Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Conformational Change due to Intramolecular Hydrophobic Interaction Leads to Large Blue-Shifted Emission from Single Molecular Cage Solutions

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Materials and Methods

Reagents and solvents were purchased from Sigma-Aldrich and used without purification. 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethene, sodium isophthalate, sodium [1,1'-biphenyl]-4,4'-dicarboxylate, *cis*-$Pt(PEt_3)_2(OTf)_2$, *cis*-$Pt(PEt_3)_2(NO_3)_2$, **Cage 1**·8OTf⁻ were synthesized according to the reported procedures.[1] Thin layer chromatography (TLC) was performed on flexible sheets (Baker-flex) precoated with SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using SiO_2 (60-200 mesh) from Fisher Scientific.

^1H, ^{31}P and 2D COSY NMR spectra were recorded on a Varian NMR 500. UV-Vis spectrum were measured on Agilent Technologies 8453 UV-Vis Spectrophotometer from Aligent Technologies and analyzed by UV-Vis ChemStation Software. Fluorescence spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrometer with excitation wavelength 355 nm. Light scattering experiments were conducted on a commercial Brookhaven instrument laser light scattering spectrometer with a solid-state green laser. The SAXS studies were performed at the 15-ID-D station with X-ray energy of 20 keV at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). The sample solutions were placed in quartz capillaries for all the measurements. For each sample test, SAXS measurements of corresponding solvents were carried out for background subtraction. Guinier analysis or Indirect flourier transformation (IFT) by Moore method was used for R_g calculation. For Guinier analysis, the maximum Q to be included in the fit is $1.3/R_g$ or less.

Synthesis of Cage 1·8NO_3^-

To a 20 mL bottle vial, *cis*-$Pt(PEt_3)_2(NO_3)_2$ (88.8 mg, 0.16 mmol), 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane (25.2 mg, 0.04 mmol), sodium isophthalate (16.8 mg, 0.08 mmol), and a mixture of H_2O and acetone (1:1, 10 mL) was added. After stirring at 70 °C for 24h, a clear pale-yellow solution was obtained. The solvent was removed by N_2 flow. The residual solid was redissolved in 10 mL acetone and precipitated out by addition of Et_2O, and then dried under vacuum. **Cage 1** was obtained as a yellow solid in the yield of 98%: ^1H NMR (500 MHz, CD_3CN, 300 K) δ (ppm): 8.69 (m, 16H, $H_{\alpha\text{-}Py}$), 7.96 (t, 4H), 7.89 (dd, 8H), 7.71 (d, J = 8 Hz, 16H, $H_{\beta\text{-}Py}$), 7.52 (d, J = 9 Hz, 16H, H_{phenyl}), 7.31 (t, J = 16 Hz, 4H), 7.23 (d, J = 9 Hz, 16H, H_{phenyl}), 1.95-1.75 (m, 96H), 1.29-1.13 (m, 144H). $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_3CN, 300K) δ (ppm): 5.64 (d, J = 21 Hz, 16P), -0.06 (d, J = 21 Hz, 16P).

Synthesis of Cage 2·8NO_3^-

To a 20 mL bottle vial, *cis*-$Pt(PEt_3)_2(NO_3)_2$ (88.8 mg, 0.16 mmol), 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane (25.2 mg, 0.04 mmol), sodium [1,1'-biphenyl]-4,4'-dicarboxylate (22.9 mg, 0.08 mmol), and a mixture of H_2O and acetone (1:1, 10 mL) was added. After stirring at 70 °C for 24h, a clear pale-yellow solution was obtained. The solvent was removed by N_2 flow. The residual solid was redissolved in 10 mL acetone and precipitated out by addition of Et_2O, and then dried under vacuum. **Cage 1** was obtained as a yellow solid in the yield of 92%: ^1H NMR (500 MHz, CD_3CN, 300 K) δ (ppm): 8.64 (m, 16H, $H_{\alpha\text{-}Py}$), 7.66 (d, J = 6 Hz, 16H), 7.62 (d, J = 8 Hz, 16H), 7.53 (d, J = 9 Hz, 16H), 7.44 (d, J = 9 Hz, 16H), 7.17 (d, J = 8 Hz, 4H), 2.03-1.71 (m, 96H), 1.33-1.11 (m, 144H). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_3CN, 300K) δ (ppm) :5.28 (d, J = 21 Hz, 16P), 0.04 (d, J = 21 Hz, 16P).

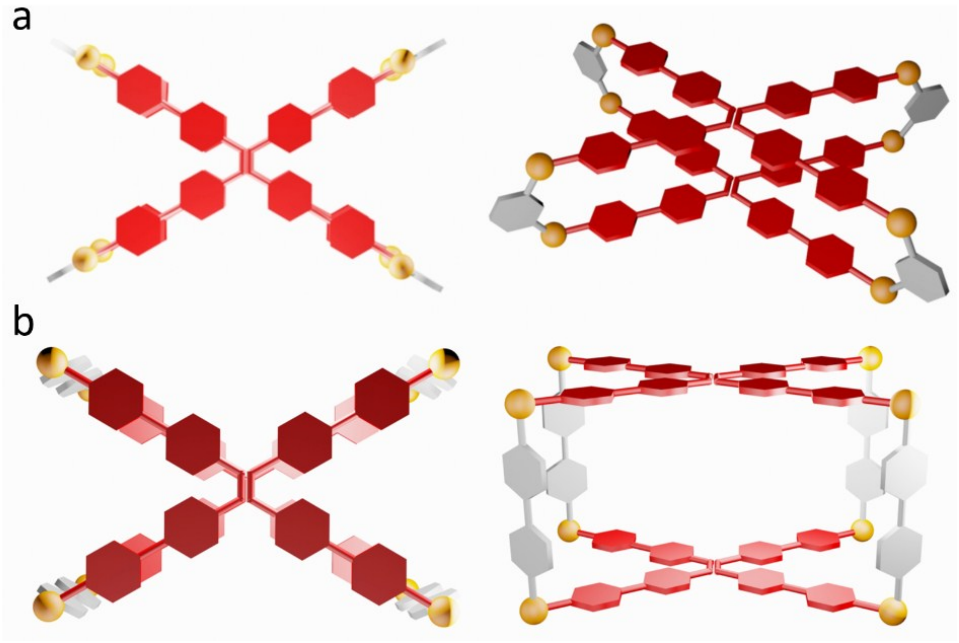

Figure S1. Illustration of molecular structures of **Cage 1** (a) and **Cage 2** (b).

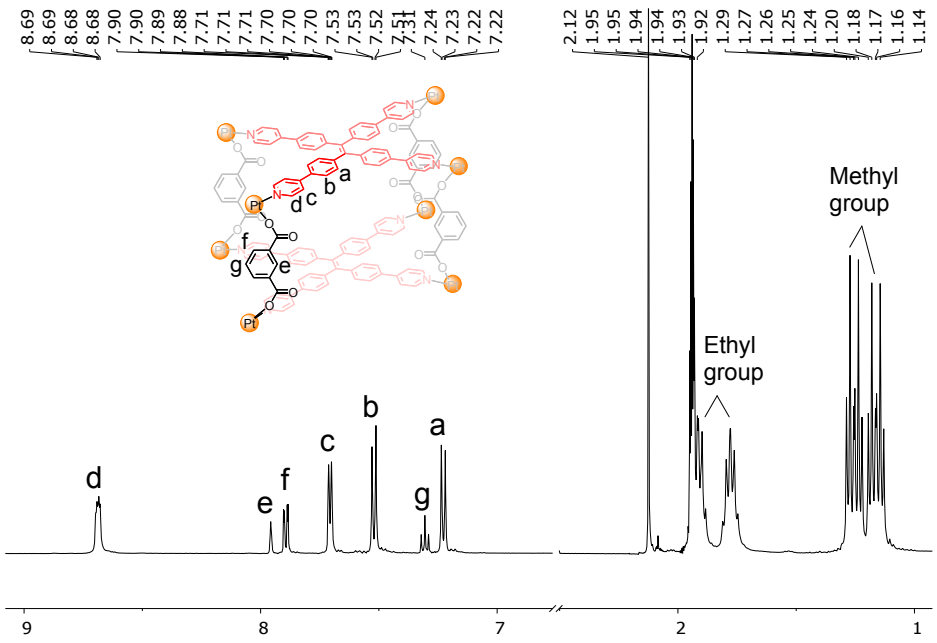

Figure S2. ^{1}H-NMR spectrum of **Cage 1** in CD_3CN at 300 K.

