# Electronic Supplementary Information

**Synthesis of a novel water-soluble cylindrical macrotricyclic host and its complexation with *N*-methylquinolinium and *N*-methylisoquinolinium salts: formation of 1:2 complexes in water**

**Fei Zeng[a,b] and Chuan-Feng Chen*[,a]**

[a]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.* [b]*University of Chinese Academy of Sciences, Beijing 100049, China*.

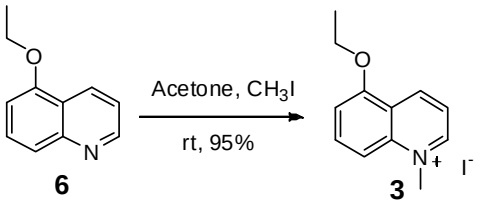
Email: cchen@iccas.ac.cn

## Contents

## 1. General information

Melting points, taken on an electrothermal melting point apparatus, are uncorrected. $^{1}$H NMR, $^{13}$C NMR spectra were recorded on a Bruker DMX300 NMR spectrometer. 2D-ROESY experiments were performed on a Bruker AVANCE 600 MHz spectrometer. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Exactive$^{TM}$ spectrometer. Compounds **2**,[S1] **4**,[S2] **5**[S3] and **6**[S4] were prepared according to the literature procedures.

**Synthesis of host 1.** A mixture of **5** (210 mg, 0.16 mmol) and NaOH (26 mg, 0.64 mmol) in $CH_3OH/H_2O$ (v/v = 9:1, 15 mL) was stirred for 12 hours at 60 $^{0}$C under nitrogen atmosphere. Then, the solvent was removed under vacuum to give host **1** (211mg, 98%) as a dark red solid. Mp: >300 ºC. $^{1}$H NMR (300 MHz, $D_2O$, 295 K): $\delta$ 6.97 (s, 8H), 3.99-3.84 (m, 16H), 3.55-3.50 (m, 32H), 2.02 (s, 12H). $^{13}$C NMR (75 MHz, $D_2O$, 295 K): $\delta$ 175.2, 147.5, 144.4, 143.6, 109.6, 69.9, 69.4, 69.3, 48.1, 13.2. HRMS cald. for $[M-2Na]^{2-}$: 633.1954. Found: 633.1966.




6 3

**Synthesis of guest 3.** A mixture of 5-ethoxyquinoline **6** (200 mg, 1.15 mmol) and $CH_3I$ (0.2 mL) was in acetone (20 mL) stirred overnight at room temperature under nitrogen atmosphere. Then, the mixture was filtrated, washed with acetone, and dried in vacuo to give guest **3** (346 mg, 95%) as a yellow solid. Mp: 198-199 ºC. $^{1}$H NMR

(300 MHz, $D_2O$, 295 K): $\delta$ 9.37-9.34 (d, $J$ = 8.7 Hz, 1H), 9.05-9.03 (d, $J$ = 5.7 Hz, 1H), 8.09-8.04 (m, 1H), 7.85-7.74 (m, 2H), 7.33-7.30 (d, $J$ = 8.1 Hz, 1H), 4.49 (s, 3H), 4.36-4.29 (m, 2H), 1.49-1.44 (m, 3H). $^{13}$C NMR (75 MHz, $D_2O$, 295 K): $\delta$ 155.7, 148.9, 142.0, 139.3, 137.1, 122.4, 119.9, 109.0, 65.8, 45.6, 13.7. HRMS cald. for $[M\text{-}I]^+$: 188.1070. Found: 188.1064.

## 2. Complexation between host 1 and guest 3

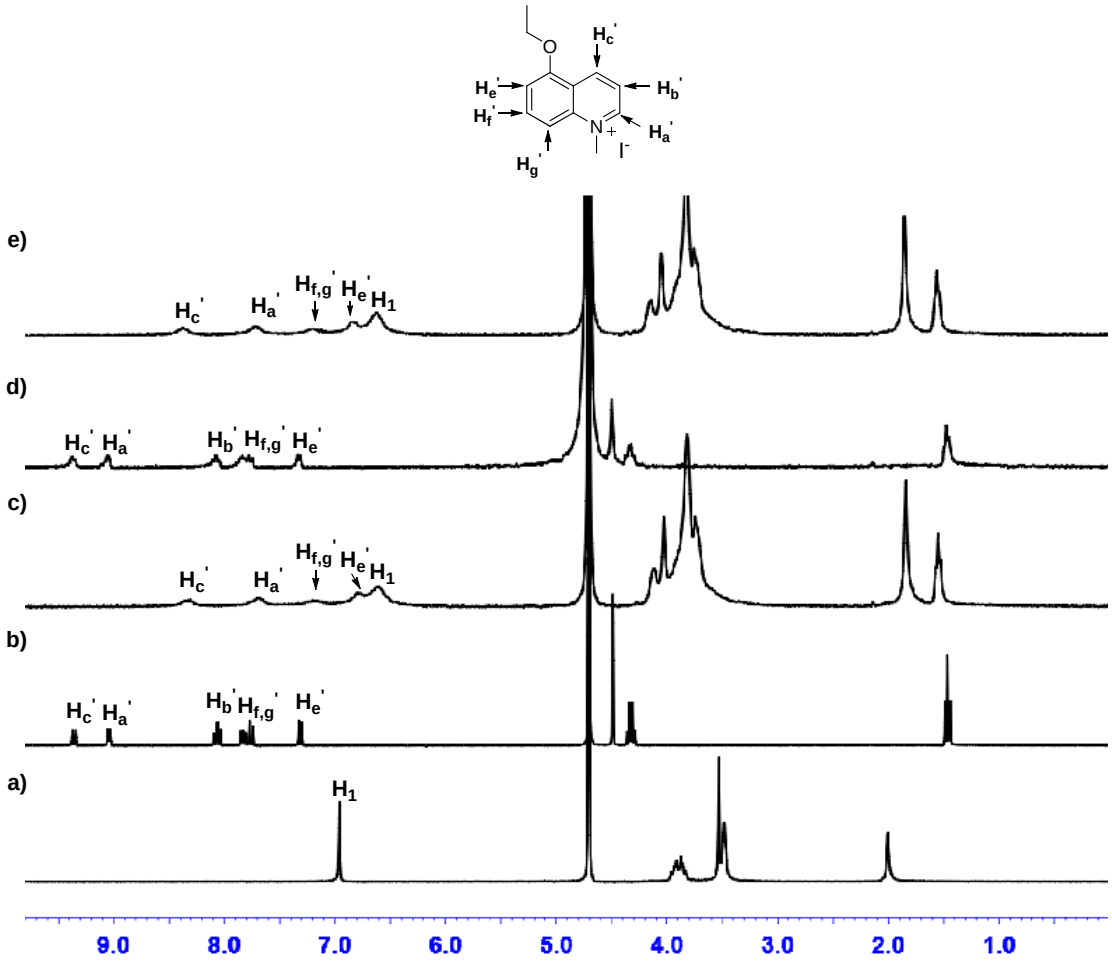



**Fig. S1** Partial $^1$H NMR spectra (300 MHz, $D_2O$, 295 K) of (a) free host **1**, (b) free guest **3**, (c) **1** and 2.0 equiv of **3**, (d) after addition of 2.0 μL of aqueous DCl solution (20 wt%) to c, and (e) after addition of 1.0 μL of aqueous NaOD solution (40 wt%) to d. $[\mathbf{1}]_0$ = 4.0 mM.

