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RESEARCH ARTICLE

Computational study of topological effects on intramolecular electron transfer in mixed-valence compounds

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The constrained density functional theory (CDFT) was used to investigate the topological effects on intramolecular electron transfer processes that have been reported in previous experimental work [*Inorg. Chem.*, 1997, *36* (22), pp 5037–5049]. The computation mainly focused on three isomers of diferrocenylbenzenes (ortho, para, and meta) and 5-substituted derivatives of m-diferrocencylbenzenes with *R* = NH_2, Cl, CH_3, CN, NO_2, $N(CH_3)_3^{3+}$, and N_2^+. The influence of a third group *R*' (*R*' = NH_2 and N_2^+) was introduced to the ortho and para isomers. The calculations were compared with the experimental results. The relation between the substituted functional groups and the effectiveness of intramolecular electron transfer was discussed on the basis of CDFT computational results.

1 Introduction

There are continuous interests in molecular mixed-valence systems involving ferrocene moieties due to the effective electronic communication between different metal centers of the compound and the resulting unique optoelectronic properties upon photoexcitation [1–10]. According to an old classification scheme proposed by Robin and Day [11], three types of mixed-valence compounds exist depending on the degree of charge delocalization or the extent of interactions between the donor and acceptor sites. Class I compounds exhibit little or no donor-acceptor interactions, whereas Class III compounds have large electronic couplings and exhibit extensive charge delocalization. Class II compounds fall into the intermediate regime between I and III. An intervalence electron transfer process in a Class II and III complex is typically ultrafast, exhibiting a characteristic metal-to-metal charge-transfer (MMCT) band in the near-infrared region. The latter is often used as an optical probe to extract the electronic coupling element V_{ab} between the donor and acceptor states according to Hush formula.

In many situations a mixed-valence system consists of a donor, an acceptor, and a bridging unit that connects them. The donor/acceptor site typically contains a transition metal center that is surrounded by some organic ligands. The ferrocenium/ferrocene redox couple is an archetypal example of a class of metallocene couples that has proven exceptionally useful for understanding intramolecular electron transfer. The relatively strong electronic coupling between the donor and acceptor states is primarily determined by two contributing factors: (i) direct overlap of the orbitals of the two metal centers (i.e., through-space interactions) and (ii) metal-ligand-metal overlap that may involve σ or π metal-ligand bonds (i.e., through-bond interactions). When the metal centers are separated by a sufficiently long distance, the contribution from the first factor will be minimal, whereas the second contribution becomes predominant, which may be readily varied by the specific ligand structure and metal-ligand bonding interactions [8–10,12–25]. A question arises on whether other spatial arrangement might also affect the electronic communication between the two metal centers.

In a previous study [26], we carried out a computational investigation to examine the bridge-mediated intervalence transfer processes for various ferrocene-bridge-ferrocene model systems. Employing the constrained density functional theory (CDFT), we calculated the electronic coupling elements between the electron donor and acceptor states for these systems, and thus quantified the relationship between the property of the bridge linkage and the electronic communication of the overall system. A practical criterion of classifying the mixed-valence compounds was suggested by gauging the computational results with the experimental observations, where it was found that for compounds with calculated H_{ab} ~ 1 kcal/mol in CH_2Cl_2 their voltammetric responses were along the borderline of Class I/II complexes in the Robin-Day classification. Based on this result, the intervalence characteristics of unknown compounds could be predicted from the CDFT calculations.

In the present paper, we report a computational study of the possible topological effects on the intramolecular electron transfer processes, which was inspired by the previous experimental work of Patoux et al. [27] Specifically, we have carried out CDFT calculations on the electronic couplings of diferrocenylbenzenes with ortho, meta, and para arrangement, and 5-substituted derivatives of m-diferrocenylbenzenes with *R* = NH_2, Cl, CH_3, CN, NO_2, $N(CH_3)_3^{3+}$, and N_2^+. This list is arranged more or less in the

