Block-Localized Wavefunction (BLW) Based Two-State Approach for Charge Transfers between Phenyl Rings

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ABSTRACT: The block-localized wave function (BLW) method is the simplest and most efficient variant of ab initio valence bond (VB) theory which defines electron-localized resonance states following the conventional VB concepts. Here, a BLW-based two-state approach is proposed to probe the charge/hole transfer reactions within the Marcus–Hush model. With this approach, both the electronic coupling and reorganization energies can be derived at the ab initio level. Pilot applications to the electron/hole transfers between two phenyl rings are presented. Good exponential correlation between the electronic coupling energy and the donor–acceptor distance is shown, whereas the inner-sphere reorganization shows little geometric dependency. Computations also support the assumption in Marcus theory that the thermal electron transfer barrier (ΔG^*), which is a sum of the reaction barrier (ΔE_a) for electron/hole transfer and the coupling energy (V_{AB}), is a quarter of the reorganization energy (λ).

■ INTRODUCTION

π-Conjugated polymers have received intensive attention due to their applications in chemical sensors and molecular electronic and photonic devices.[1−8] One of the major classes of π-conjugated polymers is poly(p-phenylene) (PPP), which is associated with its application as the organic component in LED-based devices.[9,10] Due to the limited length and disorder of polymer strands, charge transfer between polymer strands resulting from interchain interactions plays an essential role in charge transport across macroscopic distances,[11−13] although interchain transport (or "intersoliton" transfer[14]) is expected to be significantly slower than intrachain transport.[15] As the charge carriers are expected to be localized over a single unit (e.g., benzene for PPP), the transport mechanism can be described in terms of polaronic hopping between adjacent chains.[16−18] For the instance of PPP, interchain electron or hole transfer can be approximately modeled with two adjacent benzenes which are either neutral or charged.[19,20] Scheme 1 shows a model with two parallel benzene rings.

Scheme 1. Resonating States for the Electron or Hole Transfer between Two Benzene Rings
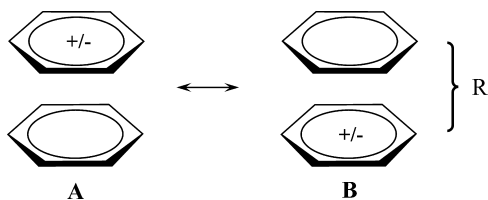
On the basis of the general Marcus–Hush model,[21−24] two diabatic states (A and B in Scheme 1) where the charge is localized on either benzene can be used to describe the above charge transfer process or self-exchange reaction. With the harmonic approximation, the potential energy for each diabatic state is represented by a parabolic curve, and the adiabatic (ground) state, which is a superposition of A and B, is characterized by a double-well potential (black curve as shown in Figure 1). Whereas the two minima, dominated by either
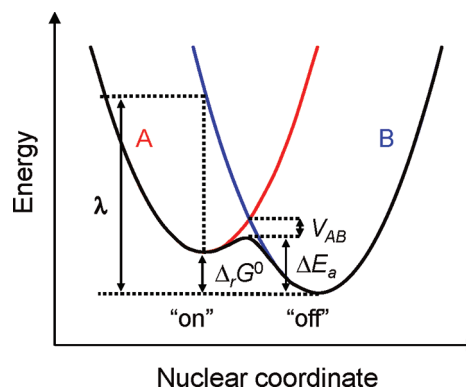

Figure 1. Illustration of the general Marcus–Hush two-state model.

A or B, correspond to "on" and "off" states in molecular electronics, the polaronic hopping between the two minima requires overcoming an activation barrier. The most intriguing issue in this model is the seam of the crossing between the two energy profiles of diabatic states, where charge transfer occurs in line with the Franck–Condon principle. Due to the electronic coupling, which is largely dictated by orbital overlap, the ground state energy will be lowered by V_{AB} compared with the diabatic state energies. The significance of V_{AB} lies in its direct relevance to the interchain transfer rate as[25,26]

$$k_{ET} = \frac{1}{\hbar}|V_{AB}|^2 \left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{(\Delta_r G^0 + \lambda)^2}{4\lambda k_B T}\right) \quad (1)$$

where λ is the reorganization energy owing to the geometric relaxation accompanying charge transfer and $\Delta_r G^0$ is the overall reaction free energy, which is zero in the present charge self-exchange reactions.

