**Supporting Information**

# Light Driven Molecular Lock comprises $Ru(bpy)_2(hpip)$ complex and Cucurbit[8]uril

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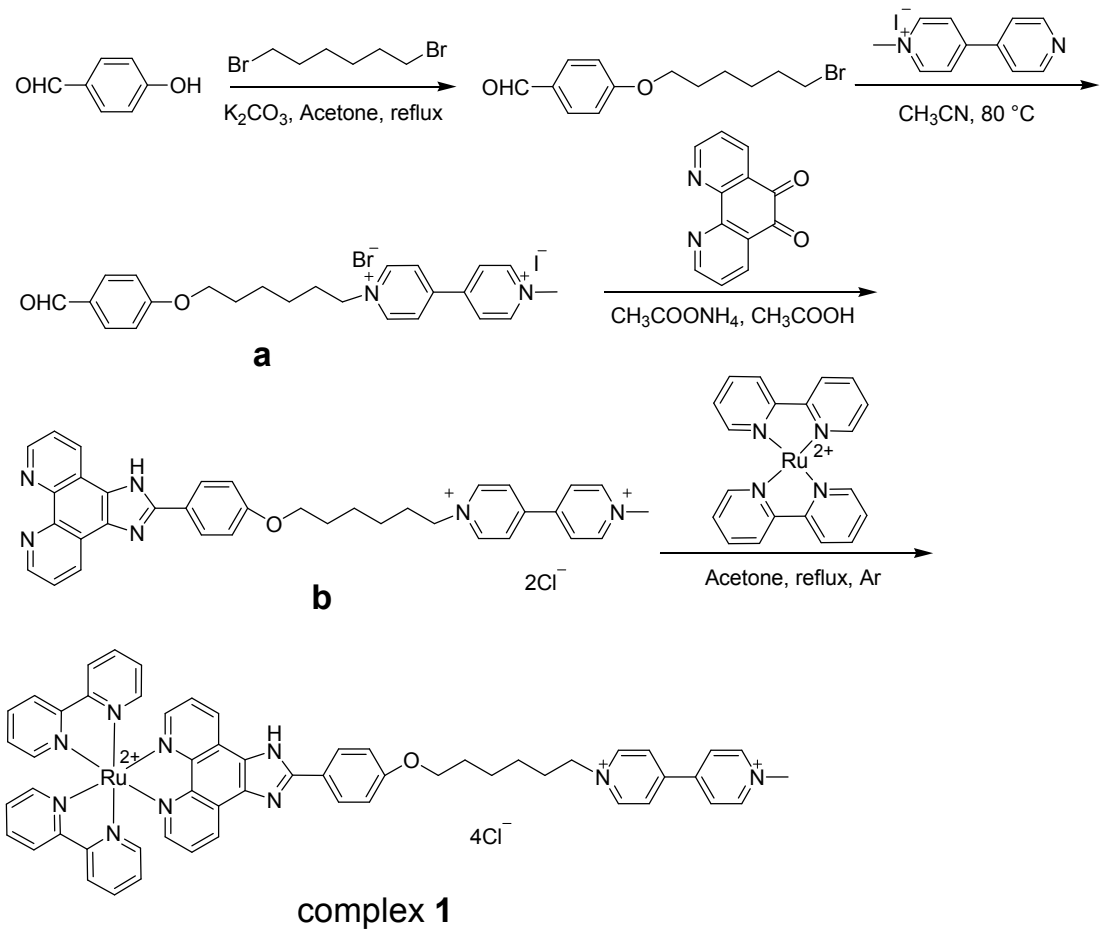
## 1. General

$^1$H NMR spectra were obtained on a Bruker AVANCE III 400 MHz spectrometer. High Resolution Mass Spectrometry (HRMS) was detected on a Agilent 6540 Q-TOF spectrometer. UV-vis Absorbance Spectra were measured on a Agilent 8453 UV-vis spectrometer. The irradiation was achieved with light from a SONY Multimedia Mobile LCD Projector. Electrochemical experiments were carried out using RST 5000 Electrochemical analyzer. Melting points were measured with an SGWX-4 microscopic apparatus without revision of the thermometer .

## 2. Materials

All materials and solvents employed were commercially available and used as supplied without purification.

## 3. Preparation of complex 1




**Scheme S1.** The synthesis route of complex **1**·**4Cl**$^-$

*Synthesis of 4-(6-Bromo-hexyloxy)-benzaldehyde*

To a suspension of $K_2CO_3$ (834 mg, 6 mmol) in 20 mL freshly distilled acetone was added 4-hydroxybenzaldehyde(488 mg, 4 mmol) and 1,6 -dibromo hexane (3 mL, 20 mmol) and the mixture was stirred at the reflux temperature for 3 h. After removal of the solid part by filtration, organic solvent was removed under reduced pressure. The crude product was dissolved in $CHCl_3$ to extract it with water. Organic layer was evaporated and resulting residue chromatographed (10:1 Petroleum ether/EtOAc) to give 4-(6-Bromo-hexyloxy)-benzaldehyde as white solid (846 mg, yield 74%). mp: 39-40 ºC. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$; 9.88 (s, 1H), 7.84 (d, *J*=8.8 Hz, 2H), 7.00 (d, *J*=8.8 Hz, 2H), 4.05 (t, *J*=6.4 Hz, 2H), 3.43 (t, *J*=6.8 Hz, 2H), 1.94-1.87 (m, 2H), 1.87-1.80 (m, 2H), 1.56-1.49 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 190.7, 164.1, 131.9, 129.8, 114.7, 68.1, 33.7, 32.6, 28.8, 27.8, 25.2.

