



Radical Cation of Tris(Triarylamine) Connected through 1,2,3-Benzenetriyl Bridge: A Three-Redox-Center Organic Mixed-Valence System

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To explore intramolecular charge-transfer (ICT) pathways in three-redox-center organic mixed-valence (MV) radical cation, a tris(triarylamine) (TTA), in which three triarylamine (TA) redox-active centers are connected in a side-by-side fashion via 1,2,3-benzenetriyl bridging unit, has been newly synthesized. The MV state of the TTA radical cation has been investigated by a combination of experimental and theoretical methods, and the

ICT pathway between three redox-active centers has been revealed. The intervalence CT (IVCT) band analysis gave an electronic coupling value comparable to the *ortho*-phenylene-bridged bis(triarylamine) radical cation. Dynamic electron spin resonance studies clarified that the TTA radical cation was a nondegenerate MV system exhibiting ICT between the central TA and the peripheral TAs through the *ortho*-phenylene-bridge.

Introduction

Partially oxidized oligotriarylamines have always played a central role as benchmark organic mixed-valence (MV) molecular systems.^[1–5] This can be ascribed to both the robustness of the radical cations generated on the triarylamine (TA) redox-active centers^[6–8] and their synthetic availability.^[9] The intervalence charge-transfer (IVCT) in the MV compounds is affected not only by the choice of a redox-active center but also by the choice of a π -conjugated bridging unit linking the redox-active centers, and the bridging topology between the redox-active centers has been recognized as a pivotal factor governing the IVCT process.^[1,2] In particular, the substitution pattern of the redox-active centers via the phenylene π -bridge were extensively studied to develop the so-called topology rule for the strength in the electronic coupling (V) between the neutral and charged redox-active units in the organic MV systems: *para*- or *ortho*-phenylene-bridging leads to a larger V , whereas *meta*-phenylene-bridging to a relatively smaller V .^[10–13]

As shown in Figure 1a, historically, Bonvoisin and co-workers commenced the optically assisted IVCT band analysis on oligotriarylamine radical cations with *meta*-topology such as *meta*-phenylene-bridged bis(triarylamine) (BTA; **4a**) and/or the

1,3,5-benzenetriyl-bridged tris(triarylamine) (TTA; **5**) radical cations.^[14,15] Thereafter, the charge-transfer process for oxidized species of hexakis(triarylamine)s (HTAs; **6**) was precisely delineated by Lambert and co-workers.^[16,17] Moreover, by utilizing the dialkylanilino moieties in place of TA redox-active centers, the toroidal charge-delocalization in **7** has been fulfilled by Kochi et al.^[18,19] In those fully amino-group-substituted MV systems, *ortho*-topology was taken in consideration in conjunction with an overcrowdedness due to *ortho*-substitution. Additionally, we have demonstrated that the V of *ortho*-phenylene-bridged BTA (**2**) radical cation was comparable in magnitude to that for *para*-phenylene-bridged BTA (**3**) radical cation, while *meta*-phenylene-bridged BTA (**4b**) radical cation exhibits a smaller V , thus leading to the above-mentioned archetypal topology rule.^[12,13]

Though the various features on the intramolecular charge-transfer (ICT) processes are being clarified by those oligotriarylamine-based organic MV compounds, the investigation on organic MV systems with multi-redox-active centers, also referred to as multi-dimensional organic MV systems,^[2] is still in its infancy with some exceptions.^[14–25] Having found that thermally assisted IVCT process in the *ortho*-phenylene-bridged BTA radical cation **2^{•+}** was observable by the variable-temperature electron spin resonance (VT-ESR) spectroscopy,^[12] we became interested in exploring the ICT in three-redox-center organic MV radical cation **1^{•+}** where three TA redox-active centers were arranged in a side-by-side fashion via 1,2,3-benzenetriyl bridging unit (Figure 1b). In the present study, we elucidated the optically and thermally assisted IVCT processes of **1^{•+}** from the absorption and VT-ESR spectroscopic analyses.

Results and Discussion

TTA **1** was obtained in four steps according to the routes shown in Scheme 1, starting from the Suzuki-Miyaura coupling reaction of 1,2,3-tribromobenzene and 4-methoxyphenylboronic acid

