

Supplementary Material (ESI) for New Journal of Chemistry  
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## Anion binding of tris-(thio)urea ligands

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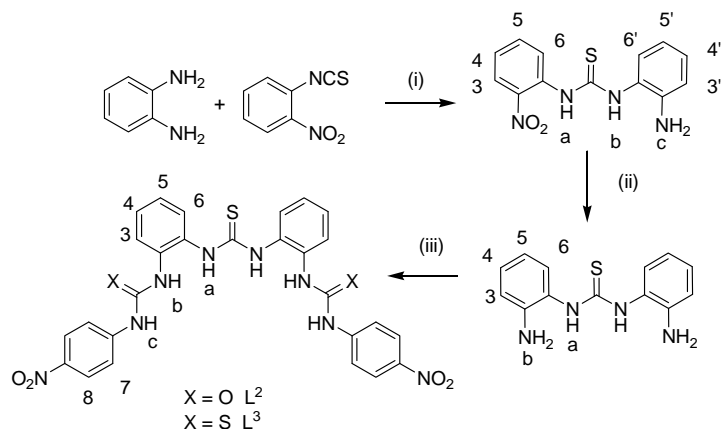
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### Experimental Section

*o*-Nitrophenyl isothiocyanate, *p*-nitrophenyl isothiocyanate, *o*-nitrophenyl isocyanate and *p*-nitrophenyl isocyanate were purchased from Alfa Aesar and used as received. All solvents and other reagents were of reagent grade quality. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Mercury plus-400 spectrometer at 400 MHz and 100 MHz, respectively, using TMS as an internal standard. UV-vis spectra were performed on an HP8453 spectrophotometer (1 cm quartz cell). Elemental analyses were performed with an Elementar Vario EL instrument. IR spectra were recorded with a Bruker IFS 120HR spectrometer. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer. Melting points were detected on an X-4 Digital Vision MP Instrument.

### Synthesis of ligands L<sup>2</sup>, L<sup>3</sup>, and complex 1



**Scheme S1.** Synthesis of ligands  $L^2$  and  $L^3$ : (i) dry  $\text{CH}_2\text{Cl}_2$ ; (ii)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , ethyl acetate; (iii)  $L^2$ : *p*-nitrophenyl isocyanate, dry THF,  $L^3$ : *p*-nitrophenyl isothiocyanate, dry  $\text{CH}_3\text{CN}$ .

### 1-(2-Nitrophenyl)-3-(2-amino-phenyl) thiourea (**1a**)

A solution of *o*-nitrophenyl isothiocyanate (0.90 g, 5.0 mmol) prepared in situ in 200 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise under 0 °C to *o*-phenylenediamine (0.56 g, 5.2 mmol) in 40 mL of  $\text{CH}_2\text{Cl}_2$ . The mixture was stirred for 4 h. Solvent was removed and the solid was recrystallized from  $\text{CH}_2\text{Cl}_2$  to give compound **1a** as a yellow solid (0.72 g, 56 %). M.p.: 153 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  10.01 (s, 1H, Ha), 8.98 (d, 1H,  $J = 8.4$  Hz, H3), 8.08 (t, 1H,  $J = 8.4$  Hz, H5), 7.71 (s, 1H, Hb), 7.65 (t, 1H,  $J = 8.4$  Hz, H4), 7.28 (d, 1H,  $J = 8.0$  Hz, H6), 7.25 (t,  $J = 8.4$  Hz, H5'), 7.21 (t, 1H,  $J = 8.4$  Hz, H4'), 6.90 (d, 1H,  $J = 4.0$  Hz, H6'), 6.87 (d, 1H,  $J = 4.0$  Hz, H3'), 3.91 (s, 2H, Hc).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  180.3 (CS), 143.8 (C), 142.7 (C), 133.6 (CH), 133.1 (C), 128.3 (CH), 127.6 (CH), 127.5 (CH), 125.2 (CH), 124.3 (CH), 123.5 (C), 122.3 (CH), 116.0 (CH), 115.5 (CH). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3420, 1612, 1508, 1347, 1178, 733. Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$ : C, 54.15; H, 4.20; N, 19.43. Found: C, 54.25; H, 4.10; N, 19.23. ESI-MS:  $m/z$  289.1 [**1a** + H] $^+$ , 95%; 311.1 [**1a** + Na] $^+$ , 96%.

### 1,3-Bis(2-aminophenyl)thiourea (**1b**)

A solution of 1-(2-nitrophenyl)-3-(2-amino-phenyl)thiourea (**1a**, 0.48 g, 1.66 mmol) in 200 mL of ethyl acetate was added dropwise to  $\text{SnCl}_2$  (1.31 g, 5.81 mmol) in 20 mL ethyl acetate. The resultant reaction mixture was stirred at room temperature and the progress of reaction was monitored by TLC. After 30 h, the reaction mixture was poured into ice-cold water and extracted with ethyl acetate ( $3 \times 50$  mL) to remove excess **1a**. The aqueous phase was neutralized by  $\text{NaHCO}_3$  and extracted with ethyl acetate ( $3 \times 50$  mL). The organic layers were

combined and concentrated to get the compound **1b** as white powders (0.22 g, 50%). M.p.: 172 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, ppm): δ 8.80 (s, 2H, Ha), 7.09 (d, *J* = 7.6 Hz, 2H, H6), 6.79 (t, *J* = 3.2 Hz, 2H, H4), 6.73 (d, *J* = 7.6 Hz, 2H, H3), 6.55 (t, *J* = 3.2 Hz, 2H, H5), 4.98 (s, 4H, Hb). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 180.3 (CS), 143.9 (C), 128.2 (CH), 126.9 (CH), 123.9 (C), 116.0 (CH), 115.4 (CH). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>S: C, 60.44; H, 5.44; N, 21.69. Found: C, 60.02; H, 5.22; N, 21.53. ESI-MS: *m/z* 259.1 [**1b** + H]<sup>+</sup>, 75%; 281.1 [**1b** + Na]<sup>+</sup>, 9%.

