Small anion-assisted electrochemical potential splitting in a new series of bistriarylamine derivatives: organic mixed valency across a urea bridge and zwitterionization

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Abstract

We report the synthesis of a new bistriarylamine series having a urea bridge and investigate its mixed-valence (MV) states by electrochemical and spectroelectrochemical methods. We found that the supporting electrolytes had unusual effects on potential splitting during electrochemical behavior, in which a smaller counteranion thermodynamically stabilized a MV cation more substantially than did a bulky one. The effects contrary to those reported in conventional MV systems were explained by zwitterionization through hydrogen bonding between the urea bridge and the counteranions, increasing the electronic interactions between two triarylamino units. Furthermore, we clarified the intervalence charge transfer characteristics of the zwitterionic MV state.

Introduction

Mixed-valence (MV) compounds have received increasing attention from the viewpoint of fundamental research on intramolecular electron transfer phenomena and application in molecular devices [1-5]. The radical cations of bistriarylamine derivatives bis(NAr\textsubscript{3}) are well-known MV compounds having \(\pi\)-conjugated bridges (where NAr\textsubscript{3} = triarylamine) [6-18]. These studies focused on evaluating the intervalence charge transfer (IVCT) transition near-infrared (NIR) absorption from NAr\textsubscript{3} to NAr\textsubscript{3}\textsuperscript{+} units [1-5]. The IVCT absorptions of MV compounds are generally more pronounced in organic species
[19,20] than in their inorganic counterparts. The strong IVCT characteristics of the bis(NAr$_3$)$_2^+$ radical cations are well documented due to their good availability through common N–C bond-forming reactions and the stability of the NAr$_3^+$ unit [6-18]. Photoswitchable mixed valency has recently been demonstrated with bis(NAr$_3$)$_2^+$ radical cations having dithienylethene bridges [21,22]. This was achieved by a regulation of the π-conjugation length through photoinduced formation/dissociation of σ bonds in the bridge, which was accomplished with changeovers from a localized system (class I) to a moderately delocalized one (class II), as well as and from moderately delocalized one to a highly delocalized one (class III) [1-5]. However, attempts to change the MV characteristics by manipulating the bridge moieties through intermolecular interactions have not been reported for bis(NAr$_3$)$_2$ derivatives.

Redox stimuli are a promising trigger to directly change the charge distributions of molecules and assemblies, potentially allowing tuning of the strength of non-covalent interactions, including hydrogen bonds (H-bonds) [23-26]. In this context, a number of redox-active compounds bearing H-bond donors and acceptors were investigated to realize electrochemically controlled H-bonding [23-36]. Especially, oxidation-active ureas are an important class of such compounds [25,26]. In the neutral state, ureas can provide two NH protons for multiple H-bonding, as often used for anion recognition [27-29]. In the oxidized state, the enhanced acidity of NH protons can increase the strength of H-bonds and give them more dynamic properties, which can be useful for refined designs of supramolecular systems [30] and proton-coupled electron-transfer systems [31-40]. In contrast to the vast majority of oxidation-active ureas, those having two redox centers at both ends have not received attention except for 1,3-bis(ferrocenyl)urea FcFc [41,42], a cyclometalated diruthenium complex [43], and bis(NAr$_3$)$_2$ counterparts, including 1a (Figure 1) [44]. The electrochemically control of H-bonding would have a dramatic impact on the field of mixed valency, which is striving to utilize charge delocalization for molecular devices. However, there is a lack of basic knowledge about the influence of an excess of supporting electrolytes on the thermodynamic stability of urea-bridged MV species. In this study, we report the synthesis and characterization of a new series of urea-bridged bis(NAr$_3$)$_2$ derivatives 1 and investigate their MV states by electrochemical and spectroelectrochemical methods. We found that the supporting electrolytes have unusual effects on the thermodynamic stability of MV ions in terms of bulkiness of the counterion. Furthermore, we clarified the IVCT characteristics of the zwitterionic organic MV state.