The major challenge therefore is to compute the electronic coupling term V_{AB} (also called transfer integral[27]) and reorganization energy λ, which center on electron transfer theory. Much progress has been made during the past decade in computing the coupling term. Among various approaches, the energy-splitting method based on Koopmans' theorem provides the simplest way to evaluate V_{AB} as half of the energies of the appropriate occupied and unoccupied orbitals,[16,27−31] e.g., half of the energy difference between the HOMO and HOMO−1 of a system with an extra electron. Another direct method to compute the couplings is based on the energy difference between the ground and the first excited states.[32] Newton and co-workers have developed the generalized Mulliken−Hush (GMH) formalism and showed that V_{AB} can be estimated from the transition dipole moment between the states of interest and the diabatic states can be defined by diagonalizing the dipole moment matrix.[33−36] Other approaches include the fragment charge difference procedure,[37] tuning the self-consistent-field (SCF) energy difference with external perturbation,[27] the perturbed ground state method,[38] the block diagonalization method,[34,39] or methods in terms of partitioning theory[40] or Green functions.[41]

A common characteristic in the above approaches is that the electronic coupling between the diabatic states stems from chosen adiabatic states. In other words, the diabatic states themselves are not directly accessible. We also note that in empirical VB approaches, the electronic coupling term (or the off-diagonal matrix element H_{AB} when S_{AB} is assumed zero) is often approximated with an exponential function,[42−44] or a generalized Gaussian form[45,46] or its improved forms,[47−51] with parameters fitted to reproduce ab initio results in the gas or solution phase or certain experimental data.

A direct evaluation of V_{AB} requires the proper definition of diabatic states with the transported electron localized. Although in general this remains a challenge in molecular orbital (MO) theory due to the delocalization nature of MOs, for certain systems where a single-determinant wave function fails, it is possible to find approximate solutions which can lead to reasonable results. Newton first introduced the charge-localized SCF wave functions derived at the unrestricted Hartree−Fock (UHF) level to denote the initial (A) and final (B) diabatic states in the process of electron transfer.[52] The subsequent solution of a 2 × 2 secular equation results in V_{AB}. This approach has been pursued and applied by many others.[16,19,53−56] Another possibility is to define the wave function of a diabatic state with the direct product of the fragmental wave functions.[57] For the instance of through-space electron transferred complex DA, the diabatic states can be defined as $|D\rangle|A\rangle$ and $|D^+\rangle|A^-\rangle$. But the relaxation (polarization) effect is not considered in these wave functions. Remarkably, Dederichs et al. proposed a general DFT method with arbitrary constraints, e.g., a number of electrons constrained in a certain volume, and demonstrated that this constrained DFT (CDFT) can derive the energies of stable magnetic configurations as well as the magnetic interactions.[58] Recently, Wu and van Voorhis introduced a Lagrange multiplier scheme to optimize the supplementary potential which is added to the usual Kohn−Sham potential in the CDFT method and applied this improved CDFT method to the study of charge transfer in the zincbacteriochlorin−bacteriochlorin complex, polyene, and alkane chains.[59] Further,

they described an approach to estimate the coupling matrix element in long-range electron transfer reactions[60] and formulated a configuration interaction (CI) method by using CASSCF-inspired charge and spin constrained configurations.[61] While the derivation of diabatic states relies on the population scheme, both V_{AB} and λ can be subsequently derived from the diabatic states.[60] This CDFT approach has been implemented into the deMon2k package by de la Lande and Salahub in the study of long-range electron transfer.[62] Warshel and co-workers also developed the frozen DFT (FDFT) algorithm to model a solute or a chemical reaction system in condensed states.[63,64]

Adopting a different strategy from CDFT and FDFT methods, we proposed the block-localized wave function (BLW) method which can be regarded as the simplest and most efficient ab initio valence bond (VB) method and can determine electron-localized states.[65−68] In the BLW method, we block-localize the molecular or Kohn−Sham orbitals, and hence the associated electron density is constrained by construction. The electron density for each diabatic state is derived from an antisymmetric wave function, consisting of both orthogonal and nonorthogonal block-localized orbitals, a feature distinct from the CDFT approach of Dederichs et al.[58] but characteristic of VB theory.[69−72] Extensive applications to the intramolecular electron transfer including conjugation and hyperconjugation, where abundant experimental data are available for the justification of theoretical methods, have demonstrated that the BLW method is applicable to both strong and weak electronic couplings.[73−81] In this work, we describe and apply the BLW-based two-state approach to the study of the self-charge transfer reactions between an ionic benzene radical and a neutral benzene.

