Amine–Amine Electronic Coupling through a Dibenzo[a,e]pentalene **Bridge**

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S Supporting Information

ABSTRACT: Three dibenzo[*a*,*e*]pentalene derivatives containing two redox-active amine substituents have been prepared. The degree of amine-amine electronic coupling through the dibenzo[a,e]pentalene bridge greatly depends on the substitution positions. Three monoamine compounds have been prepared for comparison studies. The experimental data and analysis were corroborated by time-dependent density functional theory results of mixed-valent compounds.

ibenzo [a,e] pentalene (DBP) is a ladder-type ring-fused hydrocarbon with unique electronic and antiaromatic properties.¹ Thanks to recent successes in the development of synthetic methodology,² DBP derivatives have now become readily available from ordinary starting materials. This has greatly stimulated the studies of DBP derivatives in various fields of organic electronics and optoelectronics, including organic field-effect transistors,³ organic photovoltaics,⁴ and photoluminescence.⁵ We report herein the use of DBP as a conjugated bridge to mediate the electronic coupling between two mixed-valent redox sites. Interestingly, the placement of redox sites on different positions of the DBP core gives rise to significantly different degrees of coupling.

Electronic communications between mixed-valent redoxactive components have received continuous attention since the pioneering work of Creutz and Taube.⁶ Apart from inorganic or organometallic complexes,⁷ purely organic redoxactive components have been used as redox termini in mixedvalent compounds.^{8,9} Three C_2 -symmetric compounds with two amine substituents on the 2,7- (1), 3,8- (2), and 5,10- (3) positions of the DBP core have been prepared for the purpose of electronic coupling studies (Figure 1). In addition, three DBP derivatives 4-6 with one amine substituent have been prepared for comparison. Triarylamines are useful redox sites for constructing organic mixed-valent systems due to the welldefined $N^{\bullet+/0}$ process in a relatively low potential region and a high extinction coefficient of intervalence charge-transfer (IVCT) transitions.9 The attachment of long alkyl chains (C_8H_{17}) is beneficial for improving the solubility of these compounds. These compounds were prepared via a $Pd(dba)_2$ catalyzed (dba = dibenzylideneacetone) C-N coupling of di(poctylphenyl)amine with 2,7-dichloro-5,10-diphenylDBP, 3,8dichloro-5,10-diphenylDBP, or 5,10-di(p-chlorophenyl)DBP, which were in turn synthesized via a Pd(OAc)₂/n-Bu₄NOAccatalyzed homoannulation¹⁰ of a chloro-substituted *o*-alkyny-





Figure 1. Diamine compounds 1-3 with a dibenzo [a,e] pentalene bridge and monoamine model compounds 4-6.

larvl iodide substrate. The details of synthesis and characterization are provided in the Supporting Information (SI).

Compounds 1 and 2 show two well-defined $N^{\bullet+/0}$ redox couples in the potential window between +0.4 and +1.2 V vs Ag/AgCl, as displayed by the cyclic voltammograms (CVs) in Figure 2a. The potential splitting (ΔE) between two waves is

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Figure 2. (a) CVs of 1 and 2. (b) CV and DPV of 3. (c) CVs of 4-6. Measurement conditions: glassy carbon working electrode; Pt wire counter electrode; Ag/AgCl in aq NaCl as reference electrode; 0.1 M Bu₄NClO₄/CH₂Cl₂. Potentials are summarized in Table 1.

240 and 310 mV for 1 and 2, respectively. Both compounds have a large comproportionation constant K_c for the equilibrium $[N^0 - N^0] + [N^{\bullet +} - N^{\bullet +}] \rightarrow 2[N^0 - N^{\bullet +}]$ (Table 1),

Table 1. Electrochemical Data⁴

compd	E_1 (V)	E_2 (V)	E_{cath}^{b} (V)	ΔE^{c} (mV)	$K_{\rm c}^{\ d}$
1	+0.72	+0.96	-1.19	240	1.2×10^4
2	+0.66	+0.97	-1.19	310	1.8×10^{5}
3	+0.88	+0.96	-1.28	80	23
4	+0.80		-1.17		
5	+0.79		-1.18		
6	+0.90		-1.23		
$a_{\mathbf{D}}$ to a tiple one product \mathbf{J} and $\mathbf{A} = (\mathbf{A} - \mathbf{C})$ \mathbf{D} to a tiple on formation $0/+$ and \mathbf{b}					

^{*a*}Potentials are reported vs Ag/AgCl. Potentials vs ferrocene^{0/+} can be estimated by subtracting 0.45 V. ^{*b*}Potentials of the cathodic scan. ^{*c*} $\Delta E = E_2 - E_1$. ^{*d*} $K_c = 10^{(\Delta E/59)}$.

indicating that the one-electron-oxidized state has good thermodynamic stability. In comparison, the potential splitting between two N^{$\bullet+/0$} processes of 3 is much smaller (around 80 mV, Figure 2b), and the splitting is more discernible from the differential pulse voltammogram (DPV). The monoamine compounds 4-6 show one N^{$\bullet+/0$} redox wave at similar potential region (Figure 2c). In addition, one cathodic redox wave around -1.2 V attributed to the reduction of the DBP core³ is observed for all of the six compounds prepared.