Results and Discussion

Synthesis and characterization of 1 in the neutral form

The target compounds 1 with different substituents R at the para-position of the benzene adjacent to the nitrogen centers were synthesized to tune the oxidation potential of the nitrogen centers (Figure 1). According to a previously reported method for the synthesis of ureas [45], symmetric ureas 1 were synthesized from the corresponding amines with triphosgene. An unsymmetrical reference urea having a NAr$_3$ moiety, Ph1b, was also synthesized. The new compound series was characterized by $^1$H NMR and EIMS (Figures S1–S4 in Supporting Information File 1). In the DFT-optimized structures of 1, the ureylene moiety and the phenyl groups on both sides are almost coplanar with N···N distances between the NAr$_3$ moieties of more than 13 Å (Figure S5 and Table S1 in Supporting Information File 1). Further investigations were not performed for 1c because the solubility of this compound in aprotic solvents including CH$_2$Cl$_2$ were extremely low.

The electrochemical behavior of 1a and 1b having two chemically equivalent NAr$_3$ units was investigated by cyclic voltammetry and differential pulse voltammetry. Interestingly, two reversible waves were observed for 1b in CH$_2$Cl$_2$ containing 0.10 M n-Bu$_4$NPF$_6$ (Figure 2, bottom, and Table 1 and Table S3 in Supporting Information File 1). Further investigations were not performed for 1c because the solubility of this compound in aprotic solvents including CH$_2$Cl$_2$ were extremely low.
Figure 2: Cyclic voltammograms (left) and differential pulse voltammograms (right) of (top) 1a, (middle) Ph1b, and (bottom) 1b (1.0 mM) in CH₂Cl₂ containing n-Bu₄NX (0.10 M), Scan rate: 100 mV s⁻¹. For the differential pulse voltammogram of 1b with BArF⁻, Gaussian deconvolution (black dotted line) and the sum (black dashed line) were also shown.

Table 1: Electrochemical data for 1 in CH₂Cl₂.

| Compounds | X⁻ | E₁/₂¹ | E₁/₂² | ΔE₁/₂ | Kcc |
|-----------|----|-------|-------|-------|-----|
| 1a        | PF₆⁻ | 606   | 700   | 94    | 39  |
|           | BAFeF₄⁻ | 674   | 740   | 66    | 13  |
| 1b        | PF₆⁻ | 696   | 840   | 144   | 272 |
|           | BAFeF₄⁻ | 784   | 891   | 107   | 64  |
| Ph1b      | PF₆⁻ | 724   | –     | –     | –   |

In the presence of 0.1M n-Bu₄NX. Potentials in mV vs. Fc⁺*/Fc⁺ (Fc⁺ = decamethylferrocene). ΔE₁/₂ = potential difference between two redox processes. Comproportionation constants obtained from Kcc = exp(ΔE₁/₂ F/RT).

The highest occupied molecular orbitals (HOMOs) of the NAr₃ components are hybridized, forming HOMO and HOMO⁻¹ in both 1a and 1b as the antibonding and bonding combinations, respectively (Figure 3, top, and Supporting Information File 1).
Figure 3: Key frontier orbitals (isosurface values 0.02 au) (top), DFT-optimized structures with Mulliken charges of peripheral tolyl groups (gray), nitrogen centers and bridging moieties (blue), and PF$_6^-$ (red) (middle), and electrostatic potential maps (isosurface value 0.0004 au) of 1b, 1b$, and 1b$–PF$_6^-$ (bottom).

Figure S6). The differences between the HOMO and HOMO–1 energy levels were determined as 0.151 eV for 1a and 0.155 eV for 1b. The larger splitting for 1b with respect to 1a is a common feature between DFT calculations and electrochemical investigations. This indicates that electronic interactions between the NAr$_3$ units largely contribute to the experimentally proven thermodynamic stability of the MV state. Indeed, the energy level differences in the neutral precursors have been taken as $2H_{AB}$ of the MV species in previous reports on radical cations of bis(NAr$_3$) derivatives [11]. The HOMOs of 1a and 1b are distributed over both NAr$_3$ units but not in the central carbonyl C=O moiety of the ureylene bridge. This means that the $\pi$ orbital of the central C=O moiety does not contribute to the $\pi$-conjugation in the HOMOs. Such HOMO properties would be understood by comparison with a well-known reference bis(NAr$_3$) derivative MeO-TPD, in which the NAr$_3$ units are directly connected through a $\sigma$-bond [6]. MeO-TPD shows a larger energy difference between HOMO and HOMO–1 of 0.405 eV (Supporting Information File 1, Figure S7). In addition, the HOMO of MeO-TPD is delocalized over the whole molecule through the $\sigma$-bond bridge.

