Electronic Supplementary Information

Redox-Driven Sulfate Ion Transfer between Two Tripodal Tris(urea) Receptors

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Experimental details

Synthesis.

The receptors L^1 and L^2 were synthesized as reported previously.[1]

Fluorescent emission studies.

Fluorescent spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer equipped with a PX-2 pulsed xenon lamp. Excitation and emission slit widths were 2.5 and 5.0 nm, respectively, and solutions were excited at 335 nm. A solution of **L** was prepared, e.g., 1.0×10^{-5} M in DMSO (99%), and an aliquot (2 mL) was transferred to a 1-cm fluorescence tube. The relative fluorescence changes were recorded as a function of substrate concentration.

Cyclic voltammetry.

The binding behavior of L^2 and sulfate was examined by cyclic voltammetry (CV) and the conversion between the oxidized state and neutral state of L^2 was performed by controlled-potential electrolysis (CHI 760, USA). The working electrode (with a diameter around 0.25 cm) was pretreated according to literature reports.[2] All other chemicals used were of analytical grade. Distilled water was used throughout the experiment. Tetrabuthylammonium hexafluorophosphate (0.1 M) in DMSO was used as a supporting electrolyte and oxygen in all solution was eliminated by aerating nitrogen gas for about 15 min. The electrolysis experiments were carried out at 0.02 V for the oxidation of the tripodal ferrocenyl urea L^2 and at -0.23 V for reduction of ferrocenium to ferrocene ($C_L = 1 \times 10^{-5}$ M).

NMR Spectra.

