Supporting Information for

Controlled oligomeric guest stacking by cucurbiturils in water

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Experimental Procedures

1/ Chemical compounds. **T-VPI** and **VPI-N** were obtained following previously described procedures.[1] D_2O, TFA (deuterated trifluoroacetic acid) and DCl in D_2O (3.5%) were purchased from commercial sources (Aldrich, Acros, ABCR or TCI) and used without further purification. HPLC grade water (purchased from Sigma-Aldrich) was used as deionized water. CB[8] was prepared according to a previous paper.[2] CB[10] was obtained following a previously described procedure.[3] Di-tolyl viologen (**TVT**) was obtained from a previously reported procedure.[4]

2/ NMR measurements. NMR measurements were recorded on Bruker AVL 300, 400 and 500 spectrometers (^{1}H-NMR 300.13, 400.13 and 500.13 MHz and ^{13}C-NMR 100.60, and 125.75 MHz). When using D_2O as the solvent (internal reference, 4.75 ppm) a watergate sequence (water suppress) was applied if necessary. Acetone was also used as internal reference for D_2O solutions (ref 2.22 ppm).[5] Splitting patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet. 2D NMR spectra (COSY and ROESY) were recorded using standard Bruker sequences. ROESY spectra for the CB[8]$_2$•**T-VPI**$_2$ complex was not attempted owing to large signals in the aromatic region usually affording spectra with no cross-peaks. Similarly, the ROESY of the CB[10]$_2$•**VPI-N**$_3$ complex was not recorded for the same reason, but ROESY was obtained for this complex in acidic conditions (sharper peaks compared to neutral conditions, see Figure S33).

3/ ITC measurements. Isothermal Titration Calorimetry (ITC) was performed on a Malvern MicroCal PEAQ-ITC at 25 °C. A 1 mM stock solution of **VPI-N** (syringe) was diluted in HPLC grade water (cell) for investigating dimer formation. Results were analyzed using the Malvern MicroCal PEAQ-ITC Analysis Software 1.1.0.1262 considering the dissociation model. For **T-VPI** (1 mM, syringe), titrations were performed with CB[8] solutions at 40 μM in HPLC grade water (cell). For **VPI-N** (1 mM, syringe), titrations were performed with CB[8] solutions at 40 μM in HPLC grade water (cell). Results were analyzed using the Malvern MicroCal PEAQ-ITC Analysis Software 1.1.0.1262 considering the one set of sites binding model. The reduced Chi square value [(kJ/mol)^2] for each titration is indicated hereafter: **VPI-N** dilution: 0.036, **T-VPI** with CB[8]: 0.353, **VPI-N** with CB[8]: 0.385.

4/ Absorption and fluorescence spectroscopies. UV-visible absorption spectra were recorded in spectrophotometric grade water (*ca*. 10^{-5} M) on a VARIAN CARY 50 SCAN spectrophotometer at room temperature with a 300 nm/min scan rate. Emission spectra were measured using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter equipped with a three-slit double-grating excitation and a spectrograph emission mono-chromator with dispersions of 2.1 nm.mm^{-1} (1200 grooves per mm). A 450 W xenon continuous wave lamp provided excitation. The luminescence of diluted solutions was detected at right angle using 10 mm quartz cuvettes.
Excitation: the luminescence of diluted solutions was detected at right angle using 10 mm quartz cuvettes. Fluorescence quantum yields Φ were measured in diluted absolute ethanol solution with an optical density lower than 0.1 using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{A_r(\lambda)}{A_x(\lambda)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{D_x}{D_r}\right)$$

where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. “r” and “x” stand for reference and sample. The fluorescence quantum yields were measured relative to anthracene in ethanol (Φ = 27%). Excitation of reference and sample compounds was performed at the same wavelength, *ie*. 290 nm for **T-VPI** and 310 nm for **VPI-N** and **T-V-T**.

Additional data

5/ ^{1}H NMR spectrum of T-VPI

^{1}H NMR (300 MHz, D_2O) δ 9.38 (d, *J* = 7.1 Hz, 2H, ***H5***), 9.32 (d, *J* = 7.1 Hz, 2H, ***H2***), 8.74 (d, *J* = 7.0 Hz, 2H, ***H4***), 8.69 (d, *J* = 7.0 Hz, 2H, ***H3***), 8.31 (d, *J* = 8.8 Hz, 2H, ***H7***), 7.96 (d, *J* = 8.8 Hz, 2H, ***H6***), 7.68 (dd, *J* = 5.8, 2.8 Hz, 4H, overlapped signals of ***Hy*** and ***H8***), 7.57 (d, *J* = 8.2 Hz, 2H, ***Hx***), 7.32 (dd, *J* = 6.1, 3.2 Hz, 2H, ***H9***), 2.47 (s, 3H, ***H1***).

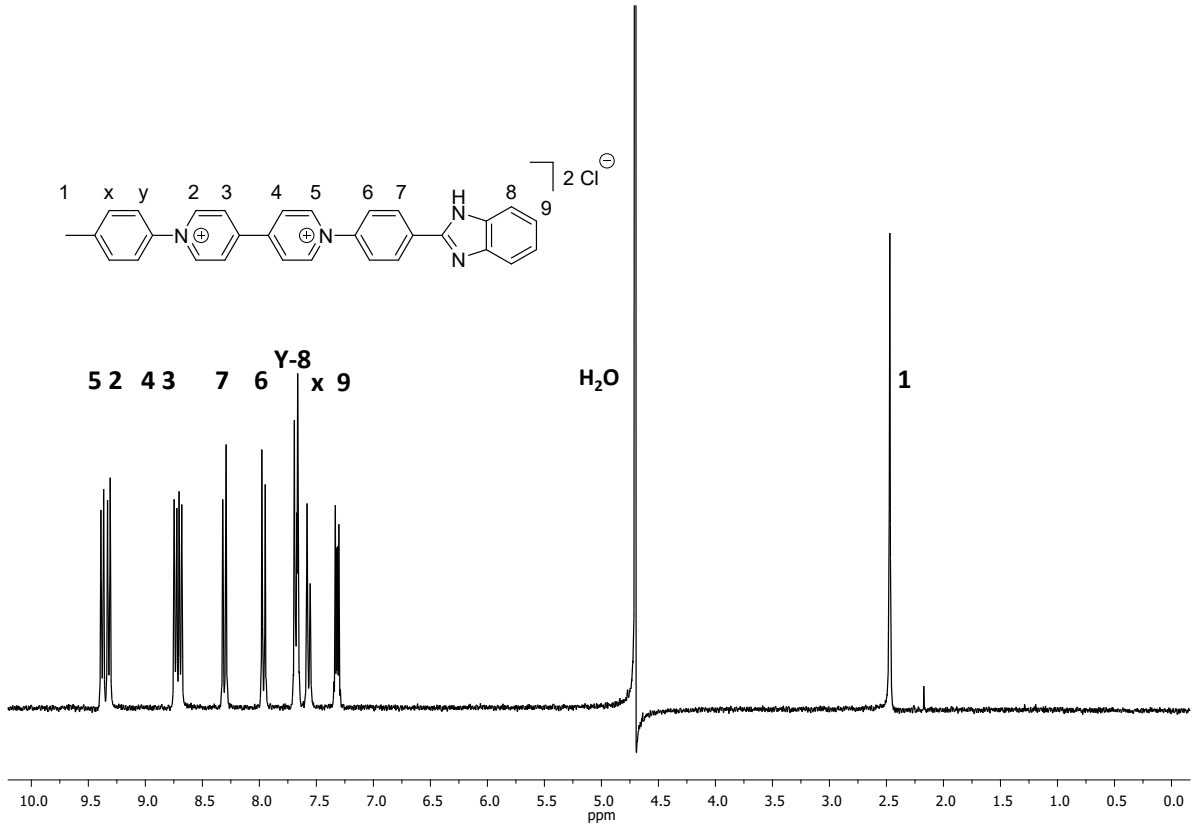


Figure S1. ^{1}H NMR spectrum (300 MHz, D_2O, 298 K, 1 M) of compound **T-VPI**.

6/ ^{1}H NMR spectrum of VPI-N

^{1}H NMR (500 MHz, D_2O) δ 8.95 (d, *J* = 5.0 Hz, 2H, ***H5***), 8.76 (d, *J* = 5.9 Hz, 2H, ***H2***), 8.19 (d, *J* = 5.0 Hz, 2H, ***H4***), 8.13 (d, *J* = 5.6 Hz, 2H, ***H3***), 8.08 (d, *J* = 8.0 Hz, 2H, ***H7***), 7.90 (br s, 2H, ***H8***), 7.73 (br s, 2H, ***H9*** or ***H10***), 7.67 (d, *J* = 8.2 Hz, 2H, ***H6***), 7.18 (m, 2H, ***H9*** or ***H10***), 4.31 (s, 3H, ***H1***).

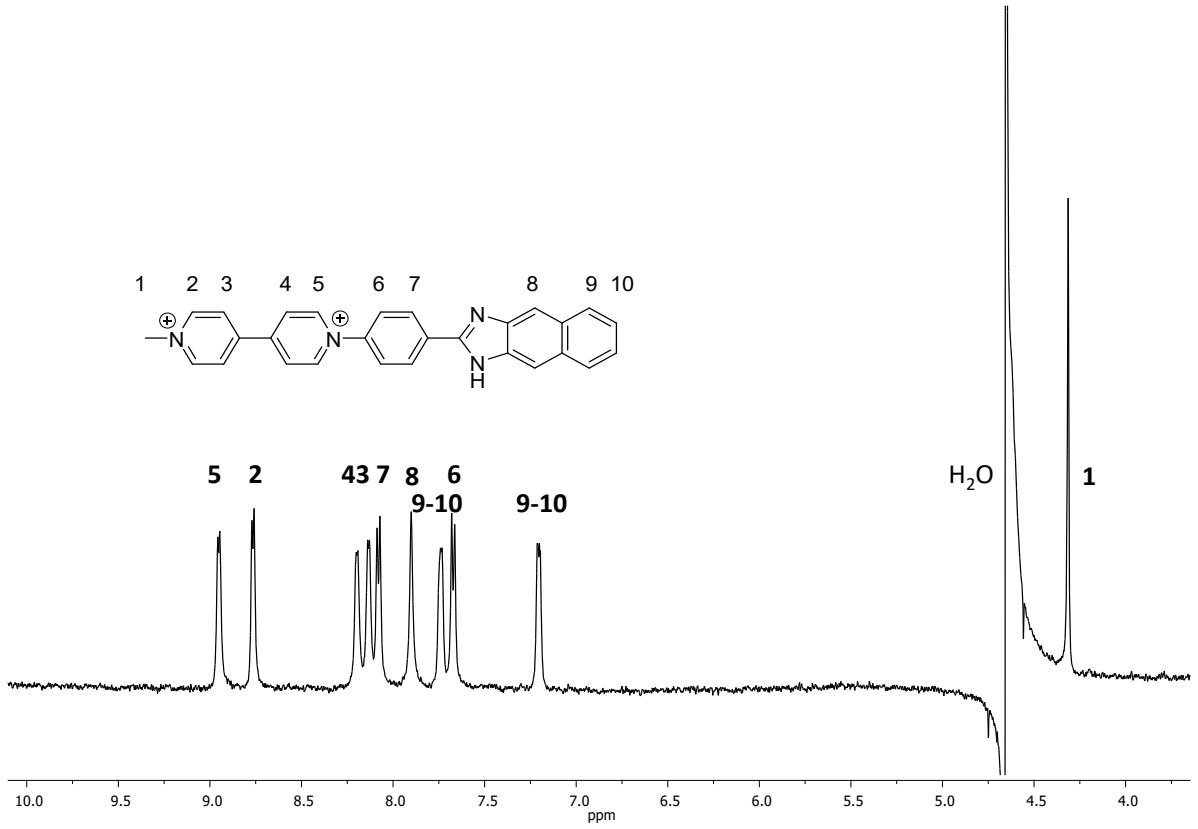


Figure S2. ^{1}H NMR spectrum (300 MHz, D_2O, 298 K, 0.33 M) of compound **VPI-N**.

7/ NMR and ITC study of VPI-N dimerization

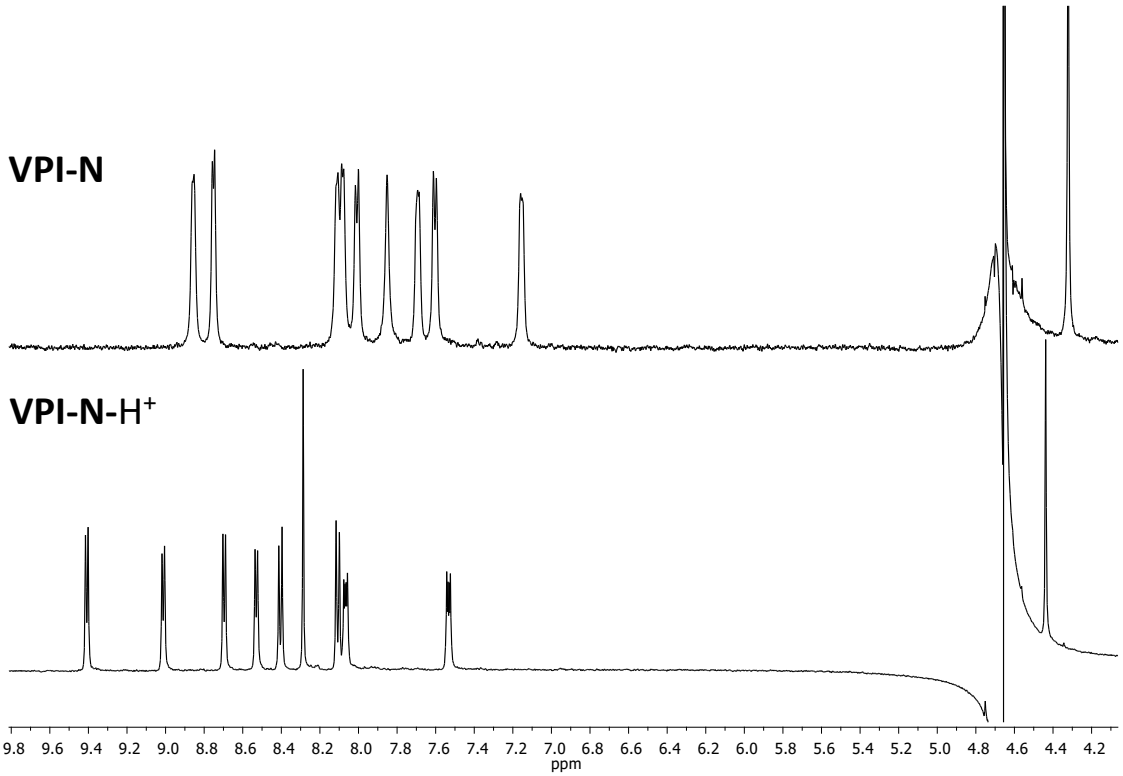


Figure S3. ^{1}H NMR spectra of **VPI-N** alone in D_2O (top) and in the presence of TFA (bottom).