### 1,3-Bis(2-(4-nitrophenyl)urea-phenyl)thiourea (**L**<sup>2</sup>)

A solution of 1,3-bis(2-aminophenyl)thiourea (**1b**, 0.26 g, 1.0 mmol) in 100 mL of THF was added dropwise into a 130 mL refluxing THF solution of *p*-nitrophenyl isocyanate (0.36 g, 2.2 mmol). The mixture was refluxed for 5 h and the precipitate was filtered off and washed several times with toluene and diethyl ether and then dried over vacuum to yield pure **L**<sup>2</sup> as a yellow solid (0.46 g, 78%). M.p.: 227 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.01 (s, 2H, Hc), 9.37 (s, 2H, Ha), 8.323 (s, 2H, Hb), 8.16 (d, *J* = 8.0 Hz, 4H, H8), 7.81 (d, 2H, H3), 7.64 (d, *J* = 8.0 Hz, 4H, H7), 7.43 (d, *J* = 8.0 Hz, 4H, H6), 7.23 (t, *J* = 4.0 Hz, 4H, H4), 7.23 (t, *J* = 4.0 Hz, 4H, H5). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 157.7 (CS), 151.7 (CO), 146.4 (C), 139.7 (C), 134.0 (C), 132.4 (C), 130.5 (CH), 129.0 (CH), 127.7 (CH), 122.9 (CH). Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>8</sub>O<sub>6</sub>S: C, 55.28; H, 3.78; N, 19.10. Found: C, 55.18; H, 3.66; N, 19.02. ESI-MS: *m/z* 585.1 (17%), [**L**<sup>2</sup>-H]<sup>-</sup>.

### 1,3-Bis(2-(4-nitrophenyl) thiourea-phenyl)thiourea (**L**<sup>3</sup>)

1,3-Bis(2-aminophenyl)thiourea (**1b**, 0.10 g, 0.4 mmol) was added to a solution of *p*-nitrophenyl isothiocyanate (0.17 g, 0.9 mmol) in dry CH<sub>3</sub>CN (130 mL). The mixture was stirred at r.t. for about 30 h. The precipitate was filtered off and washed several times with toluene and diethyl ether and then dried over vacuum to yield pure **L**<sup>3</sup> as a yellow solid (0.20 g, 81%). M.p.: 184 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.57 (s, 2H, Hc), 9.65 (s, 2H, Ha), 9.44 (s, 2H, Hb), 8.18 (d, *J* = 8.8 Hz, 4H, H8), 7.88 (d, *J* = 8.8 Hz, 4H, H7), 7.47 (m, 4H, H3 + H6), 7.25 (m, 4H, H4 + H5). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 180.7 (CS), 180.1 (CS), 148.1 (C), 142.7 (C), 134.4 (C), 134.0 (C), 128.3 (CH), 128.0 (CH), 126.9 (CH), 126.7 (CH), 124.5 (CH), 122.0 (CH). Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>8</sub>O<sub>4</sub>S<sub>3</sub>: C, 52.41; H, 3.58; N, 18.11. Found: C, 52.23; H, 3.43; N, 18.05. ESI-MS: *m/z* 619.1 (12%), [**L**<sup>3</sup> + H]<sup>+</sup>; 641.1 (100%), [**L**<sup>3</sup> + Na]<sup>+</sup>.

## X-ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). An empirical adsorption correction using SADABS was applied for the data. The structures were solved by direct methods using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on  $F^2$  by the use of the program SHELXL-97, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In complex **1**, there are additional, severely disordered solvent molecules in the crystal lattice (about 0.9 CH<sub>2</sub>Cl<sub>2</sub> molecules per formula, or 0.44 CH<sub>2</sub>Cl<sub>2</sub> molecules per asymmetric unit), and the SQUEEZE command was employed in the refinement of the structure. Moreover, the carbon atoms (C2, C3, C5, C6) on one of the aryl rings and the oxygen atoms (O2, O3) on one nitro groups of the ligand are disordered to two positions and were refined with 0.5 occupancies.

**Table S1.** Hydrogen bonds [ $\text{\AA}$  and  $^\circ$ ] in the crystal structures of complex **1**.

D–H $\cdots$ A	$d(\text{D–H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{DHA}$
N6–H6 $\cdots$ O7	0.86	2.20	2.963(4)	148
N7–H7 $\cdots$ O7	0.86	1.99	2.780(4)	153
N2–H2 $\cdots$ O7	0.86	2.01	2.852(4)	165
N3–H3 $\cdots$ O7	0.86	2.28	3.071(4)	153
N4–H4 $\cdots$ O8	0.86	1.90	2.716(5)	156
N5–H5 $\cdots$ O8	0.86	2.42	3.120(6)	141
C52–H52A $\cdots$ O6	0.97	2.67	3.510(4)	147
C52–H52A $\cdots$ O5	0.97	2.49	3.272(4)	137
C52–H52B $\cdots$ S1'	0.97	2.73	3.592(3)	148
O10 $\cdots$ O10''	---	---	2.469(4)	---
O8 $\cdots$ O9''	---	---	2.579(5)	---

Symmetry codes: "  $x, 1-y, 1/2+z$ ; '  $1-x, y, 1/2-z$ .

## Solution binding studies

(1) <sup>1</sup>H NMR titration:

A stock solution of **L** ( $5.0 \times 10^{-3} \text{ M}$ ) in DMSO (1 mL) was prepared for the <sup>1</sup>H NMR titration. A stock solution of anions (200  $\mu\text{L}$ , 0.125 M; 0.625 M) was prepared using this solution as a solvent. Small portions (2–5  $\mu\text{L}$ ) of the anion solution were added to the solution of ligand **L** (500  $\mu\text{L}$ ), and the spectrum was recorded after each addition. The association constants ( $K$ ) were determined by WinEQNMR as depicted below.

