

*Electronic Supplementary Information (ESI)*

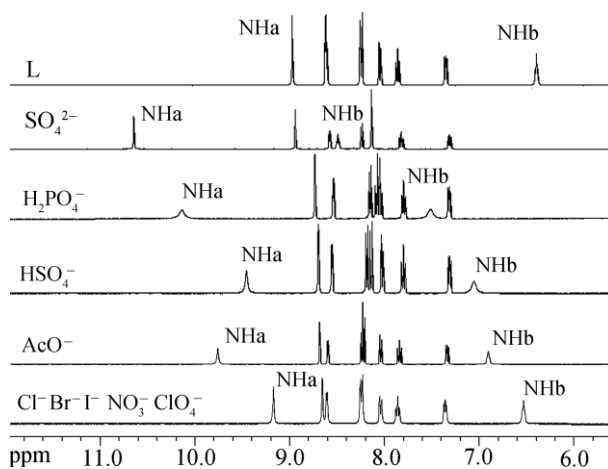
## Selective anion sensing by a ruthenium(II)–bipyridyl-functionalized tripodal tris(urea) receptor

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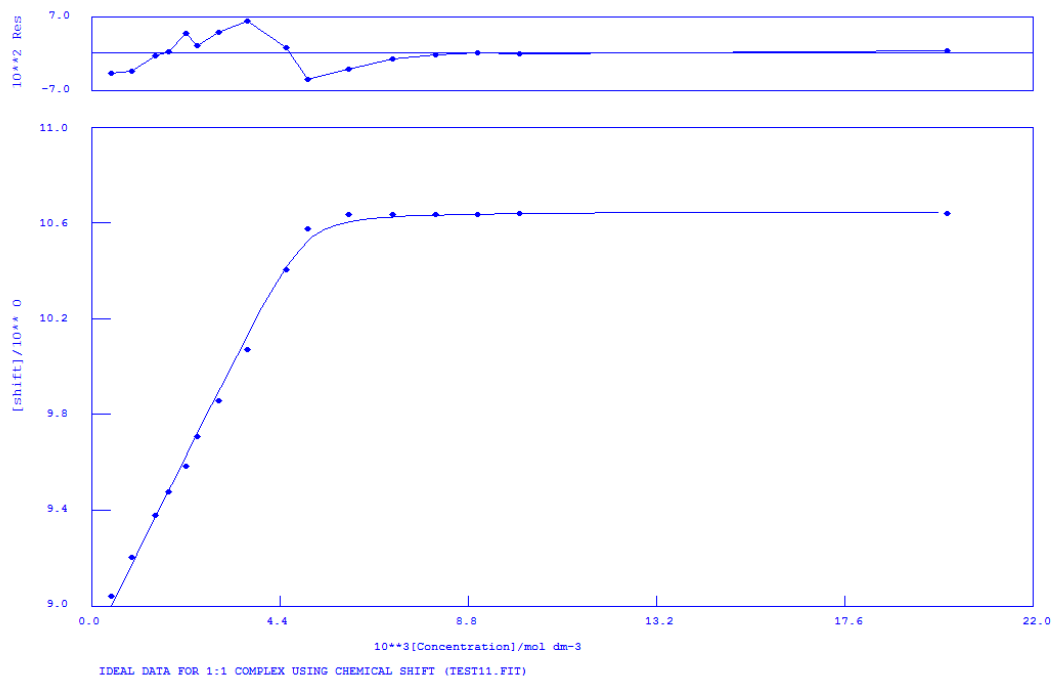
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**Fig. S1.** <sup>1</sup>H NMR spectra of L in the presence of 1 equiv. of various anions (added as Bu<sub>4</sub>N<sup>+</sup> salts, DMSO-d<sub>6</sub>-0.5% H<sub>2</sub>O, 400 MHz).