More interestingly, the supporting electrolytes were observed to cause unusual effects on the electrochemical behavior of 1b (Figure 2, bottom). In the presence of $n$-Bu$_4$NBF$_4$ (where ArF = 3,5-bis(trifluoromethyl)phenyl) as supporting electrolyte having a bulky counteranion, the potential splitting for 1b became less pronounced and decreased by 37 mV compared to that with $n$-Bu$_4$PF$_6$. A decreased potential splitting of 28 mV was also observed for 1a. These observations corresponded to a 4.3-fold and 3.0-fold reduction in $K_c$ for 1b and 1a, respectively, and implies that the larger counteranion (BArF$_4^-$) destabilized the MV state 1*. This stands in contrast to general MV compounds were $K_c$ values in the presence of larger counterions increase because they do not form strong ion-pairs with charged species, enhancing electrostatic interactions between redox components [46-52]. Thus, a different mechanism is proposed to explain the present effects of the supporting electrolytes in terms of counteranion size, as discussed in the next section.

Characterization of 1 in the MV state

DFT calculations were performed to obtain theoretical information about the MV state. The planarity of the urea moiety and the phenyl groups on both sides remained almost unchanged upon one-electron oxidation from 1 to 1$^*$ (Supporting Information File 1, Figure S5). The enhanced acidity of the NH protons in 1b$, compared to that in 1b, was well predicted by electrostatic potential maps. The positive regions (blue) were found around the two hydrogen atoms of the urea bridge in the electrostatic potential maps of 1b$^*$ (Figure 3, bottom). From these regions, 1b$^*$ can form electrostatic interactions with negatively charged species. Indeed, an optimized structure of a complex of 1b$^*$ and PF$_6^-$ was obtained and featured an intermolecular H-bonding between the N–H proton and the F atom of hexafluorophosphate. Such N–H···F hydrogen-bond formation was also reported for other urea derivatives with PF$_6^-$ as counterion in the solid state [54,55]. The N···F distance of 2.85 Å in 1b$^*$–PF$_6^-$ is slightly longer than that observed in the crystal structure of a silver complex having a pyridyl urea ligand (2.67
and 2.75 Å), primarily reflecting the absence of packing in the former. In the optimized structure of 1a⁺−PF₆⁻, the N−H···F hydrogen-bonding was comparable to that in 1b⁺−PF₆⁻ with regard to the atomic geometry and the N−F distances.

The increased acidity of 1 upon one-electron-oxidation enhances the binding strength to PF₆⁻, suggesting an involvement of the 1⁺−PF₆⁻ species during the electrochemical event of 1 described above. The comparison of DFT calculations between 1⁺ and 1⁺−PF₆⁻ revealed that upon zwitterion formation, the bound PF₆⁻ can increase the electronic interactions between the NAr₃ units. In the electrostatic potential maps of 1b⁺−PF₆⁻, the light-green and red regions face each other through the ureylene bridge, indicating the polarized nature of the zwitterionic species (Figure 3, bottom). The Mulliken charges of the central blue moiety involving redox-active nitrogen centers are 0.089 larger for 1b⁺−PF₆⁻ than for 1⁺ (Figure 3, middle), meaning the larger positive charges are delocalized between the two nitrogen centers for 1b⁺−PF₆⁻ with the assistance of charge supply from the peripheral tolyl groups. In 1b⁺−PF₆⁻, the Mulliken positive charge distributions agree well with the distributions of β-LUMO (lowest unoccupied molecular orbital) (Figure 3, top). It should be noted that the β-LUMO of 1b⁺−PF₆⁻ is distributed in both the NAr₃ units but not in the central C=O moiety of the ureylene bridge, which is in the same situation as the HOMO of 1a. Upon binding with PF₆⁻, the torsion of the central benzene rings in 1b⁺ decreased by 1.31°, accompanied with a slight shortening of the N−N distances (Supporting Information File 1, Figure S5). These structural features contribute to an increase in the electronic coupling between the NAr₃ units, thereby increasing the potential splitting seen in the electrochemical measurement. This is consistent with previous reports on bis(NAr₃)⁺⁺ derivatives that showed a positive correlation between the electron-richness of the bridge and the electronic coupling strength between the NAr₃ units [8]. In contrast, 1b⁺ does not form a complex with the larger counterion (BARF₄⁻) because of steric hindrance but instead forms a conventional ion pair, resulting in a smaller potential splitting.

