Supplementary Supporting Information

Interplay of Monomer, Intra- and Intermolecular Excimer Fluorescence in Cyclophanes and Selective Recognition of Methanol Vapors

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1. Experimental Techniques

General Methods. The equipment and procedures for melting point determination and spectral recordings have been described elsewhere.[1]Doubly distilled water was used in all the studies. Petroleum ether used was the fraction with boiling range 60-80 ºC. All experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned.

An Elico pH meter was used for pH measurements. ^{1}H and ^{13}C NMR were measured on 300 or 500 MHz Bruker spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-VIS-NIR spectrophotometer. Diffuse reflectance absorption spectra were recorded using a Shimadzu integrating sphere assembly attached to a Shimadzu UV-vis-NIR 3101 PC spectrophotometer. BaSO4 was used as the reflectance standard. Fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. Quinine sulphate ($\Phi_f = 0.54$) in 0.1 N H_2SO_4 was used as the standard. The quantum yields of fluorescence were calculated using the equation 1,

$$\phi_u = \frac{A_s F_u n_u^2}{A_u F_s n_s^2} \phi_s \quad (1)$$

where, A_s and A_u are the absorbance of standard and unknown, respectively. F_s and F_u are the areas of fluorescence peaks of the standard and unknown and n_s and n_u are the refractive indices of the solvents used for the standard and unknown, respectively. Φ_s and Φ_u are the fluorescence quantum yields of the standard and unknown compound.

Fluorescence lifetimes were measured using a IBH picosecond single photon counting system. The fluorescence decay profiles were deconvoluted using IBH datastation software V2.1 and minimizing the χ^2 values of the fit to 1 ± 0.1.

Solid-state fluorescence measurements were carried out using the front face emission scan mode on a SPEX Fluorolog F112X spectrofluorimeter. Solid-state fluorescence quantum efficiency was measured using an integrating sphere in a SPEX Fluorologspectrofluorimeter. The quantum yields in solid state were determined using a calibrated integrating sphere system. The Xe-arc lamp was used to excite the samples placed in the sphere with 355 nm as the excitation wavelength. The quantum yield was determined by comparing the spectral intensities of the lamp and the sample emission as per literature reports.[2]

2. Synthesis of the cyclophanes 1 and 2 and the model derivative 3.

Synthesis of the cyclophanes **1** and **2** were carried out as reported earlier.[3] whereas the synthesis of the model derivative**3** was achieved by the following procedure. To a solution of 9,10-bis((imidazolyl)methyl) anthracene (0.25 g, 0.74 mmol) in a mixture of acetonitrile (100mL) and DMF (50 mL) was added bromoethane (0.81 g, 0.74 mmol). The reaction mixture was then refluxed for 24 h and after cooling to room temperature the precipitated product was filtered and washed with 30 mL dry acetonitrile. It was further purified by re-crystallization from acetonitrile to yield 180 mg (40%) of **3**; m.p. 276-277 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.19 (4H, s), 6.61 (4H, s), 6.66 (2H, s), 6.81 (4H, s), 7.66 - 7.68 (4H, m), 8.00 - 8.01 (2H, t), 8.29 -

8.30 (2H, t), 8.34 - 8.36 (4H, m); ^{13}C NMR (125 MHz, DMSO-d_6) δ 45.5, 52.2, 123.57, 123.63, 124.3, 127.5, 129.7, 129.9, 134.1, 134.3; HRMS (FAB) *m/z* calcd for $C_{38}H_{30}Br_2N_4$: 622.5758, found 622.5753 $[M - Br]^+$.