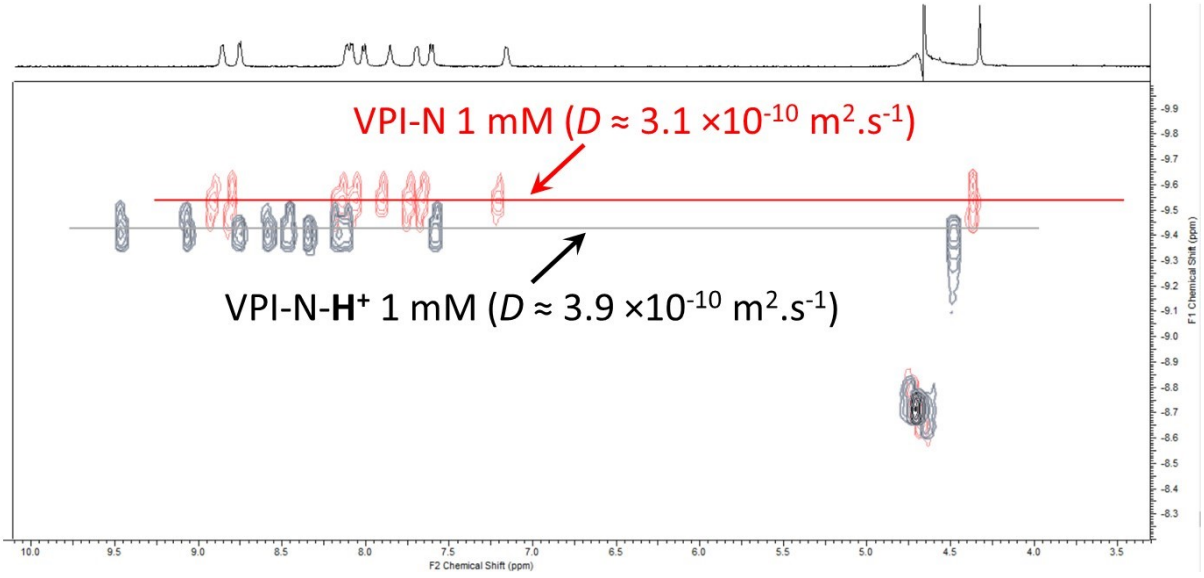


Figure S4. DOSY NMR spectra (500 MHz, D_2O, 300 K) of **VPI-N** in D_2O (top) and in the presence of deuterated-TFA (bottom).

Concentration (M)	Chemical shift (ppm)
0.000039	9.235
0.000048	9.175
0.000077	9.13
0.000113	9.108
0.00018	9.036
0.000333	8.952
0.00057	8.874
0.00075	8.834
0.001	8.806
0.002	8.658
0.003	8.646
0.004	8.585

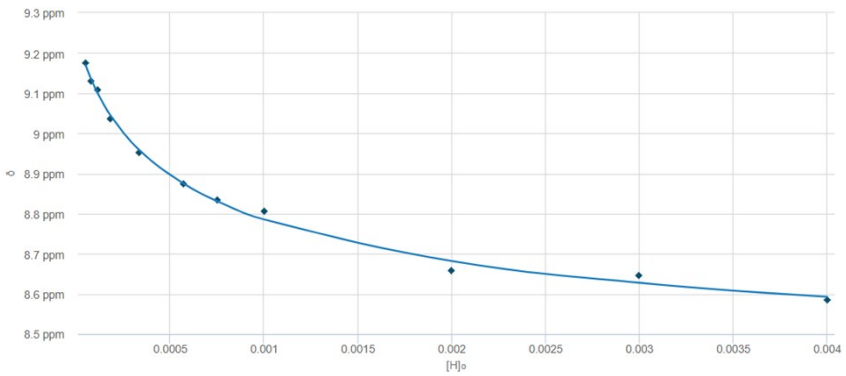
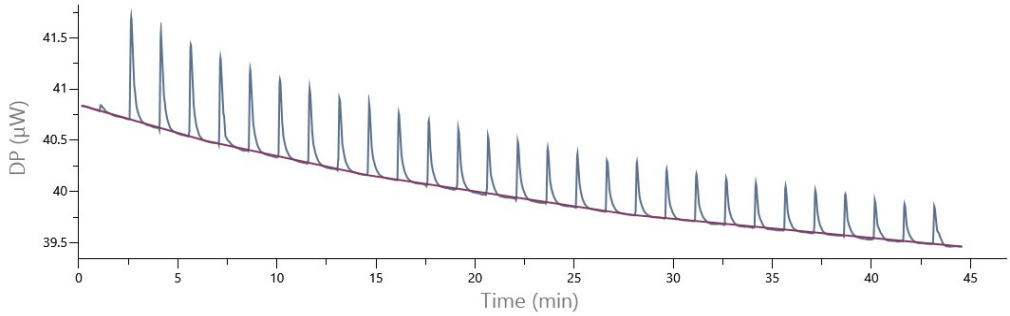


Figure S5. Evolution of the chemical shift of the ^{1}H NMR signal of proton H5 in D_2O (500 MHz, 300 K) as a function of **VPI-N** concentration (in mol.L^{-1}).



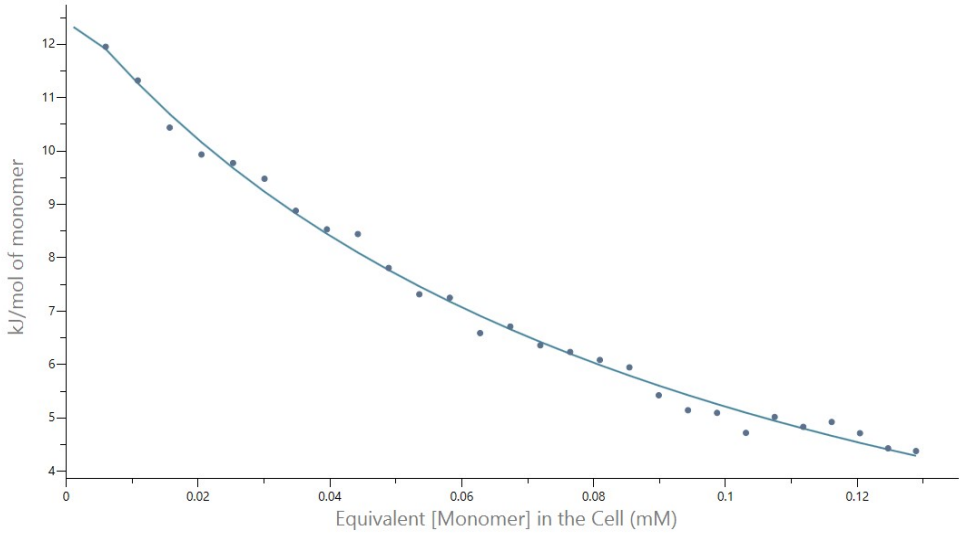


Figure S6. ITC thermogram corresponding to the dilution of a 1 mM solution of **VPI-N** in water.

8/ ^{1}H NMR titration of T-VPI with CB[8]

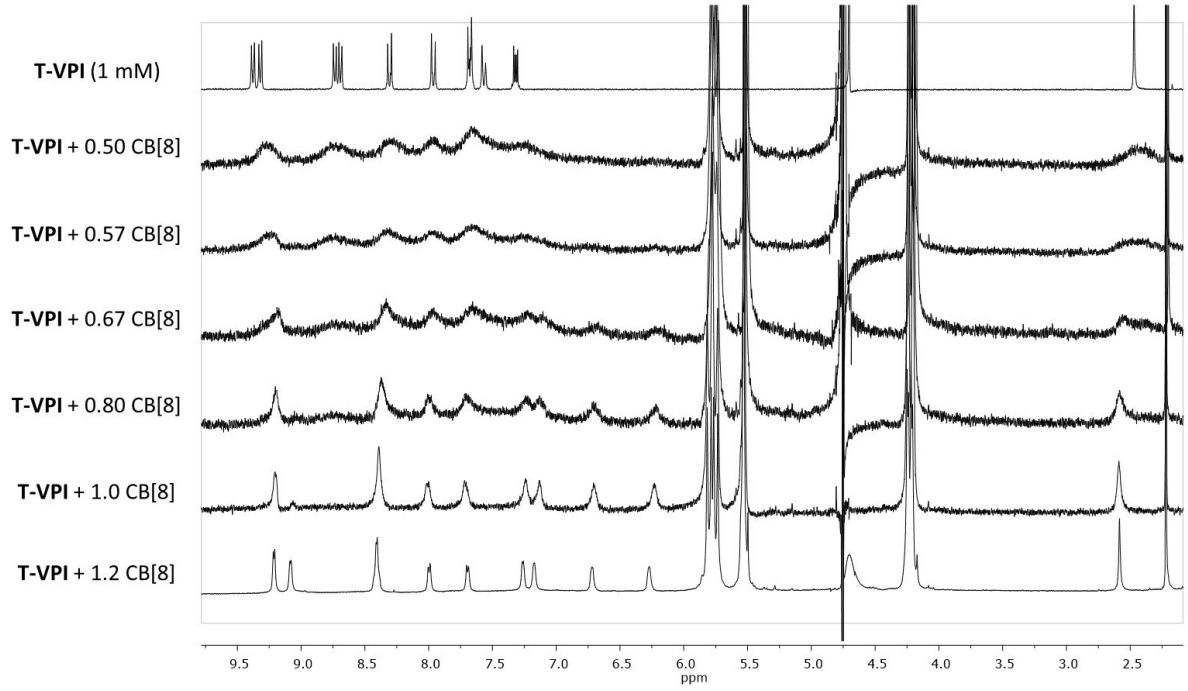


Figure S7. ^{1}H NMR (500 MHz, D_2O, 298 K, 0.45 mM) of compound $CB[8]_2$•**T-VPI**$_2$.

9/ 1H NMR titration of VPI-N with CB[8]

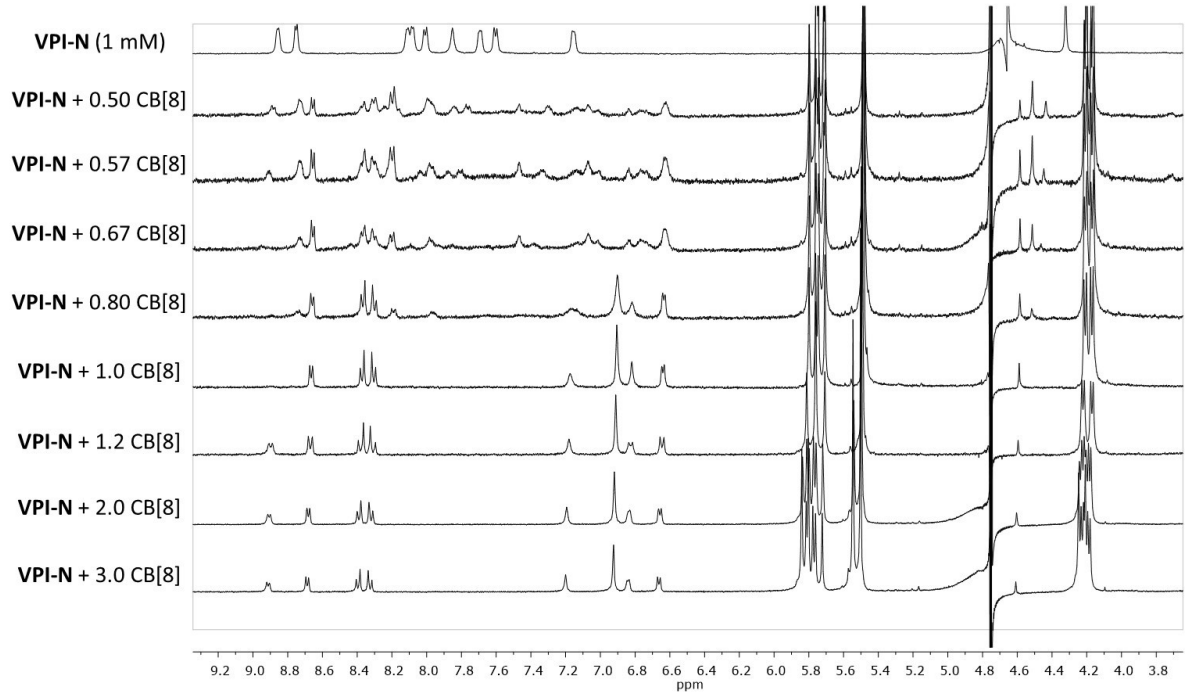


Figure S8. ^{1}H NMR (500 MHz, D_2O, 298 K, 0.45 mM) of compound $CB[8]_2$•**VPI-N**$_2$.

10/ Preparation and NMR spectra of CB[8]$_2$•T-VPI$_2$

A 0.45 mM solution of CB[8]$_2$•**T-VPI**$_2$ was prepared from a mixture of 0.84 mg of solid CB[8] (6.3×10^{-7} mol, 1.2 equiv.), 263 µL of a 2 mM stock solution of **T-VPI** (5.3×10^{-7} mol in D_2O and 370 µL of D_2O. Acetone was used as internal reference (2.22 ppm).
According to the integral value of signals ***H5*** (9.19 ppm, I = 4.00) and the integral value of CB[8] protons (5.83-5.69 ppm, I = 44.20), a CB[8]/**T-VPI** ratio of 2.76/2 is determined.
^{1}H NMR (500 MHz, D_2O) δ 9.19 (br s, 4H, ***H5***), 9.05 (br s, 4H, ***H2***), 8.38 (br s, 8H, overlapped signals of ***H6*** and ***H7***), 8.01 (br s, 4H, ***Hy***), 7.68 (br s, 4H, ***Hx***), 7.22 (s, 4H, ***H4***), 7.11 (s, 4H, ***H3***), 6.69 (s, 4H, ***H8*** or ***H9***), 6.21 (s, 4H, ***H8*** or ***H9***), 5.83 – 5.69 (m, 32H, CB[8]), 5.52 (s, 32H, CB[8]), 4.17 (app t, *J* = 37.3 Hz, 32H, CB[8]), 2.59 (br s, 6H, ***H1***), 2.22 (acetone, ref).

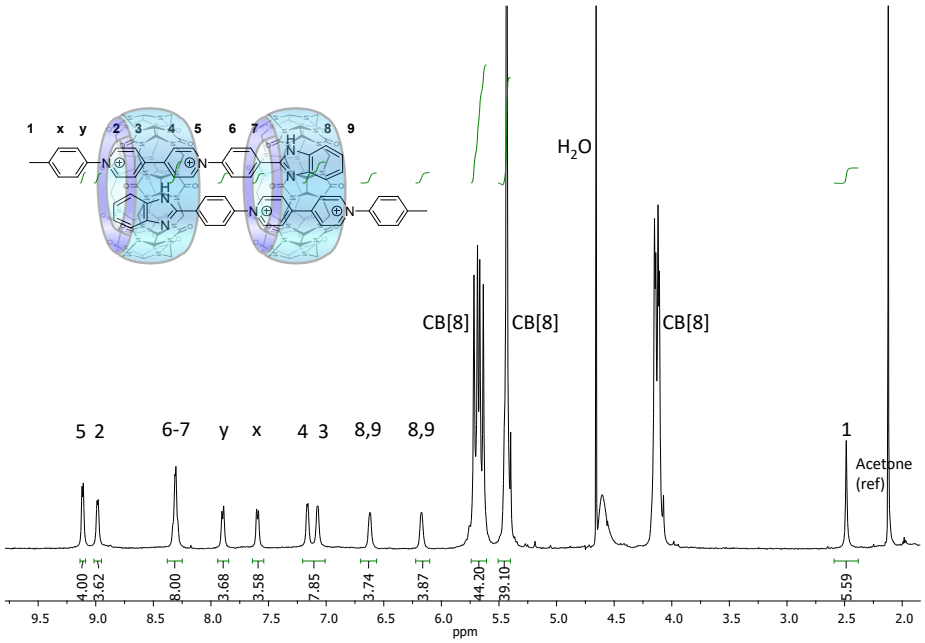


Figure S9. ^{1}H NMR (500 MHz, D_2O, 298 K, 0.45 mM) of compound CB[8]$_2$•**T-VPI**$_2$.

