

MS34-O2 Supramolecular chemistry of the *p*-carboxylatocalix[4]arenesScott J. Dalgarno¹

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Calixarenes have been used widely in supramolecular chemistry for a variety of reasons, some of which include their conformational versatility and ease of synthetic modification. The *p*-carboxylatocalix[4]arenes (pCO₄[4]s) have received relatively little attention as molecular building blocks, which is surprising as they hold great potential in the formation of both discrete and polymeric metal-organic systems. In recent times we have been exploring the synthesis of pCO₄[4]s in either cone or pinched-cone conformations, simultaneously varying the numbers of upper-rim carboxylic acid groups present at selected positions. These changes have marked effects on the resulting metal-directed assembly, as evidenced by the formation of either coordination polymers or discrete capsules.¹⁻⁴ The talk will outline these developments before moving on to discuss very recent exploration of the synthesis and metal-directed assembly of partial-cone pCO₄[4]s.⁵ In the first result obtained with this new conformer, the divergent nature of the molecule gives rise to an interesting discrete assembly that may itself act as a building block for directed assembly.

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MS34-O3 Structural Layers in High-Z' Molecular CrystalsCarolyn P. Brock¹

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More than 280 organic crystal structures archived in the CSD and having more than four molecules in the asymmetric unit and $R < 0.075$ have been investigated in detail and found to be reliable. A surprising discovery is that approximately 25 – 30% of them include easily recognizable structural layers.

There is no standard definition of a structural layer. Layers are obvious if two-dimensional regions of van der Waals contacts separate more densely packed molecular slabs; such layers are particularly obvious if they include strong intermolecular interactions such as hydrogen bonds. If there is a two-dimensional network of hydrogen bonds then layers can be described even if there is some interpenetration, such as by protruding phenyl rings. Likewise, parallel H-bonded chains are often described as forming a layer.

Layers can also be described if two-dimensional regions have higher approximate local symmetry than does the crystal as a whole. Such layer symmetry, which is often quite exact, is broken by the stacking. It has proved useful to describe such layers using the layer groups tabulated in Volume E of *International Tables*.¹ Some layer groups occur much more frequently than do others.

In some structures composed of stacked layers at least one of the layers is related to the others by rotation about an axis normal to or lying within the layer. Two sets of molecular polytypes have been found in which the same layer is stacked in different ways.

The most unusual structures are those in which two quite different layer types alternate. The H-bonding patterns in the two layers may differ and/or their symmetries may vary. One of the layers may incorporate a solvent molecule or one layer may be enantiomerically pure while the other is racemic.

It seems that these layered structures must provide hints about possible mechanisms of crystal nucleation and growth.

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²Macrae, C. F., *et al. J. Appl. Cryst.*, **2008**, 41, 466 – 470.

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