

Supporting Information (SI)

Controlling the organization of phosphonium cations relative to *p*-sulfonatocalixarene anions

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Synthesis of **2**(C₂₈H₂₁O₁₆S₄³⁻), **4**(C₂₆H₂₂P⁺), C₂₀H₃₈N₂²⁺, **22**(H₂O)

Sodium *p*-sulfonatocalix[4]arene and 1,4-bis(triethylammoniomethyl)benzene bromide were available from earlier studies.¹ Benzyltriphenylphosphonium bromide was purchased from Sigma Aldrich and used as received. A solution of a mixture containing one equimolar of 1,4-bis(triethylammoniomethyl)benzene chloride along with two equivalents each of sodium *p*-sulfonatocalix[4]arene and benzyltriphenylphosphonium, were dissolved in THF/water (1:1, 2 mL) and the solutions were left to cool and slowly evaporate, with crystals forming after several days. The homogeneity of the materials was checked from single crystal X-ray diffraction of cell dimensions for a number of crystals.

Crystallographic details

Data were measured at T = 150(2)K from a single crystal using an Oxford Diffraction Xcalibur-S diffractometer equipped with CCD detector using monochromatic CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). The images were interpreted and integrated with the program CrysAlisPRO, Oxford Diffraction Ltd. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-2014² crystallographic package. Lp and absorption corrections applied.

2(C₂₈H₂₁O₁₆S₄³⁻), **4**(C₂₆H₂₂P⁺), C₂₀H₃₈N₂²⁺, **22**(H₂O)

C₁₇₆H₂₁₂N₂O₅₄P₄S₈, $M = 3599.84$, colorless needle, 0.34 x 0.23 x 0.12 mm³, monoclinic, space group $P2_1/c$ (No. 14), $a = 17.7070(2)$, $b = 14.7731(2)$, $c = 37.6605(4) \text{ \AA}$, $\beta = 101.434(1)^\circ$, $V = 9656.0(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.238 \text{ g/cm}^3$, $\mu = 1.823 \text{ mm}^{-1}$. $F_{000} = 3804$, $2\theta_{max} = 134.7^\circ$, 50857 reflections collected, 17107 unique ($R_{int} = 0.0294$). Final $Goof = 1.032$, $R1 = 0.1200$, $wR2 = 0.2736$, R indices based on 13943

reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho_{\max}| = 1.3(1) \text{ e \AA}^{-3}$, 1057 parameters, 126 restraints.

Two of the calixarene sulfonate groups were modelled as being disordered over two sets of sites at fixed occupancies parameters with their complements obtained after trial refinement. Geometries of the disordered components were restrained to ideal values. The water molecule hydrogen atoms could not be located. All remaining H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Anisotropic displacement parameters were employed for the non-hydrogen ordered atoms.

References

1. (a) M. Makha, C. L. Raston, *Tet. Lett.*, 2001, **42**, 6215-6217. (b) I. Ling, Y. Alias, M. S. A. Rahim, B. W. Skelton, L. T. Byrne, C. L. Raston, *Aust. J. Chem.* 2012, **65**, 755–762.
2. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122; (<http://shelx.uni-ac.gwdg.de/SHELX/index.php>)