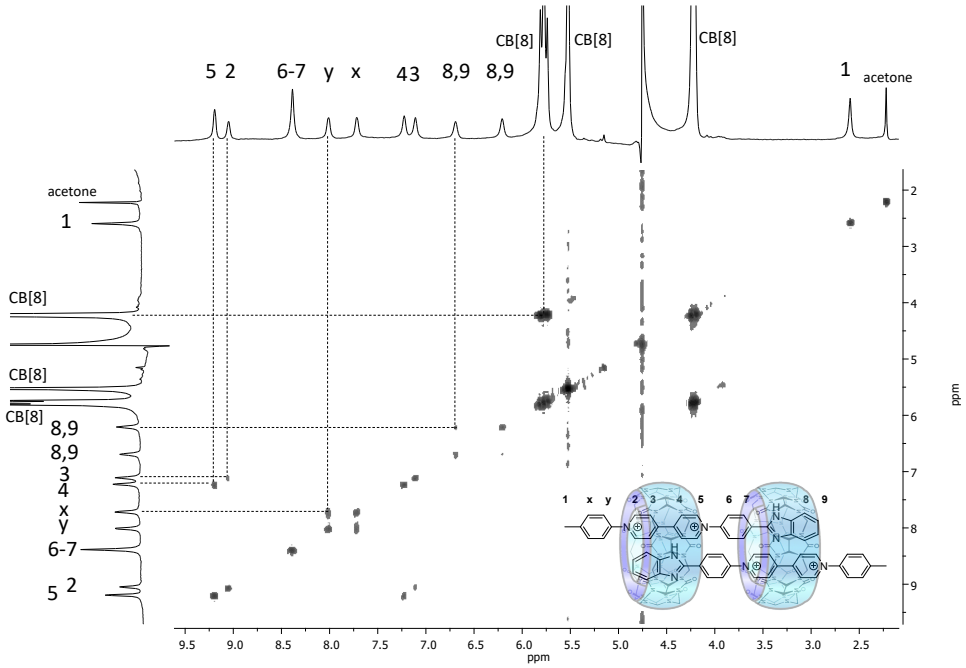


Figure S10. COSY NMR (500 MHz, D_2O, 298 K, 0.45 mM) of compound CB[8]$_2$•**T-VPI**$_2$.

11/ Preparation and NMR spectra of CB[8]$_2$•VPI-N$_2$

A 0.45 mM solution of CB[8]$_2$•**VPI-N$_2$** was prepared from a mixture of 0.74 mg of solid CB[8] (5.6×10^{-7} mol, 1.2 equiv.), 115 µL of a 4 mM stock solution of **VPI-N** (4.6×10^{-7} mol) in D_2O and 440 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

According to the integral value of signals ***H5*** (8.90 ppm, I = 4.00) and the integral value of CB[8] protons (5.75 ppm, I = 37.82), a CB[8]/**VPI-N** ratio of 2.36/2 is determined.

^{1}H NMR (500 MHz, D_2O) δ 8.90 (d, *J* = 5.9 Hz, 4H, ***H5***), 8.68 (d, *J* = 6.3 Hz, 4H, ***H2***), 8.39 (d, *J* = 8.4 Hz, 4H, ***H6*** or ***H7***), 8.32 (d, *J* = 8.4 Hz, 4H, ***H6*** or ***H7***), 7.19 (s, 4H, ***H8***), 6.91 (br s, 8H, overlapped signals of ***H9*** and ***H10***), 6.82 (d, *J* = 6.1 Hz, 4H, ***H4***), 6.65 (d, *J* = 6.2 Hz, 4H, ***H3***), 5.75 (dd, *J* = 26.9, 15.4 Hz, 32H, CB[8]), 5.49 (s, 32H, CB[8]), 4.60 (s, ***H1***), 4.19 (dd, *J* = 15.4, 6.3 Hz, 32H, CB(8]), 2.22 (acetone, ref).

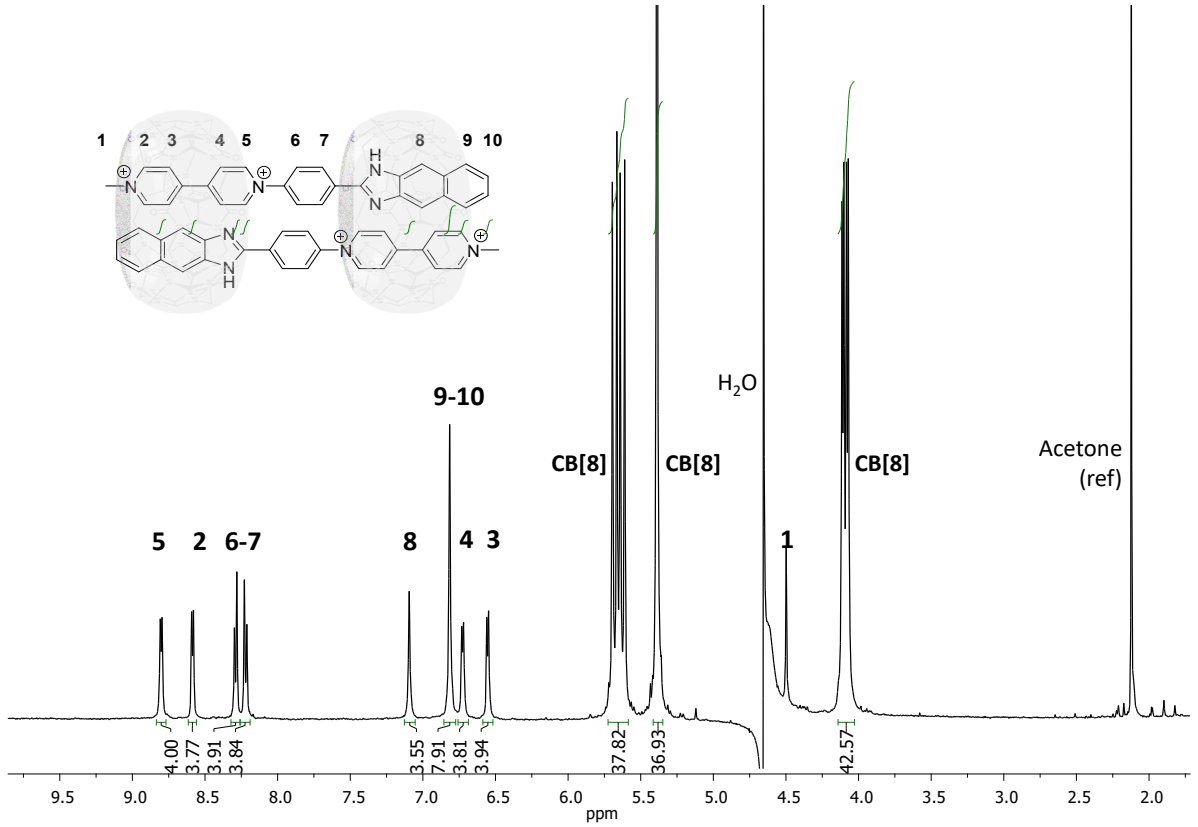


Figure S11. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 0.45 mM) of compound CB[8]$_2$•**VPI-N$_2$**.

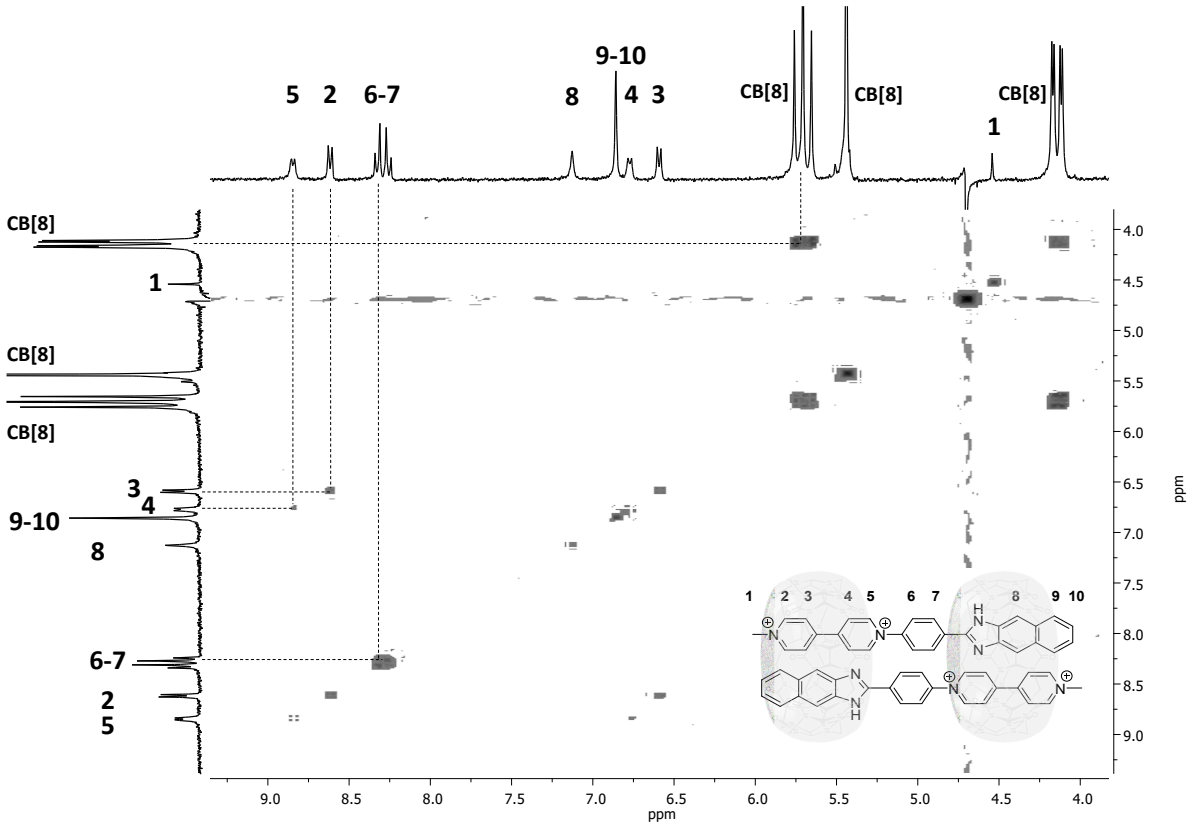


Figure S12. COSY NMR (300 MHz, D_2O, 298 K, 0.45 mM) of compound $CB[8]_2$•**VPI-N$_2$**.

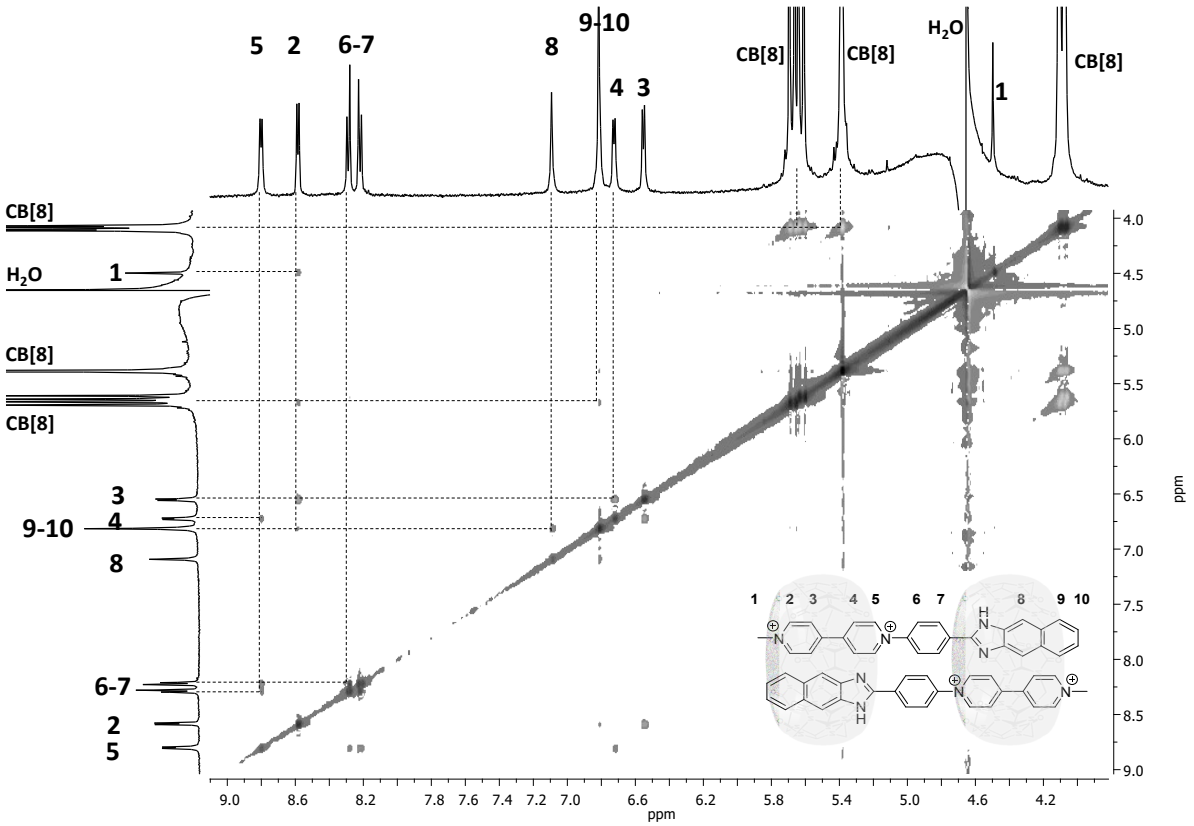


Figure S13. ROESY NMR (500 MHz, D_2O, 298 K, 0.45 mM, mixing time: 400 ms) of compound $CB[8]_2$•**VPI-N$_2$**.

12/ Preparation and NMR spectra of T-VPI with CB[10]

A solution of **T-VPI** with CB[10] was prepared from a mixture of 0.47 mg of solid CB[10] (2.7×10^{-7} mol, 1.1 equiv.), 125 µL of a 2 mM stock solution of **T-VPI** (2.5×10^{-7} mol) in D_2O and 400 µL of D_2O.

^{1}H NMR (500 MHz, D_2O, 298 K, Figure S12) δ 5.8 (br s, CB[10]), 5.5 (br s, CB[10]), 4.1 (br s, CB[10]).

^{1}H NMR (500 MHz, D_2O, 340 K, Figure S13) δ 8.86 (br s), 8.14 (br m), 7.81 (br s), 7.61 (br s), 7.48 – 7.16 (br m), 6.78 (br s), 5.80 (app d, *J* = 15.0 Hz, CB[10]), 5.50 (s, CB[10]), 4.26 – 4.20 (m, CB[10]), 2.35 (br s, ***H1***).

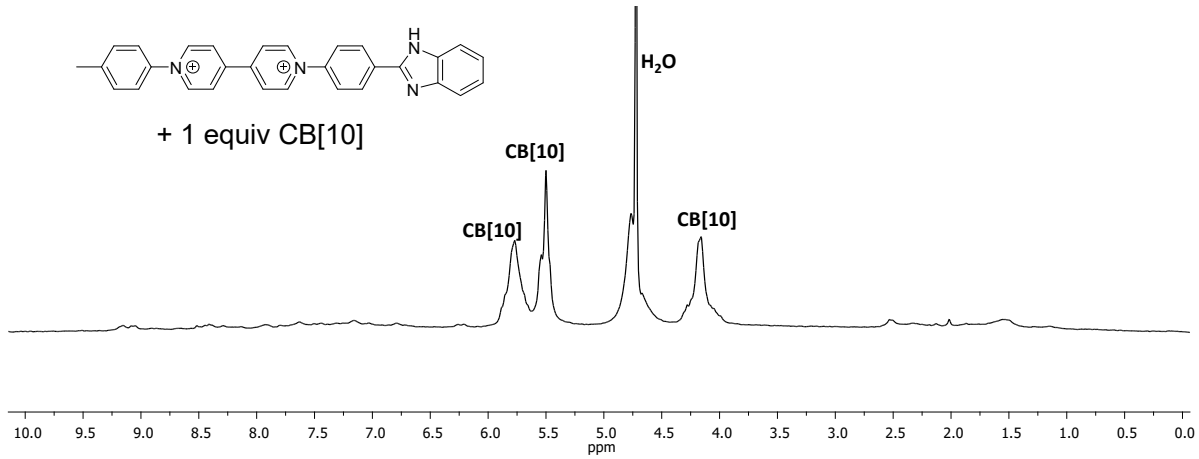


Figure S14. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 0.5 mM) of **T-VPI** with CB[10].