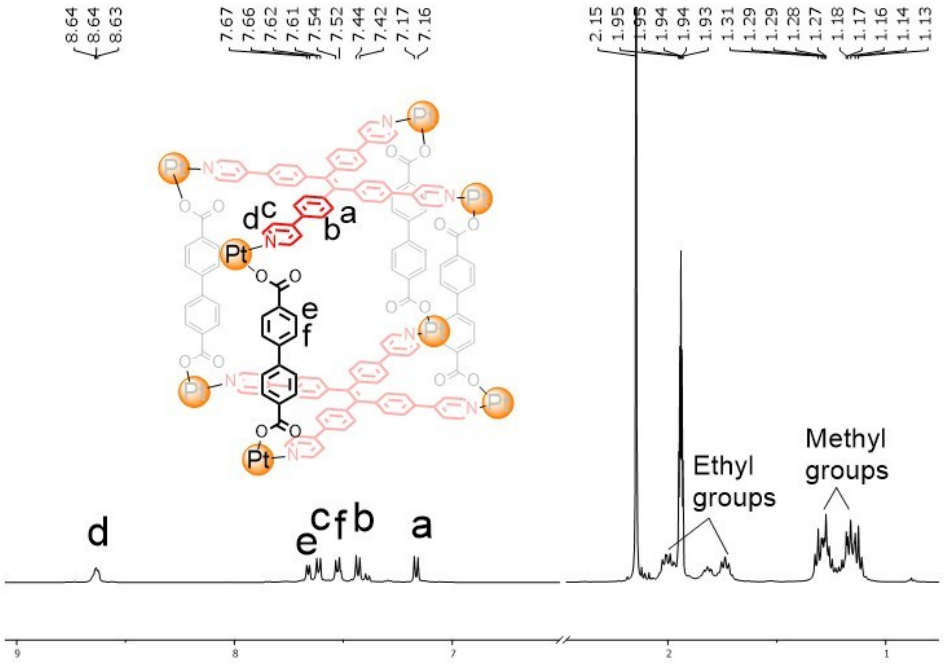

Figure S3. ^{1}H-NMR spectrum of **Cage 2** in CD_3CN at 300 K.

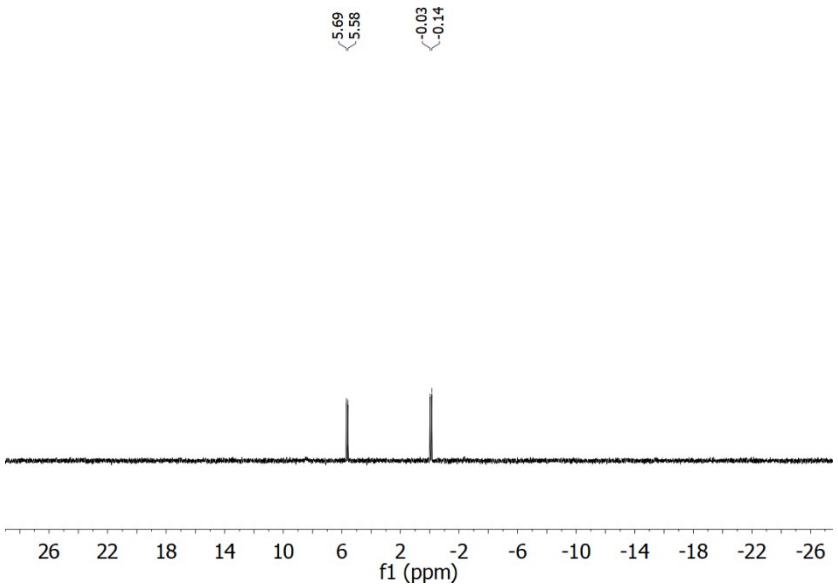

Figure S4. ^{31}P-NMR spectrum of **Cage 1** in CD_3CN at 300 K.

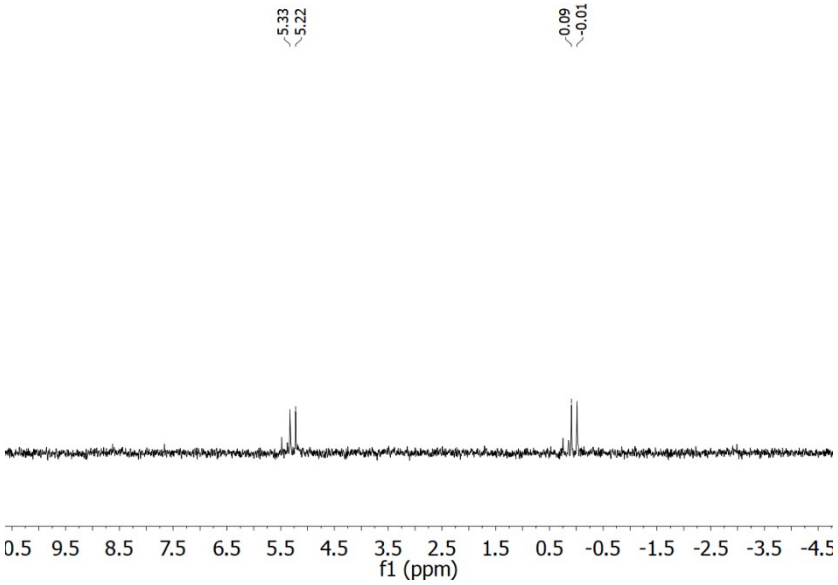

Figure S5. ^{31}P-NMR spectrum of **Cage 2** in CD_3CN at 300 K.

