

Engineering of porous π -stacked solids using mechanochemistryPeter J. Nichols,^a Colin L. Raston^{*b} and Jonathan W. Steed^{*c}^a School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia^b University of Leeds, Leeds, UK LS2 9JT^c Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS.

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Charge-assisted π -stacking interactions result in the formation of large porous arrays formed from the inclusion of metal tris(phenanthroline) cations into *p*-sulfonatocalix[4]arene anions.

A great deal of work in crystal engineering^{1–3} has focussed on the manipulation, control or prediction of solid state structure of organic^{2,4,5} and organometallic or coordination compounds^{6–9} through hydrogen bonding interactions.¹⁰ Lower in energy than many hydrogen bonds, but now reasonably well understood, are π -stacking interactions of the edge-to-face and face-to-face types.^{11–13} As early as 1989 Gavezzotti and Desiraju were able to classify the structures of a number of aromatic hydrocarbons based on the ratio of carbon to hydrogen and its effect on their mutual π -stacking interactions.¹⁴ More recently a number of studies have shown that limited π -stacked motifs may be predicted and perhaps conserved over a number of related structures. This is particularly true in cases where there is a significant donor–acceptor or ionic component to the stacking interaction.^{15,16} What is most intriguing about π -stacking interactions from a crystal engineering point of view is that such supramolecular ‘bonds’ represent the interaction of two relatively large surfaces (*cf.* the point-like nature of hydrogen bonds). Thus a well-controlled π -stacked system has the potential to command a very great deal of space within a crystal lattice. In this paper we report the initial successful results of our attempts to engineer extended π -stacked arrays based on charge assisted interactions between *p*-sulfonatocalix[4]arene anions (**1**)^{17,18} and metal 1,10-phenanthroline cations.

The molecular cavity in the *p*-sulfonatocalix[4]arene tetra- and penta-anions (**1**^{4–} or **1**^{5–}) is both electron rich and flexible (it is able to alternate between approximate C_{4v} and C_{2v} symmetry while retaining a ‘cone’ conformation).^{17–20} The cleft-shaped C_{2v} conformation is particularly suited to the inclusion of planar aromatic guest species and we reasoned that reaction of $\text{Na}_5\text{-1}$ with transition metal tris(1,10-phenanthroline) dications is likely to result in the formation of a π -stacked motif based on $[\text{M}(\text{phen})_3]^{2+} \cap \mathbf{1}^{n-}$ ($n = 4–5$). This motif should be conserved over a wide variety of structures containing different M and other co-species, particularly solvent molecules (anion **1** is commonly highly hydrated in the solid state²¹). It was found that first row transition metal tris(phen) complexes were extremely readily prepared mechanochemically.^{22,23} Simple grinding together of the appropriate stoichiometric ratio of metal salt (halide, nitrate) and phen gave rapid colour changes indicative of the formation of the desired tris(chelate) complexes. Co-complexes with **1**^{*n*–} were similarly prepared by grinding of the resulting mixture with the calixarene. The mixtures were extracted into aqueous solution in order to prepare single crystals suitable for X-ray crystallographic analysis. Thus grinding of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1,10-phenanthroline resulted in the formation of a reddish solid over a period of *ca.* two minutes. Subsequent grinding with hydrated $\text{Na}_5\text{-1}$ gave rise to a red-pink, water-insoluble mixture. Similarly, dissolution of the mechanochemically generated $[\text{Ni}(\text{phen})_3](\text{NO}_3)_2$ in water followed by addition of aqueous $\text{Na}_5\text{-1}$ gave a pink precipitate. This solid was recrystallised from

water–acetone (4:1) to give a remarkable crystalline solid of formula $[\text{Ni}(\text{phen})_3]_2[\mathbf{1}^{4-}] \cdot n\text{H}_2\text{O}$ (**2**) ($n = \text{ca. } 28$). Under slightly different conditions (small excess of phen) the related $[\text{Na}(\text{H}_2\text{O})_4(\text{phen})][\text{Ni}(\text{phen})_3]_4[\mathbf{1}^{4-}][\mathbf{1}^{5-}] \cdot n\text{H}_2\text{O}$ (**3**) ($n = \text{ca. } 22$) was formed. Complexes **2** and **3** were characterised by X-ray crystallography.[†] Reaction with a variety of metal phen complexes such as $[\text{Fe}(\text{phen})_3]^{2+}$ also gave related products which will be reported separately.

