BRIDGING SUPRAMOLECULAR ORGANOMETALLIC CHEMISTRY AND POROUS ARCHITECTURES

Shashi Kumar, Rajeev C. Nishad, and Arnab Rit

Department of Chemistry, IIT Madras, Chennai – 600036, India

N-Heterocyclic carbene (NHC)-based supramolecular chemistry lags well behind the classical Werner-type (N-/O-donor) systems, primarily due to strong, rigid M-C_{NHC} bonds that hinder the reversible bond breaking/making, which are essential for self-correction and adaptive reorganization.[1] Leveraging the uniquely labile yet robust Ag^{I}-C_{NHC} linkage, we have progressively evolved the ligand designs with coinage metals, transitioning from rigid supramolecular organometallic complexes (SOCs) to dynamic equilibrating assemblies and extended porous architectures (Fig. 1).[2-3] Accordingly, (benz)imidazole-derived tris-NHC ligands demonstrated that topological constraints and mixed NHC environments can override the typical $[M_n(\mathbf{L})_2]$ sandwich motif, enabling higher-order connectivity. Along the same line, a bis-NHC ligand combining benzimidazolylidene with a freely rotating imidazolylidene donor introduced the first C-donor system that display temperature- and concentration-dependent equilibria between tri- and tetranuclear SOCs, showing that tailored ligand topology and metal choice can mitigate the kinetic inertia of M-C_{NHC} bonds.[3a] Modification of the ligand with a 1,2,4-triazolylidene donor further slowed this equilibrium, enabling complete external stimuli control for the first selective isolation of both tri- and tetranuclear assemblies from the same ligand and metal combination using C-donor NHCs.[3b] Finally, exploiting the latent backbone N-donor of the 1,2,4-triazolylidene with flexible Cu^{I}-ion, a discrete SOC was converted into a crystalline, permanently porous 3D framework.[3c] These advances outline a coherent evolution in NHC ligand design, propelling coinage-metal supramolecular chemistry from rigid cages through stimulus-responsive equilibria to NHC-governed porous materials.

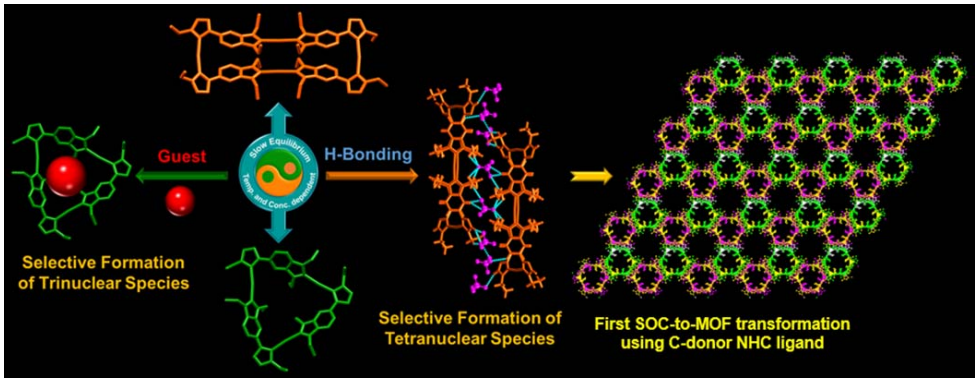

Figure 1. Coinage metal NHC complexes – spanning from SOCs to porous architecture.

---

[1] a) N. Sinha, F. E. Hahn, *Acc. Chem. Res.* **2017**, *50*, 2167–2184. b) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502–518. c) b) M. M. Gan, J. Q. Liu, L. Zhang, Y. Y. Wang, F. E. Hahn, Y. F. Han, *Chem. Rev.* **2018**, *118*, 9587–9641.

[2] R. C. Nishad, A. Rit, *Chem. Eur. J.* **2021**, *27*, 594–599.

[3] R. C. Nishad, S. Kumar, A. Rit, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206788. b) S. Kumar, A. Rit, *Angew. Chem. Int. Ed.* **2025**, *64*, e202505558. c) S. Kumar, P. Velmurugan, A. Rit, *Angew. Chem. Int. Ed.* **2025**, e202514207.