(2) UV-Vis titration:

A stock solution of L ( $1.0 \times 10^{-5}$  M) in DMSO (100 mL) was prepared for the UV/vis titration. A stock solution of the anions (2 mL, 2–10 mM) was prepared using this solution as the solvent. Small portions (2–5  $\mu$ L) of the anion solution were added to the solution of ligand L (2.0 mL), and the spectrum was recorded after each addition. The association constants ( $K$ ) were determined by Dynafit3 as depicted below.

(3) Job's plots:

$^1\text{H}$  NMR spectroscopy: Stock solutions of host (5.0 mM) and guest (5.0 mM) in DMSO- $d_6$  (5.0 mL) were prepared in separate volumetric flasks. Ten 5 mm-o.d. NMR tubes were separately filled with a total of 500  $\mu$ L solution of the host and guest in the following ratios ( $\mu$ L, host/guest) at 297 K: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. The  $^1\text{H}$  NMR spectra were obtained for each tube and the NHc signals were used to calculate the complex concentration,  $[\text{HG}] = [\text{H}]_t \times (\delta_{\text{obsd}} - \delta_{\text{free}}) / (\delta_{\text{com}} - \delta_{\text{free}})$ , where  $[\text{H}]_t$  is the total concentration of the host,  $\delta_{\text{obsd}}$  is the chemical shift observed on every point,  $\delta_{\text{free}}$  and  $\delta_{\text{com}}$  corresponds to the chemical shifts of the free ligand and the complex. This value was plotted against the molar fraction of the host.

UV/vis spectroscopy: Stock solutions of L ( $1.0 \times 10^{-5}$  M, DMSO-5% water) and of anions (the concentration is the same as that of L) were separately prepared in volumetric flasks. To a UV/visible cell, a total of 2.0 mL solution of L and  $\text{PO}_4^{3-}$  was added in the following ratios (Host/ Guest): 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10, and each spectrum was recorded. Job's plots were constructed by plotting  $[\text{HG}] \cdot \alpha$  against mol fraction of the L

$$A = A_H + A_{HG} \dots\dots (1)$$

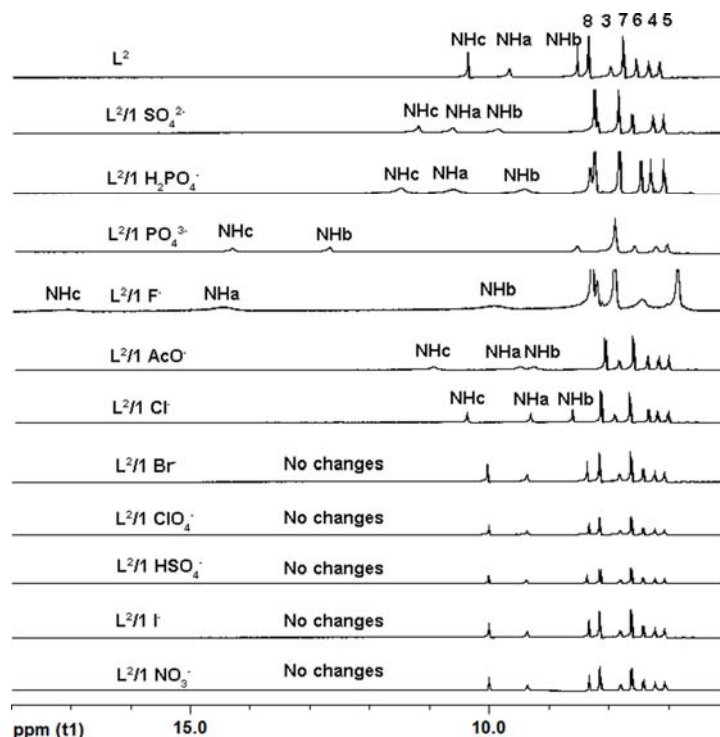
Here,  $A$  is the observed UV absorbance of the each solution, and  $A_H$  and  $A_{HG}$  correspond to the UV absorbance of the free oligoindole and its complex, respectively. According to

Beer-Lambert's law and by introducing  $r = \frac{\epsilon_{HG}}{\epsilon_H}$ , the equation (1) becomes,

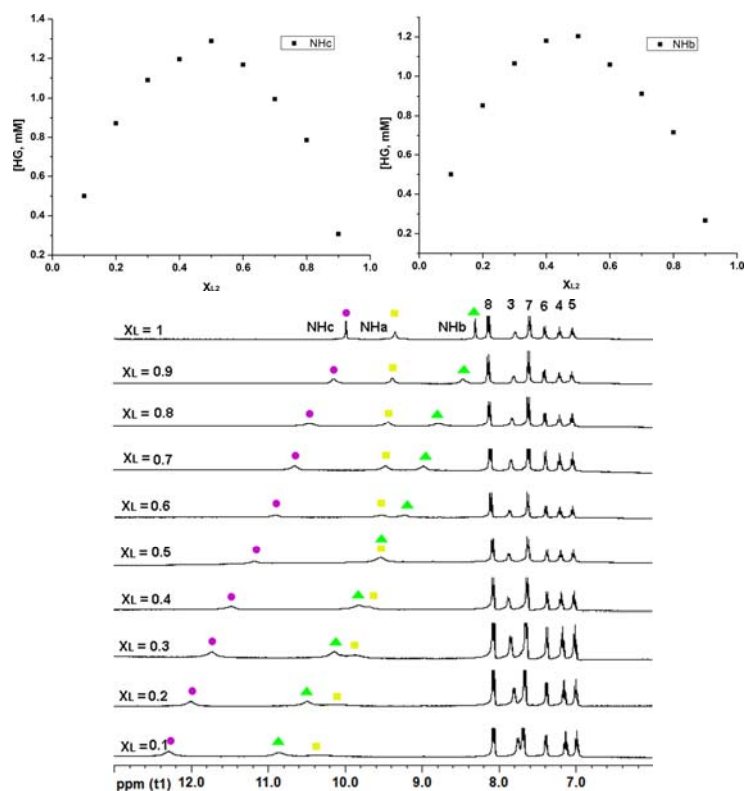
$$\frac{A}{b\epsilon_H} = [\text{H}]_0 + [\text{HG}](\gamma - 1) \dots\dots(2)$$

