Supporting Information for

Selective total encapsulation of the sulfate anion by neutral nano-jars

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GENERAL

All commercially available reagents were used as received. NMR and UV-Vis spectra were recorded at room temperature on a Jeol JNM-ECP400 and a Shimadzu UV 2101 PC spectrophotometer, respectively. X-Ray diffraction data was collected at 100 K from single crystals mounted atop a glass fiber under Paratone-N oil with a Bruker SMART APEX II diffractometer, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation.

EXPERIMENTAL DETAILS

Synthesis of $(Bu_4N)_2SO_4$. 340 mg $(Bu_4N)HSO_4$ (1 mmol) was dissolved in a minimum amount of water, and 1.00 ml aqueous Bu_4NOH ,1M (259 mg, 1 mmol) was added under stirring. The water was removed from the resulting solution under vacuum, and the product was dried for several days under high vacuum.

Synthesis of $Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)]_{\infty}$. A solution of 4.471 g KOH (pellets, 85%) (68 mmol) and 2.306 g pyrazole (34 mmol) in 150 ml H_2O was added dropwise under vigorous stirring to a solution of 8.456g $CuSO_4{\cdot}5H_2O$ (34 mmol) in 150 ml H_2O. The blue-purple precipitate formed was stirred overnight, then filtered and washed extensively with water. 4.950 g of $[Cu(\mu\text{-}OH)(\mu\text{-}pz)]_n$ was obtained as a blue-purple powder after drying (99 %).

Synthesis of $(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ *(Bu*$_4$*N-**1**), and* $(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ *(Bu*$_4$*N-**2**).*

Method A. 1.000 g $[Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)]_{\infty}$ was stirred together with 150 mg $(Bu_4N)_2SO_4$ in 50 ml THF for 14 hours under reflux. The resulting deep blue solution was filtered, the solvent removed, and the product dried in vacuum. Yield: 1.140 g dark blue powder. Similar result were obtained using toluene instead of THF.

Method B. 9.988 g $CuSO_4 \cdot 5H_2O$ (40 mmol), 5.093 g KOH (pellets, 85%) (77 mmol), 2.723 g pyrazole (40 mmol) and 3.0 ml Bu_4NOH (1M in H_2O) (3 mmol) were stirred together in 150 ml THF for 3 days. The deep blue solution was filtered and the solvent removed. Yield: 6.703 g dark blue powder (>99%).

Method C. A solution of 4.994 g $CuSO_4 \cdot 5H_2O$ (20 mmol) in 100 ml DMF was mixed with a solution of 2.546 g KOH (pellets, 85%) (39 mmol), 1.362 g pyrazole (20 mmol) and 1.5 ml Bu_4NOH (1M in H_2O) (1.5 mmol) in 20 ml methanol. The deep blue solution was stirred for 1 day, filtered and the solvent was removed under vacuum. Yield: 3.165 g (>94%).

Method D. 968 mg $CuSO_4 \cdot 5H_2O$ (3.9 mmol), 495 mg KOH (pellets, 85%) (7.5 mmol), 264 mg pyrazole (3.9 mmol) and 0.25 ml Bu_4NOH (1M in H_2O) (0.25 mmol) were added to 15 ml CH_2Cl_2, and stirred for 3 days. The deep blue solution was filtered and the solvent removed to yield 400 mg of a dark blue powder (> 62%).

Synthesis of $(Et_3NH)_2[SO_4^{2-} \subset \{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ *(Et₃NH-**1**), and* $(Et_3NH)_2[SO_4^{2-} \subset \{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ *(Et₃NH-**2**)*. 9.988 g $CuSO_4 \cdot 5H_2O$ (40 mmol) were dissolved in 100 ml DMF with stirring. 2.723 g pyrazole (40 mmol) and 14 ml Et_3N (10.164 g, 100 mmol) were added consecutively, resulting in immediate color change from green to blue to dark blue. 300 ml H_2O were added under stirring, and the blue precipitate formed was filtered, washed thoroughly with water (until no sulfate could be detected with $BaCl_2$) and dried. Yield: 6.300 g dark blue powder (>99%).

Synthesis of $(K^+ \subset 18\text{-crown-6})_2[SO_4^{2-} \subset \{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ *(K18C6-**1**), and* $(K^+ \subset 18\text{-crown-6})_2[SO_4^{2-} \subset \{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ *(K18C6-**2**)*. 968 mg $CuSO_4 \cdot 5H_2O$ (3.9 mmol), 512 mg KOH (pellets, 85%) (7.8 mmol), 264 mg pyrazole (3.9 mmol) and 73 mg 18-crown-6 (0.3 mmol) were stirred together in 15 ml THF for 2 days. The deep blue solution was filtered and the solvent removed. Yield: 664 mg dark blue powder (>99%).