In order to examine the electronic coupling of the above compounds, they are subjected to oxidative electrolysis at a transparent indium-tin oxide (ITO) glass electrode. Figure 3 shows the absorption spectral changes of three diamine compounds recorded during the oxidative spectroelectrochemical measurements. In the first one-electron oxidation step of 1 (single oxidation; potential was gradually increased from +0.70 to +0.90 V vs Ag/AgCl), some new absorption bands between 700 and 1200 nm appeared. In the second one-electron



(b)

(c)

(d)

(e)

Figure 3. Absorption spectral changes of 1 (a), 2 (b, c), and 3 (d, e) in 0.1 M Bu₄NClO₄/CH₂Cl₂ by stepwise electrolysis at an ITO glass electrode. The applied potentials shown in the insets are referenced vs Ag/AgCl.

oxidation step (double oxidation; potential was further increased to +1.20 V), these new bands continued to increase. The sharp absorption band around at 750 nm of 1^{2+} is characteristic of the N^{•+}-localized transition.^{9,11} The main absorption bands at 1100 nm of $1^{\bullet+}$ and 1^{2+} are attributable to the bridge to $N^{\bullet+}$ charge-transfer (BNCT) transitions, as supported by the time-dependent density functional theory (TDDFT) results below. It is surprising that no lower energy absorptions that could be assigned to potential IVCT transitions were observed for 1°+.

In stark contrast, an intense and broad absorption band at 2200 nm ($\varepsilon_{\rm max}$ = 8900 M⁻¹ cm⁻¹) appeared in the single oxidation of 2, which decreased in the double-oxidation step (Figure 3b,c). This band is attributed to the IVCT transitions of $2^{\bullet+}$, and this assignment is further supported by the TDDFT results discussed below. For compound 3 with a smaller potential splitting, shallow and broad IVCT absorptions were observed in the single oxidation step (Figure 3d, ε_{max} < 3000 $M^{-1} cm^{-1}$).

When the three monoamine compounds 4-6 were subjected to similar oxidative electrolysis, only the appearance of the BNCT transitions (between 800 and 1500 nm) and the N^{•+}localized transition (around 700 nm) were observed (Figure S1, SI). No other lower energy absorptions appeared. This is in agreement with the assignment of the near-infrared absorptions of $1^{\bullet+}-3^{\bullet+}$; namely, IVCT transitions are only observed for $2^{\bullet+}$ and **3**^{•+}.

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Figure 4. TDDFT results $Me-1^+$ (a), $Me-2^+$ (b), and $Me-3^+$ (c).

The IVCT band of $2^{\bullet+}$ is well separated from the higher energy absorptions (Figure S2). The full bandwidth at halfheight ($\Delta \tilde{\nu}_{1/2}$, 1700 cm⁻¹) is much narrower with respect to the theoretical value for a class II system, as determined by $\Delta \tilde{\nu}_{1/2,\text{theo}} = (2310E_{\text{op}})^{1/2} = 3200 \text{ cm}^{-1,12}$ where E_{op} is the energy of the IVCT band (4500 cm⁻¹). In addition, the IVCT band of 2^{•+} is distinctly asymmetric with some shallow shoulder bands on the high energy side (probably from vibronic structures). This indicates that $2^{\bullet+}$ is a strongly coupled system and likely belongs to a delocalized class III system. The electronic coupling V_{ab} can either be estimated by $2V_{ab} = E_{op}$ (for a class III system, $V_{ab,III} = 2250 \text{ cm}^{-1}$) or $V_{ab} = (\mu_{ge} E_{op})/$ eR_{ab} (see details in the SI for a strongly coupled class II system, $V_{\rm ab,II}$ = 480 cm⁻¹), where $\mu_{\rm ge}$ is the transition dipole moment (6.0 D), e is the elementary charge, and R_{ab} is the diabatic electron transfer (ET) distance and taken to be the geometrical N–N distance (11.6 Å). The large deviation between the $V_{ab.III}$ and $V_{\rm ab,II}$ values suggests a large error in estimating the ET distance.