The equation (2) can be rewritten into the equation (3) by replacing  $\gamma - 1 = \alpha$

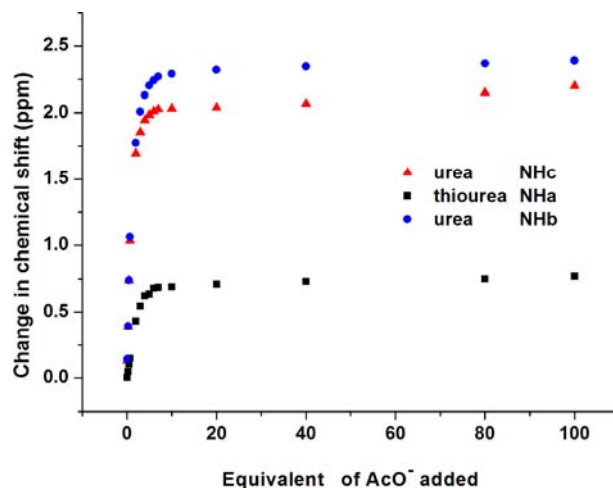
$$[\text{HG}]\alpha = \frac{A}{b\epsilon_H} - [\text{H}]_0 \dots\dots(3), \text{ where } \alpha = \frac{\epsilon_{HG}}{\epsilon_H} - 1 = \frac{\Delta\epsilon_{HG}}{\epsilon_H}$$



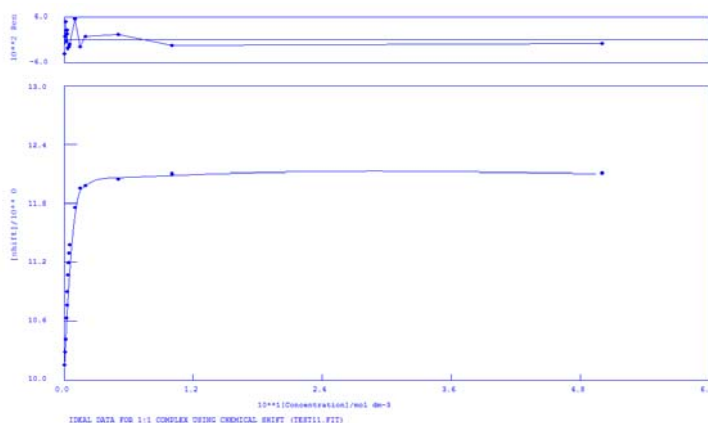
**Fig. S1**  $^1\text{H}$  NMR spectra of  $\text{L}^2$  (5 mM) in the presence of 1.0 equiv of various anions (added as  $\text{TBA}^+$  salts,  $\text{DMSO-}d_6$ -0.5% water, 400 MHz).



**Fig. S2** (Top) Job plot of  $\text{L}^2$  with  $\text{AcO}^-$  (as  $\text{TBA}^+$  salt); (Bottom) The corresponding  $^1\text{H}$  NMR spectra ( $\text{DMSO-}d_6$ -0.5% water, 400 MHz).



**Fig. S3** Change of the chemical shifts of NH signals upon titration of host  $L^2$  with  $AcO^-$  ions.



**Fig. S4**  $^1H$  NMR titration of  $L^2$  with  $AcO^-$  in  $DMSO-d_6$ -0.5% water (400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 17:32:30 on 05/10/2013

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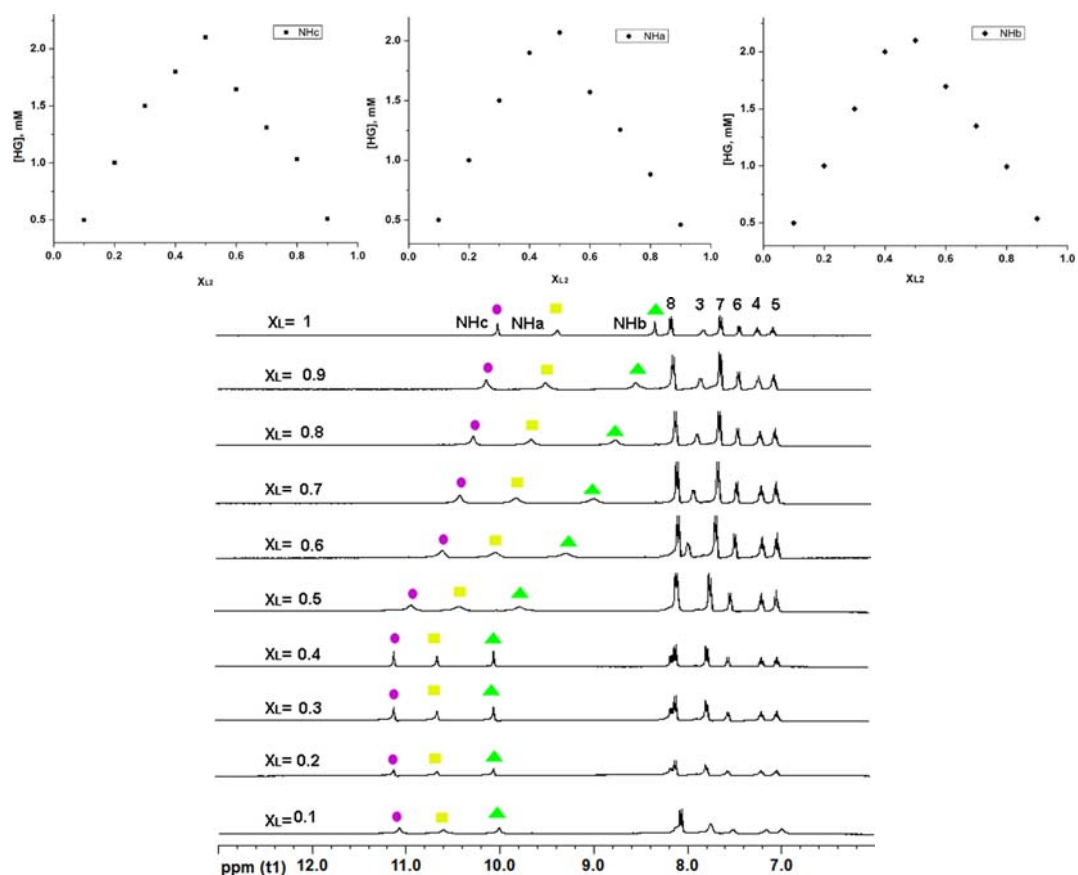
File prepared by M. J. Hynes, October 22 2000