*Synthesis of 1-(6-(4-formylphenoxy)hexyl)-1'-methyl-[4,4'- bipyridine] -1,1'-diium(compound **a**)*

A solution of 4-(6-Bromo-hexyloxy)-benzaldehyde (570 mg, 2mmol) and N-methyl-4,4′-bipyridinium (890 mg, 3mmol) in $CH_3CN$ (10 mL) was stirred at 80 °C for 2 days. After cooling to room temperature the solution was filtered to get a red precipitate **a** (748 mg, yield 63%) $^1$H NMR (400 MHz, $D_2O$) $\delta$; 9.57 (s, 1H), 9.04 (d, *J*=6.6 Hz, 2H), 8.98 (d, *J*=6.6 Hz, 2H), 8.41 (m, 4H), 7.66 (d, *J*=8.6 Hz, 2H), 6.88 (d, *J*=8.6 Hz, 2H), 4.66 (t, *J*=7.1 Hz, 2H), 4.44 (s, 3H), 3.93 (t, *J*=6.1 Hz, 2H), 2.05-1.98 (m, 2H), 1.68-1.63 (m, 2H), 1.44-1.37 (m, 2H), 1.35-1.32 (m, 2H). $^{13}$C NMR (100 MHz, $D_2O$, ppm): $\delta$ 194.5, 164.2, 149.6, 149.4, 146.3, 145.4, 132.7, 128.8, 126.9, 126.6, 115.1, 68.5, 62.0, 48.4, 30.3, 27.8, 24.7, 24.6. HRMS (ESI, *m/z*): calcd for $C_{24}H_{28}BrIN_2O_2$ $[M\text{-}I^-\text{-}Br^-+e]^+$: 376.2140, found 376.2141

*Synthesis of 1-(6-(4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2- yl)phenoxy)hexyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium(compound **b**)*

A solution of 1,10-phenanthroline-5,6-dione (0.21 g, 1.0 mmol), compound **a** (0.70 g, 1.2 mmol), and ammonium acetate (1.9 g, 25 mmol) in glacial acetic acid (10 mL)

was refluxed for 3 h, After cooling to room temperature, the cooled deep red solution was diluted with 25 mL water and neutralized with ammonium hydroxide. Then, excessive $NH_4PF_6$ was added to the solution to give a precipitate of the product which was filtered, washed with water and purified by column chromatography (10:1:1 MeCN:$H_2O$: Sat. $KNO_3$). The principal band was collected, and the counteranion exchanged with $NH_4PF_6$ to get **b·2PF$_6^-$** (385 mg, 45 %). After ion exchange the product was collected as a red powder **b·2Cl$^-$**. $^1$H NMR (400 MHz, $D_2O$, ppm): $\delta$ 8.78 (d, *J*=6.2 Hz, 2H), 8.49 (br, 2H), 8.20 (d, *J*=6 Hz, 2H), 8.02 (d, *J*=6.2 Hz, 2H), 7.87 (br, 2H), 7.81 (d, *J*=6 Hz, 2H), 7.25 (br, 4H), 6.66 (br, 2H), 4.43 (t, *J*=6.9 Hz, 2H), 3.94 (br, 2H), 3.75 (s, 3H), 1.82 (br, 2H), 1.68 (br, 2H), 1.44 (br, 2H), 1.30 (br, 2H). $^{13}$C NMR (100 MHz, $D_2O$, ppm): $\delta$ 158.9, 149.8, 148.5, 148.1, 146.7, 145.5, 145.0, 139.9, 129.5, 127.2, 126.1, 125.5, 123.3, 119.9, 114.6, 67.8, 61.7, 48.0, 30.1, 27.5, 24.9, 24.2. HRMS (ESI, *m/z*): calcd for $C_{36}H_{34}Cl_2N_6O$ $[M\text{-}2Cl^-]^{2+}$: 283.1392, found 283.1397

*Synthesis of complex **1***

The cis-Ru(bpy)$_2$Cl$_2$ (52 mg, 0.10 mmol) was dissolved in acetone (5 mL) with $AgPF_6$ (50 mg, 0.2 mmol) for 8 h. The solution was filtered and washed with acetone (10mL) into a 25 mL round bottom flask containing the crude product **b·2PF$_6^-$**. The mixture was refluxed under Ar for 2 days. After removal of the acetone the pure compound was obtained by subsequent purification by silica column with a 10:1:1 in MeCN: $H_2O$: $KNO_3$ Sat. $H_2O$. Ion exchange to $Cl^-$ ions yielded the final product **1** (43 mg, 38.4%). $^1$H NMR (400 MHz, $D_2O$, ppm): δ 9.00 (d, *J* = 6.8 Hz, 2H), 8.82 (d, *J* = 6.4 Hz, 2H), 8.73 (d, *J* = 8.6 Hz, 2H), 8.45-8.50 (m, 4H), 8.38 (d, *J* = 6.8 Hz, 2H), 8.34 (d, *J* = 6.4 Hz, 2H), 8.03 (d, *J* = 4.6 Hz, 2H), 7.97-8.01 (m, 2H), 7.88-7.92 ( m, 2H), 7.84 (d, *J* = 5.4 Hz, 2H), 7.68 (br 2H), 7.62-7.65 (m, 4H), 7.31-7.34 (m, 2H), 7.14-7.18 (m, 2H), 6.53 (br, 2H), 4.64 ( 2H), 4.16 (s, 3H), 3.69 (br, 1H ), 3.59 (br, 1H ), 1.98-2.05 (m, 2H), 1.55 (br, 2H), 1.33 (br, 4H). $^{13}$C NMR (100 MHz, $D_2O$, ppm): $\delta$ 158.9, 157.2, 156.9, 151.7, 151.0, 150.0, 149.8, 149.6, 146.2, 145.4, 145.0, 137.9, 137.8, 130.4, 130.1, 127.6, 127.5, 127.0, 126.8, 126.6, 125.5, 124.2, 124.0, 122.4,

