Poster Presentation

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Coordination-Driven self-assembly of Pd_8L_4 nanobarrels: Synthesis, Structure & Application

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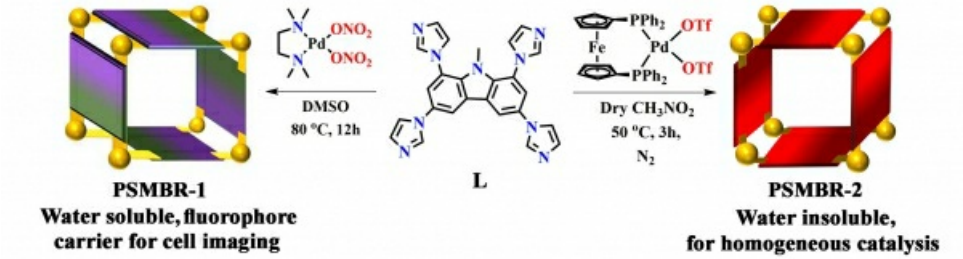
Coordination-driven self-assembly has evolved as one of the most successful methods for the construction of discrete supramolecular architectures of well-defined size, shape and functionality. A huge number of aesthetically elegant two- and three-dimensional architectures have been reported so far which have found applications in host-guest study, stabilisation of reactive species, supramolecular catalysis, drug delivery, sensing etc. The high directionality and reversible nature of certain metal-ligand bonds allow pre-designing of sophisticated molecular architectures which can be successfully obtained by 'error corrections' via a thermodynamically controlled self-assembly process. Construction of such molecular architectures uses symmetric and rigid building blocks which strictly preserves their geometrical coding and thus finally determines the fate of the self-assembly. Pyridyl-based donors have been extensively used due to their well-behaved coordination with transition metal ions. Interestingly, imidazole based donors remained almost unexplored for such purpose mainly due to the rotational flexibility of imidazole moieties owing to the lack of Pi-electron delocalization with the aromatic backbone, which makes pre-designing an architecture extremely difficult.

To explore the imidazole-based ligands in coordination-driven self-assembly, we have designed a novel 'less-symmetric' tetraimidazole donor L based on carbazole backbone. Single crystal structure of L shows that the presence of the N-Me group causes heavy twisting of the nearby imidazole moieties with respect to the other set of imidazoles. The 1:2 stoichiometric self-assembly of L with [cis-(tmeda)Pd(NO3)2] in DMSO at 80 ºC produced a water soluble single product which was characterised by 1H NMR, 1H-1H COSY and DOSY spectroscopy. ESI-MS spectra confirmed the formation of a Pd8L4 assembly, viz. PSMBR-1. SCXRD analysis of the coronene encapsulated complex of PSMBR-1 gave more insights on the sophisticated tetrafacial open barrel architecture of PSMBR-1. Such molecular barrels are rare in literature, although having great advantage due to their wide apertures compared to the close-shell architectures of most of the reported assemblies. The centrosymmetric molecule can encapsulate two aromatic guest molecules inside its hydrophobic cavity and was found to be efficiently encapsulating polyaromatic hydrocarbons (PAHs) in aqueous media. Interestingly, when the perylene encapsulated PSMBR-1 complex was incubated to the HeLa cells for fluorescence imaging, brilliant blue emission was observed from the cytoplasm part of the cells without altering the cell morphology. FACS analysis by using propidium iodide as dead cell marker showed no significant toxicity of the encapsulated complex, thus establishing the 'proof of concept' of transportation of water insoluble analyte inside live cells by using a water soluble molecular nano-vessel.

L also formed a water insoluble tetrafacial barrel (PSMBR-2) by the self-assembly with cis-[(dppf)Pd(OTf)2] (dppf=diphenylphosphino ferrocene) which interestingly has more symmetrical architecture, as evidenced from the SCXRD analysis. The formation of the symmetrical barrel is driven by the steric hindrance between the bulky phenyl groups of the nearby dppf moieties. In addition, PSMBR-2 showed good catalytic efficiency for intramolecular hetero Diels-Alder reaction of Benzyledene barbituric acid derivatives in nitromethane solvent

[1] Chakrabarty, R. et. al. (2011). Chem. Rev. 111, 6810-6918.
[2] Fujita, M. et. al. (2005). Acc. Chem. Res. 38, 369-378.
[3] Roy, B. et. al. (2015). J. Am. Chem. Soc. 137, 11916-11919.



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