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/chem.202404436>

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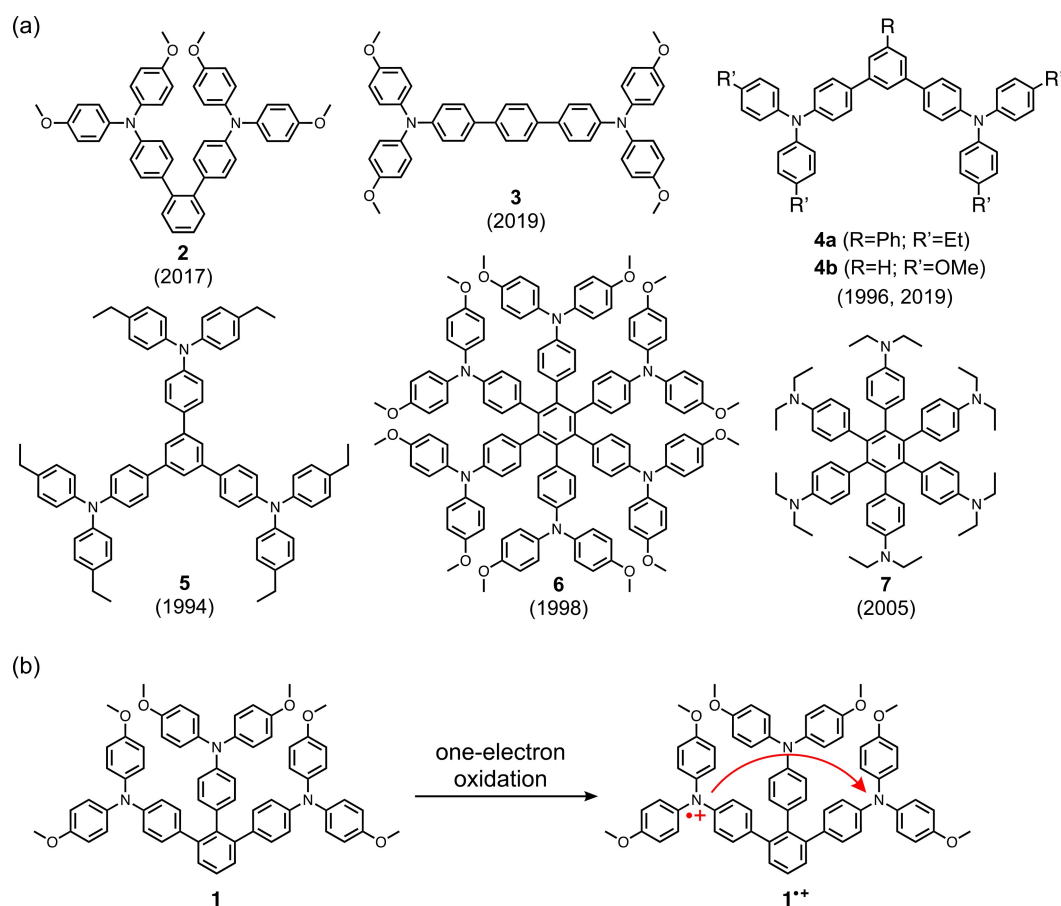
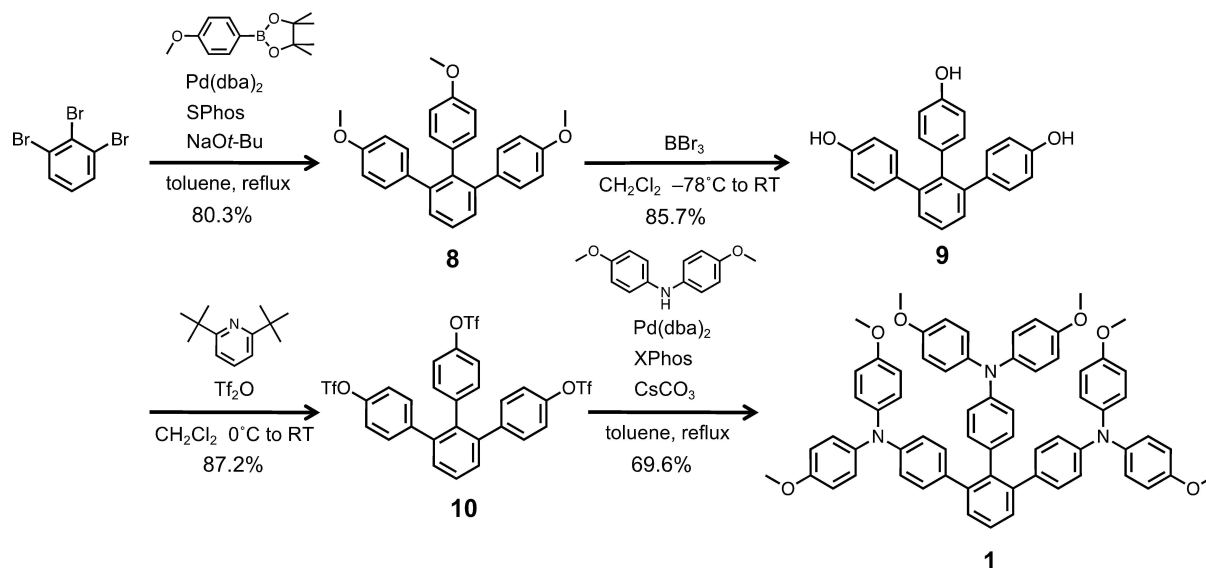


Figure 1. (a) Previously studied phenylene-bridged BTAs **2–4**, and oligotriarylamines having multi-redox-active centers **5–7**, and (b) the three-redox-center TTA **1** connected through 1,2,3-benzenetriyl bridge and its MV radical cation of interest in this study.



Scheme 1. Synthesis of TTA **1**.

pinacol ester.^[26] Compound **8** with three *p*-anisyl groups was demethylated with boron tribromide (BBr_3),^[27] and then, the hydroxy groups of compound **9** was triflated using triflic anhydride (Tf_2O) and a hindered pyridine.^[28] Finally, the

Buchwald-Hartwig amination reaction^[29] of the tris(triflate) **10** and dianisylamine afforded **1** as a white crystalline solid.

Slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **1** gave colorless prismatic crystals suitable for X-ray structure analysis

(Supporting information, Table S1 and Figure S1). As shown in Figure 2, the separations between the central nitrogen atom and the two peripheral nitrogen atoms of **1** were estimated to be 6.756 Å and 8.450 Å, respectively, designating the central TA slightly closer to one of the two peripheral TAs. Note that two nitrogen atoms were separated by 7.963 Å for **2** (Figure 2b). The dihedral angles between the 1,2,3-benzenetriyl ring and each of the NC₃ planes of three TAs were confirmed to be quite large (62.4°, 64.7°, and 39.2°), probably due to an increase in the steric congestion of **1**. Note that the corresponding dihedral angles for **2** were 42.7° and 48.2°, respectively (Figure 2b). One of the three TAs of **1** became possible to take a smaller dihedral angle due to the larger nitrogen–nitrogen separation of 8.450 Å, that is, alleviation of congestion. The observed large dihedral angles were also confirmed by the geometrical optimization (C₂-symmetry) of **1** at the B3LYP/6-31G* level of theory (Supporting Information, Figure S6).

Inspection of the Kohn-Sham orbitals at the optimized geometry of **1**, furthermore, suggested that the HOMO was mainly localized on the central TA, while the HOMO-1 was localized on the peripheral TAs, and the HOMO-2 delocalized over three TAs. In addition, the small energy gaps within 0.14 eV between the HOMO, HOMO-1, and HOMO-2, of **1** clearly indicated a quasi-degeneracy of the frontier orbitals (Supporting Information, Figure S7).

