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Exploiting phenyl embraces and π-stacking in the assembly of arrays of tetraphenylphosphonium *p*-sulfonatocalix[4]arene

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Phenyl embraces involving tetraphenylphosphonium cations feature in complexes of *p*-sulfonatocalix[4]arene where a phenyl ring of a cation is included in the cavity of the calixarene. The overall structures are based on pseudo-polymorphic supramolecular arrays and their formation is templated or induced by lanthanide ions.

Major advances made in crystal engineering in unravelling the key modes of often inherently weak interactions between moieties in molecular crystals assist our efforts to predict crystal structures.[1] Tetraphenylphosphonium cations, Ph_4P^+, can self-associate in the solid state through interdigitation of the phenyl groups from adjacent cations, forming $\{Ph_4P^+\}_2$ pairs as the 'sextuple' or lower order 'phenyl embraces'.[2,3] This self-association capability rationalises the utility of this cation in crystallising a diverse range of anions.[3] *p*-Sulfonatocalix[4]arene anions also interact with phenyl rings from adjacent anions, often by way of π-stacking as part of extended bi-layer structures or perturbations thereof.[4]

The interactions between Ph_4P^+ cations and *p*-sulfonatocalix[4]arene anions offer the possibility of building up new materials based on both types of ions based on interactions between the anions and cations beyond their attraction as ions, such as the possibility of a phenyl ring of the cation residing in the cavity of the calixarene. In developing this concept, we have embarked on a systematic study of the ability of the Ph_4P^+–*p*-sulfonatocalix[4]arene system to generate extensive self-assembled arrays and we report herein the formation of two closely related structurally authenticated arrays based on the ratio of one *p*-sulfonatocalix[4]arene to three Ph_4P^+ cations and twelve or ten water molecules, **I** and **II**, respectively. Their syntheses require the presence of a trivalent lanthanide ion that appears to template the crystallisation, but which, despite the well-documented complexation of the lanthanide ions by sulfonated calixarenes, is not included in the final product.[5] The crystals were grown by the slow evaporation of aqueous solutions of *p*-sulfonatocalix[4]arene, tetraphenylphosphonium bromide and ytterbium chloride salt.

The difference in molecular content of just two water molecules per asymmetric unit is associated with different types and modes of phenyl embrace, even though the asymmetric units in both structures are similar (Fig. 1 and 2).† The structures differ; firstly, in the manner of inclusion of the phenyl arm of Ph_4P^+ cation **A** in the cavity of the sulfonatocalix[4]arene and, secondly, in the way in which cations **B** and **C** in each structure associate predominately by only one mode of intermolecular phenyl–phenyl interaction. In respect of the interatomic distances and with reference to previous work by Dance and Scudder,[6] both structures are lacking in concerted multiple phenyl interactions, with edge-to-face (ef) interactions prevalent in structure **I** and offset face-to-face (off) interactions prevalent in structure **II**.

In structure **I** $\{(C_{28}H_{20}O_{16}S_4)(C_{24}H_{20}P)_3(H_3O)(H_2O)_{11}\}$, a cationic phenyl group (from cation **A**) included in the cavity of the calixarene is held by two CH···π interactions involving the direction of both *meta* hydrogens to a pair of opposed aromatic rings in the calixarene, with C–H···Ar distances of 2.6 and 2.7 Å, and C–H···Ar centroid angles of 160 and 146°, respectively. A phenyl of the embedded Ph_4P^+ cation (**A**), orthogonal to a phenyl of Ph_4P^+ **C**, has its *meta* and *para* hydrogens both involved in C–H···π interactions, with C–H···phenyl centroid distances of 3.3 Å for the *meta* hydrogen and 3.6 Å for the *para* hydrogen, and angles of 133 and 120°, respectively (Fig. 1). Moreover, a phenyl of the neighbouring Ph_4P^+ cation (**C**) has one *meta* hydrogen and the *para* hydrogens oriented towards the π-system of the orthogonal second phenyl of Ph_4P^+ cation **B**, with C–H···phenyl centroid distances of 3.0 Å for the *meta* hydrogen and 3.8 Å for the *para* hydrogen, and angles of 149 and 112°, respectively. Complementary C–H···π interactions holding the supermolecules together in the structure involve the *meta* hydrogen of one of the phenyls of the included Ph_4P^+ interacting with the π-system of the phenyl ring of symmetry-transformed Ph_4P^+ cation **C** ($-x + 1$, $-y$, $-z + 1$), with a shorter C–H···phenyl centroid distance of 3.2 Å.