^{1}H and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal (DMSO-d_6, 2.50 ppm for ^{1}H).
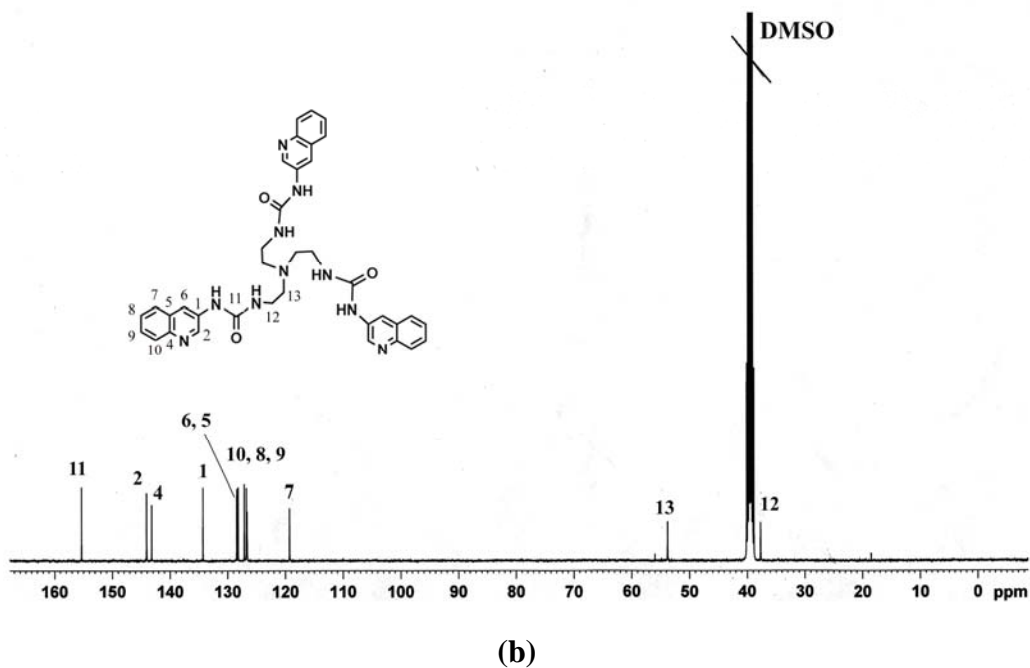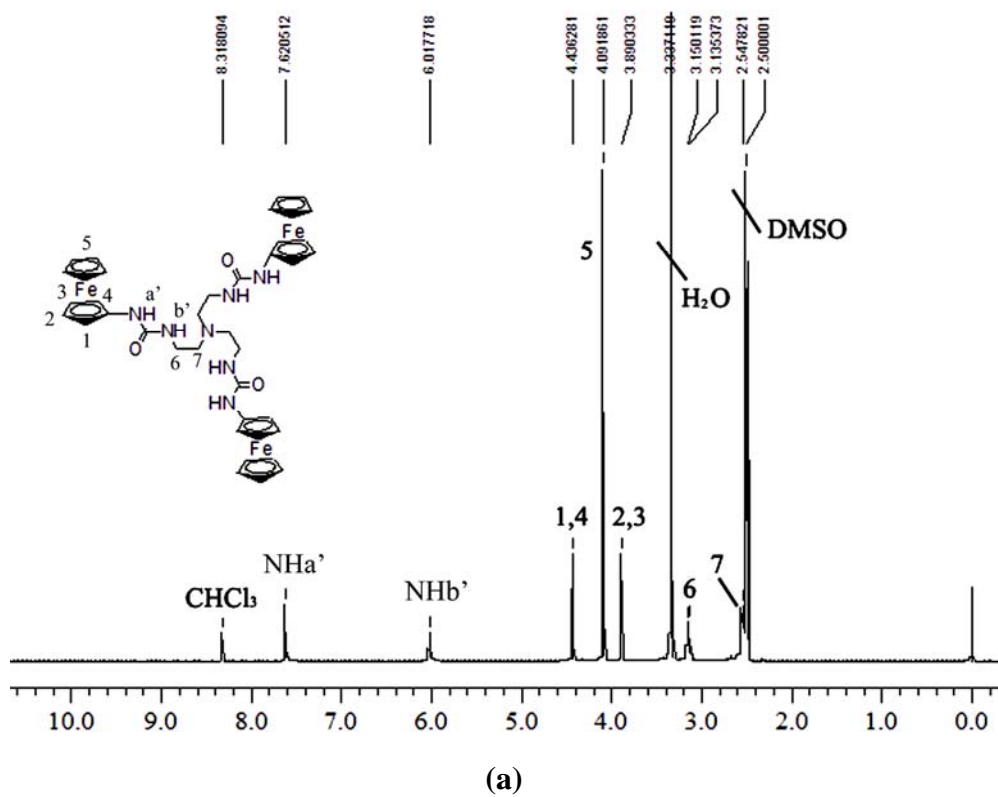

(a)

