Covalent post-assembly modification of tetrazine-edged self-assembled molecular capsules

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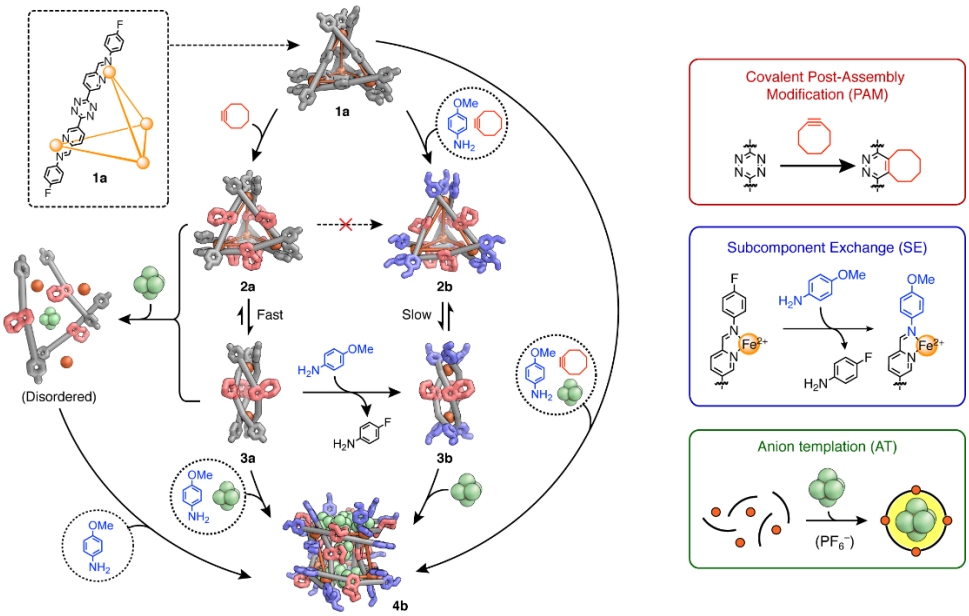
Covalent post-assembly modification (PAM) provides a versatile means of functionalizing and stabilizing self-assembled metal-organic complexes.[1] The tetrazine unit exhibits high reactivity for inverse electron-demand Diels-Alder (IEDDA) reactions, making it an ideal functional handle for performing PAM. We have recently incorporated this moiety into the panels of both an $Fe^{II}_4L_6$ tetrahedron and an $Fe^{II}_8L_{12}$ cube. The PAM of individual complexes can be accomplished quantitatively with suitable dienophiles such as cyclooctynes or norbornadienes (NBD), providing a means of tagging molecules of interest to supramolecular systems.[2] We have also been able to construct a synthetic reaction cascade from sequential PAM reactions of a tetrazine-edged cube and a maleimide-functionalized tetrahedron *via* an IEDDA-normal electron-demand Diels-Alder sequence. Initiating this cascade with 2-octadecyl-NBD leads to selective alkylation of the tetrahedron upon cascade completion, with the increased lipophilicity driving this tetrahedron into a non-polar phase, allowing the transport of cargo (an encapsulated anion) across a phase boundary in response to a chemical signal.[3] PAM can also alter the sterics and electronics of ligands to engender distinct structural changes in their parent complexes. We employed this phenomenon to trigger diverse structural transformations of a tetrazine-edged tetrahedron into a pyridazine-edged tetrahedron, helicate, or barrel, with the addition of other co-stimuli (an electron-rich aniline or a templating anion) allowing us to control the dominant product at equilibrium. We postulate this could serve as the basis for switching the functions expressed within such a system in the future.[4]



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