

Impact of Double- π -Bridge on Bis(Triarylamine)-Based Organic Mixed-Valence System: A Case Study of Diaza[1.1](4,4'')*ortho*-Terphenylophane Radical Cation

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A bis(triarylamine) (BTA) radical cation, bridged by two *o*-terphenylene moieties, was prepared and characterized to explore the impact of the double- π -bridge on the intramolecular charge/spin transfer process in the 2-site organic mixed-valence (MV) compound. Spectroscopic analyses on optically and thermally assisted intervalence charge-transfer

(IVCT) processes revealed that the doubly π -bridging enhanced the charge delocalization between two nitrogen redox-active centers, whereas the electronic coupling was not so strengthened, in comparison with the singly π -bridging reference compound.

Introduction

Electron transfer properties of π -conjugated molecular systems are being continuously investigated in conjunction with growing interest in various research areas such as organic photovoltaics,^[1,2] organic photocatalysts including water splitting,^[3,4] organic-based electrodes for batteries,^[5,6] and so forth. Charge transport through single-molecule junctions has been, in particular, actively examined and discussed for realization of molecular-scale devices.^[7–10] An emerging trend at the forefront is seemingly entering a phase to control the quantum interference (QI) pathways of charges over more complicated molecules with an interplay of molecular orbital interactions and the transient structural deformations.^[11–14] In a tutorial review by Lambert,^[15] the QI effect through multi-branched molecular structure has been introduced as an example of the more complex structure, where it has been demonstrated that the quantum of conductance even in the case of two-branches does not necessarily correspond to the sum of each branch.

In association with the intensive studies on single-molecule electron transport, various insights on intramolecular charge transfer phenomena have also been accumulated by utilizing π -bridged bis(triarylamine) (BTA) radical cations as an ideal purely

organic mixed-valence (MV) model system showing intervalence charge-transfer (IVCT).^[16–21] In the MV compounds, the two important parameters: the reorganization energy λ and the electronic coupling V govern a whole picture of IVCT. It has been clarified that those parameters were effectively tuned by various factors such as selections of both bridging unit and redox-active center, bridge length, bridge topology, molecular configuration, in the so-called singly π -bridged 2-site MV system, where the two redox-active centers were linked by a single- π -bridge. In contrast, there has been no reports on multiply π -bridged 2-site organic MV compounds.

Herein, we focused on the doubly π -bridged 2-site MV model compound including triarylamine moieties as redox-active centers. As shown in Figure 1, our previous study on phenylene-bridged BTA radical cations has demonstrated that the electronic coupling of 794 cm^{−1} for *ortho*-phenylene-bridged BTA radical cation (*ortho*-BTA^{•+}) was comparable in magnitude to that of 860 cm^{−1} for *para*-phenylene-bridged one (*para*-BTA^{•+}).^[22,23] Thus, we anticipated that the selection of *ortho*-terphenylene bridge enabled us to prepare diaza[1.1](4,4'')*ortho*-terphenylophane (1) as a doubly π -bridged BTA option with a reasonable electronic coupling between two redox-centers (Figure 1).

In the present study, we report the first analysis of doubly π -bridged organic MV model system **1**^{•+} in comparison with singly π -bridged *ortho*-BTA^{•+}. Prior to the detailed evaluation of **1**^{•+} as a MV compound, the value of 2 V for *ortho*-BTA^{•+} and **1**^{•+} was roughly estimated by the single-point calculations of a neutral state at radical cation geometries (neutral in cation geometry (NCG) method^[24,25]). As shown in Figure 2, the HOMO and HOMO-1 energy level diagrams for *ortho*-BTA^{•+} and **1**^{•+} on the basis of NCG method (B3LYP/6-31G*) show the electronic coupling constant of **1**^{•+} was almost double that of *ortho*-BTA^{•+}, thus suggesting the strengthening of the electronic coupling V between two redox-centers due to the double- π -bridge. In addition, it should be noted that the orientation of p-orbitals on the two nitrogen-redox-centers to the *ortho*-phenylene plane underwent a considerable change by the

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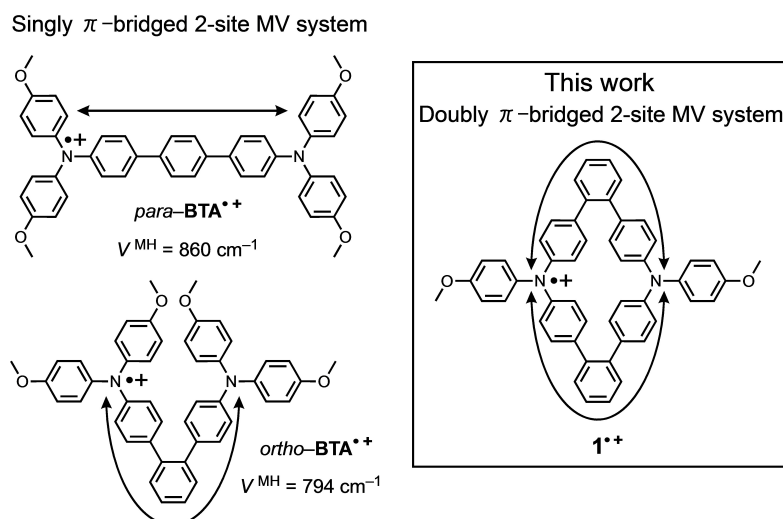


Figure 1. Previously reported BTA MV compounds, *para*-BTA $^{\bullet+}$ and *ortho*-BTA $^{\bullet+}$, as a singly π -bridged 2-site MV system (left) and **1 $^{\bullet+}$** as a doubly π -bridged 2-site MV system (right). The superscript on V designates that the electronic coupling was evaluated on the basis of the Mulliken-Hush theory.

