

How Good is Clathrochelate Framework in Facilitating Long-Range Electron-Transfer? Case Study of the Ferrocenylboron-Capped Iron(II) Clathrochelate

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A potential long-range electronic coupling between two apical ferrocenyl substituents in the clathrochelate molecule $FeDm_3(BFc)_2$ (where Dm^{2-} is dimethylglyoximate dianion) was studied using the electrochemical and the spectroelectrochemical methods with a low ion-pairing ability TBAF $\{(NBu_4)(B(C_6F_5)_4)\}$ electrolyte. Experimental data are suggestive of a rather poor ability of the quasiaromatic polyazomethine clathrochelate framework to facilitate an intramolecular long-distance electron transfer. Experimental observations were correlated with the theoretical results obtained by Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations.

Keywords: Macrocyclic compounds, clathrochelates, ferrocene, DFT calculations, electrochemistry, spectroelectrochemistry, long-range metal-metal coupling.

Насколько хороша клатрохелатная структура для облегчения переноса электронов на большие расстояния? Исследование ферроценилборатного клатрохелата железа(II)

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Потенциальное дальнее электронное взаимодействие между двумя апикальными ферроценильными заместителями в молекуле клатрохелата $FeDm_3(BFc)_2$ (где Dm^{2-} – диметилглиоксиматный дианион) было изучено электрохимическими и спектроскопическими методами исследования с использованием $(NBu_4)(B(C_6F_5)_4)$ в качестве электролита, обладающего низкой способностью к образованию ионных пар. Экспериментальные данные указывают на достаточно низкую способность квазиароматического полиазометинового клатрохелатного остова облегчить внутримолекулярный перенос электронов на большие расстояния. Экспериментальные наблюдения были сопоставлены с теоретическими результатами, полученными с использованием методов стационарной (DFT) и нестационарной (TDDFT) теории функционала плотности.

Ключевые слова: Макроциклические соединения, клатрохелаты, ферроцен, теория функционала плотности, электрохимия, спектроскопическая химия, дальнее металл-металл взаимодействие.

Introduction

Clathrochelates^[1,2] belong to the class of metal complexes with an encapsulated metal ion that have the prospective applications in hydrogen production, as single-molecule magnets, molecular switches, *et al.*^[2] The electronic structure of clathrochelate molecules can be easily tuned up by the ribbed substituents in the chelating fragments of their cage frameworks, by an encapsulated metal ion, and the functionalizing groups at their apical positions as well.^[2] An ability to alter the electronic properties of the clathrochelate molecules, as well as the stability of the macropolycyclic cages even when they undergo the redox reactions, make these molecules the ideal objects for studying outer-sphere electron transfer (ET) between the metalcenters. An ability to transfer an electron along a three-fold molecular C_3 -pseudoaxis of a clathrochelate framework is a critical property for prospective application of the polynuclear clathrochelates as molecular wires. The redox-active groups at the apical positions of a quasiaromatic cage framework can be used to probe the ET properties of the corresponding apically functionalized clathrochelates. We have recently studied a series of the hybrid porphyrinoclathrochelates in which two porphyrin macrocycles are positioned in their apical capping fragments and are connected to a macrobicyclic framework by cross-linking with Lewis-acidic hafnium or zirconium(IV) ions.^[3] It was found that their porphyrin-centered oxidation processes are separated by approximately 100 mV in DCM/0.05M TFAB system. Unfortunately, spectroelectrochemical experiments for these systems were rather inconclusive and did not allow us to probe a long-range electronic coupling between two apical porphyrin centers facilitated by a quasiaromatic clathrochelate framework. Therefore, in this work, we studied the redox properties of a diferrocenyl-containing macrobicyclic system, *bis*-ferrocenylboron-capped iron(II) *tris*-dimethylglyoximate clathrochelate, $\text{FeDm}_3(\text{BFc})_2$ (Chart 1).

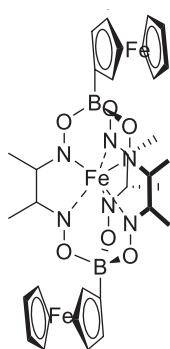


Chart 1. Chemical drawing of the molecule $\text{FeDm}_3(\text{BFc})_2$.

