solution (10 mL) of 1,6-dibromohexane (2.43 g, 10 mmol) was injected and stirred for 24 hours, purified by column chromatography on silica (PE:DCM = 2:1) to obtain white solid 1.12 g. Yield: 67.9 %. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.46 (d, *J* = 9.2 Hz, 1H), 8.13 – 8.06 (m, 3H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.98 – 1.91 (m, 2H), 1.72-1.64 (m, 2H), 1.64-1.58 (m, 2H).

**N,N,N-trimethyl-6-(pyren-1-yloxy)hexan-1-aminium bromide (Py-TMA)** 1-((6 bromohexyl)oxy)pyrene 330 mg (0.86 mmol) in 25 ml acetonitrile, stirred under the protection of nitrogen at 82 °C for 0.5 h, added excess trimethylamine (8.4 mmol), refluxed for 24 h, concentrated, precipitated in ethyl acetate (100 mL) to obtain white solid 264 mg. Yield: 69.8 %. <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$  8.38 (d, J = 9.2 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.20 (t, J = 6.4 Hz, 2H), 8.14 (d, J = 9.2 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.03 (t, J = 7.6 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 4.39 (t, J = 6.4 Hz, 2H), 3.33 – 3.30 (m, 2H), 3.05 (s, 9H), 2.02 – 1.96 (m, 2H), 1.81-1.73 (m, 2H), 1.70-1.63 (m, 2H), 1.48-1.40 (m, 2H); HRMS (ESI<sup>+</sup>) calcd for C<sub>25</sub>H<sub>30</sub>ON<sup>+</sup> *m/z* 360.2322; found *m/z* 360.2326.



Fig. S1 <sup>1</sup>H NMR spectrum (400 MHz) of Py-Br in CDCl<sub>3</sub>.



Fig. S2 <sup>1</sup>H NMR spectrum (600 MHz) of Py-TMA in DMSO-d<sub>6</sub>.



Fig. S3 <sup>13</sup>C NMR (125 MHz) spectrum of Py-TMA in DMSO-d<sub>6</sub>.



Fig. S4 HRMS (ESI) spectrum of Py-TMA.



Fig. S5  $^1\mathrm{H}$  NMR spectrum (400 MHz) of SC4 in D2O.

2. Research on particle enlargement and fluorescence-off phenomenon of Py-TMA/SC4 system



Fig. S6 Fluorescence excitation ( $\lambda_{em} = 410 \text{ nm}$ ) and emission spectra ( $\lambda_{ex} = 320 \text{ nm}$ ) of Py-TMA powder.



Fig. S7 a) UV-vis absorption and b) Optical transmittance spectra of Py-TMA at different concentrations in aqueous solution.



**Fig. S8** a) Optical transmittance spectra of Py-TMA (0.05 mM) with the addition of SC4 and b) Dependence of the optical transmittance at 390 nm of Py-TMA (0.05 mM) with SC4 at different concentrations in water.



**Fig. S9** a) UV–vis absorption spectra and b) Optical transmittance spectra of Py-TMA/SC4 with the addition of Py-TMA ([SC4] = 0.025 mM). c) Dependence of the optical transmittance at 390 nm on the Py-TMA concentration in the presence of SC4 (0.025 mM).



**Fig. S10** a) UV-vis spectra of the aqueous solution containing Py-TMA and SC4 [Py-TMA] + [SC4] =  $5*10^{-5}$  M. b) Job's plot showing 2:1 stoichiometry of the complex.



Fig. S11 Normalized emission spectrum of Py-TMA/SC4 with a) 0.5 equiv. and b) 2 equiv. SC4 after different intervals ([Py-TMA] = 0.05 mM).

**Table S1.** Detention time from cyan to blue of Py-TMA/SC4 with different proportions ([Py-TMA] = 0.05 mM).

Equivalent (SC4)	0.25	0.5	1	2
Detension	32 h	72 h	13 h	1 h

**Table S2.** Detention time from cyan to blue of Py-TMA/SC4 with different concentrations (0.5 equiv. SC4).

Concentration	1 µM	50 µM	75 µM	100 µM
(Py-TMA)				
Detension	0.5 h	72 h	50 h	53 h



**Fig. S12** The FESEM images and corresponding DLS of Py-TMA/SC4 at (a, b) 0 h, (c, d) 12 h and (e, f) 72 h.



**Fig. S13** The TEM images of Py-TMA/SC4 in 0 h at 298 K ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM).



**Fig. S14** The TEM images of Py-TMA/SC4 in 72 h at 298 K ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM).



Fig. S15 a) UV–vis absorption spectra and b) Changes in the absorbance ratio for 380 nm to 340 nm ( $A_{340 \text{ nm}}/A_{380 \text{ nm}}$ ) of Py-TMA/SC4 with time ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM).



Fig. S16 Fluorescence spectra of Py-TMA/SC4 at 495 nm after four consecutive hours of different temperature ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM) ( $\lambda_{ex}$  = 320 nm).



Fig. S17 Fluorescence spectra of Py-TMA/SC4 after resting for 72 hours and heating at 80°C for different time ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM) ( $\lambda_{ex}$  = 320 nm).

#### 3. Construction of light-harvest system of Py-TMA/SC4@SC4



Fig. S18 a) Normalized intensity of absorption spectra (EB) (2.5  $\mu$ M) and fluorescence spectra (Py-TMA/SC4). b) Fluorescence spectra of Py-TMA/SC4 and Py-TMA/SC4@EB ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM, [SC4] = 0.5  $\mu$ M) ( $\lambda_{ex}$  = 320 nm).

$$\Phi_{ET} = 1 - \frac{I_{DA}}{I_D} = 1 - \frac{8.28}{571.70} = 98.55 \%$$

 $\Phi_{ET}$ : Energy-transfer efficiency

 $I_{DA}$ ,  $I_D$ : Fluorescence intensities of the donor in the presence and absence of the acceptor at 495 nm ( $\lambda_{ex} = 320 \text{ nm}$ )



Fig. S19 The fluorescence decay trace of Py-TMA/SC4 and Py-TMA/SC4@EB ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM, [SC4] = 0.5  $\mu$ M) ( $\lambda_{ex}$  = 320 nm).



Fig. S20 Fluorescence spectra of Py-TMA/SC4@EB with time ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM, [EB] =0.5  $\mu$ M) ( $\lambda_{ex}$  = 320 nm).



Fig. S21 Fluorescence excitation ( $\lambda_{em} = 615 \text{ nm}$ ) and emission spectra ( $\lambda_{ex} = 440 \text{ nm}$ ) of EB in water ([EB] = 2.5  $\mu$ M).



Fig. S22 Fluorescence spectra of Py-TMA and Py-TMA@EB in water ([Py-TMA] = 0.05 mM, [EB] = 2.5  $\mu$ M) ( $\lambda_{ex}$  = 320 nm).



Fig. S23 Fluorescence spectra of Py-TMA/SC4, Py-TMA/SC4@EB, SC4@EB and EB in water excited by 320 nm ([Py-TMA] = 0.05 mM, [SC4] = 0.025 mM, [EB] =  $2.5 \mu$ M).

## 4. Reference

1. G. Qu, T. Jiang, T. Liu and X. Ma, ACS Appl. Mater. Interfaces, 2022, 14, 2023-2028.