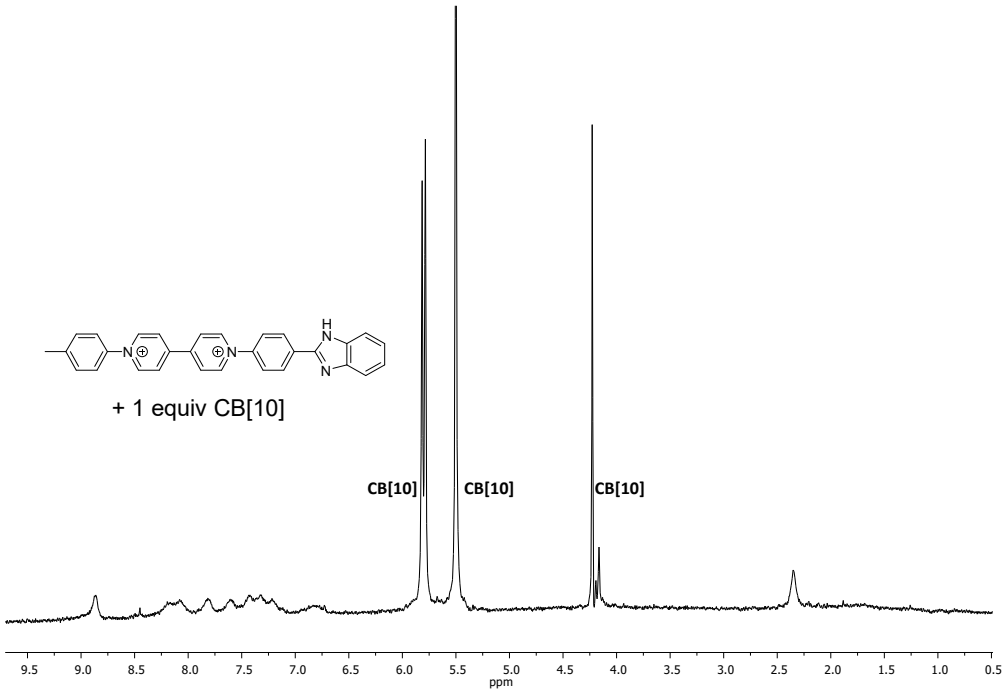


Figure S15. ^{1}H NMR spectrum (500 MHz, D_2O, 340 K, 0.5 mM) of **T-VPI** with CB[10].

13/ Preparation and NMR spectra of CB[10]$_2$•VPI-N$_3$

A 0.17 mM solution of CB[10]$_2$•**VPI-N$_3$** was prepared from a mixture of 0.46 mg of solid CB[10] (2.8×10^{-7} mol, 1.0 equiv.), 68 µL of a 4 mM stock solution of **VPI-N** (2.8×10^{-7} mol) in D_2O and 500 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

^{1}H NMR (300 MHz, 298 K, D_2O) δ 8.66 (d, *J* = 6.6 Hz, 4H, ***H5a***), 8.61 (d, *J* = 6.4 Hz, 4H, ***H2a***), 8.45-8.38 (m, 2H, ***H5b***), 8.23 (d, *J* = 5.0 Hz, 2H, ***H2b***), 8.15 (d, *J* = 8.7 Hz, 4H, ***H7a***), 7.81-7.92 (m, 6H, ***H7b*** and ***H6a***), 7.49 (d, *J* = 5.0 Hz, 2H, ***H6b***), 6.95-7.15 (br m), 6.94-6.80 (br m), 5.78 (app ddd, *J* = 17.9, 17.0, 10.7 Hz, 40H, CB[10]), 5.50 (app d, 40H, CB[10]), 4.53 (br s, ***H1a***), 4.47 (br s, ***H1b***), 4.30-4.06 (m, 40H, CB[10]), 2.22 (acetone, ref). Signals ***H3a-b***, ***H4a-b***, ***H8a-b***, ***H9a-b*** and ***H10a-b*** were not identified on the ^{1}H NMR spectrum at 298 K (300 or 500 MHz).
According to the integral value of signals ***H5a + H5b*** (8.67 ppm, I = 3.78 and 8.33 ppm, I = 1.93) and the integral value of CB[10] protons (5.92-5.69 ppm, I = 40.00), a CB[10]/**VPI-N** ratio of 2.1/3 is determined.

^{1}H NMR (500 MHz, 340 K, D_2O) δ 8.67 (d, *J* = 6.3 Hz, 4H, ***H5a***), 8.52 (d, *J* = 6.1 Hz, 4H, ***H2a***), 8.33 (d, *J* = 5.9 Hz, 2H, ***H5b***), 8.18 (d, *J* = 8.4 Hz, 4H, ***H7a***), 8.14 (d, *J* = 6.3 Hz, 2H, ***H2b***), 7.87 (two d, *J* = 11.6, 8.7 Hz, 6H, overlapped signals of ***H7b*** and ***H6a***), 7.54 (d, *J* = 8.4 Hz, 2H, ***H6b***), 7.08 (d, *J* = 6.2 Hz, 4H, ***H4a***), 7.00 (d, *J* = 6.2 Hz, 4H, ***H3a***), 6.88 (d, *J* = 8.5 Hz, 4H, ***H9a***), 6.79 (d, *J* = 6.0 Hz, 2H, ***H4b***), 6.74 (d, *J* = 6.2 Hz, 2H, ***H3b***), 6.59 (s, 4H, ***H10a***), 5.92 – 5.69 (m, 40H, CB[10]), 5.59 – 5.40 (m, 40H, CB[10]), 4.53 (br s, ***H1a***), 4.43 (br s, ***H1b***), 4.18 (app ddd, *J* = 39.1, 19.6, 11.9 Hz, 40H, CB[10]), 2.22 (acetone, ref). Signals ***H8a***, ***H8b***, ***H9b*** and ***H10b*** were not identified on the ^{1}H NMR spectrum at 340 K (500 MHz).

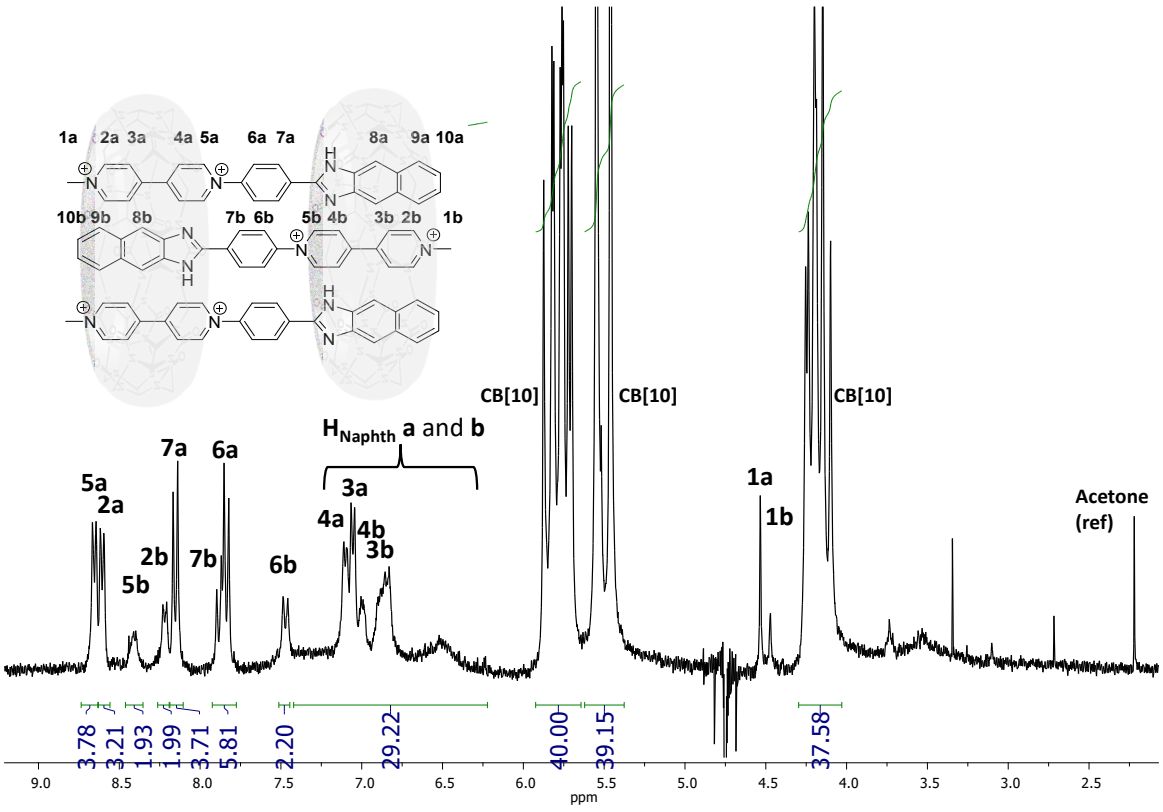
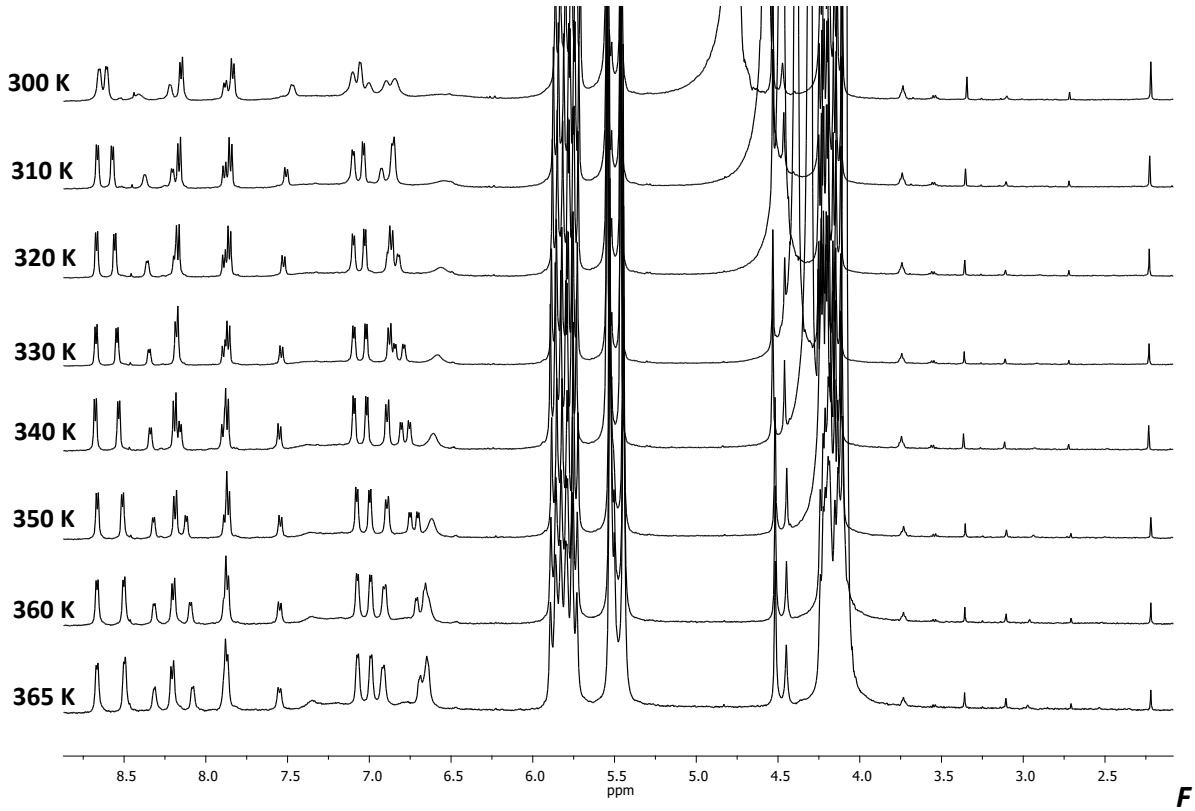


Figure S16. ^{1}H NMR spectrum (300 MHz, D_2O, 298 K, 0.17 mM) of CB[10]$_2$•**VPI-N$_3$**.



F igure S17. ^{1}H NMR spectra (500 MHz, D_2O, 300-365 K, 0.17 mM, ref. acetone 2.22 ppm) of CB[10]$_2$•**VPI-N$_3$**.

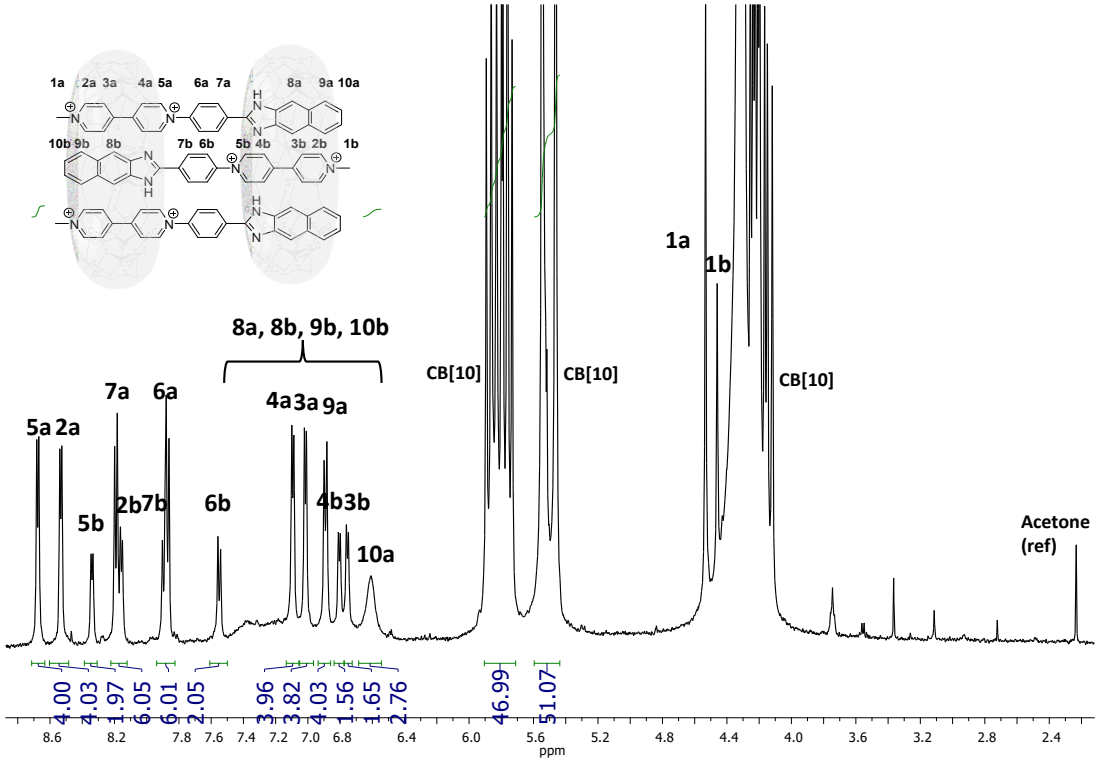


Figure S18. ^{1}H NMR (500 MHz, D_2O, 340 K, 0.17 mM, ref. acetone 2.22 ppm) of CB[10]$_2$•**VPI-N$_3$**.