## 3. Complexation between host 1 and guest 4

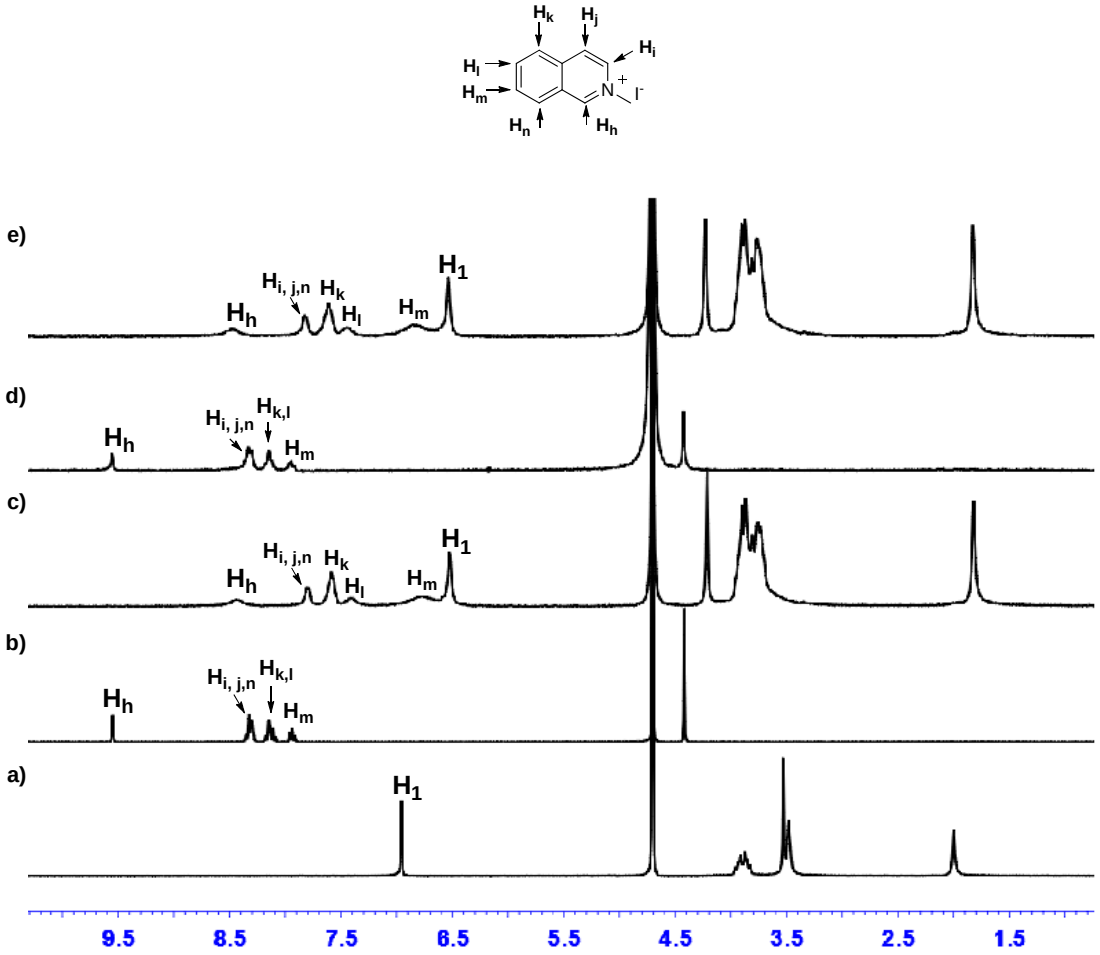



**Fig. S2** Partial $^1$H NMR spectra (300 MHz, $D_2O$, 295 K) of (a) free host **1**, (b) free guest **4**, (c) **1** and 2.0 equiv of **4**, (d) after addition of 2.0 μL of aqueous DCl solution (20 wt%) to c, and (e) after addition of 1.0 μL of aqueous NaOD solution (40 wt%) to d. $[\mathbf{1}]_0$ = 4.0 mM.

## 4. Photographs of complexation and decomplexation of complex $1{\cdot}3_2$

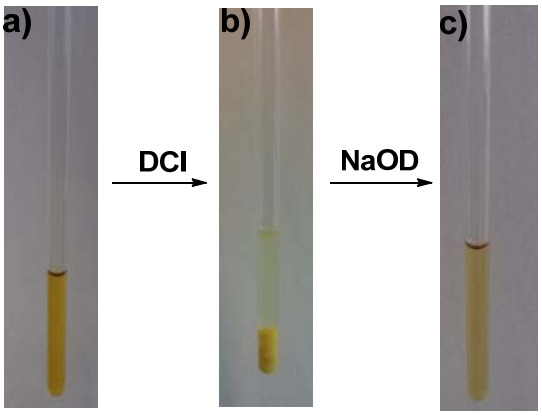



**Fig. S3** Photographs of water solutions of (a) **1** and 2.0 equiv of **3**, (b) after the addition of 2.0 μL of aqueous DCl solution (20 wt%) to a, and (c) after the addition of 1.0 μL of aqueous NaOD solution (40 wt%) to b. $[\mathbf{1}]_0 = 4.0$ mM.

## 5. Photographs of complexation and decomplexation of complex $1{\cdot}4_2$

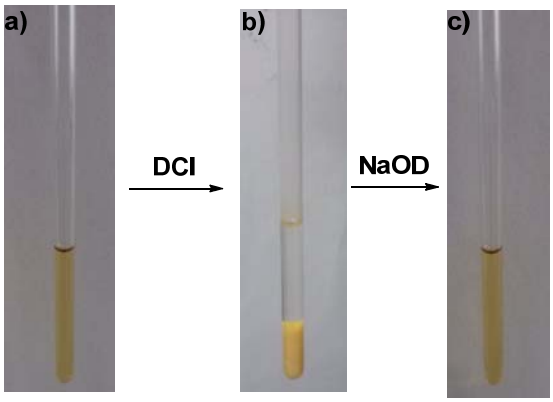



**Fig. S4** Photographs of water solutions of (a) **1** and 2.0 equiv of **4**, (b) after the addition of 2.0 μL of aqueous DCl solution (20 wt%) to a, and (c) after the addition of 1.0 μL of aqueous NaOD solution (40 wt%) to b. $[\mathbf{1}]_0 = 4.0$ mM.

## 6. Determination of the average association constants of the complexes

Δ is the observed chemical shift change relative to uncomplexed species, and $\Delta_0$ is calculated chemical shift change of fully complexed species, and is determined by

extrapolation of a plot of Δ vs 1/[**1**] in the high initial concentration range of **1**. The complex fraction ($p$) value was calculated from $p = \Delta / \Delta_0$, and $[\mathbf{1}]_{uc}$ values were calculated form $[\mathbf{1}]–0.5p[\mathbf{2}]_0$. A plot of $p / [\mathbf{1}]_{uc}$ vs $p$ was used to determine the association constant $K_{av}$, which is the average value of the slope and the intercept. The method used for the determination of average association constants of complexes **1**·$\mathbf{3}_2$ and **1**·$\mathbf{4}_2$ is similar to that of **1**·$\mathbf{2}_2$.

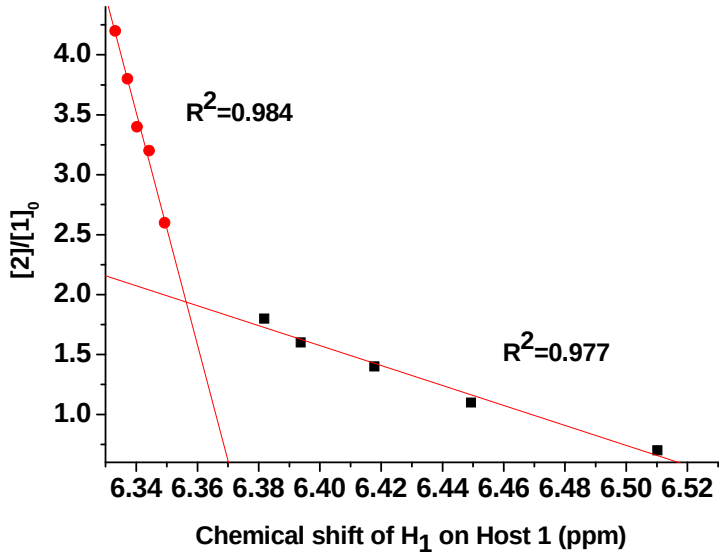



**Fig. S5** Mole ratio plot for the complexation of **1** and **2** in $D_2O$ at 295 K. $[\mathbf{1}]_0$ = 3.0 mM .

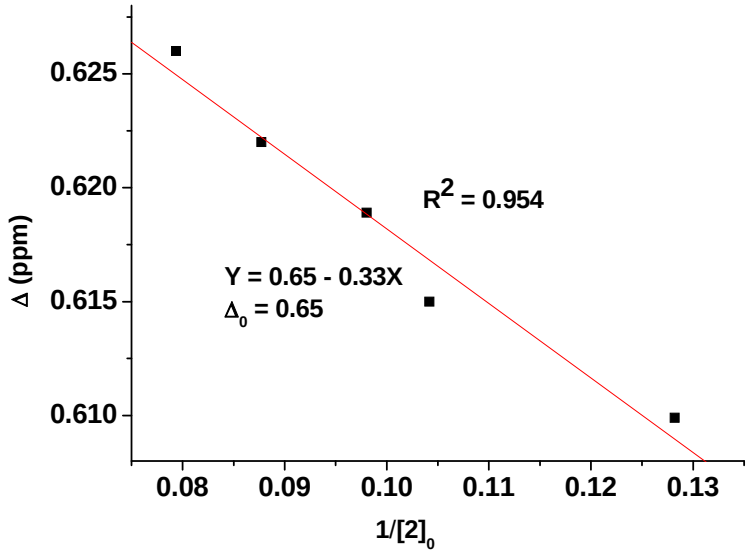



**Fig. S6** Determination of $\Delta_0$ of $H_1$ for the complexation between host **1** and guest **2** in $D_2O$ at 295K.