119.0, 113.1, 66.9, 61.9, 48.2, 30.6, 28.0, 25.4, 24.8. HRMS (ESI, *m/z*): calcd for $C_{56}H_{50}Cl_4N_{10}ORu$ $[M\text{-}4Cl^{-}\text{-}H^{+}]^{3+}$: 326.4400, found 326.4381

## 4. $^1$H NMR spectra of compounds

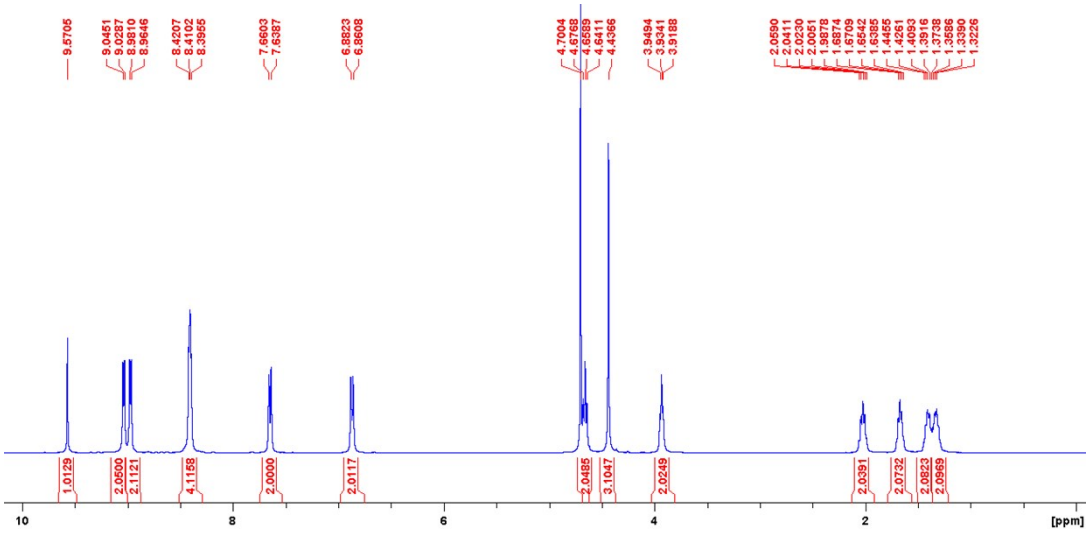



**Figure S1.** $^1$H NMR spectra (400 MHz, $D_2O$) of compound **a**

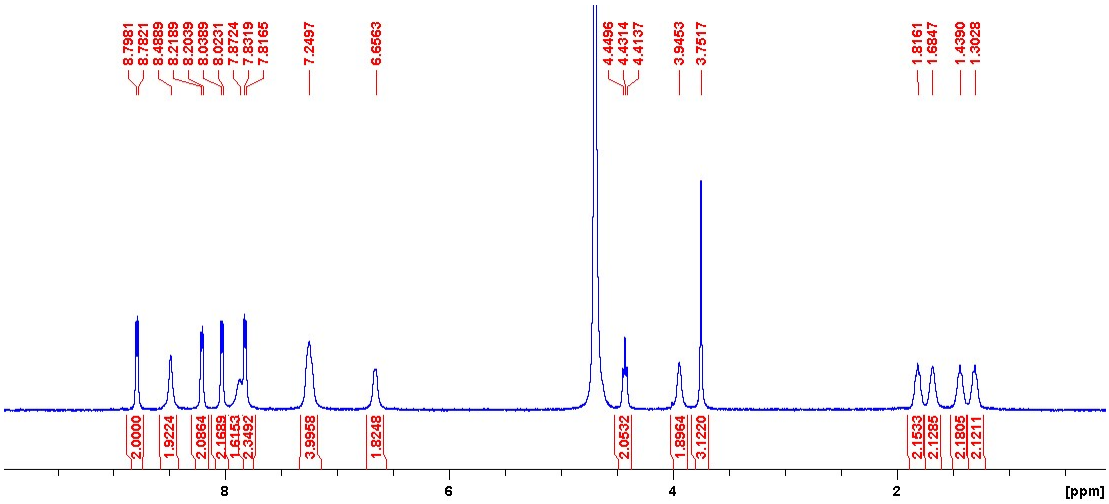



