Supporting Information

Supramolecular Organization of Calix[4]pyrrole with a Methyl-trialkylammonium Anion Exchanger Leads to Remarkable Reversal of Selectivity for Sulfate Extraction vs Nitrate

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Commercial Reagents: All reagents were used as received from the suppliers without further purification or synthesized as described below. De-ionized reverse-osmosis Milli-Q water (18.2 MΩ·cm, 3.0 ppb TOC) was used for the aqueous phase in equilibrium experiments as described in methods section. 1,2-dichloroethane (DCE) (≥99% spectrophotometric grade), and Aliquat® chloride (methyltri-$C_{8,10}$-ammonium chloride, A336 Cl) and sodium sulfate (ACS 99%+) were purchased from Sigma-Aldrich. Acros Organics furnished tetraheptylammonium chloride (95%) and tetrahexylammonium chloride was purchased from ScienceLab.com, Inc. The radiotracer used here, ^{35}S as H_2SO_4 in H_2O, was provided by Perkin Elmer (99.0% Radionuclide Purity).

Synthesis of Anion Receptor and Metathesis of Anion Exchangers: *Meso*-octamethylcalix[4]pyrrole (C4P, **1**) was prepared as adapted from the Rothemund method for synthesis of "acetonepyrrole".[1] Briefly, equimolar amounts of pyrrole (15.3 g, 0.227 moles) and acetone (131.6 g, 0.227 moles) were dissolved in 150 mL methanol. The solution was stirred vigorously and a catalytic amount of concentrated HCl was slowly added dropwise taking care to keep the reaction near room temperature. Upon the first signs of precipitate formation the acid addition was stopped. The reaction was allowed to stir for 15 minutes, during which time an off-white precipitate forms ubiquitously throughout the reaction vessel. The precipitate was filtered, washed several times with MeOH, and then recrystallized twice, once from DCM and once from a DCM/hexanes to remove traces of N-confused octamethylcalix[4]pyrrole. This provided pure octamethylcalix[4]pyrrole, as judged from mass spectrometric and ^1H NMR analyses.

Aliquat, tetraheptylammonium and tetrahexylammonium were metathesized to their respective nitrate form by dissolving ~ 1 g of the quaternary ammonium chloride salt into 25 mL $CHCl_3$ and contacting these solutions multiple times with 1 M $NaNO^{-}{}_3$ until the $AgNO_3$ test was negative for Cl^{-} for three consecutive contacts. Chloroform was removed via rotary evaporation, and the products were vacuum dried overnight at 40 °C. These salts were used directly to make up solutions with DCE and C4P.

Instrumentation and Methods

Two-phase Sulfate Extraction: Distribution experiments were performed in a similar fashion as previously reported by Fowler et al.[2] Sulfate was extracted from water using 1,2-DCE solutions of 10 mM A336 NO_3, *t*-C_7N NO_3 or *t*-C_6N NO_3 varying concentrations (~ 6 to 25 mM) of C4P (**1**). Equal volumes of organic and aqueous (10 mM Na_2SO_4) phases were placed on a rotating wheel for 1 h at 25 °C, the phases were separated by centrifugation at 25 °C, whereupon 300 mL samples of each phase were added to 10 mL of scintillation cocktail for Liquid Scintillation Analysis using ^{35}S as radiotracer for sulfate. As usual for this method, experimental uncertainty in D_{SO4} ($[SO_4^{2-}]_{org}/ [SO_4^{2-}]_{aq}$) is less than 10%, and sulfate distribution ratios were normalized as explained by ***Figure S1*** below.

Liquid Scintillation Analysis: Beta scintillation counting was performed on a Packard Tri-Carb 2500TR Model B2500P3 Liquid Scintillation Analyzer. In order to achieve a high level of counting statistical precision yet eliminate excessively long sample count times, the counting time cutoff was set at 2% of the standard deviation (%2s) with a maximum count time limited to 30 min. This yields a minimum of 40,000 counts registered for most samples, resulting in low instrumental uncertainty.