Experimental

Materials. All commercial reagents were ACS grade and were used without their further purification. Dichloromethane (DCM) was dried with CaH_2 . The $\text{FeDm}_3(\text{BFc})_2$ complex was prepared and purified as described elsewhere.^[4]

Instrumentation. All UV-Vis data were obtained on a Jasco V-670 spectrophotometer at room temperature. Electrochemical

measurements were conducted using a CHI-620C electrochemical analyzer using the three-electrode scheme. The three electrodes were a platinum working, a platinum auxiliary, and a Ag/AgCl reference electrode. A solution of 0.05 M tetrakis(pentafluorophenyl) borate (TFAB) in DCM was used in all electrochemical experiments. All redox potentials were referenced to FcH/FcH^+ couple using decamethylferrocene (Me_{10}Fc) as the internal standard. The spectroelectrochemical data were collected using a custom-made 1 mm cell, one platinum mesh working electrode, a platinum auxiliary, and a Ag/AgCl reference electrode. A 0.15 M solution of TFAB in DCM was used in spectroelectrochemical experiments. Chemical titrations were done with a solution of ~ 0.036 M of Nitrozonium Borofluorate (NOBF_4); added in 0.5–5 μL increments.

Computational details. All calculations were performed using the Gaussian 09^[5] software package running under Linux OS. Molecular orbital contributions were determined from single-point calculations using the QMForge program.^[6] The DFT and TDDFT calculations were conducted using the B3LYP exchange-correlation functional.^[7] Full-electron Wachter's basis set^[8] was used for iron and 6-311G(d) basis set^[9] was used for all other atoms. In all calculations, solvation effects were modelled using the polarizable continuum model (PCM)^[10] and DCM as a solvent. Frequencies were calculated for all optimized geometries in order to ensure that final geometries represent a minimum on the potential energy surface. TDDFT calculations were conducted for the first 80 excited states to ensure that all charge transfer (CT) and π - π^* transitions of interest were accounted for.

Results and Discussion

It was realized during the last decade that the study of the long-range metal-metal coupling in poly(ferrocenyl)-containing systems requires an elimination of the ion-pairing effect between the redox-active species under investigation and an electrolyte used in electrochemical experiments.^[11] The earlier-described electrochemical studies of $\text{FeDm}_3(\text{BFc})_2$ complex are not suitable for careful evaluation of such metal-metal coupling because these experiments have been performed using $(\text{Bu}_4\text{N})(\text{BF}_4)$ as an electrolyte that is known to possess a relatively strong ion-pairing ability.^[4] In this work, we used DCM/0.05M TFAB system for the electrochemical studies in order to suppress an ion-pairing effect. The measured cyclic voltammetry (CV) and differential pulse voltammetry (DPV) data for $\text{FeDm}_3(\text{BFc})_2$ complex are shown in Figure 1. Both CV and DPV data suggest an occurrence of two quasireversible oxidation processes. Based on the electrochemical current intensity, the first process at -180 mV (*vs* Fc/Fc^+ couple) was estimated to be two-electron in nature, while the second oxidation at approximately 1000 mV is a one-electron redox process. Based on the potential values, the first oxidation wave was assigned to an oxidation of the apical ferrocenyl groups, while the second redox couple belongs to the metal-centered oxidation $\text{Fe}^{2+/3+}$ process within a cage framework. No reduction processes were observed in the tested electrochemical window. Careful analysis of DPV data on the first and second redox processes for the $\text{FeDm}_3(\text{BFc})_2$ complex is indicative a rather broad wave in the case of the first oxidation as compared with that of the second redox-process. Since such a broadening can be associated with the different oxidation potentials for the terminal ferrocenyl groups in the molecule $\text{FeDm}_3(\text{BFc})_2$, we performed a deconvolution analysis of the first oxidation wave (Figure 1).

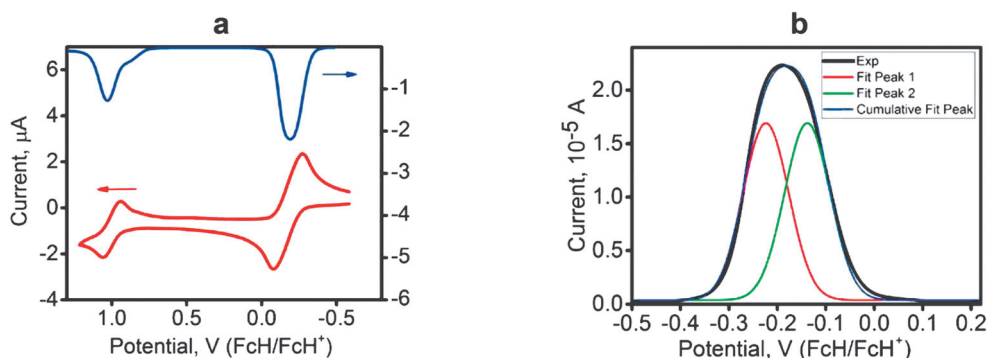


Figure 1. CV (on bottom) and DPV (on top) curves for the clathrochelate $\text{FeDm}_3(\text{BFc})_2$ in DCM/0.05 M TFAB system (a) and a deconvolution analysis of its first oxidation wave on the DPV voltammogram (b).