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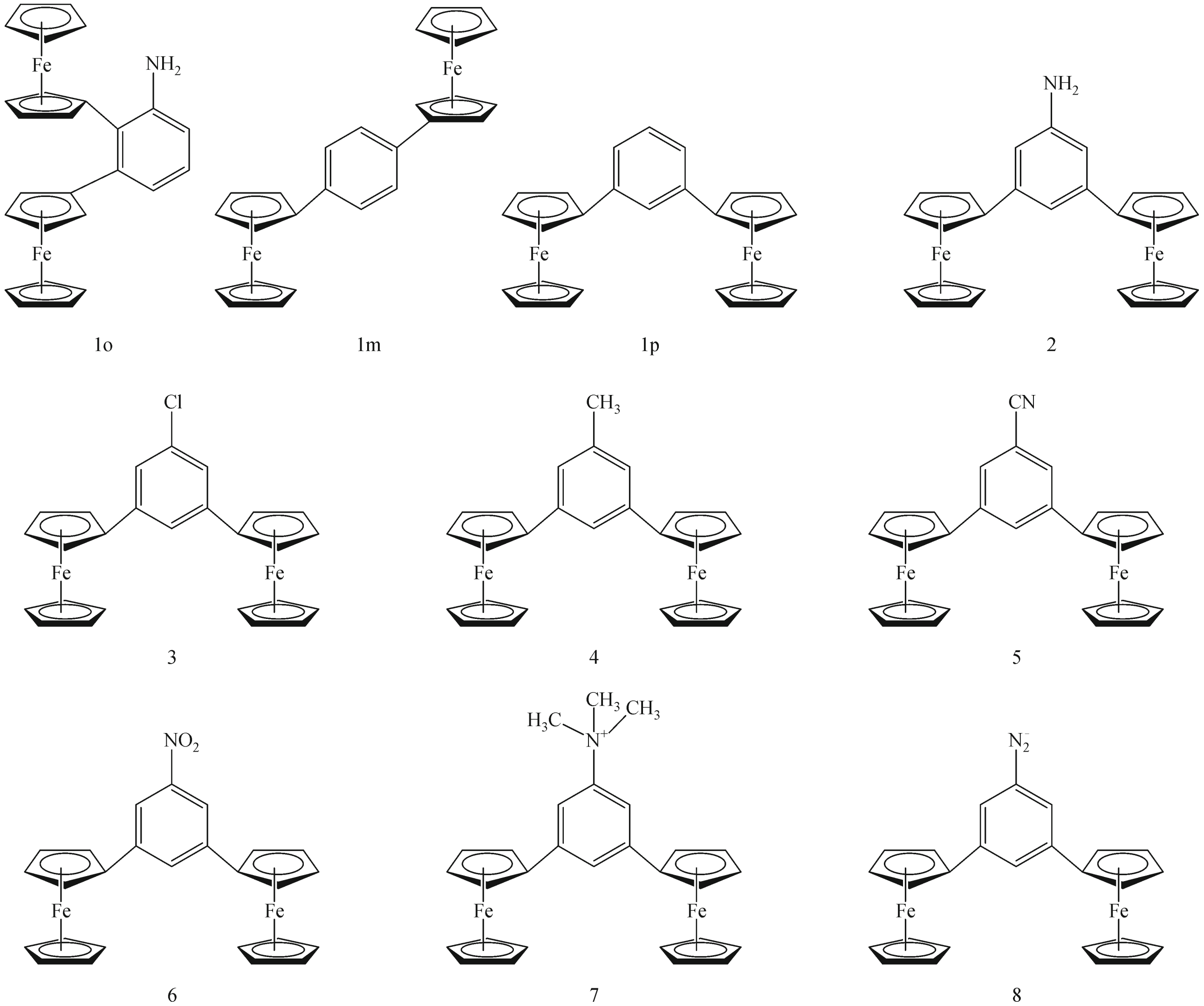
order of increasing Hammet parameters, i.e., from strong donor to strong acceptors. The primary focus is on three isomers and different derivatives of meta molecule, and additional results will be presented with a third group *R*' (*R*' = NH_2 and N_2^+) introduced to ortho and para molecules. In the next section we first describe briefly the models and the computational methods employed in our work. Then we will present the results and the detailed analysis on the intramolecular electronic coupling/communication by comparing some results with the experimental ones. In the conclusion we discuss the implications of our computational study in future experimental studies.

