

Electronic Supplementary Information

Triptycene-based tetralactam macrocycles: synthesis, structure and complexation with squaraine

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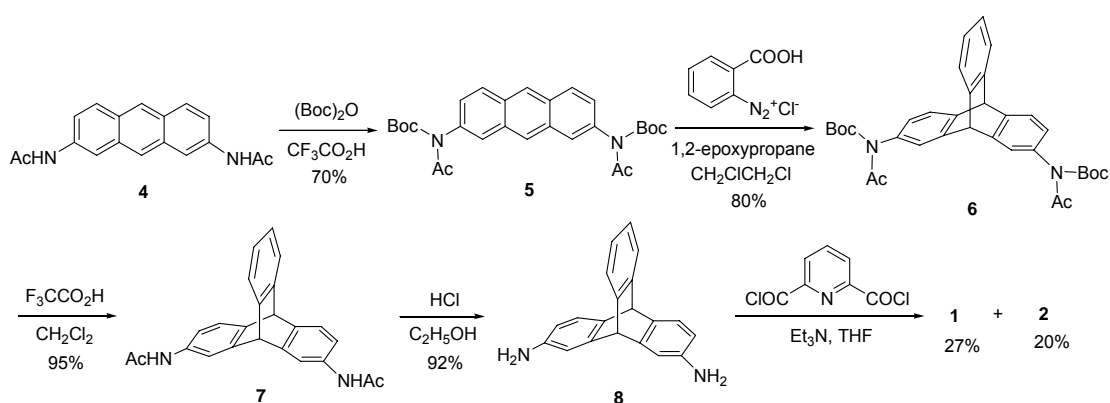
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1. Synthesis and characterization data of new compounds

General methods. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^1H NMR, ^{13}C NMR and ^1H - ^1H COSY spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. Materials obtained commercially were used without further purification. Squaraine **3** was prepared according to literature procedure.¹ The association constants for the complexes **1**·**3** and **2**·**3** were determined according to literature method.²



Scheme S1. Synthesis of hosts **1** and **2**.

2,7-Di-(*N*-*t*-butoxycarbonylacetamido)anthracene (5**).** To a suspension of **4**³ (5.84 g, 20 mmol, 1.00 equiv) in dry acetonitrile (300 mL) under argon was added 4-(*N,N*-dimethylamino)pyridine (1.83 g, 15 mmol, 0.750 equiv) and di-*t*-butyl dicarbonate (13.1 g, 60 mmol, 3.00 equiv). The reaction mixture was stirred at room temperature overnight. The reaction mixture was evaporated and the residue was dissolved in CH_2Cl_2 . The solution was washed with 1 M aqueous KHSO_4 , dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was stirred in CH_3OH for 3 h, and then filtered to give the pure product (6.88 g, 70%). Mp: > 300 °C. ^1H NMR (300 MHz, CDCl_3): δ 1.37 (s, 18H), 2.64 (s, 6H), 7.18 (dd, $J = 8.9, 2.0$ Hz, 2H), 7.72 (d, $J = 2.0$ Hz, 2H), 8.02 (d, $J = 8.9$ Hz, 2H), 8.36 (s, 1H), 8.45 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 26.4, 27.8, 83.4, 126.1, 126.5, 126.6, 126.8, 129.1, 130.9, 131.6, 152.7, 172.8. IR (KBr, cm^{-1}): 2978.5, 2935.1, 1730.5, 1258.3. EI MS:

m/z 492 (M^+). Anal. calcd. for $C_{28}H_{32}N_2O_6$: C 68.28, H 6.55, N 5.69; found: C 68.28, H 6.65, N 5.56.