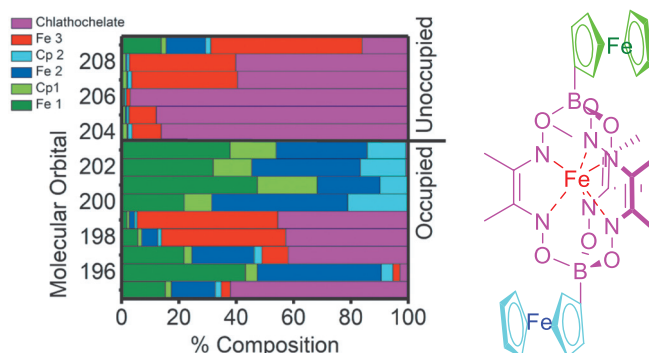


Figure 2. B3LYP-predicted compositions of the frontier molecular orbitals of the $\text{FeDm}_3(\text{BFc})_2$ complex.

Its performed deconvolution evidenced the presence of the possible electronic coupling between these two redox-active centers of the $\text{FeDm}_3(\text{BFc})_2$ complex with their individual oxidation potentials at -140 and -220 mV.

The above assignments of the electrochemically observed redox couples for the $\text{FeDm}_3(\text{BFc})_2$ complex were further confirmed by the Density Functional Theory calculations. B3LYP exchange-correlation functional was used because it correctly predicts the orbital energies, their compositions, and the nature of the excited states in the ferrocenyl-containing systems.^[12] Indeed, the DFT-predicted HOMO and HOMO-3 for the $\text{FeDm}_3(\text{BFc})_2$ complex are delocalized over two ferrocenyl substituents, while the predominant clathrochelate-based orbitals have the lower energies (Figures 2 and 3). HOMO and HOMO-1 are almost

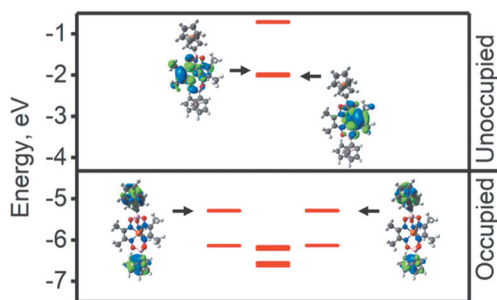


Figure 3. B3LYP-predicted energy diagram and the frontier molecular orbitals of the $\text{FeDm}_3(\text{BFc})_2$ complex.

degenerated in energy. The DFT-predicted LUMO has a predominant clathrochelate-based character and, thus, one might expect to observe several low-energy predominantly metal(Fc)-to-ligand charge transfer (MLCT) bands having the major HOMO–HOMO-2 \rightarrow LUMO contributions. Indeed, the TDDFT-predicted UV-Vis spectrum of $\text{FeDm}_3(\text{BFc})_2$ was in an excellent agreement with its experimental spectrum. Although several MLCT bands were predicted by the TDDFT calculations in a low-energy region, the TDDFT-predicted UV-Vis spectrum of the $\text{FeDm}_3(\text{BFc})_2$ complex (Figure 4) contains the predominant MLCT $\text{Fe}(\text{clathrochelate}) \rightarrow \pi^*(\text{clathrochelate})$ bands in the range 370–380 nm.

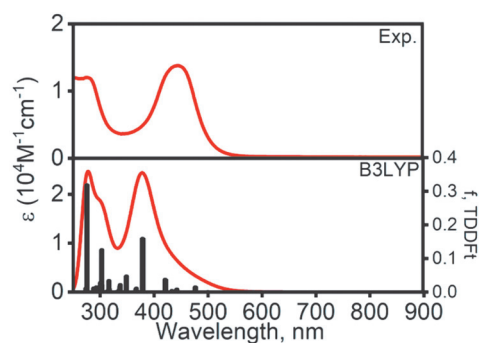


Figure 4. Comparison between the experimental (on top) and TDDFT-predicted (on bottom) UV-Vis spectra of the $\text{FeDm}_3(\text{BFc})_2$ complex.