References

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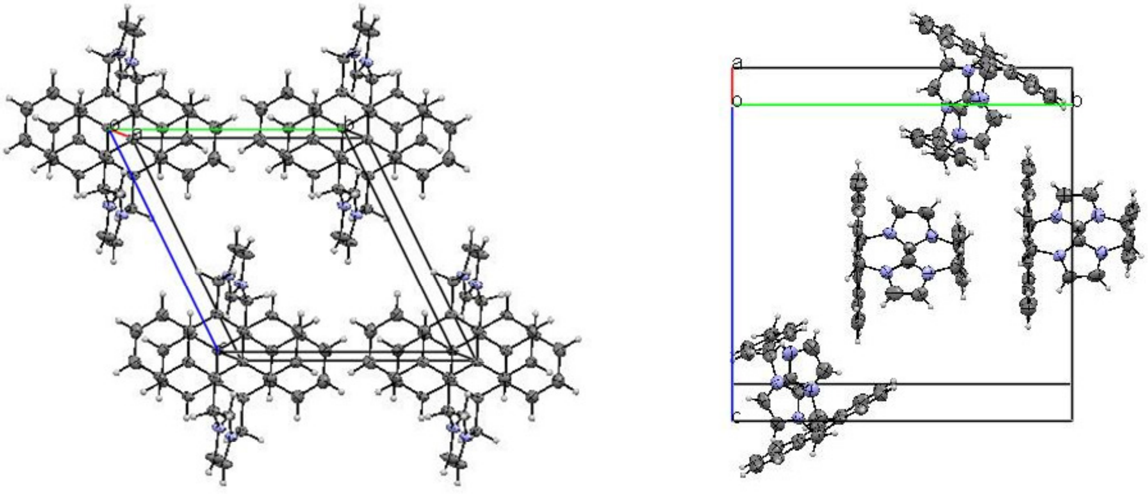
Table S1. Summary of crystallographic data for cyclophanes **1** and **2**

Parameters	**1**	**2**
Empirical formula	$C_{38}H_{30}Br_2N_4O_2$	$C_{60}H_{58}Br_2N_8O_3$
Formula weight	734.48	602.36
T, K	100(2) K	293 (2)
λ, Å	1.54178 Å	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21
a, Å	8.3588(2)	10.3953(4)
b, Å	10.3505(3)	17.2537(6)
c, Å	10.9632(3)	16.1405(6)
α, deg	63.8699(15)	90
β, deg	84.6098(15)	100.491(2)
γ, deg	83.0969(16)	90
V, $Å^3$	844.50(4)	2846.53(18)
Z	1	2
d_{calc}, Mg/m^3	1.444	1.282
F (000)	372	1136
Crystal size, mm	0.15 × 0.07 × 0.03	0.30 × 0.20 × 0.20
μ ($Mo_{K\alpha}$), mm^{-1}	3.355	1.474
Theta range for data collection, °	4.50 to 67.02	1.28 to 25.00
Limiting indices	$-9 \leq h \leq 9$, $-10 \leq k \leq 12$, $0 \leq l \leq 13$	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-19 \leq l \leq 19$
Reflections collected/ unique	2927/ 2927	25966/ 9821
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/ parameters	2927/ 0/ 212	9821/ 2/ 681
Goodness-of-fit on F^2	1.098	1.056
Final R indices [$I>2\sigma(I)$]	R1 = 0.0786, wR2 = 0.2179	R1 = 0.0637, wR2 = 0.1719
R indices (all data)	R1 = 0.0844, wR2 = 0.2278	R1 = 0.0956, wR2 = 0.1974
Largest diff. peak and hole, e-/$Å^{-3}$	4.904 and -0.630	1.804 and -0.720



1

2

Fig. S1. Unit cells of cyclophanes **1** and **2** obtained from single crystal x-ray analysis (counter ions and solvent molecules have been removed for clarity).

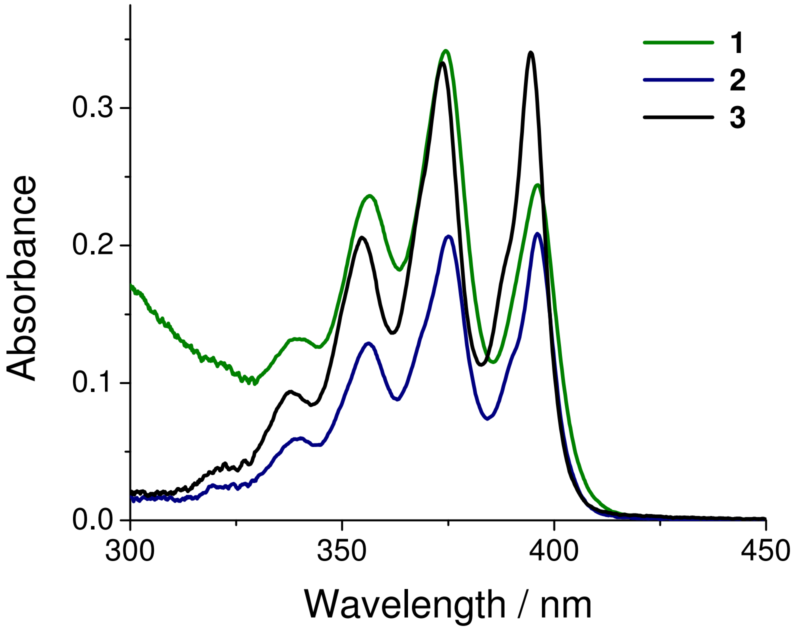


Fig. S2. Absorption spectra of the cyclophanes **1** (10µM), **2** (10µM) and **3** (12µM) in methanol.

