

## **Supporting Information**

# **Rugby Ball Shaped Sulfate–Water–Sulfate Adduct Encapsulated in a Neutral Molecular Receptor Capsule**

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## 1. Experimental procedure

**Materials and Methods:** The chemicals such as *tris*(2-aminoethyl)amine, 1-isocyanato-4-nitro-benzene and all tetrabutylammonium salts were received from Aldrich and used as such. All other chemicals were available locally and used without any further purification. Solvent such as THF and acetonitrile were dried following standard procedure prior to experiment. Microanalysis(C, H, N) was performed using a Perkin-Elmer 4100 elemental analyzer. FT—IR spectra were recorded in KBr pellets using Perkin Elmer Spectra GX 2000 spectrometer. <sup>1</sup>H NMR spectra were recorded on Bruker 200 MHz FT NMR (model: Avance-DPX 200) using DMSO-d<sub>6</sub> as the solvent and tetramethylsilane (TMS) as an internal standard. Electronic spectra were recorded with Shimadzu UV-3101 PC spectrophotometer.

### Synthesis of compound 1:

Tris(2-aminoethyl)amine (1.00 g, 6.84 mmol) was dissolved in distilled THF (100 mL) in a 250 mL RB Flask. A solution of *p*-nitrophenylisocyanate (3.39 g, 20.52 mmol) in THF was added to the above solution. Then the resulting mixture was stirred at 5°C for 5 hr. The precipitate thus obtained formed was filtered and washed with THF and methanol and dried over a vacuum pump. (3.8g) Yield: (86.5%) LC-MS: *m/z* 639.5 [<sup>1</sup>H<sup>+</sup>]; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>, TMS) δ 9.37 (s, 3H, -NH), 8.14-8.10 (d, 6H, ArH), 7.64-7.60 (d, 6H, ArH), 6.47 (s, 3H, -NH), 3.29-3.26 (t, 6H, NHCH<sub>2</sub>), 2.71-2.56 (t, 6H, NCH<sub>2</sub>). FT-IR(cm<sup>-1</sup>) 3336(s), 3093(m), 1689(m), 1659(s), 1575(br), 1502(s), 1420(m), 1344(br), 1302(vs), 1235(s), 1177(vs), 1113(vs), 844(m), 751(m), 689(m), 665(m), 535(br)., Analytical data for C<sub>27</sub>H<sub>30</sub>N<sub>10</sub>O<sub>9</sub>: Calc. C, 50.78; H, 4.74; N, 21.93. Found C, 50.45; H, 4.61; N, 21.69 X-ray quality single crystals of **1** was obtained by the slow evaporation

of acetonitrile solution of **1**. Crystals of **1.DMF** was obtained by the slow evaporation of DMF/CH<sub>3</sub>CN mixture [70:30(v/ v)] of **1**, over a period of one week.

### **Synthesis of compound 2:**

A solution of tetrabutylammonium sulfate (50 wt% solution in water) was added to a solution of **1** in CH<sub>3</sub>CN in a 25mL beaker. X-ray quality single crystals of **2** were obtained by the slow evaporation of this solution over a period of one week. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>, TMS) δ 10.972 (s, 3H, -NH), 8.59(s, 3H, -NH), 7.99-7.95 (d, 6H, ArH), 7.84-7.79 (d, 6H, ArH), 3.20-3.16 (t, 6H, NHCH<sub>2</sub>), 2.51-2.40 (t, 6H, NCH<sub>2</sub>), 1.56-1.50(t, 16H, -CH<sub>2</sub> ), 1.35-1.28(m, 16H, -CH<sub>2</sub>), 0.95-0.88(t, 24H, CH<sub>3</sub>). FT-IR (cm<sup>-1</sup>) 3455(br), 3265(m), 3065(s), 2963(s), 2875(m), 2822(m), 1698(s), 1599(s), 1555(s), 1495(br), 1381(s),1325(br), 1236(s), 1174(m), 1108(br), 859(vs), 752(vs), 619(vs). Analytical data for C<sub>118</sub>H<sub>222</sub>N<sub>24</sub>O<sub>35</sub>S<sub>2</sub>: Calc. C, 53.79; H, 8.64; N, 12.75. Found. C, 54.48; H, 8.60; N, 12.92.