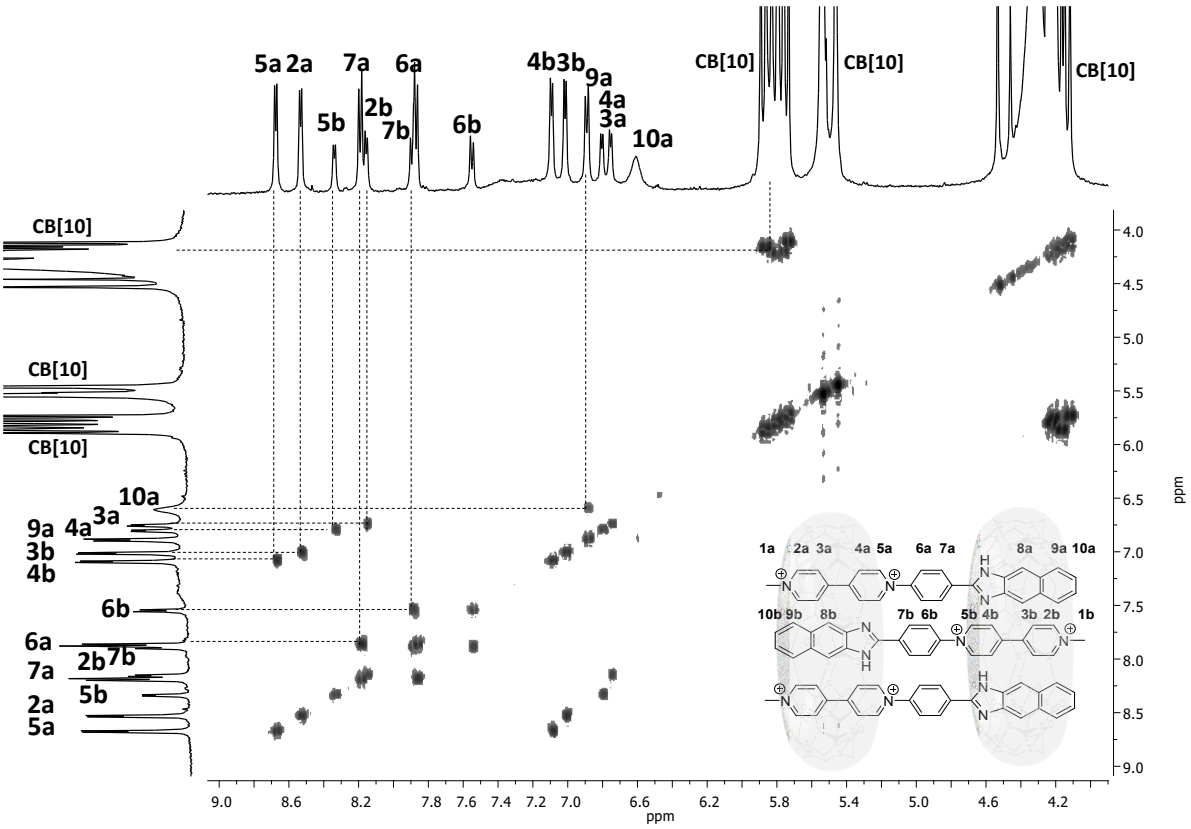


Figure S19. COSY NMR (500 MHz, D_2O, 340 K, 0.17 mM) of $CB[10]_2$•**VPI-N$_3$**.

14/ ITC study of VPI-N with CB[8]

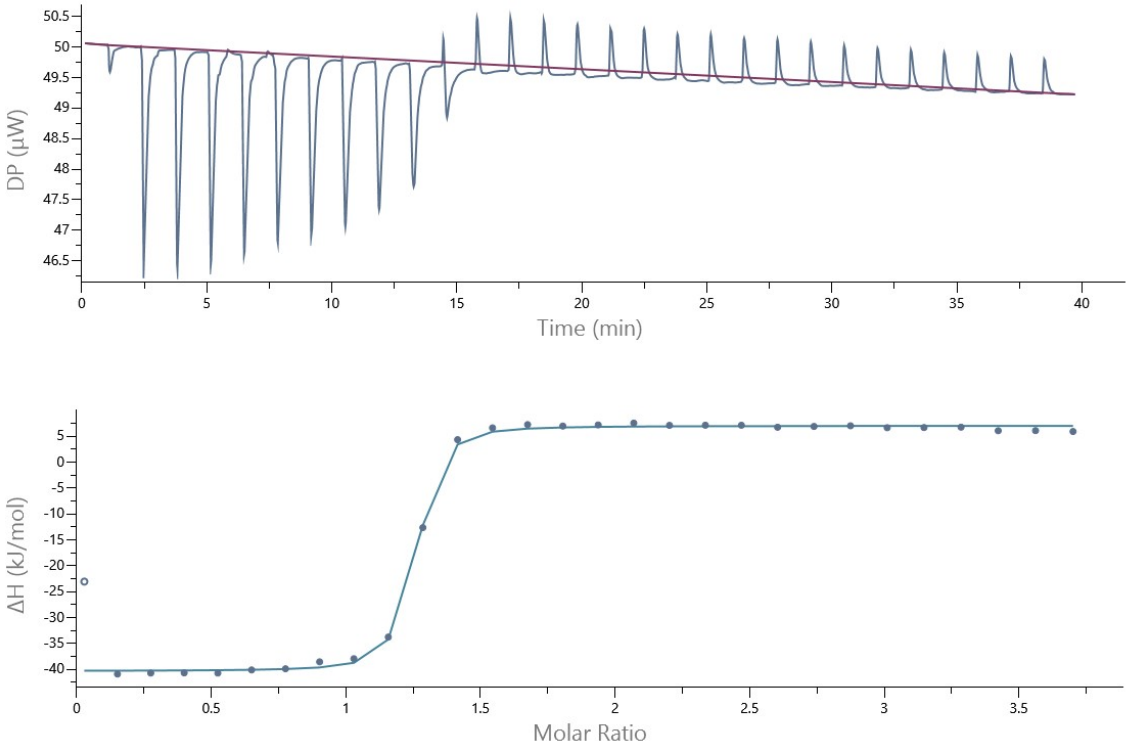


Figure S20. ITC thermogram corresponding to a solution of **VPI-N** titrated with CB[8] in water.

15/ Competition NMR for the determination of binding constants

The binding constants corresponding to the formation of CB[8]$_2$•**T-VPI$_2$** and CB[8]$_2$•**VPI-N$_2$** were evaluated using ^{1}H NMR in the presence of a competitor guest, following the procedure of Macartney and co-workers,[6] expended to CB[8] 2:2 complexes.[7] The NMR spectra were collected at 298 K on a Bruker AC500 (64 scans) from 1 mM solutions of **T-VPI** or **VPI-N** in the presence of 1 equiv. of CB[8] and 1 equiv. of competitor in D_2O (Figures S28 to S31). The first competitor guest was 1-adamantylamine•HCl (**Ad**). The binding constant correspond to formation of the CB[8]•**Ad** complex ($8.19 \pm (1.75) \times 10^8$ M^{-1}, **R1** and **Eq1**) was reported in the literature.[8] The chemical shifts of the free **Ad** and CB[8]•**Ad** were determined in D_2O from 1 mM solutions (Figure S29). The limiting chemical shift values, $\Delta\delta_{lim}$, for **Ad** and CB[8]•**Ad** were measured according to the chemical shifts of CH protons (Table S1). Then, ^{1}H NMR spectra of a mixture of **T-VPI** (1 equiv.), with CB[8] (1 equiv.) and **Ad** (1 equiv.) were recorded to determine the chemical shifts of CH protons of **Ad** (Table S2, **R3** and **Eq3**). Chemical resonances for free and complexed **Ad** suggest fast exchange on the NMR timescale (Figure S29). Following the method of Macartney et al,[6] the binding constant corresponding to the formation of the complex from CB[8] and **T-VPI** was calculated from the chemical shifts of the competitive spectra and $\Delta\delta_{lim}$ (Table S1) and considering equation **Eq4**.

On the other hand, since 1-adamantylamine•HCl (**Ad**) presents a too low CB[8] binding constant compared to **VPI-N**, we used memantine (3,5-dimethyladamantylamine•HCl, **diMeAd**) as competitor to evaluate the binding constant for CB[8]$_2$•**VPI-N$_2$** (Figures S30-31). The binding constant of CB[8] toward **diMeAd$_2$** is 4.3×10^{11} M^{-1}.[8] Because the ^{1}H NMR signals of free/complexed **VPI-N**/**diMeAd** were not clear in the aromatic and aliphatic regions (Figure S30), we evaluated the CB[8]$_2$•**VPI-N$_2$** binding constant from the integral values of the CB[8] at 5.540 and 5.490 ppm, assigned to CB[8]•**diMeAd** and CB[8]$_2$•**VPI-N$_2$**, respectively (Figure S31). The results are presented in (Table S2).

Preparation of the **Ad**/**T-VPI**/CB[8] competition solution (Figures S28-29) :

A solution of **Ad**/**T-VPI**/CB[8] was prepared from a mixture of 0.81 mg of solid CB[8] (6.1×10^{-7} mol, 1 equiv.), 304 µL of a 2 mM solution of **T-VPI** (6.1×10^{-7} mol, 1equiv.) in D_2O, 122 µL of a 5 mM solution of **Ad** in D_2O (6.1×10^{-7} mol) and 200 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

Preparation of the **diMeAd**/**VPI-N**/CB[8] competition solution (Figures S30-31) :

A solution of **diMeAd**/**VPI-N**/CB[8] was prepared from a mixture of 0.54 mg of solid CB[8] (4.1×10^{-7} mol, 1 equiv.), 102 µL of a 4 mM stock solution of **VPI-N** (4.1×10^{-7} mol, 1equiv.) in D_2O, 82 µL of a 5 mM solution of **diMeAd** in D_2O (4.1×10^{-7} mol) and 250 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

Table S1. ^{1}H NMR results considering the **Ad**/**T-VPI** competition toward CB[8].

Ratios of **Ad**/**T-VPI**/CB[8][a]	$\delta_{CH\ (Figure\ S29)}$[b]	$\Delta\delta$	% of free guest competitor	Calculated binding constant K_a[d]
1/0/0	2.134 ppm[c]	-	100	-
1/0/1	1.645 ppm[c]	$\Delta\delta_{lim}$ = 0.489 ppm	0	-
1/1/1	2.049 ppm	$\Delta\delta_{exp}$ = 0.085 ppm	17	2.3×10^{23} M^{-3}

[a] 1 mM solution in D_2O; [b] Chemical shift determined from NMR spectra of Figure S29 and using acetone (2.220 ppm) as internal reference; [c] Δδlim determined from for **Ad** and CB[8]•**Ad** spectra; [d] calculated from Eq4.

Equilibrium reactions:

R1 Ad + CB[8] = Ad•CB[8] ($K_{a\text{-Ad}}$ = 8.19 × 10^8 M^{-1})

Eq1 $K_{a\text{-Ad}} = \frac{[Ad\bullet CB[8]]}{[Ad].[CB[8]]}$

R2 2 **T-VPI** + 2 CB[8] **= T-VPI**•$CB[8]_2$

Eq2 $K_{a\text{-}\mathbf{TVPI}2.CB[8]2} = \frac{[TVPI2\bullet CB[8]2]}{[TVPI]^2.[CB[8]]^2}$

R3 Ad•CB[8] + **T-VPI =** Ad + 0.5 **$\mathbf{T\text{-}VPI_2}$**•$CB[8]_2$

Eq3 $K_{a\text{-competition}} = \frac{\sqrt{[TVPI2\bullet CB[8]2]}.[Ad]}{[Ad\bullet CB[8]].[TVPI]} = \frac{\sqrt{Ka - TVPI2.CB[8]2}}{Ka - Ad}$

Eq4 $K_{a\text{-}\mathbf{TVPI}2.CB[8]2} = [\frac{Ka - Ad.\sqrt{[TVPI2\bullet CB[8]2]}.[Ad]}{[Ad\bullet CB[8]].[TVPI]}]^2$

Table S2. ^{1}H NMR results considering the **diMeAd**/**VPI-N** competition toward CB[8].

Ratios of **diMeAd**/**VPI-N**/CB[8][a]		$\delta_{CB[8]}$	Integral values	% of complex	Calculated binding constant K_a[d]
1/1/1	CB[8]•**diMeAd**	5.540 ppm	16.11 H[c]	73%	-
	$CB[8]_2$•**VPI-N_2**	5.490 ppm	6.03 H[c]	27%	**6.4×10^{24} M^{-3}**
0/1/1	$CB[8]_2$•**VPI-N_2**	5.490 ppm[b]	*32 H*	100%	-
1/0/1	CB[8]•**diMeAd**	5.540 ppm[b]	*16 H*	100%	4.3×10^{11} M^{-1} [8]

[a] 1 mM solution in D_2O; [b] Chemical shift determined from NMR spectra of Figure S31 and using acetone (2.220 ppm) as internal reference; [c] Integral values based on -CH_3 signals of **diMeAd** in the competition solution; [d] calculated from Eq4.

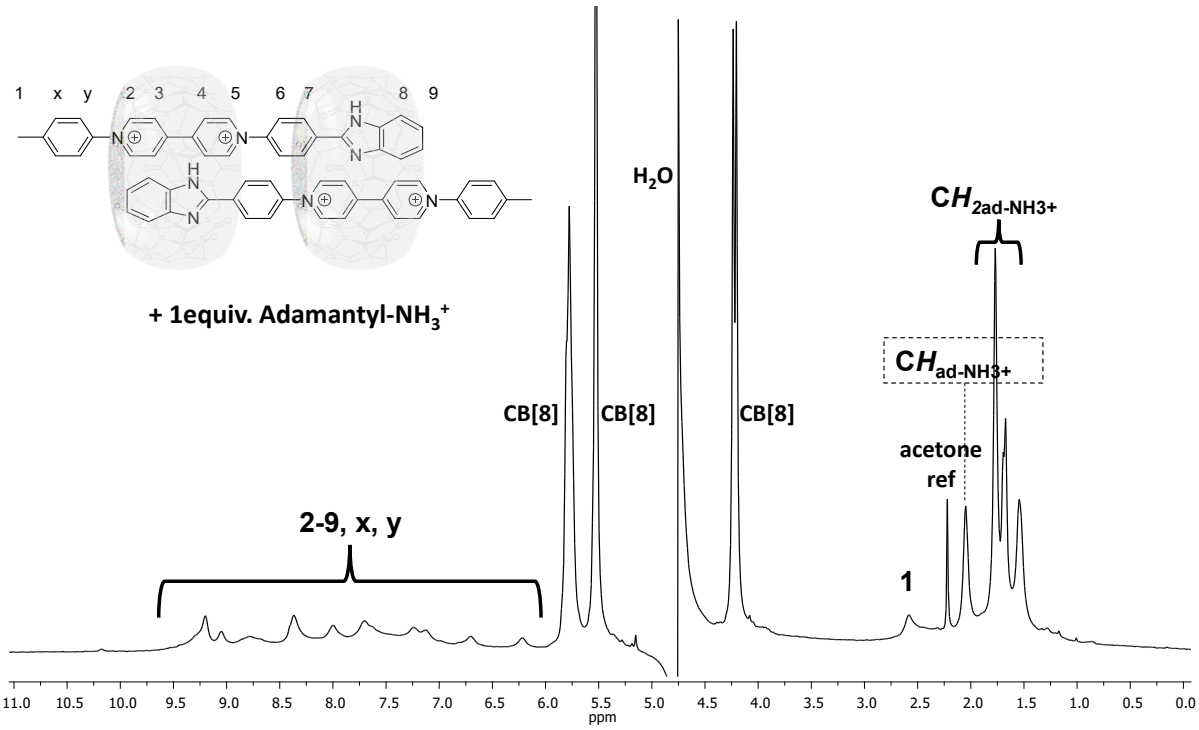


Figure S21. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K) of a mixture of 1 equiv. of **T-VPI**, 1 equiv. of CB[8] and 1 equiv. of 1-adamantylamine•HCl (**Ad**).