The structure of complex **2** comprises two independent, infinite chains of offset face-to-face π -stacked $[\text{Ni}(\text{phen})_3]^{2+}$ cations propagating in the crystal *a* and *b* directions. The strand running along *b* exhibits interplanar separations of 3.356 and 3.546 Å. The former is comparable to the distance of *ca.* 3.35 Å found in graphite and shorter than the 3.48 Å separation for the direct face-to-face overlap observed for $[\text{Cr}(\text{C}_6\text{H}_6)_2] \cdot \text{C}_6\text{F}_6$.¹⁵ Interplanar separations in the second strand (along *a*) are also short at 3.454 and 3.466 Å and of similar offset to one another, although markedly different to the *b* strand. In the strand running along *b* the independent $[\text{Ni}(\text{phen})_3]^{2+}$ cations are included within the cavities of the *p*-sulfonatocalix[4]arene(4–) anion cavities (Fig. 1) with an edge-to-face arrangement, closest $\text{C}_{\text{phen}} \cdots$ calixarene aryl ring centroid distances 3.600 and 3.739 Å. This interaction is facilitated by the C_2 symmetric ‘pinched cone’ conformation adopted by the calixarene, also noted for water inclusion.²⁰ The *a* strand also exhibits a herringbone type π -stacking intermediate between the edge-on and face-on modes, with the outside of the calixarenes (*cf.* the ‘sandwich herringbone’ structure of pyrene¹⁴). The calixarenes themselves engage in mutual intermolecular face-to-face (sulfonate head to phenolic tail) π -stacking with an interplanar separation of 3.292 Å. This gives the characteristic *p*-sulfonatocalix[4]arene clay-like bilayer packing.^{3,21} The overall result is a trapezoidal grid-like arrangement of π -stacked strands leaving void spaces corresponding to large water-filled channels running along the *b* direction, Fig. 2. The intra-channel water is partially ordered, with most oxygen positions located and being modelled as 50% occupancy. This effectively corresponds to the formation of an extremely large hydrophilic portion of the usual bilayer structure and arises from the

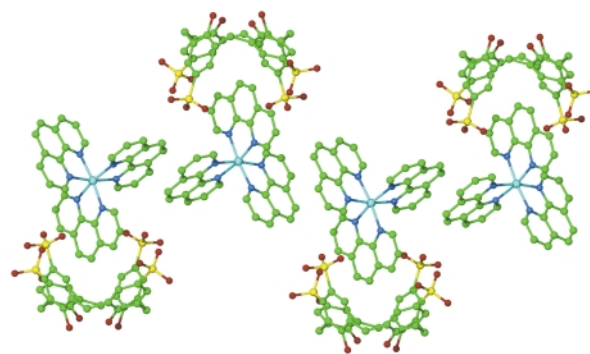


Fig. 1 Infinite π -stacked chain in **2** showing the inclusion of $[\text{Ni}(\text{phen})_3]^{2+}$ cations within the cavity of a *p*-sulfonatocalix[4]arene(4–) anion, in a C_{2v} symmetric conformation.

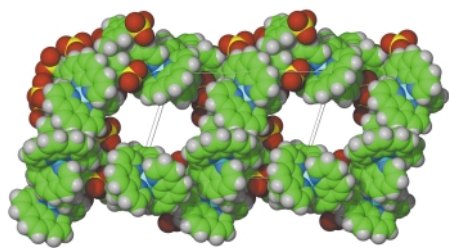


Fig. 2 Crystal packing in **2**. Only one of the two independent $[\text{Ni}(\text{phen})_3]^{2+}$ cations is included within the p -sulfonatocalix[4]arene(4 $-$) anion (crystal b direction). The calixarenes engage in mutual face-to-face π -stacking, while the second chain of $[\text{Ni}(\text{phen})_3]^{2+}$ cations runs along the crystallographic a axis. The result is large water-filled channels of approximate van der Waals dimensions $7.5 \times 10.5 \text{ \AA}$.

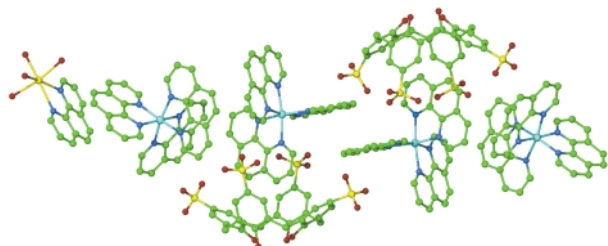


Fig. 3 The $[\text{Na}(\text{phen})(\text{H}_2\text{O})_4][\text{Ni}(\text{phen})_3]_4[p\text{-sulfonatocalix[4]arene(4-)}][p\text{-sulfonatocalix[4]arene(5-)}]$ stacked chains in **3**. The two independent $[\text{Ni}(\text{phen})_3]^{2+}$ cations both form part of the same chain.

inclusion of the second $[\text{Ni}(\text{phen})_3]^{2+}$ cation necessary for charge balance.