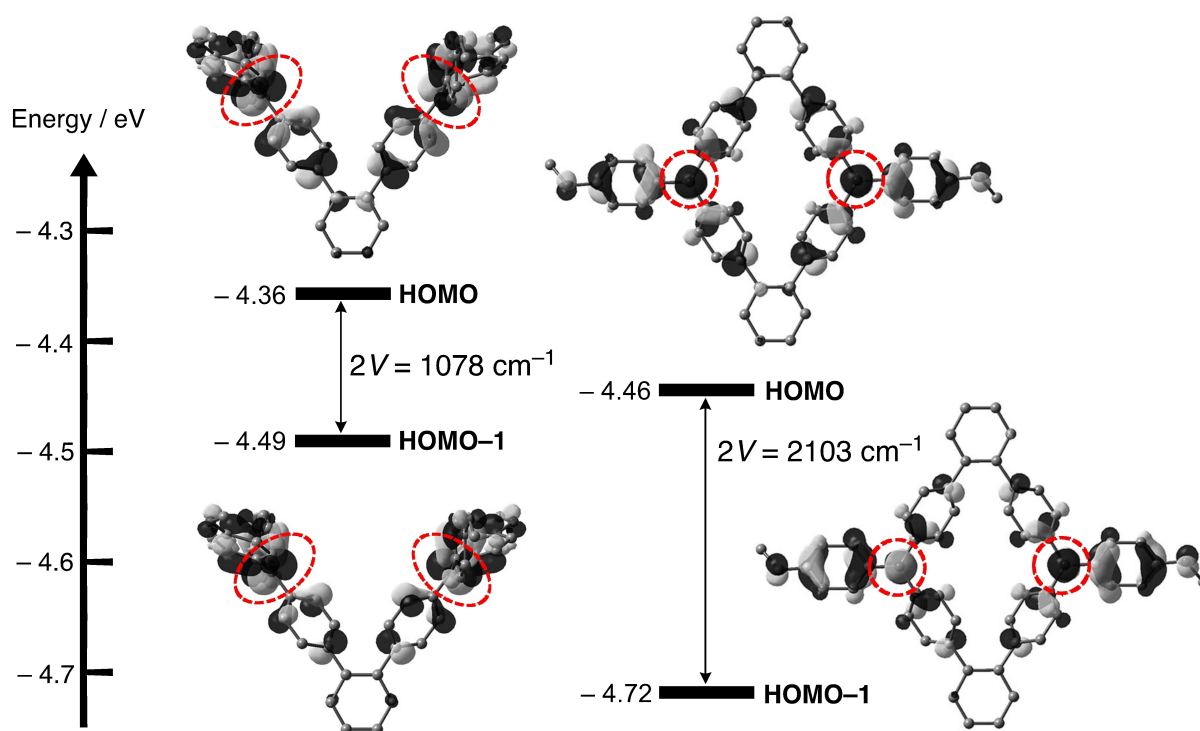


Figure 2. HOMO and HOMO–1 energy diagram for *ortho*-BTA and **1** at the optimized geometries for radical cations of *ortho*-BTA and **1** on the basis of NCG method (B3LYP/6–31G*). The p-orbitals on the nitrogen redox-centers are encircled by the dashed red line.

double- π -bridging, thus leading to a difference in reorganization energy λ between *ortho*-BTA $^{\bullet+}$ and **1 $^{\bullet+}$** (Figure 2).

Results and Discussion

The title compound **1** was prepared in 16.6% yield from the Buchwald-Hartwig amination reaction^[26] between 4,4''-dibromo-*o*-terphenyl and *p*-anisidine as shown in Scheme 1. In air-saturated dichloromethane solution, the compound **1** showed

an absorption maximum at 330 nm, and photoexcitation at 320 nm of this solution resulted in a clear emission at 460 nm with fluorescence quantum yield (Φ_F) of 29% (Figure 3). In degassed dichloromethane solution, the quantum yield increased up to 36%. Additionally, the compound **1** was fluorescent even in the solid state ($\Phi_F = 13.5\%$). Upon one-electron chemical oxidation with AgSbF₆ salt in dichloromethane, a continuous decrease in emission intensity at 460 nm was observed, and no additional emission bands appeared for neither **1 $^{\bullet+}$** or **1 $^{2+}$** (Figure S1).

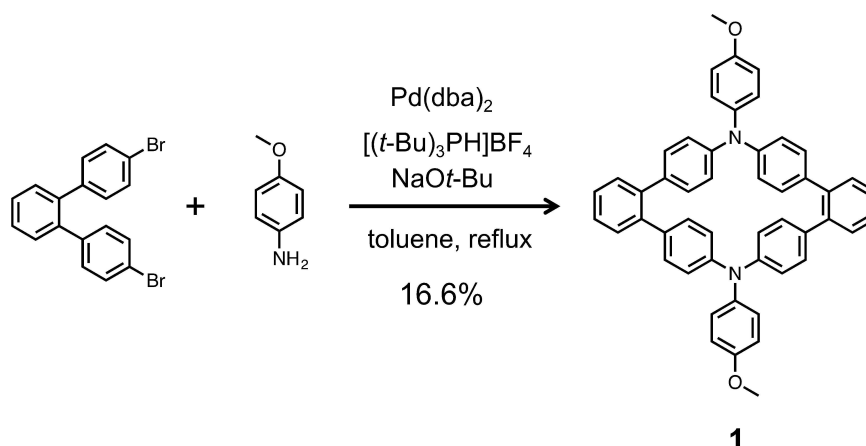
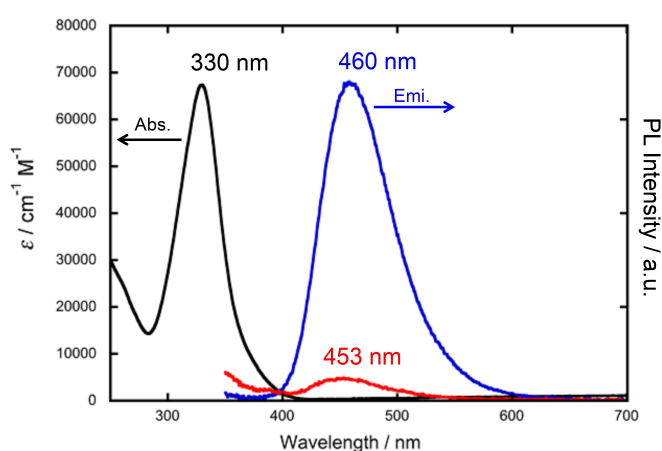
Scheme 1. Preparation of doubly π -bridged BTA **1**.

Figure 3. Absorption (black line) and photoluminescence (PL; blue line) spectra of **1** in dichloromethane (10 μ M) and in the solid state (red line) at r.t. The emission spectra were obtained at the excitation wavelength of 320 nm for dichloromethane solution and 300 nm for the solid state. An increase of the PL intensity observed in shorter wavelength region than 400 nm (red line) is a Rayleigh scattering tail of the exciting light at 300 nm.