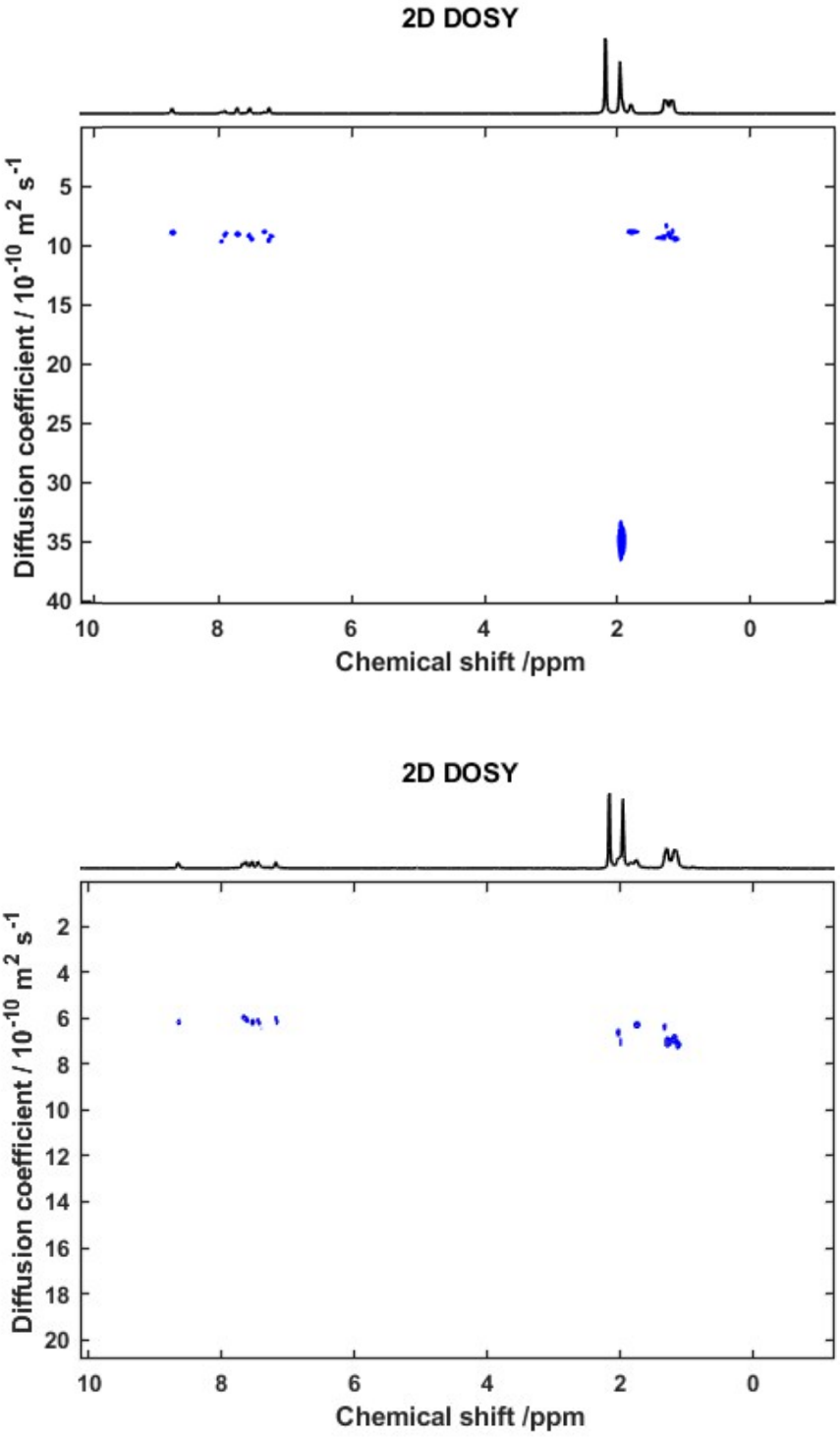

Figure S6. DOSY NMR spectra of **Cage 1** (up) and **Cage 2** (down) in CD_3CN at 300 K.

Table S1. Size calculation on cages based on the 2D DOSY NMR spectra.

Sample[a]	k ($N \cdot m \cdot K^{-1}$)	T (K)	Viscosity[b] ($N \cdot m^{-2} \cdot s$)	Diffusion Coefficient ($m^2 \cdot s^{-1}$)	R_h (nm)
Cage 1	1.38×10^{-23}	300	0.373×10^{-3}	9.0×10^{-10}	0.65
Cage 2	1.38×10^{-23}	300	0.373×10^{-3}	6.2×10^{-10}	0.94

[a] in CD_3CN; [b] at 300 K.

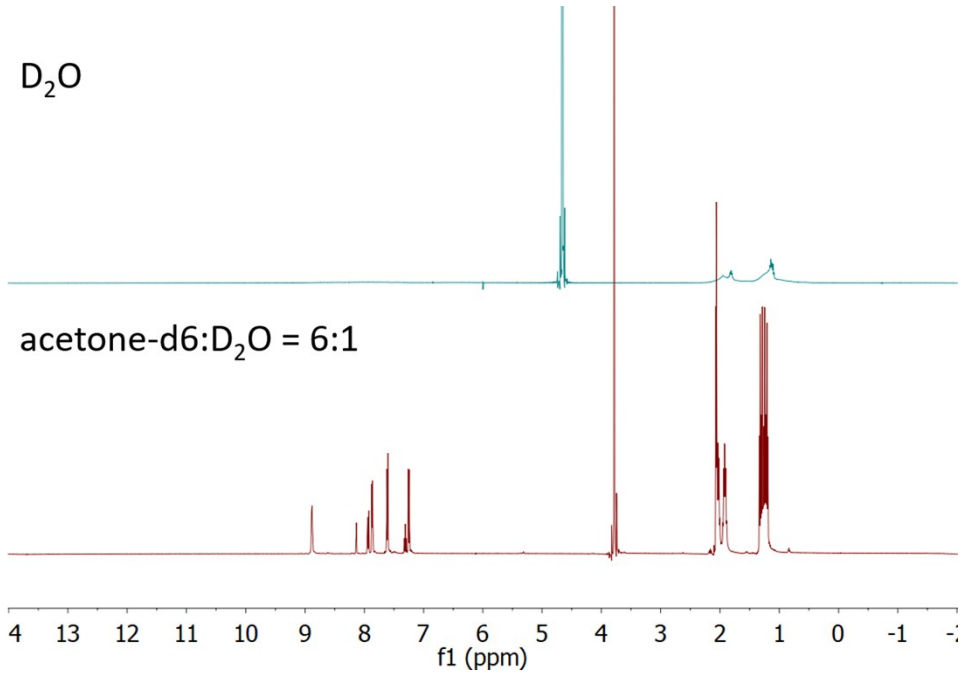

Figure S7. ^{1}H-NMR spectra of **Cage 1** in D_2O (up) and acetone-d6/D_2O mixed solvents (down) at 300 K. Relaxation time, 1.0 s.

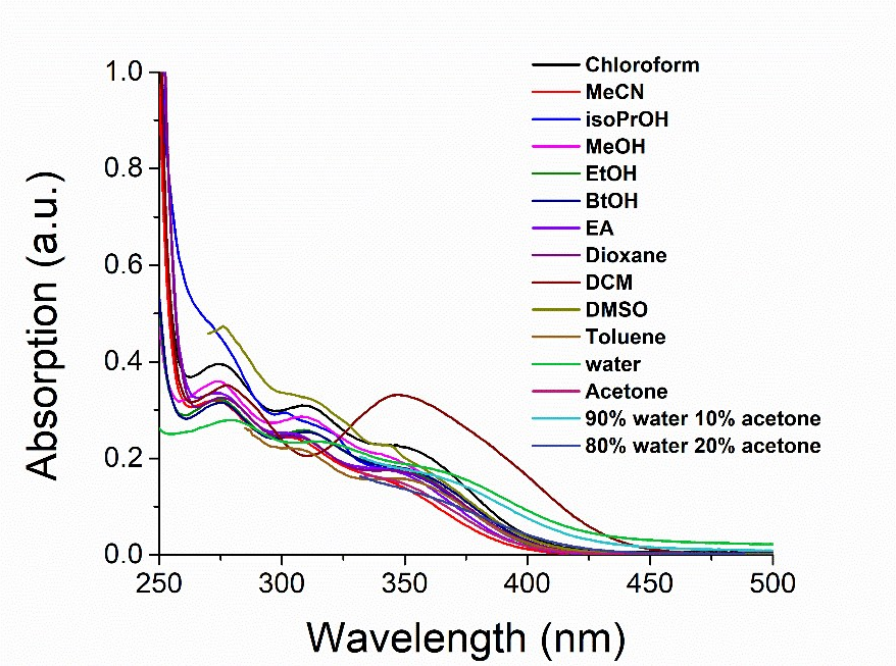

Figure S8. UV-Vis absorption of TPPE ligand in different solvents. Concentration: 0.05 mg/mL.