2 Models and computational methods

The computations were carried out on model compounds depicted in Scheme 1: diferrocenylbenzenes with ortho, meta, and para connection (compounds 1o, 1m, 1p) and 5-substituted derivatives of m-diferrocenylbenzenes with *R* = NH_2 (2), Cl (3), CH_3 (4), CN (5), NO_2 (6), $N(CH_3)_3^{3+}$ (7), and N_2^+ (8). Two computational approaches were employed in this work. The standard density functional theory (DFT) was used to optimize the structures and to obtain the equilibrium properties of the mixed-valence complexes as shown in Scheme 1. The constrained density functional theory (CDFT) [28–34] was used to define (approximately) the donor/acceptor diabatic states and to calculate the electronic coupling matrix element (or transfer integral) for the underlying intervalence transfer [35]. This calculation was carried for +1 charge counterpart of each model complex. That is, if the original complex is neutral, the calculation was performed on the +1 cation. If, on the other hand, the original compound has a charge. This charge number increases +1 in the CDFT calculation. This way the intervalence electron transfer from



Scheme 1 1o 1p 1m 2 3 4 5 6 7 8

the donor state (Fe^{2+}) to the acceptor state (Fe^{3+}) is modeled.

The DFT calculations were performed using the quantum chemical programs Gaussian 09 [36] NWCHEM [37], whereas the CDFT calculations were performed with a modified version of the quantum chemical program NWCHEM. In both simulations, the B3LYP hybrid functional, which includes the Becke three-parameter exchange [38] and the Lee, Yang, and Parr correction functionals [39], were employed. In all calculations standard 6-31G** basis sets [40] were used. Within the DFT approach, full geometric optimizations were performed in gas phase for all the systems. When applicable, the solvent effect was taken into account approximately by the COSMO approach [41].

In the CDFT calculations, an external constraint is imposed via the method of Lagrange multiplier, i.e., an effective potential $V_c w_c(\mathbf{r})$ is added to the Hamiltonian. The resulting ground-state density satisfies specific density constraints, i.e., $\int w_c(\mathbf{r})\rho_c(\mathbf{r})\mathrm{d}\mathbf{r} = N_c$, where $w_c(\mathbf{r})$ is the operator that defines the property of interest. For electron transfer processes in transition metal complexes, the constraints can be on both the charges and the spin states. In this work, we employed a simple constraint to define the diabatic states, which is represented by the charge difference (Δq) between the two metallocene groups: $\Delta q = -1$ for the donor state and $\Delta q = +1$ for the acceptor state. Similar to the standard DFT method, a self-consistent procedure is used to find the minimum energy, the electronic density (or the Kohn-Sham type orbitals), and the constrained potential (the Lagrange multiplier V_c) within the CDFT framework. The 2 × 2 Hamiltonian matrix is then obtained within the two diabatic basis states [35]. These two states are further orthogonalized via the Löwdin procedure [42,43], and the electronic coupling matrix element V_{ab} is just the matrix element H_{12} of the Hamiltonian in the Löwdin basis states.

3 Results and discussion

During the first step, all molecular compounds are fully optimized within the standard DFT-B3LYP framework using Gaussian 09 program package. A few selected optimized structures in Scheme 1 are shown in Fig. 1, and selected bond length and torsion angles are listed in Table 1. These structures are in reasonable agreement with the experimental crystallographic data [27].