2,7-Di-(*N*-*t*-butoxycarbonylacetamido)triptycene (6). A mixture of **5** (1.48 g, 3 mmol), benzenediazonium carboxylate (1.78 g, 12 mmol), and 1,2-epoxypropane (10 mL) in dichloroethane (100 mL) was refluxed overnight and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 1:4 ethyl acetate/petroleum ether) to afford 1.36 g (80%) of **6**. Mp: 180-182 °C. 1H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 18H), 2.47 (s, 6H), 5.34 (s, 1H), 5.43 (s, 1H), 6.72 (dd, $J = 7.7, 1.9$ Hz, 2H), 6.95-6.98 (m, 2H), 7.09 (d, $J = 1.8$ Hz, 2H), 7.29-7.34 (m, 2H), 7.37 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 27.8, 53.5, 53.8, 83.2, 123.6, 123.8, 123.9, 124.8, 125.3, 135.7, 144.5, 144.7, 145.8, 152.8, 172.7. IR (KBr, cm^{-1}): 2978.5, 1730.8, 1295.0, 1254.5. MALDI-TOF MS: m/z 591.3 ($M+Na^+$), 607.2 ($M+K^+$). Anal. calcd. for $C_{34}H_{36}N_2O_6 \cdot 0.5 H_2O$: C 70.69, H 6.46, N 4.85; found: C 71.01, H 6.32, N 5.01.

2,7-Diacetamidotriptycene (7). To a solution of **6** (1.14 g, 2 mmol) in dry dichloromethane (60 mL) under argon was added trifluoroacetic acid (6 mL). The reaction mixture was stirred at room temperature over four hours. Then the solution was washed with sat. aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by stirring in CH_3OH for 3 h, and then filtered to give the pure product 0.7 g (95%). Mp: 189-190 °C. 1H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 6H), 5.26 (s, 1H), 5.30 (s, 1H), 6.91-6.97 (m, 4H), 7.19 (d, $J = 7.9$ Hz, 2H), 7.26-7.33 (m, 2H), 7.53 (s, 2H), 7.57 (d, $J = 1.0$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 53.1, 54.2, 116.4, 116.6, 123.4, 123.6, 123.8, 125.2, 125.4, 135.0, 141.5, 144.7, 145.2, 146.0, 168.4. IR (KBr, cm^{-1}): 3390.2, 3273.6, 2955.4, 1661.4, 1600.6, 1470.5, 1418.4, 1286.3. EI MS: m/z 368 (M^+). Anal. calcd. for $C_{28}H_{32}N_2O_6 \cdot H_2O$: C 74.59, H 5.74, N 7.25; found: C 74.28, H 6.10, N 7.03.

2,7-Diamidotriptycene (8). To a suspension of **7** (1.47 g, 4 mmol) in ethanol (50 mL) was added hydrochloric acid (4 mol/L, 34 mL). The reaction mixture was refluxed

overnight and then cooled to room temperature. The ethanol was removed in vacuo and the residue was added sat. aqueous NaHCO₃ until the precipitate appeared, which was collected by filtration and dried. The product was afforded as a light yellow solid (1.05 g, 92%). Mp: 255-256 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.39 (s, 4H), 5.11 (s, 1H), 5.17 (s, 1H), 6.24 (dd, *J* = 7.7, 2.1 Hz, 2H), 6.73 (d, *J* = 1.9 Hz, 2H), 6.90-6.97 (m, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 7.27-7.31 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 52.4, 54.4, 110.9, 111.7, 122.9, 123.3, 123.7, 124.6, 125.1, 136.6, 143.6, 145.1, 146.5, 146.6. IR (KBr, cm⁻¹): 3448.1, 3370.0, 2954.4, 1619.9, 1473.4. HRMS (EI) *m/z* calcd for C₂₀H₁₆N₂ [M]⁺ 284.1313, found 284.1311.

Compounds 1 and 2. A solution of pyridine-2,6-dicarbonyl dichloride (0.2 mmol) in dry THF (10 mL) was added dropwise into a solution of 2,7-diaminotriptycene (0.2 mmol) and Et₃N (0.6 mmol) in dry THF (50 mL) at 0° over a period of 15 min under argon atmosphere. The mixture was stirred until it gradually warmed up to room temperature and was then stirred for 12 h. The solution was concentrated in vacuo and then the mixture was purified by column chromatography over silica gel (eluent: 1:10 ethyl acetate/DCM) to afford **1** (43 mg, 26%) and **2** (33 mg, 20%).

