

βCyclodextrin-assisted intervalence charge transfer in mixed-valent [2]rotaxane complexes having metal centres linked by interrupted π -electron systems

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The study of intramolecular electron transfer in redox active binuclear transition metal complexes is of great fundamental importance and is an area of contemporary research interest. Though there are many reports on the role of bridging ligands (BL) in tuning metal–metal interactions and intramolecular electron transfers in bi/polynuclear metal complexes, till date very little is known about the role of bridging ligands (BL) trapped in cyclodextrin cavities. With proper design it is possible to synthesise supramolecular species in which a cyclic molecular head, e.g. cyclodextrin, is threaded by a linear hydrocarbon chain bearing bulky metal complexes of different oxidation states as stoppers that prevent the complex from dissociating into cyclic and linear molecular components. This approach can enable us to investigate the effect of cyclodextrin inclusion of BL and thus the effect of nonbonding interaction on Intervalence Charge Transfer (IVCT) and metal–metal coupling. In this paper, we report syntheses of [2]rotaxane containing Fe^{II} and Ru^{III} complexes as stoppers, β CD as cyclic molecular head and 4,4'-bipyridyl derivatives (1,2-bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (tmbp)) as BL. It is possible to synthesise [2]rotaxane by self-assembly route (scheme 1). Inclusion of a bridging ligand in the β CD cavity has initiated optical electron transfer from $\text{Fe}(\text{II})$ to $\text{Ru}(\text{III})$, a feature not observed in the absence of inclusion.

