# Electronic Supplementary Information

## Redox-switchable host-guest systems based on a bisthiotetrathiafulvalene-bridged cryptand

Qi Wang,[a] Ming Cheng,[a] Yue Zhao,[b] Zhen Yang,[a] Juli Jiang,*[a] Leyong Wang*[a] and Yi Pan[b]

[a] *Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China;*

[b] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.*

*Fax: +86 25-83597090; Tel: +86 25-83592529;*

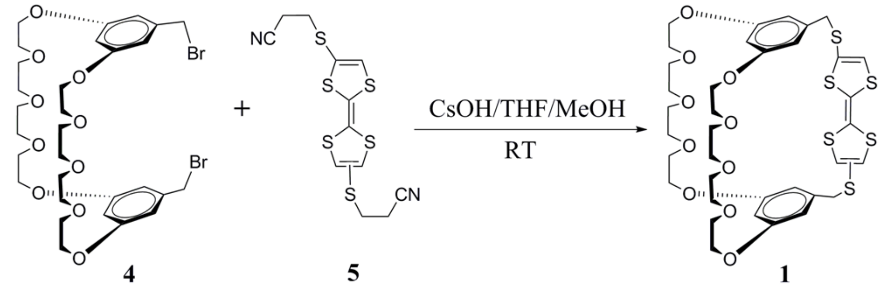
*E-mail: jjl@nju.edu.cn (JJ); lywang@nju.edu.cn (LW).*

## Table of Contents

## *1. Materials and methods*

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **2**,[S1] **3**,[S2] **4**[S3] and **5**[S4] were prepared by published literature procedures. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. 2D NOESY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

## 2. *Synthesis of compound **1***



**Scheme S1** Synthesis of cryptand **1**.

A solution of **4** (0.39 g, 0.54 mmol) and **5** (0.20 g, 0.54 mmol) in anhydrous THF (100 mL) was added very slowly to a solution of CsOH·$H_2O$ (0.45 g, 2.70 mmol) in anhydrous THF (200 mL) and MeOH (20 mL) under nitrogen gas protection. [S5] After complete addition, the mixture was stirred for 2 days. After the solvent was removed under vacuum, the residue was purified by column chromatography (silica, $CH_2Cl_2/CH_3OH$ = 100:1, *v/v*) to afford **1** as a yellow wax (0.17 g, 38%). $^1H$ NMR (400 MHz, DMSO-$d_6$): δ (ppm): 6.85 (s, 1H), 6.66 (s, 1H), 6.48 (d, $J$ = 1.9 Hz, 2H), 6.39−6.37 (m, 3H), 6.33 (t, $J$ =1.9 Hz, 1H), 4.00−3.96 (m, 8H), 3.85−3.83 (m, 4H), 3.63−3.61 (m, 4H), 3.52 (br s, 20H). $^{13}C$ NMR (75 MHz, DMSO-$d_6$): δ (ppm): 159.5, 159.4, 139.2, 139.0, 125.2, 124.7, 124.3, 122.5, 113.0, 111.6, 107.5, 106.9, 100.7, 100.4, 70.1, 70.0, 69.91, 68.85, 68.8, 67.19, 67.15. LR-ESI-MS: *m/z* calcd for $[M + H]^+$, 829.13, found 829.05 (23%); calcd for $[M + NH_4]^+$, 846.16, found 846.10 (100%); calcd for $[M + Na]^+$, 851.12, found 851.00 (35%); HR-ESI-MS: *m/z* calcd for $[M + Na]^+$ $C_{36}H_{44}O_{10}S_6Na^+$, 851.1156, found 851.1153, error 0.4 ppm.