To gain an insight into the qualitative strength of the electronic coupling in **1**^{•+}, the redox behavior of **1** was measured by the electrochemical analysis [cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M [nBu₄N]⁺[BF₄][−]/CH₂Cl₂ (ca. 1 mM) at room temperature (Supporting information, Figure S2)]. Although the observed CV was seemingly judged as a single broad reversible oxidation wave, the

wave form was derived from the close overlap of three consecutive one-electron oxidation processes by the deconvolution simulation^[30] of the observed DPV (Figure S2b). The oxidation potentials were determined to be $E_1 = +0.140$ V (1e), $E_2 = +0.204$ V (1e), and $E_3 = +0.260$ V (1e). The potential difference between E_1 and E_2 ($\Delta E_{12} = 64$ mV) indicated the electronic stabilization of **1**^{•+}, to some extent, due to the dynamic charge/spin delocalization between three TA redox centers, as compared to **1**²⁺. This is because the ΔE_{12} value corresponds to $(2RT/F)\ln 2$ ($=0.036$ V at 298 K) in the case of molecular systems with non-interacting redox centers.^[31–33] Such a redox behavior of **1** was similar to that of **2**.^[12] It should be noted that additional CV and DPV data were taken by the use of [nBu₄N]⁺[B(C₆F₅)₄][−] as a weakly coordinating electrolyte in the same conditions to investigate the electrostatic contribution for the ΔE_{12} value (Figure S3a and S3b).^[33–36] and the oxidation potentials were determined to be $E_1 = +0.033$ V (1e), $E_2 = +0.117$ V (1e), and $E_3 = +0.219$ V (1e). As a result, the ΔE_{12} value slightly increased from 64 mV–84 mV, while the potential difference between E_2 and E_3 increased from 56 mV–102 mV. This suggests that the electrostatic contribution was, to some extent, seen for the present compound **1**. Hence, this observation indicates that the oxidized charged states of **1** are not significantly affected by the ion pairing effect.

To elucidate the MV state of **1**^{•+}, we performed both experimental measurements and theoretical calculations, following the analysis procedures for 2-site MV systems.^[37] The optically assisted IVCT in oligo(triarylamine)-based MV compounds can be characterized by the electronic absorption band observed in the near IR (NIR) region.^[2,5] The UV/Vis/NIR absorption spectral changes were monitored by using an optically transparent thin-layer electrochemical cell^[38,39] during

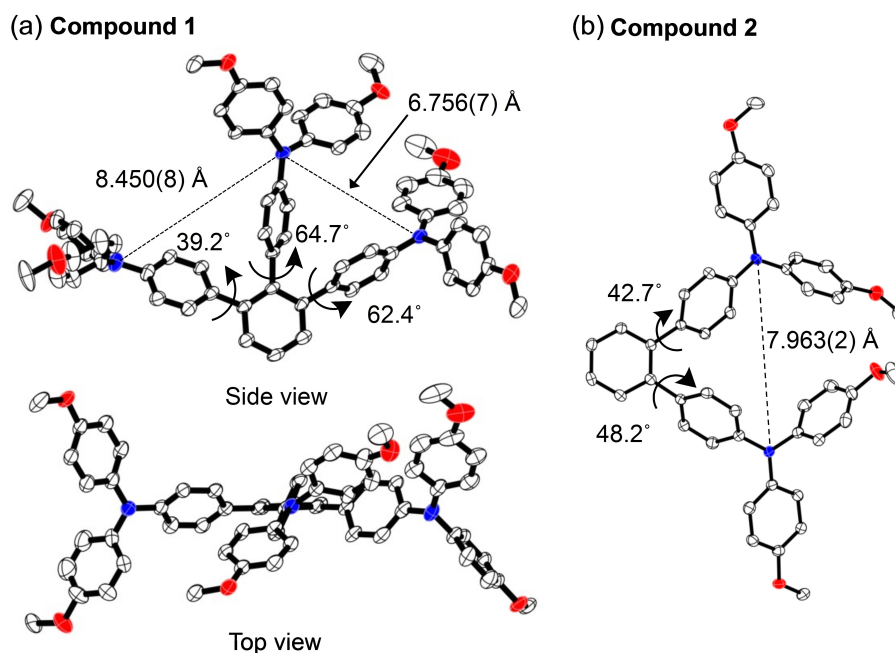


Figure 2. ORTEP views with the selected geometrical parameters of (a) **1** determined from XRD analyses (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity; blue- and red-colored ellipsoids designate nitrogen and oxygen atoms, respectively) and (b) **2** for comparison. The XRD data of **2** were taken from CCDC 1554271 (Ref.^[12]).

stepwise electrochemical oxidation of **1** in CH_2Cl_2 (Figure 3). As shown in Figure 3a, during the course of the oxidation going from **1** to 1^{++} , the absorption band at 4.04 eV (307 nm) with a

shoulder at around 3.70 eV (335 nm) gradually decreased with increasing intensity of the weak IVCT absorption band at 0.82 eV (1511 nm). The triarylaminium-localized $\pi-\pi^*$ transitions