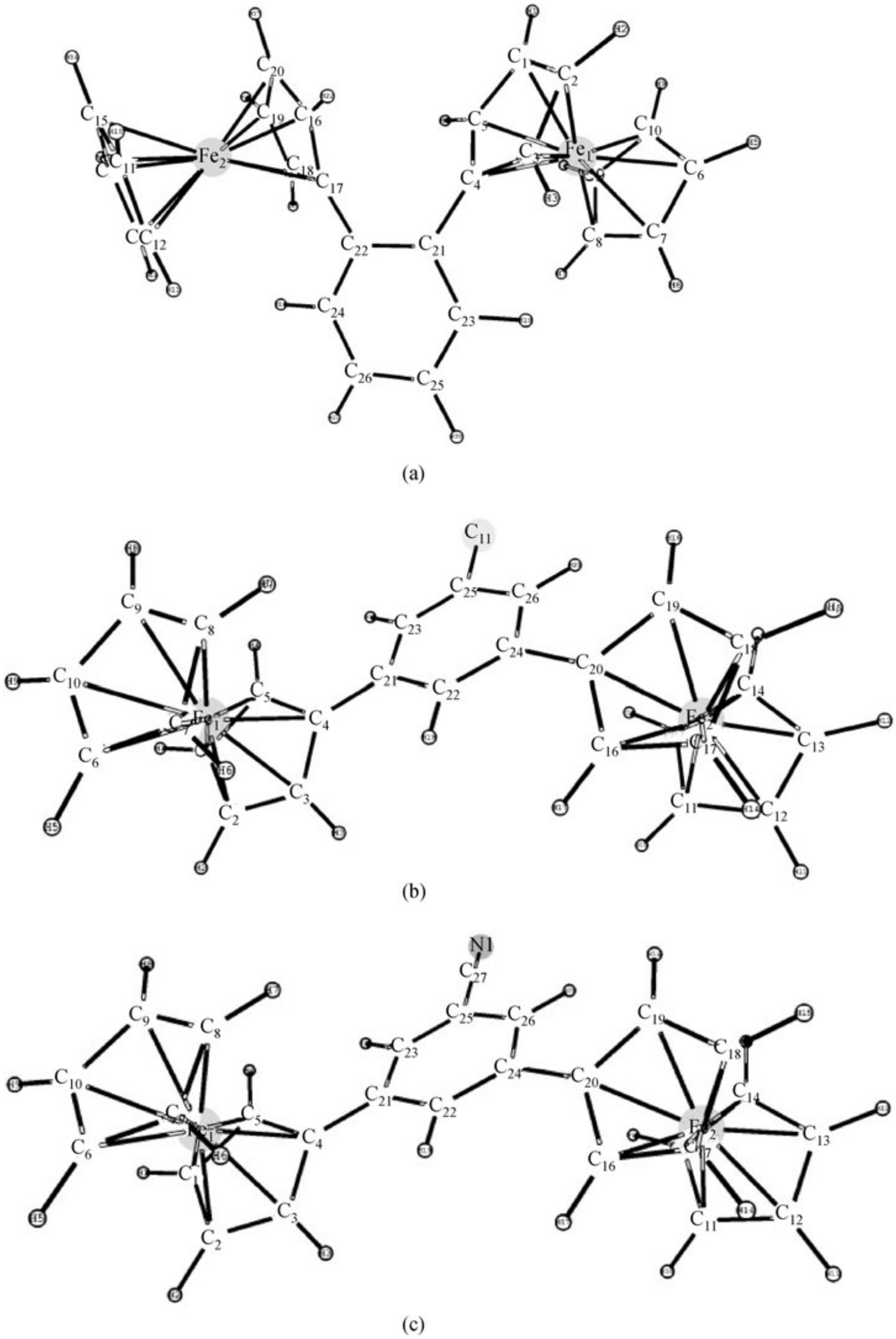
CDFT-B3LYP calculations were subsequently carried out using these optimized molecular structures by constraining the (+1) charge to one of the ferrocene groups at a time. The two diabatic states defined thereby were then used to evaluate the electronic coupling V_{ab}, which is the key parameter describing the efficiency of the molecule to perform intramolecule electron transfer.

Results for the diferrocenylbenzene isomers with ortho, meta, and para connection are summarized in Table 2. The theoretical values are in semiquantitative agreement with the experimental results: the para isomer displays the largest V_{ab}, whereas the meta isomer gives the smallest V_{ab} value. This can be explained by inspecting the bonding characteristic in Scheme 1. For both 1o and 1p, the two metal centers are linked via conjugate π bonds. However, for isomer 1m there is a break in conjugation and it decreases the electronic interaction between the metal centers. For diferrocenylbenzene isomer 1o, the two ferrocene groups are spatially too close, which slightly reduces the electronic coupling in comparison with the more relaxed 1p isomer.

Results for different meta-substituted functional groups are summarized in Table 3. The third groups introduced in the 5-position of 1m are in the order of increasing Hammet parameters. In previous work [27], it was speculated that a decrease in V_{ab} value should be observed. However, this was neither found from the experiment nor our calculations as listed in Table 3. Both the theoretical CDFT results and the experimental values show no clear variations of V_{ab} from 2 to 7. As an extreme case, we introduced a much stronger electron withdrawing group N_2^+, and this time we indeed observe a significant decrease in V_{ab}. We thus conclude that the dependence of V_{ab} on the Hammet parameter of the meta-substituted functional group is not as strong as one would expect. Only in somewhat extreme cases can one observe a significant change in the electronic communication between the two metal centers.