Sulfate binding studies. A solution of 500 mg Bu_4N-**1**/Bu_4N-**2** in 10 ml CH_2Cl_2 was vigorously stirred with a solution of 118 mg $Ba(OH)_2 \cdot 8H_2O$ in 5 ml H_2O (pH = 13.2) for two weeks. The pH was then lowered to 1 with aqueous HCl solution, which led to the formation of a white $BaSO_4$ precipitate. A control reaction ran by stirring a solution of 60 mg $(Bu_4N)_2SO_4$ in 10 ml

CH_2Cl_2 (containing the same amount of sulfate as the sample used above) with aqueous $Ba(OH)_2$ resulted in the immediate precipitation of $BaSO_4$.

Selectivity studies. 0.178 g $CuSO_4 \cdot 5H_2O$, 4.487 g $Cu(NO_3)_2 \cdot 2.5H_2O$ (or 7.148 g $Cu(ClO_4)_2 \cdot 6H_2O$), 1.362 g pyrazole and 7 ml Et_3N were stirred together in 50 ml DMF for two hours. 150 ml water was added, the blue precipitate stirred for 5 minutes, filtered, washed thoroughly with water and dried in vacuum. Similar results were obtained using an aqueous solution of the copper-salts and a CH_2Cl_2 solution of pyrazole and Et_3N, in which case the rings were extracted into the organic phase. 1000.0(±0.1) mg of the product was dissolved in 15 ml HCl 6 M at 90 °C, and a solution of 156 mg $BaCl_2 \cdot 2H_2O$ in 15 ml water was added dropwise under stirring. After keeping the solution hot for two hours, the precipitated $BaSO_4$ was filtered on a pre-weighted filter crucible, washed with water and dried in an oven to constant weight. Expected $BaSO_4$ amount: 52.6 mg if the product was pure Et_3NH -**1**, and 47.9 mg if the product was pure Et_3NH -**2**. Amount of $BaSO_4$ found: 51.8(±0.1) mg for the sulfate/nitrate experiment, and 48.9(±0.1) mg for the sulfate/perchlorate experiment. A reference experiment with Et_3NH -**1**/Et_3NH -**2** synthesized from $CuSO_4 \cdot 5H_2O$ only was also carried out; 50.3(±0.1) mg of $BaSO_4$ were obtained.

CRYSTALLOGRAPHY

Once removed from the mother liquor, all crystals reported here are extremely sensitive to solvent loss at ambient conditions, and were mounted quickly under the cryostream to prevent decomposition. The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares on F^2, using the APEX2 v2008.2-0 software package.[1]

Bu_4N-**1**$\cdot 6C_7H_8$. All non-hydrogen atoms were refined with independent anisotropic displacement parameters, except the disordered terminal tetrabutylammonium carbon atoms C100, C104, C288, and the toluene solvent molecules. C–H hydrogen atoms were placed in idealized positions and refined using the riding model, except for the disordered terminal tetrabutylammonium carbon atoms C87, C88, C288, C99, C100, C200, C103, C104, C204, and the toluene solvent molecules, on which they were not placed. O–H hydrogen atoms were located from the difference Fourier map; their displacement parameters were fixed to be 20 % larger than those of the attached O atoms, and the bond lengths were restrained to 0.82 Å. Three sulfate O-atoms are disordered over two positions around the molecule's three-fold axis. Two toluene solvent molecules are each disordered over two positions.

Bu_4N-**2**$\cdot 2.5C_7H_8\cdot 2.5C_6H_{14}\cdot 0.5C_6H_{12}$: Due to poor crystal quality, over twenty-five crystals from five different batches were screened, and three data sets were collected; the best of the three is presented here. All non-hydrogen atoms were refined with independent anisotropic displacement parameters, except the disordered Bu_4N^+ counterion and the solvent molecules (toluene, hexane, cyclohexane). Pyrazole C–H hydrogen atoms were placed in idealized positions and were refined using the riding model. Hydrogen atoms were not placed on the disordered Bu_4N^+ counterion and the solvent molecules. The hydrogen atoms of the O–H groups could not be located in Fourier difference maps. The disorder could only be modeled in the case of a toluene and a hexane molecule, which occupy the same space with SOFs of 50% each. The cyclohexane molecule (which originates in the mixture of different hexane isomers used for crystal growth), has its SOFs fixed at 50%.

