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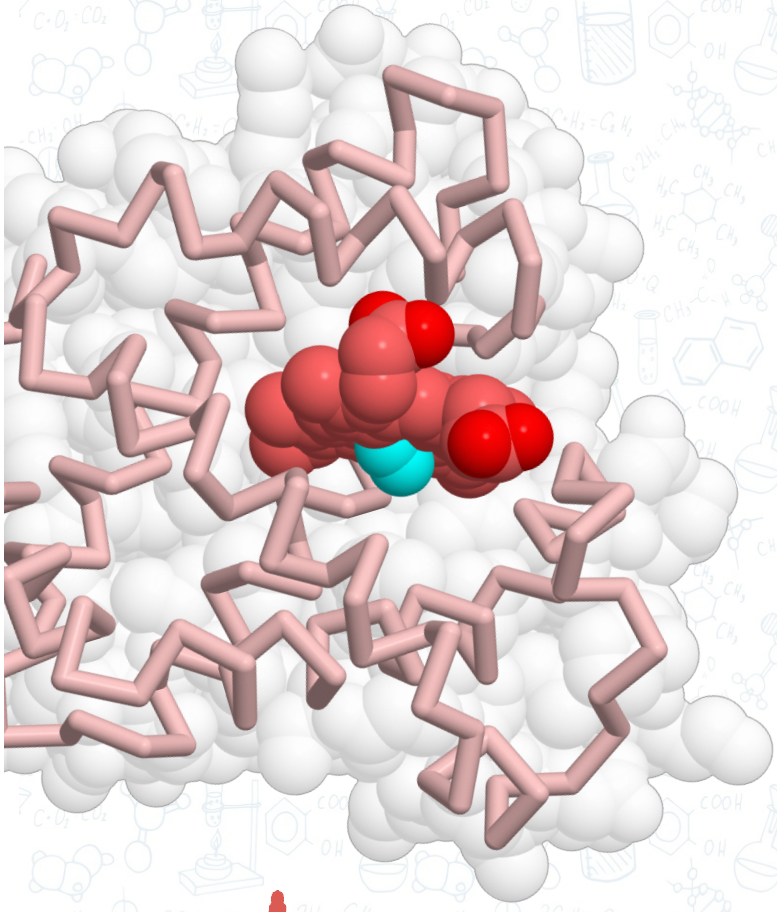

Proceedings

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Painting the Blue Box Violet

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The Blue Box (cyclobis(paraquat-p-phenylene)) is everyone's favourite building block for the make up of supramolecular assemblies. This cage needs no further introduction, being the signature molecule of one of the most recent Nobel prizes, Sir J. Fraser Stoddart. His choice of a blue shade for the depictions of electronpoor aromatics accounts for the curious nickname of the molecule.
What about the violet? As Inorganic Chemists, violet is the colour of iodine species par excellence. For long enough, Iodine has been an off-limits element to pair with the Blue Box in general, accounting to the early reports of its manifest tendency to trigger the opening and eventually reforming of the cage at high temperature, a feature which has been since exploited for the synthesis of a number of mechanically interlocked systems.
What happens in milder conditions is all another story.
Iodide and the Blue Box have a marked tendency to interact to form what we could call Supramolecularly Organized Frameworks. In their simplest form, the one having 4 I^- per Blue Box molecule, porous structures constituted by aligned infinite channels are formed in the solid state. Within these channels small molecules, like solvents' ones (e.g. H_2O, CH_3CN) and even proper supramolecular guests (eg. Naphthalene), can be hosted, with minor to no distortion of the overall structure.
But do a mere 4 I^- per cage allow us to say to have painted the Blue Box Violet? Probably not. Yet fascinating structures are generated by adding more and more iodide to the mix: at present, we consider a Blue Box to be painted for good when it interacts with 14 or even 16 I atoms at a time. The leitmotiv of these higher polyiodide structures is the trapping of the elusive I_5^- anion inside the Box, with formation of infinite polycatenates, where repeating 14 terms supramolecular I rings are encircled by two Blue Boxes at a time, producing fascinating structures such as the one displayed in Figure 1.

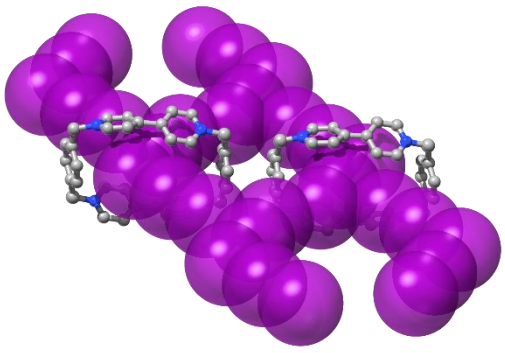

***Figure 1**: I_5^- 14 member link chains interlocked with 2 Blue Boxes, forming ([3]-catenane)$_\infty$ structures in the solid state.*