## **2.Single crystal X-ray Diffraction**

Diffraction data were collected using MoK $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation on a SMART APEX diffractometer equipped with charge-coupled device (CCD) area detector. Crystals were isolated from mother liquor and immediately immersed in paratone oil and then mounted. Data collection, data reduction, structure solution/refinement and empirical absorption correction (SADABS) were carried out using the programs provided with the software package of SMART APEX. (Bruker AXS: Madison, WI, **1999**) Graphics were generated using Mercury 1.4.1 (Mercury 1.4.1 Supplied with Cambridge Structural Database, Copyright CCDC, **2005-2006**)

All structures were solved by direct methods. In all cases, non-hydrogen atoms were treated anisotropically except in **2** where the disordered carbon atom of the tetrabutylammonium moiety was treated isotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed.

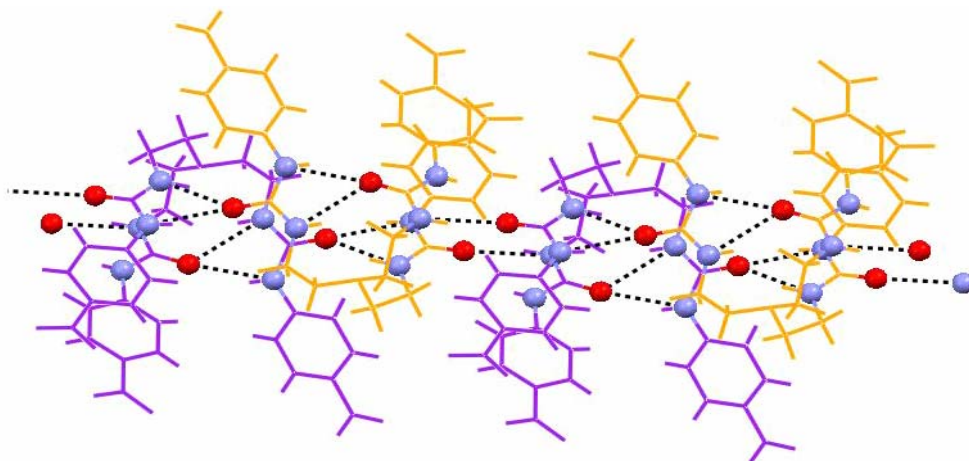
In **2**, the carbon atom of the tetrabutylammonium moiety was found to be disordered. At the final stage of refinement, the extra electron densities (three peaks) have been assigned as carbon atoms of tetrabutylammonium moiety. The SOF of these three peaks have been refined keeping the x,y,z and temperature factors fixed (at 0.05). After refinement, the refined SOF of the disordered carbon atoms were fixed and x,y,z and isotropic temperature parameters were refined in the subsequent cycle of refinements. Hydrogen bonding parameters are listed in Table S1.

### 3. Table S1: Hydrogen Bonding Parameters for 1, 1.DMF and 2

D–H...A	D–H/Å	H...A/Å	D...A/Å	D–H...A/ <sup>0</sup>	Symmetry operation for A
<b>1</b>					
N(4A)–H(4A)···O(6C)	0.85(4)	2.21(4)	2.964(5)	148(4)	x, y, z
N(4B)–H(4B)···O(6A)	0.98(4)	2.23(4)	2.995(4)	134(4)	1-x, 1-y, 1-z
N(4C)–H(4C)···O(6B)	0.94(3)	1.97(3)	2.885(5)	167(2)	-x, 1-y, -z
N(7B)–H(7B)···O(6A)	0.82(4)	2.07(4)	2.860(5)	161(4)	1-x, 1-y, 1-z
N(7C)–H(7C)···O(6B)	0.79(5)	2.45(5)	3.181(5)	155(5)	-x, 1-y, -z
C(2A)–H(2A)···O(16B)	0.99(4)	2.56(4)	3.253(6)	127(3)	1+x, 1+y, z
C(3B)–H(3B)···O(15C)	1.05(4)	2.51(4)	3.312(6)	133(3)	x, 1+y, z
C(12B)–H(12B)···O(15A)	0.97(4)	2.55(4)	3.335(6)	139(4)	1-x, -y, 1-z
C(12C)–H(12C)···O(15B)	0.99(4)	2.33(4)	3.294(6)	165(3)	-1-x, -y, -z
<b>1.DMF</b>					
N(4A)–H(4A)···O(21)	0.83(3)	2.25(3)	2.969(3)	145(3)	-x, 1-y, 1-z
N(4C)–H(4C)···O(6A)	0.92(3)	2.01(3)	2.912(3)	169(2)	1-x, 1-y, 1-z
N(7A)–H(7A)···O(21)	0.87(3)	1.97(3)	2.818(3)	165(3)	-x, 1-y, 1-z
N(7C)–H(7C)···O(6A)	0.91(3)	2.34(3)	3.159(3)	150(2)	1-x, 1-y, 1-z
N(7B)–H(7B)···O(6C)	0.81(3)	2.16(3)	2.937(3)	163(3)	x, y, z
C(10B)–H(10B)···O(15A)	0.98(3)	2.50(3)	3.270(4)	135(2)	x, y, -1+z
C(12A)–H(12A)···O(15C)	0.95(3)	2.52(3)	3.356(4)	146(2)	-x, 2-y, 1-z
C(17)–H(17B)···O(16A)	0.96	2.57	3.424(5)	149	x, -1+y, z
<b>2</b>					
O(3W)–H(3W)···O(1S)	0.73(3)	2.06(3)	2.773(4)	167(3)	x, y, z
N(4)–H(4)···O(2S)	0.88	2.01	2.870(5)	165	x, y, z
N(7)–H(7)···O(1S)	0.88	2.03	2.901(5)	170	x, y, z
C(10)–H(10)···O(6)	0.95	2.51	3.161(6)	126	2/3+x-y, 4/3-y, 1/3-z
C(13)–H(13)···O(1S)	0.95	2.58	3.353(5)	138	x, y, z
C(13)–H(13)···O(3W)	0.95	2.45	3.334(5)	155	x, y, z
C(18)–H(18B)···O(3W)	0.99	2.52	3.488(7)	165	x, y, z
C(19)–H(19A)···O(15)	0.99	2.55	3.307(7)	133	1-x+y, 1-x, z