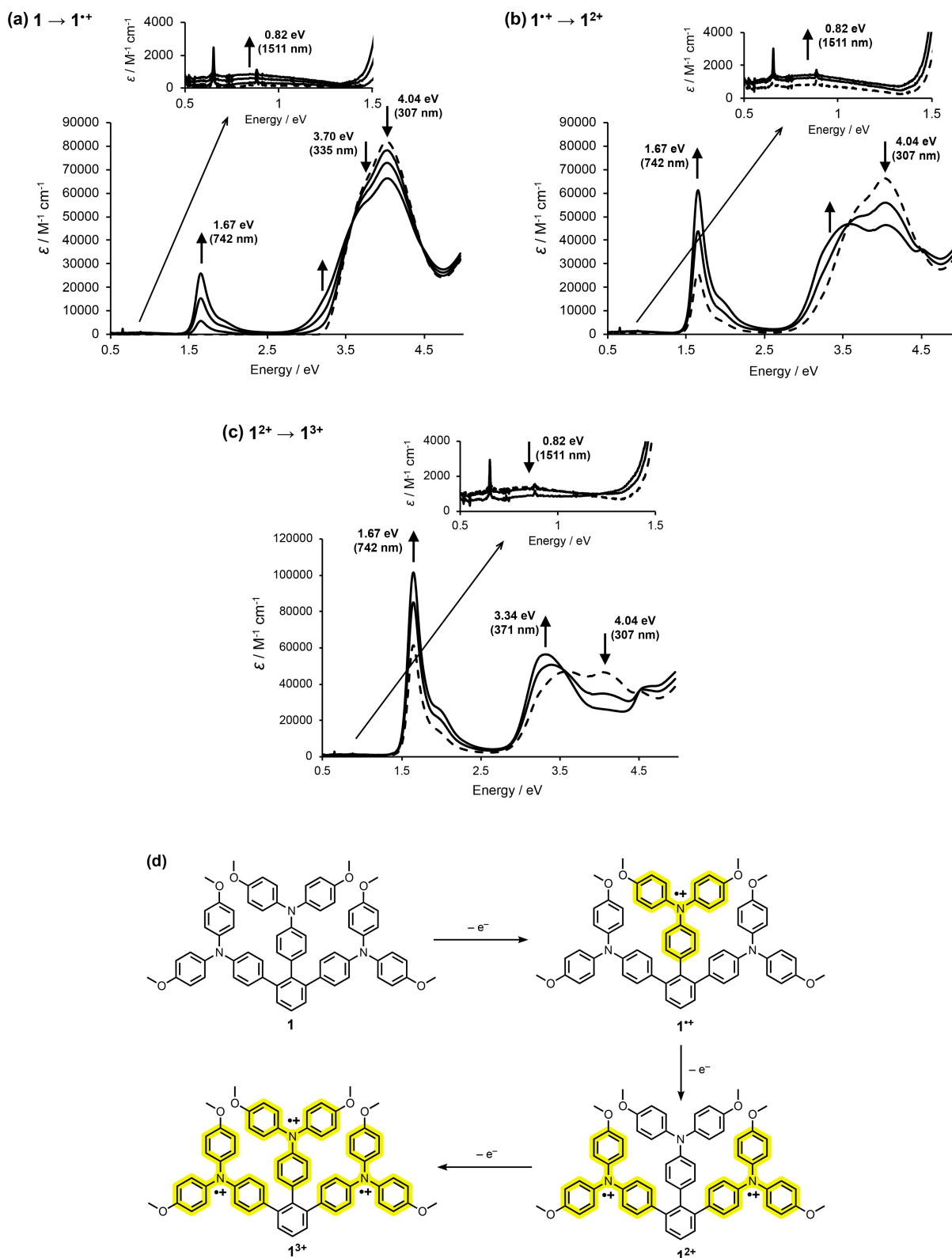


Figure 3. UV/Vis-NIR absorption spectral changes during electrochemical oxidation (a) from **1** (broken line) to 1^{++} (solid line), (b) from 1^{++} (broken line) to 1^{2+} (solid line), and (c) from 1^{2+} (broken line) to 1^{3+} (solid line) in CH_2Cl_2 (at 1×10^{-4} M) at 298 K, and (d) oxidation processes and schematic drawings of the ground state spin/charge distributions (in yellow) in each oxidation state.

at 1.67 eV (742 nm)^[6] increased simultaneously associated with two isosbestic points at 3.58 and 4.50 eV. To probe the electronic structure of 1^{*+} showing the IVCT absorption band, the DFT calculations have been carried out. The single-point time dependent DFT (TD-DFT) calculation at the UB3LYP/6-31G* optimized charge-delocalized C_2 -symmetric structures for 1^{*+} underestimated the IVCT transition energy [0.23 eV (5303 nm), $f=0.09$] (Supporting Information, Figure S9). The symmetric optimized structure was also predicted with the spin density being localized on the central TA redox-active center by the DFT geometrical optimization for 1^{*+} with use of the BLYP-based hybrid functional with 35% exact exchange (BLYP35/SVP)^[40] including the solvation effect by the conductor-like polarizable continuum (CPCM) model^[41] [CH_2Cl_2 ($\epsilon=8.93$)] (Supporting Information, Figure S10).

The IVCT transition can be assigned as the lowest-energy transition from β HOMO and/or β HOMO-1 (the MO localized on the peripheral TAs) to β LUMO (the MO localized the central TA) by the subsequent single-point TD-DFT calculation at the same level of theory. (Supporting Information, Figure S10). The IVCT transition energies ($\tilde{\nu}_{IVCT}^{DFT}$) were then estimated by DFT as 0.69 eV (1802 nm; $f=0.017$) and 0.69 eV (1788 nm; $f=0.018$), which are in reasonable agreement with the observed IVCT band maximum. Hence, the BLYP35 computations supported the present TTA MV radical cation was classified into class II MV system,^[42] where the generated charge was localized on the central TA redox-active center. More interestingly, the charge/spin localized asymmetric local minimum structure for 1^{*+} has also been found together with the partially charge/spin localized asymmetric saddle-point structure at the BLYP35/SVP + CPCM (CH_2Cl_2) level of theory (Supporting Information, Figures S11 and S12). As a whole, the DFT-predicted energy diagram for the intramolecular charge/spin transfer process in TTA radical cation 1^{*+} are shown together with schematic

adiabatic free energy surfaces for the MV compound with three redox-active centers in Figure 4. Hence, in contrast to the degenerate MV system such as 2^{*+} ,^[12] 1^{*+} can be expected to be a nondegenerate MV system.^[2,43]

During further oxidation to 1^{2+} , the intensity of IVCT band and triarylammonium-localized $\pi-\pi^*$ transition band continued to increase to almost 2-fold larger than that of 1^{*+} (Figure 3b), suggesting that 1^{2+} is still in the MV state. Finally, the IVCT band at 0.82 eV disappeared by oxidation up to 1^{3+} , and the intensity of the triarylammonium-localized $\pi-\pi^*$ band at 1.67 eV reached up to nearly 3-fold relative to that of 1^{*+} (Figure 3c). Overall oxidation processes and spin/charge distributions in each oxidation state were depicted in Figure 3d, and were mentioned below. Note that the stepwise chemical oxidation of **1** with $AgSbF_6$ also reproduced the same spectral changes as those in Figure 3 (Supporting Information, Figure S4).

For the charge/spin-localized class II MV compound 1^{*+} in the framework of Mulliken-Hush theory, the value of V can be derived by Equation (1):^[44–46]

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

where μ_{ab} is the transition moment between the adiabatic states (μ_{ab}), which can be determined from the integration of the IVCT band (Supporting Information, Figure S5), $\tilde{\nu}_{max}$ the energy of the IVCT band maximum (6618 cm^{-1} ; Figure 3a), $\Delta\mu_{12}$ the difference in the diabatic dipole moments between the ground and excited states, which was calculated by using both of μ_{ab} and the DFT-computed adiabatic dipole moment difference ($\Delta\mu_{ab}$) of 20.5 Debye [BLYP35/SVP + CPCM(CH_2Cl_2)]. Noteworthy is that the direction of the adiabatic dipole moment change in 1^{*+} by the optically assisted IVCT is parallel to the direction of connecting line between the central TA and the

