# Light driven formation of a supramolecular system with three CB[8]s locked between redox-active Ru(bpy)$_3$ complexes

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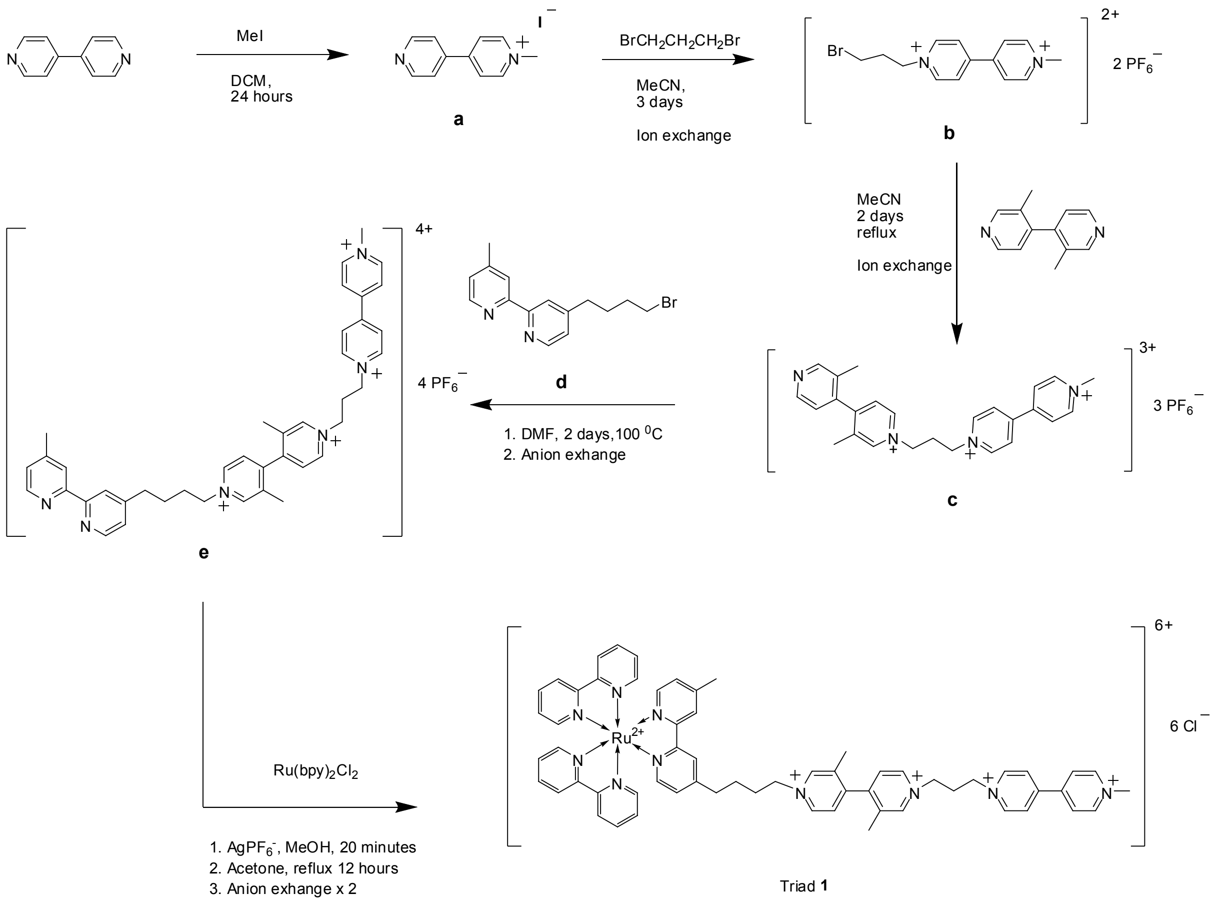
## Supporting information.

## 1. Synthesis

Preparation of 3,3'-dimethyl-4,4'-bipyridinium and cis-Ru(bpy)$_2$Cl$_2$ was performed according to litterature procedures.[1,2] Synthesis of precursor ligand and the triad were performed according to modified literature procedures as seen below. [3] Other materials and solvents employed were commercially available and used as supplied without further purification.



Scheme S1. Synthesis of triad **1**

Synthesis of **a**

1 gram of 4,4'-bipyridinium (6.4 mmol) was dissolved in a round bottom flask containing ca 50 ml dichloromethane. Methyliodide was added to the solution via syringe (1 ml, 9.6 mM) and reacted at room temperature for 24 hours. The pure product, a yellow precipitate, was filtrated and washed with dichloromethane to yield 1.7 gram of the pure product N-methyl-4,4'-bipyridinium (90%).

