

An Efficient Molecular Tool with Ferrocene Backbone: Discriminating Fe³⁺ from Fe²⁺ in Aqueous Media

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Two novel molecular probes with ferrocene backbone have been designed and synthesized for the 1st time and they were subsequently found capable of distinguishing Fe³⁺ and Fe²⁺ ion in aqueous media. The discrimination of both the oxidation states (II/III) of iron by these receptors can be established either from a striking shift in redox potential (**1**: $\Delta E_{1/2} = \sim 90$ mV and **2**: $\Delta E_{1/2} = \sim 59$ mV) for Fe²⁺ ion or from UV-vis absorption studies (using light-absorption ratio variation approach (LARVA)). The probable binding modes of these receptors with Fe²⁺ have also been suggested on the basis of the ¹H NMR spectroscopic titration, ESI-MS, Job's plot and computational (DFT) studies along with electrochemical and spectro-photochemical data. The single crystal X-ray diffraction analysis of **1** revealed that its solid state structure was stabilized *via* intermolecular C–H/O and O–H/N hydrogen bonds and by C–H/ π interactions. Interestingly, detail theoretical calculations (DFT) indicated that hydroxymethyl (-CH₂OH) group attached to naphthalene unit plays a pivotal role in sensing Fe^{2+/3+} ion selectively and in the stabilization of **2** in unusual eclipsed configuration through C–H \cdots O type hydrogen bonding. More in **Organometallics 2017**
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