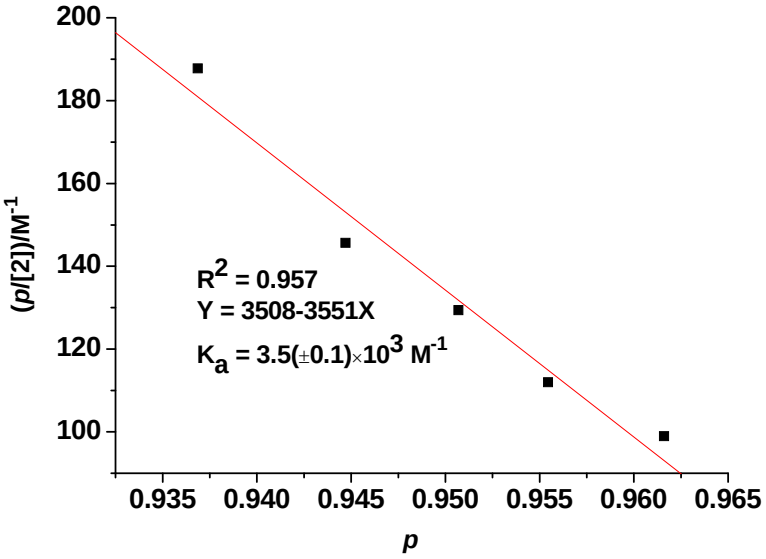



**Fig. S7** Scatchard plot for the complexation of host **1** and guest **2** in $D_2O$ at 295K.

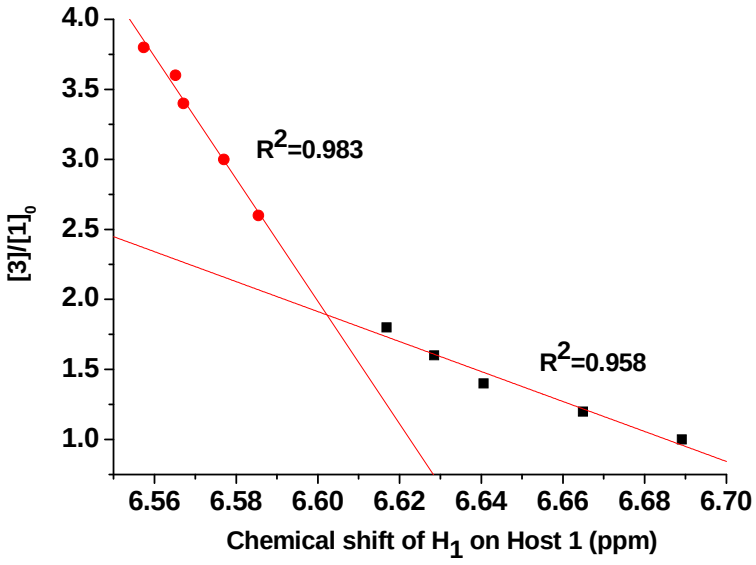



**Fig. S8** Mole ratio plot for the complexation of **1** and **3** in $D_2O$ at 295 K. $[\mathbf{1}]_0$ = 3.0 mM .

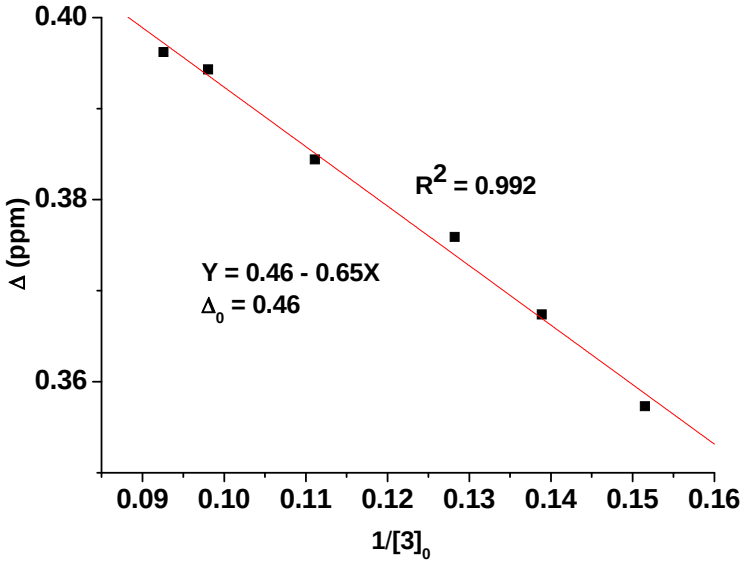



**Fig. S9** Determination of $\Delta_0$ of $H_1$ for the complexation between host **1** and guest **3** in $D_2O$ at 295K.

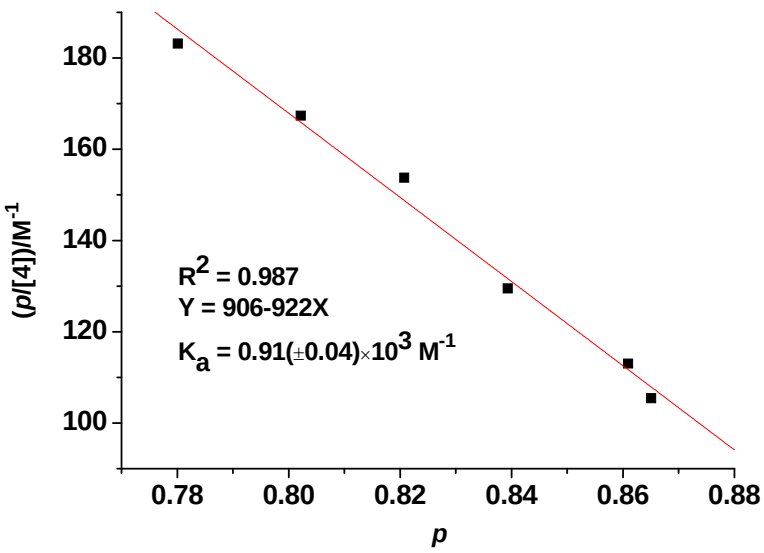



**Fig. S10** Scatchard plot for the complexation of **1** and guest **3** in $D_2O$ at 295K.

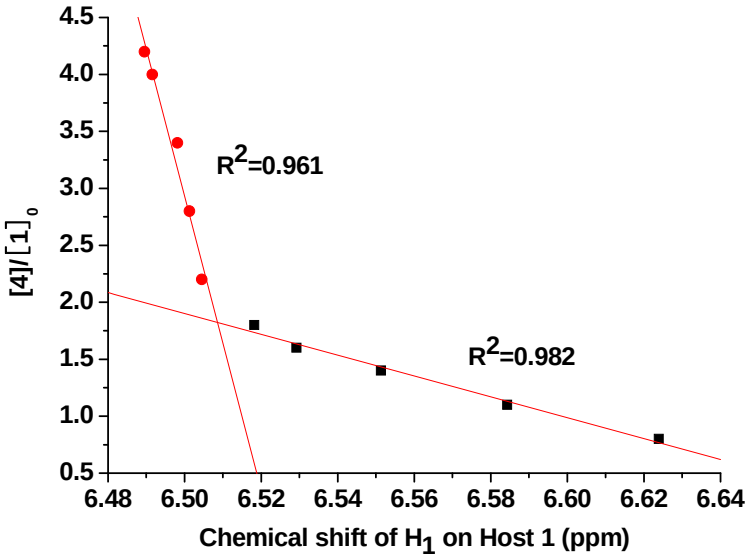



**Fig. S11** Mole ratio plot for the complexation of **1** and **4** in $D_2O$ at 295 K. $[\mathbf{1}]_0$ = 3.0 mM .

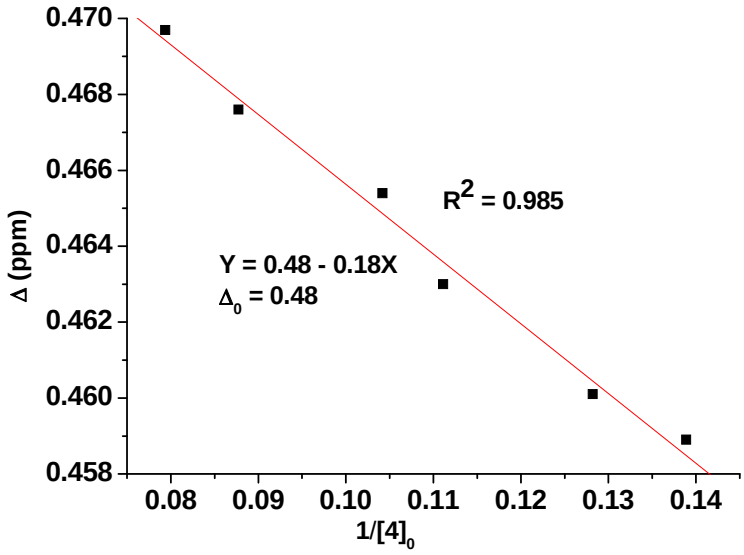



**Fig. S12** Determination of $\Delta_0$ of $H_1$ for the complexation between host **1** and guest **4** in $D_2O$ at 295K.

