Poster Presentation

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Self-assembled molecular squares as supramolecular tectons

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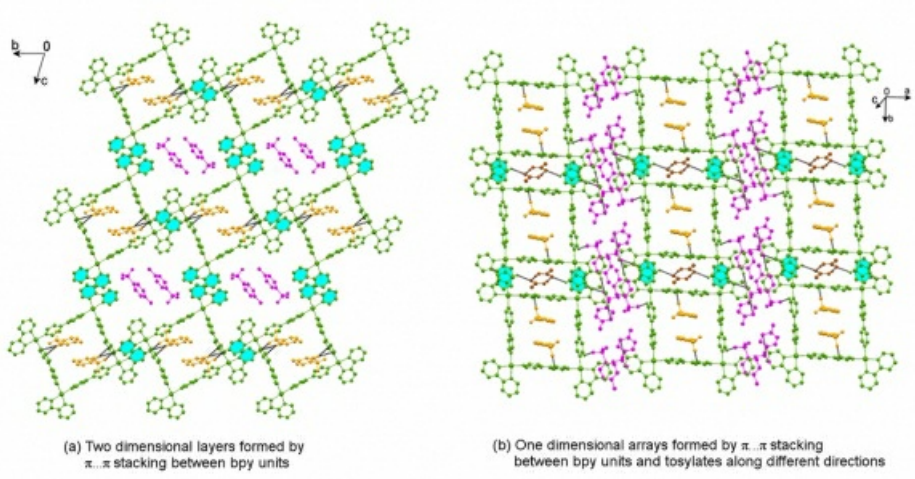
A concentration dependent equilibrating mixture of molecular squares [Pd4(L')4(L)4](NO3)8 and triangles [Pd3(L')3(L)3](NO3)6 was obtained when cis-protected Pd(II) units [Pd(L')(NO3)2] (L' = tmeda,[1] 2,2'-bpy,[2] phen) were combined in turn with 4,4'-bipyridine (L) in water. The addition of AgOTs to 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 [Pd4(L')4(L)4](OTs)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 [Pd4(bpy)4(L)4](OTs)8 and [Pd4(phen)4(L)4] (OTs)8 exhibited solvatomorphism and yielded two crystalline forms each, respectively. The cationic units in these crystals associate through π…π 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 π…π 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.

[1] Uehara, K. et al. (2007). Inorg. Chem., 46, 2563-2570.
[2] Fujita, M. et al. (1996). Chem. Commun., 1535-1536.



(a) Two dimensional layers formed by π…π stacking between bpy units

(b) One dimensional arrays formed by π…π stacking between bpy units and tosylates along different directions

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