Despite the rather poor quality of the crystals, the identity of **1** and **2** was clearly identified in all crystals studied. Crystallographic details for **1** and **2** are summarized in Table S1, and thermal ellipsoid plots are shown in Figures S1 and S2. Preliminary data for Bu_4N-**1**, Bu_4N-**2** and K^+18C6-**2,** crystallized from different solvents, are shown below. In each case, the assembly crystallizes with several disordered solvent molecules.

Table S1. Crystallographic details.

Compound	Bu_4N-**1**$\cdot 6(C_7H_8)$	Bu_4N-**2**$\cdot 2.5(C_7H_8)\cdot 2.5(C_6H_{14})\cdot 0.5(C_6H_{12})$
Formula	$C_{158}H_{232}Cu_{28}N_{58}O_{32}S$	$C_{160.5}H_{257}Cu_{31}N_{64}O_{35}S$
Formula weight	5267.20	5645.10
Crystal system	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
a / Å	20.4917(3)	20.4153(9)
b / Å	20.7379(3)	22.910(1)
c / Å	28.6519(6)	25.866(1)
α / °	99.579(1)	103.685(3)
β / °	100.964(1)	94.975(3)
γ / °	116.430(1)	110.593(3)
V/ $Å^3$	10258.3(3)	10809.7(9)
Z	2	2
D_{calc} / g cm^{-3}	1.705	1.734
μ / mm^{-1}	2.919	3.062
Reflections collected/unique	462322 /48814	206783/38159
Observed reflections	34873	27784
Goodness-of-fit (on F^2)	1.219	2.849
R(F); R_w(F) (I>2σ (I))	0.0490; 0.1519	0.1332; 0.4066

$(K^+\subset 18C6)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ from n-butyl acetate: monoclinic, C2/c, a = 50.639(1) Å, b = 27.6036(5) Å, c = 33.5667(6) Å, α = 90.000°, β = 100.038(1)°, γ = 90.000°, V = 46202(2) Å^3, Z = 8.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ from chlorobenzene: triclinic, P-1, a = 20.4484(3) Å, b = 20.7128(3) Å, c = 28.6607(6) Å, α = 100.025(1)°, β = 100.125(1)°, γ = 116.533(1)°, V = 10242.2(3) Å^3, Z = 2.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ from n-butanol: triclinic, P-1, a = 19.870(1) Å, b = 29.111(2) Å, c = 35.789(2) Å, α = 88.570(1)°, β = 77.827(1)°, γ = 77.036(1)°, V = 19714(1) Å^3, Z = 4.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ from chlorobenzene: triclinic, P-1, a = 20.548(1) Å, b = 22.937(2) Å, c = 25.545(3) Å, α = 103.374(6)°, β = 95.460(6)°, γ = 110.430(4)°, V = 10770(2) Å^3, Z = 2.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ from dichloromethane, triclinic, P-1, a = 14.7908(3) Å, b = 20.3545(3) Å, c = 35.4641(6) Å, α = 91.146(1)°, β = 97.722(1)°, γ = 101.687(1)°, V = 10348.4(3) Å^3, Z = 2.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+14+9}]$ from toluene: triclinic, P-1, a = 20.4153(9) Å, b = 22.910(1) Å, c = 25.866(1) Å, α = 103.685(3)°, β = 94.975(3)°, γ = 110.593(3)°, V = 10809.7(9) Å^3, Z = 2.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ from 1,2-dichloroethane: triclinic, P-1, a = 14.8699(6) Å, b = 20.3182(7) Å, c = 35.486(1) Å, α = 91.049(2)°, β = 96.495(2)°, γ = 101.410(2)°, V = 10433.0(7) Å^3, Z = 2.

$(Bu_4N)_2[SO_4^{2-}\subset\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_{6+12+10}]$ from n-butylamine: triclinic, P-1, a = 20.246(3) Å, b = 29.767(10) Å, c = 35.507 (6) Å, α = 96.453(2)°, β = 91.433(2)°, γ = 103.069(2)°, V = 20685(3) Å^3, Z = 4.