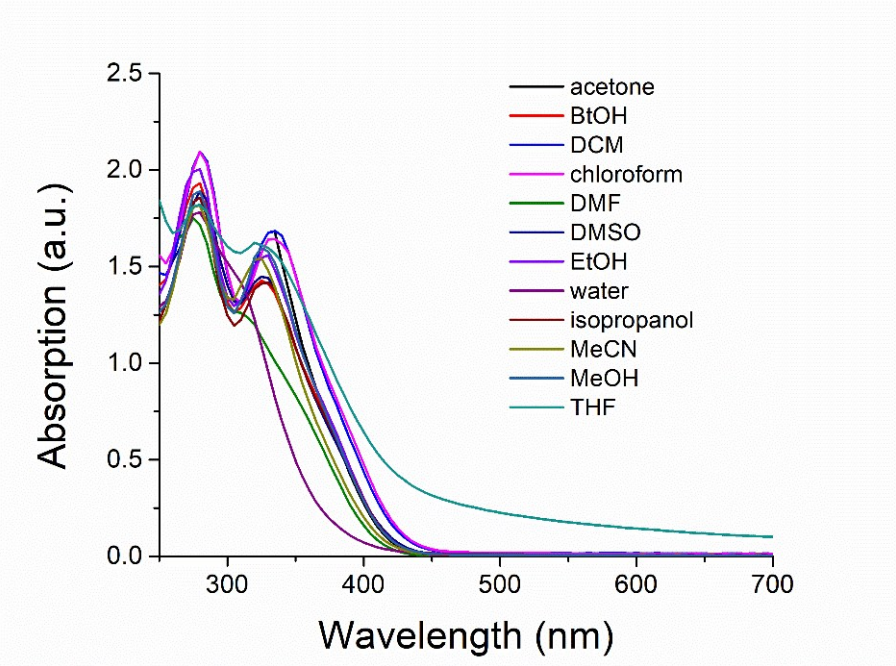

Figure S9. UV-Vis absorption of **Cage 1** in different solvents. Concentration: 0.05 mg/mL.

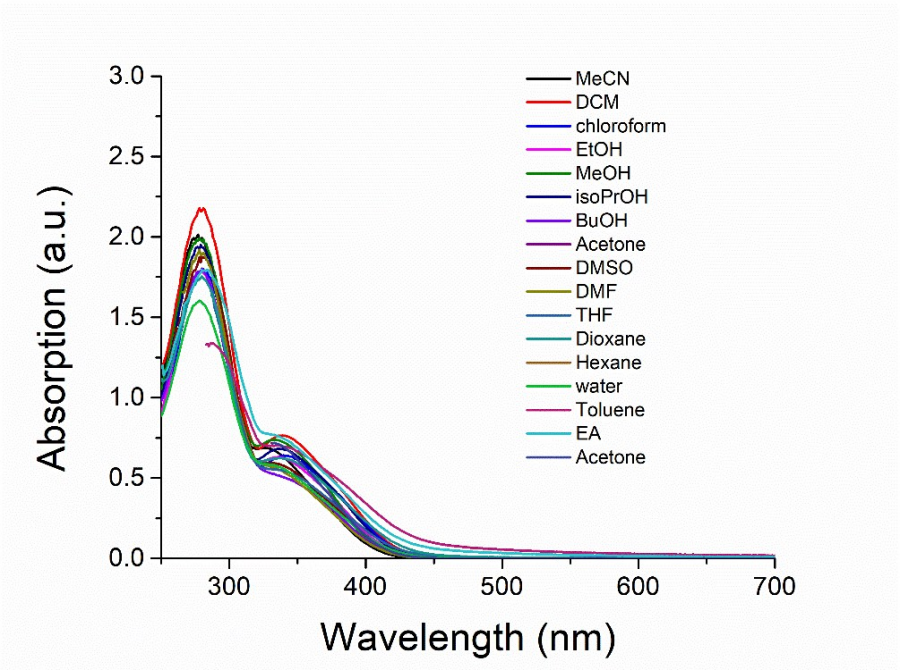

Figure S10. UV-Vis absorption of **Cage 2** in different solvents. Concentration: 0.05 mg/mL.

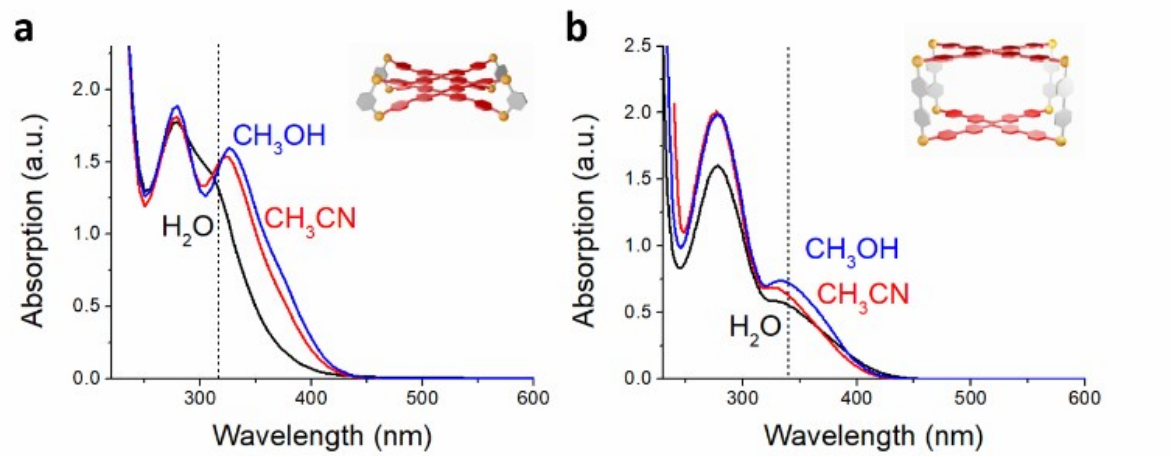

Figure S11. UV-Vis absorption spectra of **Cage 1** (a) and **Cage 2** (b) in acetonitrile, methanol and water. Concentration, 0.05 mg/mL.

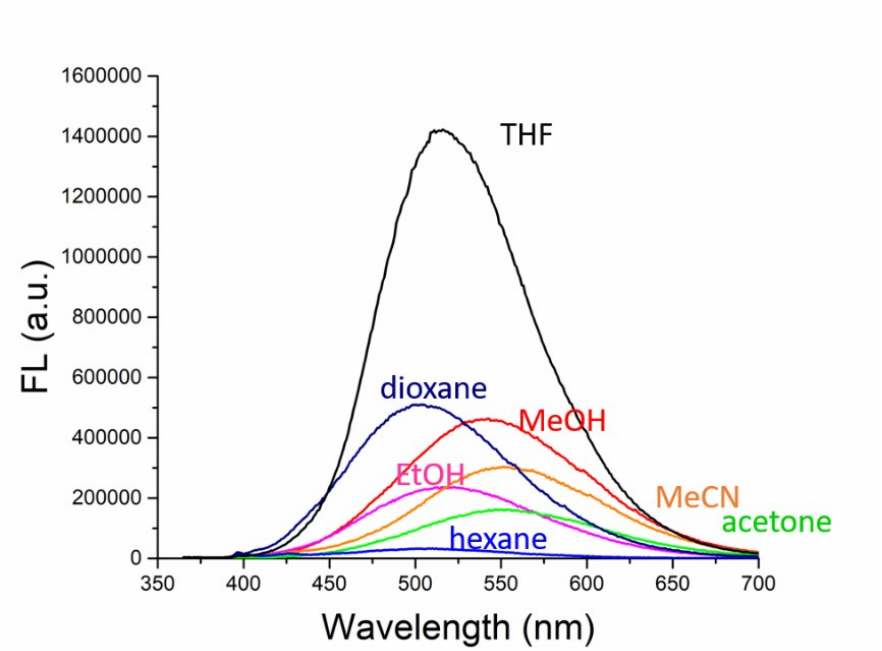

Figure S12. Fluorescence spectra of **Cage 1** in different solvents. Concentration: 0.05 mg/mL. **Cage 1** precipitates in hexane and this phase separation leads to the solution weak fluorescence.