**Fig. S2.**  $^1\text{H}$  NMR titration of **L** with  $\text{SO}_4^{2-}$  in  $\text{DMSO-}d_6$ -0.5% water (added as  $\text{Bu}_4\text{N}^+$  salt, 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes  
 Program run at 21:13:15 on 11/16/2011

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction:  $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

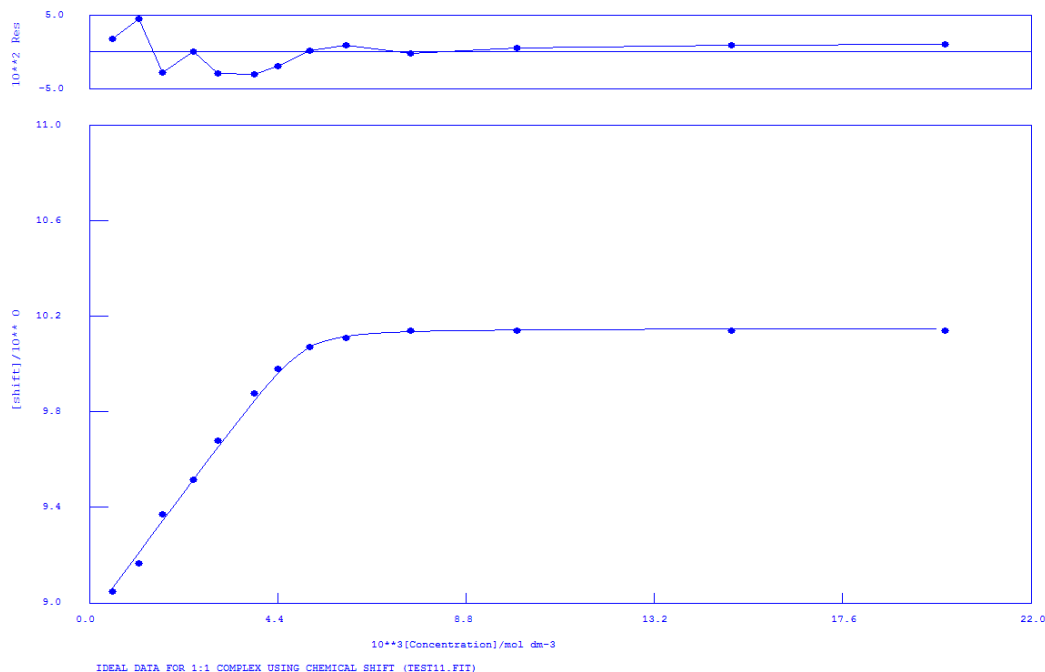
IDEAL DATA:  $\text{K1} = 46000$ ;  $\text{DELTA M} = 8.964$ ;  $\text{DELTA ML} = 10.643$

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	$3.42805\text{E}+04$	$2.000\text{E}-01$	$4.735\text{E}+02$	$1.114\text{E}+00$	K1
2	1	$8.83281\text{E}+00$	$2.000\text{E}-01$	$1.917\text{E}-02$	$1.146\text{E}+00$	SHIFT M
3	1	$1.06477\text{E}+01$	$1.000\text{E}+00$	$1.204\text{E}-02$	$1.262\text{E}+00$	SHIFT ML

ORMS ERROR =  $3.22\text{E}-02$  MAX ERROR =  $6.14\text{E}-02$  AT OBS.NO. 8

RESIDUALS SQUARED =  $1.35\text{E}-02$

RFACTOR = 0.2880 PERCENT



**Fig. S3.**  $^1\text{H}$  NMR titration of **L** with  $\text{H}_2\text{PO}_4^-$  in  $\text{DMSO-}d_6$ -0.5% water (added as  $\text{Bu}_4\text{N}^+$  salt, 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes  
 Program run at 20:47:27 on 11/16/2011

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction:  $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