■ METHODOLOGY

Different from MO theory, VB theory is established on the philosophy that any molecular state is a superposition of certain charge-localized resonating (diabatic) states, and each diabatic state (with $N − 2n$ unpaired electrons) can be well described by a Heitler−London−Slater−Pauling (HLSP) function as[82]

$$\Psi_K = M_K \hat{A}(\varphi_{1,2}\varphi_{3,4}\cdots\varphi_{2n-1,2n}\phi_{2n+1}\alpha(2n+1)\ldots\phi_N\alpha(N))$$

(2)

where M_K is the normalization constant, $\hat{A}$ is the antisymmetrizer, and $\varphi_{2i-1,2i}$ is a bond function corresponding to the bond between orbitals ϕ_{2i-1} and ϕ_{2i} (or a lone pair if $\phi_{2i-1} = \phi_{2i}$)

$$\varphi_{2i-1,2i} = \hat{A}\{\phi_{2i-1}\phi_{2i}[\alpha(i)\,\beta(j) - \beta(i)\,\alpha(j)]\}$$

(3)

Apparently, a HLSP can be expanded to 2^n Slater determinants. The overall many-electron wave function for the real adiabatic state is a linear combination of several important VB functions. The simultaneous optimization of both the configurational coefficients and the one-electron orbitals $\{\phi_i\}$ leads to the VBSCF method. Recent applications have extensively demonstrated the capability of modern ab initio VB methods in gaining novel insights into chemical properties and reaction processes.[69−72,83−89] While it is promising to use the ab initio VB theory to study inter- and intramolecular electron transfers, the computational efficiency of VB methods needs to be greatly boosted.

To alleviate the mathematical complexity of VB theory, recently we proposed the block-localized wave function (BLW) method, which uniquely combines the characters and advantages of both the MO and VB theories.[65−68] Unlike conventional MO methods where MOs are delocalized over the whole
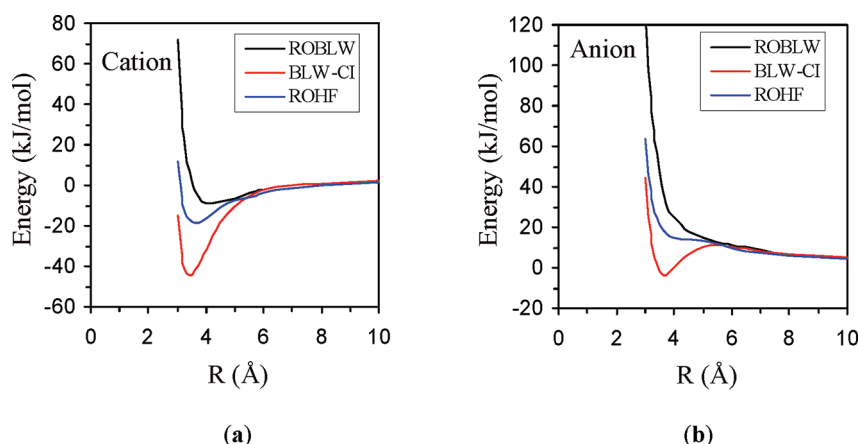
Figure 2. Binding energy potentials between a neutral benzene and (a) a cationic benzene radical and (b) an anionic benzene radical.

system, the BLW method defines a diabatic state wave function by limiting the expansion of each MO to a predefined subspace. Thus, block-localized MOs belonging to different blocks are generally nonorthogonal, whereas those belonging to the same block are constrained to be orthogonal. The BLWs for diabatic states are optimized self-consistently at the HF and DFT levels. For the two states in Scheme 1, their wave functions can be uniquely defined as

$$\psi_A = \hat{A}[\Phi_1(C_6H_6^{\pm}) \Phi_2(C_6H_6)] \tag{4a}$$

$$\psi_B = \hat{A}[\Phi_1(C_6H_6) \Phi_2(C_6H_6^{\pm})] \tag{4b}$$

where Φ denotes a successive product of occupied orbitals which are expanded in only one benzene orbital space and optimized self-consistently. Once we derive the wave functions and energy profiles for the two electron-localized diabatic states, we can easily derive the electronic coupling energy V_{AB} by resolving the following 2 × 2 secular equation:[90]