A polar solvent should interfere with the N−H···F H-bonding in the present MV state. Indeed, in MeCN/CH₂Cl₂ 9:1 containing n-Bu₄NPF₆, 1a showed a 13 mV smaller potential splitting than in CH₂Cl₂ containing n-Bu₄NPF₆ (Supporting Information File 1, Figure S9 and Table S3). This suggests a decrease in electronic interactions between the NAr₃ units upon disrupting the H-bonds. The mixed solvent was selected because of the low solubility of 1a in MeCN. In general, in a more polar solvent, electrostatic repulsions between the redox units become smaller, thus decreasing potential splitting [46-48]. This is the case with MeO-TPD in CH₂Cl₂ and MeCN/CH₂Cl₂ 9:1 (Supporting Information File 1, Table S3). However, such electrostatic contribution to a change in the potential splitting should be smaller in case of compound 1a because of the separated redox units (N−N 13.13 Å for 1a⁺ in the DFT-optimized structure). Unfortunately, no investigations of solvent effects were performed with 1b due to the low solubility in polar solvents including MeCN/CH₂Cl₂ mixed solvents.

To quantify the electronic interactions between the NAr₃ units in the MV state, 1b was investigated in CH₂Cl₂/n-Bu₄NPF₆ by a spectroelectrochemical method. The medium was chosen to reduce the influence of disproportionation to the N⁺−N⁻ species. When the electrolysis of 1b was performed at E₁/₂, two new absorption bands were observed in this solution (Figure 4a). Based on its similarity to the reported NAr₃⁺⁺ derivatives [56], the first band at 760 nm derives from the π−π* transition of the NAr₃⁺⁺ moiety of 1b⁺ [56]. However, the second band in the NIR region significantly differs in broad-

![Figure 4: UV–vis-NIR spectral changes of CH₂Cl₂/n-Bu₄NPF₆ (0.10 M) solutions containing (a) 1b (4.5 × 10⁻⁴ M) and (b) Ph1b (5.0 × 10⁻⁴ M) during the controlled potential electrolysis. Potentials in mV vs. Fc⁺⁻/Fc⁻⁻.](image-url)
ness and intensity. Because any NIR absorption was not observed for the reference Ph1b+ (Figure 4b), this second band of 1b+ is assigned to an IVCT transition from the NAr3 unit to the NAr3** unit. Indeed, using time-dependent DFT (TD-DFT) calculations, an electronic transition from the β-HOMO to β-LUMO was predicted in the NIR region (at 1745 nm) for 1b+ (Table S2 in Supporting Information File 1), which has an IVCT character corresponding to the experimentally observed one. The β-HOMO (194) and β-LUMO (195) for 1b+ are distributed over both NAr3 units (Figure 3 and Figure S6 in Supporting Information File 1). When the electrolysis is performed at E1/2 = 0.15 V, the first band deriving from the π-π transition of the NAr3** moiety increased in intensity (Supporting Information File 1, Figure S10), reflecting the presence of two chromophores in the generated two-electron-oxidized species 1b2+. The generation of the dication agreed with the decrease in the IVCT intensity.

