Orientational self-sorting in octahedral palladium cages: scope and limitations of the cis-rule

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Palladium-based metal-organic cages (MOCs) have been widely studied and have applications in medicinal chemistry as well as in catalysis. The understanding of their self-assembly is therefore of great importance. Ditopic N-donor ligands L and Pd(II) precursors form a variety of MOCs of the general formula $[Pd_nL_{2n}]^{2n+}$ in which the bend angle of L, for the most part, dictates the geometry of the cage. Using various low-symmetry heteroditopic ligands L with a bend angle of 90°, hexanuclear $[Pd_6L_{12}]^{12+}$ metal-organic cages (MOCs) were synthesized with $[Pd(CH_3CN)_4(BF_4)_{12}]$ in acetonitrile. Due to the low symmetry of the ligands many isomers can potentially be formed. The obtained structures provide additional evidence for orientational self-sorting[1,2]: Out of 112 possible isomers for $[Pd_6L_{12}]^{12+}$, we show the one isomer with *cis*-configuration at all Pd-centers is thermodynamically favored (Fig. 1a and 1b). Various characterization methods including ^{1}H NMR, ^{13}C NMR, COSY, NOESY, DOSY and single crystal XRD structure elucidation confirm the formation of a single isomer. Using ligands with different coordination vector ratios and donor groups (pyridyl-, triazolyl- and imidazolyl-donor) we discuss the scope and limitations of the aforementioned selectivity. A kinetically trapped product was obtained from imidazolyl-ligand **L5** (Fig. 1c). Furthermore, we provide a geometrical explanation using a coordination vector model for the experimentally observed *cis*-isomers.

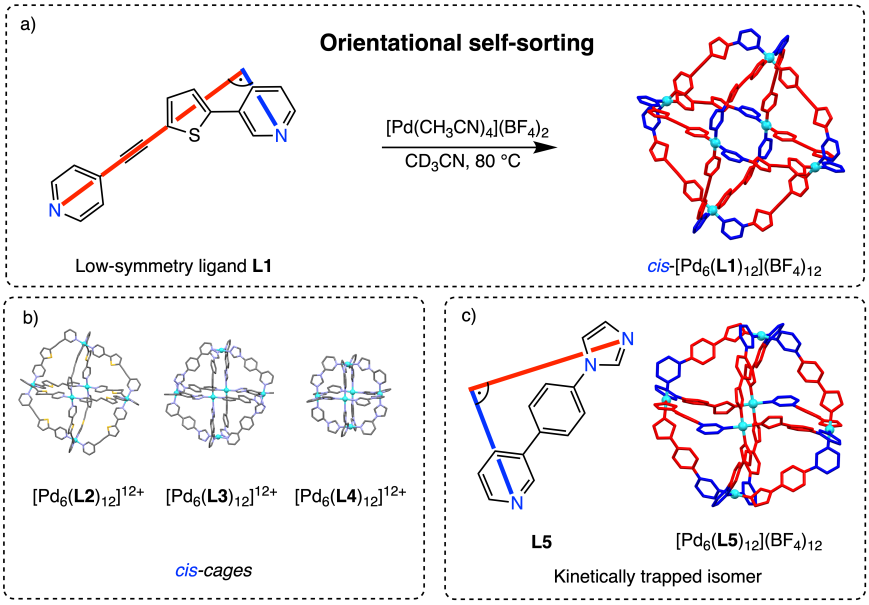

Fig. 1 Orientational self-sorting in $[Pd_6L_{12}]^{12+}$ cages using low-symmetry ligands. a+b) The thermodynamic isomers with *cis*-configuration at every Pd-center are obtained exclusively. c) A kinetically trapped isomer with *cis*-configuration at only 2 Pd-centers.

[1] Ru-jin Li, Andrew Tarzia, Victor Posligua, Kim E. Jelfs, Nicolas Sanchez, Adam Marcus, Ananya Baksi, Guido H. Clever, Farzaneh Fadaei-Tirani and Kay Severin, *Chem. Sci.*, **2022**, 13, 11912-11917.

[2] Ru-jin Li, Adam Marcus, Farzaneh Fadaei-Tirani and Kay Severin, *Chem. Commun.*, **2021**, 57, 10023-10026.