(b)
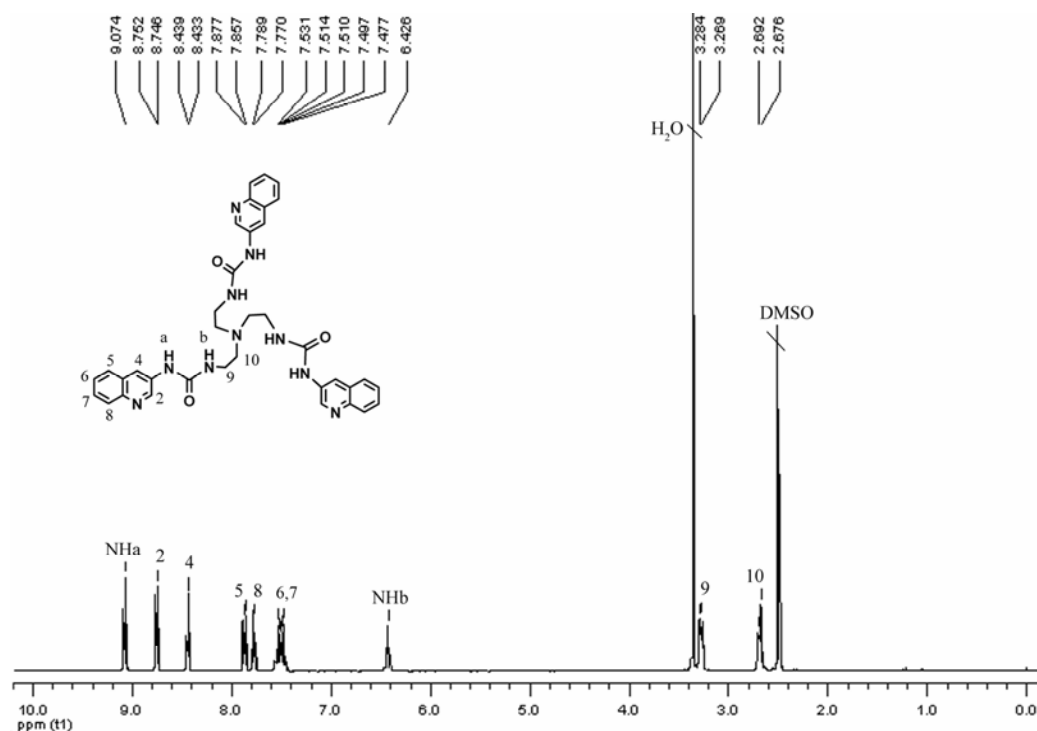
Figure S1. (a) ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of the receptor L^1 (5 mM); (b) ^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of L^1 (20 mM).
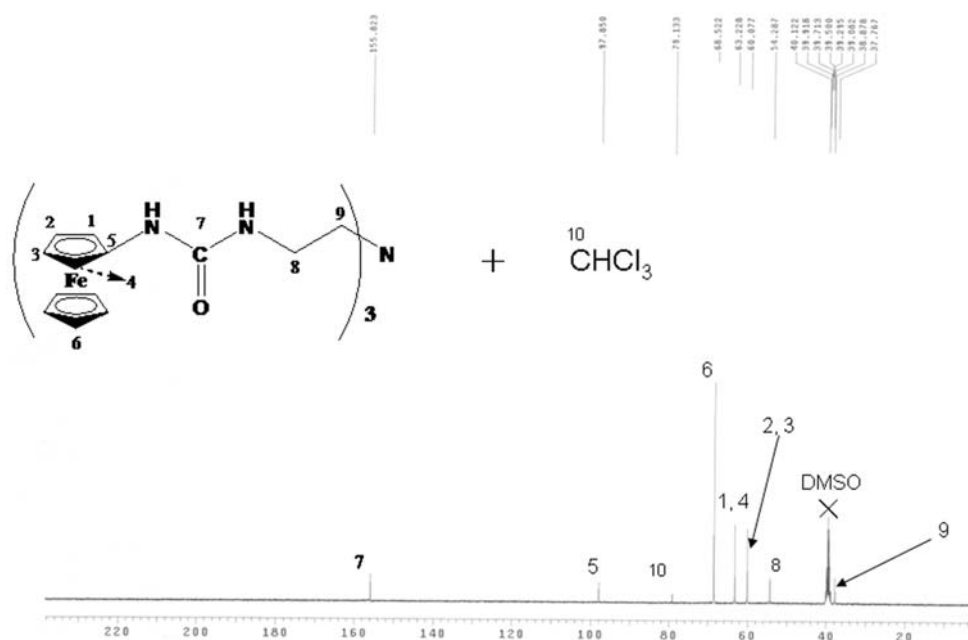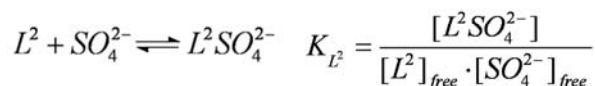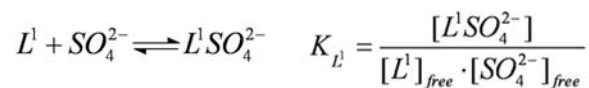

(a)

Figure S2. (a) ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of the receptor L^2 (5 mM); (b) ^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of L^2 (20 mM).