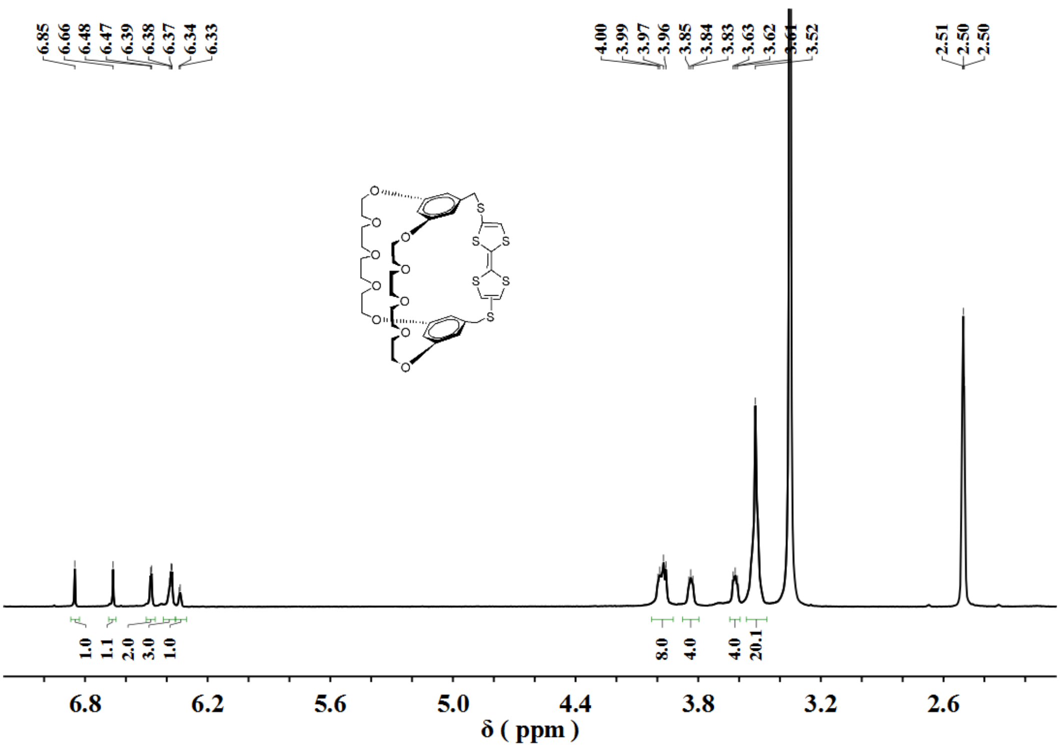


**Fig. S1** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of **1**.

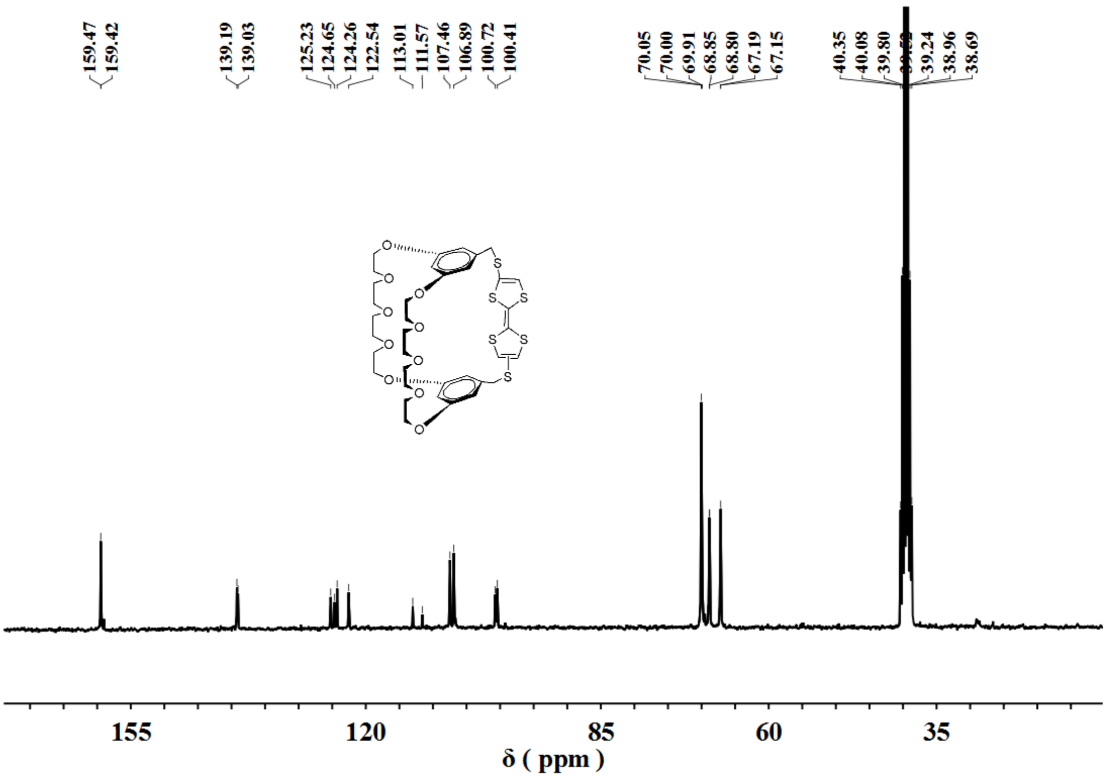
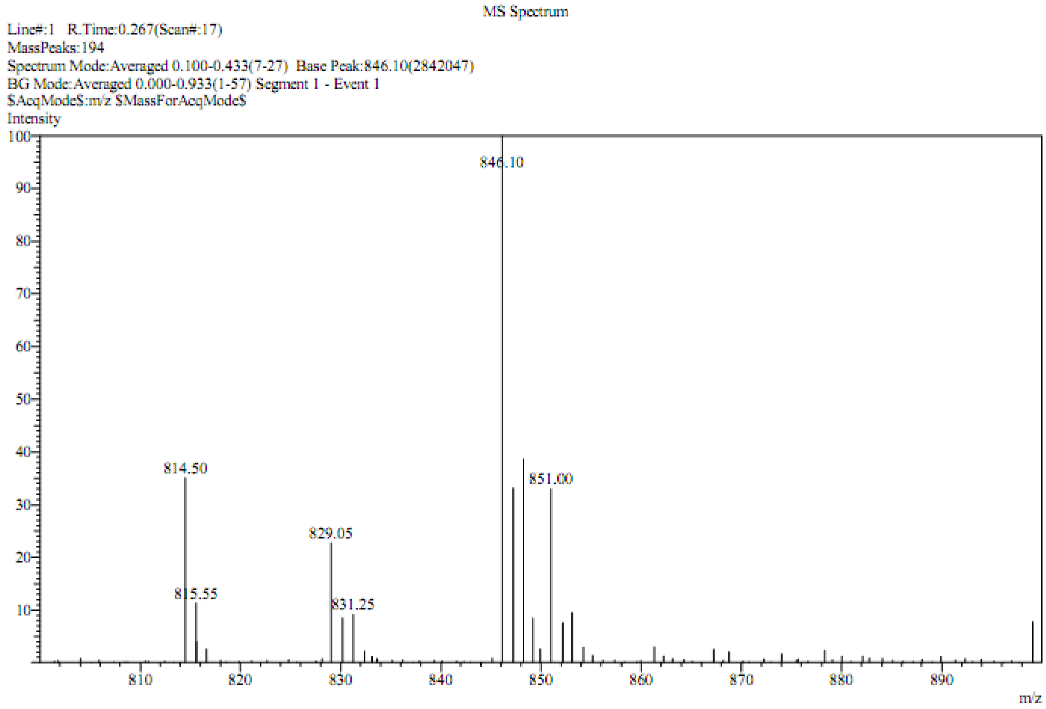
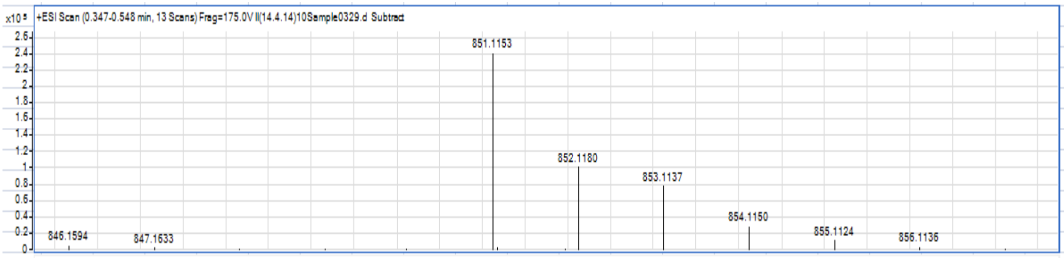


**Fig. S2** $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$, 298 K) of **1**.



```
Line#:1   R.Time:0.267(Scan#:17)
MassPeaks:194
Spectrum Mode:Averaged 0.100-0.433(7-27)  Base Peak:846.10(2842047)
BG Mode:Averaged 0.000-0.933(1-57) Segment 1 - Event 1
$AcqMode$:m/z $MassForAcqMode$
```

Fig. S3 LR-ESI-MS spectrum of **1**.



```
+ESI Scan (0.347-0.548 min, 13 Scans) Frag=175.0V II(14.4.14)10Sample0329.d  Subtract
```