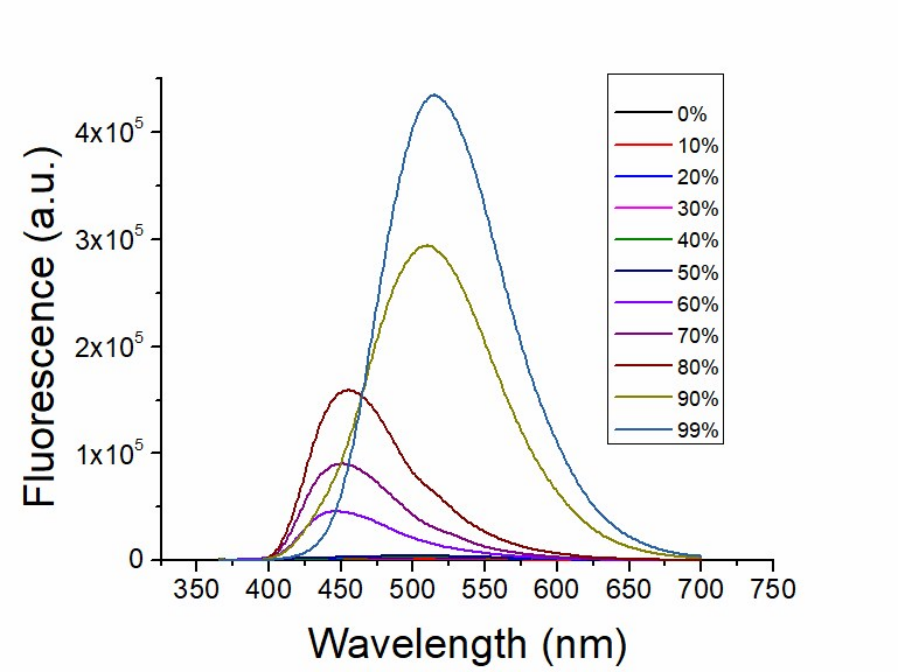

Figure S13. Fluorescence spectra of TPPE in water/acetone mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

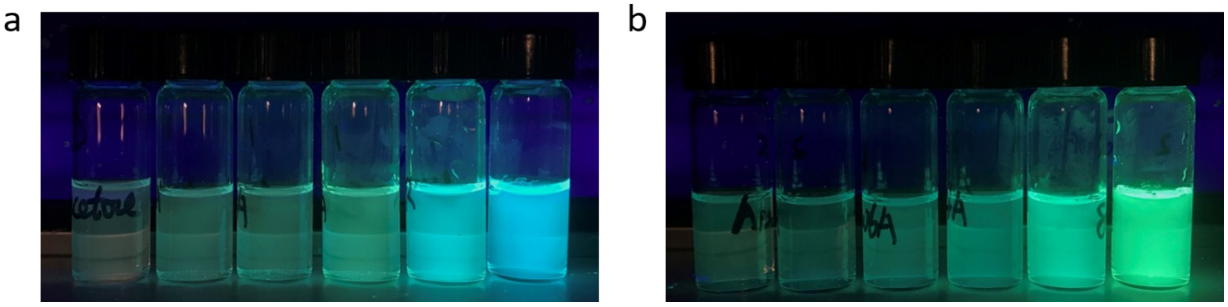

Figure S14. Photograph of **Cage 1** and **Cage 2** in water/acetone mixed solvents with different water fraction under 365 nm UV light. In each photo graph, from left to right, the water fractions are 0%, 20%, 40%, 60%, 80%, 100%.

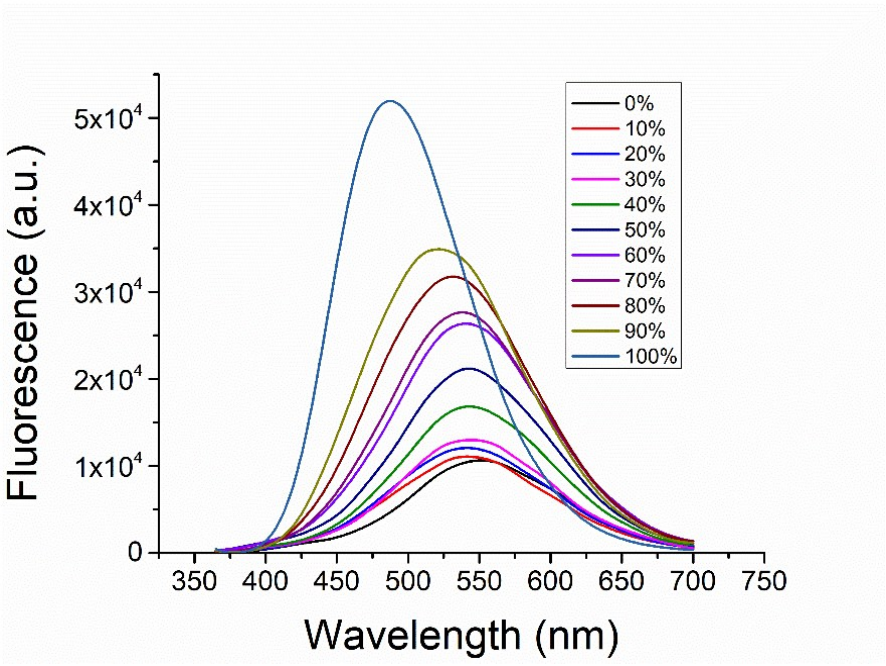

Figure S15. Fluorescence spectra of **Cage 1** in water/acetonitrile mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

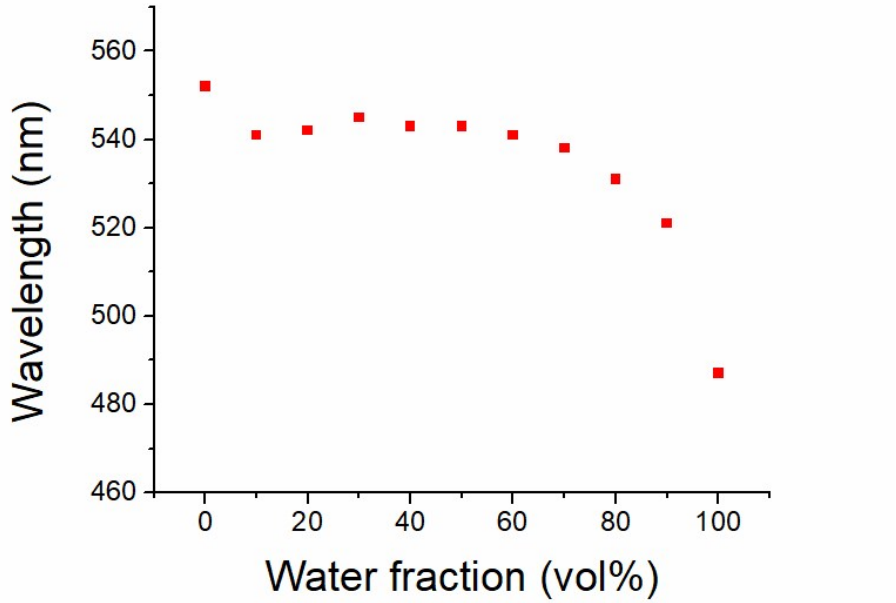

Figure S16. The wavelength of the maximum fluorescence of **Cage 1** in water/acetonitrile mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