**Figure S2.** $^1$H NMR spectra (400 MHz, $D_2O$) of compound **b**

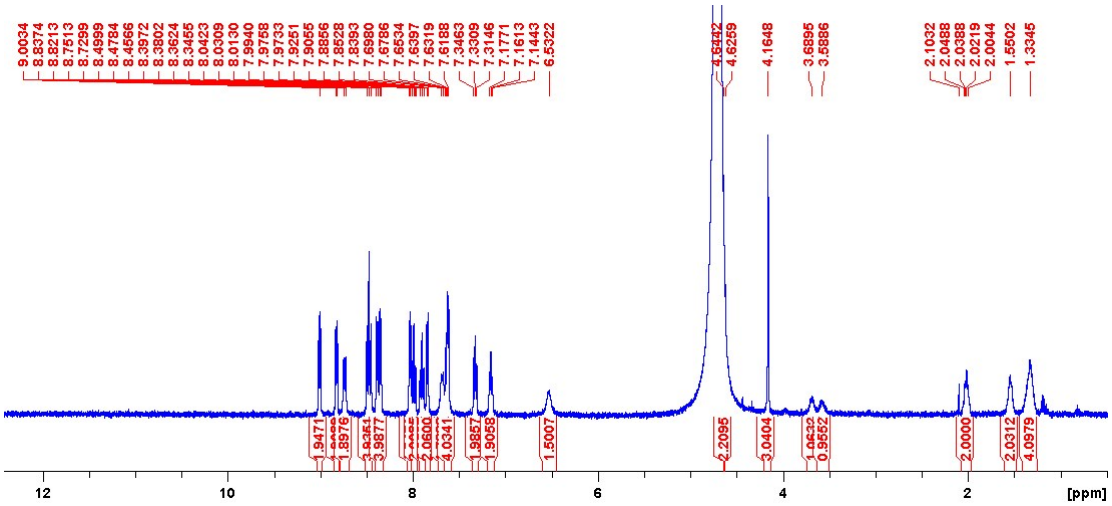



**Figure S3.** $^{1}H$ NMR spectra (400 MHz, $D_2O$) of complex **1**

## 5. $^{13}C$ NMR spectra of compounds

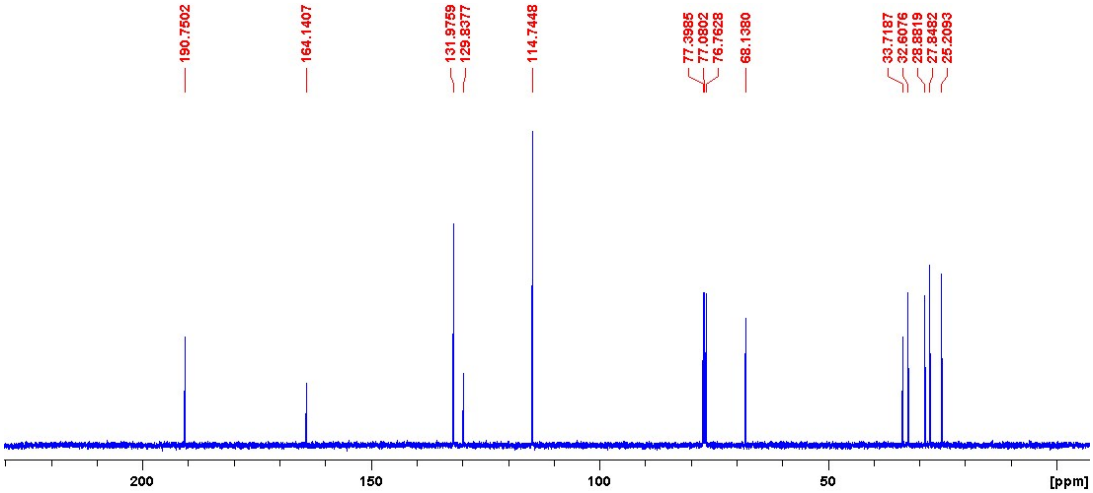



**Figure S4.** $^{13}C$ NMR spectra (100 MHz, $CDCl_3$) of 4-(6-Bromo-hexyloxy)-benzaldehyde

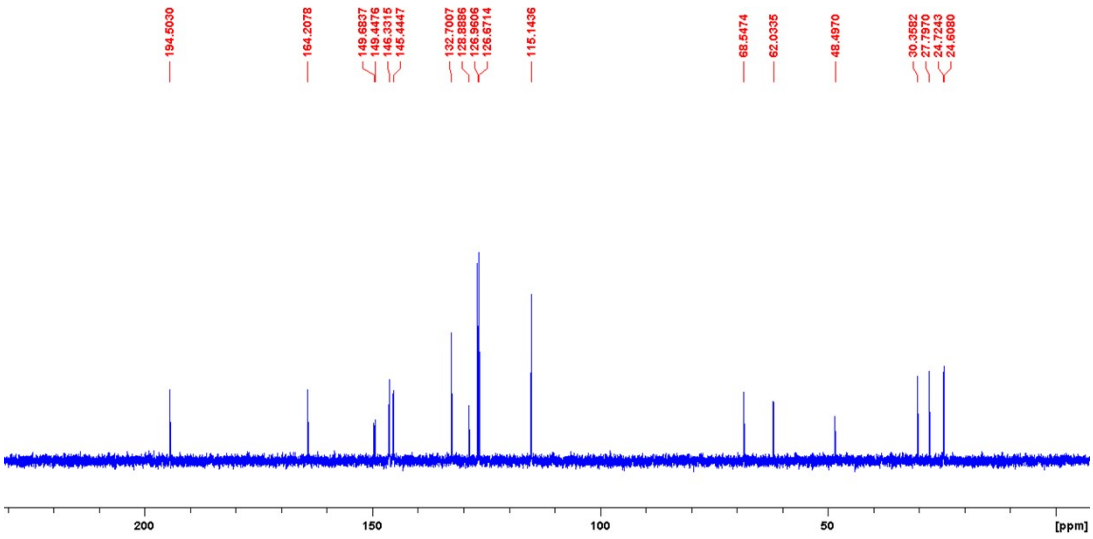