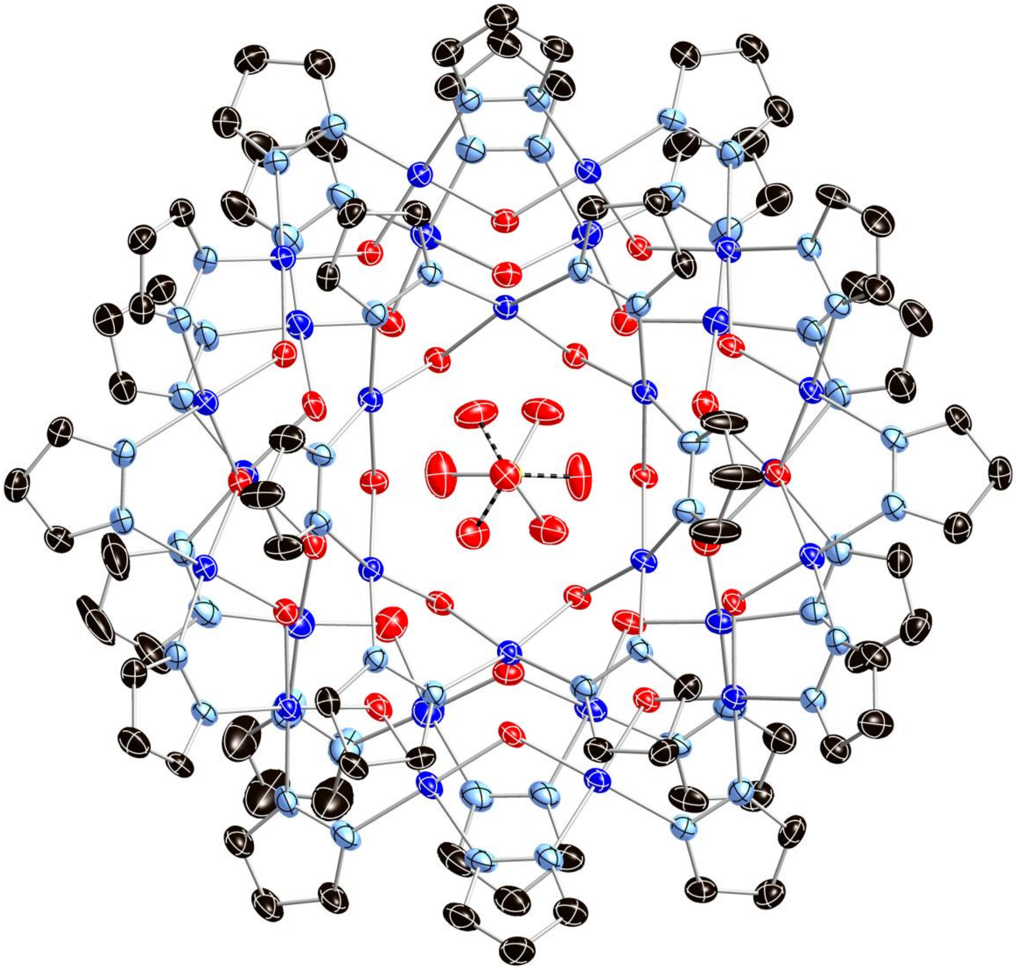

Figure S1. Thermal ellipsoid plot (50%) of Bu$_4$N-**1**·6C$_7$H$_8$. H atoms, Bu$_4$N$^+$ counterions and solvent molecules are omitted for clarity.