$^1$H NMR (500 MHz, *D$_2$O*), δ ppm= 8.91 (d, *J* = 6.69 Hz, 1H), 8.77 (d, *J* = 6.27 Hz, 2H), 8.39 (d, *J* = 6.70 Hz, 1H), 7.91 (d, *J* = 6.28 Hz, 1H), 4.45 (s, 3H)
$^{13}$C NMR (126 MHz, *D$_2$O*), δ ppm 153.47 (s,1C), 149.96 (s,1C), 145.60 (s,1C), 142.59 (s,1C), 125.76 (s,1C), 122.46 (s,1C), 47.86 (s,1C)
ESMS calculated for [**a** -I$^-$]$^+$, 171.09; found 171.10.

## Synthesis of **b**

550 mg ( 1.83mmol) of **a** was dissolved in hot acetonitrile, when the solution became clear 1 ml (19.4 mmol) of dibromopropane was added via syringe to the solution and reacted for 3 days at reflux and the reaction process was controlled via TLC (10:1:1 MeCN:$H_2O$: Sat $KNO_3$). After the reaction mixture cooled down to room temperature the crude product was filtrated and washed with acetonitrile to yield 821 mg (1.41mmol) of the pure product as a yellow precipitate (77 %).

$^1$H NMR (500 MHz, *$D_2O$*), δ ppm 9.20 (d, *J* = 5.40 Hz, 2H), 9.08 (d, *J* = 5.55 Hz, 2H), 8.60 (d, *J* = 5.47 Hz, 1H), 8.55 (d, *J* = 5.51 Hz, 1H), 4.95 (t, *J* = 6.85, 6.85 Hz, 1H), 4.53 (s, 1H), 3.57 (t, *J* = 6.02, 6.02 Hz, 2H), 2.69 (q, 2H)
$^{13}$C NMR (126 MHz, *$D_2O$*), δ ppm 150.46 (s,1C), 149.72 (s,1C), 146.33 (s,1C), 145.78 (s,1C), 127.18 (s,1C), 126.71 (s,1C), 60.31 (s,1C), 48.39 (s,1C), 32.71 (s,1C), 28.76 (s,1C)
ESMS calculated for [**b** -2$PF_6^-$]$^{2+}$, 146.03; found 146.08.

## Synthesis of **c**

The product **b** was converted to $PF_6^-$ counterions as described above and 352 mg (0.6 mmol) was dissolved in 20 ml acetonitrile. 111 mg (0.6 mmol) of 3,3’-dimethyl-4,4’-bipyridine was added to the solution and the solution reacted for 2 days at 80°C and the reaction process was controlled via TLC (4:1:1 MeCN:$H_2O$: Sat $KNO_3$). After the reaction mixture cooled down to room temperature the solvent was removed in vaccum and dissolved into a minimum amount of solvent mixture (10:1:1 MeCN:$H_2O$: Sat $KNO_3$) for 10 minutes. The product was attained by chromathography on a silica column (10:1:1→4:1:1 of MeCN:$H_2O$: Sat $KNO_3$). After ion exchange the product was collected as a pale white powder (320 mg, 65%).

1H NMR (500 MHz, *$CD_3CN$*), δ ppm 8.94 (d, *J* = 6.52 Hz, 2H), 8.86 (d, *J* = 6.47 Hz, 2H), 8.68 (d, *J* = 10.11 Hz, 2H), 8.62 (t, *J* = 5.88, 5.88 Hz, 1H), 8.46 (d, *J* = 6.41 Hz, 1H), 8.38 (d, *J* = 6.25 Hz, 1H), 7.85 (d, *J* = 6.21 Hz, 1H), 7.24 (d, *J* = 5.08 Hz, 1H), 4.82-4.73 (m, 2H), 4.70-4.64 (m, 1H), 4.41 (s, 3H), 2.84-2.66 (m, 2H), 2.25 (s, 3H), 2.12 (s, 3H)
$^{13}$C NMR (126 MHz, *$CD_3CN$*), δ ppm 158.21, 153.65, 149.58, 148.92, 148.11, 147.52, 144.64, 144.31, 140.03, 131.63, 130.27, 129.44, 128.78, 123.58, 118.63, 60.77, 60.11, 50.48, 34.15, 18.29, 17.41
ESMS calculated for [**c** -2$PF_6^-$]$^{2+}$, 270.1; found 270.03.