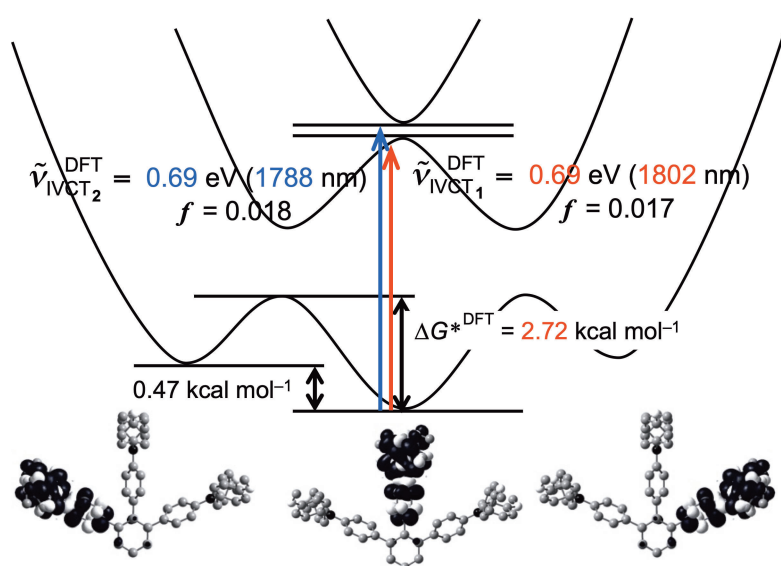


Figure 4. Schematic representation of adiabatic free energy surfaces for the MV compound with three redox-active centers like 1^{*+} and the DFT- and TD-DFT-predicted energy diagram for the intramolecular charge/spin transfer process of 1^{*+} [BLYP35/SVP + CPCM(CH_2Cl_2)]. The depicted symmetrical and asymmetrical molecular structures and their spin density distributions were determined by the geometrical optimization at BLYP35/SVP + CPCM(CH_2Cl_2) level of theory.

1,2,3-benzenetriyl bridging unit, whereas that in $2^{+\bullet}$ is parallel to the direction of connecting line between two TAs (Support-

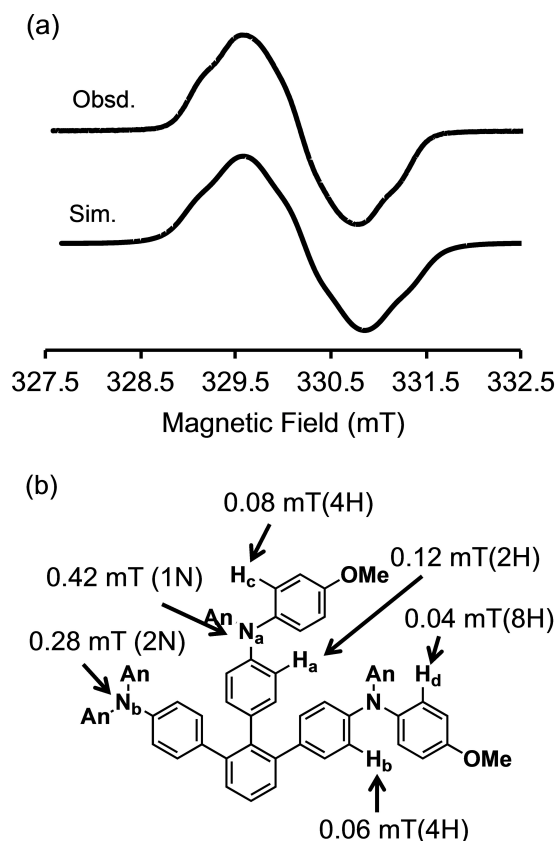


Figure 5. (a) Observed and simulated X-band ESR spectra at 298 K, and (b) the designation of nitrogen and hydrogen nuclei used in the simulation together with the hyperfine coupling constants.

ing Information, Figure S13). From the IVCT band analysis, the value of V for $1^{+\bullet}$ in CH_2Cl_2 has been determined to 874 cm^{-1} , which was comparable to that of $2^{+\bullet}$ (794 cm^{-1}).^[12] More interestingly, additional IVCT bands corresponding to the direct charge/spin transfer between two peripheral TA redox-active centers were not confirmed for $1^{+\bullet}$, in contrast with the Bonvoisin's TTA radical cation possessing two kinds of charge/spin transfer pathways.^[15]

As has been established for the BTA-based organic MV systems,^[47–49] an insight into the thermally assisted IVCT process of $1^{+\bullet}$ was directly monitored by VT-ESR spectroscopy at X-band frequencies. As shown in Figure 5, the sample generated by chemical oxidation of **1** by 0.5 equivalent of AgSbF_6 gave a hyperfine-structured ESR spectrum of $1^{+\bullet}$ in CH_2Cl_2 at 298 K. The spectrum was reasonably reproduced by hyperfine interactions of the radical spin with ^{14}N nuclei ($|a_{\text{Na}}| = 0.42\text{ mT}$) and two sets of equivalent ^1H nuclei ($|a_{\text{Ha}}| = 0.12\text{ mT}$ (2H), $|a_{\text{Hc}}| = 0.08\text{ mT}$ (4H)) in the central triarylamine redox-center and two equivalent ^{14}N nuclei ($|a_{\text{Nb}}| = 0.28\text{ mT}$ (2N)) and two sets of equivalent ^1H nuclei ($|a_{\text{Hb}}| = 0.06\text{ mT}$ (4H), $|a_{\text{Hd}}| = 0.04\text{ mT}$ (8H)) in two peripheral TA redox-active centers (Figure 5b), indicating the generated charge/spin was dynamically delocalized over the three TAs at room temperature. As shown in Figure 6a, temperature-dependence of the ESR spectra of $1^{+\bullet}$ in CH_2Cl_2 clearly showed a thermally assisted IVCT process between three TA redox-active centers, thereby indicating the radical cation $1^{+\bullet}$ can be classified into charge-localized class II MV systems. This is in accordance with the aforementioned results on the optical IVCT band analysis. The IVCT rate constants (k_{th}) at various temperatures were determined by spectral simulations with the Heinzer's dynamic ESR-EXN program based on the stochastic Liouville scheme, which simulates the ESR line shape