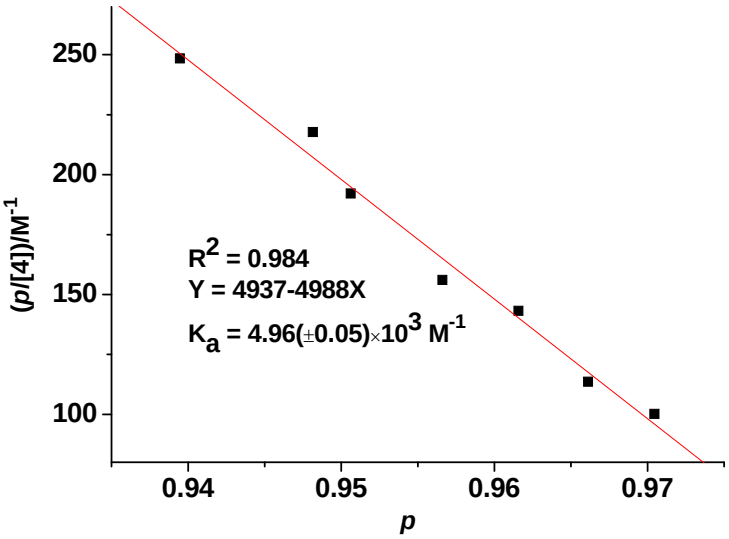



**Fig. S13** Scatchard plot for the complexation of host **1** and guest **4** in $D_2O$ at 295K.

## 7. Partial $^1$H-$^1$H COSY and ROESY spectra of complexes $1{\cdot}2_2$, $1{\cdot}3_2$ and $1{\cdot}4_2$

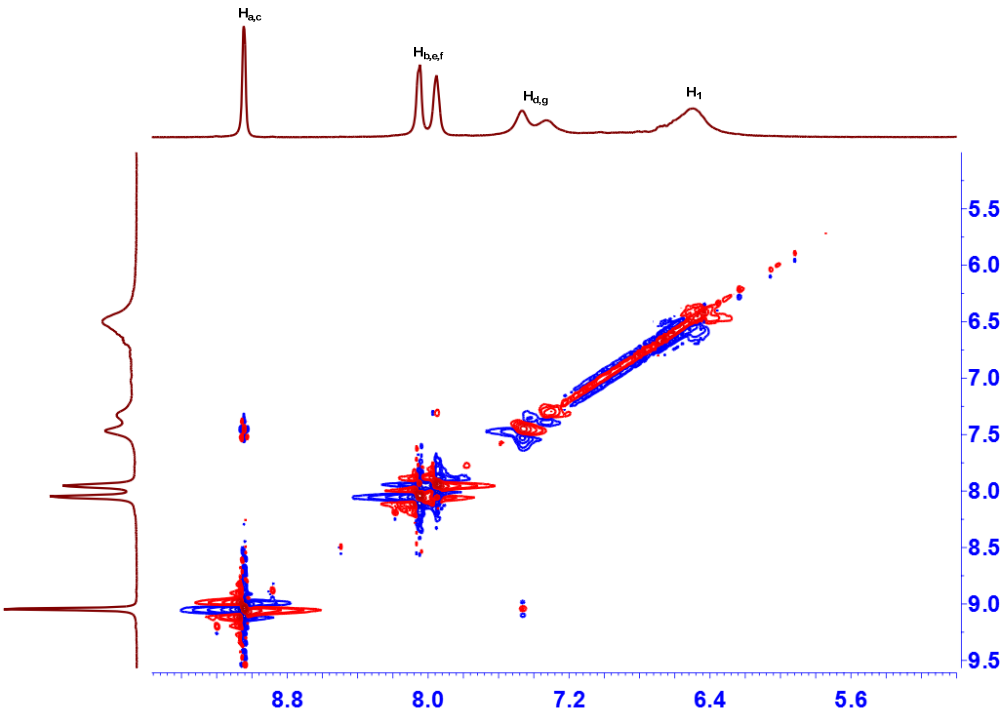



**Fig. S14** Partial $^1$H-$^1$H COSY spectrum (600 MHz, $D_2O$, 295 K) of a solution of host **1** and 2.0 equiv of guest **2**. $[\mathbf{1}]_0$ = 8.0 mM.

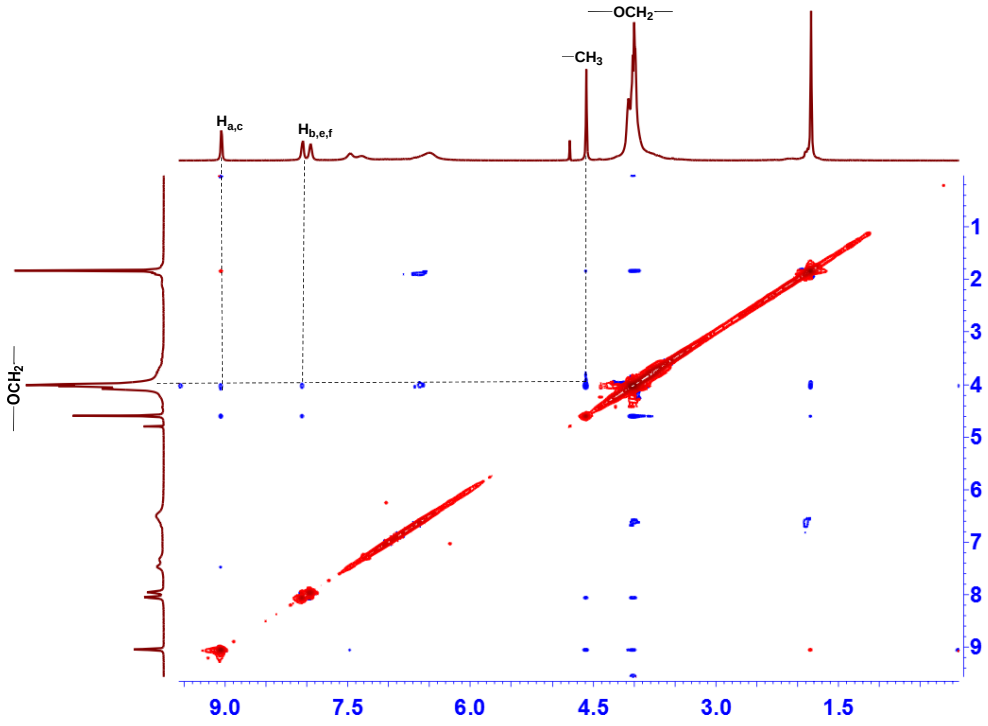



**Fig. S15** Partial $^1$H-$^1$H ROESY spectrum (600 MHz, $D_2O$, 295 K) of a solution of host **1** and 2.0 equiv of guest **2**. $[\mathbf{1}]_0$ = 8.0 mM.

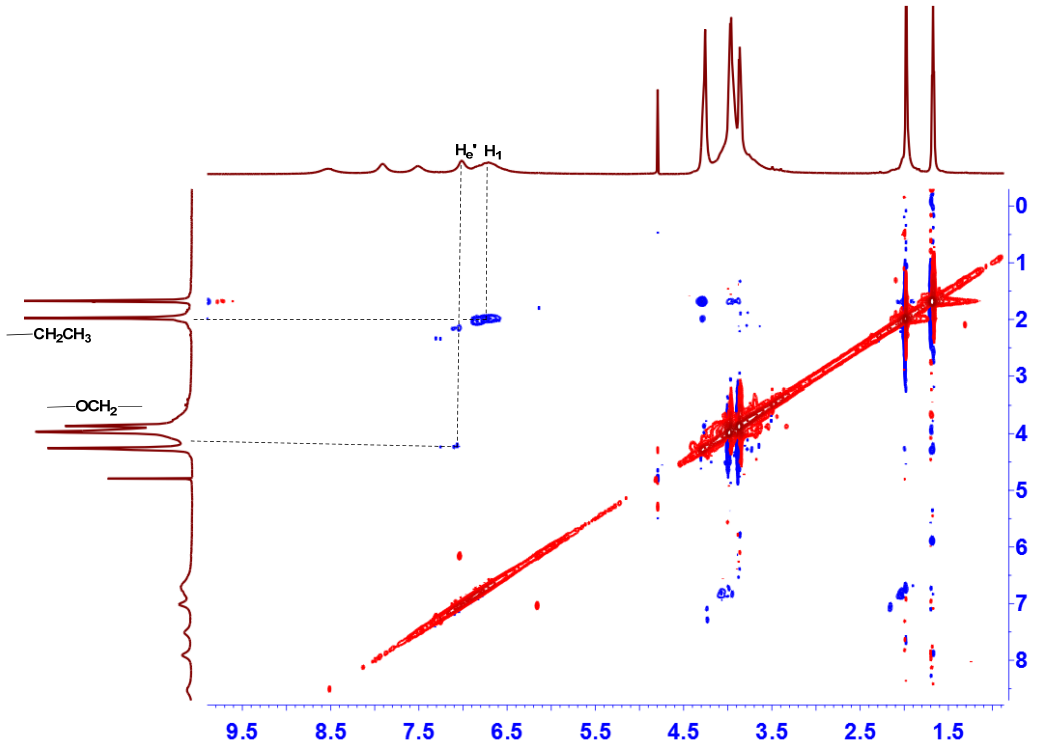



**Fig. S16** Partial $^1$H - $^1$H ROESY spectrum (600 MHz, $D_2O$, 295 K) of a solution of host **1** and 2.0 equiv of guest **3**. $[\mathbf{1}]_0$ = 8.0 mM.

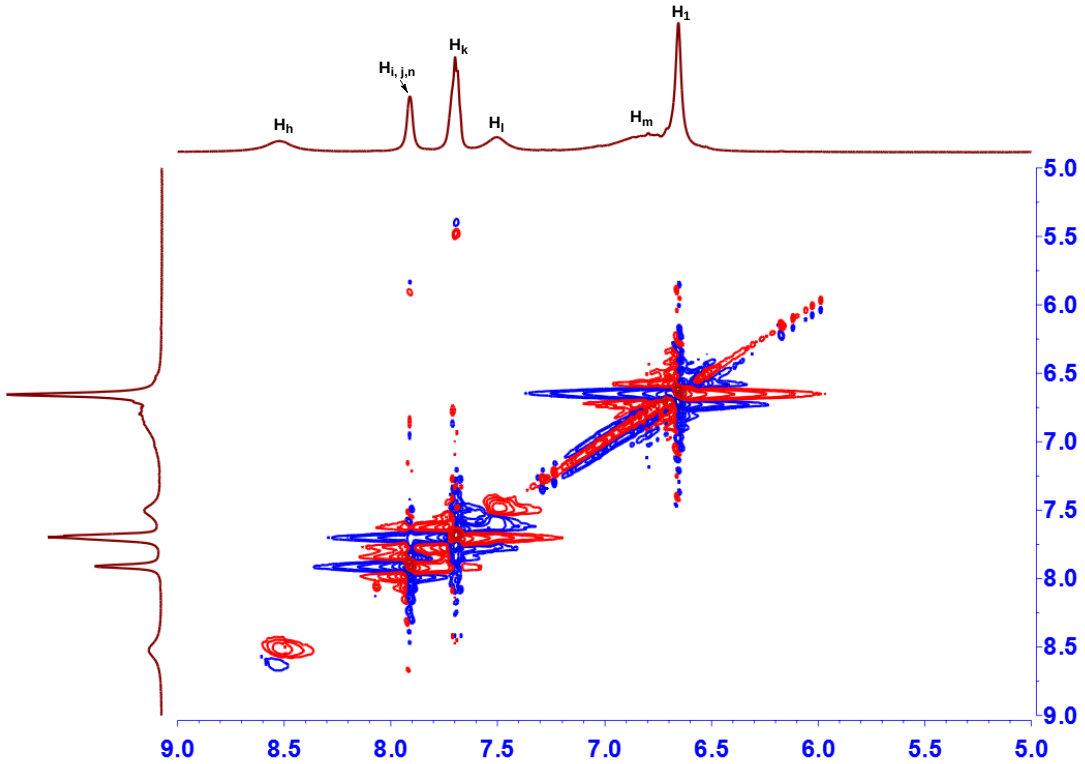



**Fig. S17** Partial $^1$H-$^1$H COSY spectrum (600 MHz, $D_2O$, 295 K) of a solution of host **1** and 2.0 equiv of guest **4**. $[\mathbf{1}]_0$ = 8.0 mM.

