Invited Lecture

Do supramolecular synthons predetermine crystal packing of giant supramolecules?

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Supramolecules, or giant metallasupramolecular cages, are formed upon coordination of metal cations and organic ligands and possess various molecular structures [1]. Thanks to the hollow structure many of them are successfully used as molecular containers, and current research focuses mainly on exploring host-guest interactions aiming to use them for effective inclusion-release cycle as well as for the immobilization of various guests [1]. However, preferable intermolecular interactions are formed not only inside metallasupramolecular cages, but also should influence to some extent the type and efficiency of a molecular packing.

Our research is related to a special class of supramolecules based on coinage metal salts and organometallic complex pentaphosphaferrocenes $[Cp^RFe(\eta^5\text{-}P_5)]$ in which R = alkyl or aryl can be varied according to the desired properties. Metal cations coordinate to rigid and chemically stable pentagonal P_5 rings of the organometallic ligand and give rise to hollow inorganic cores reaching 2.2-3.2 nm [2]. A series of supramolecules with 70-, 80- and 90 non-carbon atoms in the inorganic cores, $[(CuX)_{20-n}(Cp^*Fe(\eta^5\text{-}P_5))_{12-x}]$ and $[(Cp^*Fe(\eta^5\text{-}P_5))_{12}(CuX)_{25}(MeCN)_{10}]$ (x = 0, 1; n = 0-4, X = F, Cl, Br, I) possess fullerene topology and nearly spherical shape [3]. Beside them, a series of cages like 110-vertex nano-capsule $[Cp^*FeP_5]@[\{Cp^*FeP_5\}_9\{CuCl\}_{10}]$ or 99-vertex closed architecture $C_{60}@[Cu_{26}Cl_{26}(H_2O)_2\{Cp^*FeP_5\}_{13}(CH_3CN)_9]$ have fullerene-like topology [2]. Various CuI derivatives demonstrate non-fullerene cage topology [4, 5].

What determines the crystal packing of these giant molecules? The outer surface in the supramolecules in all cases is confined by the organic cyclopentadienyl ligands Cp^R. When R is small, π–π interactions between Cp* or Cp^{Et} ligands and σ–π interactions between terminal or bridging halides X and Cp^R ligands are enabled. Our study showed that these directed X–π and/or π–π intermolecular interactions occur from structure to structure, and their geometrical characteristics are reproducible, allowing us to formulate existence of unique supramolecular synthons (Fig. 1), which support molecular packing. However, do these directed interactions predetermine the packing in the presence of hundreds of non-specific intermolecular interactions that involve not only surface of the giant supramolecules but also numerous solvent molecules?

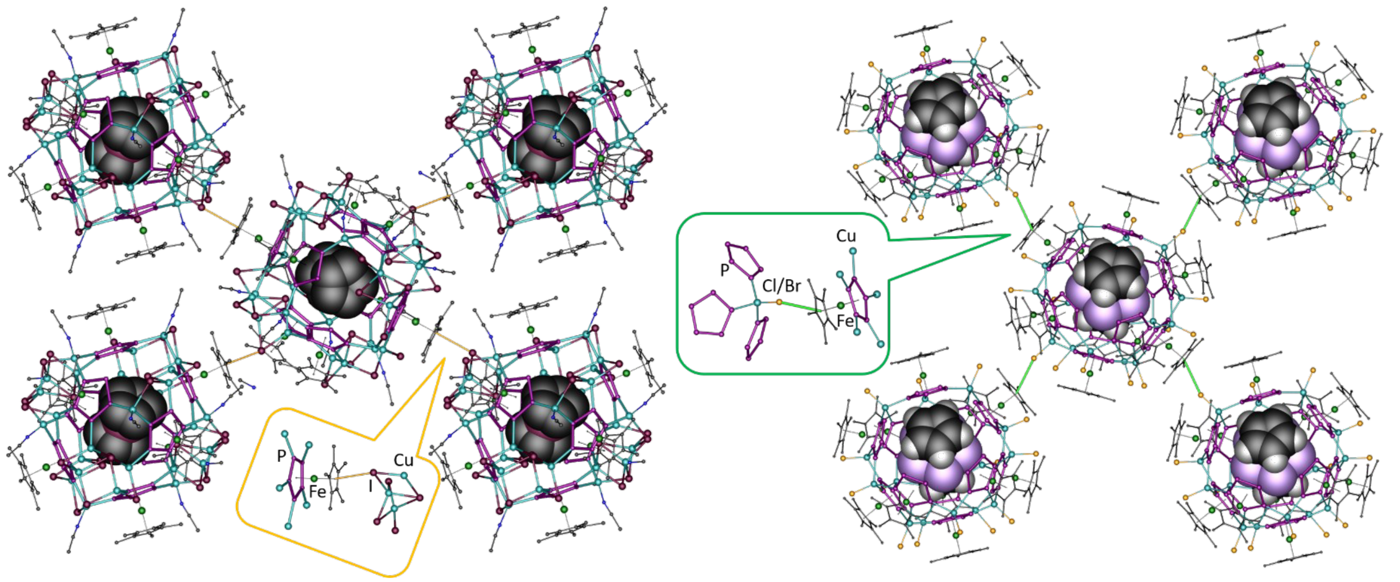

Figure 1. Supramolecular synthons in crystal structures of different supramolecules.

[1] Virovets, A. V., Peresypkina, E., Scheer, M. (2021). *Chem. Rev.* **121**, 14485.

[2] Peresypkina, E., Virovets, A.V., Scheer, M. (2021). *Coord. Chem. Rev.* **446**:213995.

[3] Brake, H., Peresypkina, E., Heindl, C., Virovets, A.V., Kremer, W., Scheer, M. (2019) Chem. Sci., **10**, 2940.

[4] Peresypkina, E., Heindl, C., Virovets, A., Brake, H., Mädl, E., Scheer, M. (2018). *Chem.-Eur. J.*, **24**, 2503.

[5] Schwarzmaier, C., Schindler, A., Heindl, C., Scheuermayer, S., Peresypkina, E.V., Virovets, A.V., et al (2013). *Angew. Chem.-Int. Ed.*, **52**, 10896.