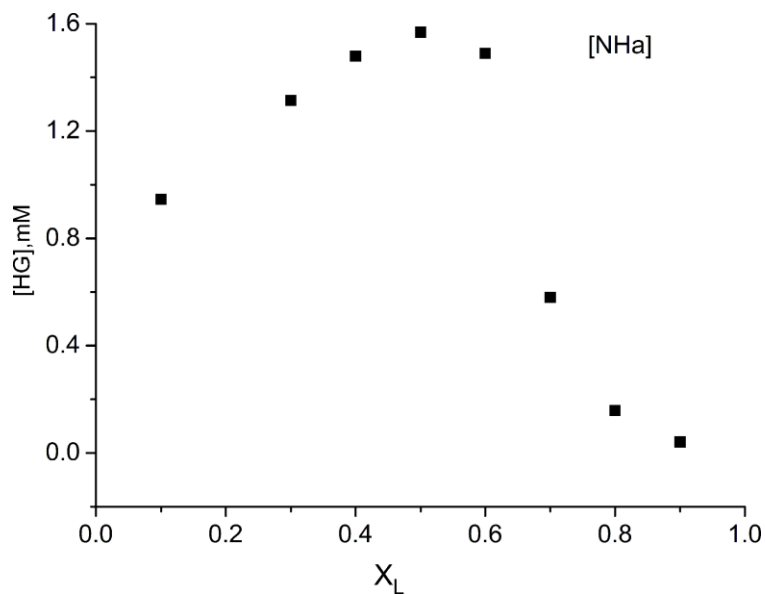
IDEAL DATA:  $K_1 = 22208$ ;  $\Delta M = 8.964$ ;  $\Delta M_L = 10.137$

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	$3.05393\text{E}+04$	$2.000\text{E}-01$	$5.839\text{E}+03$	$1.738\text{E}+00$	$K_1$
2	1	$8.93110\text{E}+00$	$2.000\text{E}-01$	$1.635\text{E}-02$	$1.131\text{E}+00$	SHIFT M
3	1	$1.01485\text{E}+01$	$1.000\text{E}+00$	$1.135\text{E}-02$	$1.803\text{E}+00$	SHIFT ML

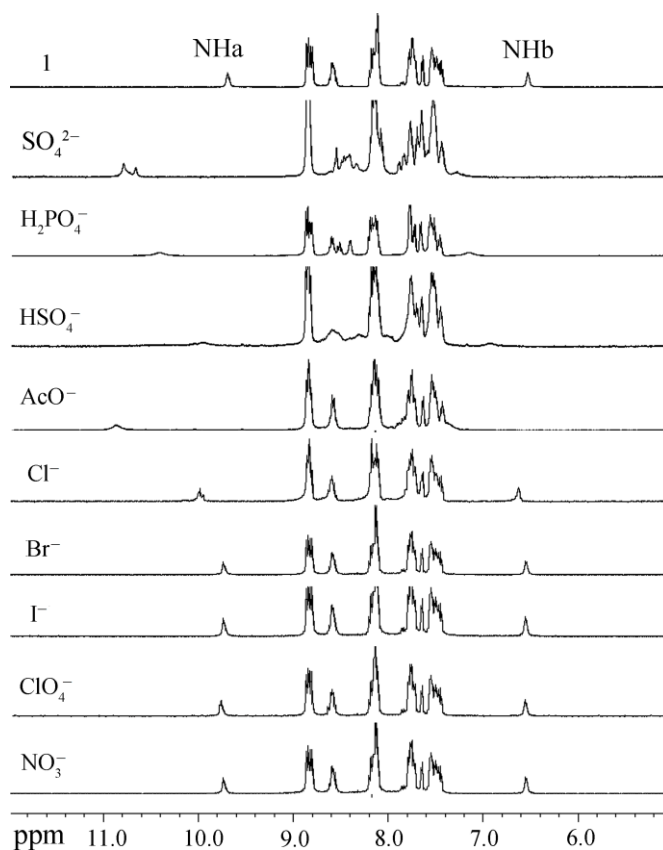
ORMS ERROR =  $2.36\text{E}-02$  MAX ERROR =  $4.34\text{E}-02$  AT OBS.NO. 2