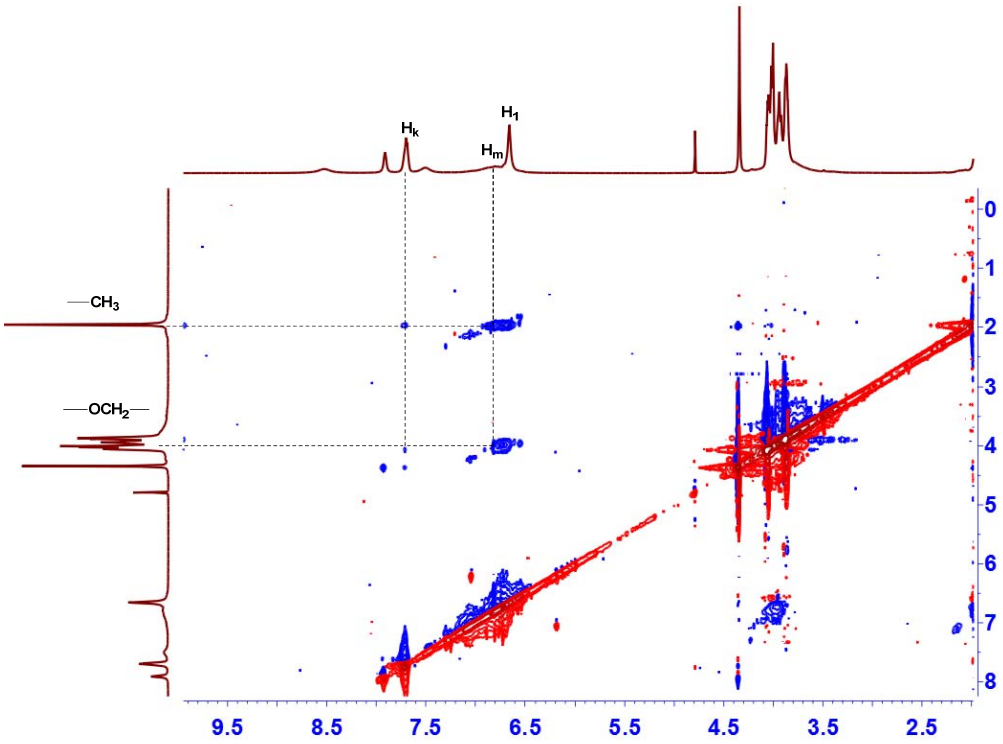



**Fig. S18** Partial $^{1}$H-$^{1}$H ROESY spectrum (600 MHz, $D_2O$, 295 K) of a solution of host **1** and 2.0 equiv of guest **4**. $[\mathbf{1}]_0$ = 8.0 mM.