1. Mp: >300 °C. ¹H NMR (300 MHz, CDCl₃): δ 5.55 (s, 2H), 5.61 (s, 2H), 7.11-7.14 (m, 4H), 7.35 (d, *J* = 2.0 Hz, 4H), 7.50-7.55 (m, 8H), 8.06-8.15 (m, 6H), 8.46 (d, *J* = 7.8, 4H), 9.53 (s, 4H). IR (KBr, cm⁻¹): 3448.1, 3371.0, 1686.4, 1612.2, 1538.9. HRMS (EI) *m/z* calcd for C₅₄H₃₄N₂O₆ [M]⁺ 830.2642, found 830.2636.

2. Mp: 276-277 °C. ¹H NMR (300 MHz, CDCl₃): δ 5.31 (s, 2H), 5.51 (s, 2H), 6.96-7.06 (m, 4H), 7.11 (d, *J* = 1.7 Hz, 4H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.87 (dd, *J* = 8.0, 1.8 Hz, 4H), 7.93 (t, *J* = 7.8 Hz, 2H), 8.30 (d, *J* = 7.7, 4H), 9.31 (s, 4H). IR (KBr, cm⁻¹): 3441.4, 3371.9, 1685.5, 1611.2, 1533.1. HRMS (EI) *m/z* calcd for C₅₄H₃₄N₂O₆ [M]⁺ 830.2642, found 830.2637.

2. Comparison of ^1H NMR spectra of **1** and **2**

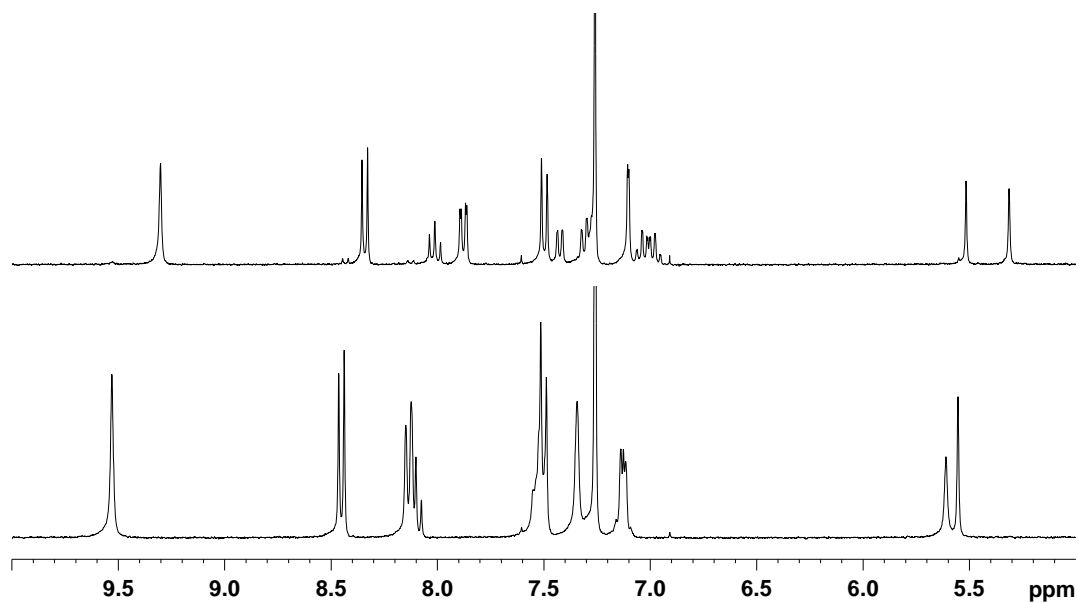


Figure S1. ^1H NMR Spectra (300 MHz, CDCl_3) of **1** (bottom) and **2** (top).