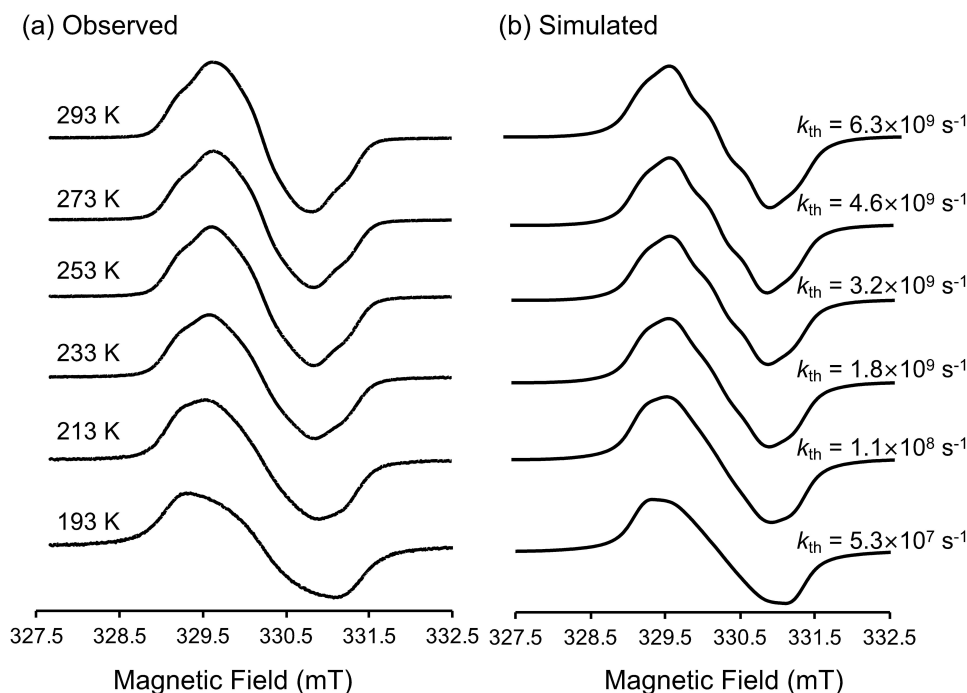


Figure 6. (a) Observed X-band VT-ESR spectra and (b) simulated spectra with determined IVCT rates (k_{th}) of $1^{+\bullet}$ in CH_2Cl_2 at $1 \times 10^{-4}\text{ M}$.

when there exists the intramolecular dynamic spin transfer among the multi-redox-active centers (Figure 6b).^[50] As shown in Figure 7, in the present dynamic ESR simulations, the spin configurations of 50% at the central TA and 25% at the peripheral two TAs has been assumed on the basis of the hyperfine coupling constants observed at 298 K (Figure 5), and the fictitious hyperfine coupling constants, a_{N} , $a_{\text{H1}}(2\text{H})$, and $a_{\text{H2}}(4\text{H})$, for each of three TA redox-active centers were estimated to be 0.9, 0.24, and 0.16 mT, respectively. The activation barrier (ΔG^*) for the thermally assisted IVCT in 1^{*+} in CH_2Cl_2 was evaluated to be 986 cm^{-1} ($2.82\text{ kcal mol}^{-1}$) from the Arrhenius plots of $\ln(k_{\text{th}})$ versus $1/T$ in the temperature range (Figure S14). It should be noted that the experimentally determined activation barrier (ΔG^*) for 1^{*+} showed good agreement with the TD-DFT-computed value [950 cm^{-1} ($2.72\text{ kcal mol}^{-1}$)] at the BLYP35/SVP+CPM(CH_2Cl_2) level of theory (Figure 4). Again, the direct charge/spin transfer pathway between two peripheral TA redox-active centers could not be extracted from the VT-ESR analysis for 1^{*+} , as can be seen from the energy diagram in Figure 4. This is probably because the electronic coupling value via *meta*-phenylene bridge ($200\text{--}300\text{ cm}^{-1}$)^[13,15] is smaller than that via *ortho*-phenylene bridge ($\sim 800\text{ cm}^{-1}$),^[12] thus leading to a high activation barrier through *meta*-phenylene bridge. Hence, it is strongly suggested that the thermally assisted IVCT pathway between two peripheral TA redox-active centers is virtually forbidden due to such high activation barrier.

Finally, it may be worth mentioning the dicationic species 1^{2+} , though the present study focuses on the MV state of radical cation 1^{*+} . The UB3LYP/6-31G* calculations predicts that 1^{2+} has a biradical character with a very small singlet-triplet energy difference (0.6 kcal mol^{-1} , which value is almost the same value as thermal energy at room temperature), strongly suggesting virtually no magnetic interaction between two electron spins. Figure S15 shows spin density distributions for both singlet and triplet states of 1^{2+} ; the spin/charge distribution in the singlet state is localized on the two peripheral TAs,

while that in triplet state is delocalized over three TAs. As shown in Figure S16a, the measured ESR spectrum for frozen CH_2Cl_2 solution of 1^{2+} exhibited no forbidden signal at half field region ($\sim 165\text{ mT}$) as well as no fine structure originating from the existence of triplet species, indicating again a biradical character of 1^{2+} . Furthermore, in contrast to the 1^{*+} , the VT-ESR measurement for 1^{2+} in CH_2Cl_2 resulted in no temperature dependence on the spectral shape (Figure S16b). Tentatively, the spectral simulation of the observed spectrum at 293 K gave the following hyperfine coupling constants of 1^{2+} : ^{14}N nuclei ($|a_{\text{Na}}| = 0.37\text{ mT}$) and two sets of equivalent ^1H nuclei ($|a_{\text{Ha}}| = 0.06\text{ mT}$ (2H), $|a_{\text{Hc}}| = 0.04\text{ mT}$ (4H)) in the central triarylamine redox-center and two equivalent ^{14}N nuclei ($|a_{\text{Nb}}| = 0.29\text{ mT}$ (2 N)) and two sets of equivalent ^1H nuclei ($|a_{\text{Hb}}| = 0.10\text{ mT}$ (4H), $|a_{\text{Hd}}| = 0.07\text{ mT}$ (8H)) in two peripheral TA redox-active centers (Figure S16c), suggesting the generated charge/spin was dynamically delocalized over the three TAs at room temperature. The IVCT absorption band for 1^{2+} in CH_2Cl_2 showed a similar feature with that for 1^{*+} in CH_2Cl_2 , and the intensity of 1^{2+} increased to nearly 2-fold larger than that of 1^{*+} (Figure S17). Judging from these experimental facts, the generated charges/spins are considered to be localized into the two peripheral TAs to avoid charge repulsion (Figure 3d). Unfortunately, the IVCT band analysis of 1^{2+} is beyond the scope of the present work, simply because the understanding of mutual interactions between the magnetic exchange interaction and electronic coupling is required for the analysis of the MV state of 1^{2+} .^[51,52] Additionally, the small potential difference between E_1 and E_2 ($\Delta E = 84\text{ mV}$) of **1** might cause the comproportionation reaction of 1^{2+} , leading to contamination of 1^{*+} in the sample.^[53]