The electronic transitions to the singlet excited states of **1** were calculated at the B3LYP/6-31G* level of theory using the time-dependent DFT (TD-DFT) approach for the optimized ground-state molecular geometry of **1**. As shown in Figure 4, the unoccupied frontier orbitals were localized on the *o*-terphenylene bridges, while the occupied frontier orbitals were of triarylamine redox-center localized ones, and therefore, the HOMO-LUMO ($H \leftarrow L$) transition ($S_1 \leftarrow S_0$) of **1** was virtually forbidden (410 nm, $f=0.0001$) similar to that of triarylamine. The absorption band at 330 nm can be assigned to the $S_2 \leftarrow S_0$ ($H-1 \rightarrow L$; 365 nm, $f=0.32$), $S_3 \leftarrow S_0$ ($H \rightarrow L+1$; 353 nm, $f=0.56$), and $S_4 \leftarrow S_0$ ($H \rightarrow L+2$; 342 nm, $f=0.23$) electronic excitations.

To check the electron-donating ability of **1** and its oxidative stability, the redox properties of **1** were investigated at room temperature in dichloromethane by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) while comparing with the previously reported data^[22] for *ortho*-BTA (Figure 5). The two reversible redox waves were detected in the CV and the DPV, respectively, hence indicating stepwise

oxidation of **1** through $1^{+\bullet}$ to 1^{2+} . The first oxidation potential of **1** ($E_1 = +0.25$ V (1e) vs $Fc^{0/+}$) exhibited an anodic shift of +0.05 V, as compared with *ortho*-BTA ($E_1 = +0.20$ V (1e) vs $Fc^{0/+}$), reflecting the impact of double- π -bridging in **1**. The second oxidation potential of **1** ($E_2 = +0.38$ V (1e) vs $Fc^{0/+}$) was found to be more anodically shifted than that of *ortho*-BTA ($E_2 = +0.29$ V (1e) vs $Fc^{0/+}$), indicating the larger redox potential splitting $\Delta E \equiv E_2 - E_1 = 130$ mV for **1** than that for *ortho*-BTA ($\Delta E = 90$ mV). The strength of ΔE can be frequently utilized as a qualitative indicator for electronic communication between two redox-centers in 2-site MV systems,^[27] thus promising a large electronic coupling in $1^{+\bullet}$.

Herein, prior to the detailed analysis and discussion on the MV state of $1^{+\bullet}$, we briefly overview the experimental procedures and the analyses to extract the two kinds of key parameters, the reorganization energy λ and the electronic coupling V , while referring to the schematic representation of adiabatic free energy surfaces (FESs) for degenerate MV states (Figure 6).^[16,17,20] The separated diabatic FESs corresponding to those of two identical redox-active centers are mixed to result in two adiabatic FESs shown in Figure 6, as a result of electronic coupling V between the redox-active centers through interaction with the π -bridge orbitals. The abscissa axis designates the charge transfer coordinate X indicating two minima of the lower adiabatic FESs at $X=0$ and 1. The lower energy double-well FES means the existence of charge/spin localized ground state for one-electron oxidized MV state, which is referred to as charge-localized class II MV state in the Robin-Day classification.^[28] At $X=0$ and 1 (and at this point, the MV molecule adopts the asymmetric geometrical structure), the energy gap between upper and lower FESs equals with λ , and hence, the quantum chemical single-point transition energy calculation at this point gives the theoretical estimation of λ . Moreover, at $X=0.5$ (and at this point, the MV molecule adopts the symmetric geometrical structure), the energy gap between upper and lower FESs equals with $2V$, and hence, the same single-point transition energy calculation at this point provides the theoretical estimation of $2V$. Experimentally, the value of λ is directly obtained from the optical absorption band maximum

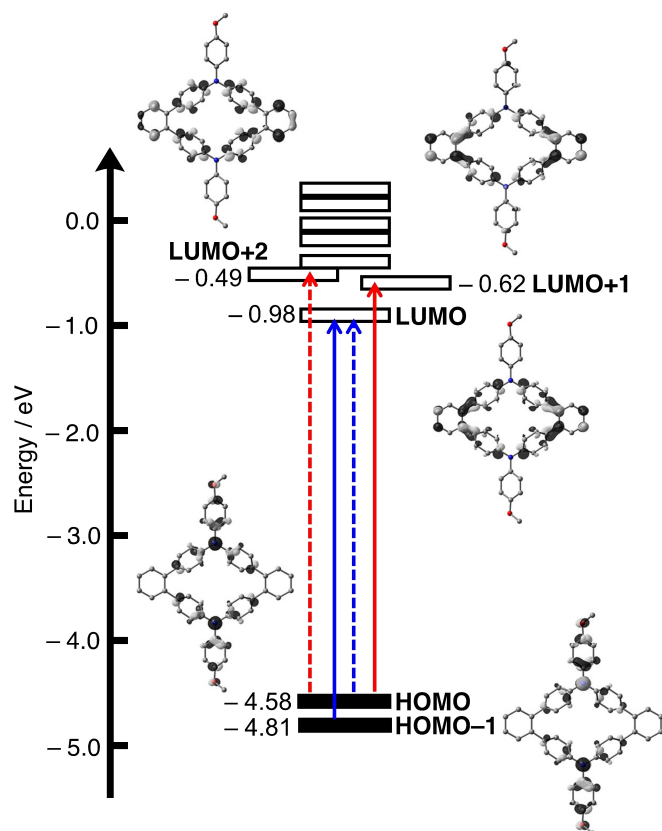


Figure 4. Frontier Kohn-Sham orbitals and their energy levels for **1** at the B3LYP/6-31G* level of theory. The arrows denote the major contributions related to the $S_1 \leftarrow S_0$ (dashed blue), $S_2 \leftarrow S_0$ (solid blue), $S_3 \leftarrow S_0$ (solid red), and $S_4 \leftarrow S_0$ (dashed red) electronic transitions on the basis of single-point TD-DFT calculations (B3LYP/6-31G*).