3. ^1H - ^1H COSY and NOESY spectra of the complexes

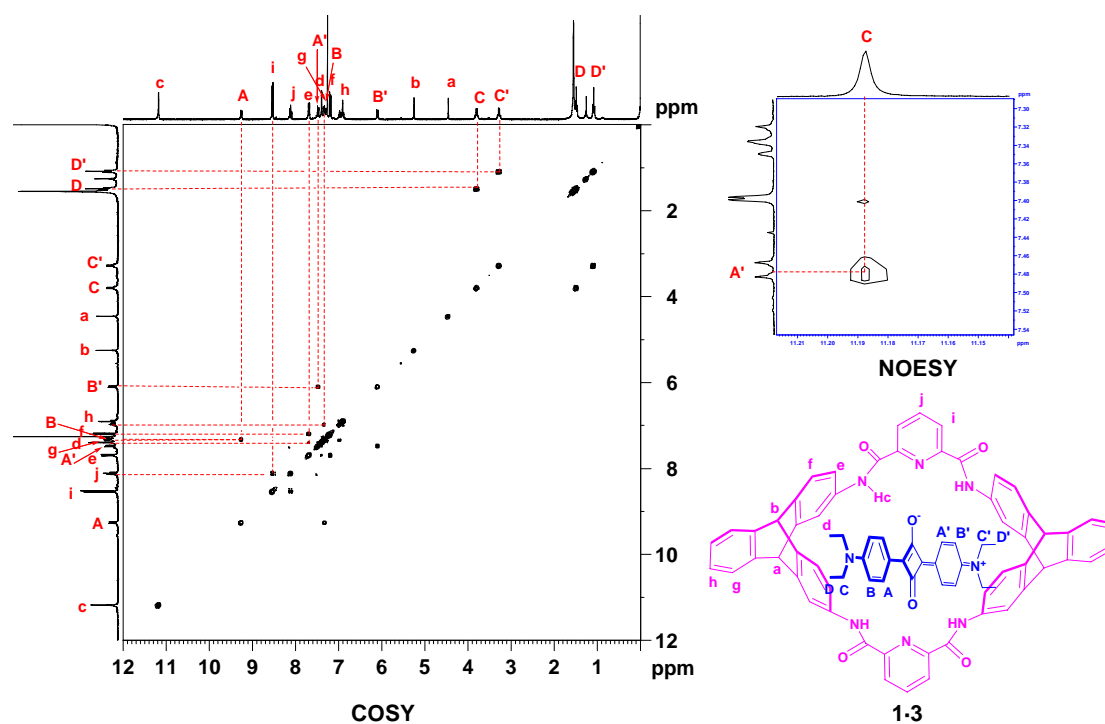


Figure S2. ^1H - ^1H COSY and NOESY spectra of complex **1·3** in CDCl_3 .