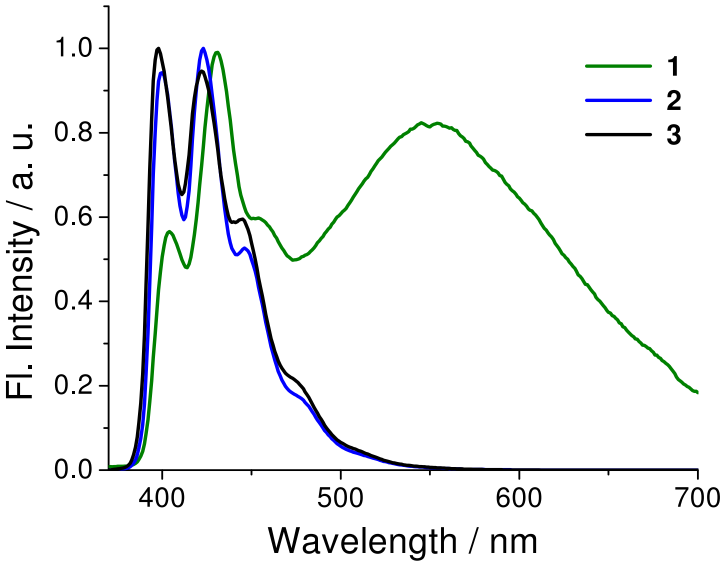


Fig. S3. Fluorescence spectra of the cyclophanes **1** (10μM), **2** (10μM) and **3** (10μM) in water. λ_{ex}, 355 nm.

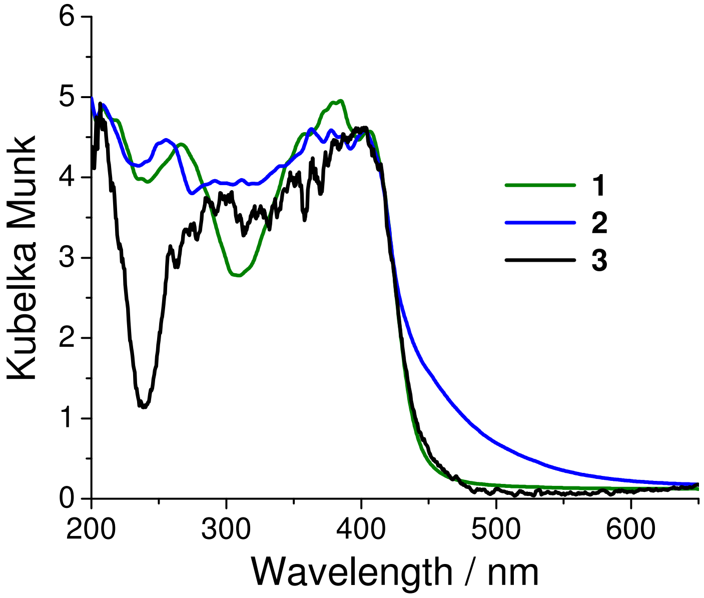


Fig. S4. Absorption spectra (obtained by transforming the reflectance spectra) of **1**-**3** in the solid state.