## **Triad 1**

A mixture of **c** (210 mg, 0.25 mmol) and **d** (152 mg, 0.50 mmol) was dissolved in DMF (3 ml) and reacted at 100 $^0$C for two days. The solvent was concentrated by evaporation and after addition dichloromethane (10 ml) a precipitate was formed. The crude compound was washed with dichloromethane and dissolved in minimum amount of water. The crude product precipitated from the water phase by addition of a sat solution $TBAPF_6$ in water. After drying the crude ligand **e** was used directly. The cis-Ru(bpy)$_2$Cl$_2$ (135 mg, 0.26 mmol) was dissolved in acetone (5 ml) with $AgPF_6$ (142 mg, 0.57 mmol) for 20 min. The solution was filtered and washed with acetone (10ml) into a 25 ml round bottom flask containing the crude product **e**. The mixture was refluxed under nitrogen for 2 days. After removal of the acetone the pure compound was obtained by subsequent purification by silica column with a 10:1:1→4:1:1 in MeCN: $H_2O$: $KNO_3$ Sat. $H_2O$. Ion exchange to $Cl^{-}$ ions yielded the final product **1** (71 mg, 22.4% over two steps).

$^1H$ NMR (500 MHz, $D_2O$), δ ppm=9.22 (d, 2H), 9.09 (s, 1H), 9.06 (d, 2H), 9.00 (s, 1H), 8.99 (d, 1H), 8.90 (d, 1H), 8.61 (d, 2H), 8.53 (m, 6H), 8.37 (s, 2H), 8.00 (m, 6H), 7.82 (m, 4H), 7.68 (d, 1H), 7.62 (d, 1H), 7.34 (m, 4H), 7.23 (d, 1H), 7.20 (d, 1H), 4.99 (t, 2H), 4.93 (t, 2H), 4.71 (t, 2H), 4.51 (s, 1H), 2.92 (m, 4H), 2.52 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 2.17 (q, 2H), 1.81 (q, 2H).
$^{13}C$ NMR (126 MHz, $D_2O$), δ ppm=157.133, 156.880, 156.414, 153.080, 152.287, 151.462, 151.288, 150.883, 150.782, 150.496, 150.213, 149.668, 146.377, 145.935, 145.769, 145.667, 142.482, 142.254, 138.211, 137.740, 137.362, 127.991, 127.823, 127.453, 127.401, 127.106, 127.054, 126.803, 124.820, 123.939, 61.716, 58.317, 58.196, 48.457, 33.875, 31.865, 30.210, 26.130, 23.179, 20.450, 19.190, 16.505, 12.888
HRMS calculated for [**1** -6$Cl^-$]$^{6+}$, 172.7367; found 172.7471.