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0 \tag{5}$$

where H and S are the Hamiltonian and overlap matrix, respectively, and E is the energy eigenvalue and has two roots E_1 and E_2. At the crossing point of energy curves of diabatic states when their energies are identical ($H_{AA} = H_{BB}$), the electronic coupling strength V_{AB} is defined as the difference between the diabatic state energy and the lower root of eq 5

$$V_{AB} = H_{AA} - E_1 = \frac{H_{AA}S_{AB} - H_{AB}}{1 + S_{AB}} \tag{6}$$

Note that $V_{AB} = -H_{AB}$ when the overlap between the two diabatic states is neglected.

In this work, optimal geometries and primitive integrals were obtained with Gaussian 98,[91] while the subsequent BLW computations were performed with our own codes, and the 6-31G(d) basis set was used.

■ RESULTS AND DISCUSSION

The Dependence of Charge Transfer Rates on the Distance. We started from the MP2/6-31G(d) geometry of benzene ($R_{CC} = 1.398$ Å) and fixed the benzene rings at this geometry in the computations of the charge transfer rates with the variation of the transfer distance (R) between two benzene

rings, as shown in Scheme 1. The BLW computations to derive the wave functions ψ_A and ψ_B (eqs 4a and 4b) were performed under the restricted open-shell constraint. Figure 2 compared the energy profiles from the ROHF (blue line), ROBLW (black line), and BLW-CI (red line) computations. For the cation, all of these levels can locate a minimum, indicating the significant electrostatic attraction between benzene and the benzene cation. However, the ROHF energy curve is more similar to the ROBLW curve than to the BLW-CI curve. The latter leads to a minimum at $R = 3.40$ Å with a binding energy of about 49 kJ/mol. For the anion, both ROBLW and ROHF computations cannot locate a minimum, while the BLW-CI method can successfully identify a shallow minimum at $R = 3.75$ Å with a binding energy of 6.7 kJ/mol. Apparently, the attractive interaction in the cationic complex is much stronger than in the anionic complex. These computations also demonstrated that MO methods based on one Slater determinant may not work well for the biphenyl radicals, and two-state methods are essential in the description of the interactions between benzene and its radical ions. We also note that the minima derived by the current two-state approach (at $R = 3.40$ Å and 3.75 Å, respectively) are close to the distance (3.37 Å) between layers in graphite.[92]

Figure 3 shows the dependence of the electronic coupling energy on the charge transfer distances. McConnell[93] first proposed that the rate of intramolecular electron transfer decreases exponentially with the chain length of the polymethylene chain r_{AB}, in other words

$$V_{AB} \propto e^{-\beta r_{AB}/2} \tag{7}$$

where β is an energy-dependent parameter characterizing the molecule. Since then, the β value has been widely used as a measure for the charge transfer efficiency both computationally and experimentally. Very interestingly, in our attempt to derive the β values for the cationic and anionic complexes, we observed two distinctive electronic coupling mechanisms separated at $R = 4.6$ Å in both $C_6H_6\cdots C_6H_6^{\pm}$ complexes (Figure 3): when $R < 4.6$ Å, the exponential decay constant is about 2.6–2.9 Å^{-1}, but when $R > 5$ Å, the exponential decay constant is doubled to around 5.4 Å^{-1}. For comparison, electron transfer across linear alkyl chains and polyethylene decays at rates of 1.0 and 0.2 Å^{-1}, respectively.[90] Thus, interchain charge transport is significantly slower than intrachain transport.[13] Experimentally, the exponential decay constant
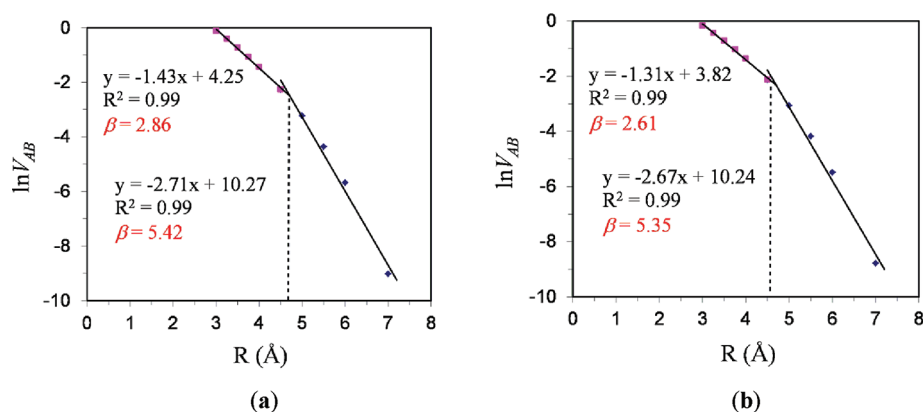
Figure 3. Correlation between the electronic coupling energy (V_{AB} in eV) and the electron-transfer distance between a neutral benzene and (a) a cationic benzene and (b) an anionic benzene radical.

