

## Electronic Supplementary Information

### **Influence of the cavity dimension on encapsulation of halide within the capsular assembly and side-cleft recognition of sulphate-water cluster assisted by polyammonium tripodal receptor**

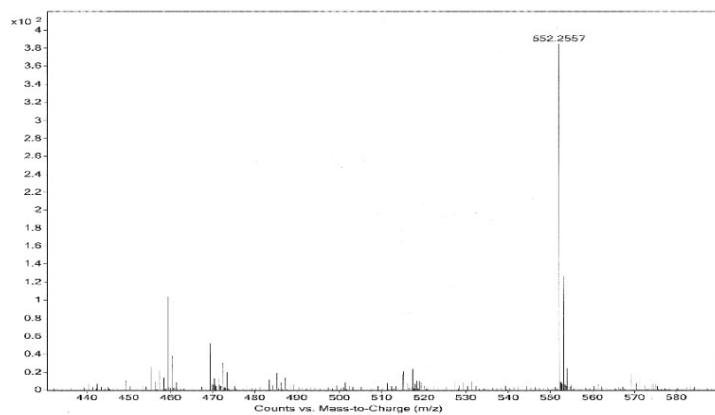
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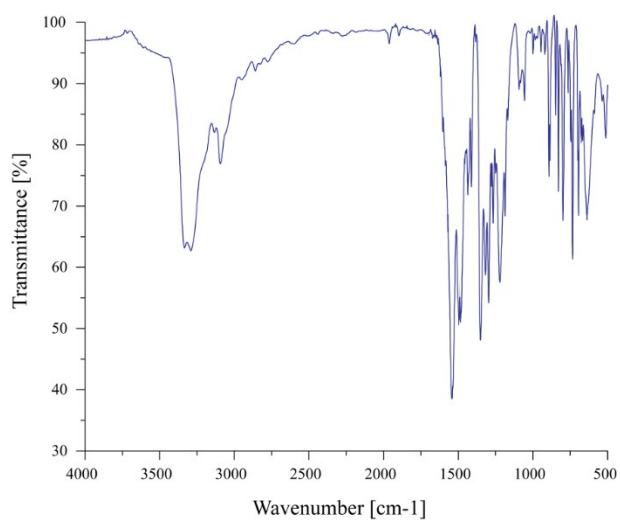
*Fax: +91-361-258-2349; Tel: +91-361-258-2313*

*E-mail: [gdas@iitg.ernet.in](mailto:gdas@iitg.ernet.in)*

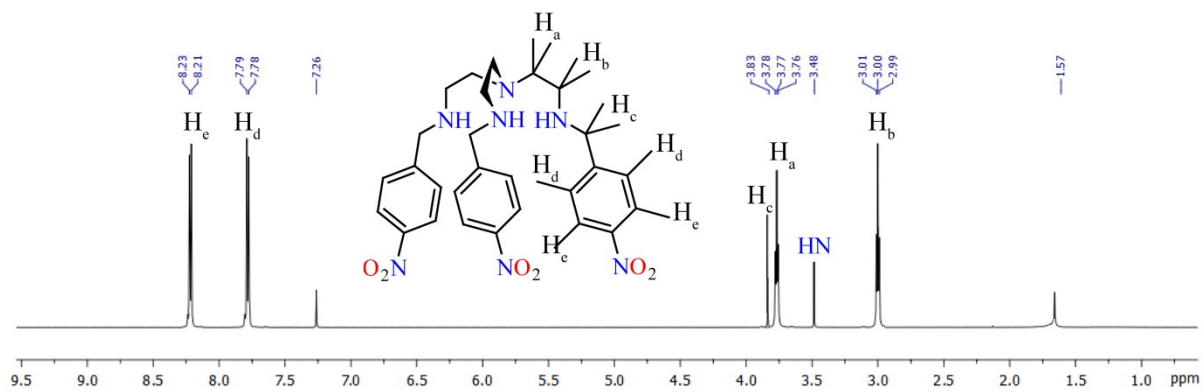
## Characterization of receptor L<sub>1</sub>:



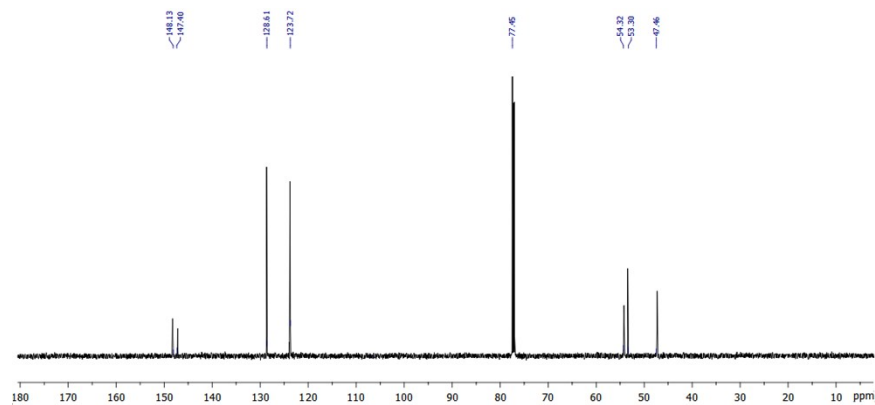
**Fig. S1.** ESI-mass spectrum of receptor L<sub>1</sub>