## 2. $^1$H NMR of triad 1

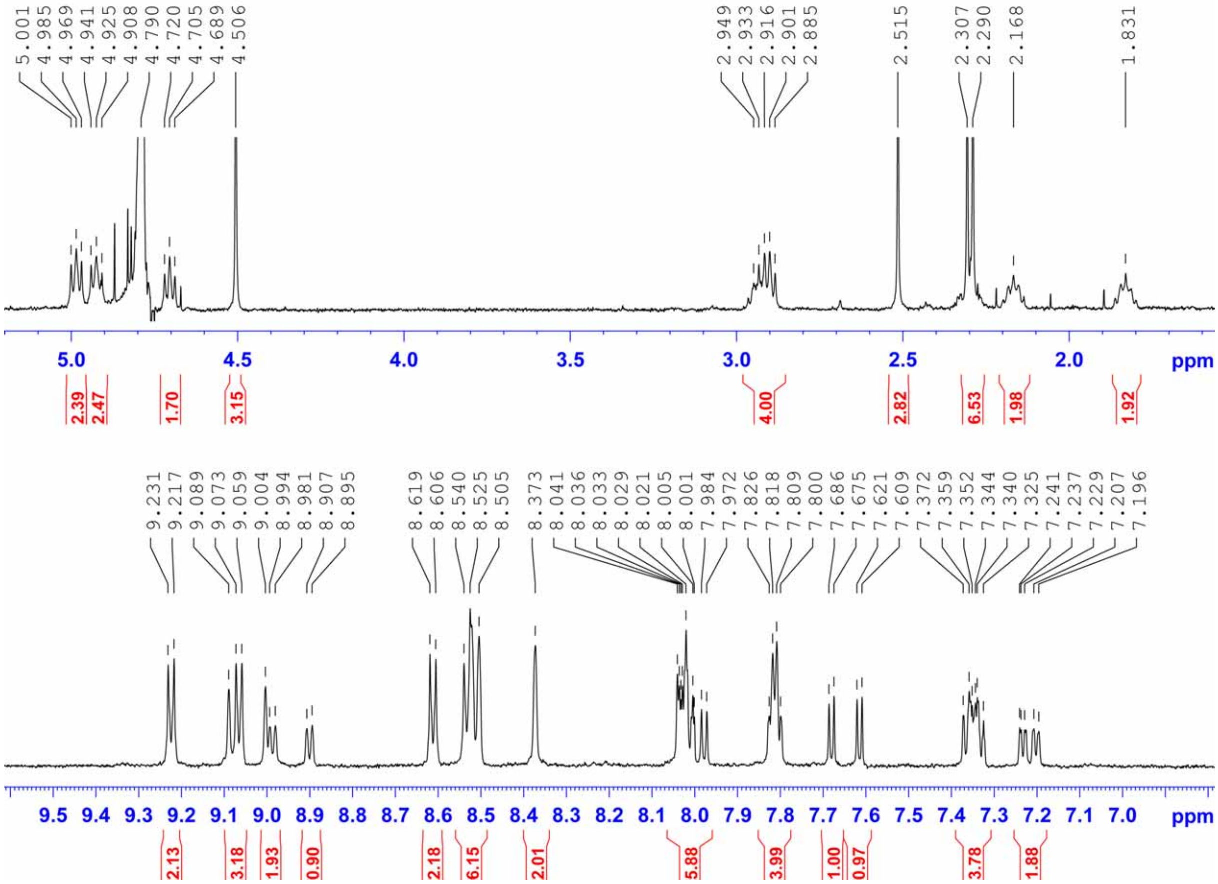


Figure S1. $^1$H NMR spectrum (500 MHz, $D_2O$) of triad **1**.

## 3. $^1$H NMR of triad 1 with CB[8]

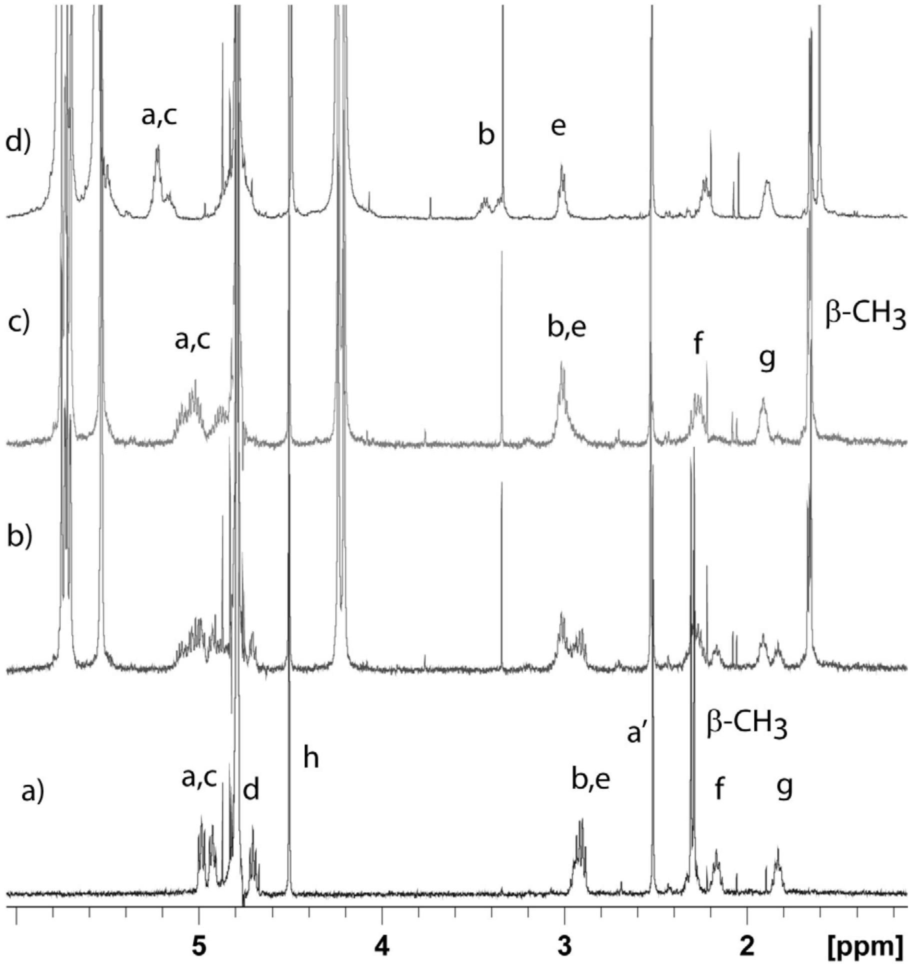


Figure S2. $^1$H NMR spectrum (500 MHz, $D_2O$) of the triad **1** at the concentration of 2.9 mM. a) shows **1**, while b), c) and d) shows **1** with 0.5, 1.0, 2.0 equivalents of CB[8] respectively.