(the so-called IVCT band maximum) corresponding to the electron transition at $X=0$ and 1 , and the optical transition causes the optically assisted IVCT. Additionally, the integration of the observed IVCT band is proportional to the transition dipole moment μ_{abr} and the value of V can be finally evaluated from the energy of the IVCT band maximum and the change of static dipole moment before and after the charge transfer event, in addition to the transition dipole moment. To determine the change of static dipole moment, the charge transfer distance is needed for the studied MV system. However, in the organic MV systems such as BTA radical cations, the exact charge transfer distance is difficult to define, simply because the generated charge/spin on one redox-active center is partially delocalized on the periphery. Therefore, the change of static dipole moment is usually estimated from the quantum chemical calculations of adiabatic dipole moment difference.

From the viewpoint of thermally assisted IVCT for 2-site MV systems, the activation barrier ΔG^* at $X=0.5$ along the lower FES in Figure 6 determines the ease of charge delocalization between two redox-active centers: the lower the activation barrier becomes, the more delocalized the charge/spin is. Theoretically, the value of ΔG^* can be obtained by the energy difference between the charge-localized asymmetric structure (at $X=0$ and 1) and the charge-delocalized symmetric structure

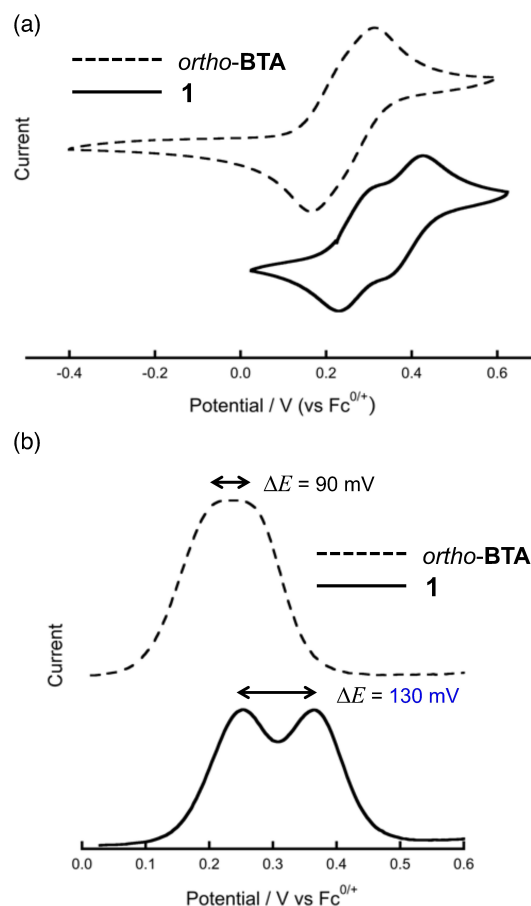


Figure 5. (a) Cyclic voltammograms and (b) differential pulse voltammograms of **1** (solid curve) and *ortho*-BTA (dashed curve) measured in 0.1 M $[n\text{Bu}_4\text{N}]^+[\text{BF}_4]^-$ /dichloromethane (ca. 1 mM) at a scan rate of 0.1 V s^{-1} . The potential values were corrected for ferrocene/ferrocenium redox couple ($\text{Fc}^{0/+}$) as an internal standard.

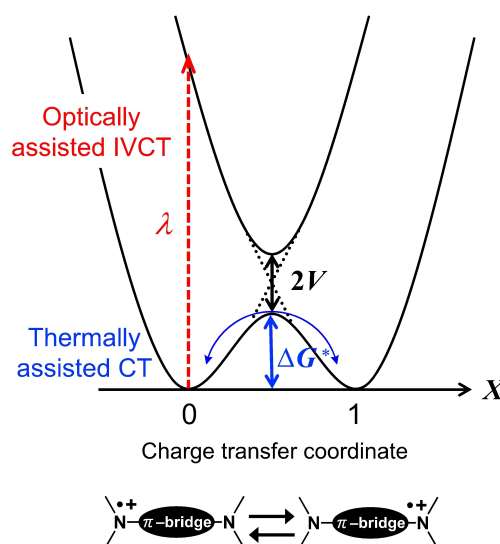


Figure 6. Schematic representation of adiabatic free energy surfaces (FES) for a 2-site MV compound (such as BTA radical cations) with degenerate MV states classified into a charge-localized class II MV system ($0 < 2V < \lambda$). The values of $2V$ and ΔG^* are determined at the crossing point of the diabatic FESs ($X=0.5$), where the MV compound adopts a symmetrical structure.

(at $X=0.5$), when both structures are optimized quantum-chemically as well. Experimentally, the value of ΔG^* can be evaluated by the ESR spectroscopy. As is often the case with the BTA radical cations,^[29–31] if the solution ESR line-shape exhibits a temperature dependency in measurable temperature range, the rate constant k_{th} of the IVCT at each temperature can be derived from the spectral simulations, and hence the Arrhenius plot gives the activation barrier ΔG^* . However, we cannot discern whether the charge/spin is delocalized statically or dynamically, in case of the value of k_{th} exceeding the ESR time-scale in the measured temperature range. Obviously, the MV system with $\Delta G^*=0$, that is $\lambda \leq 2 V$, is of charge-delocalized class III MV system in the Robin-Day classification.^[28]

Above-mentioned analytical procedures are also applicable to the present doubly π -bridged BTA radical cation $1^{+\bullet}$. The key parameters, the reorganization energy λ and the electronic coupling V , obtained in this way affect a whole picture of the IVCT process. The larger the reorganization energy λ is, the more the double-well of the lower-energy FES in Figure 6 deepens, leading to the charge localization. The larger the electronic coupling V is, the shallower the double-well becomes, leading to the dynamic charge delocalization. As an extreme case such as $\lambda \leq 2 V$, the double-well FES degenerates into a single well FES, where the charge is statically delocalized over the MV system, resulting in the charge-delocalized class III MV state. It should be noted that the observed IVCT absorption band shape also tells us the degree of charge delocalization in the MV system.^[32] the small electronic coupling of $0 < 2V < \lambda$ gives a symmetric Gaussian-shaped IVCT band, while the large electronic coupling of $2V > \lambda$ an asymmetric IVCT band with cut-off in the lower-energy side. Hence, we can safely judge the charge-localized class II or charge-delocalized class III MV systems whether the observed IVCT band shape is symmetric or asymmetric.