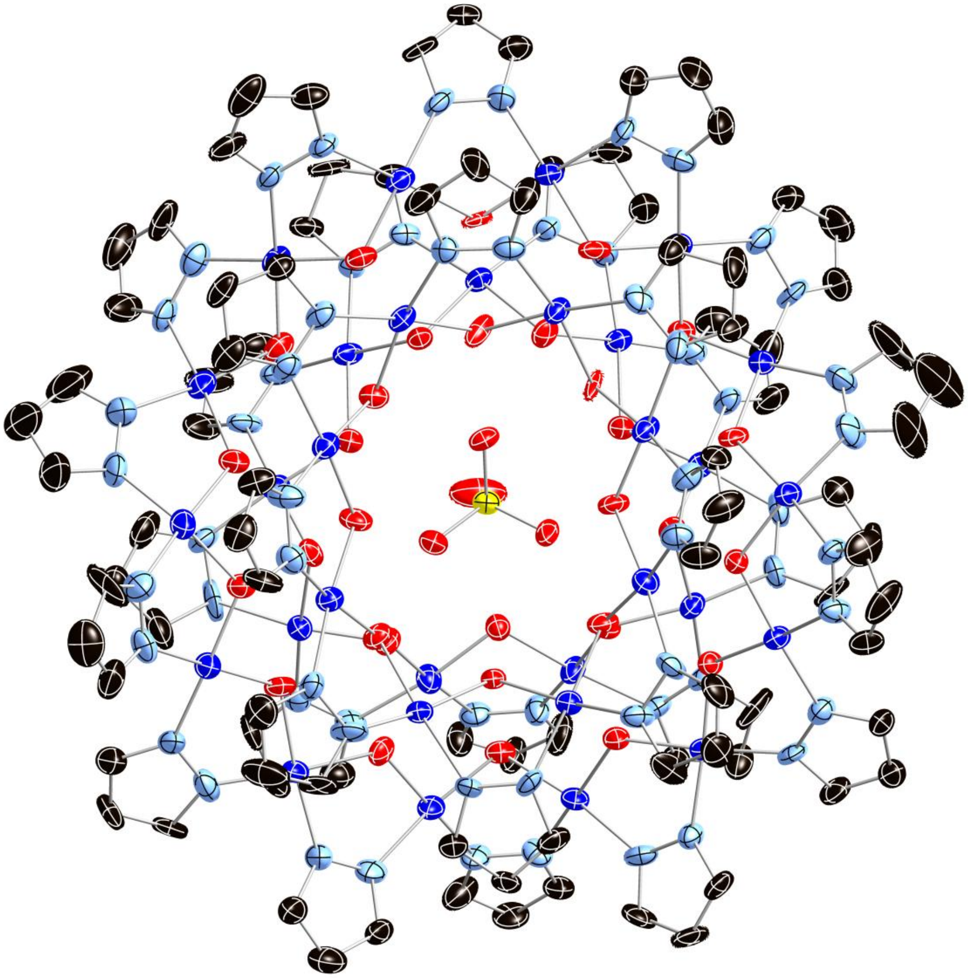

Figure S2. Thermal ellipsoid plot (50%) of Bu_4N-**2**·$2.5C_7H_8$·$2.5C_6H_{14}$·$0.5C_6H_{12}$. H-atoms, Bu_4N^+ counterions and solvent molecules are omitted for clarity.