**Figure S5.** $^{13}C$ NMR spectra (100 MHz, $D_2O$) of compound **a**

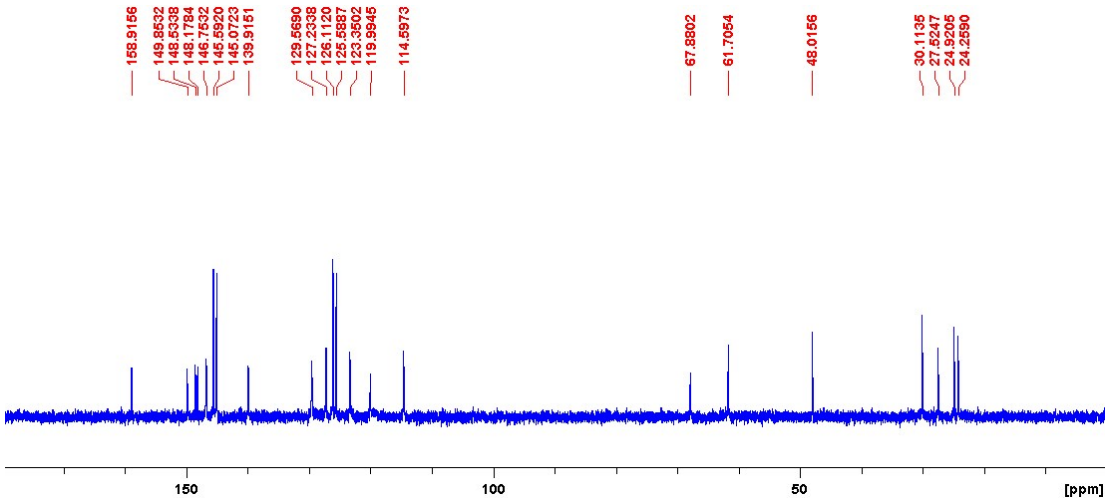



**Figure S6.** $^{13}C$ NMR spectra (100 MHz, $D_2O$) of compound **b**

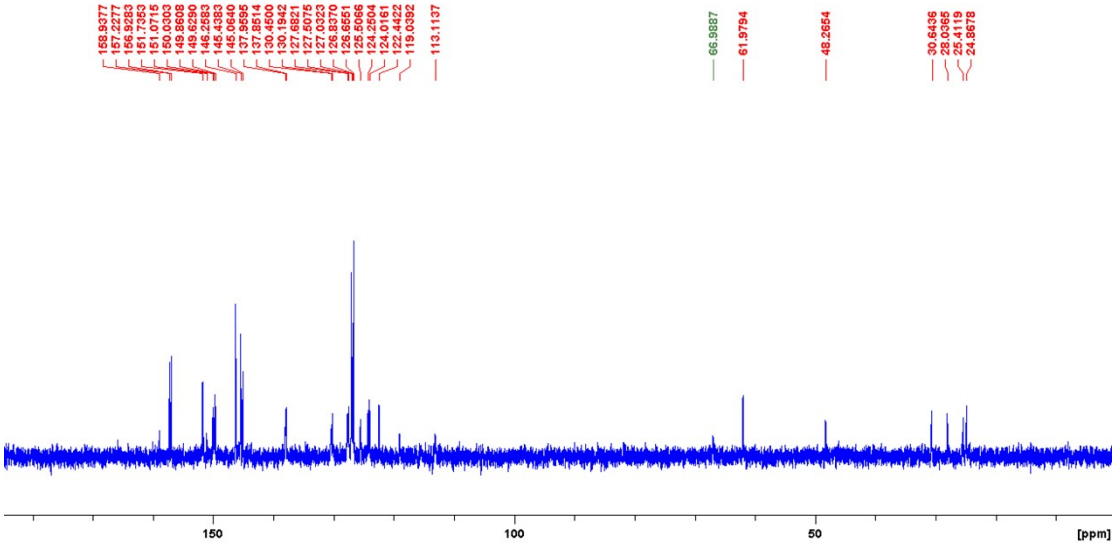



**Figure S7.** $^{13}C$ NMR spectra (100 MHz, $D_2O$) of complex **1**

## 6. COSY and NOESY NMR spectra of complexs

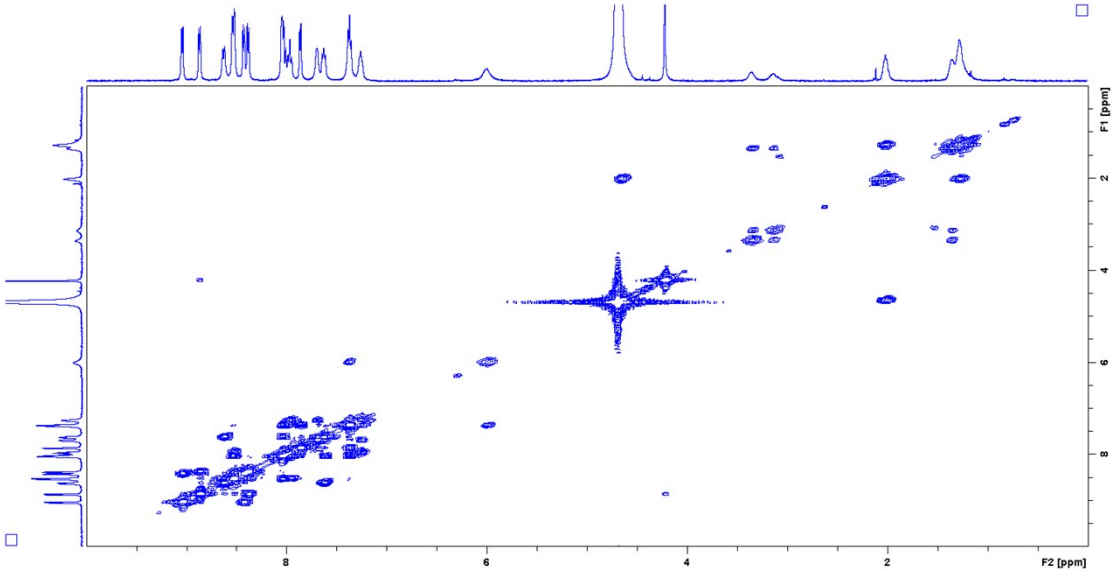