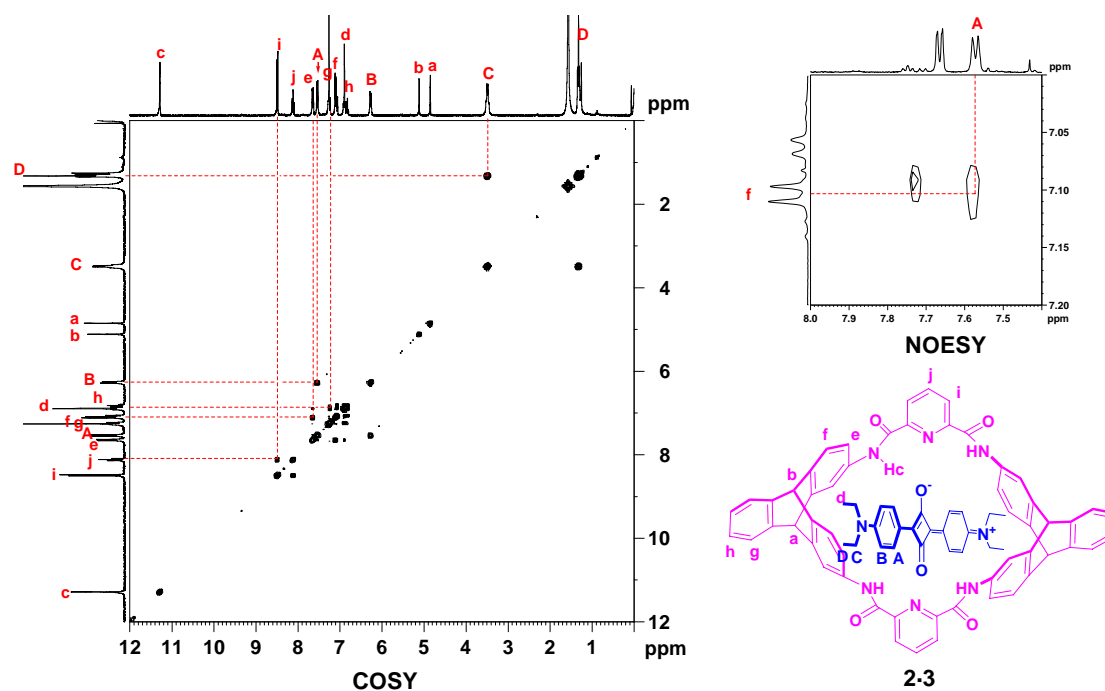
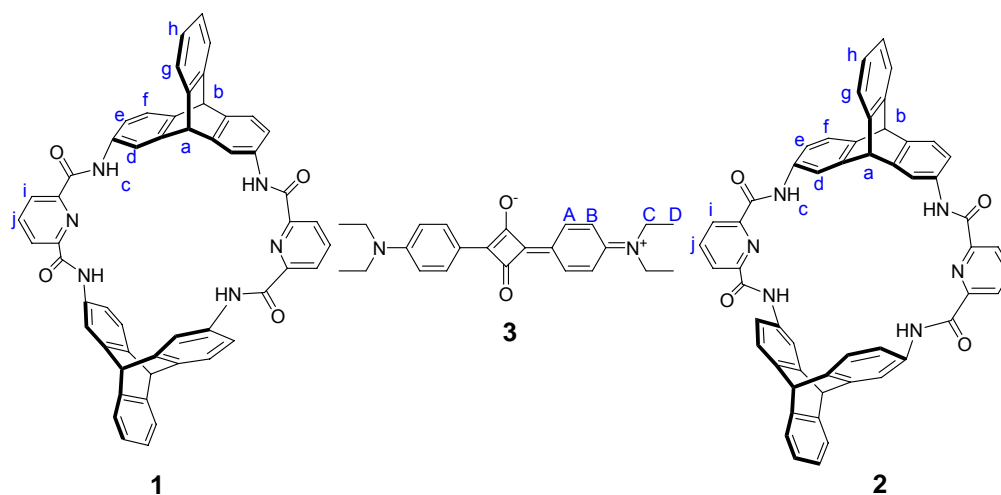


Figure S3. ^1H - ^1H COSY and NOESY spectra of complex **2·3** in CDCl_3 .

4. Complexation induced changes in chemical shift for the complexes

Table S1. Changes in chemical shift ($\Delta\delta$, ppm) on formation of **1·3** and **2·3** in CDCl_3 .



| | a | b | c | d | e | f | g | h | i | j | A | B | C | D |
|------------|-------|-------|------|-------|-------|-------|--------------|-------|------|-------|-------------|-------------|-------------|-------------|
| 1·3 | -1.10 | -0.36 | 1.64 | 0.05 | -0.45 | -0.32 | -0.19 | -0.18 | 0.07 | -0.01 | 0.87, -0.91 | 0.55, -0.68 | 0.27, -0.25 | 0.21, -0.19 |
| 2·3 | -0.46 | -0.40 | 1.95 | -0.21 | -0.21 | -0.38 | -0.18, -0.24 | -0.13 | 0.19 | 0.19 | 0.10 | -0.44 | -0.04 | 0.04 |