The IVCT band of 1b+ was fitted using a Gaussian function (Figure 5) to obtain the spectroscopic parameters of energy (υmax), intensity (σ), and bandwidth at the half-height (Δυ1/2) (Table 2). An electronic coupling for 1b+−PF6− was calculated to be HAB = 810 cm−1 using Hush analysis [1-5,19,20] with the three parameters. According to previous studies on bis(NAr3)+ radical cations [6,8], we adopted the N−N distance of the DFT-optimized structure of 1b+−PF6− (13.12 Å) to determine HAB, although there is an uncertainty associated with the electron transfer distances in general organic MV systems [57,58]. As the IVCT bandwidth at half-height for 1b+ is broader than the high-temperature limit (47.94 × (Δυ1/2)1/2 = 4,120 cm−1) [6], 1b+ is regarded as a class II system.

The HAB value for 1b+ is by a factor of 4.9 greater than that reported for its ferrocenyl counterpart (FcFc+) in the one-electron-oxidized form (HAB = 165 cm−1) [42]. In conventional π-conjugated bis(NAr3) derivatives [8], it was clearly demonstrated that electron-rich bridges increased HAB values. In the previous and present urea-bridged MV systems, the involved counteranions can enhance the electron-richness of the bridge moieties through interactions with NH protons. Such interactions can contribute to the relatively large HAB values seen in 1b+ and FcFc+. The interaction parameter (α) is determined by the ratio of HAB to λ and quantifies the degree of delocalization [1-4,5]. Changing the redox-active components from ferrocene to NAr3 led to a 4.3-fold increase in the α value. The degree of delocalization in the MV species can be understood in terms of the properties of the redox-active components; the positive charge of the ferrocenium moiety is accommodated largely on the d orbital, while that of the NAr3** moiety is delocalized from the nitrogen center to the benzene ring adjacent to the urea bridge.

The MV species 1a+ and the dication 1a2+ were also generated by the controlled-potential electrolysis and characterized by UV–vis-NIR spectroscopy (Figures S11, S12 in Supporting Information File 1 and Table 2). The replacement of the Me group at the para position by a OMe group decreased the HAB values by 110 cm−1. Indeed, the Mulliken positive charges of the moieties covering the central bridge and nitrogen centers (blue regions) for 1a−−PF6− decreased by 0.142 compared to those for 1b−−PF6− (Figure S8 in Supporting Information File 1). This means that the peripheral electron-donating group of the NAr3 unit decreases the extent of delocalized positive charges. This is consistent with the previous reports on conventional π-conjugated bis(NAr3) derivatives [8]. In their pioneering work on polyacetylene-bridged bis(NAr3) derivatives, Lambert et al. demonstrated a negative linear correlation of ln (HAB) versus n − 1, where n is the bond number bridging the nitrogen centers of NAr3 moieties [6]. The HAB value of 1a+ (n = 12) was almost comparable to that of a polyacetylene-bridged counterpart (HAB = 710 cm−1 with n = 13). We found that the present urea bridge can maintain electronic coupling in

### Table 2: IVCT band shape and electronic coupling factor of 1+.a

|          | υmax (cm−1) | σ (M−1·cm−1) | Δυ1/2 (cm−1) | HAB (cm−1) | αc |
|----------|-------------|--------------|--------------|------------|----|
| 1a+      | 8550        | 3050         | 7590         | 700        | 0.082 |
| 1b+      | 7400        | 3810         | 9590         | 820        | 0.110 |
| FcFc+    | 8745        | 143          | 3323         | 165        | 0.019 |

aIn CH3Cl2/0.1 M n-Bu4NPF6. bDetermined by the equation: HAB = 0.0206 (υmax) Δυ1/2)1/2/ρDA (where ρDA is the N−N distance between NAr3 moieties). cDelocalization parameter α = HAB/υmax. dIn CH3Cl2 with AgSbF6 as reported in reference [42].
terms of the N···N distances between the NAr₃ moieties with a small decrease of $H_{\text{AB}}$ values.

**Conclusion**

A new series of urea-bridged bis(NAr₃) derivatives was electrochemically characterized. This study represents the first example of ionic MV species whose thermodynamic stability was enhanced more by smaller counterions than by larger counterions. This was achieved by introduction of a urea bridge and subsequent H bonding with counteranions. The resultant zwitterionic MV species was well modeled by DFT calculations. Through the spectroelectrochemical method, we confirmed that the urea bridge can maintain electronic coupling between the NAr₃ moieties in the MV cations. These findings provide new insights into controlling MV characteristics and fabricating sophisticated molecular devices through supramolecular methods.

