

Transformative Cages and Luminous Chains: Functional Systems through Subcomponent Self-assembly

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The materials that we depend on rely upon ever-increasing structural complexity for their function. The use of chemical self-assembly as a synthetic technique can simplify materials preparation by shifting intellectual effort away from designing molecules, and towards the design of *chemical systems* that are capable of self-assembling in such a way as to express desired materials properties and functions. Below are shown the subcomponent precursors and structures of three of products that can form functional constituents of these systems (Figure 1).

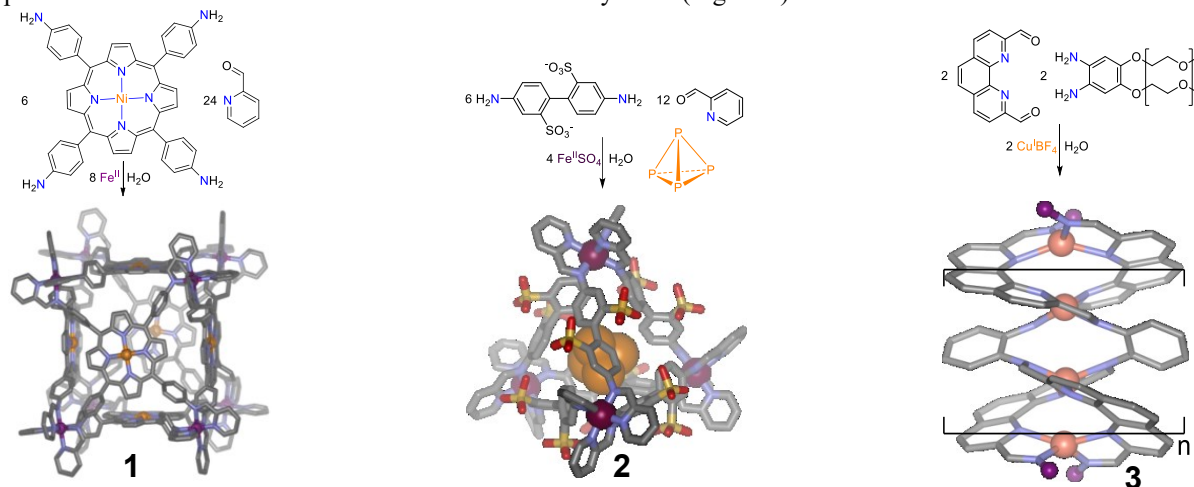


Figure 1. Fe^{II}_8 cubic cage **1**,¹ Fe^{II}_4 tetrahedral cage **2**,² and electroluminescent Cu^{I}_n double-helical polymer **3**³

Current challenges involve inducing multiple structures to form in parallel,⁴ such that they may act in concert to achieve a catalytic goal,⁵ our techniques allow entry into the emerging field of *systems chemistry*.⁶ Functional systems that we have recently developed include a fuel-controlled self-assembly process (Figure 2)⁷ and a triphasic sorting system, wherein three guests are selectively encapsulated within three cages, each in turn soluble in only one of three mutually-immiscible phases (water and two different ionic liquids).⁸

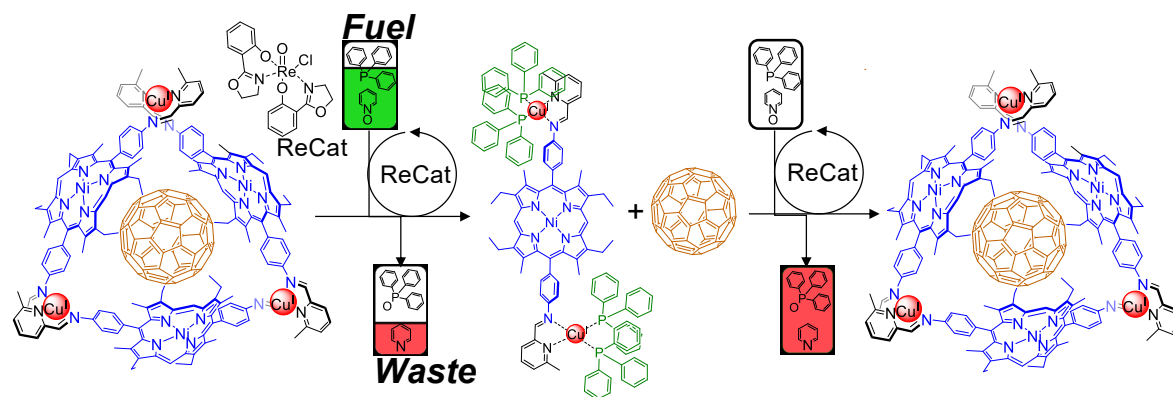


Figure 2. A system wherein the duration of release of a guest (C_{60}) can be programmed by the amount of fuel (PPh_3) present

- (1) Meng, W.; Breiner, B.; Rissanen, K.; Thoburn, J. D.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 3479.
- (2) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* **2009**, *324*, 1697.
- (3) de Hatten, X.; Asil, D.; Friend, R. H.; Nitschke, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 19170.
- (4) Jiménez, A.; Bilbeisi, R. A.; Ronson, T. K.; Zarra, S.; Woodhead, C.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 4556.
- (5) Salles, A. G.; Zarra, S.; Turner, R. M.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 17052.
- (6) Nitschke, J. R. *Nature* **2009**, *462*, 736.
- (7) Wood, C. S.; Browne, C.; Wood, D. M.; Nitschke, J. R. *ACS Cent. Sci.* **2015**, *1*, 504.
- (8) Grommet, A. B.; Bolliger, J. L.; Browne, C.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 15100.