## 4. COSY spectra of triad 1 with CB[8]

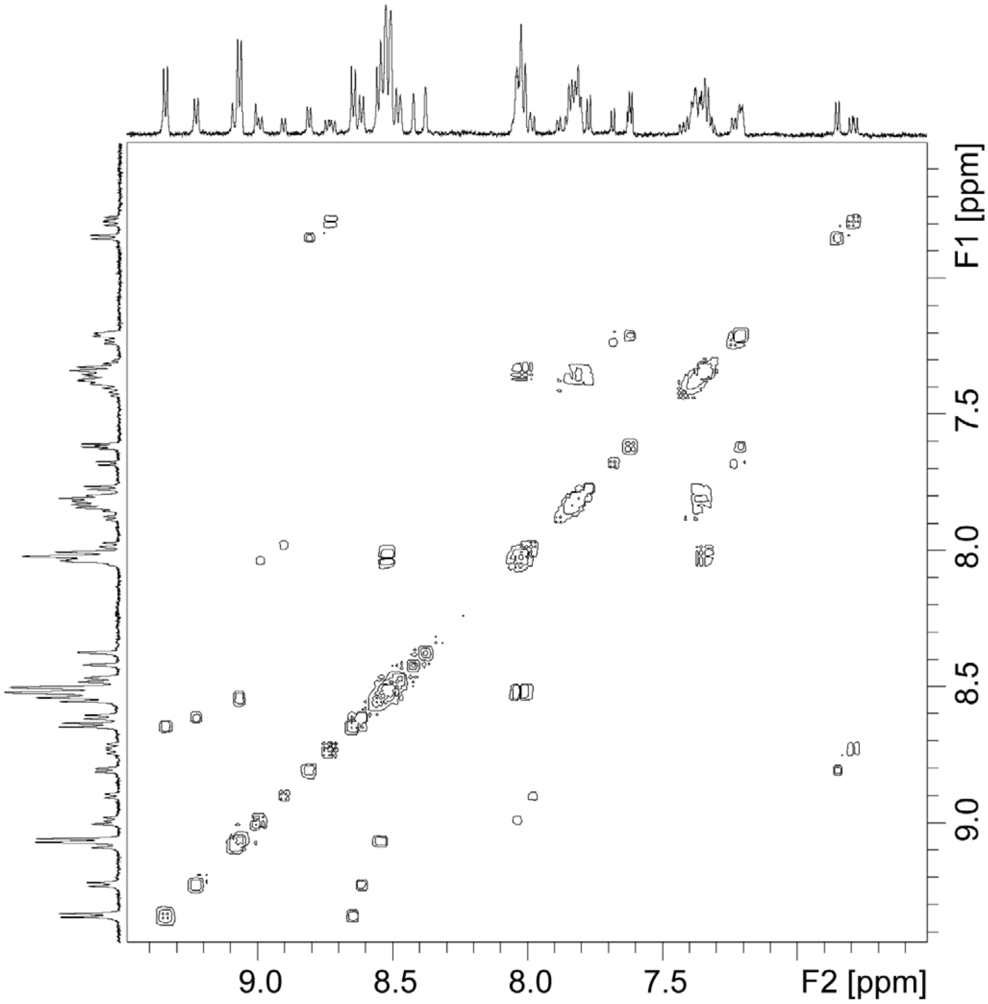


Figure S3. COSY spectrum (500 MHz, $D_2O$) of the triad **1** at the concentration of 2.9 mM. with 0.5 equiv CB[8]