The percentage of [L·SO$_4{}^{2-}$] was estimated as the value $\Delta\delta_{mix}/\Delta\delta_{sat.}$,[3] where $\Delta\delta_{mix}$ is the downfield shift of the urea groups in the mixed system (L^1/ L^2/ SO$_4{}^{2-}$ 1:1:1) and $\Delta\delta_{sat.}$ is the saturated value induced by sulfate (L^1/ SO$_4{}^{2-}$ 1:1 or L^2/ SO$_4{}^{2-}$ 1:1, both receptors form complex of 1:1 stoichiometry with SO$_4{}^{2-}$).

$$\frac{[L^1SO_4^{2-}]}{[L^1]_{tot}} = \frac{\Delta\delta^1_{mix}}{\Delta\delta^1_{sat.}} = a^1 \qquad \frac{[L^2SO_4^{2-}]}{[L^2]_{tot}} = \frac{\Delta\delta^2_{mix}}{\Delta\delta^2_{sat.}} = a^2 \qquad [L^1]_{tot} = [L^2]_{tot}$$

$$\Rightarrow r = \frac{a^1}{a^2} = \frac{[L^1SO_4^{2-}]}{[L^2SO_4^{2-}]} \qquad (1)$$

$$L^1 + SO_4^{2-} \rightleftharpoons L^1SO_4^{2-} \qquad K_{L^1} = \frac{[L^1SO_4^{2-}]}{[L^1]_{free} \cdot [SO_4^{2-}]_{free}}$$

$$L^2 + SO_4^{2-} \rightleftharpoons L^2SO_4^{2-} \qquad K_{L^2} = \frac{[L^2SO_4^{2-}]}{[L^2]_{free} \cdot [SO_4^{2-}]_{free}}$$

$$[L^1]_{free} + [L^1SO_4^{2-}] = [L^1]_{tot} \quad [L^2]_{free} + [L^2SO_4^{2-}] = [L^2]_{tot}$$

$$\Rightarrow \frac{K_{L^1}}{K_{L^2}} = r \cdot \frac{1-a^1}{1-a^2} \qquad (2)$$

The results were obtained from both the urea NH protons, (NHa & NHa') r_1 = 7/1, and (NHb & NHb') r_2 = 5/1, and the corresponding percentage of [$L^1 \cdot SO_4^{2-}$] is 88% and 83%.

The calculated value of $K(L^1)/ K(L^2)$ is from 2.33 to 2.78, and the experimental value is 2.69, which is consistent with the percentage values obtained from the downfield shifts of NH protons in ^{1}H NMR.

UV-vis spectral titration for the binding studies.