**Fig. S4** HR-ESI-MS spectrum of **1**.

## *3. $^1$H NMR spectra of **1**, **1⊃2** and **1⊃3** in CD$_3$CN*

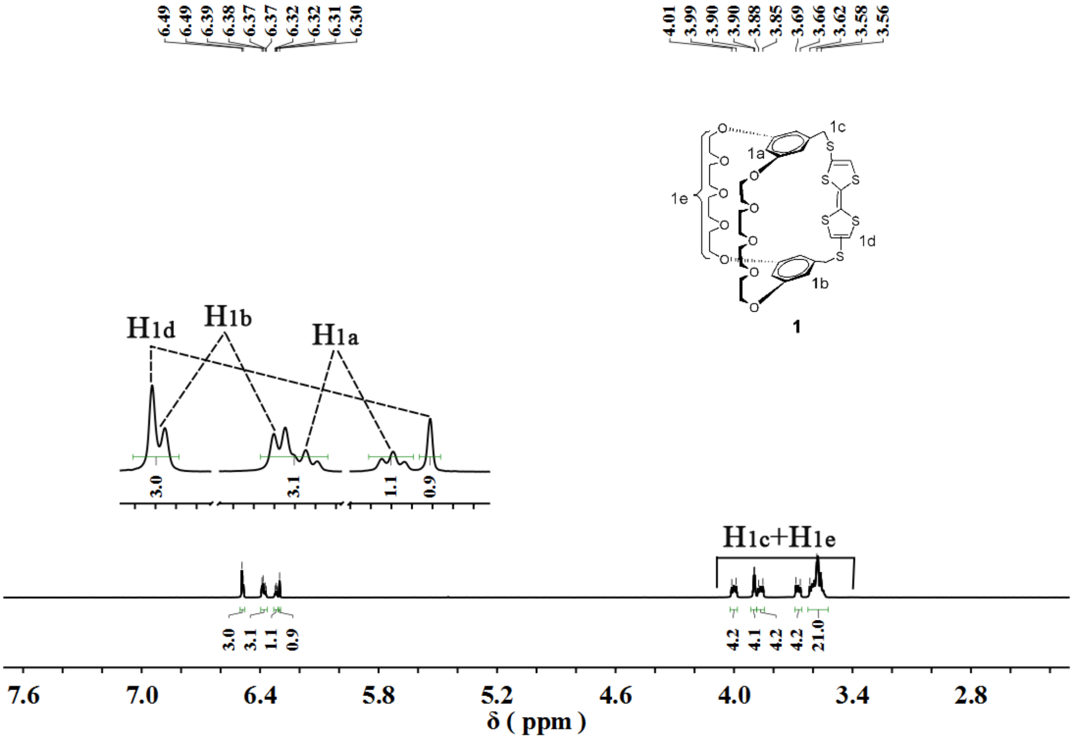


**Fig. S5** $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of **1**.

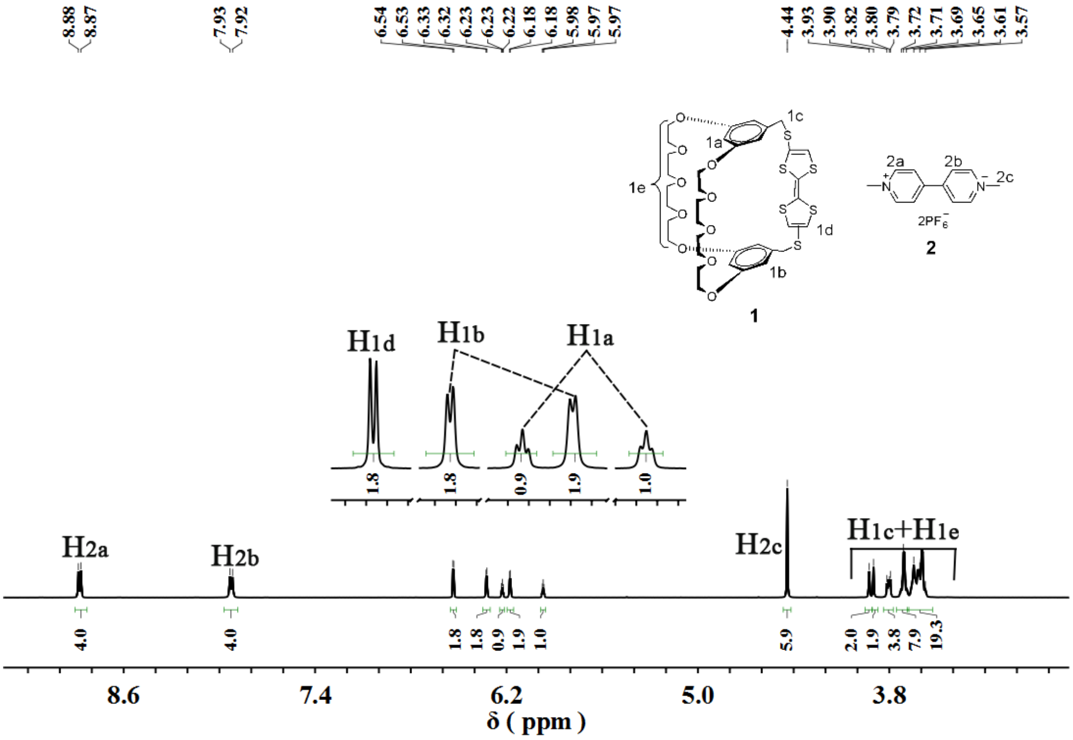


**Fig. S6** $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of a solution of 4.50 mM **1** and 4.50 mM **2**.

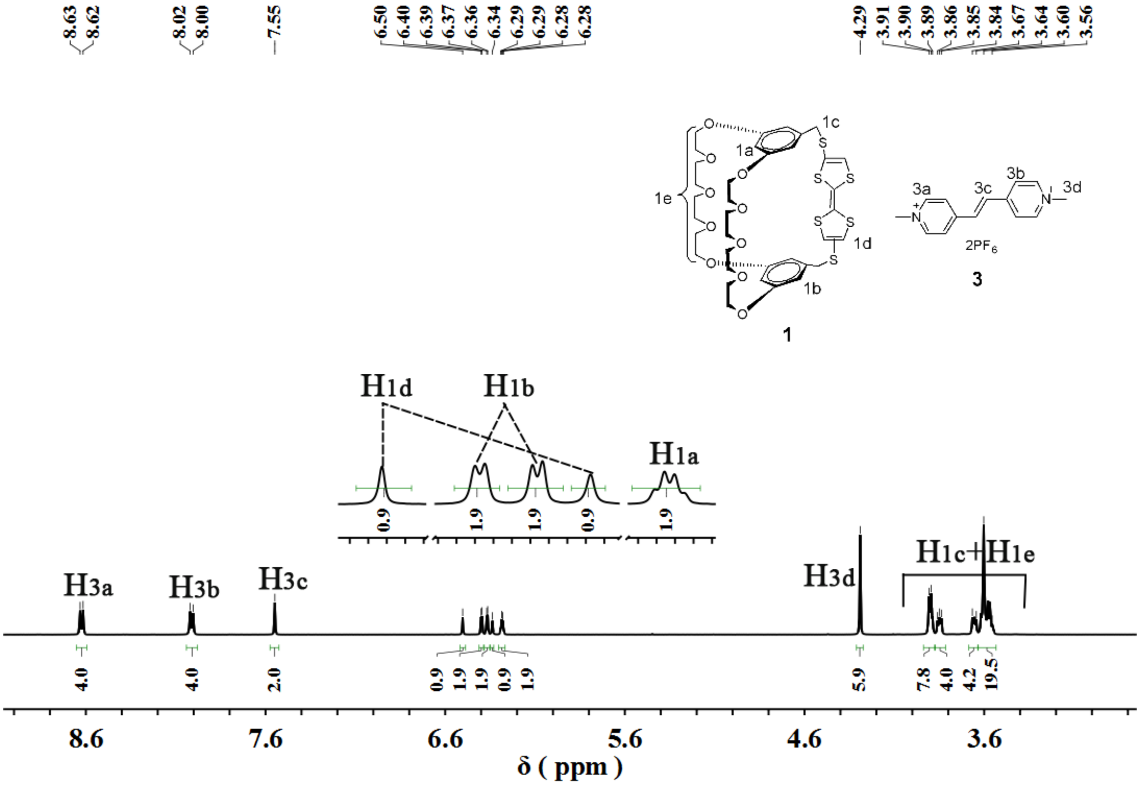
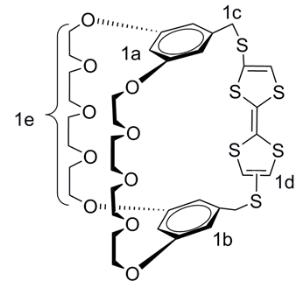
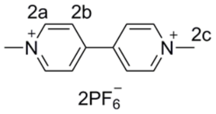


**Fig. S7** $^1$H NMR spectrum (400 MHz, $CD_3CN$, 298 K) of a solution of 4.50 mM **1** and 4.50 mM **3**.

## 4. *Partial 2D NOESY spectra of **1⊃2** and **1⊃3***



**1**



**2**

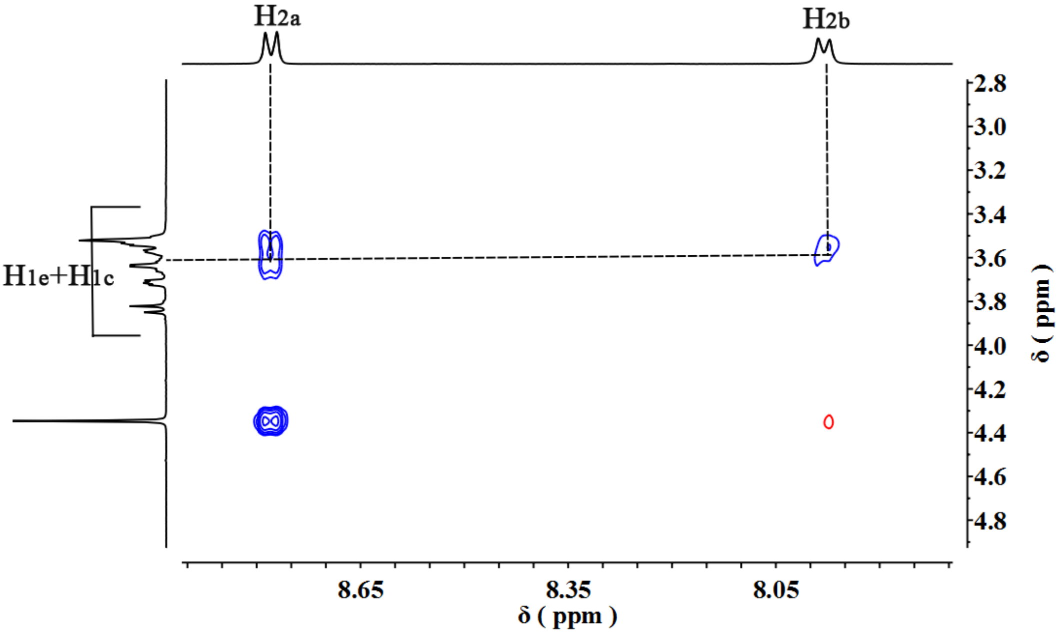
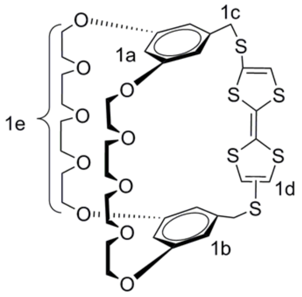
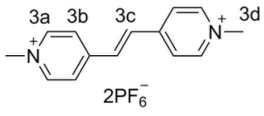