To confirm the electronic states of the oxidized species of **1**, the changes in the optical absorption spectra during the electrochemical oxidation in dichloromethane were recorded by using an optically transparent thin-layer electrochemical cell^[33] (Figure S2); firstly, a weak band due to the formation of $1^{+\bullet}$ grew at 0.59 eV (2097 nm) in the near IR (NIR) region, accompanied by an intense absorption band due to the triarylaminium-localized π - π^* transition^[18,20,34] at 1.61 eV (769 nm), and secondly, the weak band gradually disappeared, whereas the intense π - π^* band continued to increase until further oxidation to 1^{2+} . This indicates that the observed lowest-energy weak band can be characterized as the IVCT band for $1^{+\bullet}$. The optical absorption spectrum of $1^{+\bullet}$, which was generated with 1 equiv. AgSbF_6 as an oxidizing agent in dichloromethane, is shown in Figure 7, together with the IVCT band for *ortho*-BTA $^{+\bullet}$. The DFT geometrical optimizations by using the BLYP-based hybrid functional^[35,36] with 35% exact exchange term and the SVP basis set^[37] (BLYP35/SVP)^[38] obviate the overestimation of charge-delocalized geometries originating from the self-interaction error,^[39] and in particular, the selection of exchange-correlation functionals is of great importance for the organic MV systems.^[40,41] Additionally, the solvation effect was included by the conductor-like polarizable

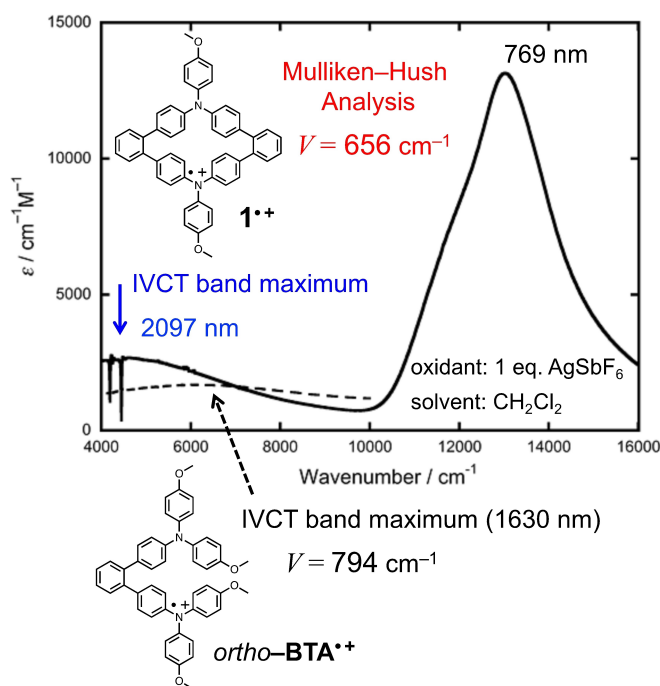


Figure 7. UV/Vis/NIR optical absorption spectrum of $1^{+\bullet}$ generated with 1 equiv. AgSbF_6 as an oxidizing agent in dichloromethane (at 0.1 mM) at r.t. The IVCT band of *ortho*-BTA $^{+\bullet}$ generated under the same conditions was also shown in dashed line.

continuum (CPCM) model (dichloromethane ($\epsilon=8.93$) in the present case).^[42] The BLYP35-optimization for $1^{+\bullet}$ provided the charge-localized asymmetric structure as energetically most stable structure, as shown in Figure 9b. The single-point TD-DFT calculation (BLYP35/SVP) at the asymmetrical geometry of $1^{+\bullet}$ indicated that the lowest-energy electronic transition corresponds to the IVCT transition from HOMO(β) to LUMO(β) [$D_1 \leftarrow D_0$], and the transition energy was computed to be 0.69 eV (1792 nm; $f=0.11$), in reasonable agreement with the observed IVCT band maximum of 2097 nm (Figure S3 and Figure 7). Moreover, the intense absorption band at 1.61 eV (769 nm) is assignable to the $D_2 \leftarrow D_0$ (H-1 and H-2 $\rightarrow$ L; 707 nm, $f=0.18$) and $S_3 \leftarrow S_0$ (H-3 $\rightarrow$ L; 702 nm, $f=0.30$) electronic excitations (Figure S4). Hence, judging from the computational result as well as the observed symmetric IVCT band shape, it can be safely said that $1^{+\bullet}$ was classified into the charge-localized class II MV system similar to *ortho*-BTA $^{+\bullet}$. Additionally, the observed optical excitation energy of the IVCT band ($\tilde{\nu}_{max}$) corresponds to the reorganization energy (λ) for the charge-localized Robin-Day class II MV systems.^[28] The doubly π -bridged $1^{+\bullet}$ had the reorganization energy of 4769 cm^{-1} ($= 2097 \text{ nm}$ in wavelength), which was in contrast to the value of 6135 cm^{-1} ($= 1630 \text{ nm}$ in wavelength) in the singly-bridged analog of *ortho*-BTA $^{+\bullet}$ (Figure 7).

On the basis of Mulliken-Hush theory, the electronic coupling (V) was evaluated by Eq. (1):^[43–45]

$$V = \frac{\mu_{ab}}{\Delta\mu_{12}} \tilde{\nu}_{max} = \frac{\mu_{ab}}{\sqrt{(\Delta\mu_{ab})^2 + 4(\mu_{ab})^2}} \tilde{\nu}_{max} \quad (1)$$

where μ_{ab} is the transition dipole moment between the adiabatic states, which can be determined from the integration of the IVCT band, $\tilde{\nu}_{max}$ the energy of the IVCT band maximum, $\Delta\mu_{12}$ the difference in the diabatic dipole moments between the ground and excited states, which is calculated by using both of μ_{ab} and the DFT-computed adiabatic dipole moment difference ($\Delta\mu_{ab}$) of 36.4 Debye [BLYP35/SVP + CPCM(CH₂Cl₂)]. From the lowest-energy band fitting to several Gaussian functions, the observed IVCT band fit well with a single Gaussian function, indicating the charge localized class II MV system of 1^{*+} . Based on the IVCT band analysis, the electronic coupling V for 1^{*+} in dichloromethane was evaluated to be 656 cm⁻¹. It should be noted that the experimentally determined value for 1^{*+} was quite small as compared with the rough estimation by the NCG method (1052 cm⁻¹; Figure 1), and furthermore it was a smaller value than that for *ortho*-BTA^{•+} (794 cm⁻¹; Figure 7).