All solutions were freshly prepared prior to use. The association constants[4] were determined by adding increasing amounts of a stock solution of sulfate to 2 mL of L^1 (5.0×10^{-5} M) and L^2 (4.0×10^{-4} M). After each addition, the absorption spectrum was recorded. Absorption spectra were obtained on a HP-8453 spectrophotometer (1-cm quartz cell).
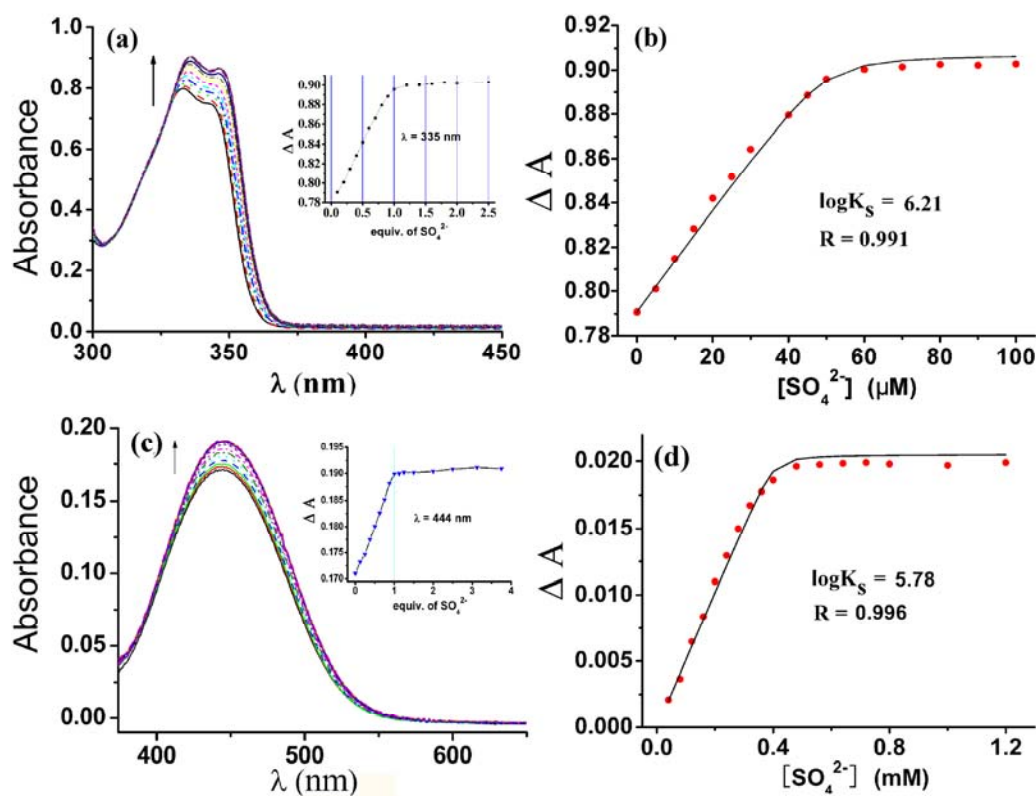

Figure S3. (a) Absorption spectra recorded over the course of the titration of a 5×10^{-5} M solution of L^1 with a standard solution of (TBA)$_2$SO$_4$ in DMSO. Inset: titration curve for L^1 with SO$_4^{2-}$. (b)Variation in absorbance of L^1 in DMSO as a function of SO$_4^{2-}$ concentration. (c) Absorption spectra recorded over the course of the titration of a 4×10^{-4} M solution of L^2 with a standard solution of (TBA)$_2$SO$_4$ in DMSO. Inset: titration curve for L^2 with SO$_4^{2-}$. (d) Variation in absorbance of L^2 as a function of SO$_4^{2-}$ concentration.
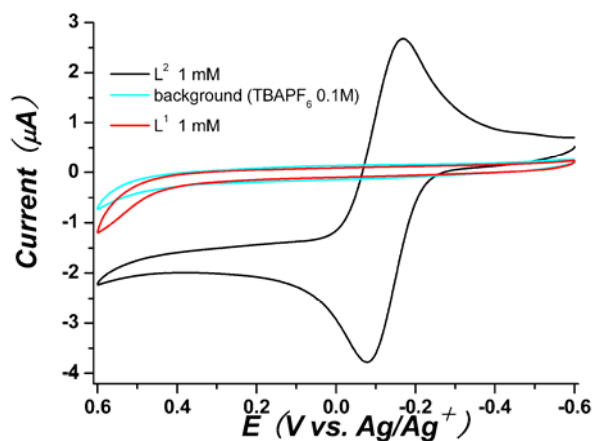
Figure S4. Cyclic voltammetry of L^2 (1×10^{-3} M) (black), blank background (blue), and L^1 (1×10^{-3} M) (red) in DMSO. Scan rate: 50 mV/s. Supporting electrolyte: $TBAPF_6$ (0.1 M).
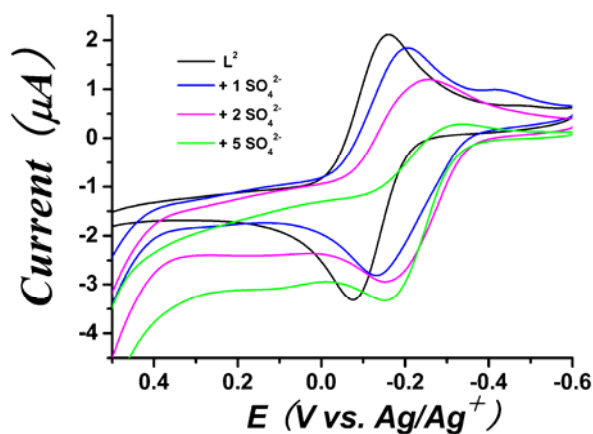