RESIDUALS SQUARED =  $5.57\text{E}-03$

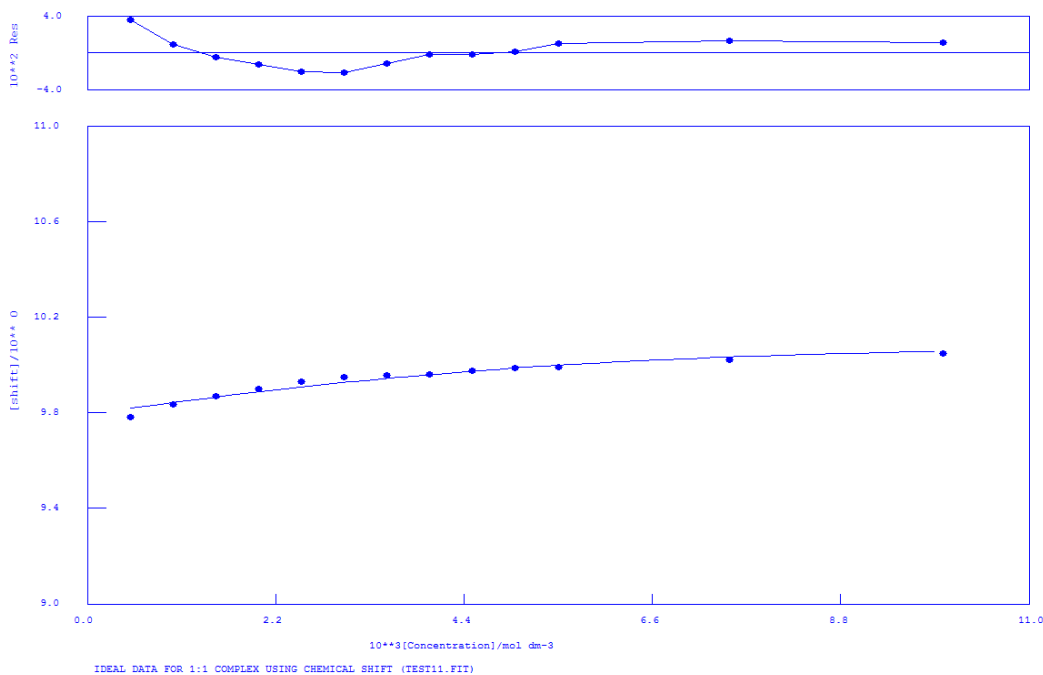
RFACTOR = 0.2112 PERCENT



**Fig. S4.** Job's plot of receptor **1** with addition of  $\text{H}_2\text{PO}_4^-$  ions in  $\text{DMSO}-d_6$ -0.5%  $\text{H}_2\text{O}$ . Data were obtained based on the changes of the NHa signal.



**Fig. S5.**  $^1\text{H}$  NMR spectra of **1** (5 mM) in the presence of 1 equiv. of various anions (added as  $\text{Bu}_4\text{N}^+$  salts,  $\text{DMSO}-d_6$ -0.5% water, 400 MHz).



**Fig. S6.**  $^1\text{H}$  NMR titration of **1** with  $\text{Cl}^-$  in  $\text{DMSO-}d_6$ -0.5% water (added as  $\text{Bu}_4\text{N}^+$  salt, 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes  
 Program run at 22:41:52 on 04/11/2012

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

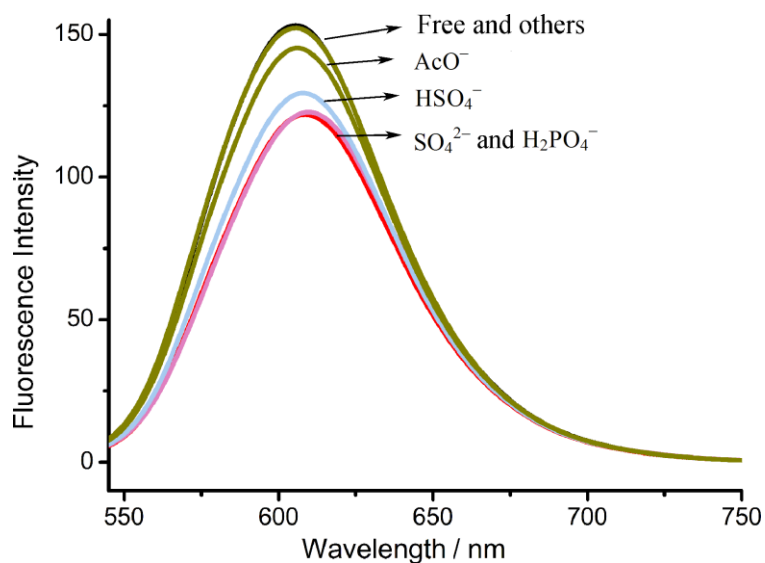
Reaction:  $\text{M} + \text{L} = \text{ML}$