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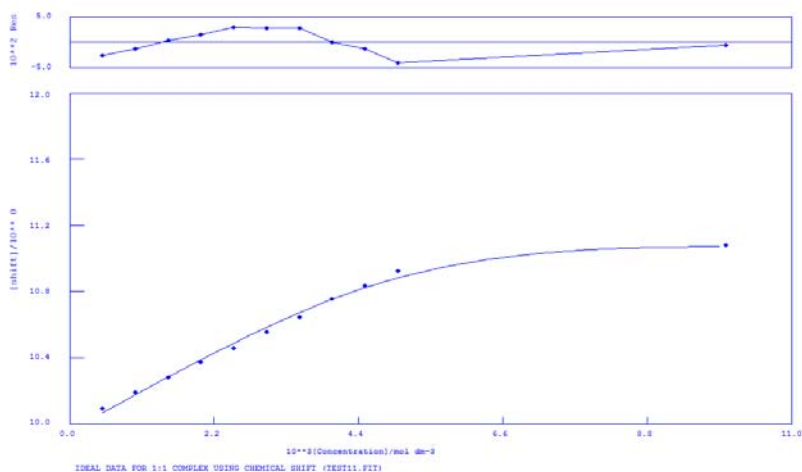
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RESIDUALS SQUARED = 1.03E-02

RFACTOR = 0.2250 PERCENT



**Fig. S5** (Top) Job plot of  $L^2$  with  $SO_4^{2-}$  (as  $TBA^+$  salt); (Bottom) The corresponding  $^1H$  NMR spectra (DMSO- $d_6$ -0.5% water, 400 MHz).



**Fig. S6**  $^1H$  NMR titration of  $L^2$  with  $SO_4^{2-}$  in DMSO- $d_6$ -0.5% water, 400 MHz.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 16:03:59 on 03/08/2013

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Reaction:  $M + L = ML$



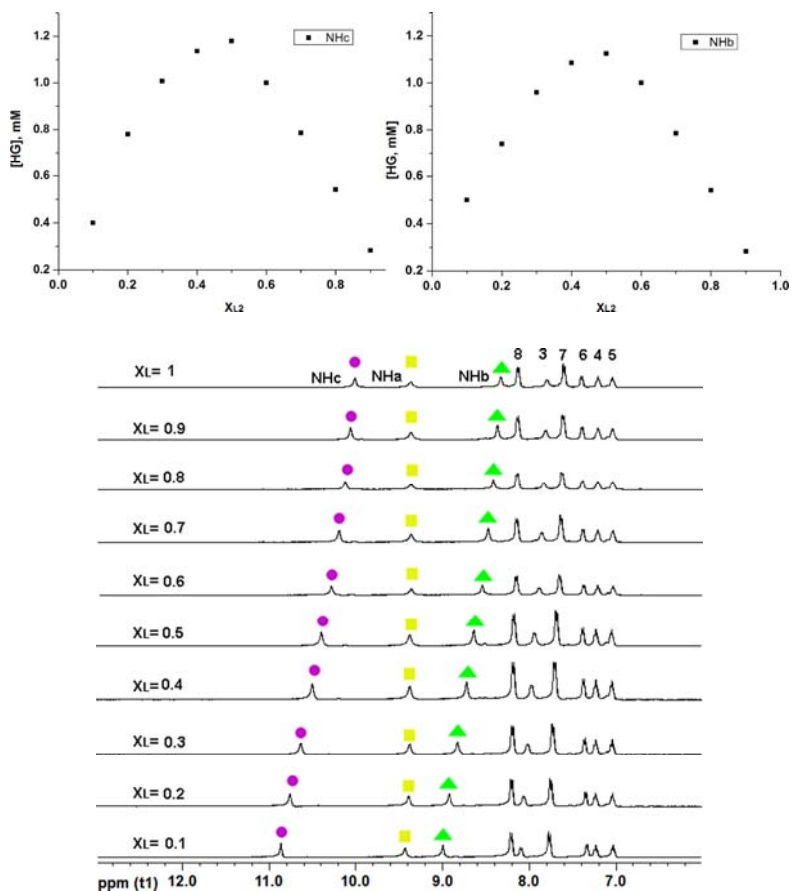
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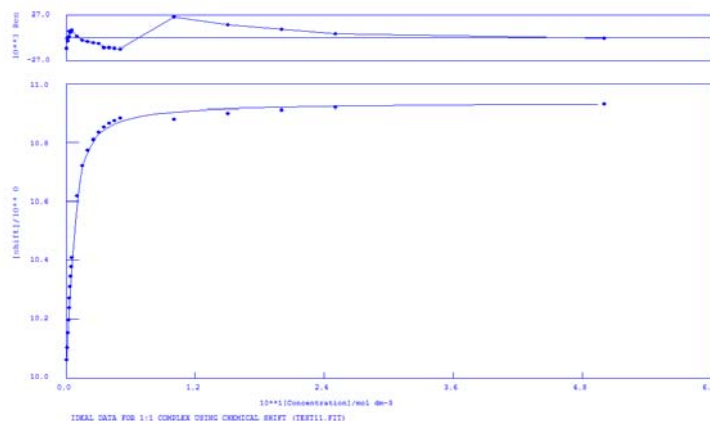
File prepared by M. J. Hynes, October 22 2000

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RESIDUALS SQUARED = 5.26E-03  
RFACITOR =        0.2069 PERCENT



**Fig. S7** (Top) Job plot of L<sup>2</sup> with Cl<sup>-</sup> (as TBA<sup>+</sup> salt); (Bottom) The corresponding <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>-0.5% water, 400 MHz).