The packing diagram for structure **I** shows that pairs of Ph_4P^+ cations form columnar arrays and are arranged in a three-dimensional grid where a pair of calixarenes side-by-side in up–down/zig-zag fashion form channels through the network (Fig. 3).

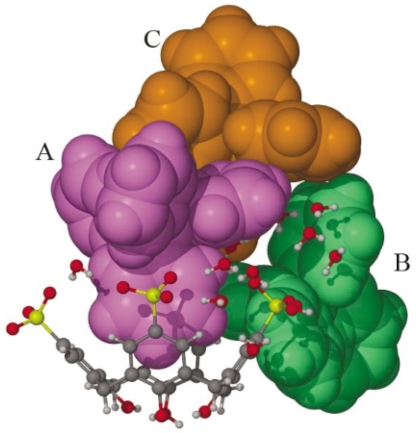

Fig. 1 Asymmetric unit of structure **I** showing the edge-to-face modes of interaction.

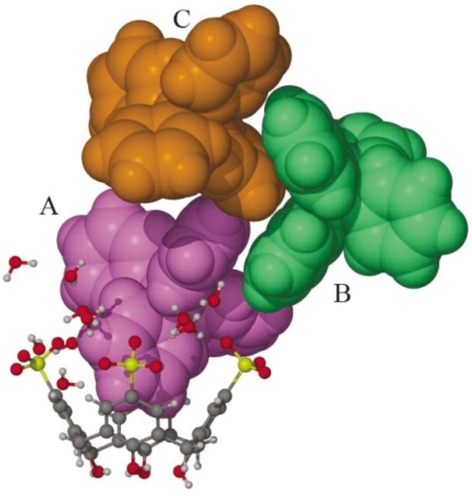

Fig. 2 Asymmetric unit of structure **II** showing the prevalence of offset face-to-face interactions.

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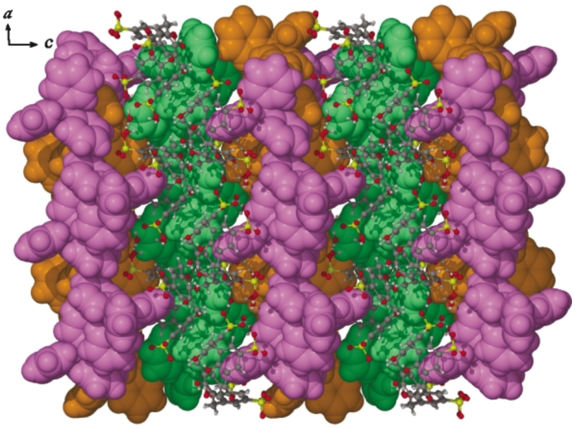

Fig. 3 Cross-section slice (×5) of the packing diagram for structure **I** projected down the *b* axis, showing the channels of calixarenes and water molecules.

The water molecules lie around the sulfonates of the calixarenes as well as clustering between the three Ph_4P^+ cations involved.

In the structure of **II** $\{(C_{28}H_{20}O_{16}S_4)(C_{24}H_{20}P)_3(H_3O)(H_2O)_9\}$, the inclusion of the phenyl from Ph_4P^+ cation **A** takes a different form, this time being slightly tilted and not orthogonal to any of the aromatic rings of the calixarene, with *meta* and *para* hydrogens involved in 'bidentate' interactions to two adjacent aromatic rings of the calixarene. The C–H···aryl(calixarene) centroid distances and the associated angles are as follows: C–H14A···ring 4 centroid 3.0 Å (134°), C–H14A···ring 1 centroid 3.2 Å (124°), C–H15A···ring 3 centroid 2.7 Å (134°) and C–H15A···ring 2 centroid 3.4 Å (117°). In contrast to the structure of **I**, the predominant interactions are the off interactions between neighbouring Ph_4P^+ cations, **A** with **B** and **C** with **B**, having centroid···centroid distances of 4.6 and 3.8 Å, respectively, as illustrated in Fig. 2. In addition, there is also one vertex-to-face (vf) association involving a phenyl from a symmetry-transformed Ph_4P^+ $(x, y - 1, z)$ and one phenyl of the included Ph_4P^+ which has its *para* hydrogen directed into the π-system of the other, with a C–H···phenyl centroid distance of 2.6 Å and an angle of 160°.