## 8. $^{1}$H NMR, $^{13}$C NMR and HRMS spectra of new compounds

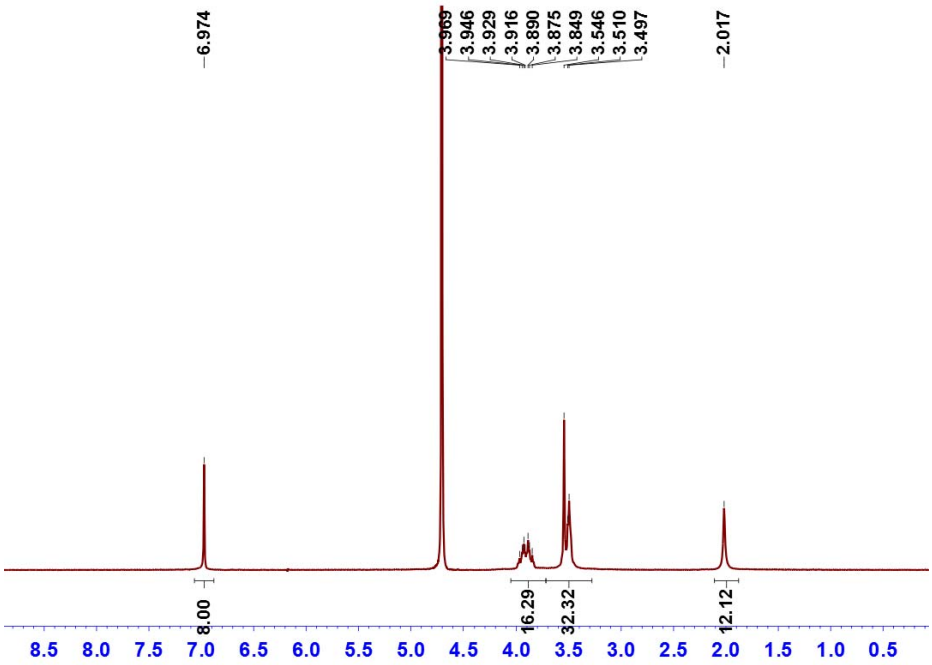



**Fig. S19** $^{1}$H NMR spectrum (300 MHz, $D_2O$, 295 K) of host **1**.

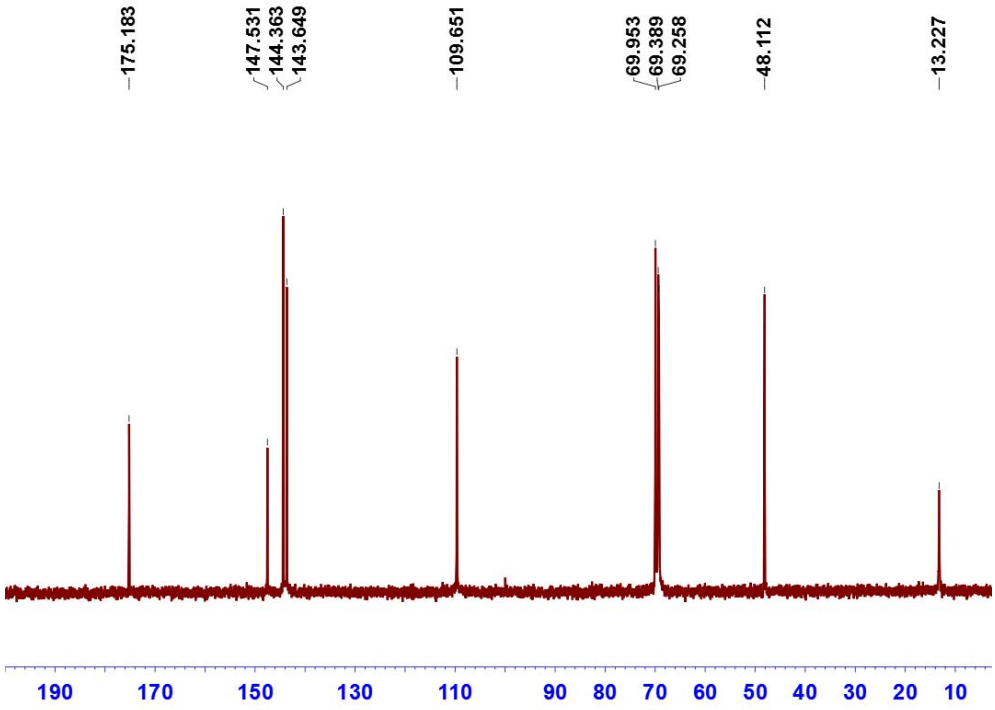



**Fig. S20** $^{13}$C NMR spectrum (75 MHz, $D_2O$, 295 K) of host **1**.

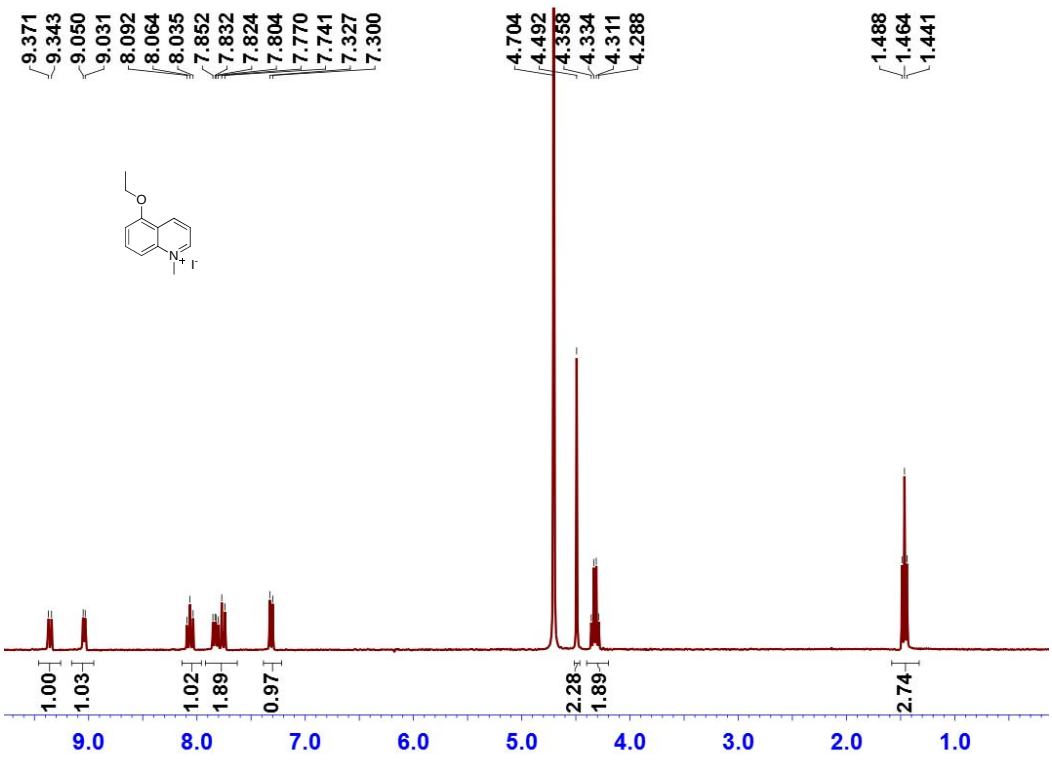



**Fig. S21** $^{1}$H NMR spectrum (300 MHz, $D_2O$, 295 K) of guest **3**.

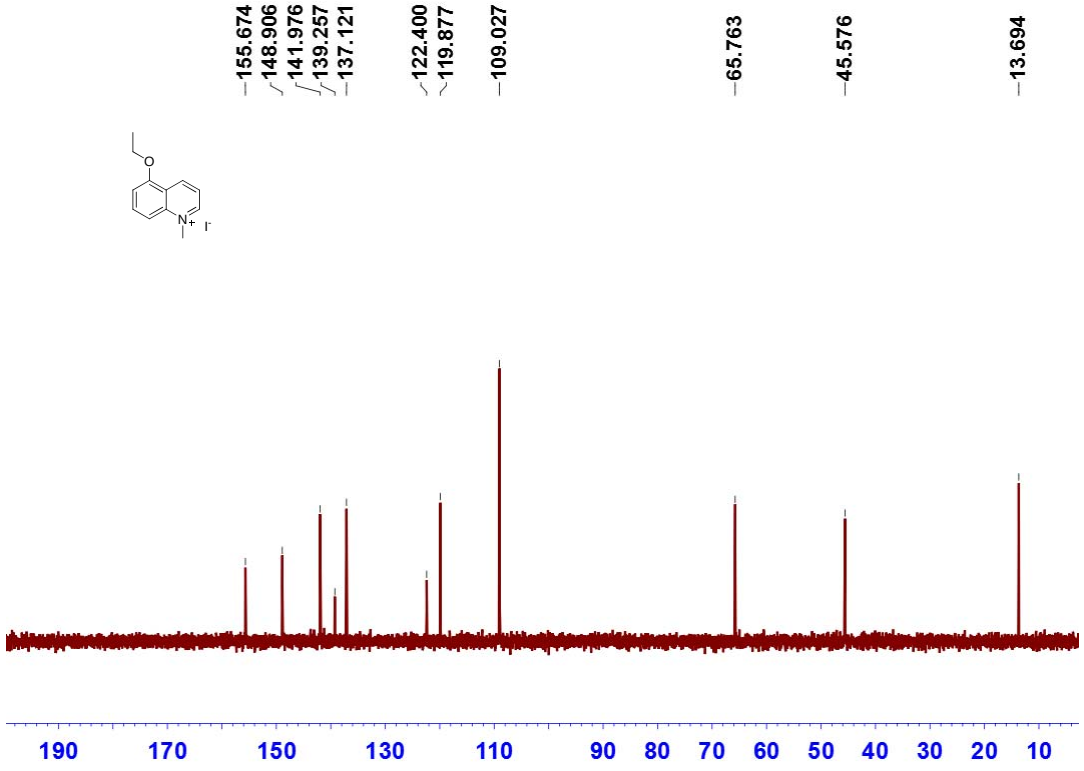



**Fig. S22** $^{13}$C NMR spectrum (75 MHz, $D_2O$, 295 K) of guest **3**.

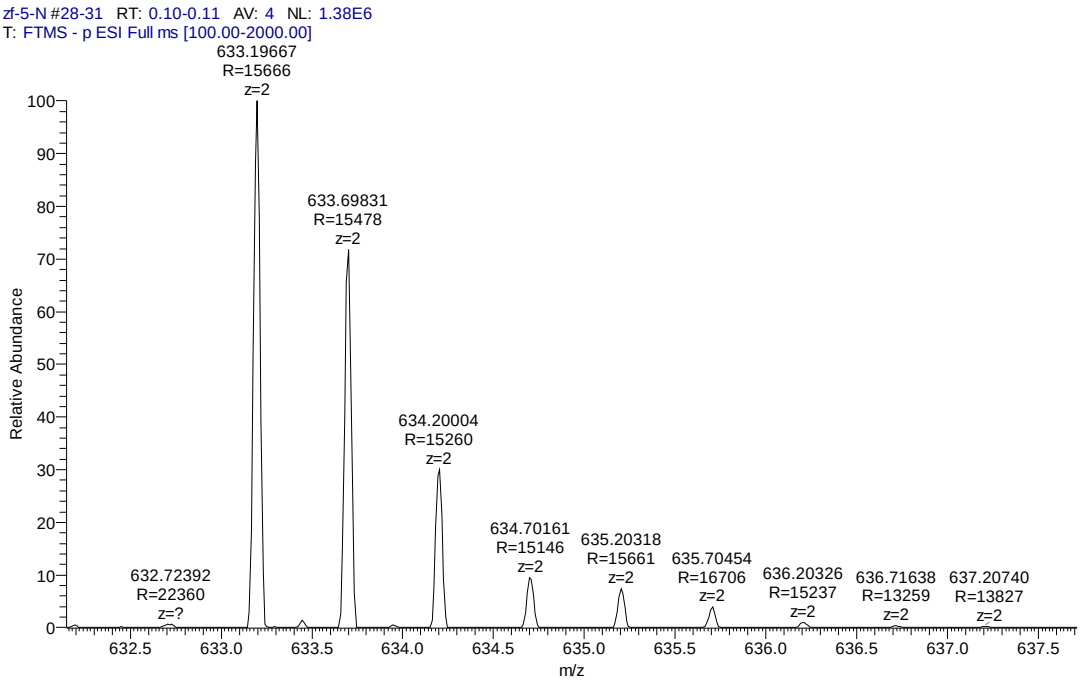



**Fig. S23** HRESI mass spectrum of host **1**.

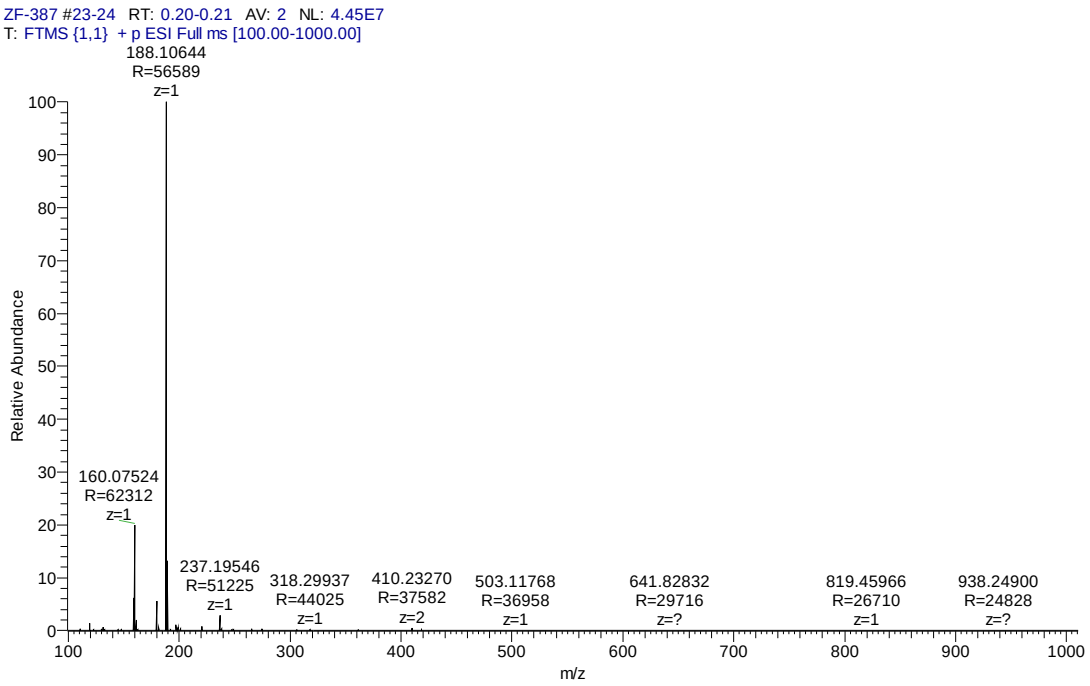



**Fig. S24** HRESI mass spectrum of guest **3**.

## 9. UV/Vis spectra of complexes $1{\cdot}2_2$, $1{\cdot}3_2$ and $1{\cdot}4_2$

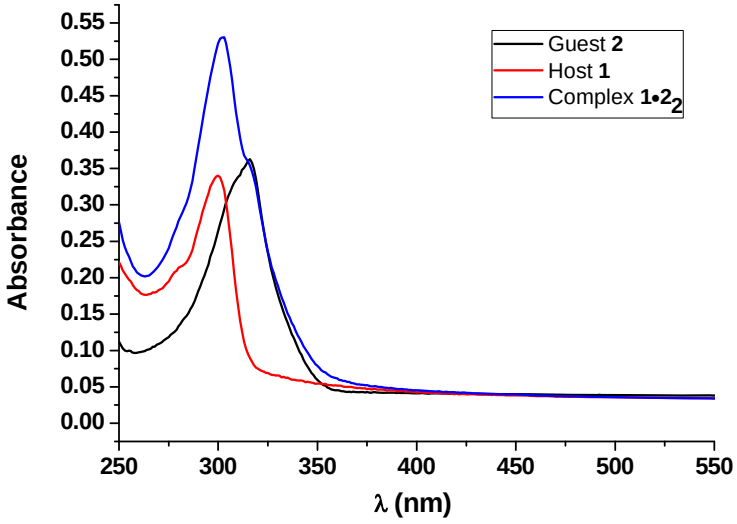



**Fig. S25** UV/Vis absorption spectra of host **1**, guest **2** and complex $\mathbf{1{\cdot}2_2}$. [**1**]= $2.0\times10^{-5}$ M.

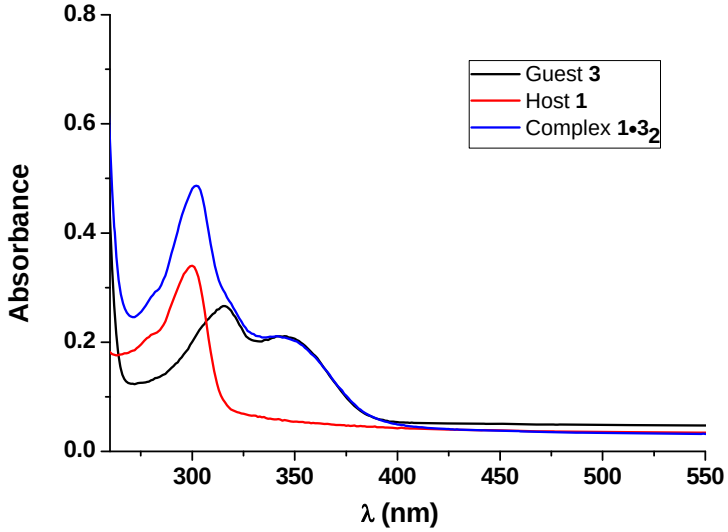