**Experimental Materials and general measurements**

All solvents and chemicals of reagent grade were used without purification except tetra-n-butylammonium phosphate (n-Bu₄NPF₆), which was recrystallized from methanol. 4-Aminotriphenylamine [59], 4,4'-dimethoxy-4''-nitrotetraphenylamine [38], 4,4'-dimethyl-4''-nitrotetraphenylamine [60], and n-Bu₄NBArF₄ [61] were synthesized as described in the literature. A JASCO V-670 spectrometer was used for UV–vis-NIR measurements at room temperature. The $^1$H NMR spectra were recorded using a JEOL JNM-ECP400 spectrometer with tetramethylsilane (TMS) as internal standard (0 ppm). EIMS measurements were performed using a JEOL JMS-700 MStation spectrometer.

**Synthesis and characterization of compounds**

**Synthesis of 1a**

The mixture of 4,4'-dimethoxy-4''-nitrotetraphenylamine (0.351 g, 1.00 mmol) and Pd/C (0.0145 g) was refluxed in dry ethanol (10 mL) for 1 h. After dropwise addition of hydrazine monohydrate (0.30 mL) to the reaction mixture, the reaction mixture was refluxed overnight. After filtration of Pd/C and concentrating the filtrate to dryness, the resulting white solid (0.320 g) was identified as 4-amino-4',4''-dimethoxytriphenylamine by NMR comparison to reported data [62] which was used in the next step without further purification. To a solution of triphosgene (0.296 g, 1.00 mmol) in 15 mL of dry dichloromethane (15 mL) was added at 0 °C. After 10 min of stirring, 2.5 mL of dry pyridine were added and the mixture heated at 50 °C overnight. The reaction mixture was filtrated and concentrated to dryness. The resulting solid was dissolved in ethyl acetate and washed with water. After drying the organic layer over Na₂SO₄, the solution was concentrated to dryness. Compound 1a was isolated by column chromatography on silica gel using ethyl acetate/n-hexane 1:1 as the eluent. Yield: 0.043 g (13%). $^1$H NMR (400 MHz, DMSO-d₆, ppm) $\delta$ 3.71 (s, 2H, -CH₃), 6.80 (m, 4H, -NCC(H)C(H)CN(H)-), 6.85, 6.90 (m, 16H, -OCC(H)C(H)CN-), 7.28 (m, 4H, -NCC(H)C(H)CN(H)-), 8.44 (s, 2H, -NH-); HREIMS (m/z): [M + Na]$^+$ calcd for C₄₁H₃₈N₄NaO₅, 689.27399; found: 689.27404.

**Synthesis of 1b**

Following a similar procedure as described for 1a and starting from 4,4'-dimethyl-4''-nitrotetraphenylamine (0.637 g, 2.00 mmol), the target compound was synthesized and purified. Yield: 0.165 g (27%). $^1$H NMR (400 MHz, DMSO-d₆, ppm) $\delta$ 2.23 (s, 12H, -CH₃), 6.83 (m, 8H), 6.89 (m, 4H, -NCC(H)C(H)CN(H)-), 7.25 (m, 8H), 7.34 (m, 4H, -NCC(H)C(H)CN(H)-), 8.54 (s, 2H, -NH-); HREIMS (m/z): [M + Na]$^+$ calcd for C₄₁H₃₈N₄NaO₅, 625.29533; found: 625.29533.

**Synthesis of 1c**

To a solution of triphosgene (0.296 g, 1.00 mmol) in 15 mL of dry dichloromethane a solution of the crude product of 4-aminotriphenylamine (0.520 g, 2.00 mmol) and 0.70 mL of triethylamine in dry dichloromethane (15 mL) was added at 0 °C. The reaction mixture was heated at 50 °C overnight and filtered. The filtrate was concentrated to dryness, the resulting solid was dissolved in chloroform and washed with water. After drying the organic layer over Na₂SO₄, the solution was concentrated to afford the target product 1c. Yield: 0.231 g (42%). $^1$H NMR (400 MHz, DMSO-d₆, ppm) $\delta$ 6.96 (m, 16H, -C(H)C(H)C(H)N-, -NC(H)C(H)CN(H)-), 7.25 (m, 8H, -C(H)C(H)C(H)N-), 7.41 (m, 4H, -NC(H)C(H)CN(H)-), 8.63 (s, 2H, -NH-); HREIMS (m/z): [M + Na]$^+$ calcd for C₄₅H₃₉N₅NaO₅, 659.23173; found: 659.23174.