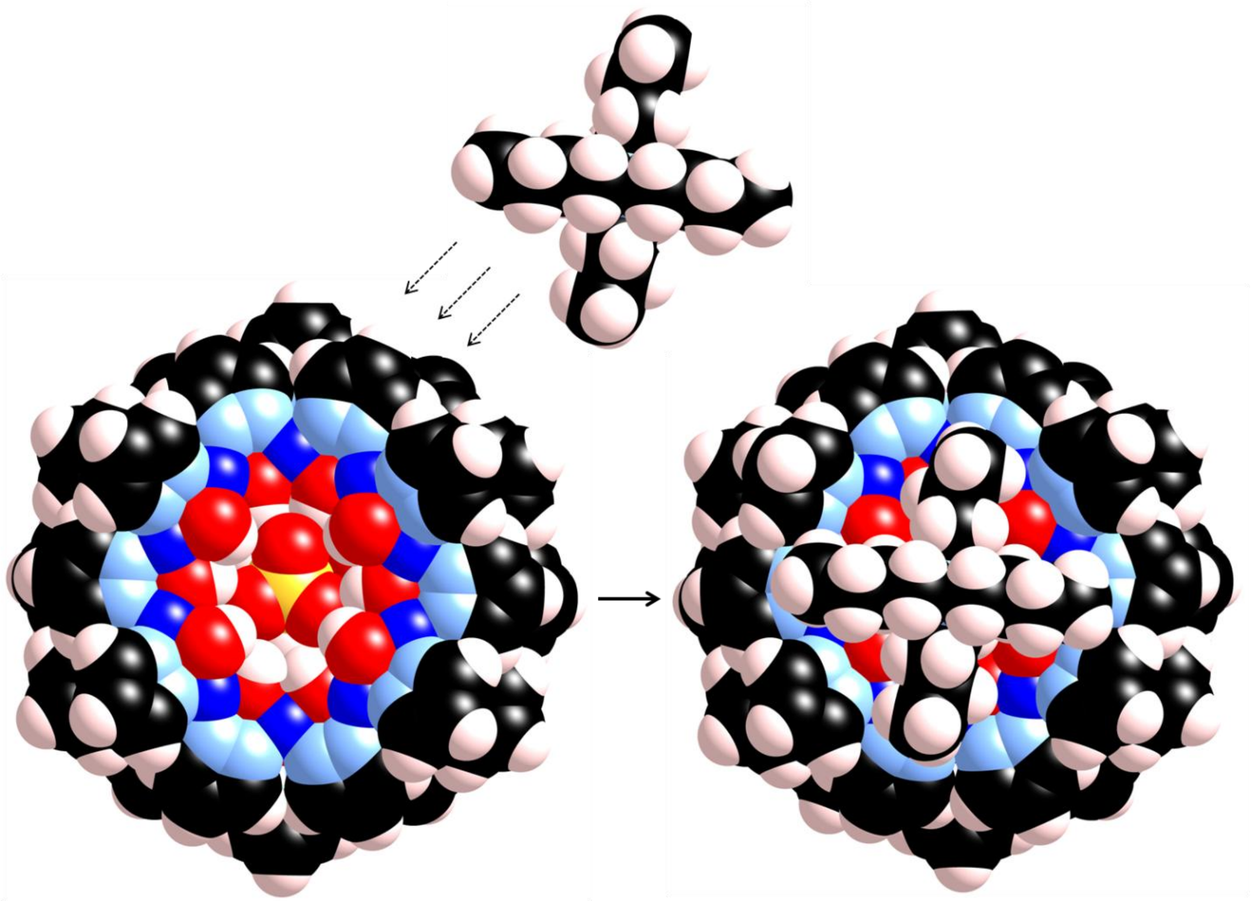

Figure S3. Illustration of the ion-association between Bu_4N^+ and the sulfate-encapsulating nano-toroid **1** (top-view). Color-code: S-yellow, O-red, Cu-blue, N-light blue, C-black, H-pink.

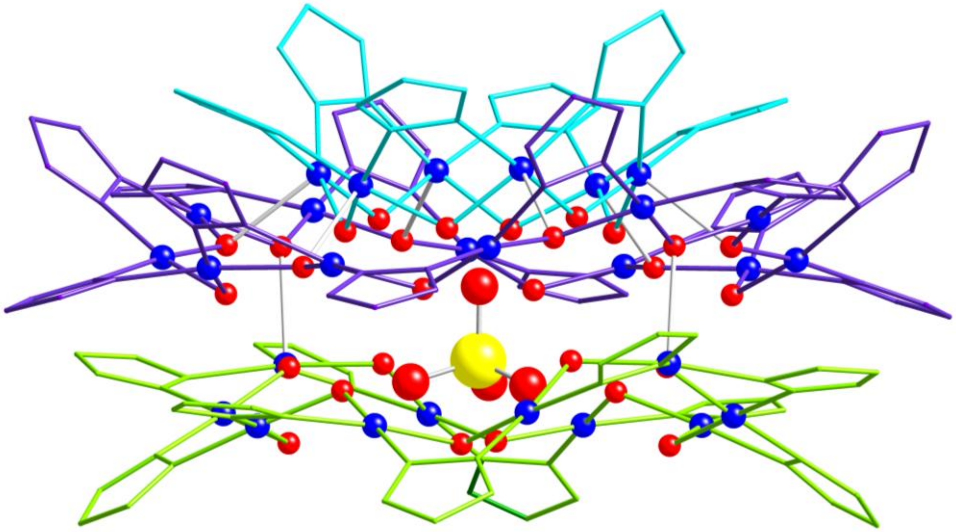

Figure S4. Illustration of the 6+12+10 ring assembly encapsulating the sulfate anion (side-view). Color code for atoms: Cu-dark blue, O-red, S-yellow. Pentagons denote pyrazole ligands (light blue: 6-membered ring, violet: 12-membered ring, lime green: 10-membered ring).