Conclusions

The foregoing results unequivocally demonstrated that the present TTA radical cation, bearing three TA redox-active centers in a side-by-side fashion via 1,2,3-benzotriyl bridge, exhibited optically and thermally assisted IVCT phenomenon, and these features were fully characterized by the Mulliken-Hush analysis of the observed IVCT band, the exchange rate analysis based on VT-ESR measurements, and the DFT calculations. As opposed to the previously studied TTA radical cations with trigonal topology, the present TTA radical cation was found to be a nondegenerate MV system, and the overall charge/spin transfer pathway was revealed by the dynamic ESR spectroscopy on the basis of the DFT prediction with use of the BLYP35 functional. More noteworthy is that the IVCT pathway through *ortho*-phenylene overwhelms the IVCT pathway through *meta*-phenylene, probably due to a large difference in electronic couplings for *ortho*- and *meta*-conjugation. The present study may provide a clue for designing multi-dimensional MV systems to control many aspects of electronic communication.

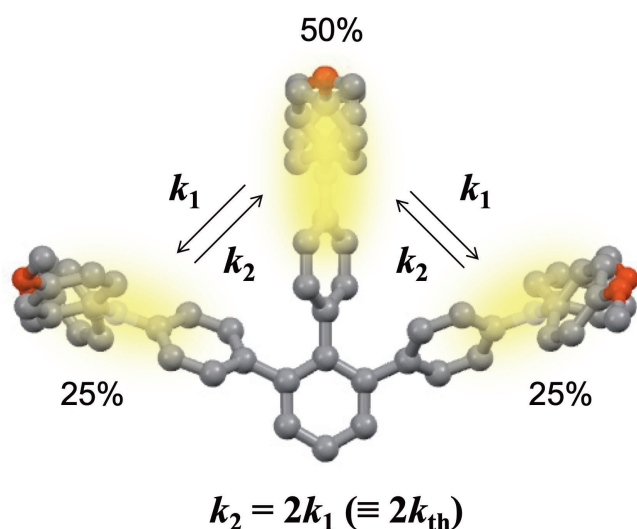


Figure 7. Spin configurations for the dynamic ESR analysis of 1^{*+} .

Experimental Section

General

All the purchased reagents were of standard quality, and used without further purification. All the 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-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. Crystallographic data for **1** were collected at 144 K on a Rigaku Saturn70 CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda=0.71075\text{ \AA}$) generated from a rotating anode. The data collection and processing was performed with CrystalClear software.^[54] The structures was solved by direct method [SHELXT-2014/5]^[55] and refined by full-matrix least-squares procedures on F^2 [SHELXL-2018/1].^[56] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on the calculated positions, and refined isotropically as a riding model. All the calculations except for the refinement procedures were performed by using CrystalStructure crystallographic software package.^[57] 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 (TBABF $_4$) as supporting electrolyte (scan rate 100 mV s $^{-1}$) using an ALS/chi Electrochemical Analyzer model 612 A. A three-electrode assembly was used, which was equipped with a platinum disk (2 mm 2) and a platinum wire as the working and counter electrodes, respectively, and Ag/0.01 M AgNO $_3$ (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. The computational simulation for the observed differential pulse voltammogram was conducted according to the method of Bond and co-workers.^[58] Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) 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 AgNO $_3$ (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 8

A mixture of 1,2,3-tribromobenzene (4.00 g, 12.7 mmol), 4-methoxyphenylboronic acid pinacol ester (10.7 g, 44.5 mmol), NaOt-Bu (6.48 g, 67.4 mmol), SPhos (0.80 g, 1.9 mmol), and Pd(dba) $_2$ (1.00 g, 1.74 mmol) in toluene (100 mL) was refluxed with stirring under argon atmosphere for 24 h. The reaction mixture was washed with brine and the organic layer was dried over Na $_2\text{SO}_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane : *n*-hexane = 1:4 as eluent) to afford **8** (4.06 g, 80.3%) as a white solid; ^1H NMR (400 MHz, CDCl $_3$) δ = 3.69 (s, 3H, -Ar $_B$ OCH $_3$), 3.75 (s, 6H, -Ar $_C$ OCH $_3$), 6.54 (d, J = 8.8 Hz, 2H, -Ar $_B$ -H 3), 6.69 (d, J = 8.8 Hz, 4H, -Ar $_C$ -H 3), 6.72 (d, J = 8.8 Hz, 2H, -Ar $_B$ -H 2), 6.97 (d, J = 8.8 Hz, 4H, -Ar $_C$ -H 2), 7.33–7.42 (m, 2H + 1H, Ar $_A$ -H 4 and Ar $_A$ -H 5); ^{13}C NMR (100 MHz, CDCl $_3$) δ = 55.0, 55.1 (–Ar $_B$ -OCH $_3$ and –Ar $_C$ -OCH $_3$), 112.8, 113.0, 126.9, 129.3, 130.8, 132.1,

132.6, 134.5, 138.6, 141.6, 157.4, 157.8; HRMS (ESI): m/z calcd for C $_{27}\text{H}_{24}\text{O}_3\text{Na}$ [M + Na] $^+$: 419.1623; found: 419.1615.

Synthesis of 9

To a dichloromethane (20 mL) solution of **8** (1.19 g, 3.00 mmol), BBr $_3$ (13.5 mL, 1.0 M in dichloromethane) was added at -78°C , and the mixture was stirred at room temperature for 1 day. The reaction mixture was cooled to 0°C , then quenched with H $_2\text{O}$. The mixture was extracted with dichloromethane and ethyl acetate. The combined organic layer was dried over Na $_2\text{SO}_4$, filtrated, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (toluene : ethyl acetate = 1:1 as eluent) to afford white powder **9** (0.91 g, 85.7%); ^1H NMR (400 MHz, DMSO- d_6) δ = 6.36 (d, J = 8.4 Hz, 2H, -Ar $_B$ -H 3), 6.47–6.53 (m, 2H + 4H, -Ar $_B$ -H 2 + -Ar $_C$ -H 3), 6.76 (d, J = 8.8 Hz, 4H, -Ar $_C$ -H 2), 7.20 (d, J = 7.6 Hz, 2H, Ar $_A$ -H 4), 7.33 (dd, J = 8.0 Hz, J = 6.8 Hz, 1H, Ar $_A$ -H 5), 9.10 (s, 1H, -Ar $_B$ -OH), 9.23 (s, 2H, -Ar $_C$ -OH); ^{13}C NMR (100.5 MHz, DMSO- d_6) δ = 114.3, 114.5, 126.9, 128.8, 130.3, 130.6, 132.2, 132.6, 138.6, 141.6, 155.0, 155.6; HRMS (ESI): m/z calcd for C $_{24}\text{H}_{18}\text{O}_3\text{Na}$ [M + Na] $^+$: 377.1154; found: 377.1147.