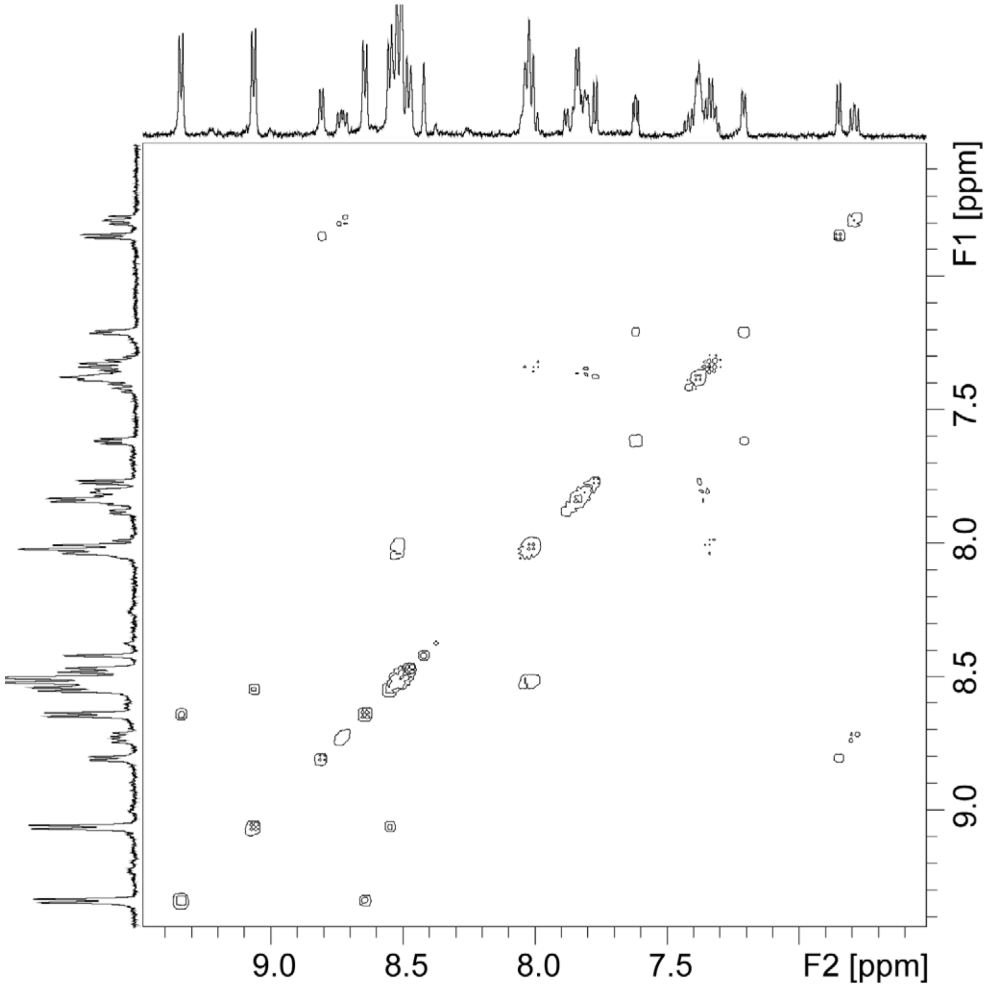


Figure S4. COSY spectrum (500 MHz, $D_2O$) of the triad **1** at the concentration of 2.9 mM. with 1 equiv CB[8]