5. Time dependent ^1H NMR spectrum of **1**·**3** in CDCl_3

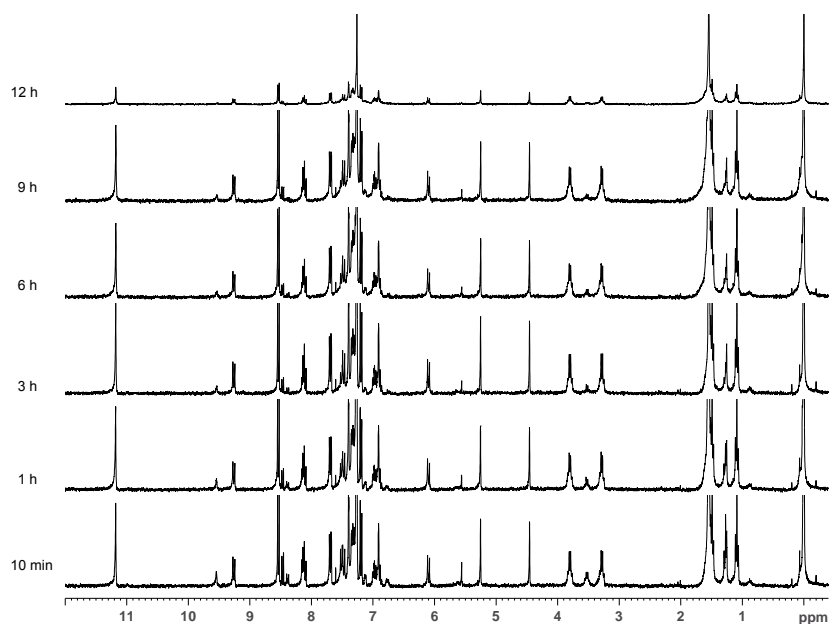


Figure S4. Time dependent ^1H NMR spectrum of **1**·**3** in CDCl_3 .

6. Determination of the stoichiometries

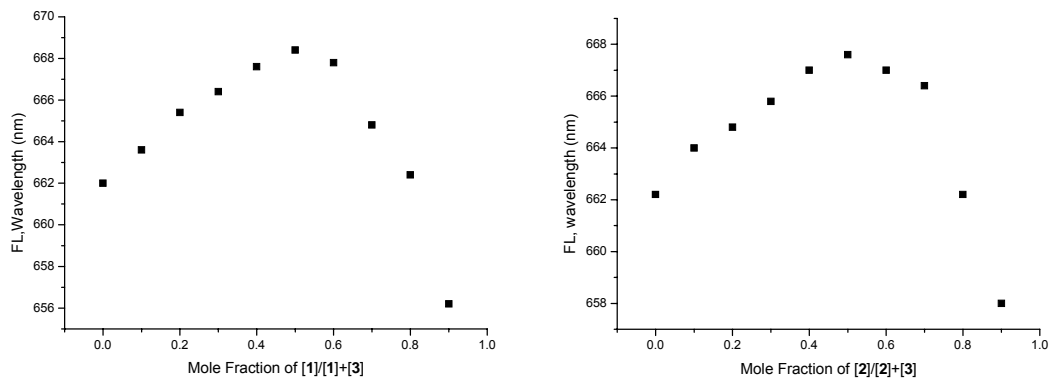


Figure S5. Molecular ratio plots of **1**·**3** and **2**·**3**.

7. Determination of the quantum yields⁴

Measurements of all reported quantum yields followed a previously described Procedure. The quantum yield was determined by the relative method using Equation below:

$$\Phi_u = \frac{A_s F_u n_u^2}{A_u F_s n_s^2} \Phi_s$$

Each experiment was performed in spectroscopic grade chloroform at 20 °C. Fluorescence quantum yields were determined using 4,4-[bis-(*N,N*-dimethylamino)-phenyl]squaraine dye as the standard (Φ_f) 0.70 in CHCl_3 .

8. X-ray crystal structures and/or packing of **1**, **2**, and the complex **2·3**

All data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 113 K. Intensities were collected for absorption effects using the multi-scan technique SADABS. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. All non-hydrogen atoms were refined anisotropically and H atoms were located from difference electron density maps. Especially for **2** (CCDC: 697890), the disordered solvent molecules were deleted with SQUEEZE program.