Figure S5. CVs of L^2 upon addition of SO_4^{2-} (0 – 5 equivalents). Scan rate 50 mV·s^{-1}, $L^2 = 1\times10^{-3}$ M in DMSO. Supporting electrolyte: $TBAPF_6$ (0.1 M).
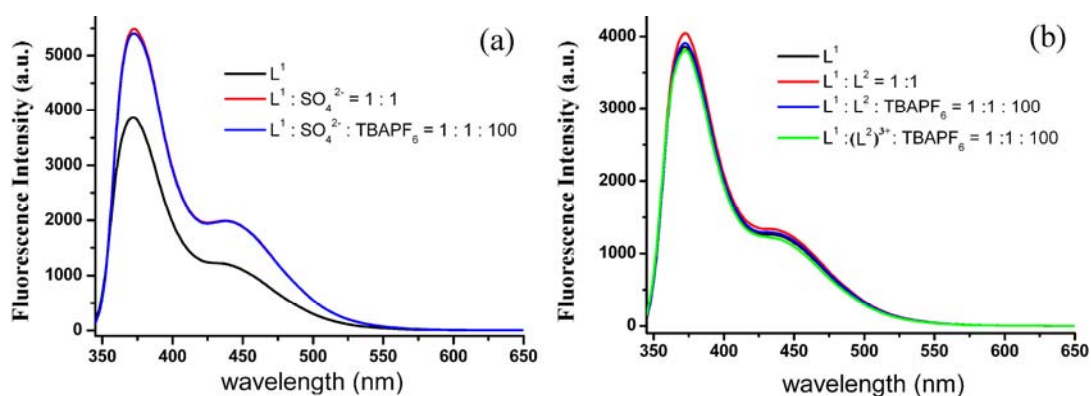