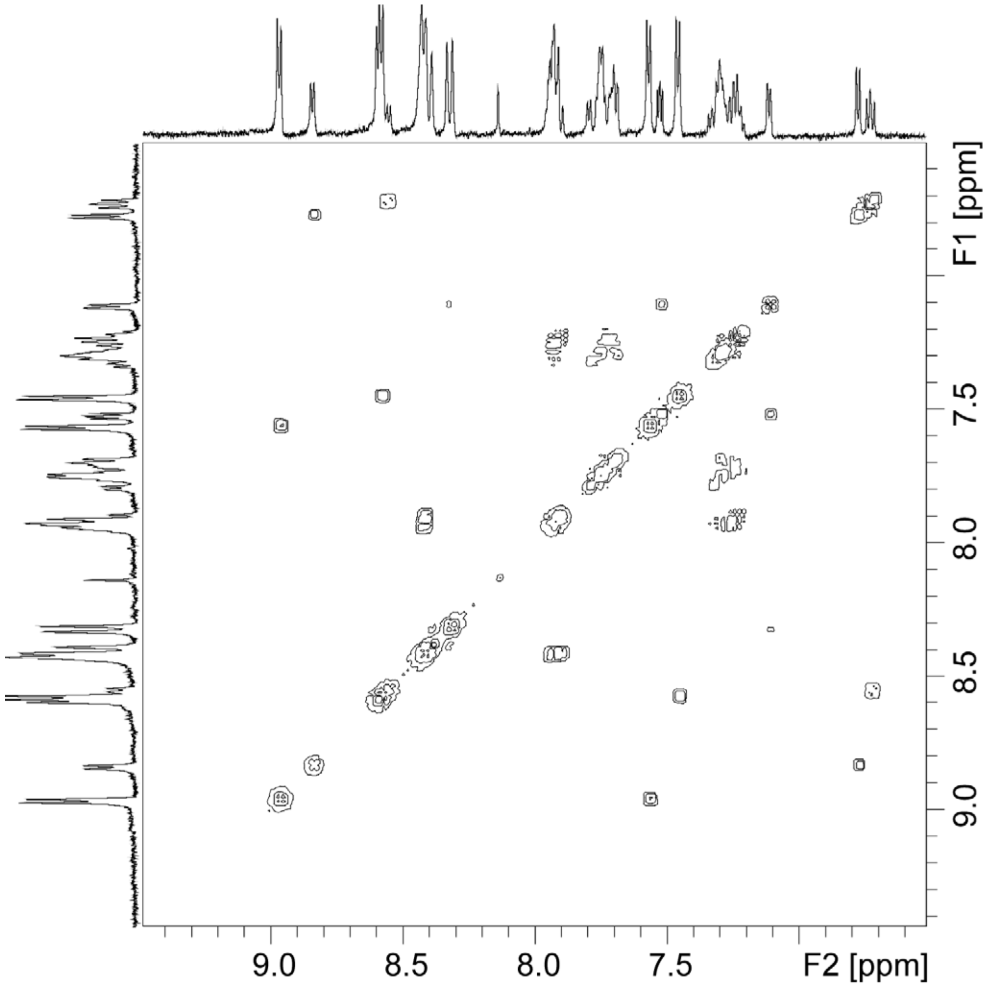


Figure S5. COSY spectrum (500 MHz, $D_2O$) of the triad **1** at the concentration of 2.9 mM. with 2.0 equiv CB[8]

## 6. $^1$H NMR of triad 1 after irradiation

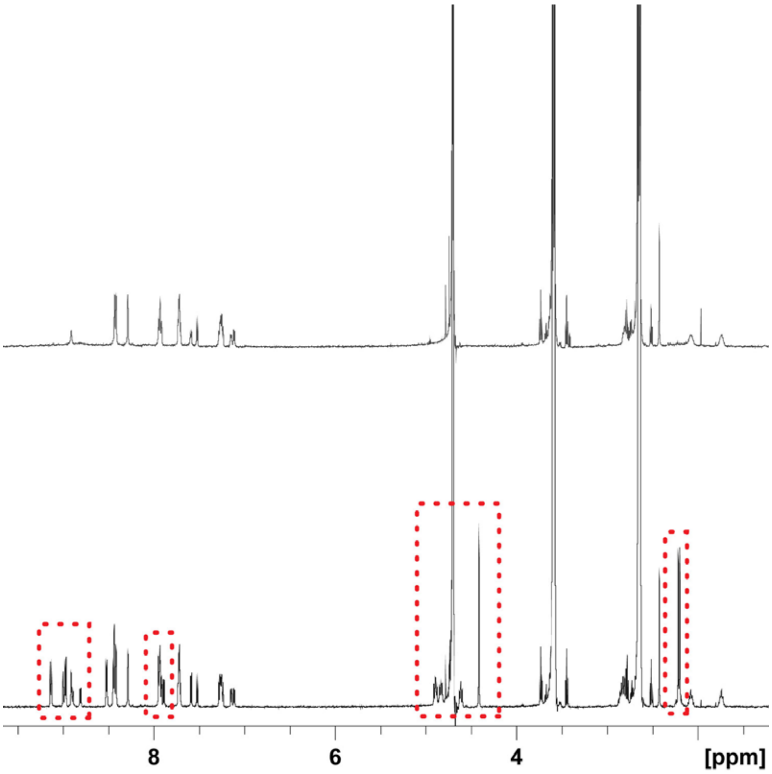


Figure S3. $^1$H NMR spectra (500 MHz, $D_2O$) of the **1** at the concentration of 2.9 mM with TEOA, before (below) and after 5 min irradiation (above) without CB[8].