Alternatively, the thermally assisted IVCT picture of 1^{*+} is provided by the variable-temperature ESR (VT-ESR) spectroscopy. As shown in Figure 8, a five-line spectrum was observed at 293 K, thereby indicating the dynamic delocalization of spin/charge between two triarylamine redox-active centers at room temperature. However, the ESR spectral shape of 1^{*+} in dichloromethane remained unchanged in the measured temperature range (193–293 K). The observed spectrum of 1^{*+} at 293 K was well characterized by the splitting of the main five-line by the two equivalent nitrogen nuclei from the two redox-active centers [$|a_N| = 0.45$ mT (2 N)] and relatively smaller splitting by the two sets of hydrogen nuclei surrounding the two nitrogen redox-active centers [$|a_{H1}| = 0.08$ mT (8H); $|a_{H2}| =$

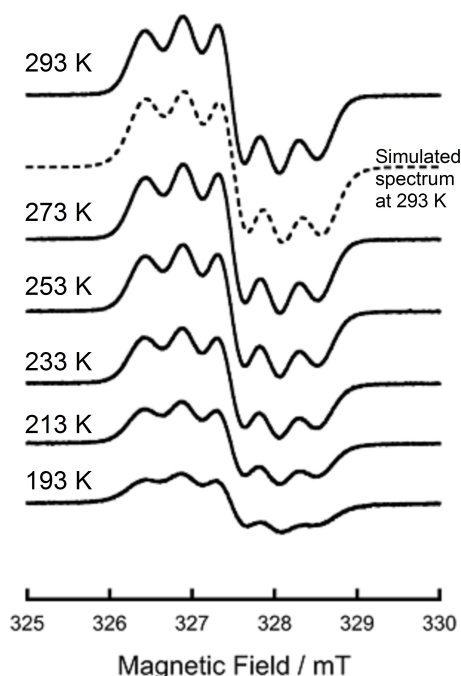


Figure 8. Observed X-band variable-temperature ESR spectra of 1^{*+} generated with 1 equiv. AgSbF₆ as an oxidizing agent in dichloromethane (at 0.1 mM). The simulated spectrum for the observed one at 293 K was depicted in dashed line.

0.06 mT (4H)]. The observed temperature-independent spectral behavior strongly suggested that the rate of the thermally assisted IVCT in 1^{*+} (k_{th}) was rapid enough compared to the ESR time-scale ($> 10^9$ s⁻¹), indicating a shallow activation barrier (ΔG^*) in the adiabatic double-well FES for the thermally assisted IVCT of doubly π -bridged 1^{*+} (Figure 6). In contrast, the VT-ESR measurements for singly π -bridged *ortho*-BTA^{•+} exhibited a clear temperature-dependent spectral change with the ΔG^* value of 3.09 kcal mol⁻¹.^[22] Hence, it was demonstrated that the double- π -bridging in a 2-site MV system effectively enabled the dynamic charge-delocalization in comparison with the usual singly π -bridged one. The activation barrier (ΔG^*) can be represented by the electronic coupling V and the reorganization energy λ by Eq. (2).^[43]

$$\Delta G^* = \frac{(\lambda - 2V)^2}{4\lambda} \quad (2)$$

From the experimentally determined values for both V (656 cm⁻¹) and λ (4769 cm⁻¹; Figure 7), the ΔG^* value was calculated to be 1.79 kcal mol⁻¹, thus certainly providing a small value for the observation of dynamic charge-delocalization in 1^{*+} within the ESR time-scale.

The DFT- and TD-DFT-computed energy profiles are summarized in Figure 9 for the singly π -bridged *ortho*-BTA^{•+} and the doubly π -bridged 1^{*+} at the BLYP35/SVP level of theory. For both compounds, the charge-localized asymmetric structures were optimized as the energetically most stable structures. Note that no other asymmetric structures were found for 1^{*+} in which the charge was mainly localized on one *o*-terphenylene-bridge. The DFT-computed V for *ortho*-BTA^{•+} and 1^{*+} was estimated to be 651 and 959 cm⁻¹, respectively, as the lowest excitation energies computed at the optimized symmetric structures (2 V in Figure 9). In contrast to the values obtained by the simplistic NCG method, it was found that the value of V for 1^{*+} was reduced to approximately 1.5 times that for *ortho*-BTA^{•+} on the basis of the BLYP35/SVP level of theory. However, the experimentally determined value of V (656 cm⁻¹) for 1^{*+} is still low as compared with the theoretical prediction (959 cm⁻¹), and the origin is currently unclear. For the experimental determination of V according to Eq. (1), the adiabatic dipole moment difference ($\Delta\mu_{ab}$) is solely dependent on the DFT calculations. Hence, there may be room for improvement of the value of V by considering further on the validity of computational values of $\Delta\mu_{ab}$.

The DFT-computed activation barriers (ΔG^*) for *ortho*-BTA^{•+} and 1^{*+} were determined to be 2.66 and 1.40 kcal mol⁻¹, respectively, by the energy difference between the symmetric and asymmetric structures, thereby indicating that the thermally assisted IVCT rate could be accelerated by double- π -bridge between two redox-active centers in accordance with the VT-ESR results. Note that the DFT-computed ΔG^* value of 1.40 kcal mol⁻¹ showed good consistency with the ΔG^* value obtained from Eq. (2) (1.79 kcal mol⁻¹). Such a low activation barrier for 1^{*+} was considered to be derived from the small reorganization energy: both *ortho*-BTA^{•+} and 1^{*+} showed a similar trend of experimental and theoretical λ with significant