**Fig. S2.** FTIR spectrum of receptor L<sub>1</sub>

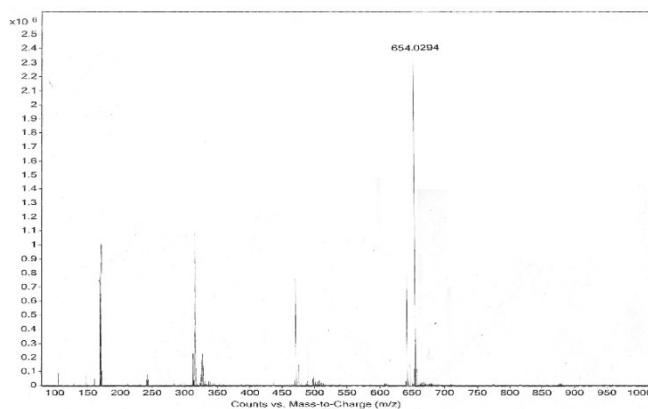


**Fig. S3.** <sup>1</sup>H NMR spectrum of receptor **L**<sub>1</sub> in CDCl<sub>3</sub> at 298 K

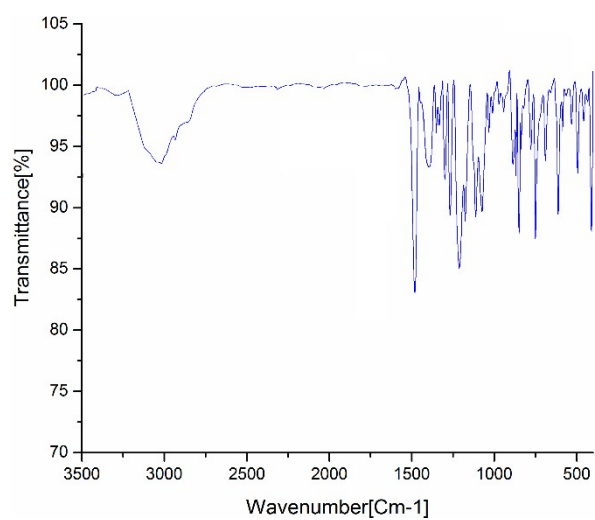


**Fig. S4.** <sup>13</sup>C NMR spectrum of receptor **L**<sub>1</sub> in CDCl<sub>3</sub> at 298 K

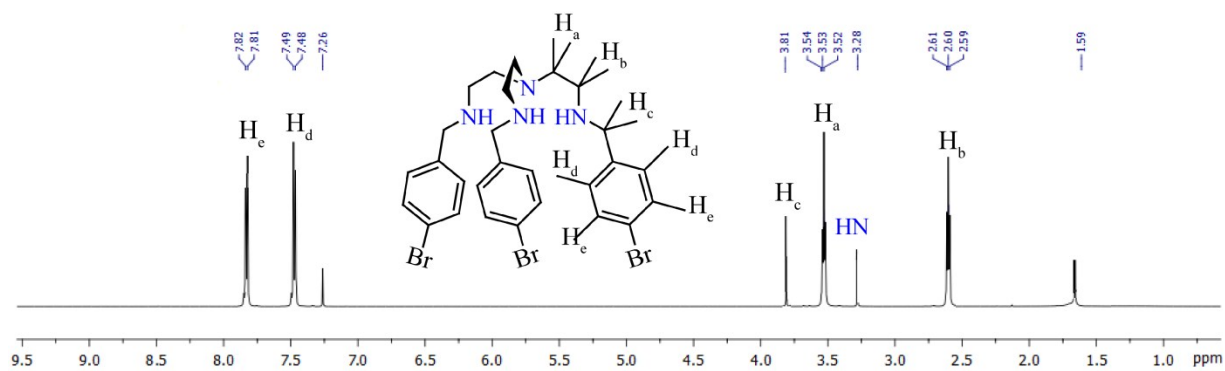
## Characterization of receptor $L_2$ :



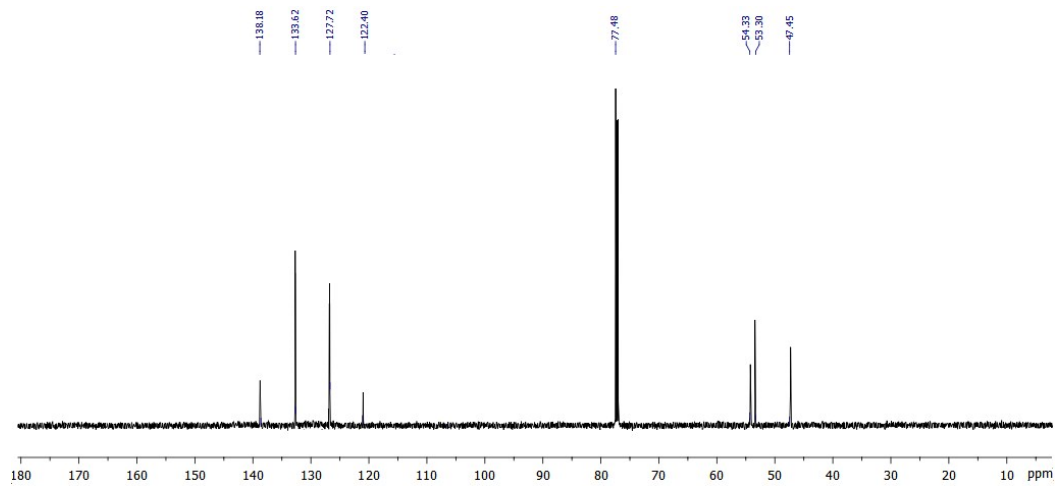
**Fig. S5.** ESI-mass spectrum of receptor  $L_2$