#### 4. Illustration of the Crystal structures

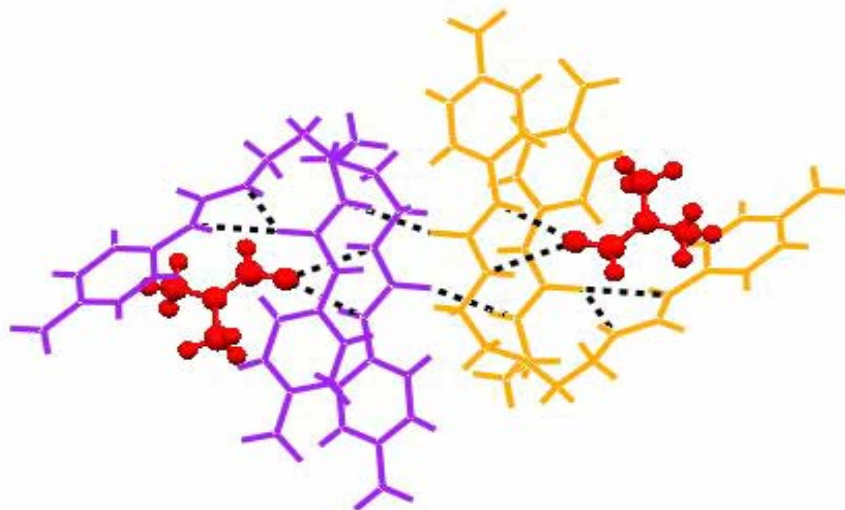
Two different crystal structures of **1**, one devoid of solvent crystallized from CH<sub>3</sub>CN and one with one molecule of DMF included in the crystal structure; crystallized from DMF (**1.DMF**) have been obtained. In **1** the urea moiety displays its complementary hydrogen bonding with the neighboring molecule arranged in a head and tail fashion. As a result a one-dimensional hydrogen bonded network is formed; propagating along the diagonal of the a-c plane. Such chains are further packed along the b-axis to form a two-dimensional hydrogen bonded network.



**Figure S1:** Illustration of the crystal structure of **1**; Complementary hydrogen bonding of urea moiety forming 1D network in **1**, [nitrogen (blue) and oxygen (red) atoms of urea are shown in ball and stick model].

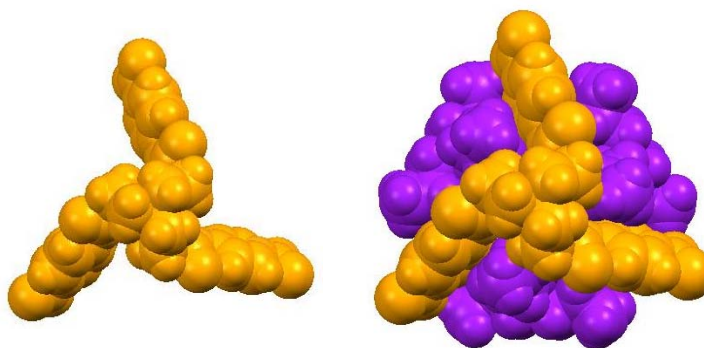
In **1.DMF**, the oxygen atom of the DMF molecule is hydrogen bonded to one of the urea moieties of **1**. The other urea moieties are involved in self-complementary hydrogen bonds with the adjacent molecule. Thus, a hydrogen-bonded dimer is formed involving two solvate DMF and two molecules of **1**. It is interesting to note that in both the cases, **1** does not display C<sub>3</sub> symmetry as expected. This may be presumably due to

the strong hydrogen bonding involving the N-H of the urea moiety and the carbonyl groups.