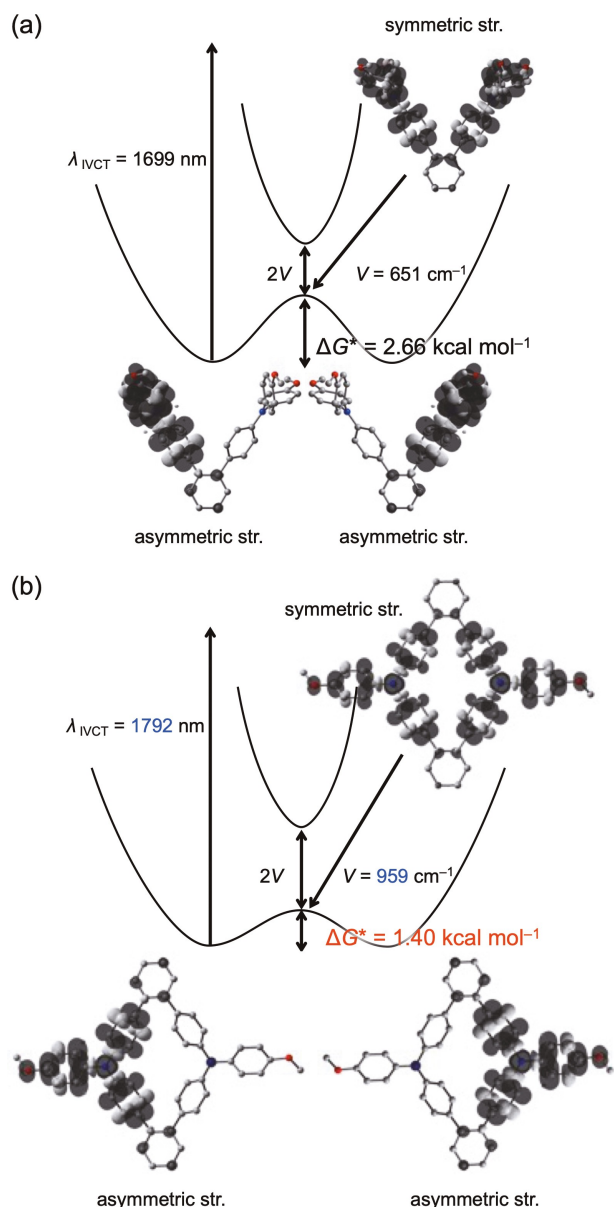


Figure 9. DFT-predicted energy diagrams for the optically and thermally assisted IVCT of (a) *ortho*-BTA^{•+} and (b) **1**^{•+} [BLYP35/SVP + CPCM(CH₂Cl₂)]. The depicted symmetrical and asymmetrical molecular structures with spin density distribution were determined by the geometrical optimization at BLYP35/SVP + CPCM(CH₂Cl₂) level of theory.

reduction by the double- π -bridge. Indeed, the slight geometrical change was seen in the symmetric and asymmetric structures of **1**^{•+} optimized at BLYP35/SVP level of theory, as shown in Figure 10. Only the peripheral anisyl group underwent a quinoidal distortion as well as a decrease in the dihedral angle against the sp^2 plane of the nitrogen redox-active center (Figure 10b).

Herein, the spin state of the dication of **1** is worth a mention in passing. On the basis of UB3LYP/6-31G* level of theory, it was predicted that the closed-shell singlet state lay 6.2 kcal mol⁻¹ above the triplet state, and furthermore, the singlet-triplet energy difference ΔE_{S-T} was estimated to be -1.0 kcal mol⁻¹ according to the DFT-based broken symmetry

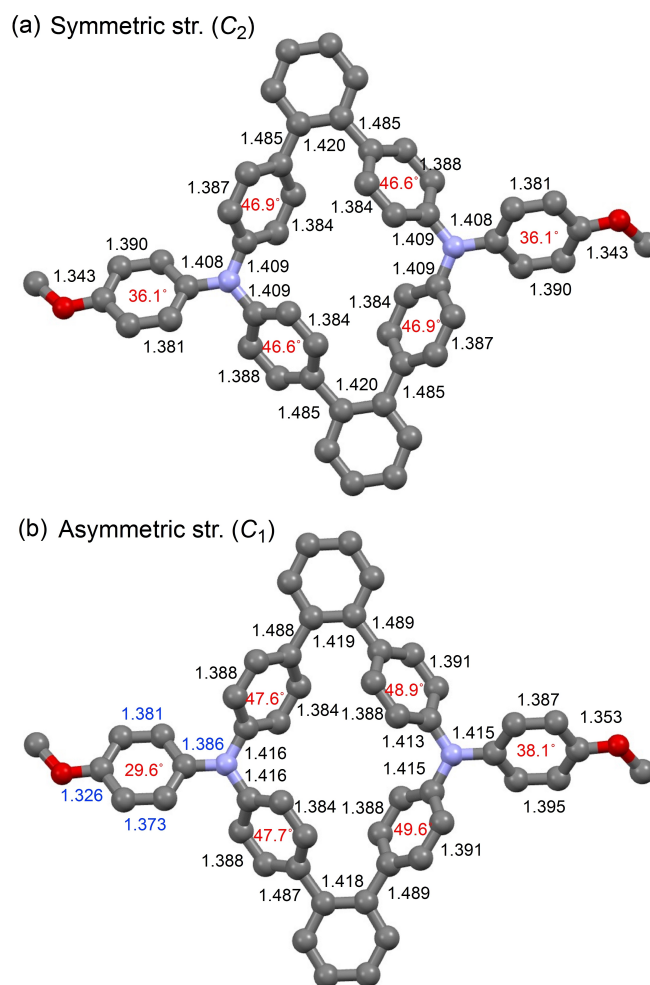


Figure 10. DFT-optimized geometrical parameters for (a) symmetric structure (C_2 -symmetry) and (b) asymmetric structure (C_1 -symmetry) of **1**^{•+} at the BLYP35/SVP + CPCM(CH₂Cl₂) level of theory; the bond length (in Å) is written in black, the dihedral angle of peripheral phenyl groups to the sp^2 plane of the nitrogen redox-center (shown in yellow triangles) in red. The left-side triarylamine moiety in the asymmetric structure is the spin/charge-localized center, and the relatively short bond lengths are written in blue.

approach,^[46–48] indicating the open-shell singlet ground state of **1**²⁺. As a result, the small ΔE_{S-T} value means very weak spin-spin interaction. As shown in Figure S5, the observed ESR spectrum in a frozen dichloromethane matrix exhibited a single resonance with no definite fine structure at 123 K. Moreover, the forbidden resonance was not observed in the half-field region (the inset in Figure S5), strongly suggesting virtually no intramolecular magnetic interaction between two spins-1/2 in **1**²⁺.