**Fig. S8** Partial 2D NOESY spectrum (400 MHz, $CD_3CN$, 298 K) of a solution of 4.00 mM **1** and 4.00 mM **2**.



**1**



**3**

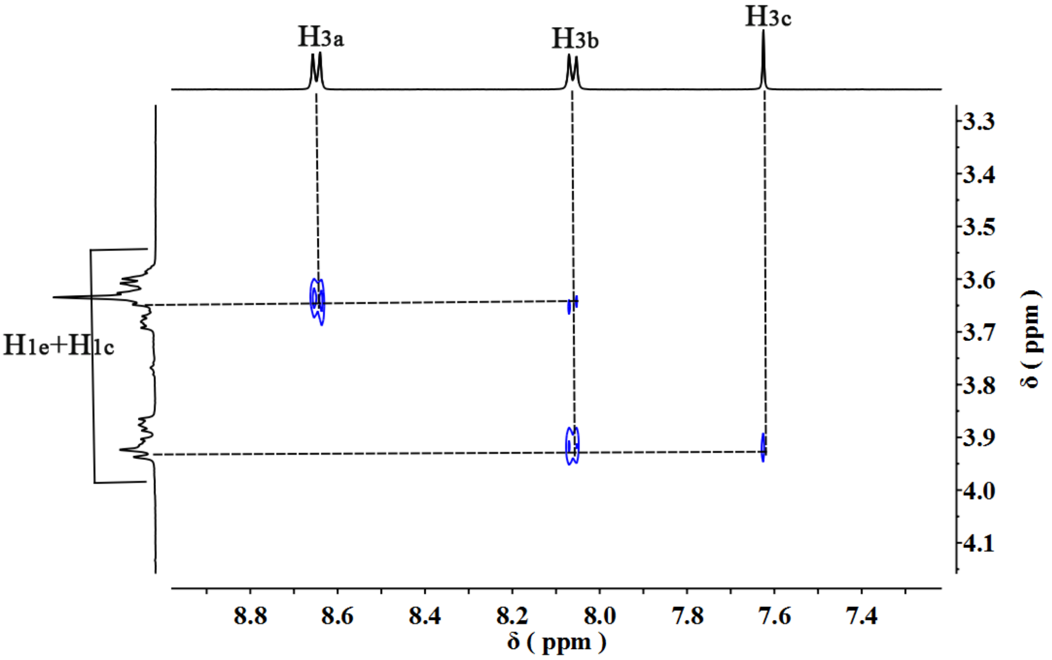


**Fig. S9** Partial 2D NOESY spectrum (400 MHz, $CD_3CN$, 298 K) of a solution of 4.00 mM **1** and 4.00 mM **3**.

## 5. *Job plots for the complexes of **1⊃2** and **1⊃3***

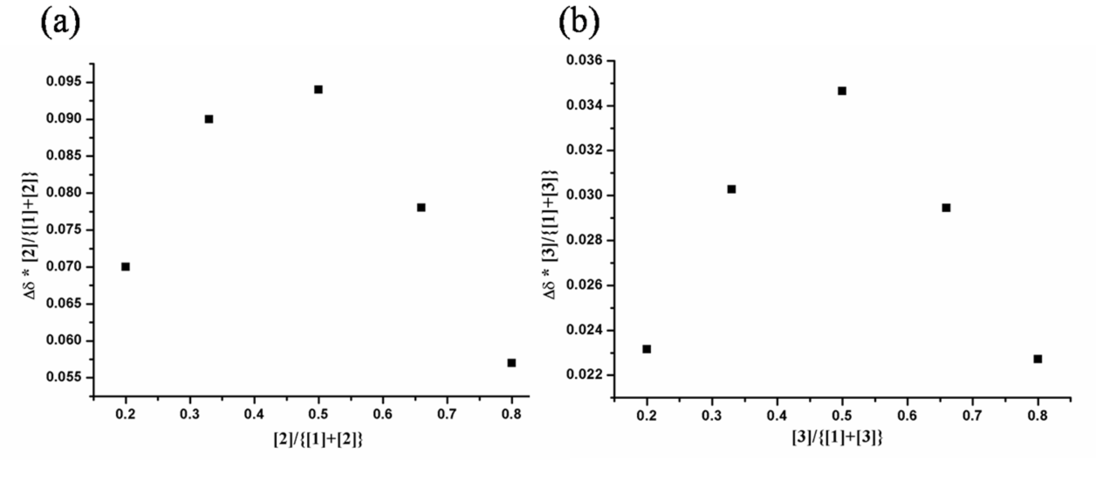


**Fig. S10** Job Plots showing the 1:1 stoichiometry of the complexation between **1** and **2** (a) and **1** and **3** (b) in $CD_3CN$. ([H] + [G] = 4 mM).

## 6. *LR-ESI-MS for the complexes of **1**⊃**2** and **1**⊃**3***

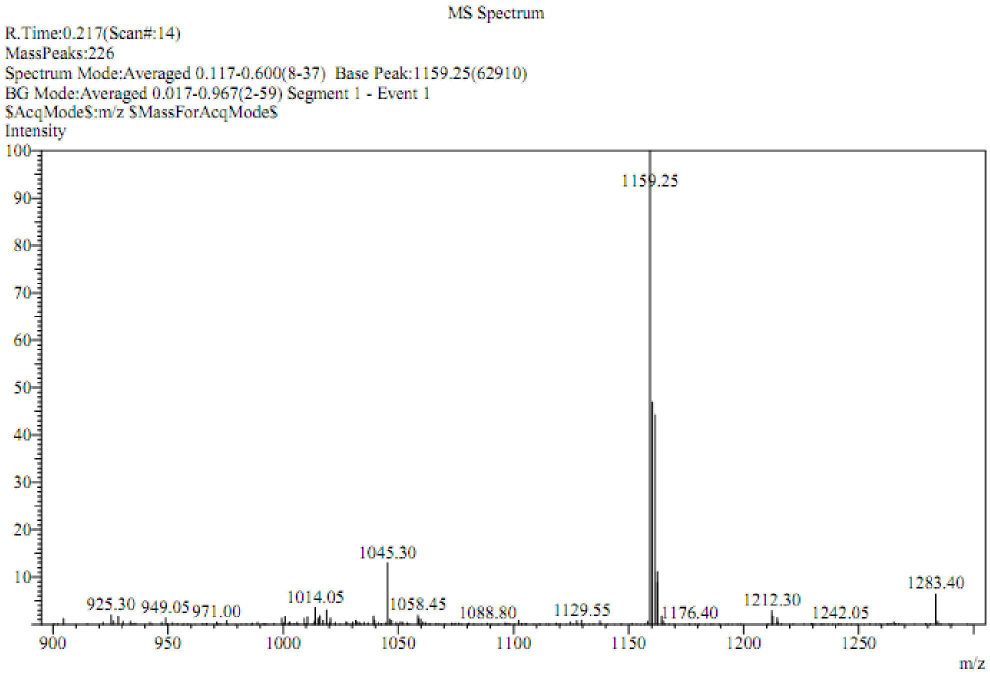


**Fig. S11** LR-ESI-MS of an equimolar mixture of **1** and **2**. Assignment of main peaks: *m/z* 1159.25 (100%) for [**1**⊃**2** – $PF_6$]$^+$. This result confirmed the 1:1 stoichiometry of the complex between **1** and **2** further.