**Fig. S6.** FTIR spectrum of receptor  $L_2$

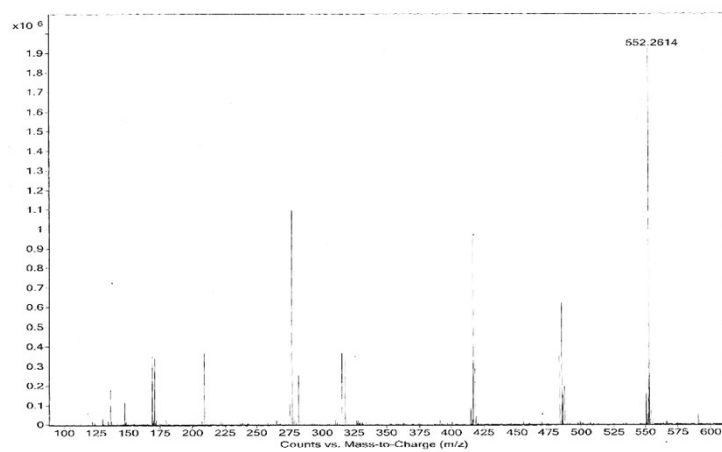


**Fig. S7.** <sup>1</sup>H NMR spectrum of receptor **L**<sub>2</sub> in CDCl<sub>3</sub> at 298 K

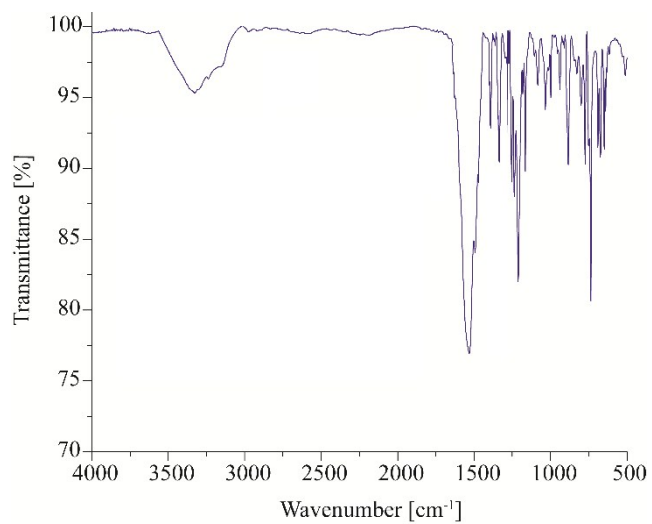


**Fig. S8.** <sup>13</sup>C NMR spectrum of receptor **L**<sub>2</sub> in CDCl<sub>3</sub> at 298 K

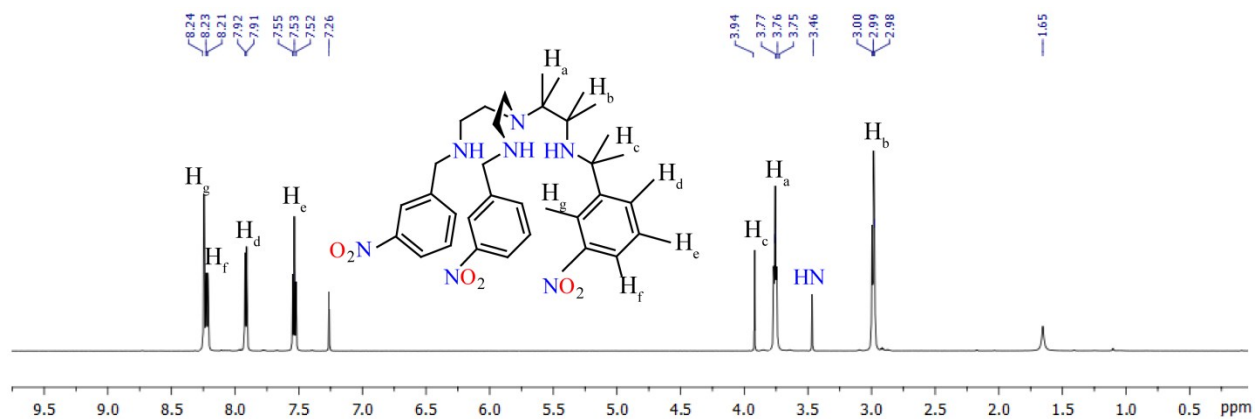
### Characterization of receptor $L_3$ :



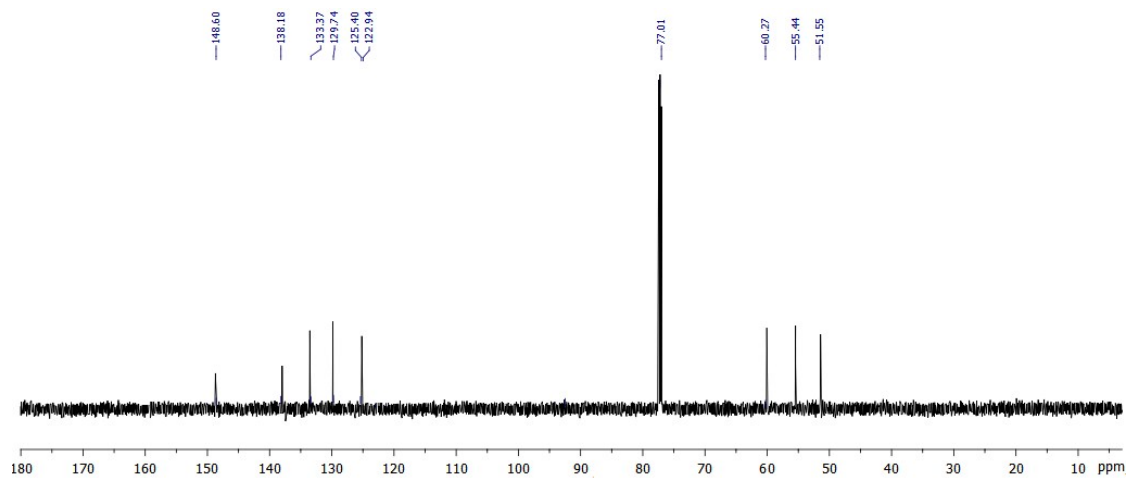
**Fig. S9.** ESI-mass spectrum of receptor  $L_3$