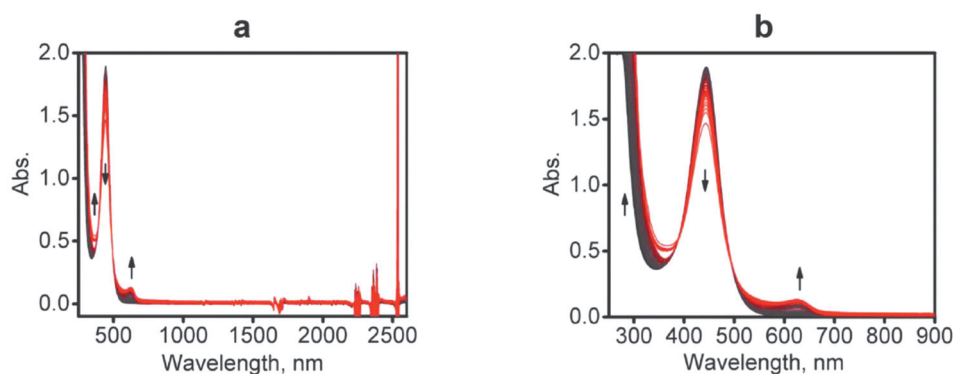


Figure 5. Stepwise oxidation of the $\text{FeDm}_3(\text{BFc})_2$ complex with nitrozonium tetrafluoroborate in DCM solution: the full-range spectra in the range 250–2650 nm (a) and their visible-range fragments (b).

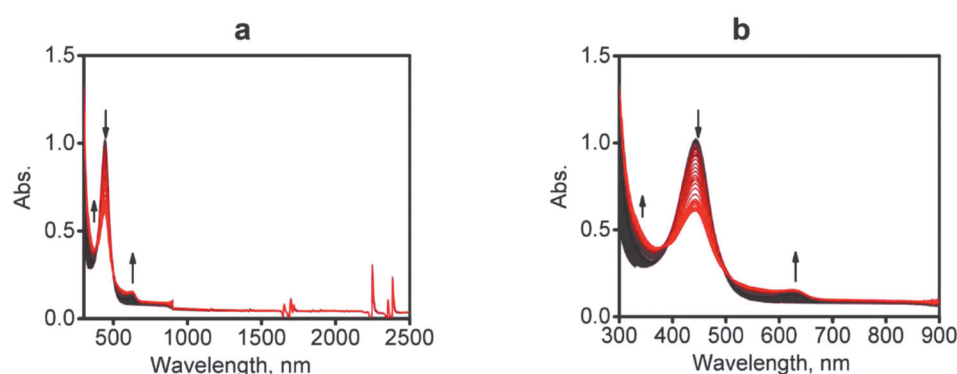


Figure 6. Stepwise oxidation of the $\text{FeDm}_3(\text{BFc})_2$ complex under spectroelectrochemical conditions in DCM/0.15M TFAB system: the full-range spectra between 250 and 2500 nm (a) and their visible-range fragments (b).

A rather small (~ 80 mV) separation between two oxidation waves for the clathrochelate $\text{FeDm}_3(\text{BFc})_2$ in DCM/0.05M TFAB system cannot be viewed as a proof of the long-range electronic communication in this molecule and, therefore, we performed its stepwise oxidation under chemical and spectroelectrochemical conditions (Figures 5 and 6). The results of both the chemical and electrochemical oxidation experiments were found to be consistent with each other. Indeed, in the visible range upon an oxidation of the $\text{FeDm}_3(\text{BFc})_2$ complex, an intensity of the strong absorption band at 443 nm goes down, while a new band at approximately 625 nm appears. The presence of a clathrochelate-centered MLCT band at 443 nm in an oxidized form of the $\text{FeDm}_3(\text{BFc})_2$ complex suggests a removal of electron from its ferrocenyl group. This is consistent with an appearance of the classical ferricinium transition band at approximately 625 nm.^[13] More importantly, we did not observe a formation of very characteristic and intense intervalence CT band expected for the class II or the class III (in the Robin-Day classification)^[14] mixed-valence compounds in the 1000–2500 nm range. So, both the chemical and electrochemical oxidations of the $\text{FeDm}_3(\text{BFc})_2$ complex cause a simultaneous oxidation of its two apical ferrocenyl groups, thus suggesting a rather poor ability of a given clathrochelate quasiaromatic framework to provide an ET pathway for a long-range metal–metal coupling.

Conclusions

In conclusion, we probed a potential long-range metal–metal coupling between two apical ferrocene groups in $\text{FeDm}_3(\text{BFc})_2$ complex using electrochemical and spectroelectrochemical methods in TBAF electrolyte with low-pairing ability. The electrochemical, spectroelectrochemical, and chemical oxidation data suggest a rather poor ability of clathrochelate cage framework to facilitate a long-distance ET because two terminal ferrocenyl groups undergo simultaneous oxidation. Experimental observations were compared with the theoretical results obtained using DFT and TDDFT calculations.

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