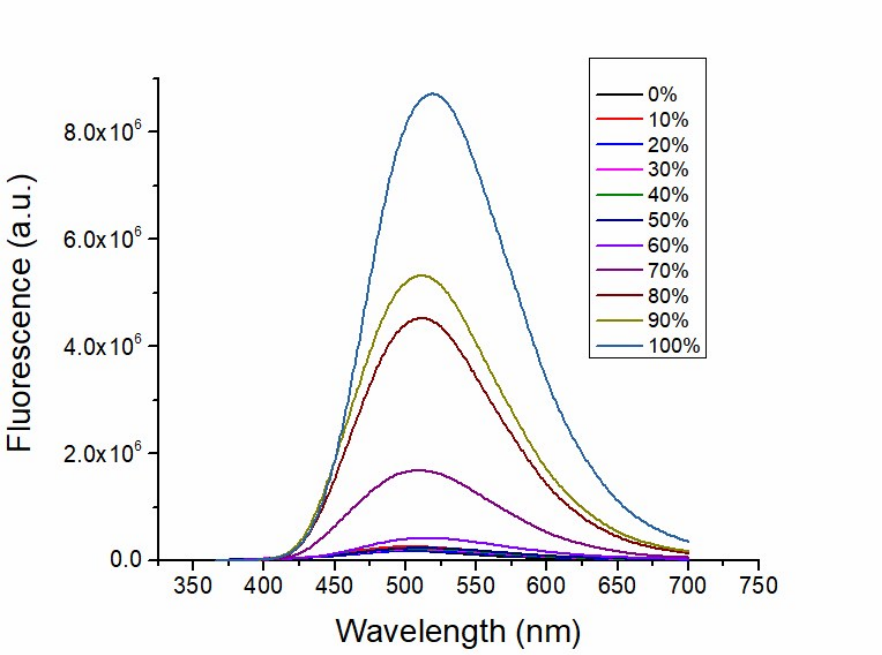

Figure S17. Fluorescence spectra of **Cage 2** in water/acetonitrile mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

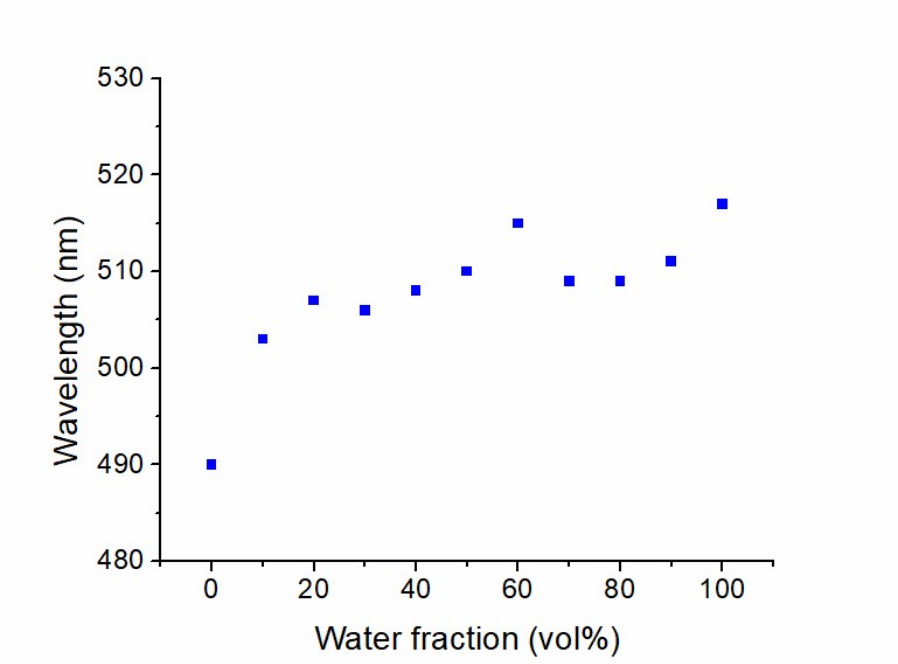

Figure S18. The wavelength of the maximum fluorescence of **Cage 2** in water/acetonitrile mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

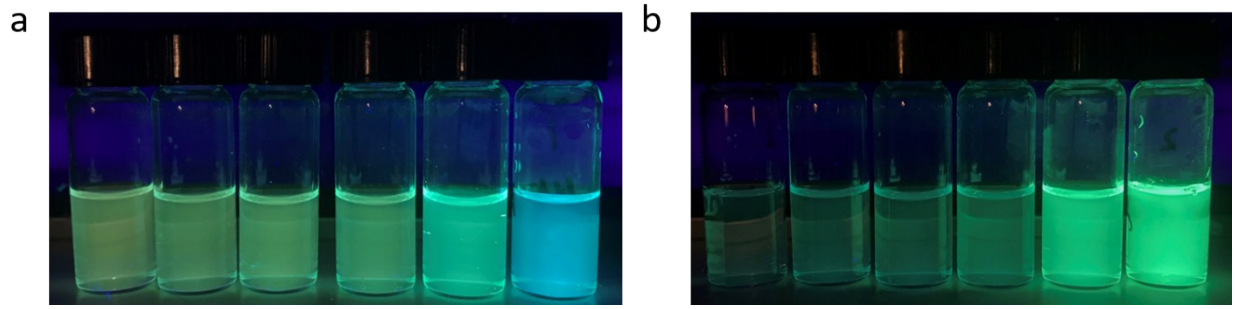

Figure S19. Photograph of **Cage 1** and **Cage 2** in acetonitrile/water mixed solvents with different water fraction under 365 nm UV light. In each photo graph, from left to right, the water fractions are 0%, 20%, 40%, 60%, 80%, 100%.

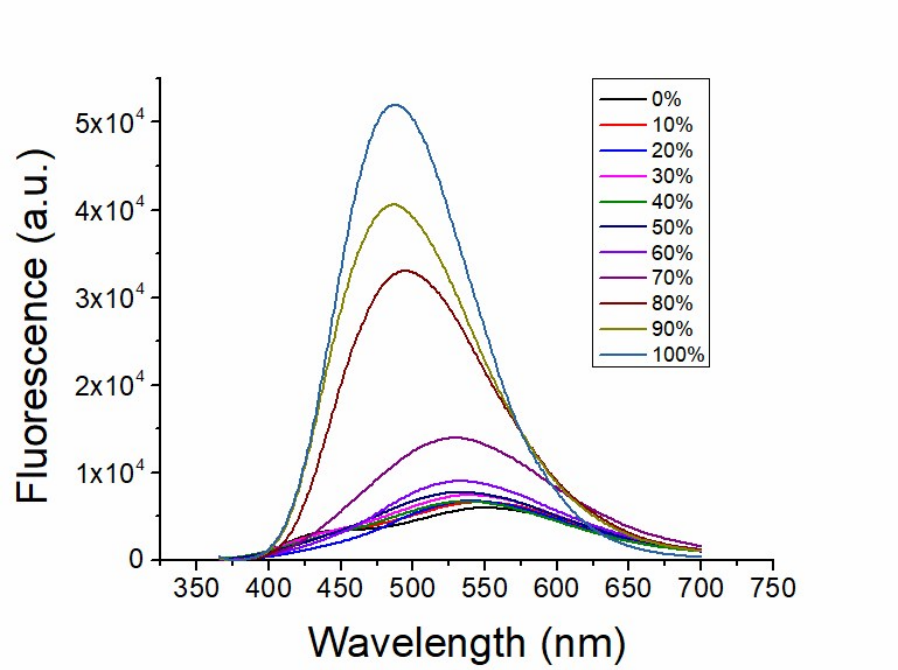

Figure 20. Fluorescence spectra of **Cage 1** in water/methanol mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