Figure S6. Emission spectra of blank experiments: (a) L^1 (1×10^{-5} M) in DMSO (black); L^1/ SO_4^{2-} 1:1 (red) and L^1/SO_4^{2-}/$TBAPF_6$ 1:1:100 (blue). (b) L^1 (1×10^{-5} M) in DMSO (black); L^1/ L^2 1:1 (red) (1:1); L^1/L^2/$TBAPF_6$ (1:1:100) (blue); L^1/ $(L^2)^{3+}$ /$TBAPF_6$ (1:1:100) (green).
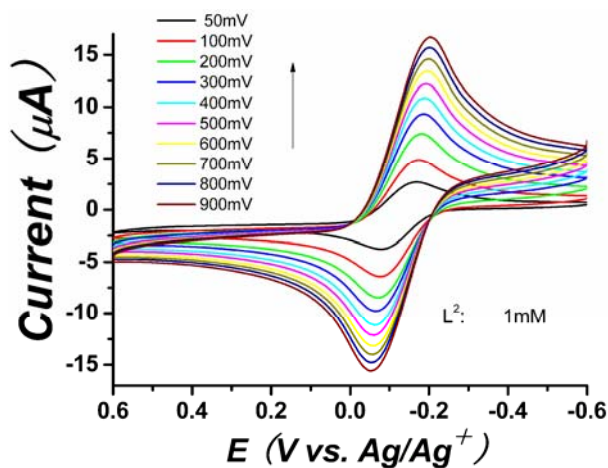
Figure S7. Cyclic voltammetry of L^2 (1×10^{-3} M) in DMSO. Scan rate: 50–900 mV/s. Supporting electrolyte: $TBAPF_6$. Working and counter-electrode: platinum. Reference electrode: Ag/Ag^+.
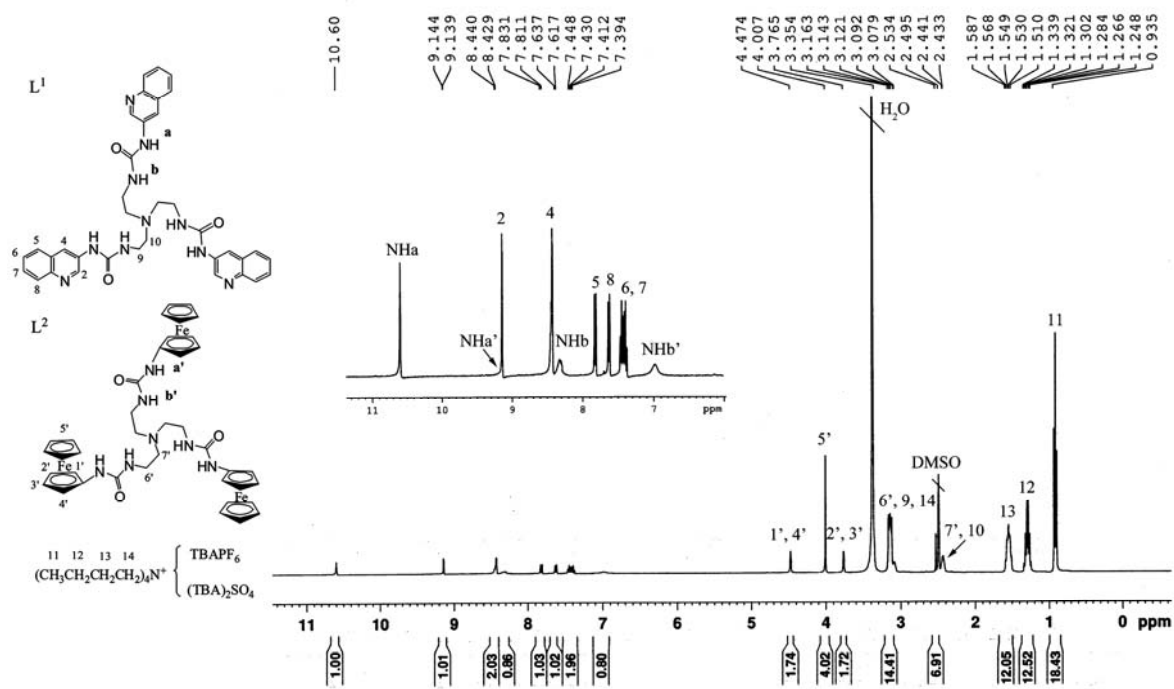