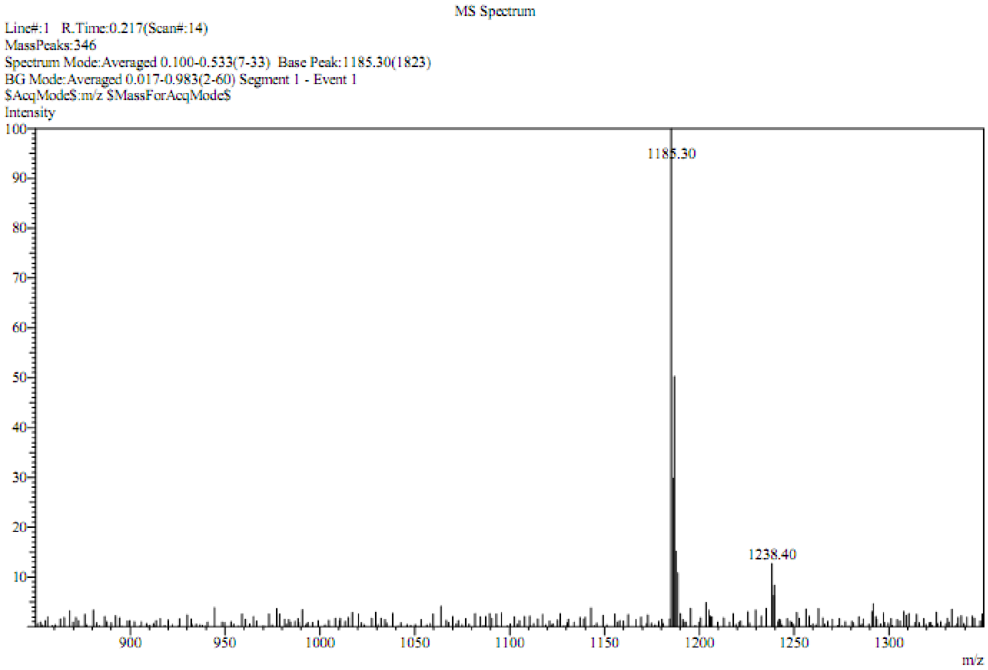


**Fig. S12** LR-ESI-MS of an equimolar mixture of **1** and **3**. Assignment of main peaks: *m/z* 1185.30 (100%) for [**1**⊃**3** – $PF_6$]$^+$. This result confirmed the 1:1 stoichiometry of the complex between **1** and **3** further.

## *7. Determination of the association constants of **1⊃2** and **1⊃3** by $^1$H NMR*

$^1$H NMR titrations were performed with a constant concentration of guest (2.00 mM) and varying concentrations of host in the range of 1.0 – 40.0 mM. Using a non-linear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation:

$\Delta\delta = (\Delta\delta_\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5\ ([H]_0^2 + (2[H]_0(1/K_a - [G]_0)) + (1/K_a + [G]_0)^2)^{0.5}))$ (Eq. S1)

Where $\Delta\delta$ is the chemical shift change of $H_a$ on G at $[H]_0$, $\Delta\delta_\infty$ is the chemical shift change of $H_a$ when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the initial concentration of the host.

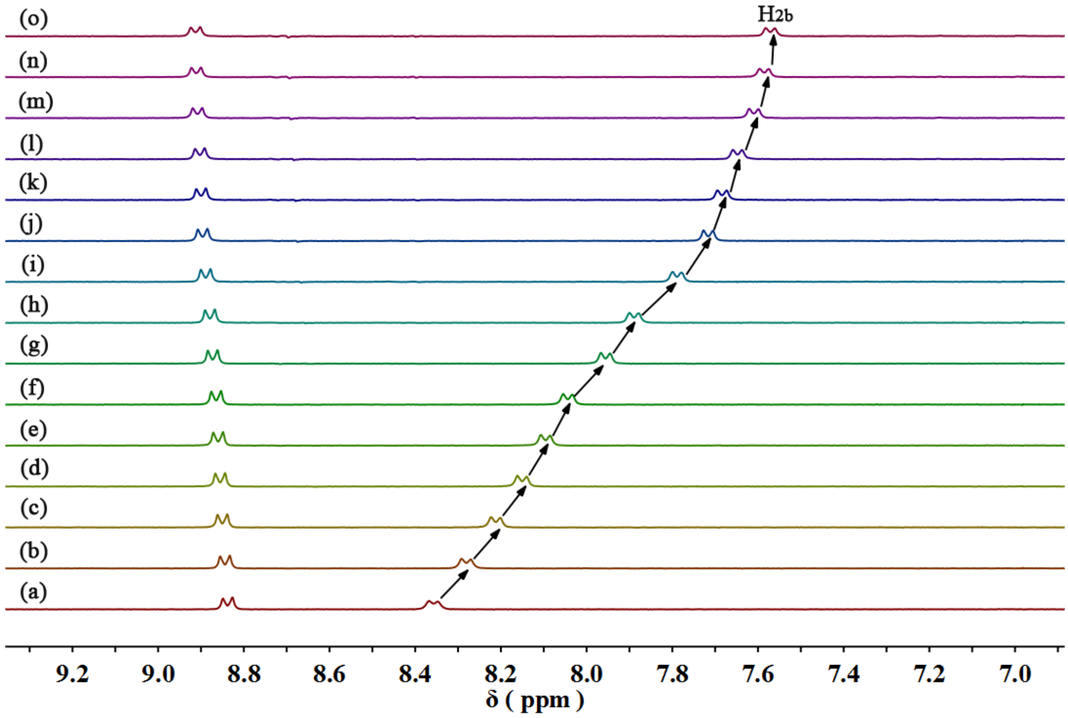


**Fig. S13** Partial $^1$H NMR spectral changes (300 MHz, $CD_3CN$, 298 K) of **2** at a concentration of 2.00 mM upon gradual addition of **1**: (a) 0.00, (b) 1.00, (c) 2.00, (d) 3.00, (e) 4.00, (f) 5.00, (g) 7.00, (h) 9.00, (i) 13.00, (j) 17.00, (k) 20.00, (l) 24.00, (m) 30.00, (n) 36.00, (o) 40.00 mM.

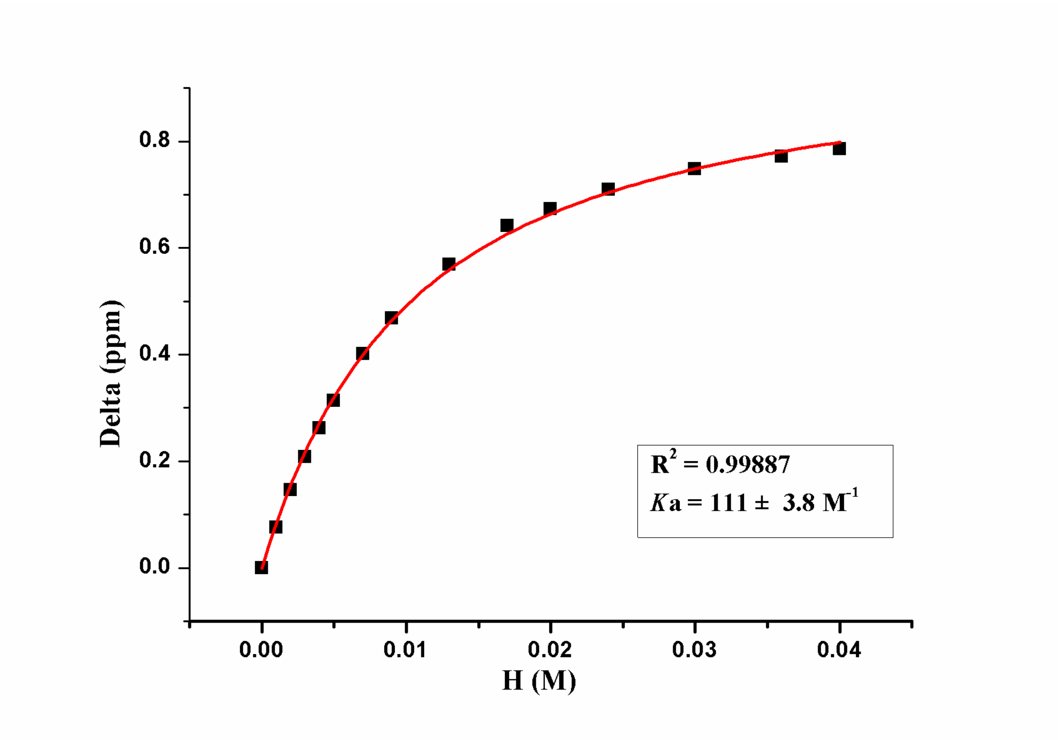


**Fig. S14** The chemical shift changes of $H_{2b}$ on **2** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The association constant ($K_a$) of **1⊃2** was estimated to be about 111 ± 3.8 $M^{-1}$.