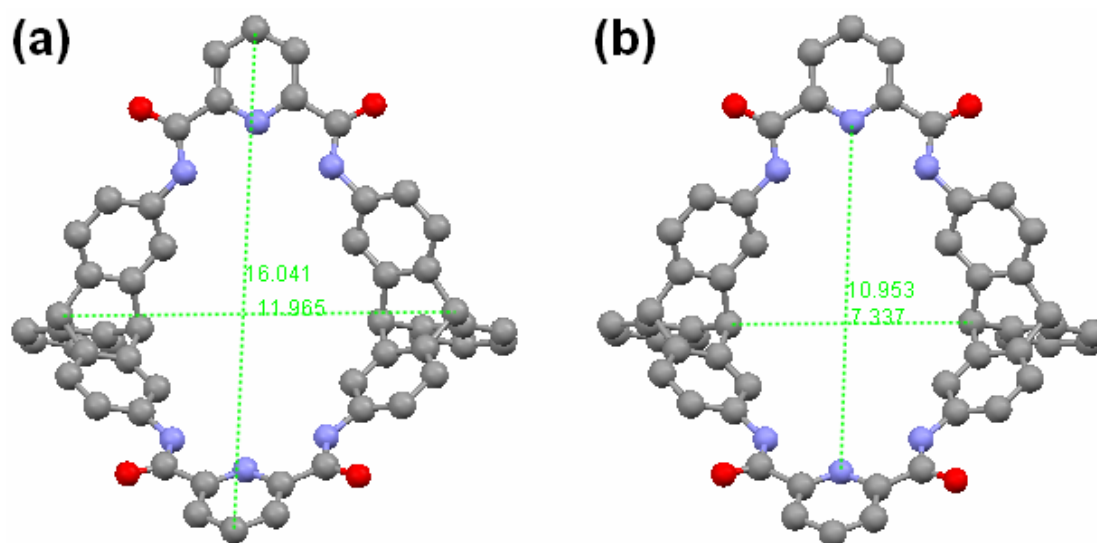


Figure S6. Crystal structure of **1** showing 11.97×16.04 Å of the wider rim (a), and 7.34×10.95 Å of the narrower rim (b).

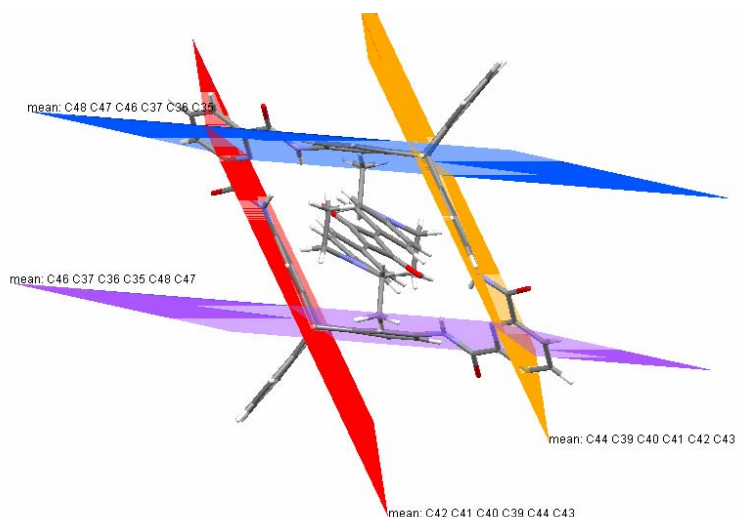


Figure S7. Crystal structure of complex **2·3** showing the prism cavity of host **2** for encapsulating guest **3**.

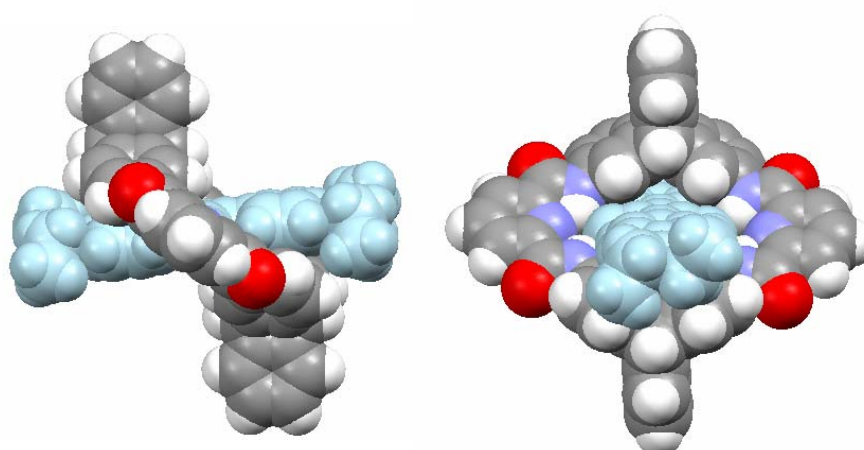


Figure S8. Spacefilling models of **2·3**. The light blue thread structure denotes the squaraine dye.