**Figure S8.** $^{1}$H-$^{1}$H COSY spectra (400 MHz, $D_2O$) of complex **1**

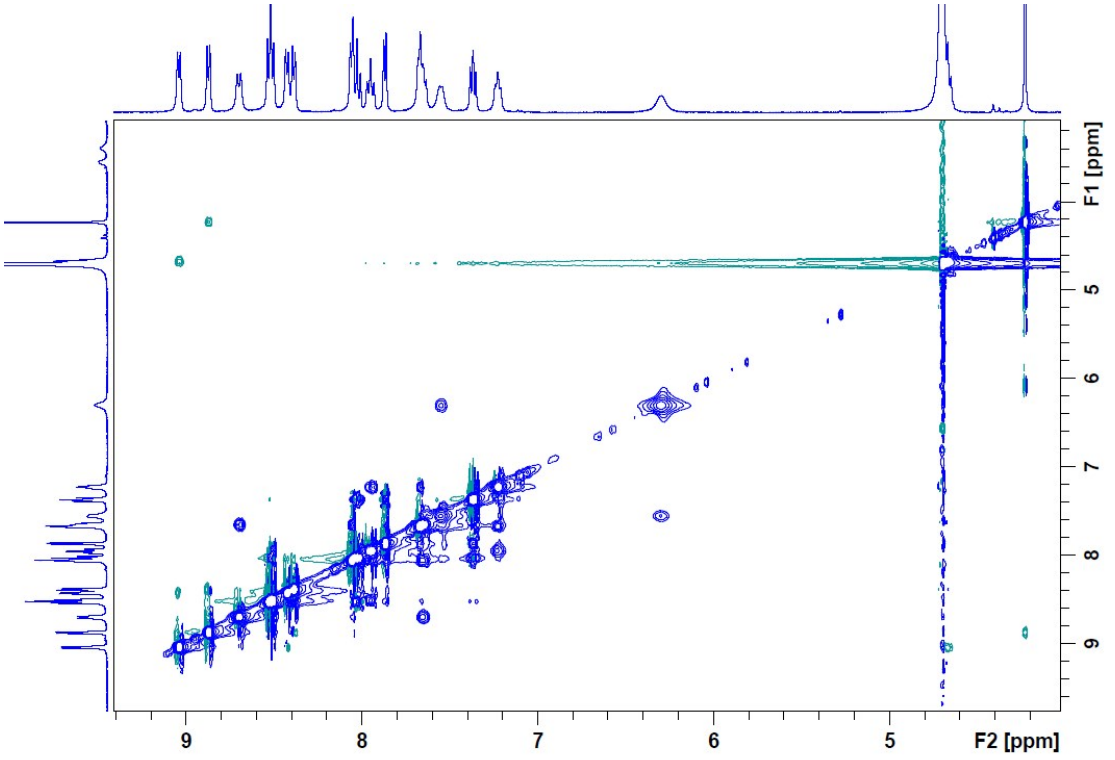



**Figure S9.** Partial $^{1}$H–$^{1}$H NOESY spectrum of complex **1** in $D_2O$ at 298 K.

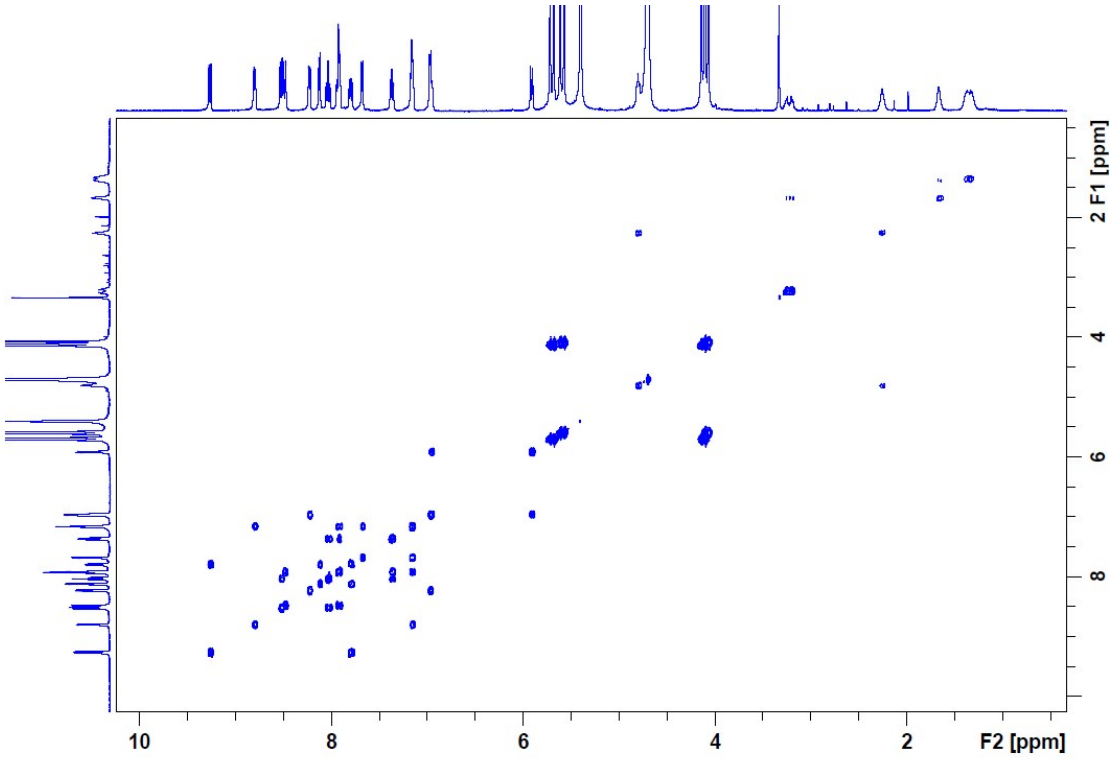



**Figure S10.