Figure S8. ^1H NMR (DMSO-d_6, 400 MHz) spectrum of the $L^1/L^2/(TBA)_2SO_4/TBAPF_6$ (1:1:1:2) solution after one redox cycle (5 mM).
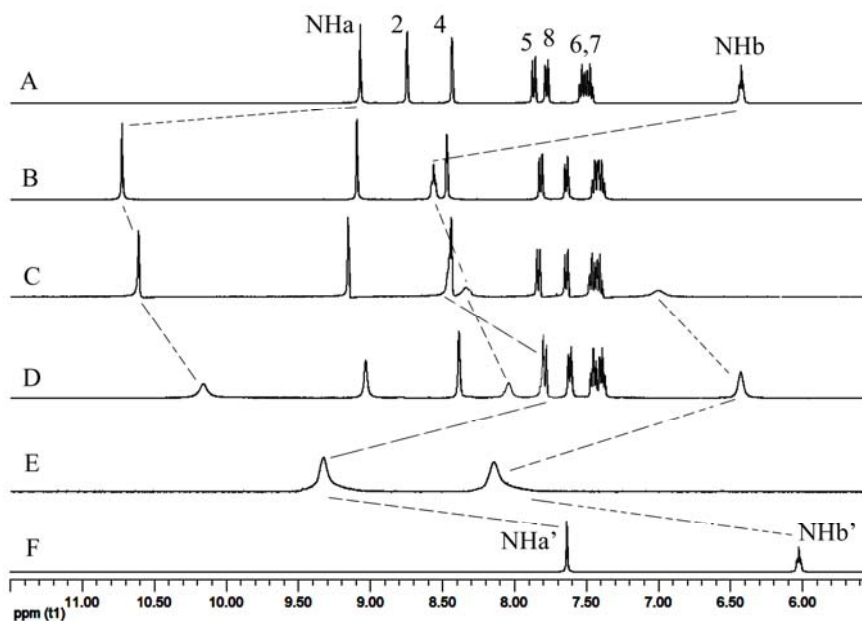
Figure S9. ^{1}H NMR spectra of A) L^1; B) L^1/SO_4^{2-} (1:1); C) $L^1/L^2/ SO_4^{2-}/TBAPF_6$ (1:1:1:2) solution after one redox cycle; D) $L^1/ L^2/ SO_4^{2-}$ (1:1:1); E) L^2/ SO_4^{2-} (1:1); F) L^2 in DMSO-d_6 (5 mM).

^{1}H NMR spectrum of the solution $L^1/L^2/SO_4^{2-}/TBAPF_6$ (1:1:1:2) after one redox cycle was measured (Figs. S8 and S9). Notably, the urea NH protons of L^1 shifted further downfield ($\varDelta\delta_{NHa}$ 1.55 and $\varDelta\delta_{NHb}$ 1.91 ppm; Fig. S9, B/C) than those (1.13 ppm and 1.59 ppm; Fig. 1C) before the redox processes, and the values are only slightly smaller than those (1.68 and 2.15 ppm; Fig. 1B) of L^2 with sulfate. Although the NH protons of L^2 also showed further downfield shifts, the degree is much smaller than L^1 ($\varDelta\delta_{NHa'}$ 0.83 and $\varDelta\delta_{NHb'}$ 0.93 ppm; Fig. S9, C/E). Apparently, the sulfate binding affinity of L^1 is now much larger than L^2 in the mixture. These results are also consistent with the fluorescence experiments which demonstrated that L^2 could not quench the emission again after one redox cycle. The missing of the competition ability of L^2 upon redox treatment might be due to that the receptor L^2 is unstable under the experimental conditions and can partially decompose or deposit on the electrode during the redox processes. This is supported by the decrease of the integral proportion of the ferrocene protons by ca. 15% ~ 20% (Fig. S8, H1' ~ H5'). Moreover, during the first redox cycle (5 mM, DMSO-d_6, $L^1/L^2/SO_4^{2-}/TBAPF_6$ 1:1:1:2), deposition of some dark material on the surface of the counter Pt electrode was observed. As a result, the ferrocenyl-substituted ligand L^2 had a lower concentration and could not compete with L^1 again even at the oxidized state.

Reference:

1. (a) M. Li, B. Wu, C. Jia, X. Huang, Q. Zhao, S. Shao, X.-J. Yang, *Chem. Eur. J.* 2011**, 17**, 2272; (b) Y. Hao, C. Jia, B. Wu, M. Li, S. Li, X. Huang, X.-J. Yang, *to be submitted*.

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3. G. J. E. Davidson, S. Sharma, S. J. Loeb, *Angew. Chem. Int. Ed.* 2010, **49**, 4938.

4. (a) B. Valeur, J. Pouget, J. Bouson, M. Kaschke and N. P. Ernsting, *J. Phys. Chem.*, 1992, **96**, 6545; (b) J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.