across van der Waals contacts ranges from 2.9 to 4.0 $Å^{-1}$,[94] but a value in the range of 3.5−5 $Å^{-1}$ has been estimated for donors and acceptors separated by a vacuum. While in reasonable agreement with the experimental estimates, our data seem to suggest that 4.6 Å may be the boundary for van der Waals contacts. For $R < 4.6$ Å, there is still diffusive orbital overlap which benefits the charge transfers, but after $R > 4.6$ Å, the charge transfer proceeds through a vacuum. In addition, our computations indicate that the electrical conductivity is similar in the electron and hole transfer reactions.

Reorganization along the Charge Transfers. The application of the BLW method to the same system at different geometries provides a robust way to derive the molecular reorganization energy at the ab initio level. By incorporating the BLW method with Monte Carlo simulation techniques, the important solvent reorganization energy can be computed.[95] Here, however, we focus on the inner-sphere (solute) reorganization energy. Since the current BLW computations were performed at the ROHF level (one Slater determinant), we first optimized the geometries of monomers at this level, where the neutral benzene adopts a D_{6h} symmetry and ionic radicals imposed a D_{2h} symmetry. Table 1 listed the optimal bond lengths.

Table 1. Optimal Bond Lengths in Benzene, Benzene Cationic Radical, and Benzene Anionic Radical

bond length (Å)	C_6H_6 (D_{6h})	$C_6H_6^+$ (D_{2h})	$C_6H_6^-$ (D_{2h})
R(C−C)	1.388	1.379/1.446	1.370/1.428
R(C−H)	1.076	1.074/1.073	1.081/1.077

As the charge transfer reactions accompany the rearrangement of nuclear conformations and the energy change is related to the reorganization energy λ, we define a reaction coordinate Q_i as a linear combination of reactant coordinates Q_A and product coordinates Q_B.

$$Q_i = (1 - \alpha)Q_A + \alpha Q_B \qquad (8)$$

where A or B corresponds to a diabatic state composed of a neutral benzene and an ionic radical of the separated geometries, as shown in Table 1. We studied the charge transfer processes along the reaction coordinate Q_i by gradually changing α from 0 to 1 at the fixed donor−acceptor distances of 5−10 Å. Figure 3 plots the diabatic and adiabatic energy curves at the distances of 5, 6, and 7 Å. While the diabatic energy

curves are essentially independent of the donor−acceptor distance and similar in both reactions, the adiabatic energy curves vary significantly due to the different coupling magnitude at different distances. At $R = 5$ Å, the coupling in the anionic complex is so strong that the adiabatic energy curve exhibits only one minimum at the midpoint, suggesting that the system is conductive. With the increasing separation of the donor and acceptor, the activation energy (ΔE_a) required for moving the charge increases and the adiabatic energy curve shows two minima.

For symmetric electron transfer reactions, such as the ones studied in this work, it can be derived from eq 2 that in the diabatic limit (also see Figure 2 in ref 96)[21,22,96]

$$\Delta G^* = \Delta E_a + V_{AB} \approx \lambda/4 \qquad (9)$$

where ΔG^* refers to the thermal electron transfer barrier, while ΔE_a is the activation energy required for moving the electron at the adiabatic state.

