Self-assembled molecular squares as supramolecular tectons

Shobhana Krishnaswamy¹, Soumyakanta Prusty¹, Daniel Chartrand², Garry Hanan², Dillip Kumar Chand¹
¹Dept. Of Chemistry, Indian Institute Of Technology Madras, Chennai, India, ²Dept. of Chemistry, University of Montreal, Montreal, Canada
E-mail: cy14ipf04@smail.iitm.ac.in

A concentration dependent equilibrating mixture of molecular squares \([\text{Pd}_4(L')_4(L)_4](\text{NO}_3)_8\) and triangles \([\text{Pd}_3(L')_3(L)_3](\text{NO}_3)_6\) was obtained when cis-protected Pd(II) units \([\text{Pd}(L')(\text{NO}_3)_2]\) \((L' = \text{tmeda}, [1] 2,2'-\text{bpy}, [2] \text{phen})\) were combined in turn with 4,4'-bipyridine \((L)\) in water. The addition of AgOTs to the mixture led to a shift in the equilibrium, resulting in the disappearance of the triangles and exclusive formation of the squares in case of all the complexes. The crystal structures of the molecular squares \([\text{Pd}_4(L')_4(L)_4](\text{OT}_s)_8\) revealed a pair of tosylate anions encapsulated in the hydrophobic cavity of the square and the presence of several water molecules outside the cavity. The complexes \([\text{Pd}_4(\text{bpy})_4(L)_4](\text{OT}_s)_8\) and \([\text{Pd}_4(\text{phen})_4(L)_4](\text{OT}_s)_8\) exhibited solvatomorphism and yielded two crystalline forms each, respectively. The cationic units in these crystals associate through \(n\ldots n\) stacking interactions between the aromatic rings of the four bpy/phen units and form either one-dimensional arrays or two-dimensional layers. The formation of a one-dimensional array occurs when one pair of bpy/phen units of the square engage in \(n\ldots n\) stacking interactions with the tosylate anions instead of other adjacent bpy/phen units. Therefore, the cations in the bpy and phen squares may be considered as ‘tectons’ which contain four supramolecular ‘synthons’ apiece, i.e. the cis-protecting units bpy/phen. The knowledge of common patterns of molecular association and identification of supramolecular synthons in these structures can help in the crystal engineering of coordination compounds with desired solid-state properties/functions.


Keywords: crystal engineering, Pd(II) molecular square, solvatomorphism