**Fig. S26** UV/Vis absorption spectra of host **1**, guest **3** and complex **1·3$_2$**. [**1**]= $2.0\times10^{-5}$ M.

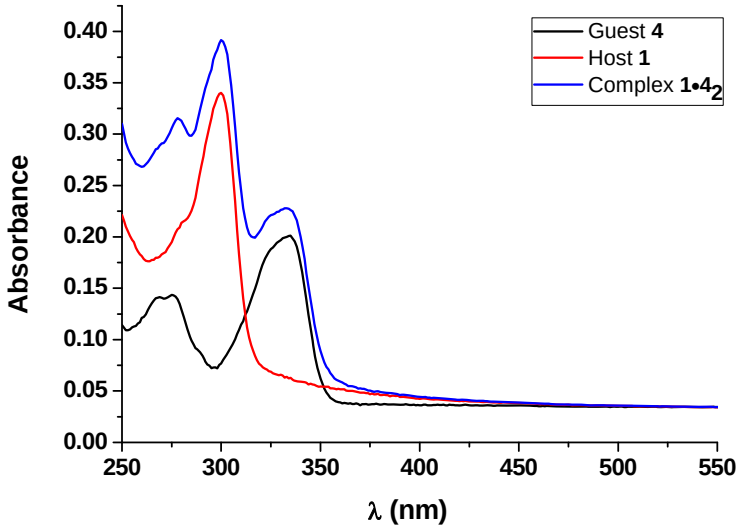



**Fig. S27** UV/Vis absorption spectra of host **1**, guest **3** and complex **1·3$_2$**. [**1**]= $2.0\times10^{-5}$ M.

## 10. The $^1$H-NMR titrations spectra of complexes $1{\cdot}2_2$, $1{\cdot}3_2$ and $1{\cdot}4_2$

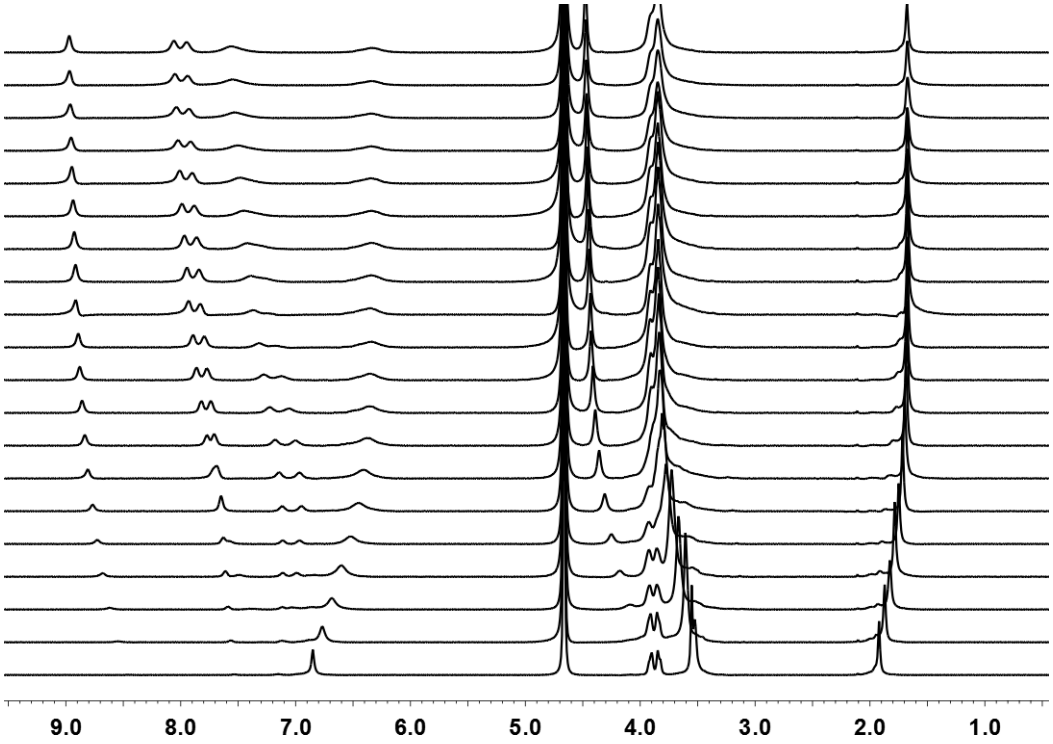



**Fig. S28** $^1$H-NMR (500 MHz, $D_2O$, 295 K) titrations spectra of guest **2** to host **1**, From bottom to top the addition of guest **2** are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2 equivalent of **1**. [**1**]= 3.0 mM.

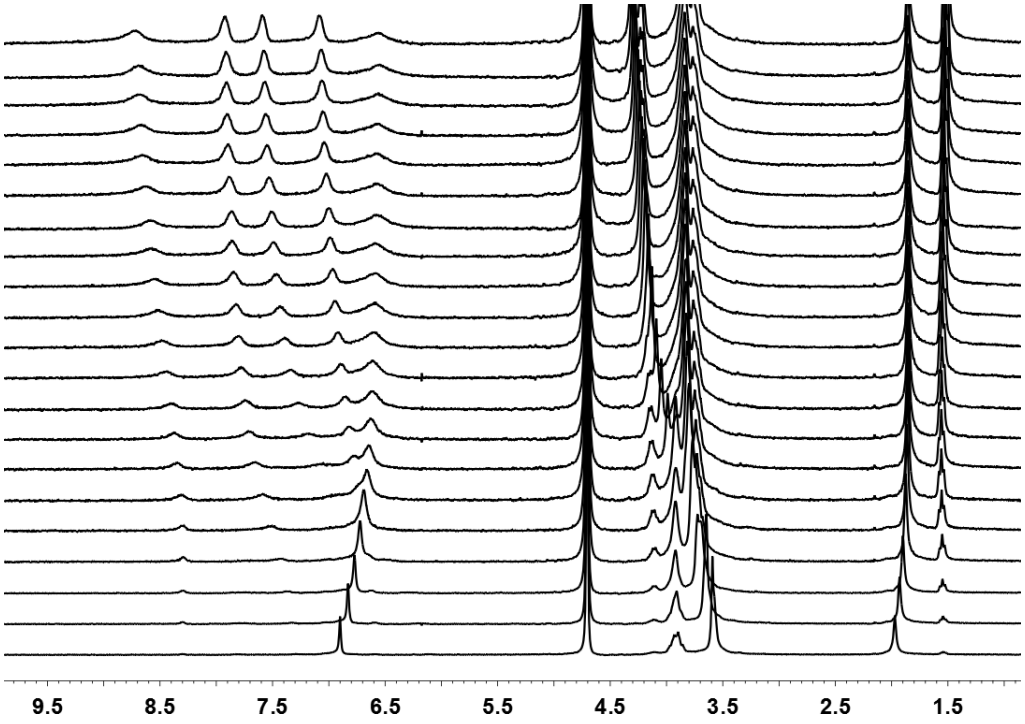



**Fig. S29** $^1$H-NMR (300 MHz, $D_2O$, 295 K) titrations spectra of guest **3** to host **1**, From bottom to top the addition of guest **3** are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2 equivalent of **1**. [**1**]= 3.0 mM.