Table 2 listed the coupling energy V_{AB}, charge transfer barrier ΔE_a, and reorganization energy λ in the charge self-exchange

Table 2. Coupling Energy V_{AB}, Charge Transfer Barrier ΔE_a, and Reorganization Energy λ (in eV) at Several Distances When the Donor and Acceptor Groups Are Weakly Coupled

	anion			cation		
R (Å)	V_{AB}	ΔE_a	λ	V_{AB}	ΔE_a	λ
6.0				0.018	0.074	0.369
7.0	0.053	0.046	0.366	4.7×10^{-3}	0.087	0.371
8.0	0.028	0.066	0.365	1.0×10^{-3}	0.091	0.371
9.0	0.013	0.079	0.365	2.0×10^{-4}	0.093	0.372
10.0	5.0×10^{-3}	0.087	0.365	5.7×10^{-5}	0.093	0.372

reactions between benzene ionic radicals and neutral benzene at separations of 6−10 Å, where the donor and acceptor monomers are weakly coupled (except for the anion at $R = 6$ Å where the coupling is strong, as shown in Figure 4). While the coupling energy is highly geometry-dependent and falls off exponentially, the charge transfer reaction barriers converge to around 0.09 eV. For both cationic and anionic complexes, the inner-sphere reorganization energies are similar and have little geometric dependency. Significantly, we found that the Marcus hypothesis stands and eq 9 holds with negligible errors.
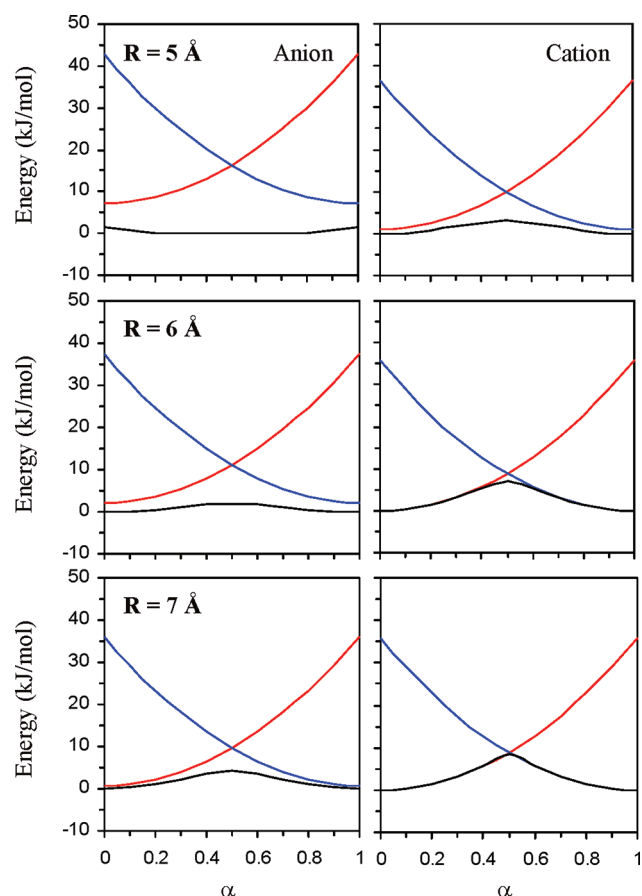
Figure 4. Potential energy curves for the charge transfer reactions between benzene and its ionic form at the distances of 5, 6, and 7 Å. Blue and red curves denote the diabatic energy potentials, whereas the black curve refers to the adiabatic energy potential.

CONCLUSION

In conclusion, the BLW method, which combines the characteristics and advantages of MO and VB theories, can effectively define the wave function for an electron-localized diabatic state. The subsequent BLW-based two-state approach can derive the quantities such as the coupling energy V_{AB} and reorganization energy λ, which are directly related to the electron transfer rate and thus center on most theoretical works on electron transfer processes. Applications of this BLW-based two-state method to the complexes of a neutral benzene and a benzene ionic radical, which are the simple models for the study of poly(p-phenylene) interchain electron/hole transfer, shows that there is an effective electron tunneling. Our computations also showed that the thermal electron transfer barrier, which is a sum of the reaction barrier for electron/hole transfer and the coupling energy, is a quarter of the reorganization energy. This finding is in good agreement with Marcus theory.

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Notes

The authors declare no competing financial interest.

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