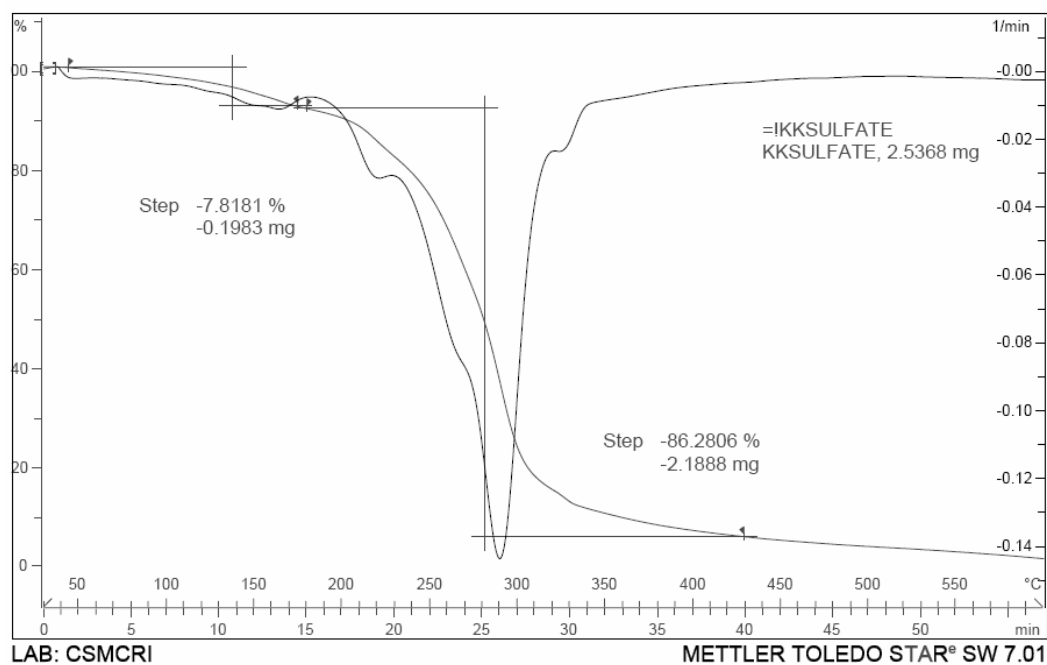
**Figure S2:** Representation of the dimer in **L.DMF** through complementary hydrogen bonding. (DMF molecules are shown in ball and stick model).

**Illustration of the formation of Bowl architecture in 2**



**Figure S3.** (a) Space filling model of the host in **2**; (b) Bowl type architecture formed in **2**, where the tetrabutylammonium cations (purple color) located between the arms of **1**

## 5. Thermal Analysis



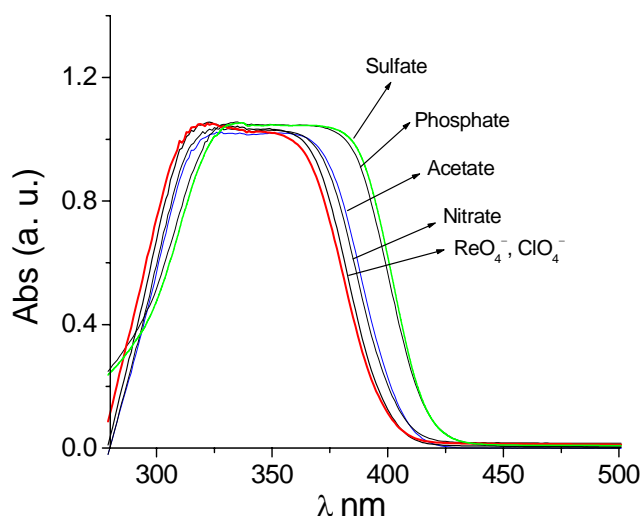
**Figure S4:** TGA plot of **2**.

Thermal Analysis performed on a filter paper dried crystals of **2**; indicate the loss of all water molecules (encapsulated as well as solvated) with a weight 7.8% as multi-step process from 40° C and 170 ° C. This value agrees well with the calculated value of 7.5% for four solvate water molecule (5.5%) and 1.5 encapsulated water molecules (2.0%). The host molecule decomposed at a peak temperature of 298° C.



