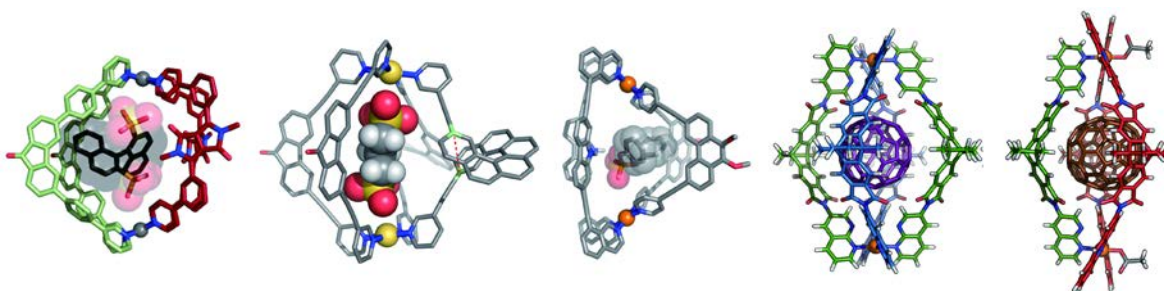

Non-statistical Assembly of Functional Coordination Cages

Guido H. Clever

Fakultät für Chemie und Chemische Biologie, Technische Universität Dortmund, Germany.

Contact: guido.clever@tu-dortmund.de

Advanced self-assembly strategies enable the targeted synthesis of supramolecular systems and materials with increasing structural and functional complexity. We use bis-monodentate ligands, reacting with transition metal cations such as Pd(II) to coordination compounds showing a broad range of topologies from small Pd₂L₄ cages, their interpenetrated dimers, rings of various size up to large Pd₂₄L₄₈ spheres.¹ We introduce stimuli-responsive behaviour triggered by small molecules or light leading to, e.g., the modulation of guest affinity² or complete structural reorganization.³ In order to combine different functionalities in the same metallosupramolecular assembly, we develop non-statistical assembly strategies to obtain heteroleptic cages with defined structures and composition. In particular, the “shape complementary assembly” (SCA) and “coordination sphere engineering” (CSE) approaches will be presented.⁴ Examples of functional heteroleptic cages include hosts that show guest-modulated circularly polarized luminescence (CPL) based on chirality transfer, phosphate ester binding through endohedral hydrogen bond donors and fullerene encapsulation,⁵ followed by confinement-controlled reactivity, e.g. long-term C₆₀ radical anion stabilization.⁶



Examples of heteroleptic coordination cage structures with guest-modulated chiroptical emission (left), phosphate binding (middle) and fullerene uptake (right).

1. S. Pullen, G. H. Clever, *Acc. Chem. Res.* **2018**, *51*, 3052.2.
2. H. Lee, J. Tessarolo, D. Langbehn, A. Baksi, R. Herges, G. H. Clever, *J. Am. Chem. Soc.* **2022**, *144*, DOI: 10.1021/jacs.1c12011.
3. M. Han, Y. Luo, B. Damaschke, L. Gómez, X. Ribas, A. Jose, P. Peretzki, M. Seibt, G. H. Clever, *Angew. Chem. Int. Ed.* **2016**, *55*, 445.
4. S. Pullen, J. Tessarolo, G. H. Clever, *Chem. Sci.* **2021**, *12*, 7269.
5. B. Chen, J. J. Holstein, A. Platzek, L. Schneider, K. Wu, G. H. Clever, *Chem. Sci.* **2022**, *13*, 1829.
6. S. Hasegawa, S. L. Meichsner, J. J. Holstein, A. Baksi, M. Kasanmascheff, G. H. Clever, *J. Am. Chem. Soc.* **2021**, *143*, 9718.

KEYWORDS: Coordination Cages, Self-Assembly, Host-Guest Chemistry, Chirality