**Fig. S10.** FTIR spectrum of receptor  $L_3$

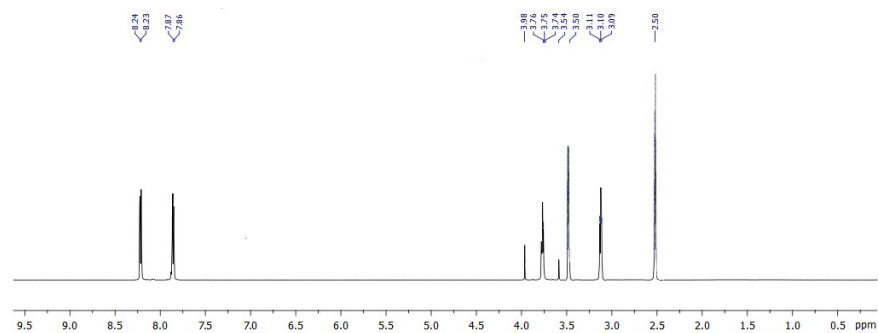


**Fig. S11.** <sup>1</sup>H NMR spectrum of receptor **L**<sub>3</sub> in CDCl<sub>3</sub> at 298 K

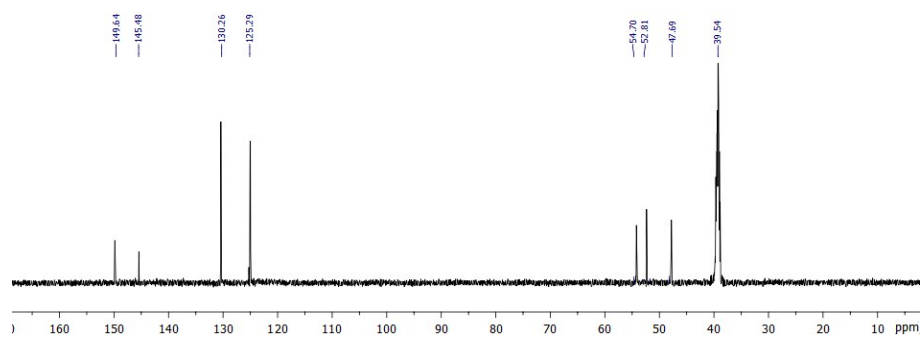


**Fig. S12.** <sup>13</sup>C NMR spectrum of receptor **L**<sub>3</sub> in CDCl<sub>3</sub> at 298 K

### Characterization of complex **1a**:

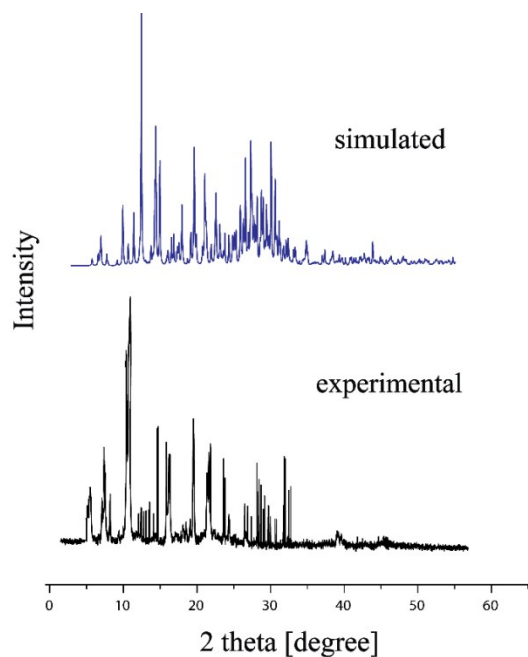


**Fig. S13.** <sup>1</sup>H NMR spectrum of complex **1a** in DMSO-d<sub>6</sub> at 298 K



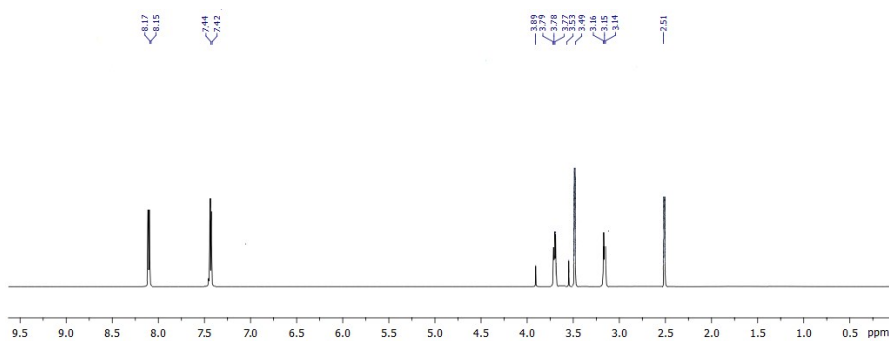
**Fig. S14.** <sup>13</sup>C NMR spectrum of complex **1a** in DMSO-d<sub>6</sub> at 298 K



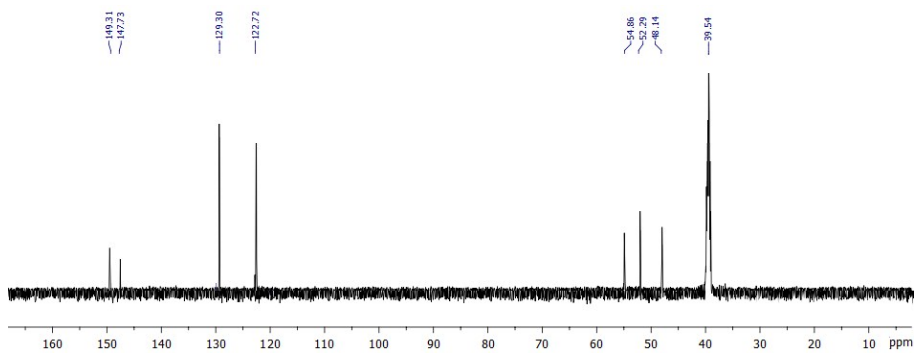


**Figure S15.** Powder X-ray diffraction: simulated pattern from the single-crystal X-ray of complex **1a** (blue), experimental pattern from the crystalline solid of complex **1a** (black).

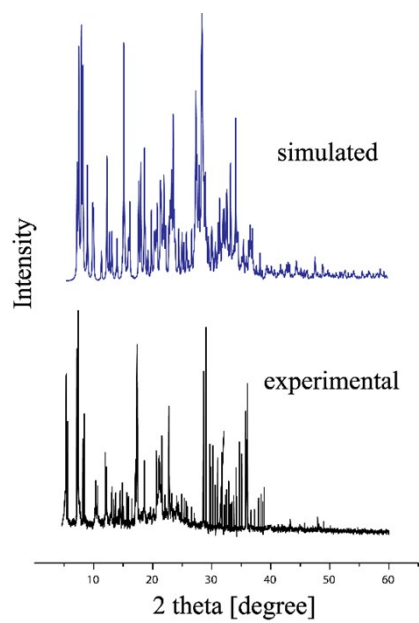
### Characterization of complex **1b**:



**Fig. S16.**  $^1\text{H}$  NMR spectrum of complex **1b** in  $\text{DMSO-d}_6$  at 298 K

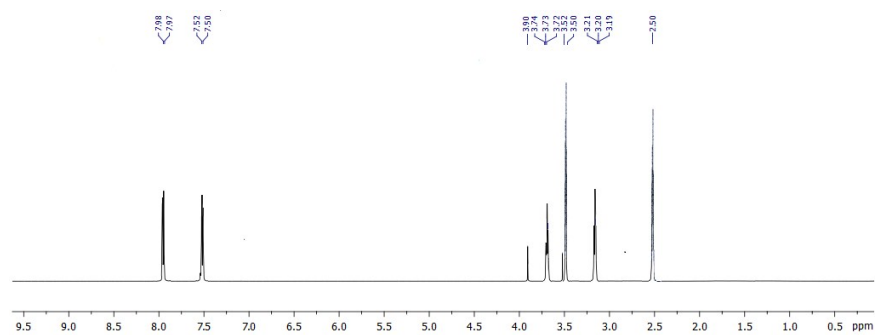


**Fig. S17.**  $^{13}\text{C}$  NMR spectrum of complex **1b** in  $\text{DMSO-d}_6$  at 298 K.

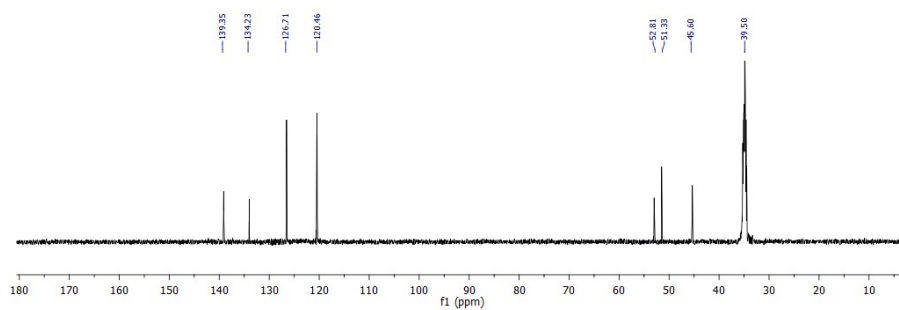


**Figure S18:** Powder X-ray diffraction: simulated pattern from the single-crystal X-ray of complex **1b** (blue), experimental pattern from the crystalline solid of complex **1b** (black).

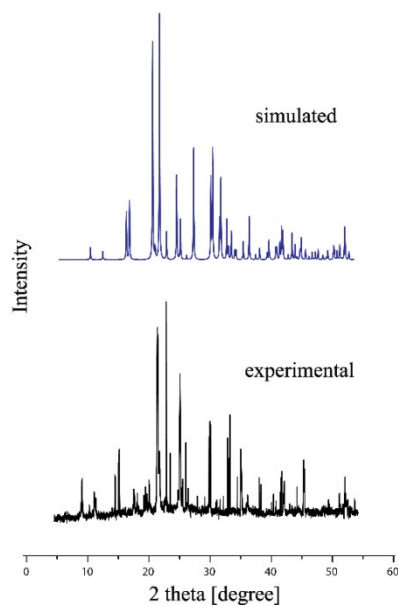
## Characterization of complex **2a**:



**Fig. S19.** <sup>1</sup>H NMR spectrum of complex **2a** in DMSO-d<sub>6</sub> at 298 K

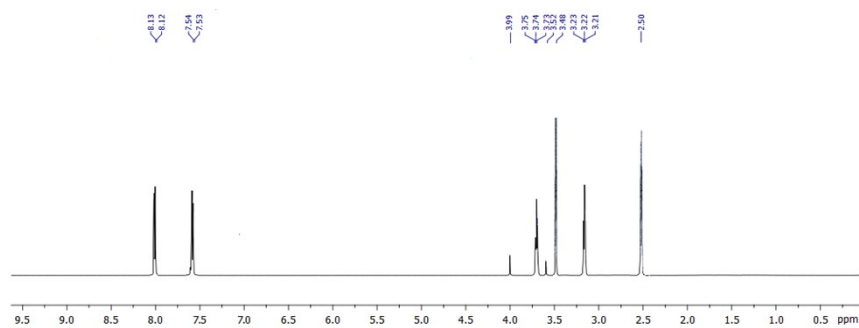


**Fig. S20.** <sup>13</sup>C NMR spectrum of complex **2a** in DMSO-d<sub>6</sub> at 298 K

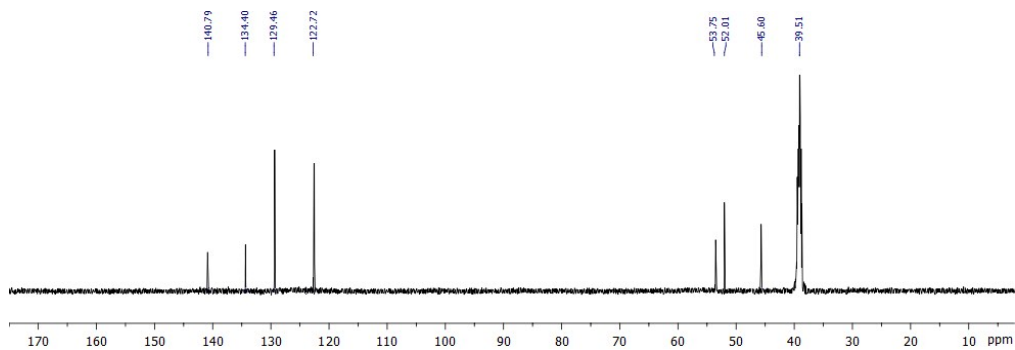


**Figure S21:** Powder X-ray diffraction: simulated pattern from the single-crystal X-ray of complex **2a** (blue), experimental pattern from the crystalline solid of complex **2a** (black).

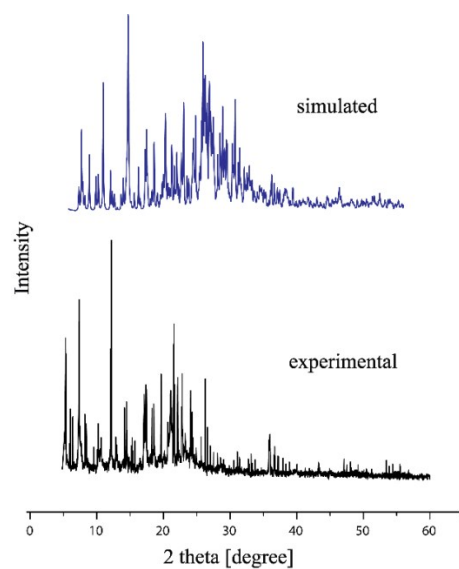
### Characterization of complex **2b**:



**Fig. S22.**  $^1\text{H}$  NMR spectrum of complex **2b** in  $\text{DMSO-d}_6$  at 298 K

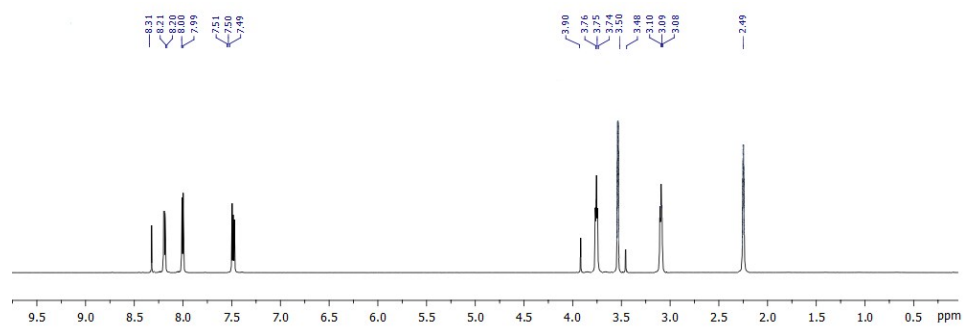


**Fig. S23:**  $^{13}\text{C}$  NMR spectrum of complex **2b** in  $\text{DMSO-d}_6$  at 298 K

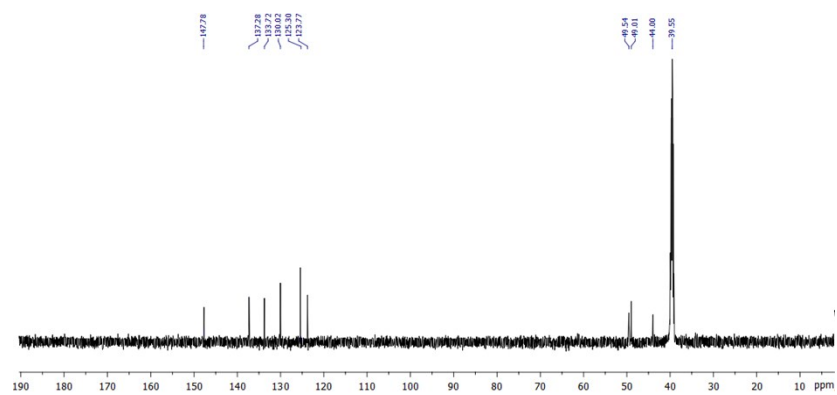


**Figure S24:** Powder X-ray diffraction: simulated pattern from the single crystal X-ray of complex **2b** (blue), experimental pattern from the crystalline solid of complex **2b** (black).

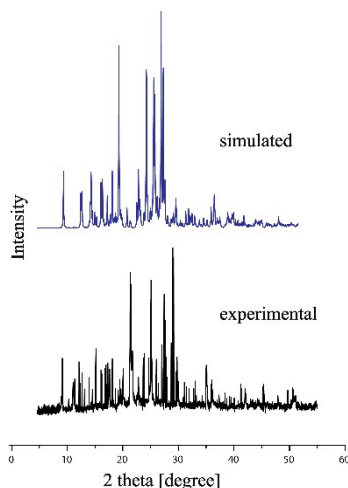
## Characterization of complex **3a**:



