From Heteroleptic Coordination Cages to Complex Molecular Systems

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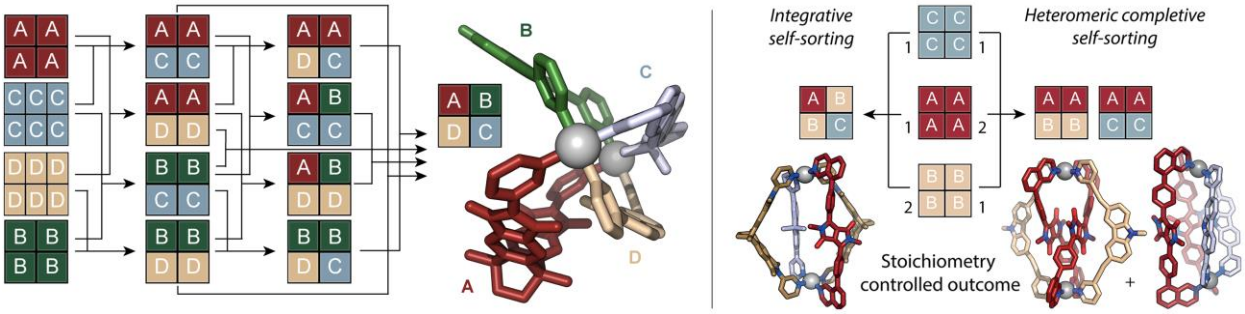
Advanced self-assembly strategies enable the targeted synthesis of supramolecular systems and materials with increasing structural and functional complexity. We react bis-monodentate ligands with transition metal cations to coordination compounds showing a broad range of topologies. To combine different functionalities in the same metallosupramolecular structure, we develop non-statistical assembly strategies such as “shape complementary assembly” (SCA) and “coordination sphere engineering” (CSE).[1]

We then implement various functionalities, with a focus on multi-chromophore systems.[2] These are studied then, e.g., for light-induced charge separation, vectorial excitation transport and as potential photo-redox catalysts. By combining chiral with emissive ligands, heteroleptic cages showing guest-modulated circularly polarized luminescence (CPL) were obtained.[3] We further introduce stimuli-responsive behaviour in photochromic cages[4] allowing to control guest affinity[5] and established a light-fueled dissipative system.[6] Cages capable of fullerene encapsulation[7] give rise to confinement-controlled reactivity, such as long-term C_{60} radical anion stabilization.[8]

Recently, we mastered the non-statistical and robust assembly of dinuclear Pd(II) cages containing four chemically different ligands [Pd_2ABCD].[9] The collected results now set the stage for looking into ‘complex systems’ behaviour by following the stimuli-responsive population and evolution of co-existing species in mixtures.[10] In this direction, we study multi-step cage interconversions, guest-binding/release cascades and propagation of chiral information.



References:
[1]Pullen, S.; Tessarolo, J.; Clever, G. H. *Chem. Sci.* **2021**, *12*, 7269, https://doi.org/10.1039/D1SC01226F
[2]Regeni, I.; Chowdhury, R.; Terlinden, K.; Horiuchi, S.; Holstein, J. J.; Feldmann, S.; Clever, G. H. *Angew. Chem. Int. Ed.* **2023**, *e202308288*, https://doi.org/10.1002/anie.202308288
[3]Wu, K.; Tessarolo, J.; Baksi, A.; Clever, G. H. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205725, https://doi.org/10.1002/anie.202205725
[4]Benchimol, E.; Tessarolo, J.; Clever, G. H. *Nat. Chem.* **2024**, https://doi.org/10.1038/s41557-023-01387-8 (Perspective Article)
[5]Li, R.-J.; Tessarolo, J.; Lee, H.; Clever, G. H. *J. Am. Chem. Soc.* **2021**, *143*, 3865, https://doi.org/10.1021/jacs.0c12188
[6]Lee, H.; Tessarolo, J.; Langbehn, D.; Baksi, A.; Herges, R.; Clever, G. H. *J. Am. Chem. Soc.* **2022**, *144*, 3099, https://doi.org/10.1021/jacs.1c12011
[7]Chen, B.; Holstein, J. J.; Platzek, A.; Schneider, L.; Wu, K.; Clever, G. H. *Chem. Sci.* **2022**, *13*, 1829, https://doi.org/10.1039/D1SC06931D
[8]Hasegawa, S.; Meichsner, S. L.; Holstein, J. J.; Baksi, A.; Kasanmascheff, M.; Clever, G. H. *J. Am. Chem. Soc.* **2021**, *143*, 9718, https://doi.org/10.1021/jacs.1c02860
[9]Wu, K.; Benchimol, E.; Baksi, A.; Clever, G.H. *Nat. Chem.* **2024**, https://doi.org/10.1038/s41557-023-01415-7
[10]Benchimol, E.; Regeni, I.; Zhang, B.; Kabiri, M.; Holstein, J. J.; Clever, G. H. *J. Am. Chem. Soc.* **2024**, *accepted*.