**Fig. S8**  $^1\text{H}$  NMR titration of  $\text{L}^2$  with  $\text{Cl}^-$  in  $\text{DMSO-}d_6$ -0.5% water, 400 MHz.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes  
Program run at 17:11:23 on 05/10/2013

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

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

FILE: TEST11.FIT

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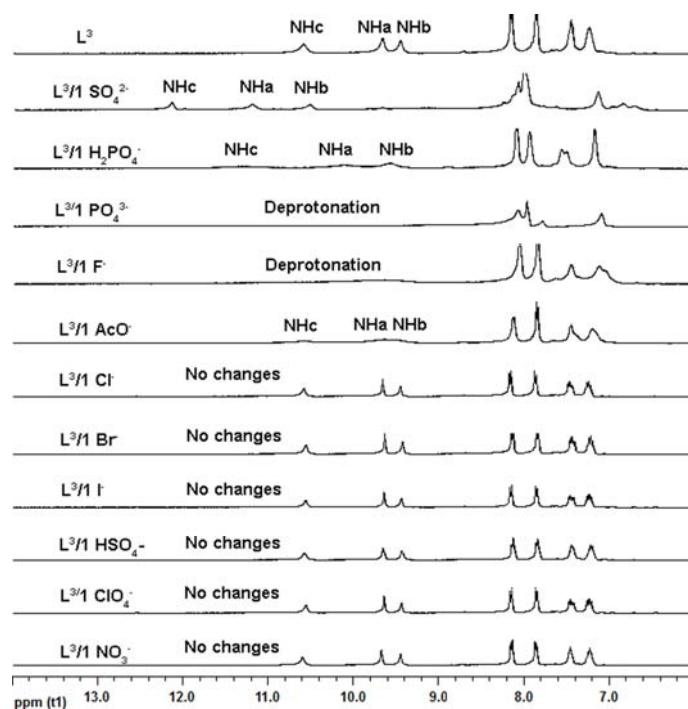
File prepared by M. J. Hynes, October 22 2000

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3	1	1.09339E+01	1.000E+00	4.324E-03	2.206E+00	SHIFT ML

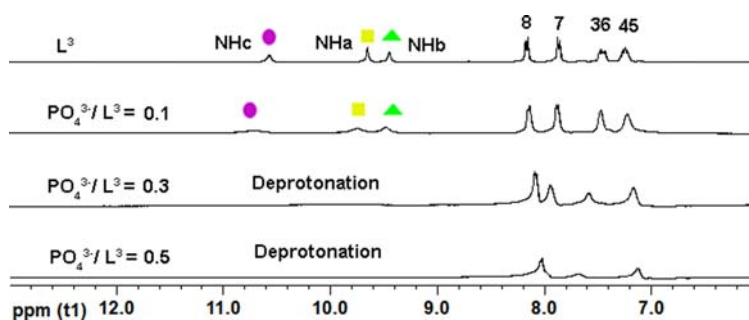
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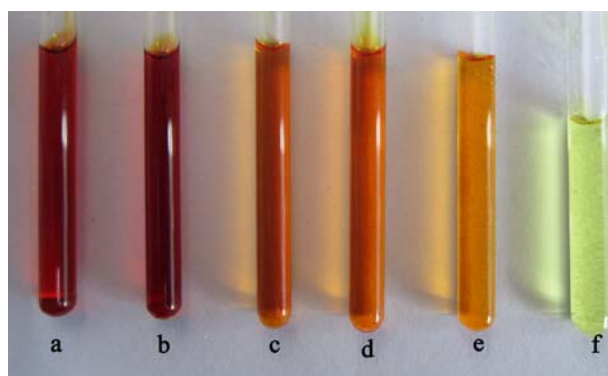
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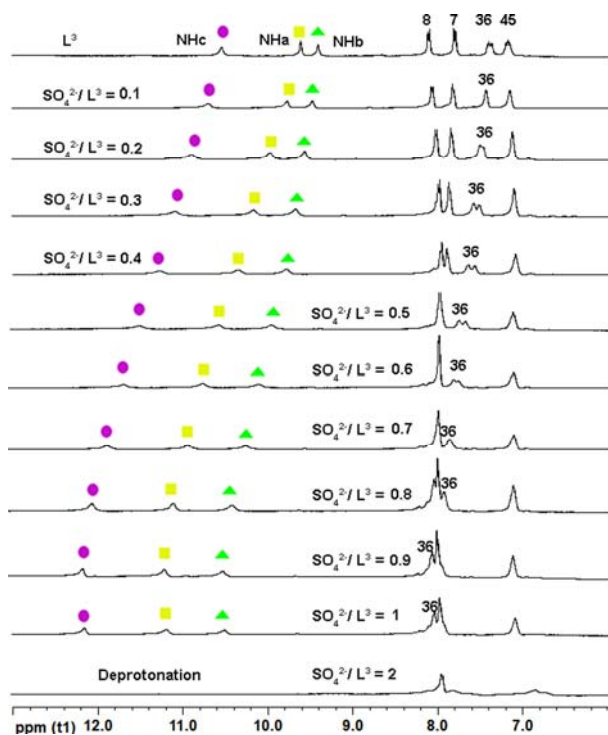
**Fig. S9**  $^1\text{H}$  NMR spectra of  $\text{L}^3$  (5 mM) in the presence of 1.0 equiv of various anions (added as  $\text{TBA}^+$  salts,  $\text{DMSO-}d_6$ -0.5% water, 400 MHz).



