

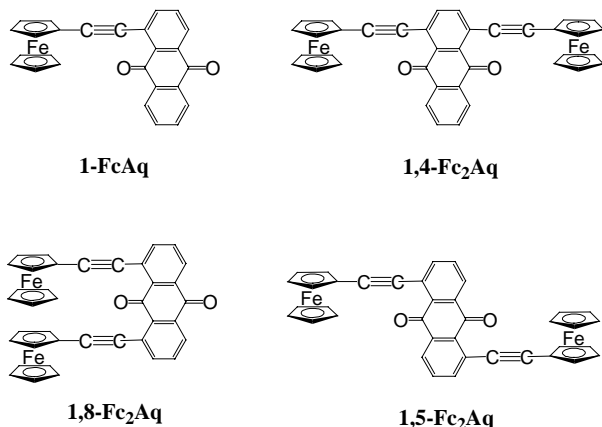
**Protonation-induced Intramolecular Electron Transfer and Electrochemical Properties in the Ferrocene-quinone  $\pi$ -Conjugated Donor-acceptor System**

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Recent attention has been focused on electronic communication between redox molecular units linked by a  $\pi$ -conjugated chain. In the direct combination of a donor (D) and an acceptor (A) either of which redox potential can be changed by external stimulation, the control of the reversible electron transfer would be possible if the donor and acceptor levels can be close enough to conduct strong electronic interaction.

Quinonoid compounds are representative acceptor molecules of which redox properties can be readily controlled by external perturbation, such as protonation and solvation. Also, the redox-conjugated systems involving ferrocene units showing a fast redox response have been systematically investigated. From these points of view, we considered it intriguing to investigate a system in which D (ferrocene) and A

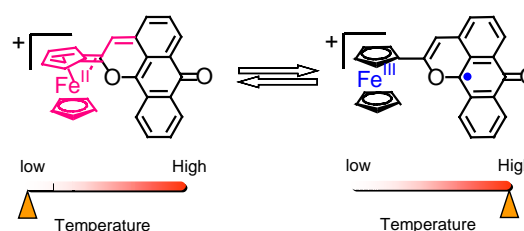


(quinone) molecules are combined by a  $\pi$ -conjugated linker and the A (quinone) undergoes proton-coupled redox reactions.

In the present research, we focused on the creation of a novel  $\pi$ -conjugated D-A system with multiple functionalities, involving ethynylene-bridged ferrocene-anthraquinone complexes with a variation of substitution position and/or the different number of D and A units such as, 1-ferrocenylethynylantraquinone (**1-FcAq**), 1,4-bis(ferrocenylethynyl)anthraquinone (**1,4-Fc<sub>2</sub>Aq**), 1,8-bis(ferrocenylethynyl)anthraquinone (**1,8-Fc<sub>2</sub>Aq**) and 1,5-bis(ferrocenylethynyl)anthraquinone (**1,5-Fc<sub>2</sub>Aq**). Actually, protonation-induced intramolecular electron transfer occurs in all **FcAq** complexes[1-2], but the structures of the protonated complexes depend on several factors in the structure of the original complexes and in the nature of matrix (Scheme 1)[1-4].

These are the first series of functional molecules exhibiting protonation-induced complete and reversible structural and magnetic alteration. We will report details of preparation methods and their electrochemical

properties.



**Figure 1.** Protonated structure in the solid state with a structural phase transition.

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