** $^{1}$H-$^{1}$H COSY spectra (400 MHz, $D_2O$) of complex **1+CB[8]**

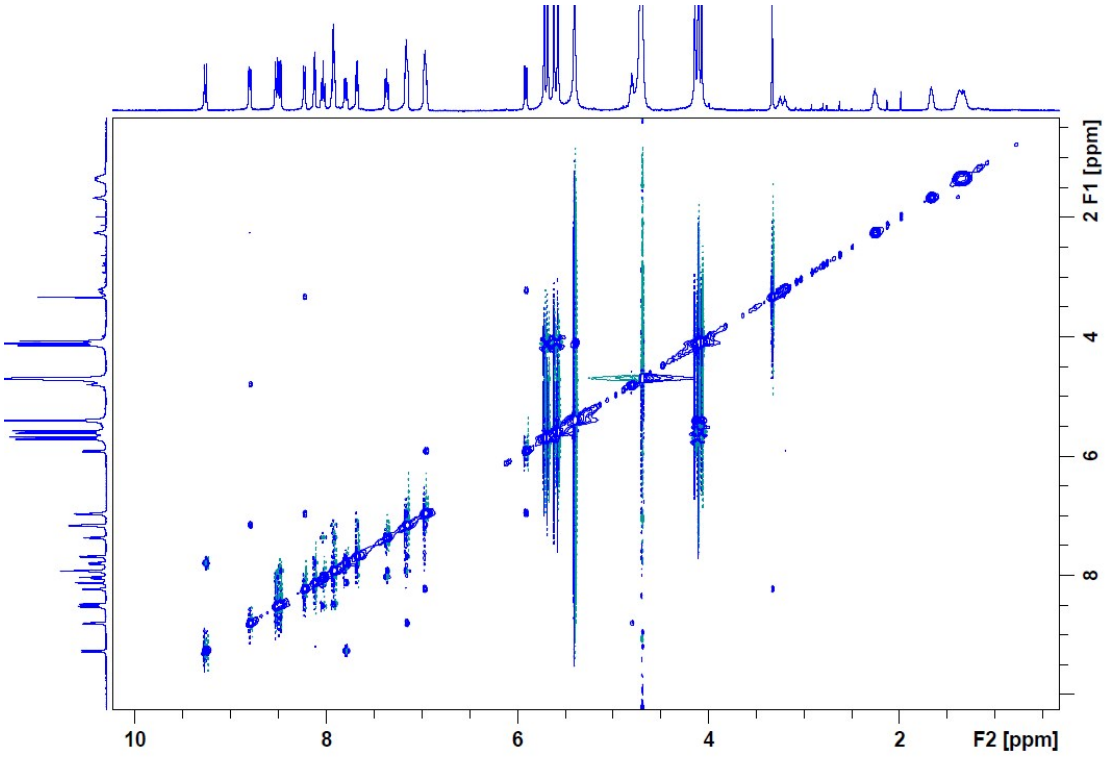



**Figure S11.** $^{1}$H–$^{1}$H NOESY spectrum of complex **1+CB[8]** in $D_2O$ at 298 K.

## 7. DOSY NMR spectra of complexs

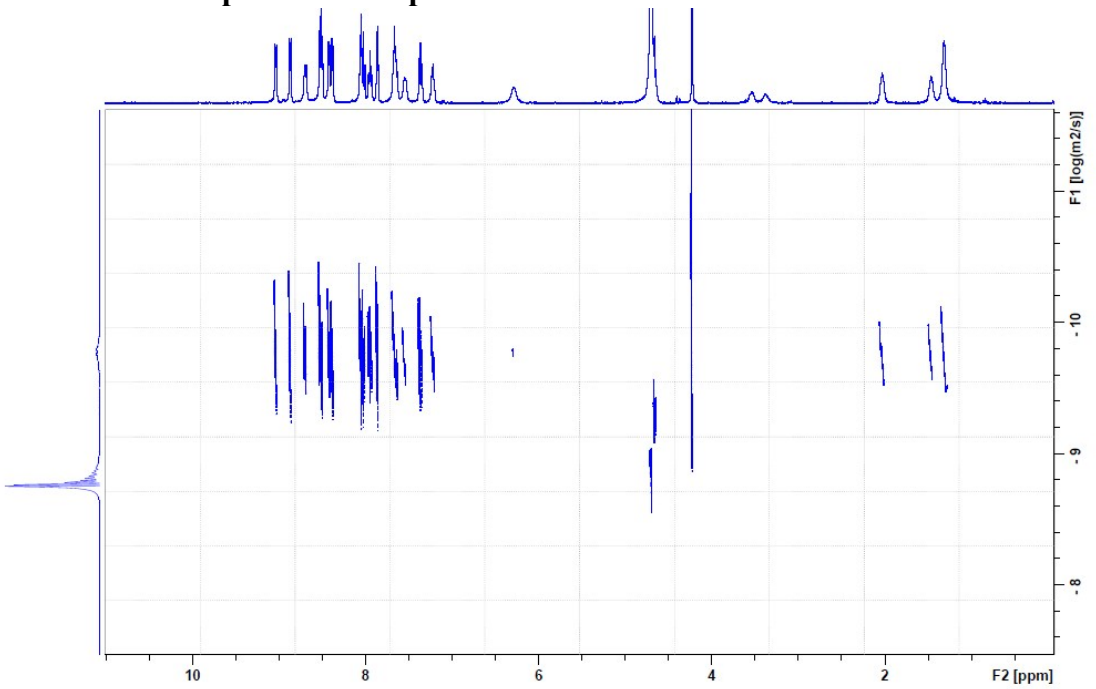



**Figure S12.** DOSY-NMR spectrum (400 MHz, $D_2O$, 298 K) of complex **1**, plotted using the log values of the diffusion constant.