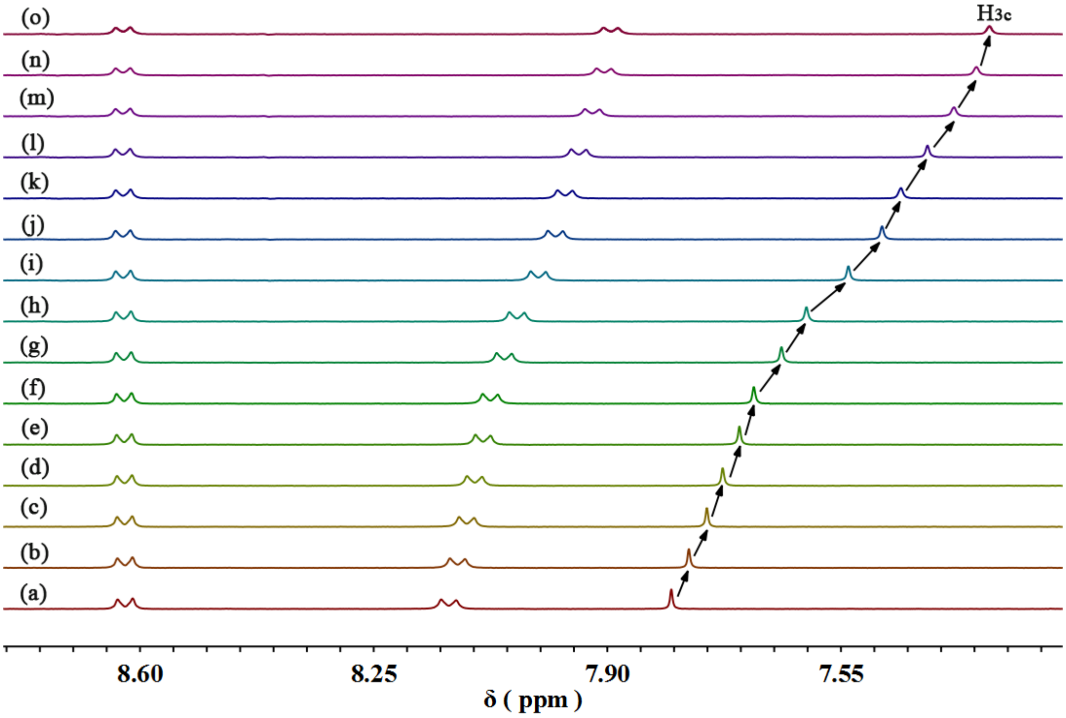


**Fig. S15** Partial $^1H$ NMR spectral changes (300 MHz, $CD_3CN$, 298 K) of **3** at a concentration of 2.00 mM upon gradual addition of **1**: (a) 0.00, (b) 1.00, (c) 2.00, (d) 3.00, (e) 4.00, (f) 5.00, (g) 7.00, (h) 9.00, (i) 13.00, (j) 17.00, (k) 20.00, (l) 24.00, (m) 30.00, (n) 36.00, (o) 40.00 mM.

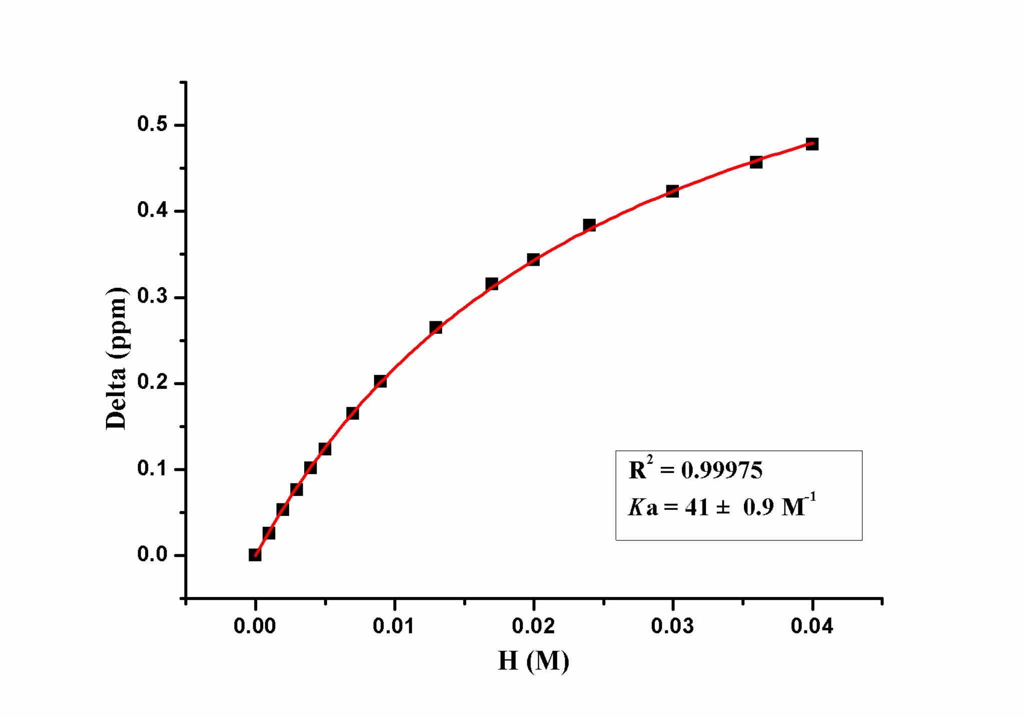


**Fig. S16** The chemical shift changes of $H_{3c}$ on **3** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The association constant ($K_a$) of **1**⊃**3** was estimated to be about 41 ± 0.9 $M^{-1}$.

## *8. Studies of charge transfer interactions by UV-vis spectra*

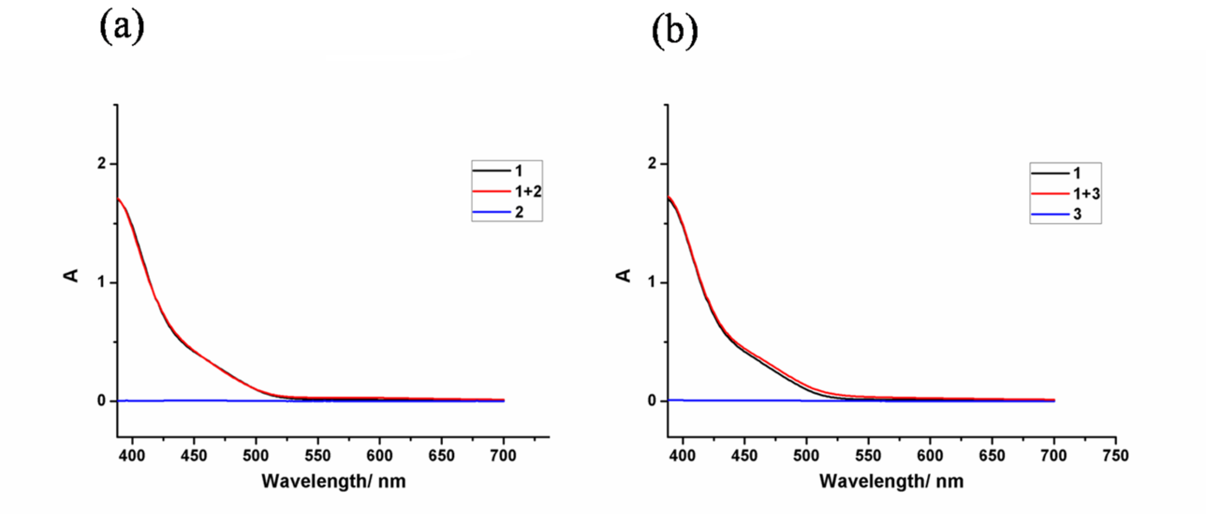


**Fig. S17** UV-vis absorption spectra of between 1.00 mM **1** and 1.00 mM **2** (a) and 1.00 mM **1** and 1.00 mM **3** (b) in $CH_3CN$.