**Synthesis of Ph1b**

The mixture of 4,4'-dimethyl-4''-nitrotetraphenylamine (0.318 g, 1.00 mmol) and Pd/C (0.0145 g) in dry ethanol (10 mL) was refluxed for 1 h. After dropwise addition of hydrazine monohydrate (0.30 mL), the reaction mixture was refluxed overnight. After filtration and concentrating the filtrate to dryness, the resulting white solid (0.320 g) was identified as 4-amino-4',4''-dimethyltriphenylamine by NMR [62] and used in the next step without further purification. To a solution of triphosgene (0.296 g, 1.00 mmol) in 15 mL of dry dichloromethane at 0 °C a solution of aniline (0.093 g, 1.00 mmol) and 0.56 mL of triethylamine in dry dichloromethane (15 mL) was added. After 10 min of stirring, 5.0 mL of dry pyridine were added followed
by crude product of 4-aminoo-4’,4”-dimethyltriphenylamine (0.288 g). The resulting reaction mixture was heated at 50 °C overnight. After filtration the filtrate was concentrated, diluted with dichloromethane and washed with water. After drying the organic layer over Na2SO4, the solution was concentrated to dryness. Compound Phib was isolated by column chromatography on silica gel using ethyl acetate/n-hexane 1:1. Yield: 0.086 g (21%). 1H NMR (400 MHz, DMSO-d6, ppm) δ 2.23 (s, 6H, -CH3), 6.83 (m, 4H, -NCC(H)C(H)C(CH3)-), 6.90 (m, 2H, -N(H)CC(H)C(H)CN-), 6.94 (m, 1H, -C(H)C(H)C(H)CN-), 7.05 (m, 4H, -NCC(H)C(H)C(CH3)-), 7.26 (m, 2H, -C(H)C(H)C(H)CN-), 7.35, 7.43 (m, 4H, -C(H)C(H)C(H)CN-, -N(H)CC(H)C(H)CN-), 8.58, 8.59 (s, 2H, -NH2). HREIMS (m/z): [M + Na]+ calcld for C27H25N3NaO, 430.18953; found: 430.18889.

DFT calculations
The DFT calculations were performed using the Gaussian09 software [63]. The three-parameterized Becke–Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional [64] was selected using the 6-31G(d) basis set for 1a and 1b with a restricted method and using the 6-311++G(d,p) basis set for the MV species with an unrestricted method. Vibrational frequencies were calculated to check the stability of the optimized MV species with an unrestricted method. Vibrational frequencies were calculated to check the stability of the optimized MV species with an unrestricted method. The DFT calculations were also performed to predict electronic transitions with energies and oscillator strengths to obtain insight into UV–vis-NIR spectral data.

Electrochemical investigations
The electrochemical behavior was investigated using a BAS electrochemical analyzer (Bioanalytical Systems Inc. West Lafayette, IN, USA) with a three-electrode system composed of a platinum wire (1.6 mm diameter) counter electrode, a glassy carbon working electrode (3.0 mm diameter), and a Ag/AgCl (3.0 M NaCl) reference electrode in CH2Cl2 solutions (1.0 mM) of the target compound containing 0.1 M n-Bu4NPF6. Additional experiments were carried out in the presence of decamethylferrocene (Fc*). The potentials versus the Fc+/Fc couple (where Fc = ferrocene) are also included in Table S4 (Supporting Information File 1), which are based on an independent experiment containing Fc and Fc*.

Supporting Information
Supporting Information File 1
Copies of 1H NMR spectra of new compounds, DFT calculation data, and electrochemical data. [https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-15-220-S1.pdf]

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