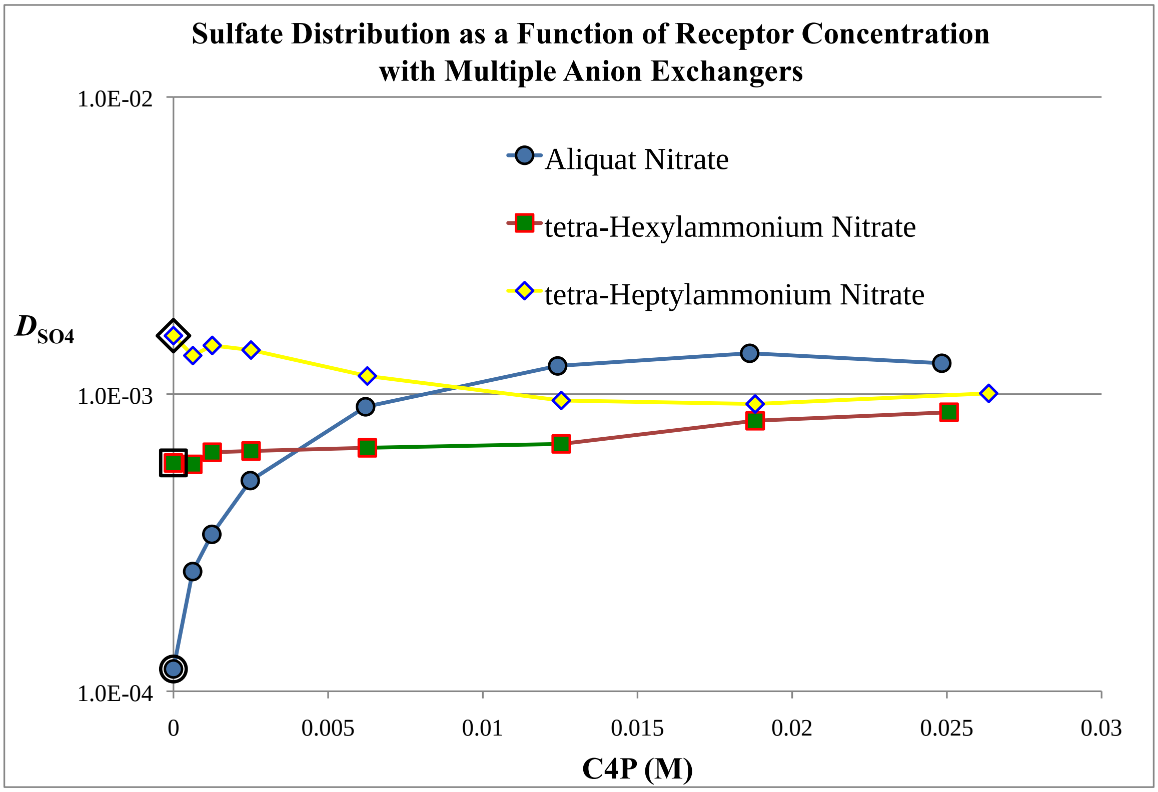

Figure S1 – Equilibrium sulphate distribution ratios at several receptor concentrations for sulphate extraction by the anion exchangers: Aliquat® 336N (**2a**), tetrahexylammonium (**2b**), and tetraheptylammonium (**2c**) nitrate. The values for each of the data points corresponding with 0 M C4P (**1**), which are each highlighted by an outer data marker, were used to provide normalized sulphate distribution coefficients in the paper. The quotient of all non-zero [C4P] D_{SO4} values and the value for that data set at 0 M C4P D_{SO4} value were plotted vs [C4P] producing ***Figure 1*** of the accompanying communication.

X-Ray Crystallography: X-ray quality single crystals of $(TMA)_2 \bullet (SO_4) \bullet (C4P) \bullet (EtOH)_2 \bullet (CH_2Cl_2)_2$ were obtained by slow evaporation of a dichloromethane/ethanol solution. Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus Mo Kα radiation (λ = 0.71073 Å), operated at 50 kV and 30 mA. The structure was solved by direct methods and refined on F^2 using the SHELXTL software package.[3] Absorption corrections were applied using SADABS, part of the SHELXTL package. There was significant disorder in one of the Me_4N^+ cations that could not be completely resolved. As a result, some Me groups were refined isotropically. The ethanol molecule included in the crystal displayed moderate disorder and was therefore refined isotropically. The source of the relatively large R_1 and wR_2 factors could not be identified, and it presumably indicates partial twinning. Repeated attempts to obtain higher quality data using different crystals did not lead to significant improvements. Fig. S2 shows the observed molecular structure of $(TMA)_2(SO_4)(C4P)$, and the interactions between C4P, sulfate, Me_4N^+ cations, and included ethanol.

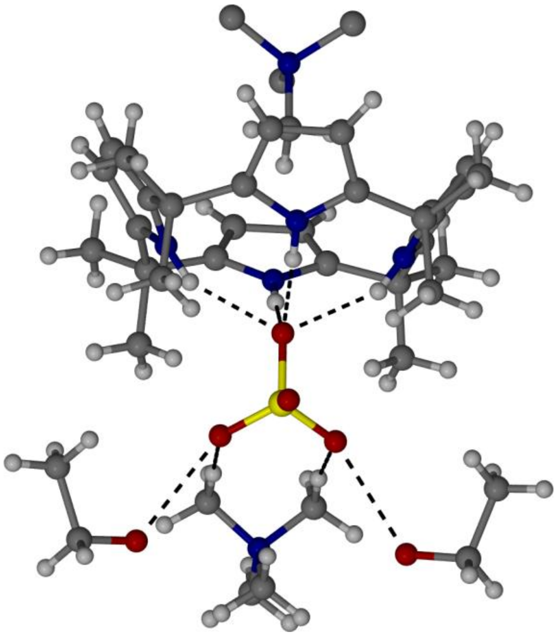

Figure. S2 – Molecular structure of $(TMA)_2(SO_4)(C4P)$ obtained by single crystal X-ray diffraction. One of the the Me_4N^+ cations is bound inside the C4P cup, while the second one interacts with sulfate via C–H···O hydrogen bonds (d(H···O) = 2.44 Å, < C– H···O = 161.9º). The sulfate is additionally hydrogen-bonded by two ethanol molecules, with observed O···O distances of 2.692 Å.

References

1. P. Rothemund, C. L. Gage, *J Am Chem Soc*, **1955**, 77, 3340-3342.
2. C. J. Fowler, T. J. Haverlock, B. A. Moyer, J. A. Shriver, D. E. Gross, M. Marquez, J. L. Sessler,* Md. A. Hossain, and K. Bowman-James, *J Am Chem Soc*, 2008, **130**, 14386–14387
3. SHELXTL 6.12; Bruker AXS, Inc., Madison, WI, **1997**.