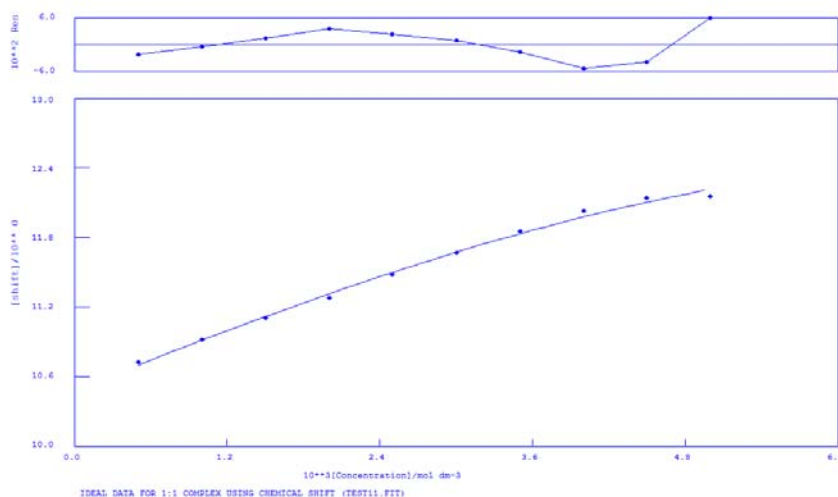
**Fig. S10**  $^1\text{H}$  NMR titration of  $\text{L}^3$  with  $\text{PO}_4^{3-}$  (as  $\text{TBA}^+$  salt;  $\text{DMSO-}d_6$ -0.5% water, 400 MHz).



**Fig. S11** Color change of  $\text{L}^3$  in the presence of 3.0 equiv of various anions added as TBA salts,  $\text{PO}_4^{3-}$  as  $\text{Na}^+$  salt: a)  $\text{SO}_4^{2-}$ , b)  $\text{F}^-$ , c)  $\text{PO}_4^{3-}$ , d)  $\text{AcO}^-$ , e)  $\text{H}_2\text{PO}_4^-$ , f) free  $\text{L}^3$ .



**Fig. S12**  $^1\text{H}$  NMR titration of  $\text{L}^3$  with  $\text{SO}_4^{2-}$  (as  $\text{TBA}^+$  salt;  $\text{DMSO-}d_6$ -0.5% water, 400 MHz).



**Fig. S13**  $^1\text{H}$  NMR titration of  $\text{L}^3$  with  $\text{SO}_4^{2-}$  in  $\text{DMSO-}d_6$ -0.5% water, 400 MHz.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes  
 Program run at 15:56:55 on 03/23/2013

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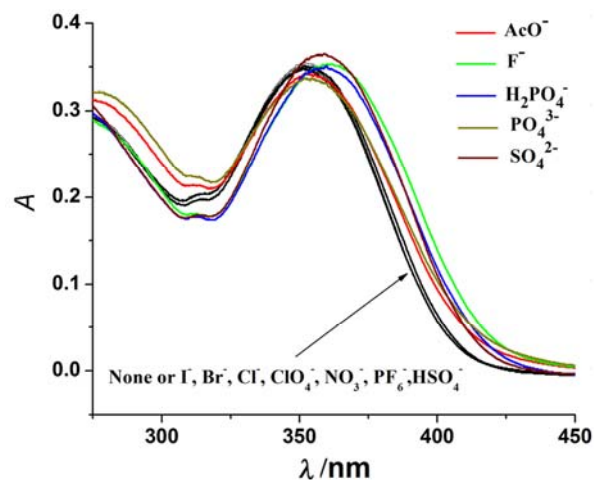
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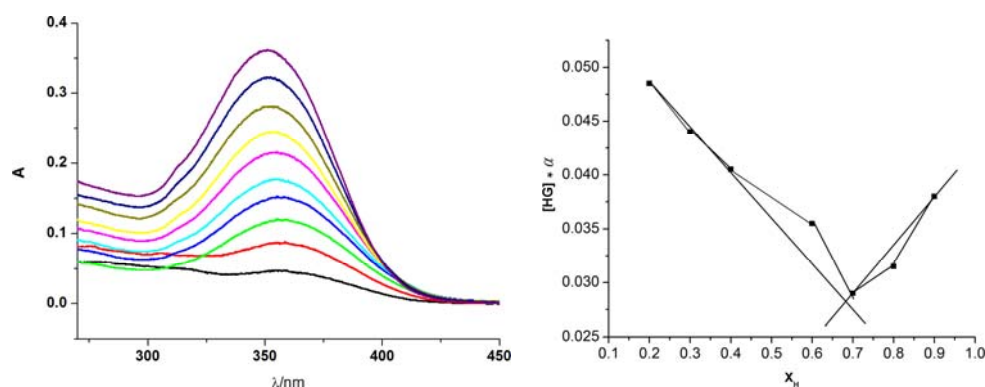
File prepared by M. J. Hynes, October 22 2000