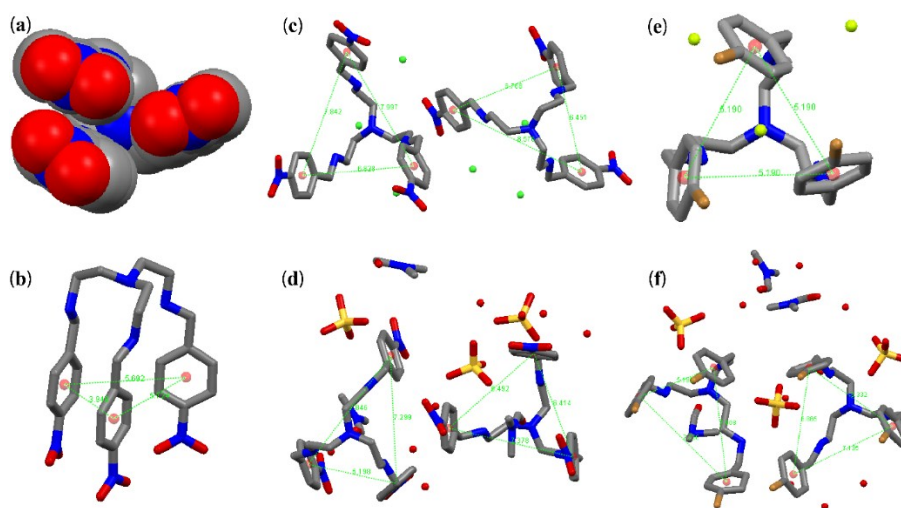
**Fig. S25:** <sup>1</sup>H NMR spectrum of complex **3a** in DMSO-d<sub>6</sub> at 298 K.



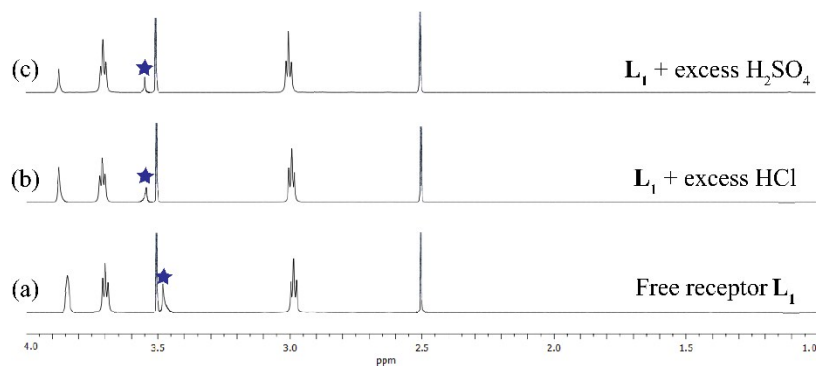
**Fig. S26:** <sup>13</sup>C NMR spectrum of complex **3a** in DMSO-d<sub>6</sub> at 298 K.



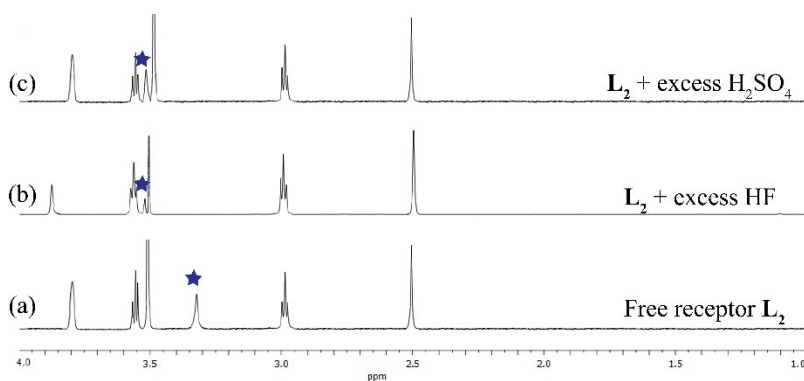
**Figure S27:** Powder X-ray diffraction: simulated pattern from the single-crystal X-ray of complex **3a** (blue), experimental pattern from the crystalline solid of complex **3a** (black).



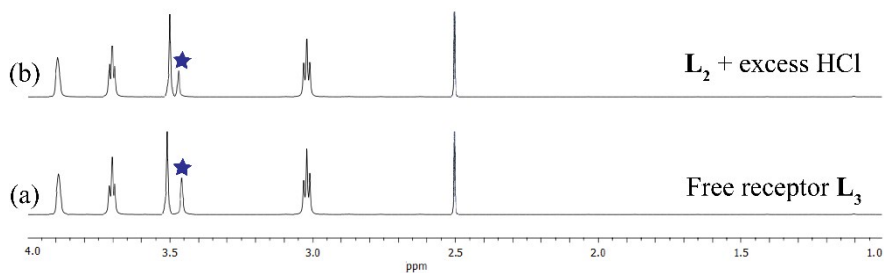
**Fig. S28:** (a) space-fill view of  $L_1$  receptor from crystallographic b axis showing there is almost no space or no cavity, (b) depicting distances among each  $L_1$  receptor arms, (c) depicting distances among each three arms of two  $L_1$  receptor units in salt **1a**, (d) depicting distances among each three arms of two  $L_1$  receptor units in salt **1b**, (e) depicting distances among each three arms of two  $L_2$  receptor units in salt **2a** and (f) depicting distances among each three arms of two  $L_2$  receptor units in salt **2b**.



**Fig. S29:** Partial <sup>1</sup>H NMR spectra (600 MHz, DMSO d<sub>6</sub>) of (a) free receptor L<sub>1</sub>, (b) addition of excess HCl to L<sub>1</sub> and (c) addition of excess H<sub>2</sub>SO<sub>4</sub> to L<sub>1</sub>.



**Fig. S30:** Partial <sup>1</sup>H NMR spectra (600 MHz, DMSO d<sub>6</sub>) of (a) free receptor L<sub>2</sub>, (b) addition of excess HCl to L<sub>2</sub> and (c) addition of excess H<sub>2</sub>SO<sub>4</sub> to L<sub>2</sub>.



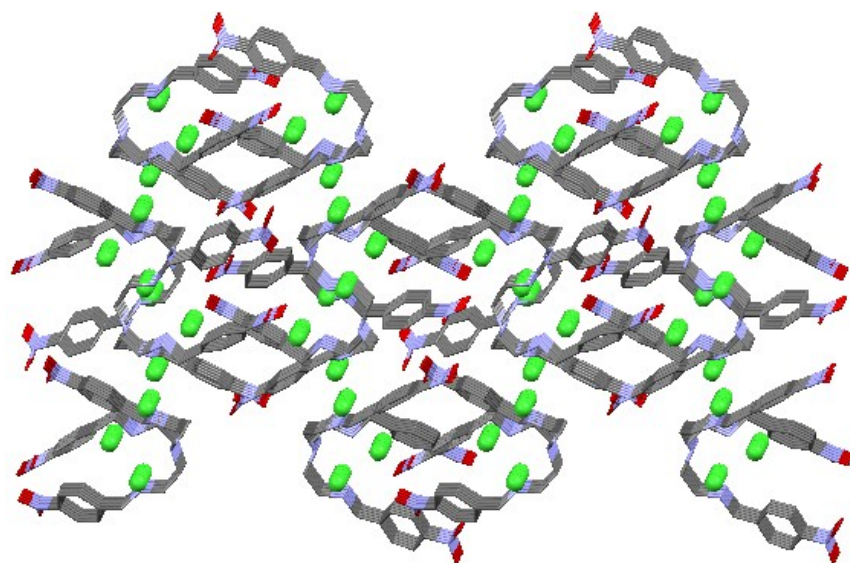
**Fig. S31:** Partial <sup>1</sup>H NMR spectra (600 MHz, DMSO d<sub>6</sub>) of (a) free receptor L<sub>3</sub> and (b) addition of excess HCl to L<sub>3</sub>.