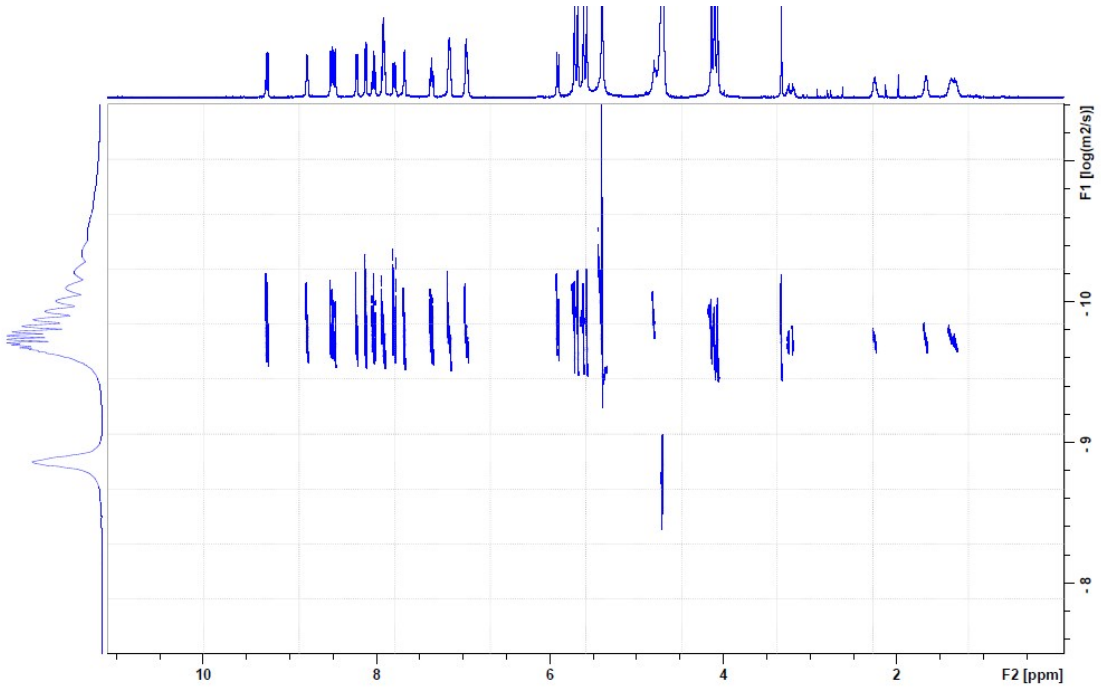



**Figure S13.** DOSY-NMR spectrum (400 MHz, $D_2O$, 298 K) of complex **1+CB[8]**, plotted using the log values of the diffusion constant.

**Table S1.** Diffusion coefficients (D) obtained from DOSY measurements

| Complex | Diffusion coefficient ($m^2$ $s^{-1}$) |
|---|---|
| **1** | 1.70 ß$10^{-10}$ |
| **1+CB[8]** | 1.55 ß$10^{-10}$ |

## 8. ESI-MS spectra of complex of 1–CB[8]

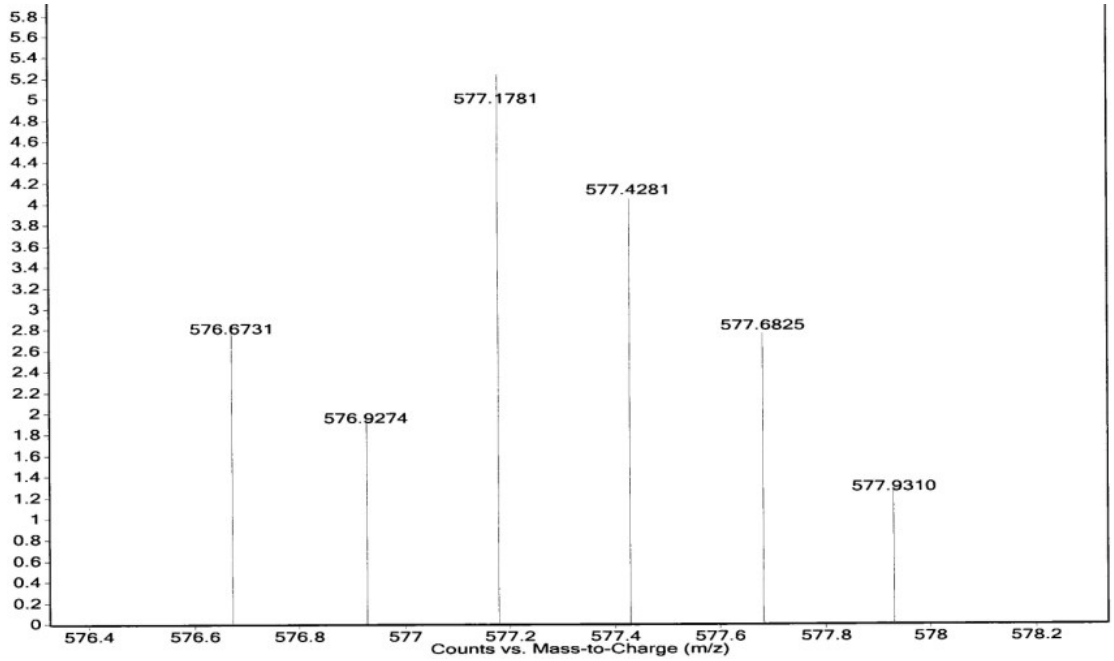



**Figure S14.** ESI-MS spectra of 1: 1 inclusion complex of **1+CB[8]** (calculated for [**1** + CB[8] - 4$Cl^-$]$^{4+}$, 577.1779).

## 9. UV-vis Absorbance Spectra of complex 1 with CB[8]

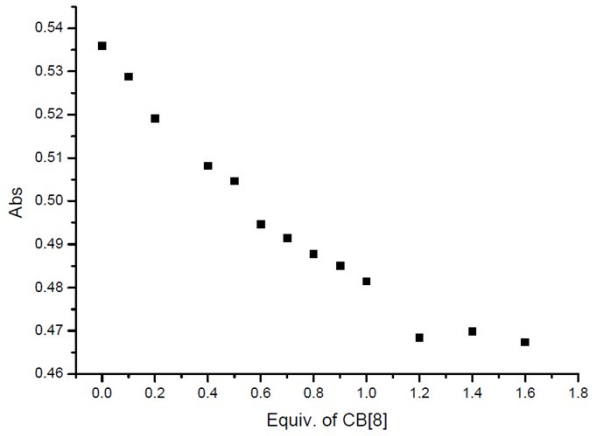



**Figure S15.** UV-vis titration curve at 284 nm versus equivalents of CB[8].