FILE: 2.FIT

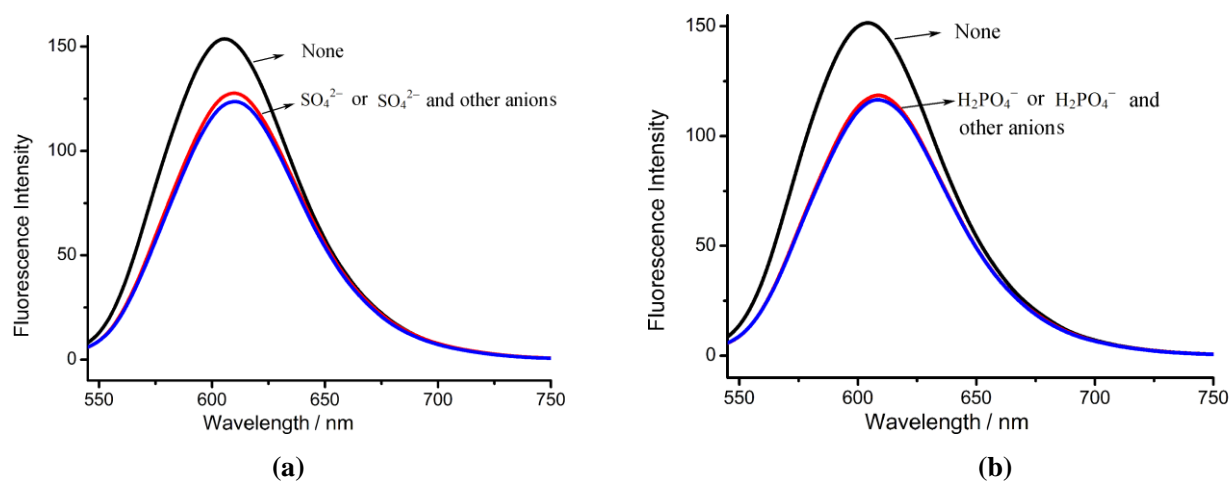
IDEAL DATA:  $K_1 = 200$ ;  $\Delta M = 9.77$ ;  $\Delta \text{ML} = 10.047$

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	7.34519E+02	2.000E-01	7.453E+01	2.266E+00	K1
2	1	9.79338E+00	2.000E-01	1.105E-02	1.882E+00	SHIFT M
3	1	1.01170E+01	1.000E+00	1.710E-02	3.110E+00	SHIFT ML

ORMS ERROR = 1.73E-02 MAX ERROR = 3.51E-02 AT OBS.NO. 1  
 RESIDUALS SQUARED = 2.98E-03  
 RFACTOR = 0.1524 PERCENT



**Fig. S7.** Fluorescence emission spectra of the receptor **1** ( $5 \times 10^{-6}$  M in CH<sub>3</sub>CN–5% H<sub>2</sub>O) upon addition of 10 equiv. of different anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> as Bu<sub>4</sub>N<sup>+</sup> salts). Excitation at 447 nm.



**Fig. S8.** Fluorescence titration of **1** ( $5 \times 10^{-6}$  M in CH<sub>3</sub>CN–5% water) with 10 equiv. of SO<sub>4</sub><sup>2-</sup> (a) or H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (b) and various competitive anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, HSO<sub>4</sub>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>).