From the CDFT results for the 1m family compounds with different meta-substituted functional groups, we found clear differences between compounds with the strongest electron donor $R = NH_2$ and the strongest acceptor $R = N_2^+$. This led us carry out some further theoretical calculations, where we introduced these two R groups to the 1o and 1p compounds. For compound 1o we introduced the R group either in 3- or 4-position, i.e., 1o(1) and 1o(2) are 3-substituted derivatives of 1o, and 1o(3) and 1o(4) are 4-substituted derivatives. There is only one type of substitution for 1p, i.e., 1p(1) and 1p(2) for different R groups.

The CDFT results are summarized in Table 4. For compound 1p and its derivatives, the observation is the same as for the 1m family, the electronic coupling of 1p(1) ($R = NH_2$) does not vary significantly from that of 1p, whereas compound 1p(2) ($R = N_2^+$) shows a clear decrease in the V_{ab} value. However, for compound 1o and its derivatives, the trend is not clear. This suggests that besides the electron donating/withdrawing ability of the substituted group, steric effect may also play an important role in determining the



(a)

(b)

(c)

Figure 1 Selected optimized molecular structures. (a) Molecular structure of 1o in Scheme 1; (b) Molecular structure of 3 in Scheme 1; (c) Molecular structure of 5 in Scheme 1

Table 1 Selected bond lengths

Internuclear C(Cp) –C(phenyl) bond distances				
1o	C(17) – C(22)	1.48406	C(4) – C(21)	1.48406
3	C(17) – C(22)	1.47640	C(4) – C(21)	1.47665
5	C(17) – C(22)	1.47573	C(4) – C(21)	1.47619

Table 2 Experimental and theoretical V_{ab} couplings (eV) for three isomers

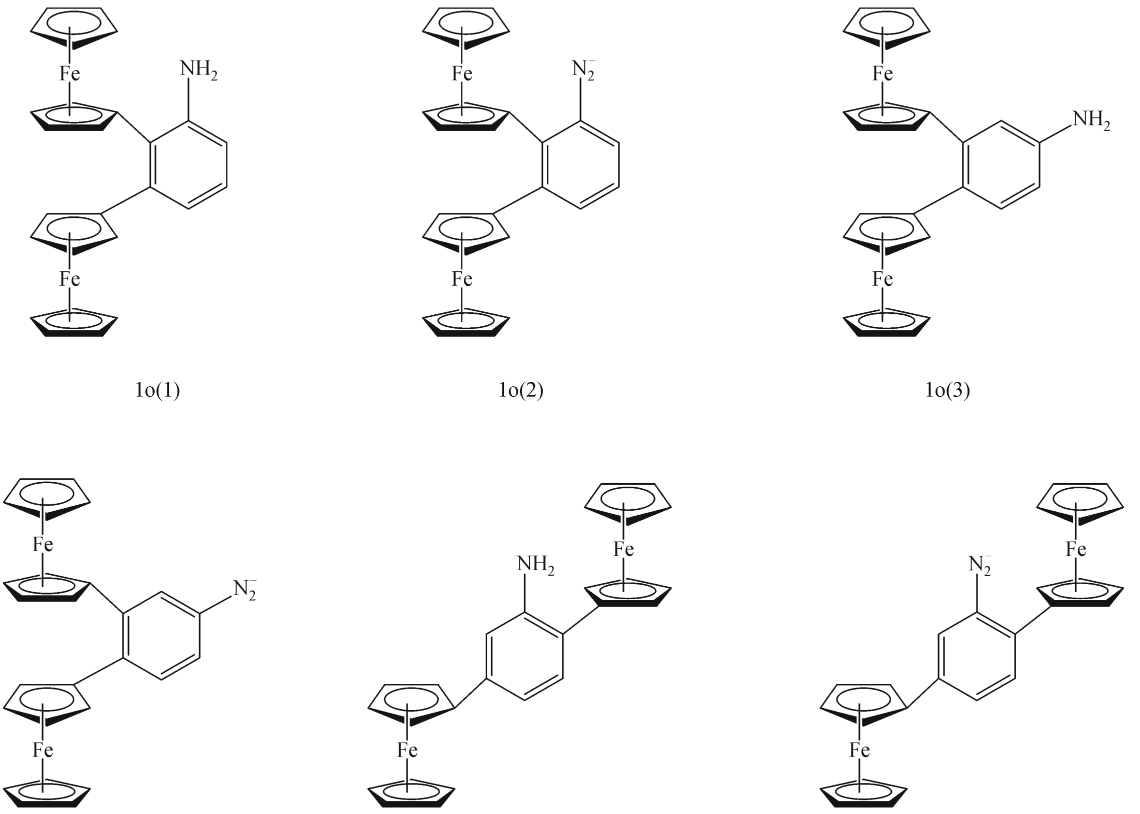
Compound	CDFT calculation		Experimental[a)]	Calculated[a)]
	Gas phase	CH_3CN solution		
1o	0.028	0.022	0.025±0.002	–
1p	0.078	0.056	0.043±0.001	0.0768
1m	0.013	0.009	0.013±0.001	0.0110