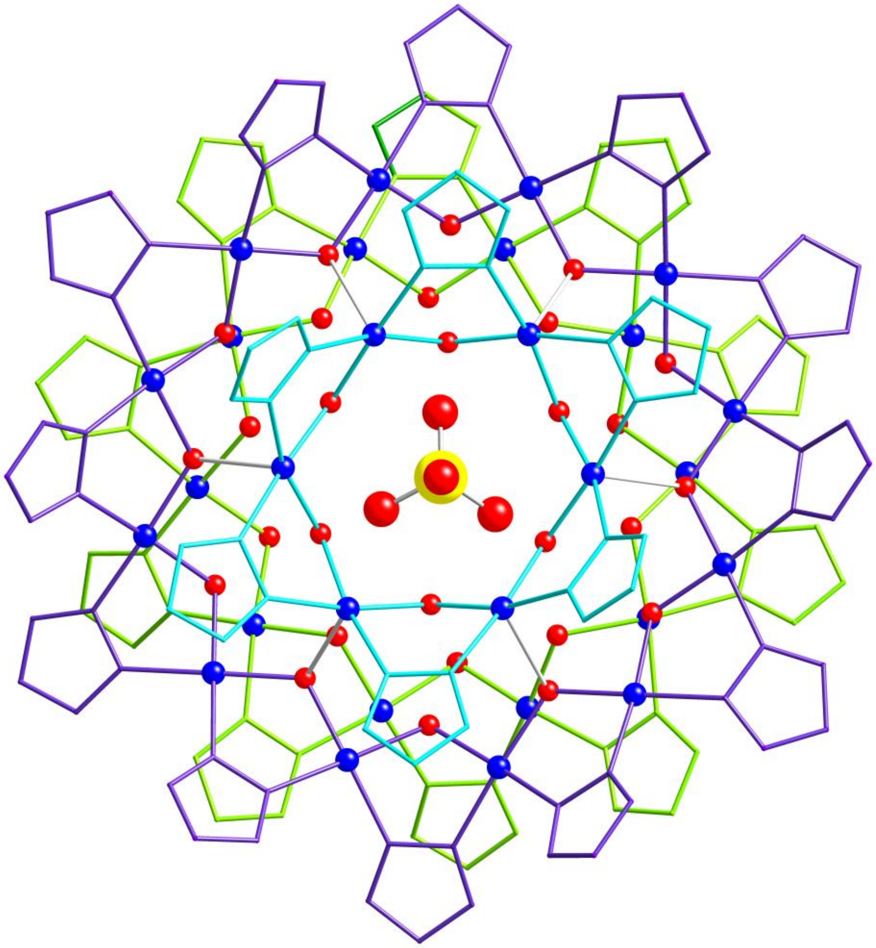

Figure S5. Illustration of the 6+12+10 ring assembly encapsulating the sulfate anion (top-view).

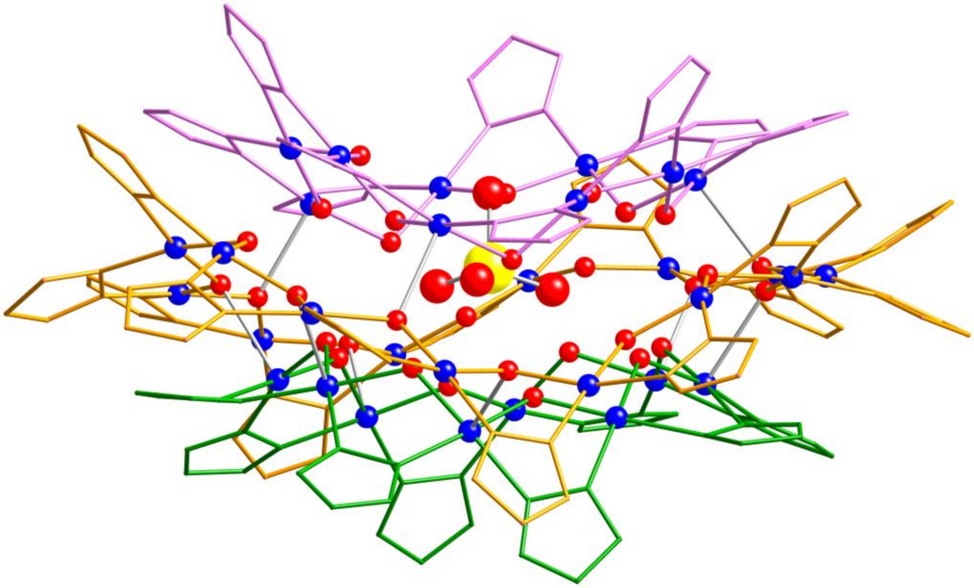

Figure S6. Illustration of the 8+14+9 ring assembly encapsulating the sulfate anion (side-view). Color code for atoms: Cu-dark blue, O-red, S-yellow. Pentagons denote pyrazole ligands (pink: 9-membered ring, orange: 14-membered ring, green: 8-membered ring).