## 9. *Switchable behaviors of **1⊃2** investigated by $^{1}$H NMR experiment*

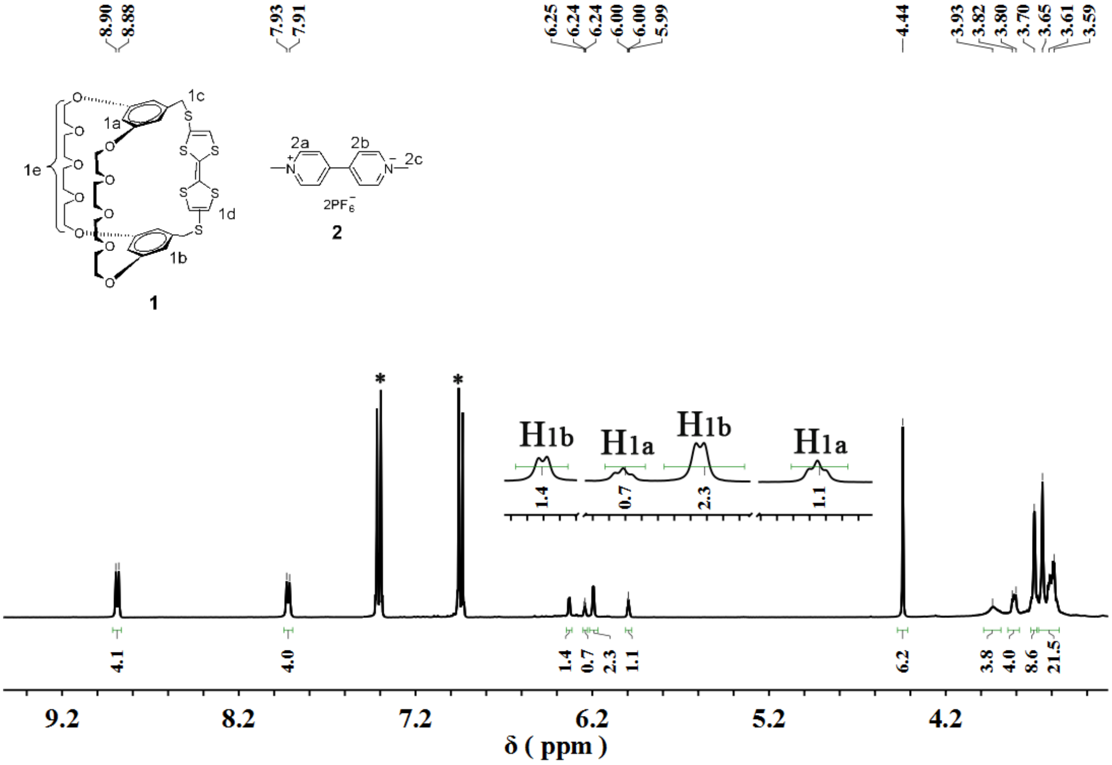


**Fig. S18** Partial $^{1}$H NMR spectrum (400 MHz, $CD_3CN$, 298 K) of **1⊃2** (1:1, 4.50 mM each) after one oxidation/reduction cycle. The resonances indicated by an asterisk arise from the oxidant.

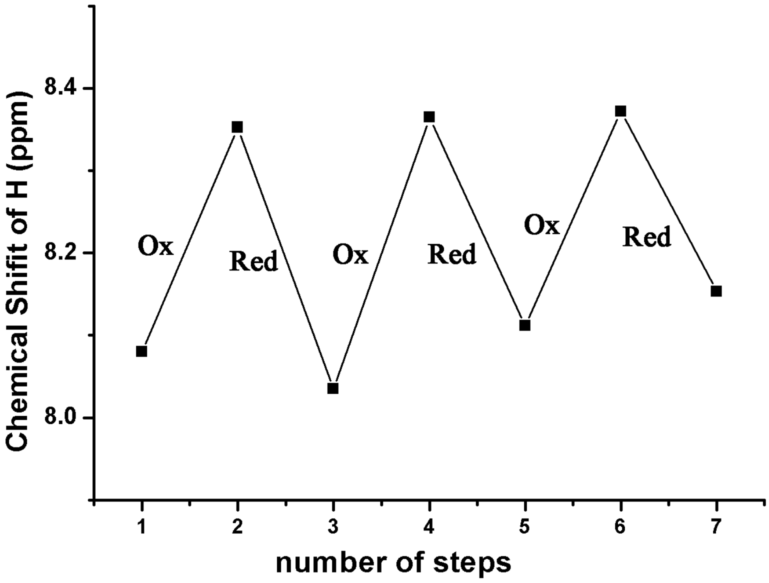


**Fig. S19** The chemical shift changes of $H_{2b}$ on **1⊃2** (1:1, 4.00 mM each, 400 MHz, $CD_3CN$, 298 K) upon stepwise addition of oxidant or reductant.