The IVCT band of $3^{\bullet+}$ is very broad, and the center of the band is located around 2700–2800 nm, where big noises from the solvent are present. It is difficult to distinguish the whole shape of the IVCT band. The near-infrared absorptions of $3^{\bullet+}$ were thus fitted to multiple symmetric curves using Gaussian functions (Figure S3). The deconvoluted IVCT band has a reasonable $\Delta \tilde{\nu}_{1/2}$ value of 3200 cm^{-1} (see details in the SI). The V_{ab} value is estimated to be 250 cm^{-1} by analyzing the higher energy side of the deconvoluted IVCT band using $V_{ab} = 0.0206(\varepsilon_{max}E_{op}\Delta \tilde{\nu}_{1/2})^{1/2}/(R_{ab})$,¹² where R_{ab} is again taken to be geometrical N–N distance (14.6 Å). Note that for a symmetric IVCT band, this equation gives exactly the same value as $V_{ab} = (\mu_{ge}E_{op})/eR_{ab}$. Due to the error in deconvoluting the IVCT band and estimating the ET distance, the calculated V_{ab} value should be taken with care.

The V_{ab} values of $1^{\bullet+}$ ($V_{ab,II}$) and $3^{\bullet+}$ are smaller than that of 4,4'-bis(N,N-di-p-anisylamino)tolane with a conjugated bridge but comparable N–N distance ($R_{ab} = 12.48$ Å; $V_{ab} = 3.1$ kcal/mol =1080 cm⁻¹).¹⁴ However, this comparison should be taken with great care because the estimated V_{ab} values are greatly dependent on the measurement conditions and calculation methods.

TDDFT calculations have been performed on the DFToptimized structures of the open-shell compounds Me-1⁺, Me- 2^+ , and Me- 3^+ by replacing the octyl chains of 1^+-3^+ with methyl groups (see details in Table S1, Figure 4, and Figures S4–S6). The predicted D_1 excitation of Me-1⁺ have potential IVCT character, which is dominated by the spin transition from the β -highest occupied spin orbital (HOSO) to the β -lowest unoccupied spin orbital (LUSO). However, this excitation has very weak oscillator strength (f = 0.01) and very low energy (λ = 7442 nm), which means that the IVCT transition of this compound is essentially forbidden. The predicted D_3 excitation of Me-1⁺ (f = 0.3783, $\lambda = 1060$ nm) is responsible for the observed absorptions at 1100 nm of 1⁺. This excitation has the dominant spin transition from β -HOSO-1 to β -LUSO, attributable to the BNCT transitions. In comparison, IVCT transitions with large oscillator strengths have been reproduced for Me-2⁺ and Me-3⁺ at 2144 and 2629 nm, respectively. Both transitions are dominated by the β -HOSO $\rightarrow \beta$ -LUSO excitations, where the p orbitals of the amine atom are in out-of-phase and in-phase combination, respectively, and both orbitals have large contributions from the bridge segment. This kind of excitations and orbital compositions are observed in most TDDFT results of mixed-valent bistriarylamines.^{9d,h,15} In the higher energy region, BNCT, amine-to-bridge charge transfer, and bridge-localized transitions are predicted (Table S1). It should be kept in mind that DFT calculations often tend to overestimate delocalization and give symmetrical delocalized structures. The TDDFT results based on these structures should be taken with care since $3^{\bullet+}$ is clearly a class II compound from the experimental side.

It is strange that the no IVCT band has been observed and predicted for $1^{\bullet+}$ or $Me-1^+$. The β -HOSO and β -LUSO orbitals of $Me-1^+$ are localized on the triarylamine segment; however, those of $Me-2^+$ and $Me-3^+$ are delocalized. A similar situation is present for the spin density distribution (Figure S7, again keeping in mind the apparent delocalization of DFT calculations). The DFT-calculated energy splitting between the highest occupied molecular orbital (HOMO) and HOMO-1 of neutral Me-1, Me-2, and Me-3 is 0.022, 0.31, and 0.22 eV, respectively (Figure S8). This trend does reproduce that of the experimentally determined degree of electronic coupling of $1^{\bullet+}-3^{\bullet+}$. The attachment of two amine substituents on the 2,7-positions of the DBP core results in near-degenerate HOMO and HOMO-1 orbitals, which is in agreement with the absence of efficient amine-amine coupling in $1^{\bullet+}$.

In summary, the degree of amine–amine electronic coupling through the DBP bridge was found to be greatly dependent on the substitution pattern of the redox sites. Efficient coupling is present between two amine substituents on the 3,8- and 5,10positions of DBP. However, little coupling is present between the two distal amine sites through the 2,7-positions of the bridge. The latter system is dominated by the bridge to aminium charge transfer in the one-electron oxidized state. This information is of great significance for the design of new mixedvalent systems and DBP derivatives for optoelectronic applications. In addition, the amine-substituted DBP derivatives possess appealing electrochemical properties and rich electronic absorptions at different redox states, which may make them useful in near-infrared electrochromism and redox-driven molecular switches.¹⁶

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.5b03408.

Complete synthesis and experimental details, TDDFT results, and NMR and mass spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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