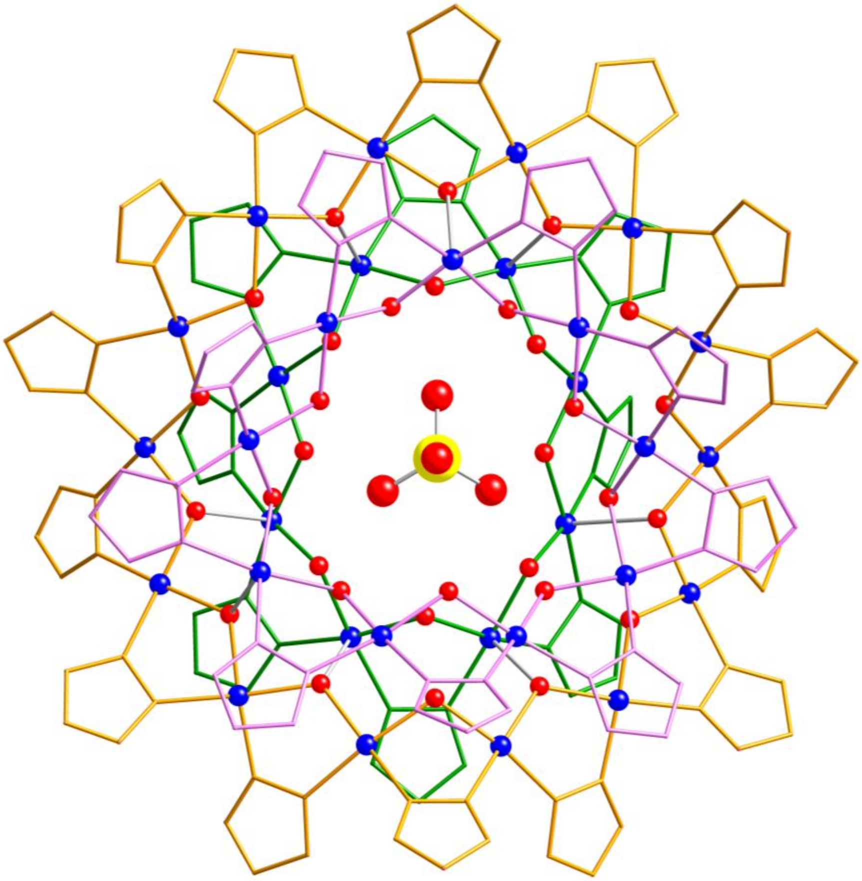

Figure S7. Illustration of the 8+14+9 ring assembly encapsulating the sulfate anion (top-view).

SPECTROSCOPY

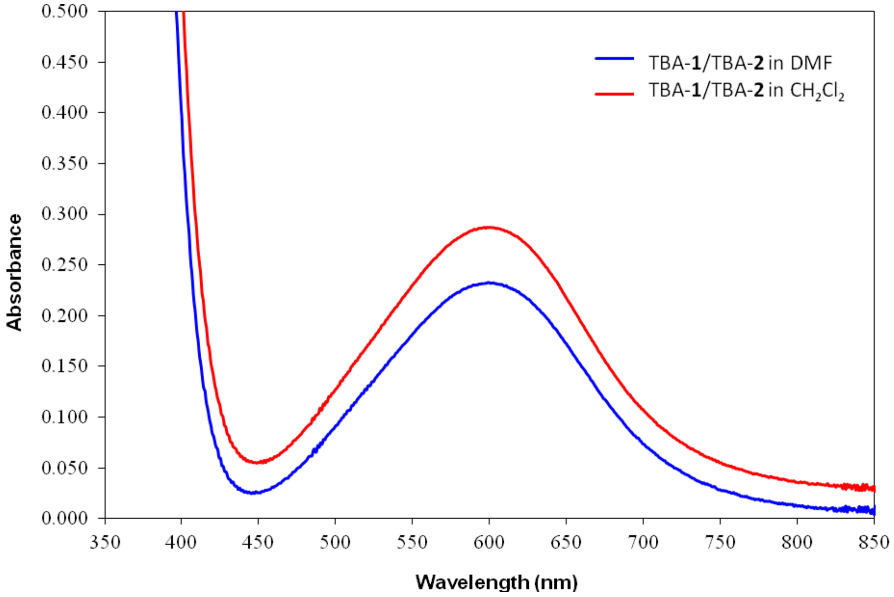

Figure S8. UV-vis spectrum of Bu_4N-**1**/Bu_4N-**2** in DMF and CH_2Cl_2.

Table S2. ^{1}H NMR chemical shifts of the $[N(CH_2CH_2CH_2CH_3)_4]^+$ counterion protons in DMSO-d_6, CD_3CN, $(CD_3)_2CO$ and $CDCl_3$.

	DMSO-d_6	CD_3CN	$(CD_3)_2CO$	$CDCl_3$	DMSO-d_6	CD_3CN	$(CD_3)_2CO$	$CDCl_3$
	$(Bu_4N)_2[SO_4\{Cu(\mu\text{-}OH)(\mu\text{-}pz)\}_n]$				**$Bu_4N[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3Cl_3]$**			
CH_2	3.25	3.48	4.22	4.40	3.15	3.07	3.43	3.97
CH_2	1.67	2.75	3.39	~4.2	1.56	1.61	1.84	2.37
CH_2	1.58	2.14	2.71	3.16	1.30	1.37	1.48	2.37
CH_3	1.18	2.03	2.30	2.97	0.93	0.98	1.01	1.49
	$(Bu_4N)_2SO_4$				**Bu_4NCl**			
CH_2	3.17	3.14	3.59	3.49	3.18	3.13	3.54	3.38
CH_2	1.57	1.60	1.77	1.62	1.57	1.60	1.80	1.65
CH_2	1.31	1.34	1.43	1.42	1.30	1.34	1.41	1.43
CH_3	0.93	0.96	0.96	0.93	0.93	0.95	0.96	0.98