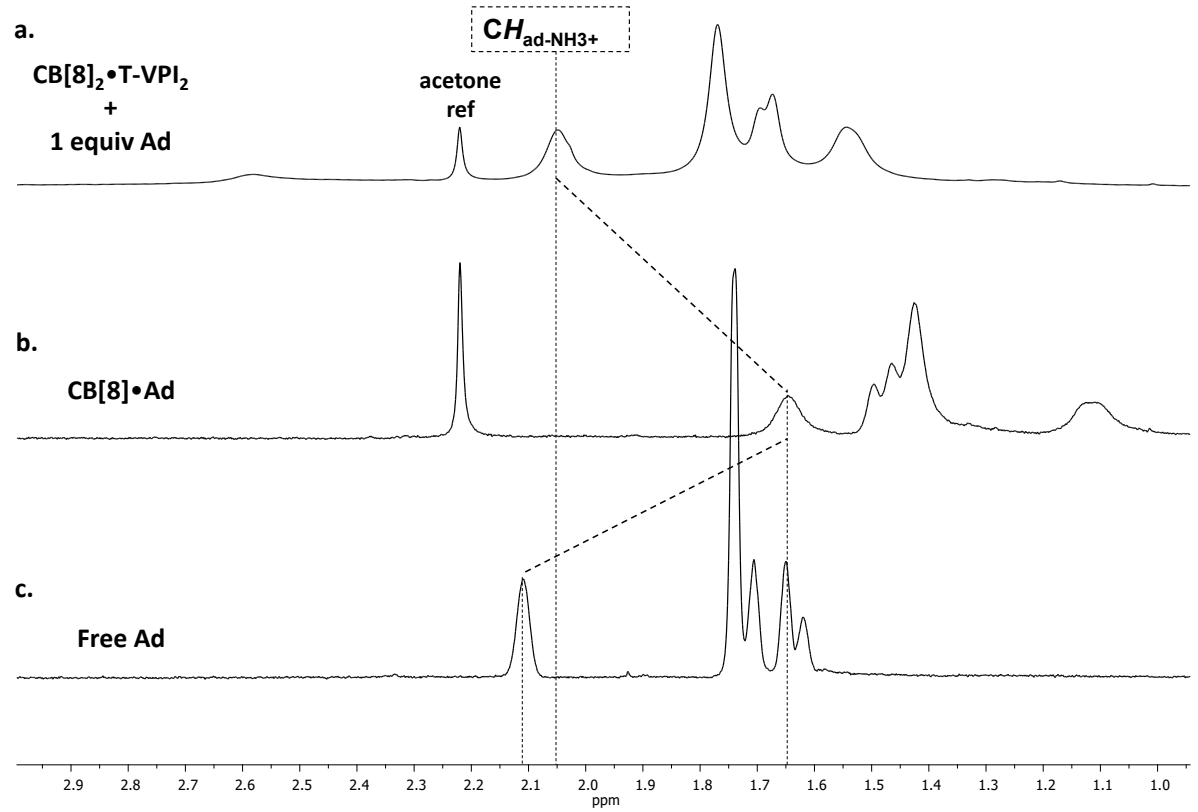


Figure S22. ^{1}H NMR spectra (500 MHz, D_2O, 298 K, zoom of 0.9-3 ppm region) of: **a.** a mixture of **T-VPI**/CB[8]/**Ad** (1 equiv.), **b.** of a mixture of 1.2 equiv. of CB[8] and 1 equiv. of 1-adamantylamine•HCl (**Ad**), and **c.** 1-adamantylamine•HCl (**Ad**, 1 mM) in D_2O.

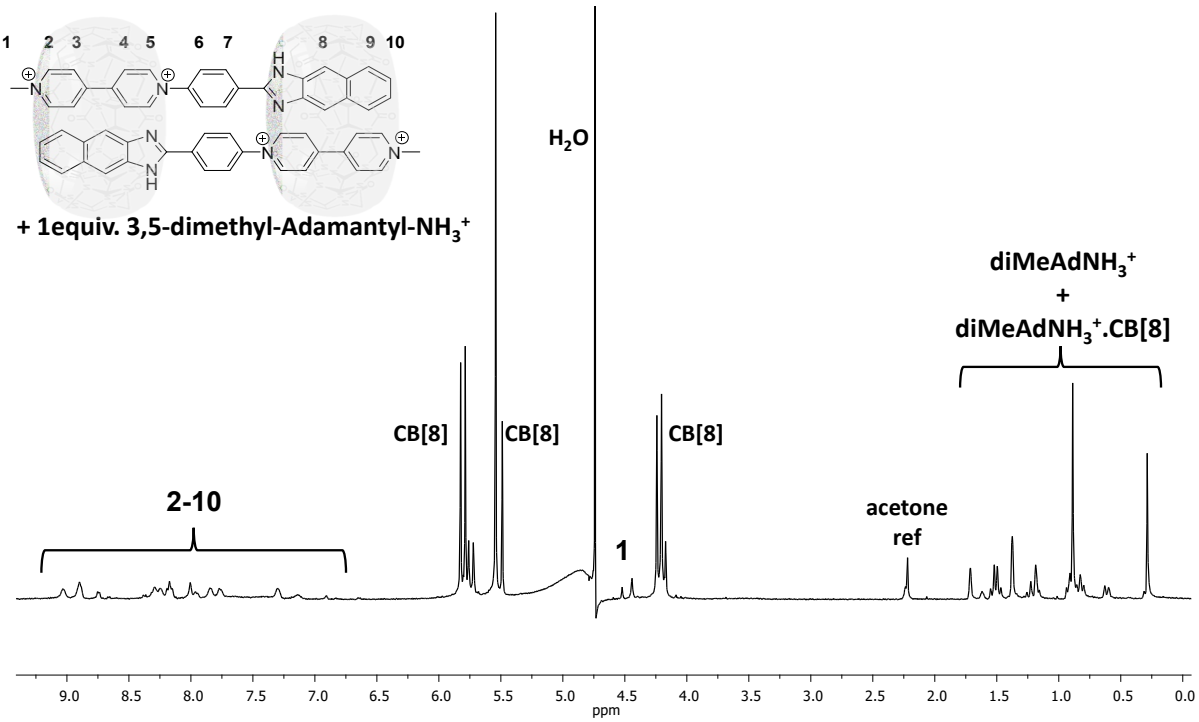


Figure S23. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K) of a mixture of 1 equiv. of **VPI-N**, 1 equiv. of CB[8] and 1 equiv. of **diMeAd** (1 mM).

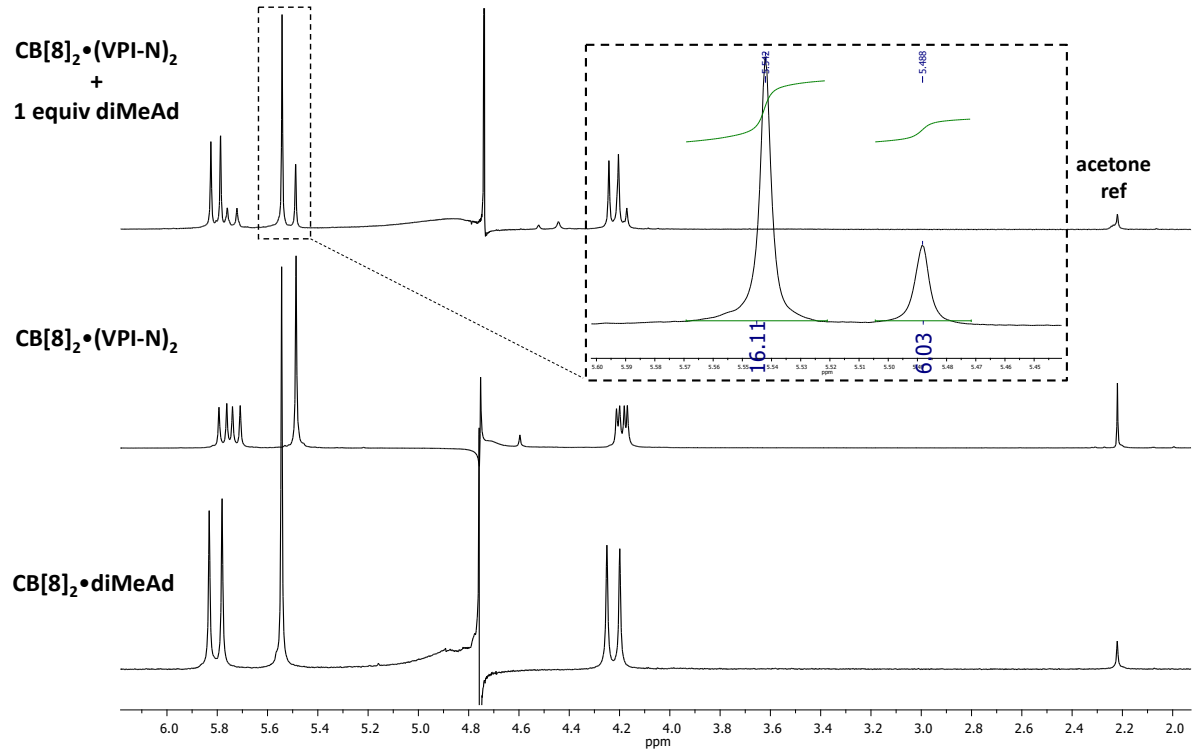


Figure S24. ^{1}H NMR spectra (500 MHz, D_2O, 298 K, zoom of 2-6.2 ppm region) of: **a. VPI-N**/CB[8]/**diMeAd** (1 mM), **b.** CB[8]$_2$•**VPI-N**$_2$ and **c.** CB[8]•**diMeAd** (1 mM).

16/ UV-visible and fluorescence spectra

Table S3. Summary of the optical properties in water solution.

	λ_{abs} [nm] (ε [M^{-1} cm^{-1}])	λ_{em} [nm]	Φ [%][a]
T-VPI	344 (16000), 295 (22500), 247 (16900)	378	0.88
T-VPI + CB[8] (1:1)	378 (12900), 300 (19200), 246 (15500)	381	0.65
T-VPI + CB[10] (2:1)	360 (15200), 296 (21500), 245 (16700)	381	0.68
T-VPI + CB[10] (1:1)	371 (14800), 299 (19400), 245 (15400)	385	0.47
VPI-N	343 (19400), 273 (44500), 221 (38900)	424	0.45
VPI-N + CB[8] (1:1)	365 (13900), 274 (32500)	415	0.36
VPI-N + CB[10] (1:1)	359 (14700), 275 (33000)	422	0.11
T-V-T	338 (18100), 252 (14500)	528	~1.3[b]

[a] Fluorescence quantum yields in deionized water, relative to anthracene in ethanol (Φ = 27%). Excitation of reference and sample compounds was performed at the same wavelength, *i.e.* 290 nm for **T-VPI** and 310 nm for **VPI-N** and **T-V-T**.

[b] Slightly underestimated value due to the recording conditions.

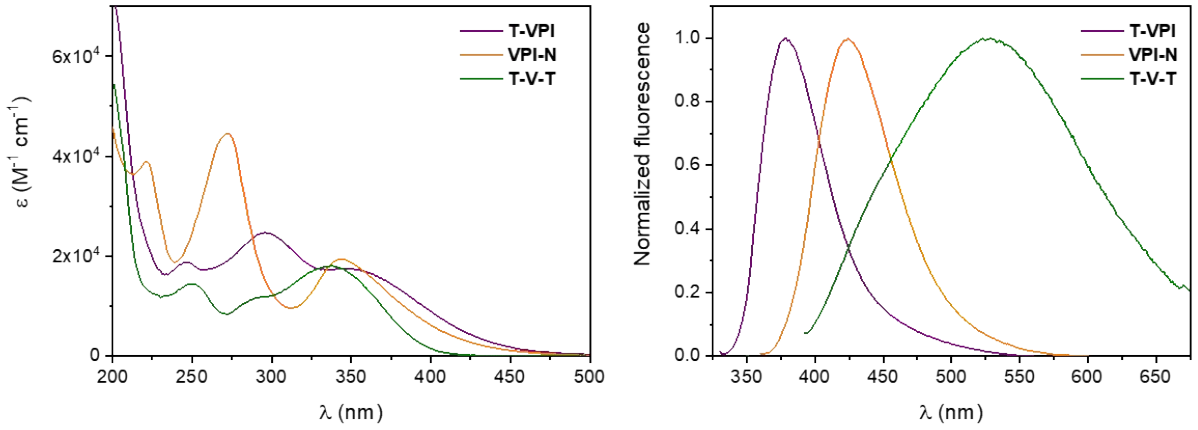


Figure S25. Electronic absorption (left) and normalized emission (right) spectra of compounds **T-VPI** (purple), **VPI-N** (orange) and **T-V-T** (green) in water solution (*ca*. 10^{-5} M).

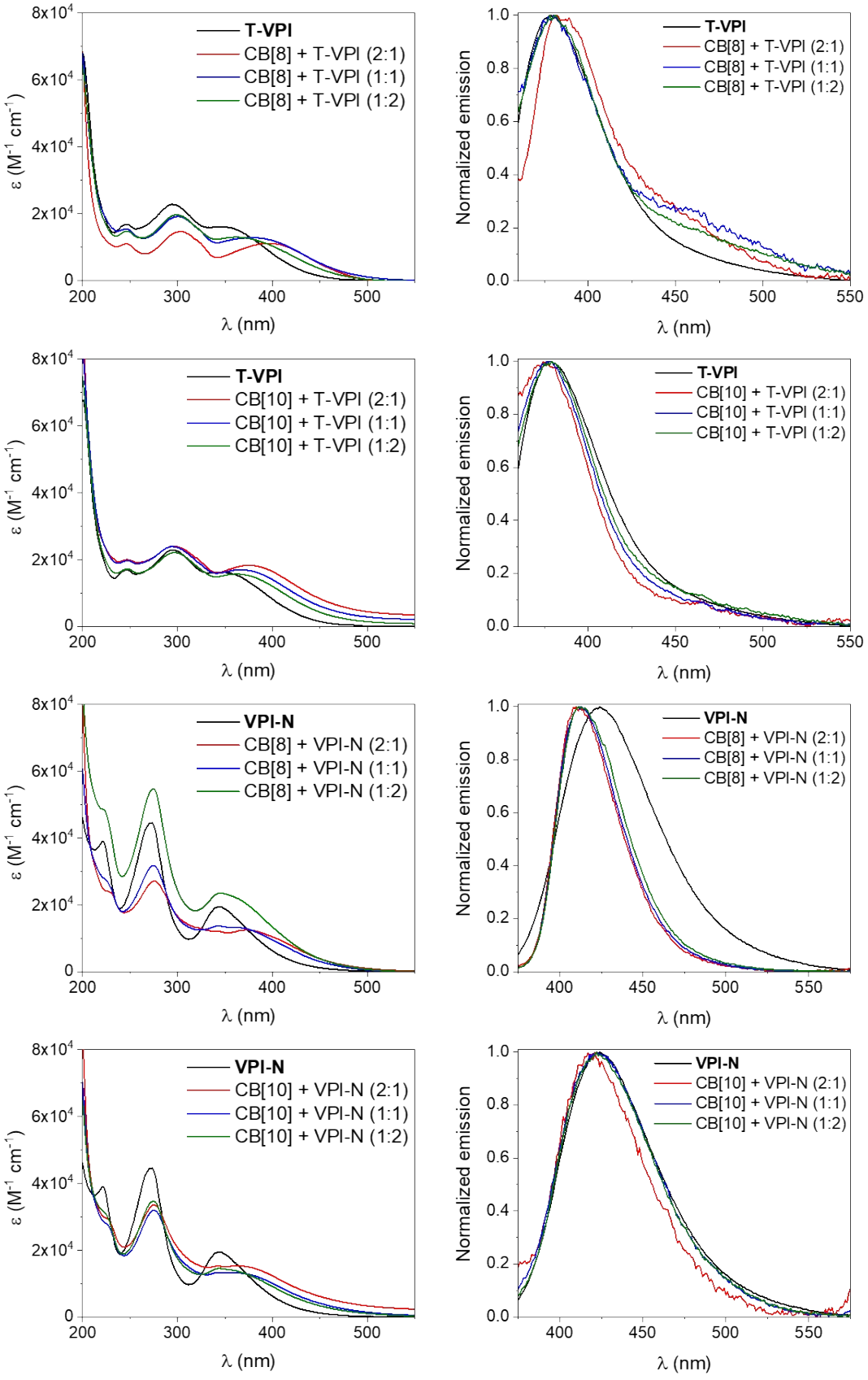


Figure S26. Electronic absorption (left column) and emission (right column) spectra of **T-VPI** or **VPI-N** in the presence of CB[8] or CB[10] in water (10^{-5} M).

17/ Preparation and NMR spectra of CB[8]$_2$•T-VPI$_2$•Ag$^+_2$

A 0.45 mM solution of CB[8]$_2$•**T-VPI**$_2$•**Ag**$^+_2$ was prepared from a mixture of 0.64 mg of solid CB[8] (4.8×10^{-7} mol, 1.2 equiv.), 200 µL of a 2 mM stock solution of **T-VPI** (4×10^{-7} mol) in D_2O, 40 µL of a 0.2 M solution of $AgNO_3$ (8.0×10^{-6} mol) and 300 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

^{1}H NMR (500 MHz, D_2O) δ 9.37 (d, *J* = 5.8 Hz, 4H, ***H5***), 9.07 (s, 4H, ***H2***), 8.47 (d, *J* = 7.6 Hz, 4H, ***H7*** or ***H6***), 8.17 (s, 4H, ***H7*** or ***H6***), 7.98 (d, *J* = 7.5 Hz, 4H, ***Hy*** or ***Hx***), 7.68 (d, *J* = 7.5 Hz, 4H, ***Hy*** or ***Hx***), 7.40 (s, 4H, ***H4***), 7.18 (br s, 4H, ***H3***), 6.67 (br s, 4H, ***H8*** or ***H9***), 6.38 (s, 4H, ***H8*** or ***H9***), 5.92 – 5.66 (m, 32H, CB[8]), 5.55 (s, 32H, CB[8]), 4.25 (dd, *J* = 15.3, 9.1 Hz, 32H, CB[8]), 2.57 (s, 6H, ***H1***), 2.22 (acetone, ref).