The crucial aspect from a crystal engineering perspective is the prediction and conservation of the $[\text{Ni}(\text{phen})_3]^{2+} \cap p\text{-sulfonatocalix[4]arene}(n-)$ motif with its large, accessible π -surface, resulting in π -stacked chain formation. In this system addition of a small excess of the basic phen is sufficient to deprotonate some of the calixarene anions further to give $[\text{Na}(\text{H}_2\text{O})_4(\text{phen})][\text{Ni}(\text{phen})_3]_4[1^{5-}][1^{5-}] \cdot n\text{H}_2\text{O}$ (**3**). Compound **3** displays an entirely novel packing mode for the much studied p -sulfonatocalix[4]arene which is not based on a clay-like bilayer, nor the recently reported spherical or tubular types.²⁴ Each calixarene is almost entirely surrounded by $[\text{Ni}(\text{phen})_3]^{2+}$ cations in order to maximise π -stacking interactions. The core of the structure is again the $[\text{Ni}(\text{phen})_3]^{2+} \cap p\text{-sulfonatocalix[4]arene}(n-)$ motif and again an infinite 'sandwich herringbone'¹⁴ type π -stacked chain is observed, although it is very different to that found in **2**. In this case the included $[\text{Ni}(\text{phen})_3]^{2+}$ cation stacks with a symmetry equivalent of itself on one side and the second independent $[\text{Ni}(\text{phen})_3]^{2+}$ unit on the other (interplanar distances *ca.* 3.50 and 3.59 Å). Thus the two independent $[\text{Ni}(\text{phen})_3]^{2+}$ cations form part of the same chain, which zig-zags across the unit cell body diagonal. The $[\text{Na}(\text{phen})(\text{H}_2\text{O})_4]^+$ cation forms the pivot of the chain at which point the face-to-face π -stacking of the $[\text{Ni}(\text{phen})_3]^{2+}$ cations gives way to a herringbone type edge-to-face interaction. Thus the full chain exhibits an $\cdots\text{ABCCBABCCB}\cdots$ arrangement in which A = $[\text{Na}(\text{phen})(\text{H}_2\text{O})_4]^+$, B = $[\text{Ni}(\text{phen})_3]^{2+}$ and C = $[\text{Ni}(\text{phen})_3]^{2+} \cap p\text{-sulfonatocalix[4]arene}(n-)$, Fig. 3. The water molecules of the $[\text{Na}(\text{phen})(\text{H}_2\text{O})_4]^+$ cation hydrogen bond to calixarene sulfonato functionalities and one solvent water molecule. The result is again large water filled channels running in the crystallographic b direction that are bounded by the interlocking, zig-zag π -stacked chains, Fig. 4. The included water is predominantly ordered with half the oxygen sites being full occupancy and the other half being split across more than one position.

This study has shown that there is a strong solid-state preference for maximising π -stacking interactions and π -surface contact to such an extent that the $[\text{Ni}(\text{phen})_3]^{2+} \cap p\text{-sulfonatocalix[4]arene}(n-)$ motif is conserved over two very different structures. A further $[\text{Fe}(\text{phen})_3]^{2+}$ analogue has also been isolated and will be reported separately. In each case channel structures are a direct and predictable consequence of

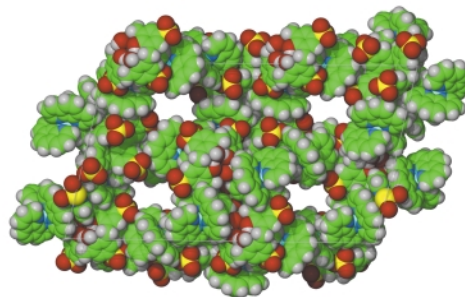


Fig. 4 Water-filled channels in **3**. Approximate channel van der Waals dimensions $4 \times 7 \text{ \AA}$.

the very bulky nature of the crystal synthons. Such new porous materials may prove highly interesting in separation/adsorption applications since the intra-channel interactions are very different and distinct from the forces holding the channel framework together.

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Notes and references

† Crystal data for **2**: $\text{C}_{100}\text{H}_{140}\text{N}_{12}\text{Ni}_2\text{O}_{50}\text{S}_4$, M 2555.90, triclinic, space group $P\bar{1}$, $a = 16.306(3)$, $b = 18.802(4)$, $c = 23.787(5) \text{ \AA}$, $\alpha = 104.84(3)$, $\beta = 104.54(3)$, $\gamma = 98.56(3)^\circ$, $U = 6644(2) \text{ \AA}^3$, $D_c = 1.278 \text{ Mg m}^{-3}$, $Z = 2$, $\mu = 4.32 \text{ cm}^{-1}$, $T = 123(2) \text{ K}$, reflections measured: 117 913, unique data: 32 533, parameters: 1423, $R1 [F^2 > 2\sigma(F^2)]$ 0.1322, $wR2$ (all data) 0.4148. For **3**: $\text{C}_{106}\text{H}_{119.5}\text{N}_{13}\text{Na}_{0.5}\text{Ni}_{2}\text{O}_{39.75}\text{S}_4$, M 2468.80, monoclinic, space group $C2/c$, $a = 51.7470(8)$, $b = 14.8734(3)$, $c = 30.5036(6) \text{ \AA}$, $\beta = 102.440(6)^\circ$, $U = 22 926.0(7) \text{ \AA}^3$, $D_c = 1.431 \text{ Mg m}^{-3}$, $Z = 8$, $\mu = 4.94 \text{ cm}^{-1}$, $T = 123(2) \text{ K}$, reflections measured: 33 241, unique data: 19 118 ($R_{\text{int}} = 0.0573$), parameters: 1652, $R1 [F^2 > 2\sigma(F^2)]$ 0.0739, $wR2$ (all data) 0.2263. CCDC 157786 and 157787. See <http://www.rsc.org/suppdata/cc/b1/b103411c/> for crystallographic data in .cif or other electronic format.

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