In the present study, unexpectedly, the electronic coupling for doubly π -bridged **1**^{•+} (656 cm⁻¹) has become smaller than that for singly π -bridged *ortho*-BTA^{•+} (794 cm⁻¹). However, as is apparent from the ESR study, the activation barrier ΔG^* of **1**^{•+} has been lowered enough to realize the dynamic charge/spin delocalization, in comparison with *ortho*-BTA^{•+}. In the recent studies,^[49,50] it has been clarified that the charge delocalization in a MV system is governed by an exquisite balance of two key parameters, the reorganization energy λ and the electronic

coupling V . Although the activation barrier ΔG^* increases with decreasing electronic coupling V , a whole picture of the IVCT process possibly leads to a dynamic or static charge delocalization by a greater decrease of reorganization energy λ , as compared to the small electronic coupling. For the present doubly π -bridged 1^{*+} , it is inferred that the rigidity of triarylamine redox-active units due to the macrocyclization by two *o*-terphenylene bridges brought about a small reorganization energy.

Conclusions

In conclusion, this work explored the intramolecular charge/spin transfer in a newly designed 2-site organic MV compound where two redox-active centers were connected by double- π -bridge. Contrary to the simplistic theoretical prediction that the electronic coupling of doubly π -bridged MV system becomes larger than that of singly π -bridged one, it has been found that the doubly π -bridged MV compound possessed a smaller electronic coupling than the singly π -bridged one as a reference compound, on the basis of the optically assisted IVCT band analysis. However, in the thermally assisted IVCT process, the doubly π -bridged MV compound exhibited virtually dynamic charge-delocalization, whereas the singly π -bridged MV gave temperature-dependent ESR spectral change originating from the significant activation barrier. This work exemplifies the possibility that multi-branched organic MV systems give rise to unexpected charge delocalization among the redox-active centers. Such compounds also expand the molecular design possibilities toward the realization of molecular-scale devices. Further studies on this line are in progress.

Experimental Section

General: 4,4'-dibromo-*o*-terphenyl and *p*-anisidine were purchased from TCI chemicals and used without further purification. All the other purchased reagents were of standard quality, and used without further purification. All the purchased solvents were purified, dried, and degassed by standard procedures. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc., silica gel 60 N, spherical neutral). ^1H and ^{13}C NMR spectra were measured by a JEOL JNM-AL300 and JNM-AL400 FT-NMR spectrometers. Chemical shifts of NMR spectra were determined relative to internal tetramethylsilane (TMS) standard (δ), and are given in parts per million (ppm). UV/Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 950 spectrometer. High resolution (HR) electrospray ionization (ESI) mass spectra were acquired using a Thermo Fischer EXACTIVE mass spectrometer. Fluorescence spectra were recorded on an absolute PL quantum yield measurements system (HAMAMATSU Quantaaurus-QY). The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 solution at 298 K with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte (scan rate 100 mVs⁻¹) using an ALS/chi Electrochemical Analyzer model 612 A. A three-electrode assembly was used, which was equipped with a platinum disk (2 mm²) and a platinum wire as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The redox potentials were referenced against a ferrocene/ferrocenium (Fc^{0/+})

redox potential measured in the same electrolytic solution. Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OT-TLE) cell (light pass length = 1 mm) equipped with a platinum mesh and a platinum coil as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The potential was applied with an ALS/chi Electrochemical Analyzer model 612 A. ESR spectra were recorded on a JEOL JES-X310 X-band ESR spectrometer, in which temperature was controlled by a JEOL ES-13060DVT5 variable temperature unit.

Synthesis of 1: A mixture of 4,4'-dibromo-*o*-terphenyl (2.00 mmol, 776 mg), *p*-anisidine (2.00 mmol, 246 mg), Pd(dba)₂ (0.17 mmol, 100 mg), [(*t*-Bu)₃PH]BF₄ (0.34 mmol, 100 mg), sodium *tert*-butoxide (6.00 mmol, 576 mg) in anhydrous toluene (200 mL) was refluxed with stirring under argon atmosphere for 48 h. The reaction mixture was cooled down to room temperature and washed with brine. The organic layer was dried over Na₂SO₄, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (dichloromethane : toluene = 1:1), and precipitated from MeOH (dissolution in dichloromethane and precipitation by pouring the solution into MeOH) to afford **1** as a white powder (116 mg (0.166 mmol), 16.6%). ^1H NMR (400 MHz, CD₂Cl₂): δ = 7.48 (m, 4H), 7.39 (m, 4H), 7.04 (d, J = 8.0 Hz, 8H), 6.97 (d, J = 8.4 Hz, 4H), 6.92 (d, J = 8.0 Hz, 8H), 6.80 (d, J = 8.4 Hz, 4H), 3.72 ppm (s, 6H); ^{13}C NMR (75 MHz, CDCl₃): δ = 154.7, 147.8, 141.2, 139.6, 135.3, 131.2, 130.0, 127.5, 124.9, 123.5, 114.4, 55.5 ppm; HRMS (ESI): m/z calcd for C₅₀H₃₈N₂O₂: 698.2933 [M]⁺; found: 698.2928.

Density functional theory calculations: Quantum chemical calculations were performed with using a hybrid Hartree-Fock/density functional theory (HF/DFT) method (B3LYP).^[51] Full geometrical optimizations for *ortho*-TBA^{•+}, **1**, **1**^{•+}, and **1**²⁺ were carried out, and furthermore, their local minimum structures were confirmed by performing subsequent frequency analyses. Excitation energies were examined on the basis of time-dependent density functional theory (TD-DFT)^[52] by using the B3LYP/6-31G* optimized structures. All the computations employed the 6-31G* basis sets.^[53] In addition, the symmetric and asymmetric optimized structures for *ortho*-TBA^{•+} and **1**^{•+} were determined by using the BLYP35 functional with the SVP basis sets,^[37,40,41] and their excitation energies were also computed on the basis of TD-DFT at the same level of theory. In addition, the solvent effect has been included by the CPCM version of polarizable continuum solvent model for CH₂Cl₂ (ϵ = 8.93).^[37] All these computational approaches are implemented in Gaussian 16 package of ab initio quantum chemical calculation.^[54]

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Conflict of Interests

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: redox chemistry • radical ions • mixed-valence compounds • arylamine • charge delocalization

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