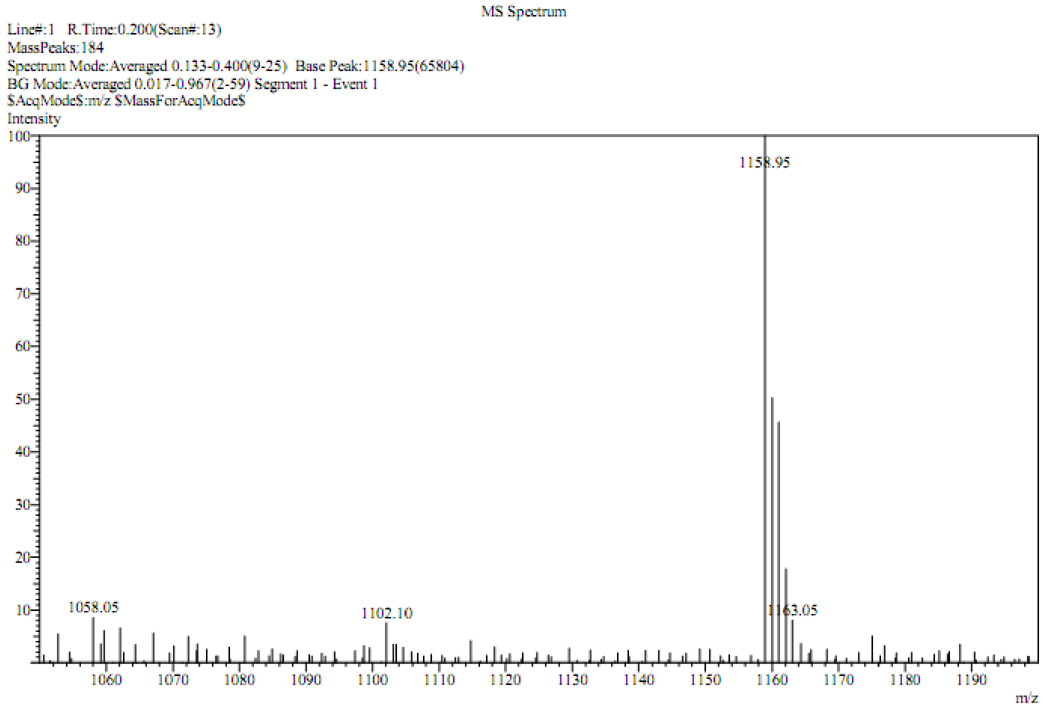


**Fig. S20** LR-ESI-MS of **1**⊃**2** after one oxidation/reduction cycle.

## *10. Redox-responsive complexation between **1** and **3***

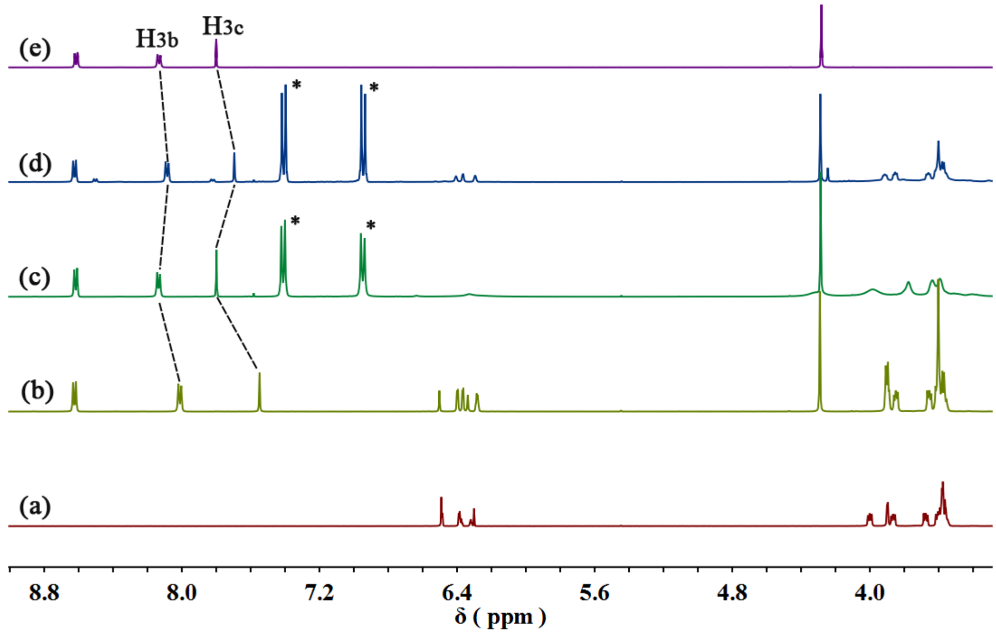


**Fig. S21** Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 298 K): (a) **1**; (b) 4.50 mM **1** and 4.50 mM **3**; (c) after addition of 2.2 equiv. of tris(p-bromophenyl)aminium hexachloroantimonate to (b); (d) after addition excess Zn powder to (c); (e) **3**. The resonances indicated by an asterisk arise from the oxidant.

## 11. $^1$H NMR spectrum of the single crystal of **1⊃2**

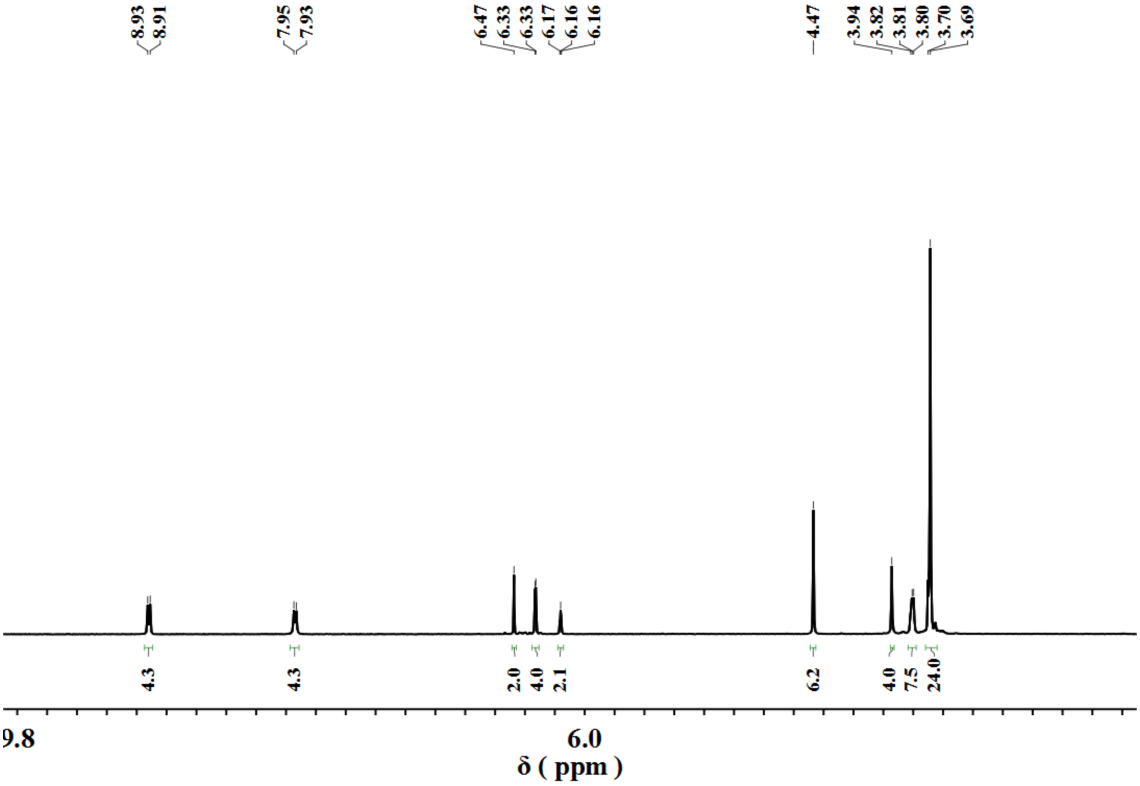


**Fig. S22** $^1$H NMR spectrum (400 MHz, $CD_3CN$, 298 K) of the single crystal of **1**⊃**2**.

## 12. X-ray crystal data for **1⊃2**

**Table 1** Crystal data and structure refinement for **1**⊃**2**

| | |
|---|---|
| CCDC number | 1004106 |
| Empirical formula | $C_{96}H_{116}F_{24}N_4O_{20}P_4S_{12}$ |
| Formula weight | 2610.53 |
| Temperature | 293(2) |
| Wavelength | 1.54178 Å |
| Crystal system | monoclinic |
| Space group | *Pc* |
| *a* | 11.7180(2) Å |
| *b* | 25.4446(4) Å |
| *c* | 26.3628(3) Å |
| *α* | 90.00° |
| *β* | 105.6740(10)° |
| *γ* | 90.00° |
| Volume | 7568.0(2) Å$^3$ |
| Z | 2 |

| | |
|---|---|
| Density (calculated) | 1.146 |
| Absorption coefficient | 2.711 |
| F(000) | 2696.0 |
| Crystal size | 0.26 × 0.24 × 0.19 $\mathrm{mm}^3$ |
| Theta range for data collection | 2.46 to 55.23° |
| Index ranges | −13<=h<=10, −28<=k<=29, −30<=l<=30 |
| Reflections collected | 29348 |
| Independent reflections | 15250 [R(int) = 0.0459] |
| Completeness to theta = 65.00° | 97.4 % |
| Absorption correction | multi-scan |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on *F*2 | 1.030 |
| Final R indices [$I > 2\mathrm{sigma}(I)$] | $R1 = 0.0680$, $wR2 = 0.1512$ |
| *R* indices (all data) | $R1 = 0.1064$, $wR2 = 0.1611$ |
| Largest diff. peak and hole | 0.417 and −0.295 $\mathrm{e{\cdot}Å^{-3}}$ |

## *References*

S1. W. S. Bryant, J. W. Jones, P. E. Mason, I. Guzei, A. L. Rheingold, F. R. Fronczek, D. S. Nagvekar and H. W. Gibson, *Org. Lett.*, 1999, **1**, 1001.

S2. M. T. McCall and D. G. Whitten, *J. Am. Chem. Soc.*, 1969, **91**, 5681.

S3. H. W. Gibson and D. S. Nagvekar, *Can. J. Chem.*, 1997, **75**, 1375.

S4. X. Guo, D. Zhang, H. Zhang, Q. Fan, W. Xu, X. Ai, L. Fan and D. Zhu, *Tetrahedron*, 2003, **59**, 4843.

S5. C. Wang, S. M. Dyar, D. Cao, A. C. Fahrenbach, N. Horwitz, M. T. Colvin, R. Carmieli, C. L. Stern, S. K. Dey, M. R. Wasielewski and J. F. Stoddart, *J. Am. Chem. Soc.*, 2012, **134**, 19136.