a) Data are the results taken from the Patoux et al.'s paper. See Ref. [27].

Table 3 Experimental and theoretical V_{ab} couplings (eV) for 1m family

Compound	CDFT calculation		Experimental[a)]	Prev. calc[a)]
	Gas phase	CH_3CN solution		
1m	0.013	0.009	0.013±0.001	0.0110
2	0.011	0.0088	0.011±0.001	0.0079
3	0.012	0.0074	0.011±0.001	0.0107
4	0.008	0.0099	0.015±0.001	0.0108
5	0.009	0.0063	0.012±0.002	0.0117
6	0.006	0.0045	0.013±0.002	0.0122
7	0.010	0.0072	0.012±0.002	0.0113
8	0.006	0.0006	-	-

a) Data are the results taken from the Patoux et al.'s paper. See Ref. [27].



1o(1) 1o(2) 1o(3)

1o(4) 1p(1) 1p(2)

Scheme 2 1o(1) 1o(2) 1o(3) 1o(4) 1p(1) 1p(2)

Table 4 Experimental and theoretical V_{ab} couplings (eV) for three isomers and their derivatives

Compound	CDFT calculation		Experimental[a)]	Prev. calc.[a)]
	Gas phase	CH_3CN solution		
1m	0.013	0.009	0.013±0.001	0.0110
2	0.011	0.0088	0.011±0.001	0.0079
8	0.006	0.0006	-	-
1o	0.028	0.022	0.025±0.002	-
1o(1)	0.018	0.0142	-	-
1o(2)	0.027	0.0205	-	-
1o(3)	0.025	0.0193	-	-
1o(4)	0.006	0.1274	-	-
1p	0.078	0.056	0.043±0.001	0.0768
1p(1)	0.068	0.0486	-	-
1p(2)	0.015	0.0110	-	-

a) Data are the results taken from the Patoux et al.'s paper. See Ref. [27].

electronic communication between the metal centers.

4 Conclusion

In this study, the constrained density functional theory (CDFT) was employed to study the topological effects on intervalence electron transfer processes. By calculating the electronic coupling between the electron donor and acceptor states, CDFT method provides a quantitative measure of extent for the intramolecular electron transfer. For the three isomers 1o, 1m, and 1p of diferrocenylbenzene, the calculations show a strong influence of the molecular topology on the electronic coupling, which is in agreement with the previous experimental work done by Patoux et al. [27]

To investigate the influence of a third group R introduced in the 5-position of the m- diferrocenylbenzene, i.e., the family of substituted compound 1m, CDFT calculations were carried out for a series of compounds (Scheme 1: 2–7) that have been investigated previously in the experiment [27]. The calculated electronic coupling does not show significant variation when the Hammett parameter of the substituted group is changed, which is consistent with the previous experimental findings [27].

Additional calculations were carried out by introducing a much stronger acceptor $R = N_2^+$ to the 5-position of 1m. A significant decrease in the electronic coupling element V_{ab} has been observed, which suggests possible future experimental studies. Furthermore, two representative third groups $R = NH_2$ and $R = N_2^+$ are introduced to compounds 1o and 1p. More complex steric effect has been observed to have influenced the overall electronic communication between the two metal centers.

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