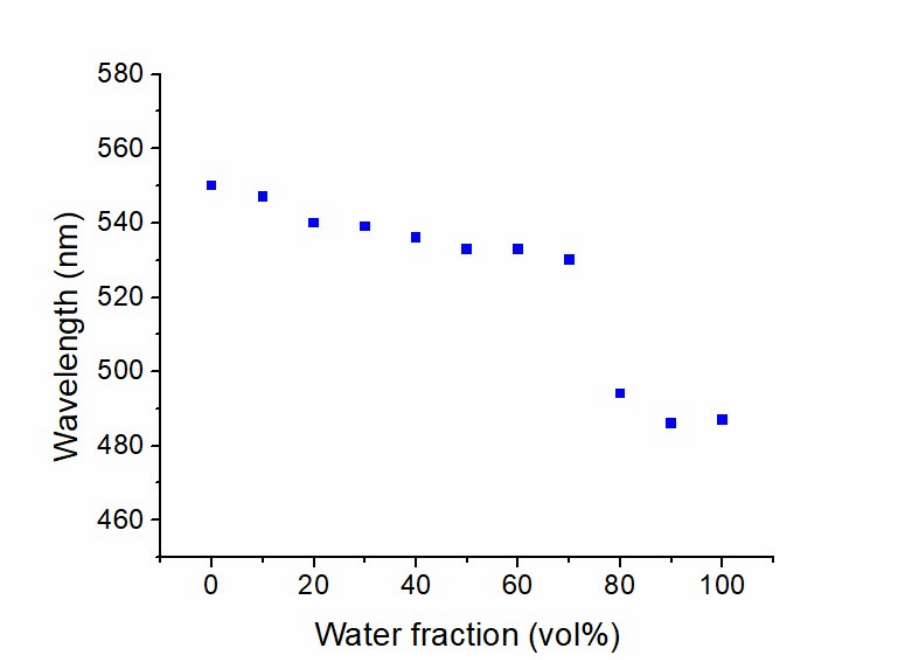

Figure S21. The wavelength of the maximum fluorescence of **Cage 1** in water/methanol mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

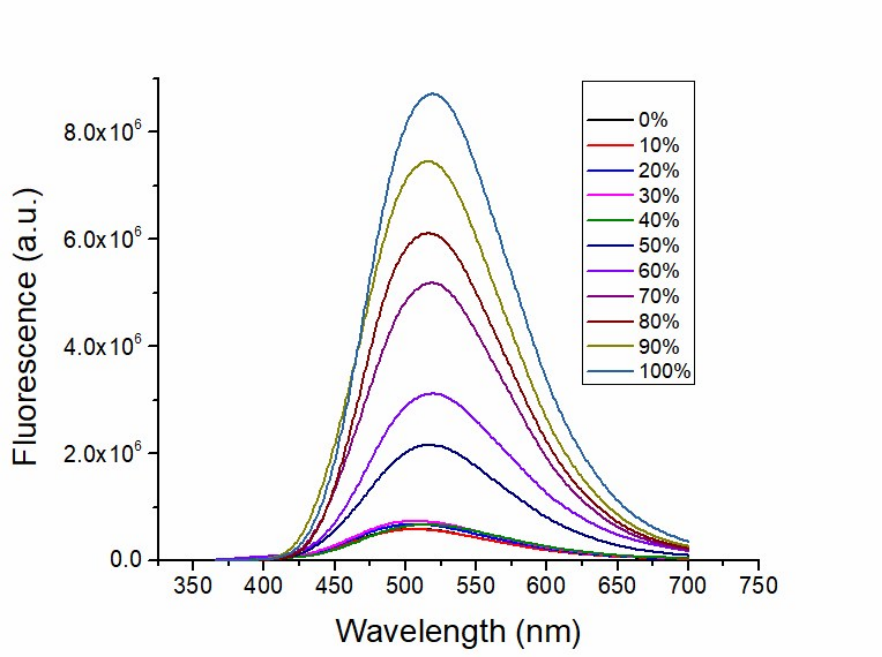

Figure 22. Fluorescence spectra of **Cage 2** in water/methanol mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

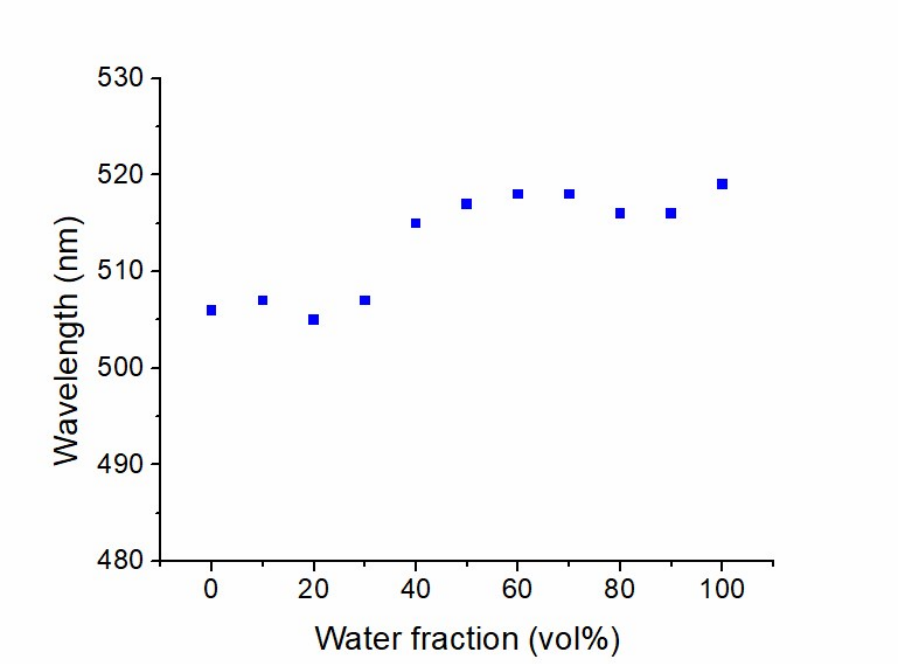

Figure S23. The wavelength of the maximum fluorescence of **Cage 2** in water/methanol mixed solvents with different water fraction. Excitation wavelength: 355 nm; concentration: 0.05 mg/mL.

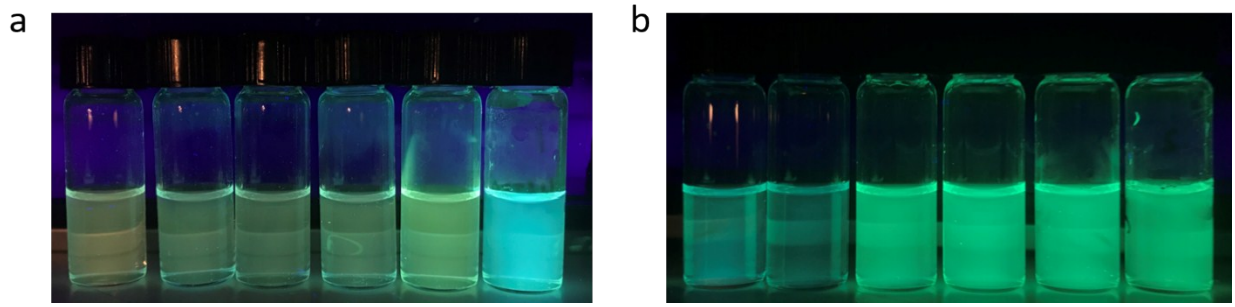

Figure S24. Photograph of **Cage 1** and **Cage 2** in methanol/water mixed solvents with different water fraction under 365 nm UV light. In each photo graph, from left to right, the water fractions are 0%, 20%, 40%, 60%, 80%, 100%.