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
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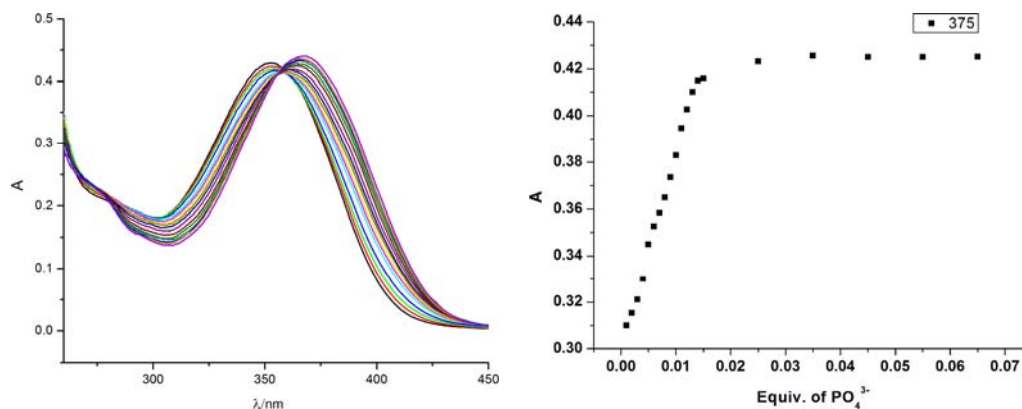
2 1 1.04835E+01 2.000E-01 2.938E-02 2.091E+00 SHIFT M  
3 1 1.29777E+01 1.000E+00 8.605E-02 1.042E+01 SHIFT ML  
0RMS ERROR = 3.92E-02 MAX ERROR = 5.83E-02 AT OBS.NO. 10  
RESIDUALS SQUARED = 1.08E-02  
RFACTOR = 0.2843 PERCENT



**Fig. S14** UV-vis spectra of  $L^2$  ( $1.0 \times 10^{-5}$  M) in DMSO-0.5% water (v/v), alone and in the presence of 1.0 equiv of various anions (added as TBA salts,  $PO_4^{3-}$  as  $Na^+$  salt).



**Fig. S15** UV-vis spectra (DMSO-5% water) and Job plot of  $L^2$  with  $PO_4^{3-}$  (as  $Na^+$  salt, 350 nm).



**Fig. S16** UV-vis titration of  $L^2$  ( $1.0 \times 10^{-5}$  M) with  $PO_4^{3-}$  (as  $Na^+$  salt) in DMSO-25% water (v/v) in the presence of 1 mM  $Et_3N$  to exclude the influence of hydrolysis.

Program DynaFit version 3.28.070 [04-21-2010]

Execution started Mon Apr 01 21:14:25 2013

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 SCRIPT FILE

.\examples\enzymology\DNA+promoter\mlp1.txt

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 TASK

Fit of complex equilibria

MODEL = fixed

DATA

file .\examples\enzymology\DNA+promoter\data\NaPO4处375nm.txt

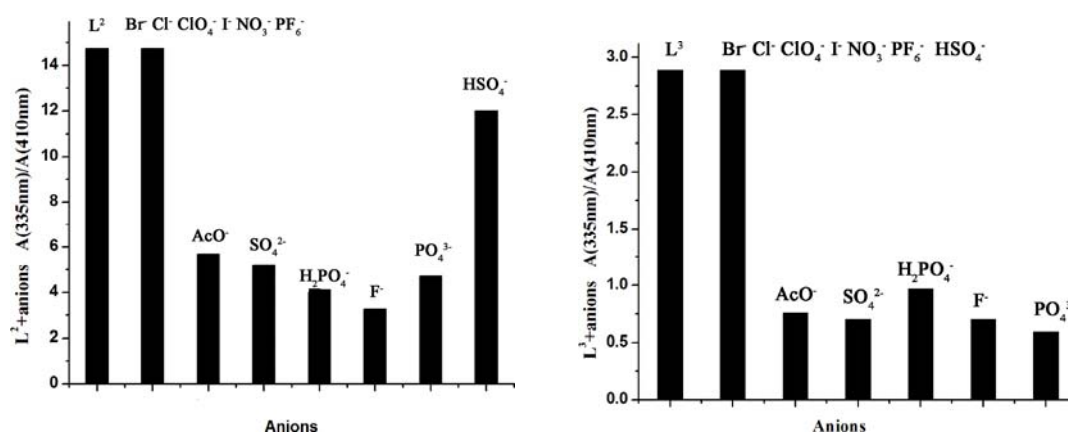
REACTION MECHANISM

P.D <=> P + D : K1 dissociation

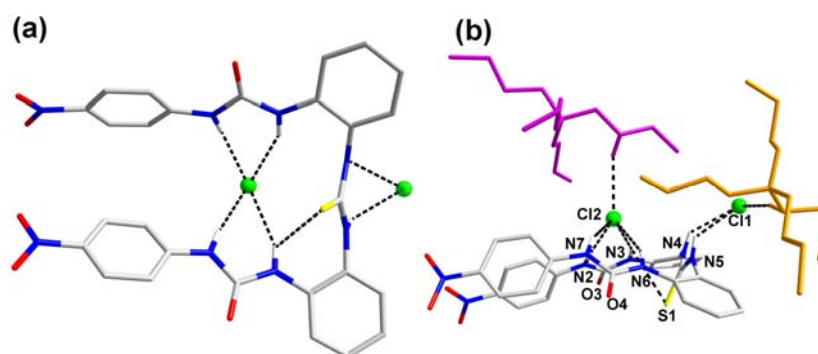
PARAMETERS & STANDARD ERRORS

Set	Parameter	Initial	Fitted	Error	%Error
	K1	0.001494	0.001494	0.0002	13
	r:P.D	43.29	43.18	0.25	0.58

$K = 1/K1 = 6.69 \times 10^2 \text{ (mM}^{-1}\text{)} = 6.69 \times 10^5 \text{ (M}^{-1}\text{)}$ ;  $\log K = 5.82$



**Fig. S17** [A(335nm)/A(410nm)] upon the addition of 1.0 equiv of various anions (as TBA<sup>+</sup> salts) into the DMSO-0.5% water solutions of L<sup>2</sup> and L<sup>3</sup> ( $1 \times 10^{-5}$  M) at room temperature.



**Fig. S18** Preliminary crystal structure of the dichloride complex (TBA)<sub>2</sub>[L<sup>2</sup>Cl<sub>2</sub>]. (a) Top view; (b) Side view.