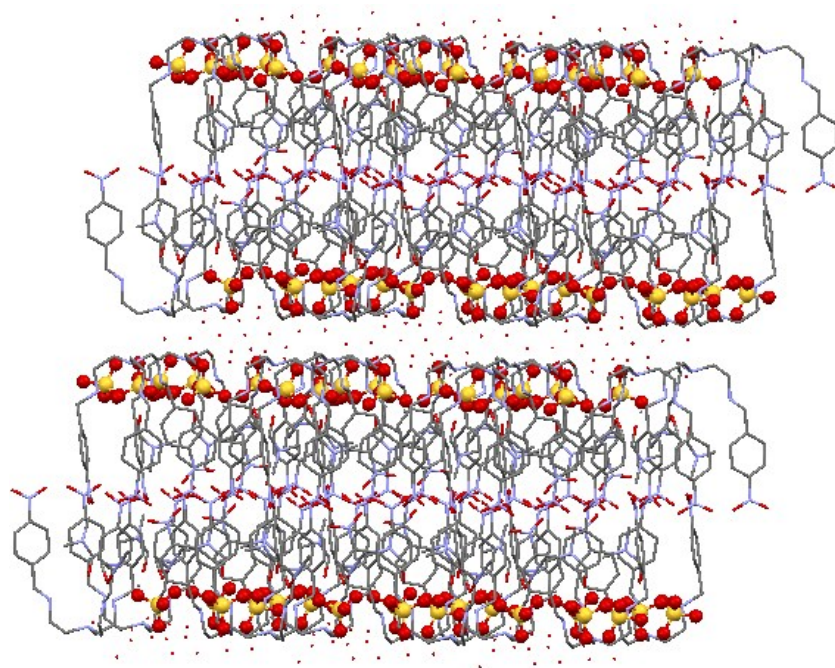
**Table S1.** Hydrogen bonding contacts in complexes **1a-b**, **2a-b** and **3a**

Complex	D-H...A	$d(\text{D}\cdots\text{H})/\text{\AA}$	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\angle\text{D-H}\cdots\text{A}/^\circ$	Symmetry codes
<b>1a</b>	N2-H2C...Cl6	0.90	2.22	3.092(5)	164	x,y,z
	N2-H2D...Cl3	0.90	2.28	3.155(4)	163	x,y,z
	N4-H4C...Cl3	0.90	2.21	3.077(5)	162	x,y,z
	N4-H4D...Cl2	0.90	2.21	3.098(5)	170	-x, y-1/2, -z+3/2
	N6-H6C...Cl3	0.90	2.31	3.177(4)	163	x,y,z
	N6-H6D...Cl2	0.90	2.28	3.140(5)	161	-x+1/2, -y+1, z-1/2
	N9-H9C...Cl1	0.90	2.35	3.237(4)	167	x,y,z
	N9-H9D...Cl5	0.90	2.18	3.073(5)	171	x,y,z
	N11-H11C...Cl1	0.90	2.31	3.184(5)	164	x,y,z
	N11-H11D...Cl4	0.90	2.25	3.094(5)	157	-1/2+x, 1/2-y, -z
	N13-H13C...Cl1	0.90	2.25	3.129(5)	167	x,y,z
	N13-H13D...Cl4	0.90	2.21	3.085(5)	162	-1+x,y,z
	C2-H2B...O2B	0.97	2.56	3.406(11)	146	1-x, 1/2+y, 3/2-z
	C15-H15...O12	0.93	2.48	3.391(10)	168	-1/2-x, -y, 1/2+z
	C35-H35...O1A	0.93	2.51	3.385(10)	157	3/2-x, -y, -1/2+z
	C35-H35...O1B	0.93	2.39	3.296(11)	165	3/2-x, -y, -1/2+z
	C37-H37B...O4B	0.97	2.52	3.382(17)	148	-x, 1/2+y, 1/2-z
	C50-H50...O4A	0.93	2.50	3.411(9)	167	-1/2+x, 1/2-y, -z
<b>1b</b>	N2-H2N...O13	0.86	2.14	2.951(9)	158	x,y,z
	N4-H4N...O13	0.86	2.30	3.063(8)	148	x,y,z
	N9-H9N...O14	0.86	2.21	2.919(9)	140	x,y,z
	N11-H11N...O14	0.86	2.30	3.108(9)	156	x,y,z
	N13-H13N...O14	0.86	2.37	3.134(8)	148	x,y,z
	C11-H11B...O21	0.97	2.59	3.529(14)	163	x,y,z
	C19-H19B...O23	0.97	2.55	3.497(10)	164	-x, 1-y, 1-z
	C23-H23...O18	0.93	2.45	3.283(12)	149	-1+x,y,z
	C28-H28B...O23	0.97	2.53	3.469(9)	163	1-x, -y, 1-z
	C44-H44...O2A	0.93	2.46	3.300(2)	151	1-x, 1-y, 1-z
	C47-H47A...O28	0.97	2.59	3.415(14)	143	x,y,z
	C54-H54...O16	0.93	2.54	3.368(13)	148	x,y,z
	C55-H55C...O24	0.96	2.44	3.295(11)	148	-x, 1-y, 1-z
	C59-H59B...O20	0.96	2.54	3.414(13)	151	x,y,z
<b>2a</b>	N2-H2C...F1	0.90	1.72	2.614(6)	173	2/3+x, 1/3+y, -2/3+z
	N2-H2D...F2	0.90	1.76	2.663(10)	178	1-x+y, 1-x,z
	C1-H1B...F3	0.97	2.47	3.346(12)	150	2/3-y, 1/3+x-y, 1/3+z
	C3-H3A...F3	0.97	2.49	3.443(9)	167	x,y,z