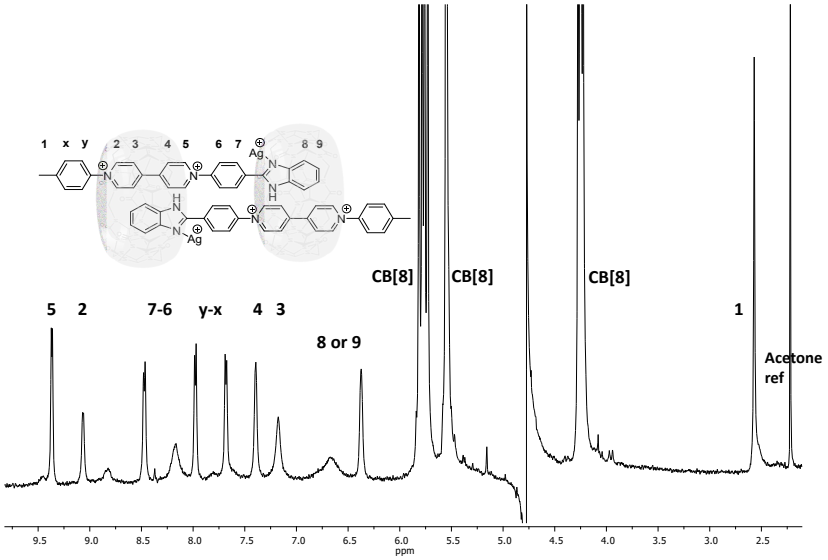


Figure S27. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**T-VPI**$_2$•**Ag**$^+_2$.

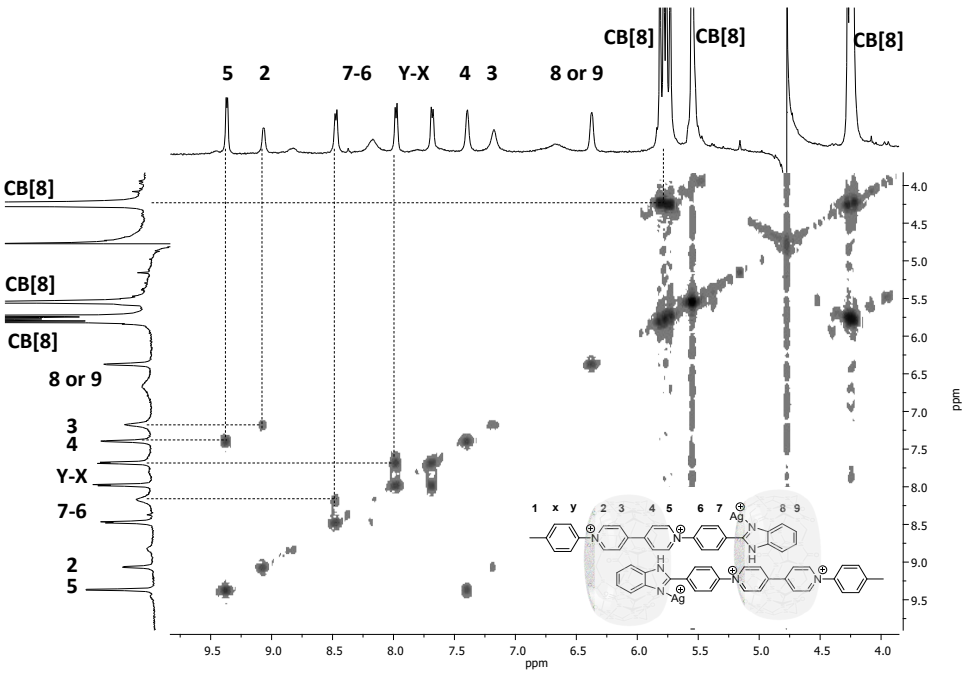


Figure S28. COSY NMR (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**T-VPI**$_2$•**Ag**$^+_2$.

18/ Preparation and NMR spectra of CB[8]$_2$•VPI-N$_2$•Ag$^+_2$

To 500 µL of a 0.45 mM solution of CB[8]$_2$•**VPI-N$_2$** were added 50 µL of a 0.2 M solution of $AgNO_3$ (10^{-5} mol) in D_2O. Acetone was used as internal reference (2.22 ppm).

^{1}H NMR (500 MHz, D_2O) δ 8.94 (d, *J* = 5.3 Hz, 4H, ***H5***), 8.75 (d, *J* = 6.3 Hz, 4H, ***H2***), 8.48 (d, *J* = 8.4 Hz, 4H, ***H6*** or ***H7***), 8.31 (d, *J* = 8.6 Hz, 4H, ***H6*** or ***H7***), 7.16 (br s, 4H, ***H8***, ***H9*** or ***H10***), 6.93 (br s, 8H, ***H8***, ***H9*** or ***H10***), 6.83 (d, *J* = 4.6 Hz, 4H, ***H4***), 6.69 (d, *J* = 6.3 Hz, 4H, ***H3***), 5.73 (app dt, *J* = 43.3, 21.6 Hz, 32H, CB[8]), 5.52 (d, *J* = 24.6 Hz, 32H, CB[8]), 4.64 (br s, ***H1***), 4.20 (d, *J* = 15.4 Hz, 32H, CB[8]), 2.22 (acetone, ref).

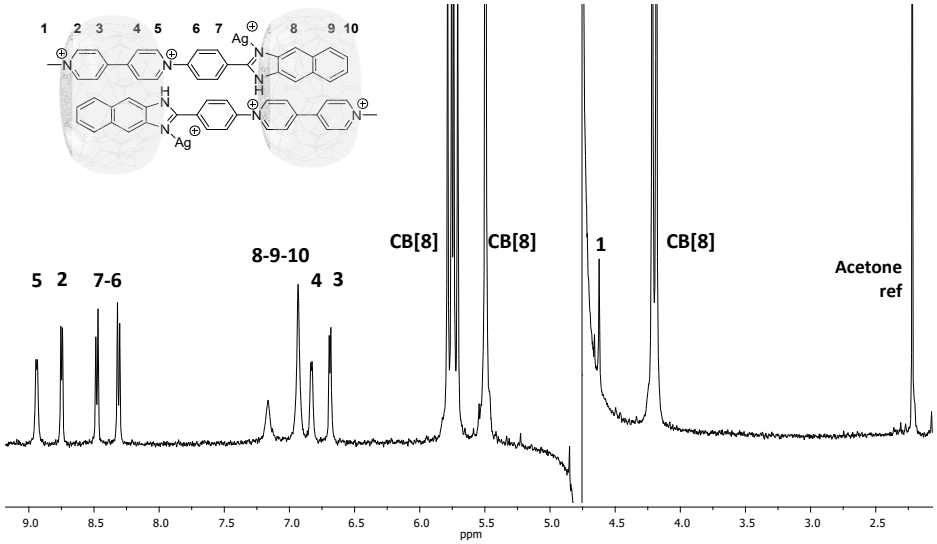


Figure S29. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**VPI-N$_2$**•Ag$^+_2$.

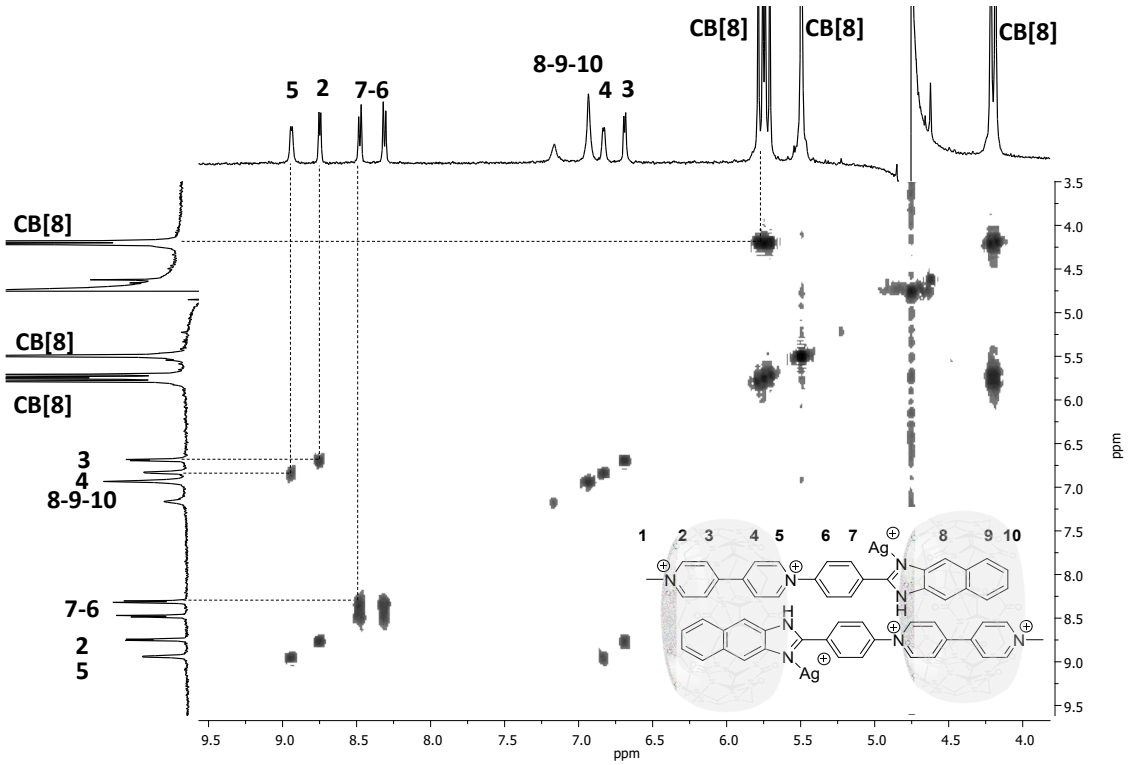


Figure S30. COSY NMR (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**VPI-N$_2$**•Ag$^+_2$.

19/ Preparation and NMR spectra of CB[8]$_2$•VPI-N-H$^+_2$

A 0.45 mM solution of CB[8]$_2$•**VPI-N**-H$^+_2$ was prepared from a mixture of 0.61 mg of solid CB[8] (4.6×10^{-7} mol, 1.2 equiv.), 95 µL of a 4 mM stock solution of **VPI-N** (3.8×10^{-7} mol) in D_2O, 20 µL of a 0.2 M solution of **TFA** (4.0×10^{-6} mol) and 360 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

^{1}H NMR (500 MHz, D_2O) δ 8.95 (d, *J* = 6.4 Hz, 4H, ***H5***), 8.81 (d, *J* = 6.3 Hz, 4H, ***H2***), 8.49 (d, *J* = 8.6 Hz, 4H, ***H6*** or ***H7***), 8.39 (d, *J* = 8.6 Hz, 4H, ***H6*** or ***H7***), 7.32 (s, 4H, ***H8***), 6.97 (two d, *J* = 6.3 Hz, 8H, , ***H9*** and ***H10***), 6.87 (d, *J* = 6.5 Hz, 4H, , ***H4***), 6.75 (d, *J* = 6.4 Hz, 4H, , ***H3***), 5.76 (app dd, *J* = 29.5, 15.4 Hz, 32H, CB[8]), 5.50 (br s, 32H, CB[8]), 4.65 (br s, ***H1***), 4.22 (d, *J* = 15.3 Hz, 32H, CB[8]), 2.22 (acetone, ref).

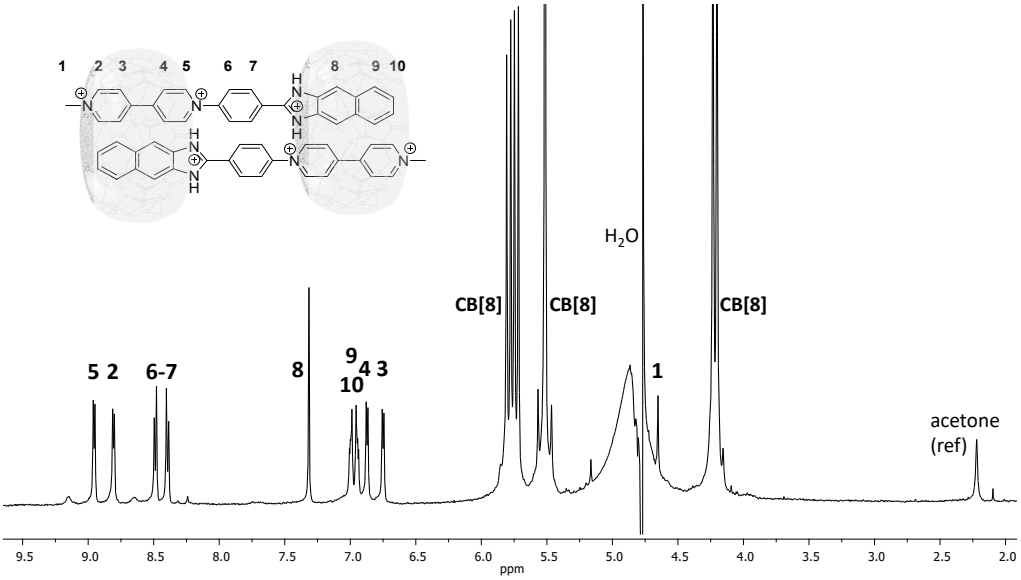


Figure S31. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**VPI-N**-H$^+_2$.

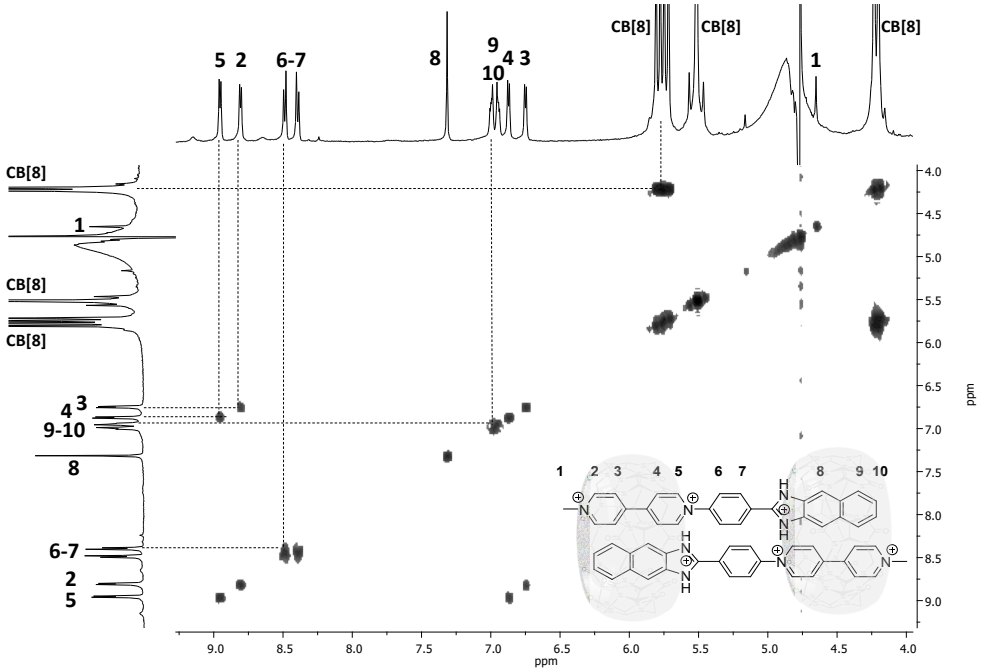


Figure S32. COSY NMR (500 MHz, D_2O, 298 K, 0.45 mM) of CB[8]$_2$•**VPI-N**-H$^+_2$.