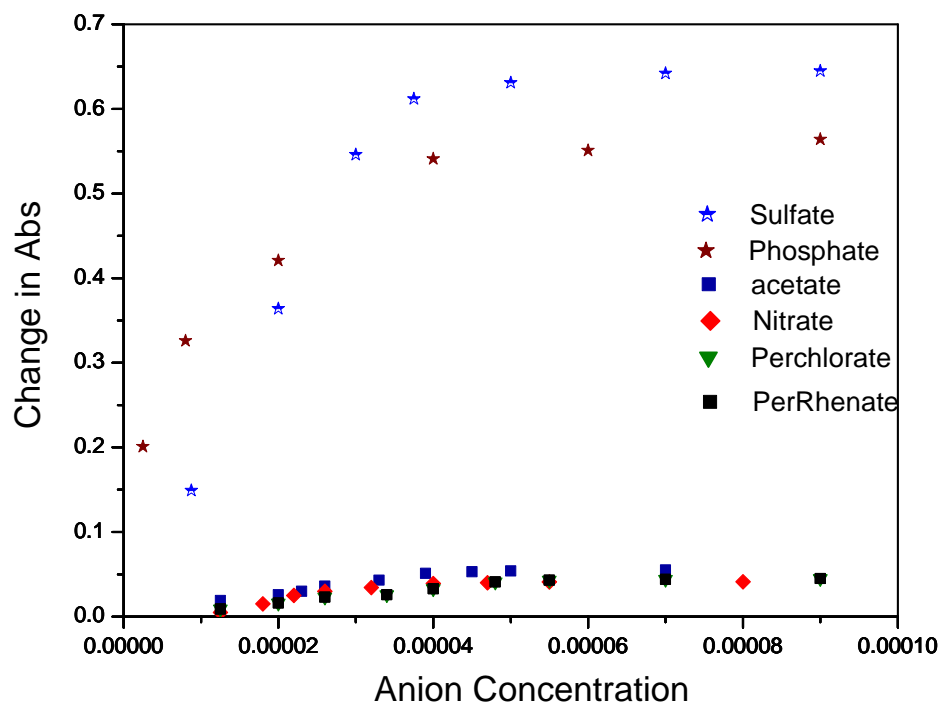
## 6. UV-Visible changes with different anions

**Experimental method:**  $1.0 \times 10^{-4}$  M solution of the receptor **1** was prepared in acetonitrile. All Uv-Vis titrations were carried out using these solutions, after appropriate dilution.  $1.0 \times 10^{-3}$  M solutions of tetrabutylammonium salts of respective anions were prepared in distilled acetonitrile, prior to use and were stored under inert atmosphere. All titration experiments were performed using  $4.0 \times 10^{-5}$  M solutions of receptor **1** in  $\text{CH}_3\text{CN}$  and various concentrations of anions ( $2.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  M) in acetonitrile. Affinity constant values were evaluated from the absorbance data of the titration curve using 380 nm as the probe wavelength.



**Figure S5:** Changes in Absorption spectra of **1** with different anions.

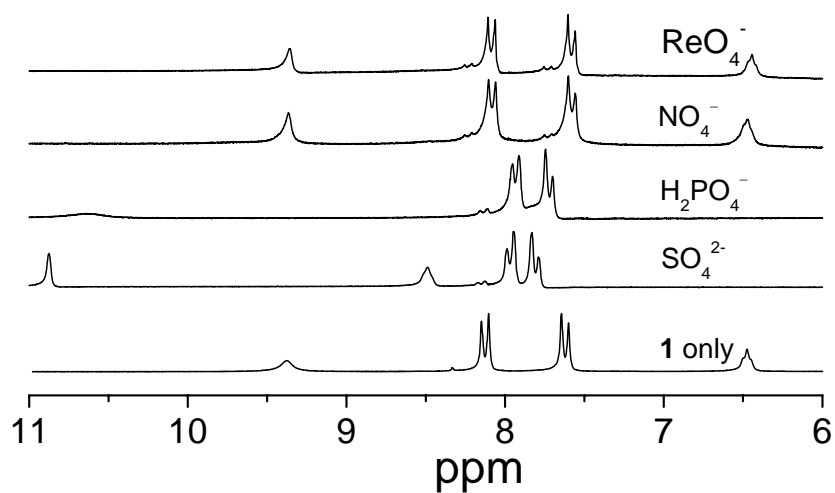
**Titration profile of 1 with different anions**



**Figure S6:** Titration profile of receptor **1** with different anions.

## 7. $^1\text{H}$ NMR with different anions

### Change in NMR Spectra with different anions



**Figure S7:** Change in NMR spectra of **1** upon addition of 5 equivalents of different anions