The overall structure in **II** is considerably different from that of **I** in having three distinct columns of $\{Ph_4P^+\}_2$ pairs running in all directions, forming a scaffolded network, and also having layers involving intercalation of dissimilar columns. Pockets within the structure are filled with pairs of sulfonated calixarenes and water molecules. It is noteworthy that water molecules have their usual proximity to the sulfonate groups of the calixarenes, with, on this occasion, the water cluster about only one sulfonate filling the interstitial space. It is noteworthy that the disruption of the usual bi-layer arrangement of the *p*-sulfonatocalix[4]arene in **II** is associated with the intercalation of the aryl moieties of the phosphonium cations and water molecules, disrupting the infinite up and down assembly so that the calixarenes associate only as pairs (Fig. 4).

In conclusion, we have established two closely related structures differing only in their included water molecule content, but showing remarkably different arrays. This suggests rich supramolecular/crystal engineering possibilities for materials built up from Ph_4P^+ cations and sulfonatocalix[4]arene anions, with applications also to the larger calixarenes and phosphonium cations with more extended arms, an area we are actively engaged in.

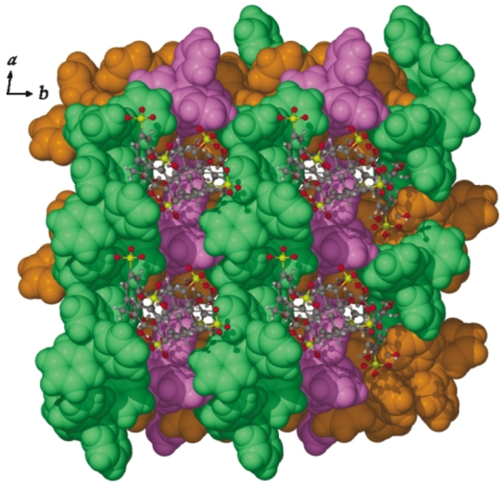

Fig. 4 Packing diagram for structure **II** projected down the *c* axis, showing the 3D grid-like structure wherein the columns of $\{Ph_4P^+\}_2$ pairs form a scaffolding network.

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Notes and references

† All data were measured using a Bruker AXS CCD diffractometer at $T \approx 153$ K with monochromatic Mo-Kα radiation ($\lambda = 0.7107_3$ Å). The structures were solved by direct methods and refined by full matrix least-squares procedures on F^2 using all reflections with SHELX programs and Xseed graphics.

Crystal data for **I**: $(C_{28}H_{20}O_{16}S_4)(C_{24}H_{20}P)_3(H_3O)(H_2O)_{11} \equiv C_{100}H_{105}O_{28}P_3S_4$, $M = 1976$, $a = 13.775(3)$, $b = 18.262(4)$, $c = 21.173(4)$ Å, $\alpha = 79.456(3)$, $\beta = 89.192(3)$, $\gamma = 68.566(3)°$, $V = 4866\ (2)$ Å^3, space group $P\bar{1}$, D_c $(Z = 2) = 1.34_9$ g cm^{-3}; $\mu_{Mo} = 0.23$ cm^{-1}, $2\theta_{max} = 58°$; $N_t = 43\,532$, $N = 23\,209$ ($R_{int} = 0.047$); $R = 0.078$, $R_w = 0.18$ for $N_o = 13\,269$ with $I > 2\sigma(I)$ reflections. For **II**: $(C_{28}H_{20}O_{16}S_4)(C_{24}H_{20}P)_3(H_3O)(H_2O)_9 \equiv C_{100}H_{101}O_{26}P_3S_4$, $M = 1939.9$, $a = 13.562(2)$, $b = 15.255(2)$, $c = 23.895(3)$ Å, $\alpha = 73.796(3)$, $\beta = 87.726(2)$, $\gamma = 85.040(2)°$, $V = 4728.8(11)$ Å^3, space group $P\bar{1}$, D_c $(Z = 2) = 1.36_9$ g cm^{-3}; $\mu_{Mo} = 0.23$ cm^{-1}, $2\theta_{max} = 58°$; $N_t = 43\,574$, $N = 22\,774$ ($R_{int} = 0.033$); $R = 0.066$, $R_w = 0.18$ for $N_o = 13\,062$ with $I > 2\sigma(I)$ reflections. CCDC 231281 and 231282. See http://www.rsc.org/suppdata/cc/b4/b402327g/ for crystallographic data in CIF or other electronic format.

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