## 7. $^1$H NMR of triad 1 with CB[8] after irradiation

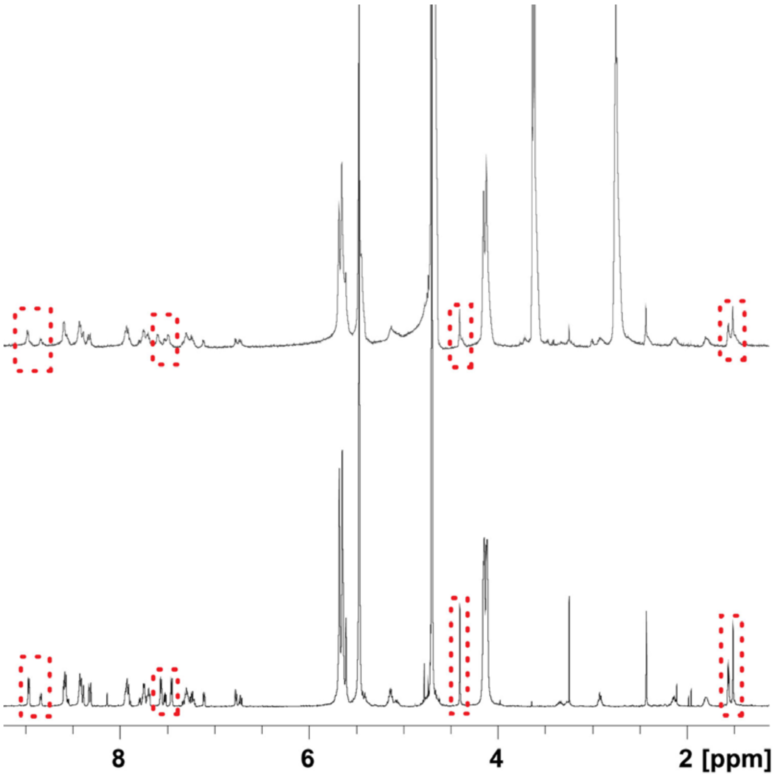


Figure S4. $^1$H NMR spectra (500 MHz, $D_2O$) of **1** with two equivalent CB[8] and TEOA before irradiation (below) after 10 min irradiation (above).

## 8. Cyclic voltammogram of triad 1 in acetonitrile

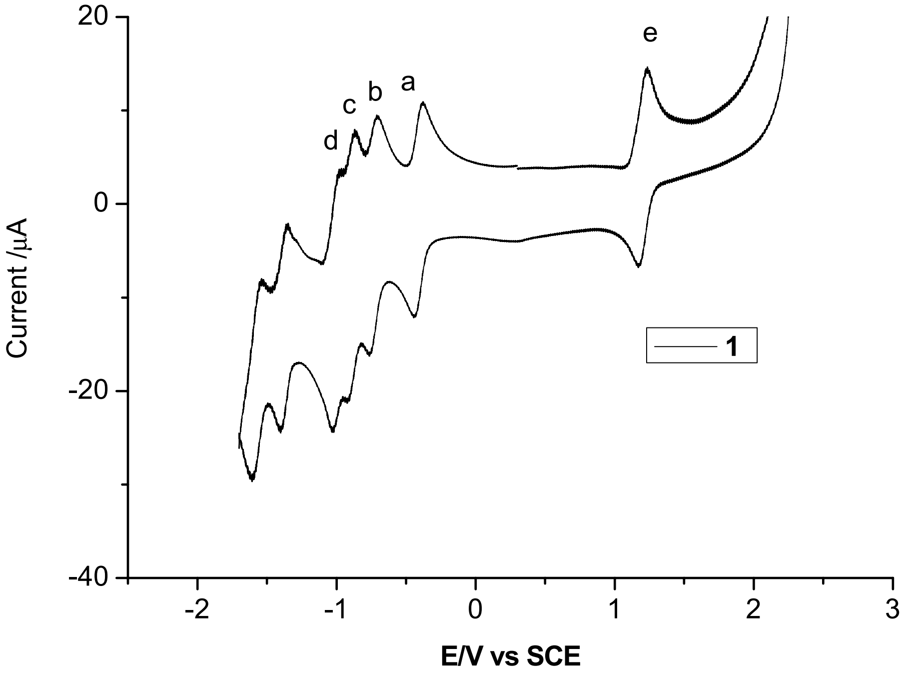


Figure S5. Cyclic-voltammogram of **1** in acetonitrile (0.5mM), scan rate 0.1Vs$^{-1}$. The reversible redox peaks are assigned as: (a) MV$^{2+}$/MV$^{+\cdot}$; (b) DMV$^{2+}$/DMV$^{+\cdot}$; (c) MV$^{+\cdot}$/MV$^{0}$; (d) DMV$^{+\cdot}$/DMV$^{0}$; (e) Ru$^{2+}$/Ru$^{3+}$.

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[1] Rebek, J.; Costello, T.; Wattley, R. *J. Am. Chem. Soc.* **1985**, *107*, 7487-7493.

[2] E.H.Yonemoto, R. L. Riley, Y. I.Kim, S. J. Atherton,R.H. Schmehl, T. E. Mallouk, *J. Am. Chem. Soc* **1992**, 114, 8081

[3] H. Durr, M. Seiler, *Synthesis* **1994**, *1*, 83-86.