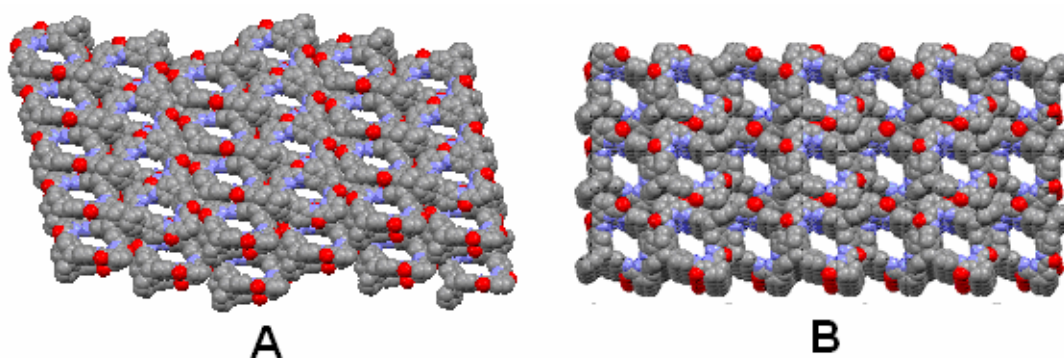


Figure S9. Packing of (A) **2**, and (B) complex **2·3** in the absence of guest **3**.

9. Photophysical properties and chemical stabilities of **3**, **1·3**, and **2·3**.

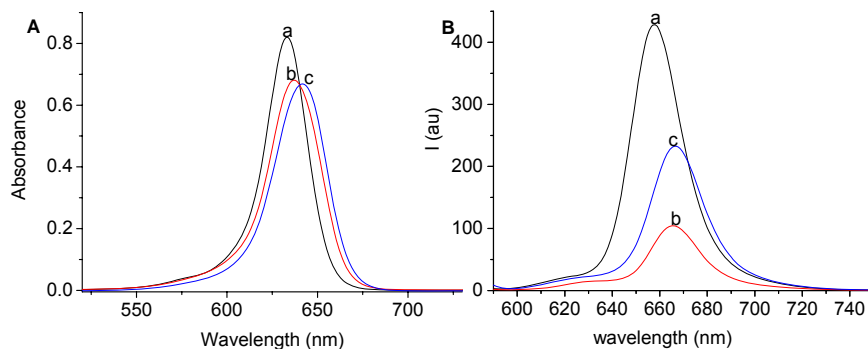


Figure S10. Absorption spectra (A) and fluorescence emission spectra (B) of (a) **3**, (b) **1·3**, (c) **2·3** in CHCl₃, 2.5 μM for A and 10 μM for B, ex: 580 nm.

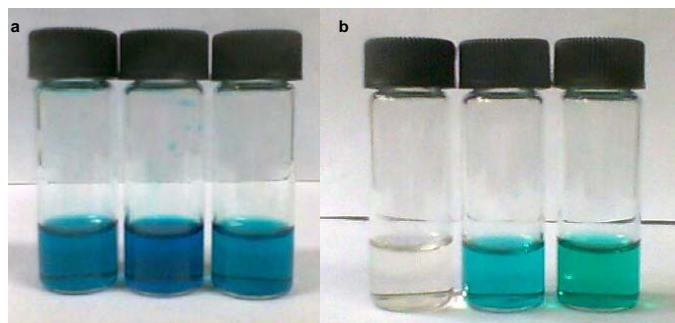


Figure S11. Photographs of (a) the solutions in THF/water (4:1) containing **3**, **1·3**, and **2·3** (from left to right), (b) 4 days later.

References

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