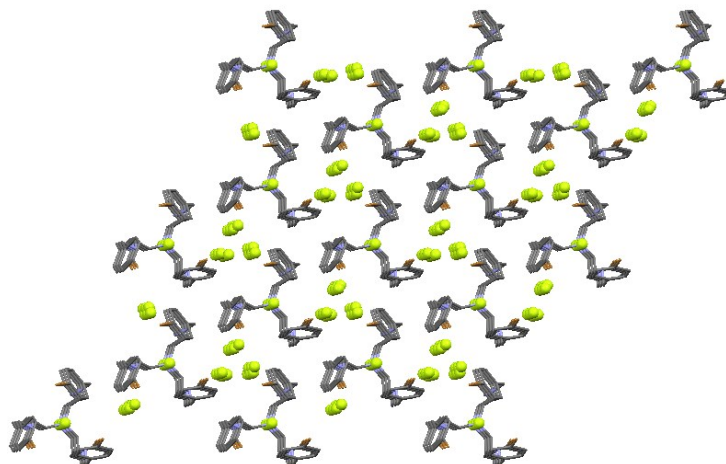
<b>2b</b>	N2-H2A...O4A	0.97	1.77	2.738(18)	173	x,1+y,z
	N2-H2A...O4B	0.97	1.78	2.715(13)	162	x,1+y,z
	N3-H3B...O12	0.97	1.75	2.710(10)	168	x,y,z
	N6-H6A...O3	0.90	1.86	2.758(9)	173	x+1, y, z
	N6-H6B...O5	0.90	2.09	2.871(8)	145	x,y,z
	N7-H7A...O3	0.97	2.18	2.932(9)	134	x+1,y,z
	N7-H7B...O9	0.97	1.85	2.806(9)	167	x+1,y,z
	N8-H8C...O9	0.97	2.07	2.910(9)	144	x+1,y,z
	N8-H8D...O5	0.97	1.88	2.841(9)	172	x,y,z
	C2-H2D...O11A	0.97	2.54	3.490(2)	166	x,y,z
	C5-H5...O12	0.93	2.42	3.258(11)	150	x,y,z
	C11-H11B...O7B	0.97	2.58	3.550(2)	177	x,y,z
	C20-H20B...O1	0.97	2.57	3.535(15)	175	x,1+y,z
	C21A-H21C...O14	0.86	2.55	3.260(4)	141	x,1+y,z
	C45-H45...O3	0.93	2.51	3.317(16)	146	-x,1-y,1-z
	C47-H47A...O11A	0.97	2.44	3.320(2)	151	x+1,y,z
	C50-H50...O5	0.93	2.50	3.379(16)	158	1-x,1-y,1-z
	C56-H56C...O9	0.96	2.37	3.316(15)	170	-x,1-y,1-z
	<b>3a</b>	N2-H2C...Cl2	0.90	2.24	3.075(10)	153
N2-H2D...Cl1		0.90	2.28	3.152(10)	164	1+x,1+y,z
N4-H4C...Cl2		0.90	2.40	3.285(12)	167	x,y,z
N4-H4D...Cl6		0.90	2.21	3.078(11)	163	x,y,z
N6-H6C...Cl5		0.90	2.25	3.137(11)	166	1+x,1+y,z
N6-H6D...Cl3		0.90	2.25	3.110(11)	159	x,y,z
N9-H9C...Cl6		0.90	2.27	3.143(11)	163	x,y,z
N9-H9D...Cl1		0.90	2.21	3.078(10)	162	x,y,z
N11-H11C...Cl4		0.90	2.42	3.312(12)	172	x,y,z
N11-H11D...Cl5		0.90	2.18	3.051(11)	162	x,-1+y,z
N13-H13C...Cl3		0.90	2.28	3.160(10)	167	x,y,z
N13-H13D...Cl4		0.90	2.24	3.080(10)	156	x,y,z
C21-H21B...O5A		0.97	2.57	3.462(2)	154	-1+x,y,z
C23-H23...O5A		0.93	2.23	3.120(2)	160	-1+x,y,z
C23-H23...O5B		0.93	2.50	3.190(2)	160	-1+x,y,z
C23-H23...O6		0.93	2.57	3.375(18)	145	-1+x,y,z
C30-H30B...O7A		0.97	2.54	3.450(2)	157	-1+x,y,z
C32-H32...O7A		0.93	2.39	3.260(2)	155	-1+x,y,z
C32-H32...O7B		0.93	2.38	3.270(2)	159	-1+x,y,z
C32-H32...O8		0.93	2.51	3.339(18)	148	-1+x,y,z



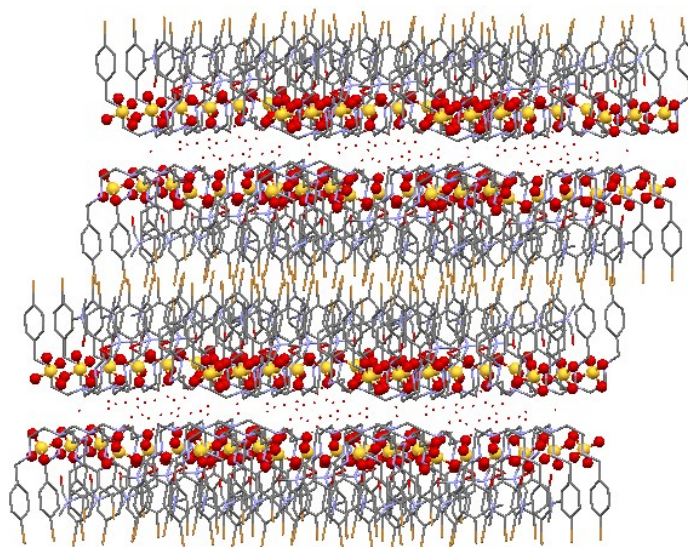
**Figure S32:** Packing motif of crystal structure of complex **1a** (as viewed down the *a*-axis) showing capsular assembly formation.



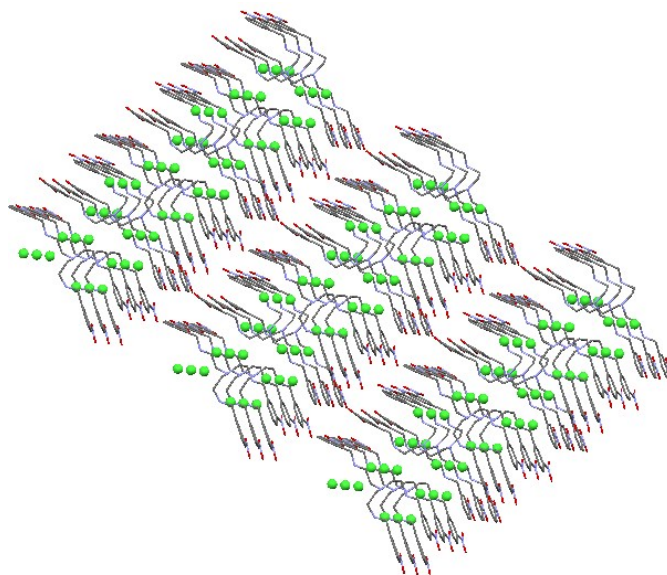
**Figure S33:** Packing motif of crystal structure of complex **1b** (as viewed down the *a*-axis) showing side-cleft binding of sulphate ions around DMF encapsulated receptor **L<sub>1</sub>**.



**Figure S34:** Packing motif of crystal structure of complex **2a** (as viewed down the *c*-axis) showing encapsulation of fluoride ion (F1) supported by H-bonding interactions with exterior fluorides (F2 and F3)



**Figure S35:** Packing motif of crystal structure of complex **2b** (as viewed down the *c*-axis) showing side-cleft binding of sulphate ions around DMF encapsulated receptor **L<sub>2</sub>**.



**Figure S36:** Packing motif of crystal structure of complex **3a** (as viewed down the *c*-axis) showing linear architecture of chloride via Y-shaped layer like assembly of receptor **L<sub>3</sub>**.