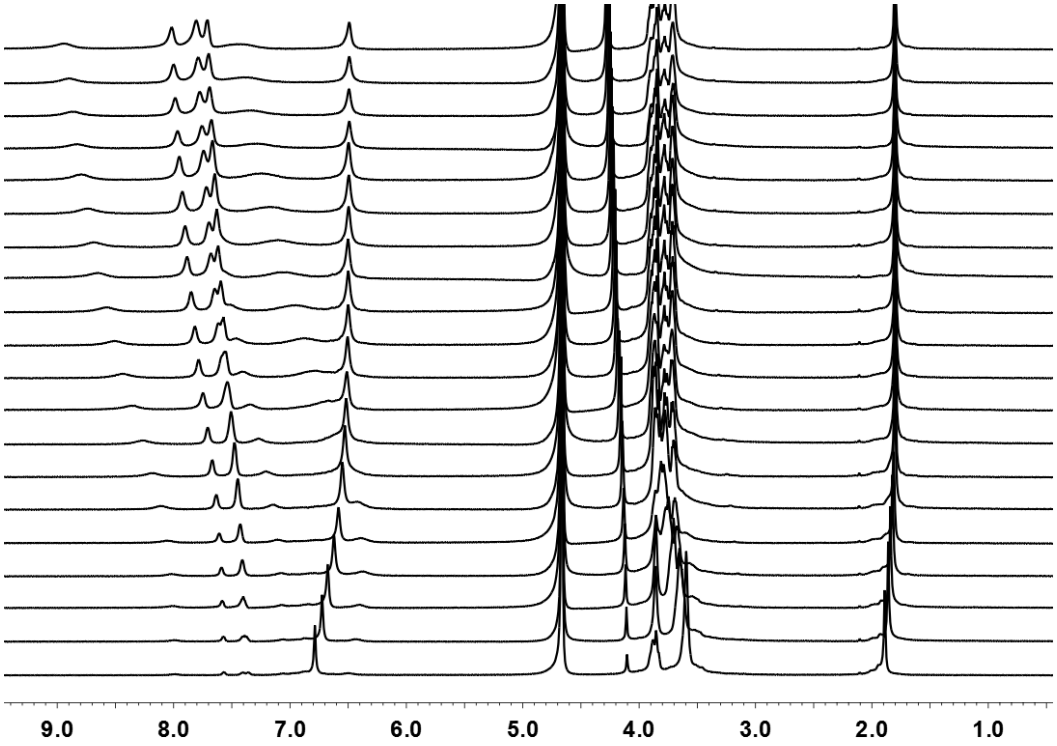



**Fig. S30** $^{1}$H-NMR (500 MHz, $D_2O$, 295 K) titrations spectra of guest **4** to host **1**, From bottom to top the addition of guest **4** are 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2 equivalent of **1**. [**1**]= 3.0 mM.

## 11. The Job-Plot for complexes $1{\cdot}2_2$, $1{\cdot}3_2$ and $1{\cdot}4_2$

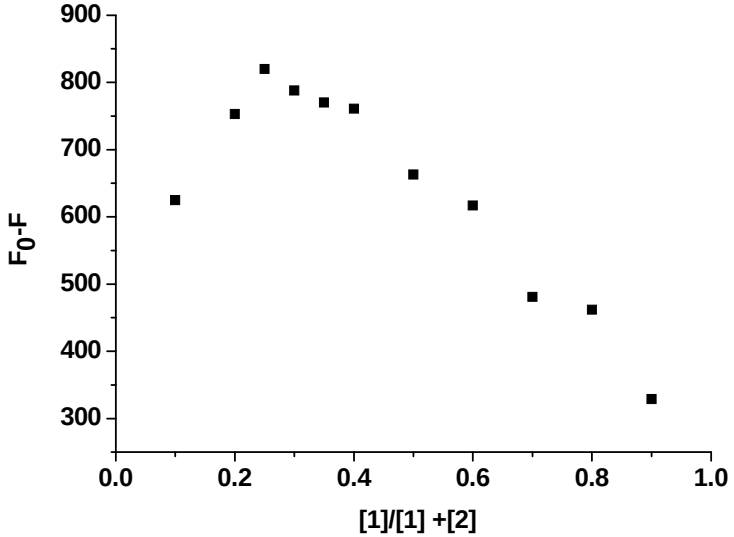



**Fig. S31** The Job plot for $\mathbf{1{\cdot}2_2}$ complex in water ([**1**]=[**2**], [**1**]+[**2**]=$8\times10^{-5}$ M, $\lambda_{ex}$ = 316 nm).

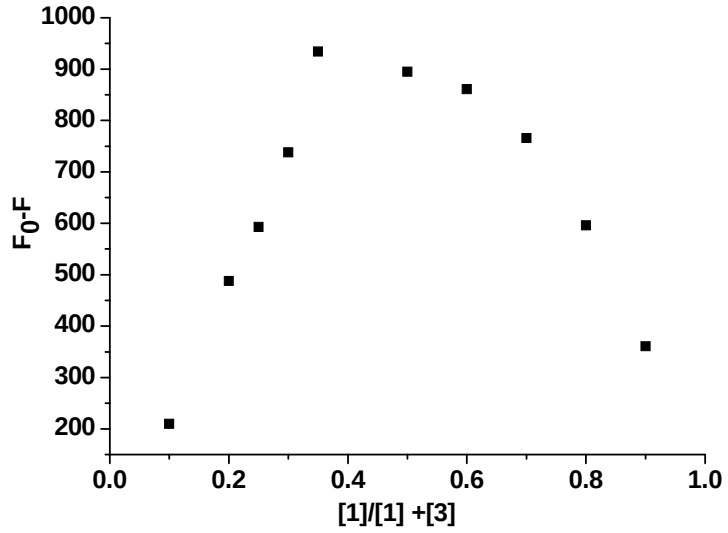



**Fig. S32** The Job plot for **1·3₂** complex in water ([**1**]=[**3**], [**1**]+[**3**]=8×10$^{-5}$ M, $\lambda_{ex}$ = 316 nm).

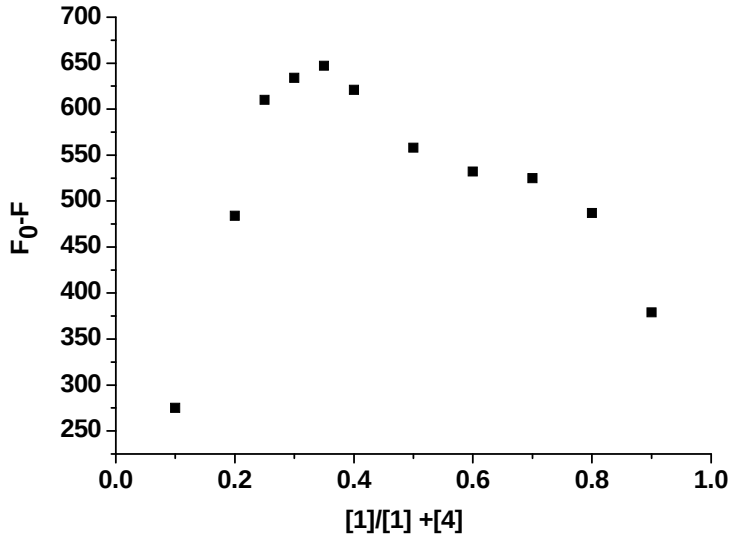



**Fig. S33** The Job plot for **1·4₂** complex in water ([**1**]=[**4**], [**1**]+[**4**]=8×10$^{-5}$ M, $\lambda_{ex}$ = 320 nm).

## 12. Crystal data

| | |
|---|---|
| Empirical formula | C84 H90 N2 O24 |
| Formula weight | 1511.57 |
| Temperature | 173.1500 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |

| | | |
|---|---|---|
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 15.814(4) Å | α= 90°. |
| | b = 14.779(3) Å | β= 96.603(4)°. |
| | c = 21.657(5) Å | γ = 90°. |
| Volume | 5027.9(19) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 0.998 $Mg/m^3$ | |
| Absorption coefficient | 0.073 $mm^{-1}$ | |
| F(000) | 1600 | |
| Crystal size | 0.26 x 0.17 x 0.15 $mm^3$ | |
| Theta range for data collection | 1.672 to 27.482°. | |
| Index ranges | -20<=h<=20, -19<=k<=19, -28<=l<=26 | |
| Reflections collected | 40163 | |
| Independent reflections | 11480 [R(int) = 0.0638] | |
| Completeness to theta = 26.000° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.0000 and 0.6554 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11480 / 402 / 580 | |
| Goodness-of-fit on $F^2$ | 1.622 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1131, wR2 = 0.2870 | |
| R indices (all data) | R1 = 0.1401, wR2 = 0.3004 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.069 and -0.600 $e.Å^{-3}$ | |

## 13. References

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