Synthesis of 10

To a dichloromethane (30 mL) solution of **9** (0.91 g, 2.6 mmol) and 2,6-di-*tert*-butylpyridine (1.5 mL, 6.8 mmol), Tf $_2\text{O}$ (4.3 mL, 26 mmol) was added at 0°C , and the mixture was stirred at room temperature for 1 day. The reaction mixture was cooled to 0°C , then quenched with 1 M HCl (15 mL). The combined organic layer was dried over Na $_2\text{SO}_4$, filtrated, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 4:1 as eluent) to afford white powder **10** (1.68 g, 87.2%); ^1H NMR (400 MHz, CDCl $_3$) δ = 6.85 (d, J = 8.8 Hz, 2H, -Ar $_B$ -H 3), 6.96 (d, J = 8.8 Hz, 2H, -Ar $_B$ -H 2), 7.10 (s, 8H, -Ar $_C$ -H 2 + -Ar $_C$ -H 3), 7.46–7.49 (m, 2H, Ar $_A$ -H 4), 7.54–7.59 (m, 1H, Ar $_A$ -H 5); ^{13}C NMR (100.5 MHz, CDCl $_3$) δ = 117.7, 119.9 (assigned to two CF $_3$ groups; all the signals could not be detected due to C–F couplings), 120.8, 121.0, 128.7, 130.3, 131.7, 133.2, 137.3, 139.3, 140.3, 141.5, 148.3, 148.5; HRMS (ESI): m/z calcd for C $_{27}\text{H}_{15}\text{F}_9\text{O}_9\text{S}_3\text{Na}$ [M + Na] $^+$: 772.9632; found: 772.9627.

Synthesis of 1

A mixture of **10** (750 mg, 1.00 mmol), 4,4'-dimethoxydiphenylamine (1.37 g, 5.98 mmol), Pd(dba) $_2$ (100 mg, 0.17 mmol), XPhos (100 mg, 0.21 mmol), and CsCO $_3$ (3.00 g, 9.20 mmol) in toluene (30 mL) was refluxed under argon atmosphere for 1 day with stirring. The reaction mixture was washed with brine and the organic layer was dried over Na $_2\text{SO}_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane : *n*-hexane = 1:1 as eluent), then purified by HPLC to afford **1** (688 mg, 69.6%) as a white crystal; ^1H NMR (400 MHz, acetone- d_6) δ = 3.75 (s, 6H, -Ar $_D$ OCH $_3$), 3.77 (s, 12 H, -Ar $_E$ OCH $_3$), 6.68 (s, 4H, -Ar $_B$ -H 2 + -Ar $_B$ -H 3), 6.73 (d, J = 12 Hz, 4H, -Ar $_D$ -H 3), 6.81 (d, J = 12 Hz, 4H, -Ar $_C$ -H 3), 6.85–6.95 (m, 8H + 4H + 4H, -Ar $_E$ -H 2 + -Ar $_D$ -H 2 + -Ar $_C$ -H 2), 7.01 (d, J = 12 Hz, 8H, -Ar $_E$ -H 2), 7.35–7.47 (m, 2H + 1H, Ar $_A$ -H 4 and Ar $_A$ -H 5); ^{13}C NMR (100.5 MHz, acetone- d_6) δ = 55.7 (two signals were observed to be accidentally overlapped, -Ar $_D$ -OCH $_3$ and -Ar $_E$ -OCH $_3$), 115.5, 115.6, 120.5, 121.9, 126.4, 127.2, 128.0, 129.5, 131.4, 133.3, 134.4, 135.3, 140.0, 141.8, 142.2, 142.7, 147.5, 148.0, 156.6, 157.0; HRMS (ESI): m/z calcd for C $_{66}\text{H}_{57}\text{N}_3\text{O}_6$ [M] $^+$: 987.4247; found: 987.4237; Elemental analysis (%) calcd for C $_{66}\text{H}_{57}\text{N}_3\text{O}_6$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.23; H, 5.96; N, 4.11.

Density Functional Theory Calculations

Quantum chemical calculations were performed with using a hybrid Hartree–Fock/density functional theory method (B3LYP).^[59] Full geometrical optimizations for 1 and 1^{•+} 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)^[60] by using the B3LYP/6-31G* optimized structures. All the computations employed the 6-31G* basis sets.^[61] In addition, the symmetric and asymmetric optimized structures for 1^{•+} were determined by using the BLYP35 functional with the SVP basis set,^[40,62–64] 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 ($\epsilon = 8.93$).^[41] All these computational approaches are implemented in Gaussian 16 package of ab initio quantum chemical calculation.^[65]

Acknowledgements

This work was supported by Grant-in-Aid for Transformative Research Area “Condensed Conjugation” and by Grant-in-Aid for Scientific Research (Nos. 22H00314, 20H05867, 20H05862, and 19H02174) from the Japan Society for the Promotion of Science (JSPS), and also supported by JST, the establishment of university fellowships towards the creation of science technology innovation (JPMJFS2123). Numerical calculations were partly performed at the Research Center for Computational Science in Okazaki (Japan) (Project: 24-IMS–C042). K. Y. thanks to the fellowship program of Fellowship for Future Human Resources Development to Create Materials Innovation (FS-MAT), Kyoto University.

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 transfer

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- be overestimated due to contamination of 1^{2+} . However, it can be safely said that the electronic coupling of 1^{*+} still has comparable value ($\sim 700\text{ cm}^{-1}$) to that of 2^{*+} (794 cm^{-1} ; Ref.^[12]). The oxidation with 0.5 equiv. of oxidizing agent might obviate a contamination of proportionated species. The sample treated with 0.5 equivalent oxidizing agent was used for the present VT-ESR analysis (Figure).
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Manuscript received: December 1, 2024

Accepted manuscript online: February 18, 2025

Version of record online: March 3, 2025