20/ Preparation and NMR spectra of CB[8]$_2$● T-VPI$_2$ with TFA

A solution of **T-VPI**/CB[8]/TFA was prepared from a mixture of 0.66 mg of solid CB[8] (5.0×10^{-7} mol, 1.2 equiv.), 205 µL of a 2 mM stock solution of **T-VPI** (4.1×10^{-7} mol, 1equiv.) in D_2O, 20 µL of a 0.2 M solution of TFA in D_2O (4.0×10^{-6} mol) and 280 µL of D_2O. Acetone was used as internal reference (2.22 ppm).

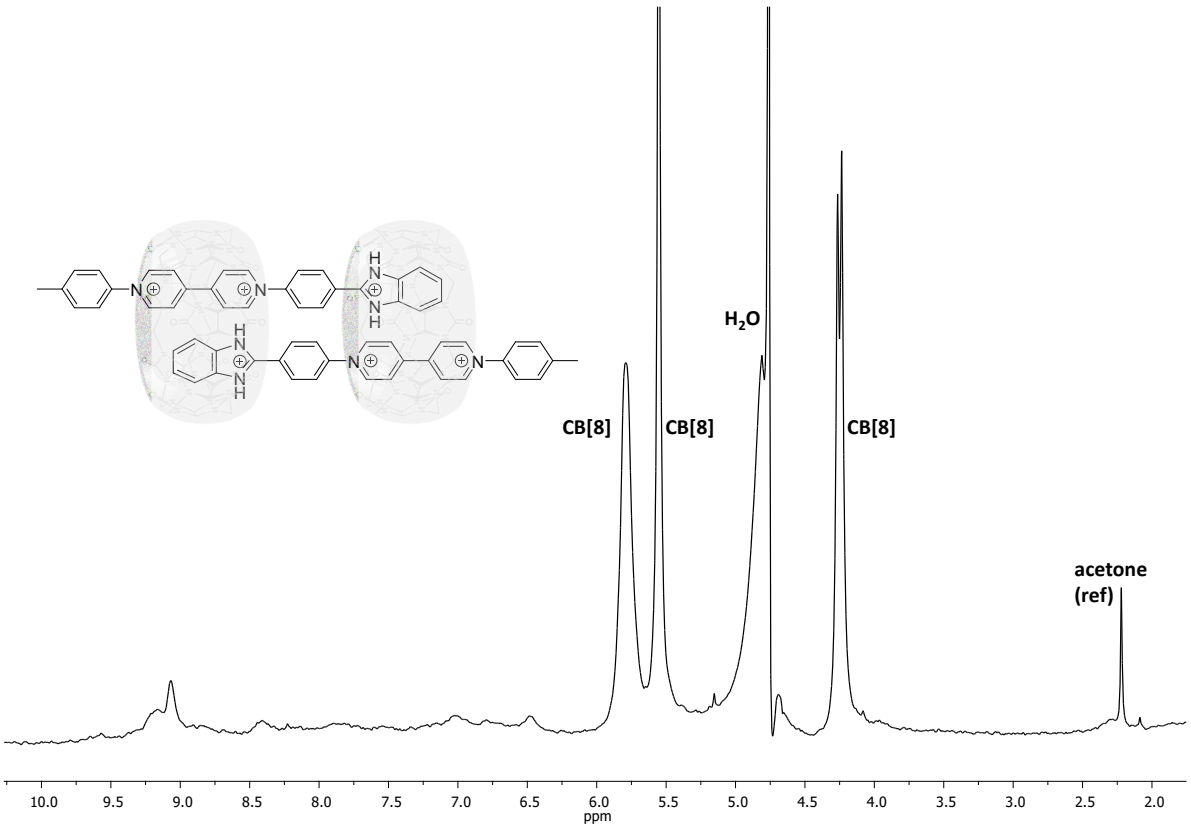


Figure S33. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K, 1 mM) of 1 equiv. of **T-VPI**, with 1.2 equiv. of CB[8] and 10 mM of TFA.

21/ Preparation and NMR spectra of CB[10]$_2$•VPI-N-H$^+_3$

To 500 µL of a 0.17 mM solution of CB[10]$_2$•**VPI-N$_3$** were added 10 µL of a 0.2 M solution of TFA in D_2O (2×10^{-6} mol, 12 equiv.). Acetone was used as internal reference (2.22 ppm).

^{1}H NMR (500 MHz, D_2O) δ 9.13 (br s, 2H, ***H2b***), 8.94 (d, *J* = 6.1 Hz, 4H, ***H2a***), 8.36 (br s, 4H, ***H5a***), 8.27 (d, *J* = 8.4 Hz, 4H, ***H7a***), 8.07 (br s, 2H, ***H7b***), 7.94 (br s, 2H, ***H5b***), 7.84 (d, *J* = 7.8 Hz, 4H, ***H6a***), 7.74 (br s, 2H, ***H8b***), 7.64 (br s, 2H, ***H3b***), 7.43 (br s, 4H, ***H3a***), 7.36 (s, 4H, ***H8a***), 7.28 (br s, 2H, ***H6b***), 7.16 (m, 6H, overlapped signals of ***H4a*** and ***H9b***), 6.97 (m, 6H, overlapped signals of ***H4b*** and ***H9a***), 6.48 (m, 4H, ***H10a***), 6.30 (br s, 2H, ***H10b***), 5.91 – 5.69 (m, 48H, CB[10]), 5.52 (d, *J* = 33.7 Hz, 43H, CB[10]), 4.61 (br s, ***H1a-b***), 4.20 (ddd, *J* = 23.3, 15.2, 7.4 Hz, 49H, CB[10]), 2.22 (acetone, ref).

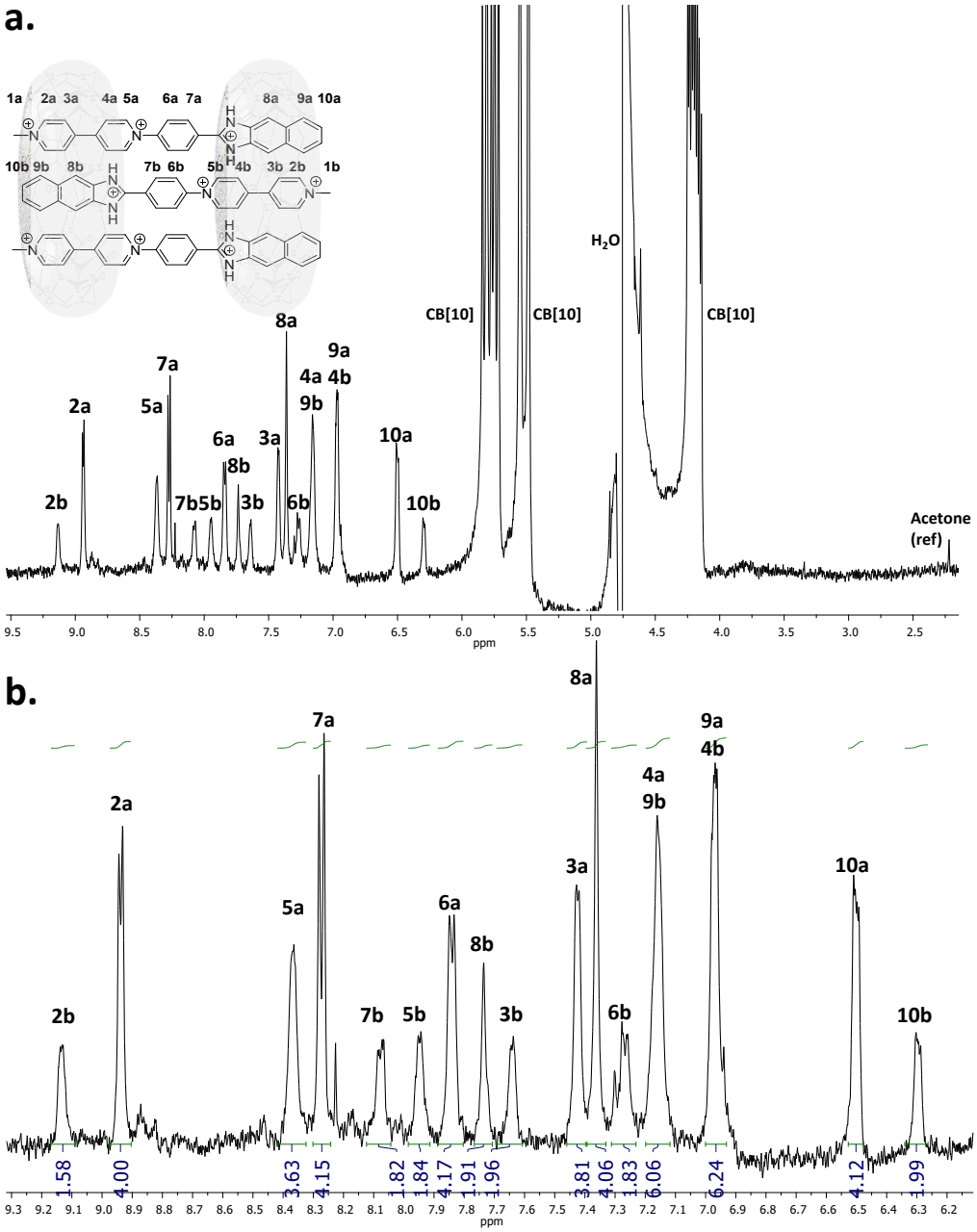


Figure S34. ^{1}H NMR spectrum (500 MHz, D_2O, 300 K, 0.17 mM, full a., zoom b.) of CB[10]$_2$•**VPI-N**-H$^+_3$ recorded after 5 days.

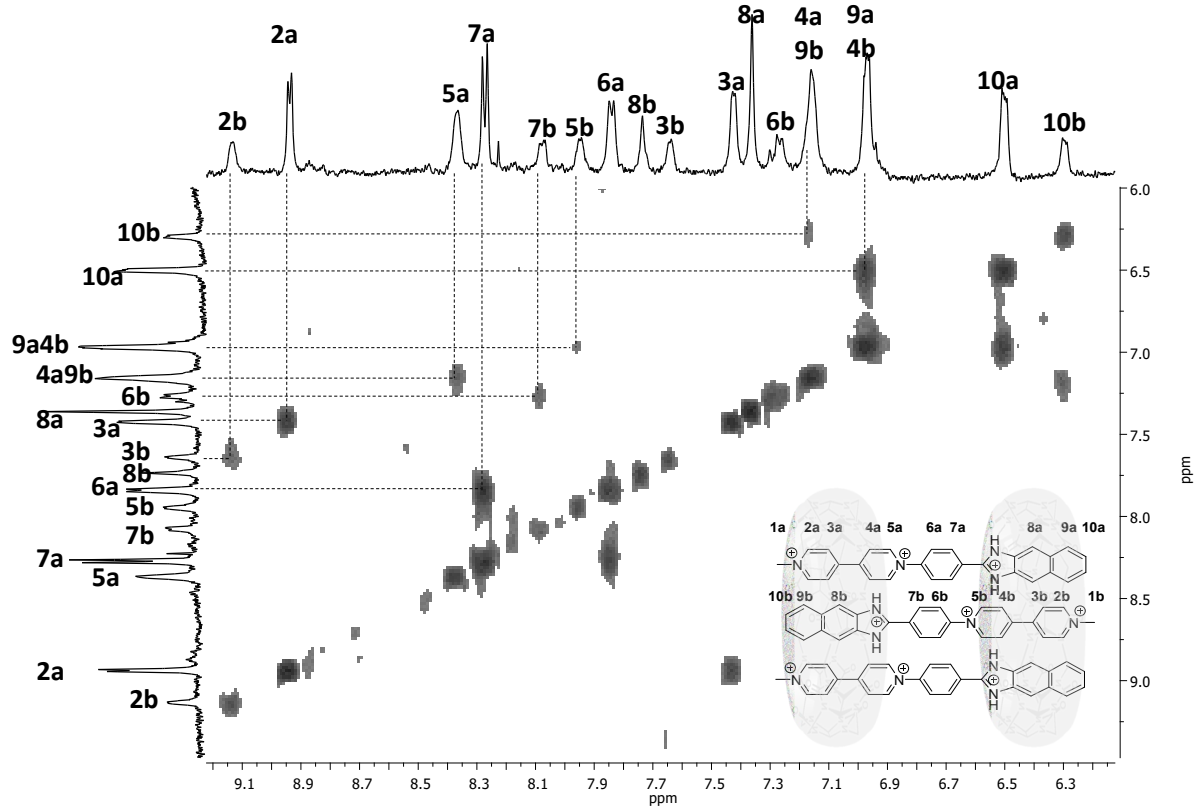


Figure S35. COSY NMR (500 MHz, D_2O, 300 K, 0.17 mM) of $CB[10]_2$•**VPI-N**-H^+_3.

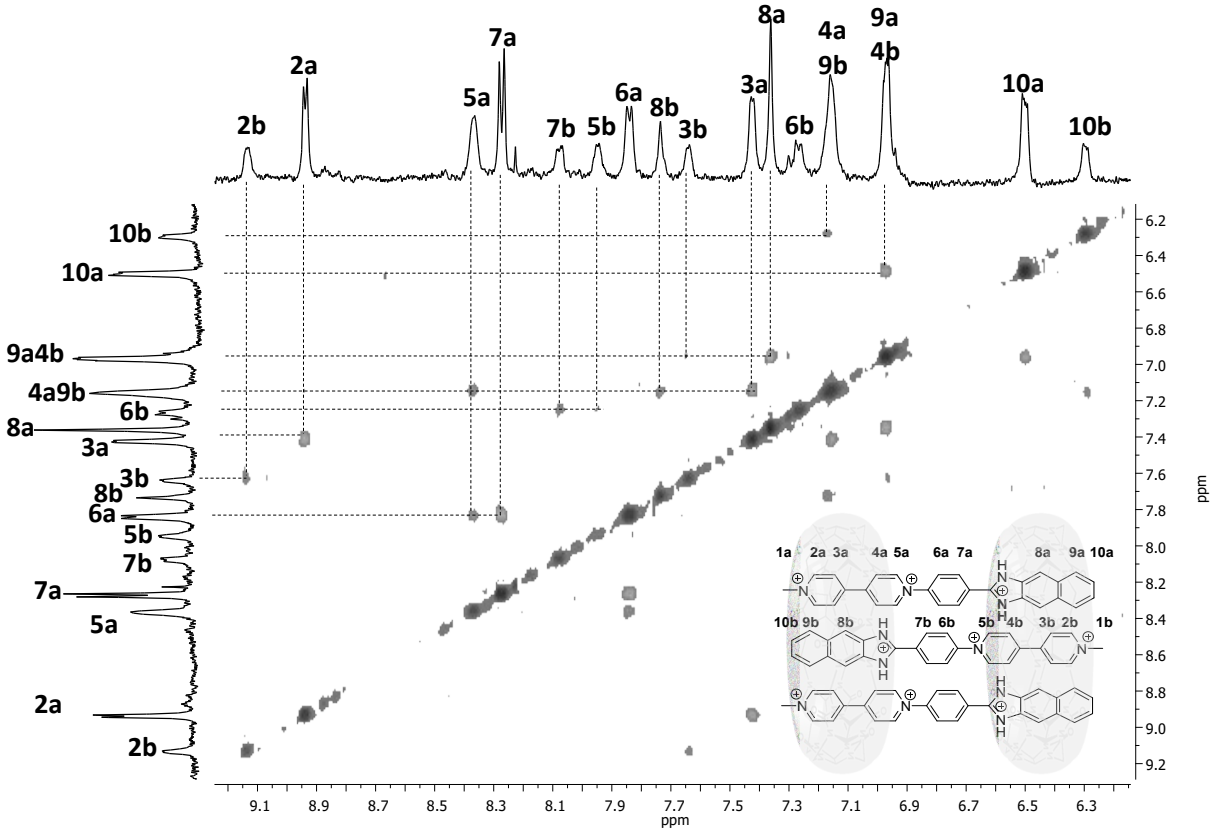


Figure S36. ROESY NMR (500 MHz, D_2O, 300 K, 0.17 mM, mixing time: 400 ms) of $CB[10]_2$•**VPI-N**-H^+_3.

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