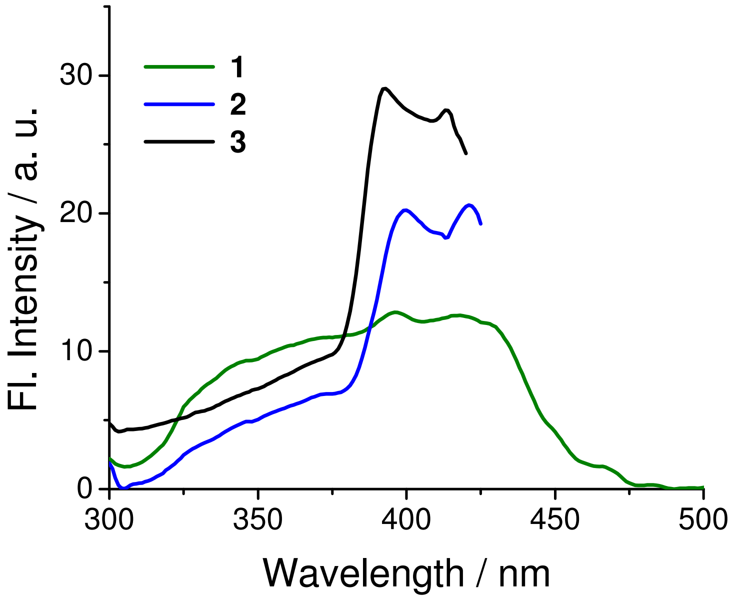


Fig. S5. Fluorescence excitation spectra of **1-3** in the solid state monitored at 565, 430 and 430 nm, respectively.

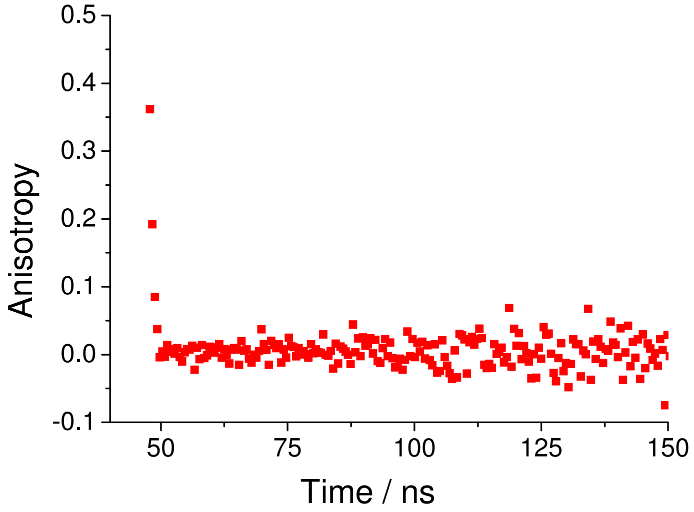


Fig. S6. Fluorescence anisotropy decay of cyclophane **1** in water monitored at 435 nm.

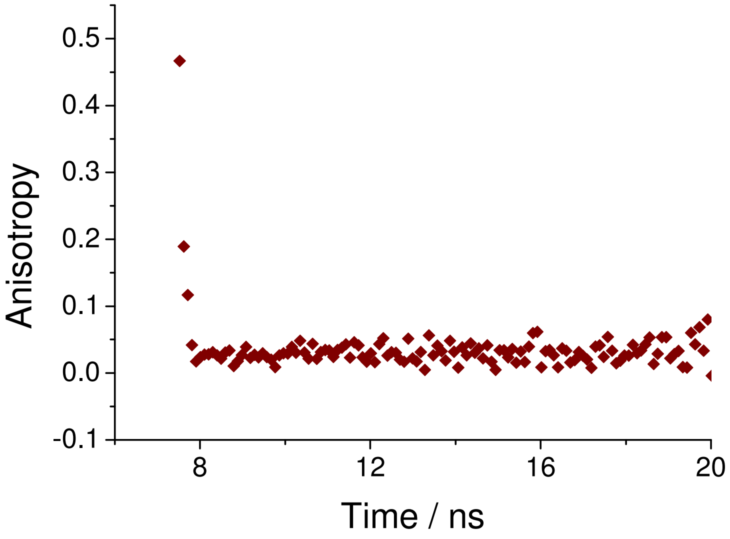


Fig. S7. Fluorescence anisotropy spectra of cyclophane **1** in the solid state monitored at 565 nm.

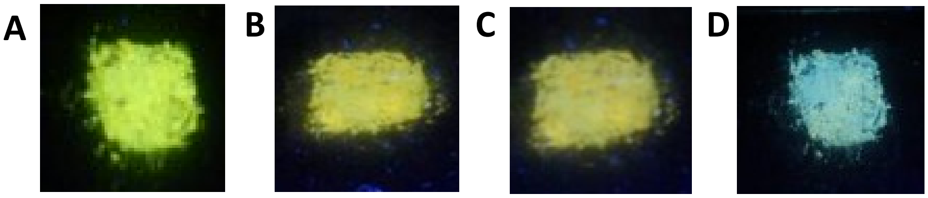


Fig. S8. Fluorescence images of cyclophane **1** coated on a glass plate A) before and after the exposure to B) ethanol, C) water and D) methanol vapors. $\lambda_{ex} = 365$ nm.