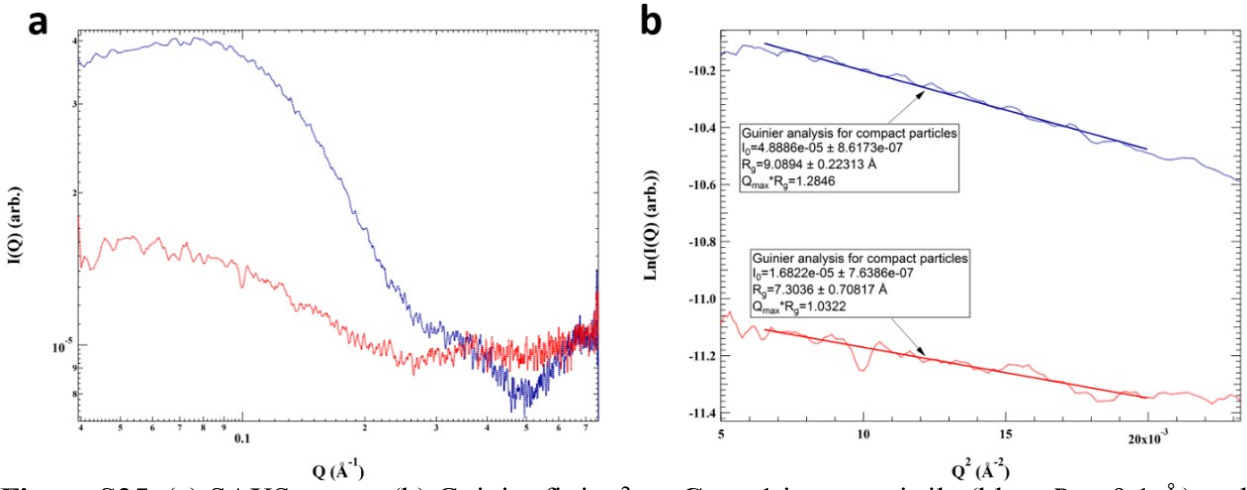

Figure S25. (a) SAXS curves (b) Guinier fitting[2] on **Cage 1** in acetonitrile (blue, R_g ~ 9.1 Å) and water (red, R_g ~ 7.3 Å) at concentration of 10 mg/mL.

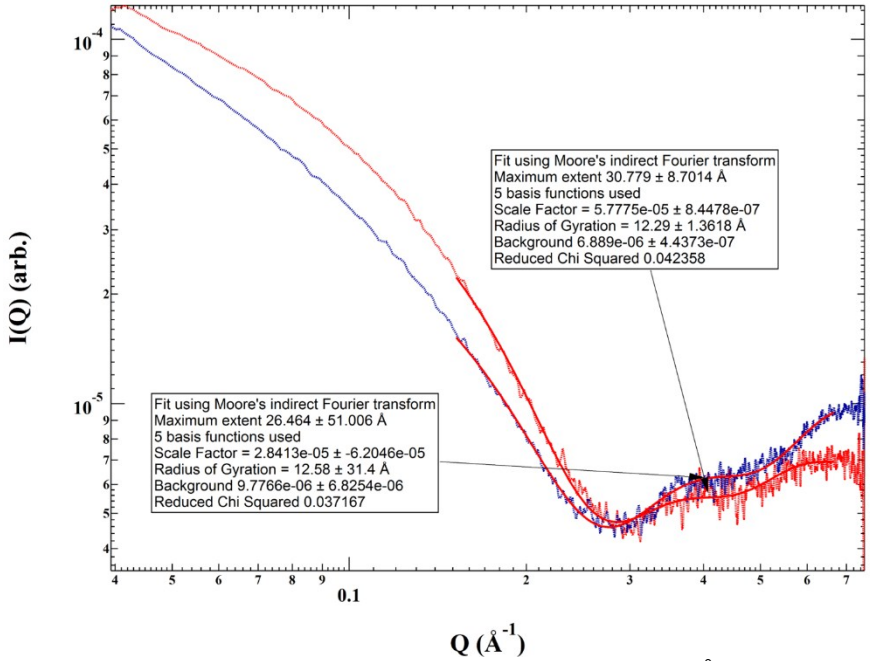

Figure S26. SAXS study on **Cage 2** in acetonitrile (red, R_g ~ 12.6 Å) and water (blue, R_g ~ 12.9 Å) at concentration of 20 mg/mL. Moore method[3] (indirect Fourier transformation) was used to fit the data instead of Guinier fitting because the high concentration causes small portion of aggregation and increases intensity in low q zone.

Table S2. Static light scattering study (Scattered intensity) on different cage solutions.

		Scattered intensity *I* (kcps)										
Water fraction[a]		0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100 %
Cage 1	Acetone -water	9	9	10	13	20	13	17	20	15	15	20
	CH_3CN -water	7	9	7	10	9	17	20	20	18	13	20
	CH_3OH -water	8	10	14	10	10	13	12	16	21	22	20
Cage 2	Acetone -water	10	14	13	20	13	14	18	19	21	13	22
	CH_3CN -water	11	13	14	19	12	17	11	19	20	22	22
	CH_3OH -water	9	10	19	20	18	18	19	18	19	22	22

[a] in volume;

[b] The size of small molecules (usually < 5 nm) cannot be precisely determined by dynamic light scattering (DLS) in a short time and therefore is not applied here. However, according to Rayleigh scattering, when the particles are much smaller (2-4 nm) than the wavelength of the laser (532 nm in our study), scattered intensity (*I*) is proportional to the sixth power of the particle size. Therefore, any large aggregation formation will be shown as great increase in *I*. In this study, all scattered intensity is as low as solvent level (3-10 kcps for different solvent composition), indicating there is no aggregation in any of the solutions.

[c] As a comparison, **Cage 2** can form assemblies/aggregations in 0.05 mg/mL ethyl acetate solution (Figure S23) with average hydrodynamic radius ~ 57 nm[4], where the solution could show high scattered intensity *I* ~ 7200 kcps.

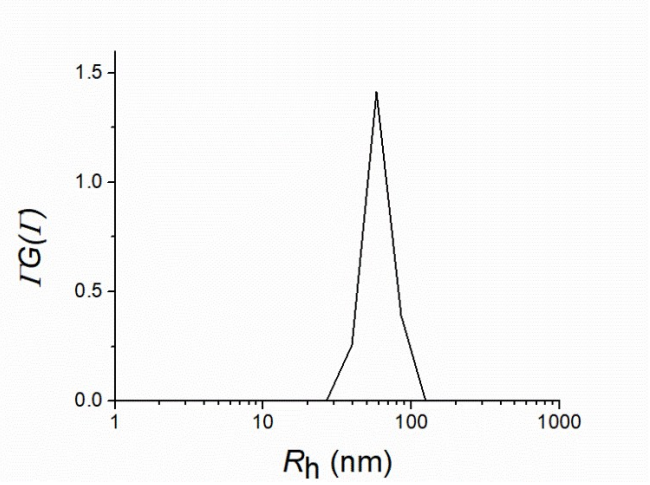

Figure S27. Size distribution of assemblies/aggregations of **Cage 2** formed in ethyl acetate. Concentration, 0.05 mg/mL.

Reference:
1. X. Yan, T. R. Cook, P. Wang, F. Huang and P. J. Stang, *Nature chemistry*, 2015, **7**, 342.
2. S. R. Kline, *J. Appl. Crystallogr.*, 2006, **39**, 895-900.
3. P. B. Moore, *J. Appl. Crystallogr.*, 1980, **13**, 168-175.
4. S. Provencher, *Biophys. J.*, 1976, **16**, 27.