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Synthesis of Azoaromatic Dyes via Redox Driven C−N Bond Fusion

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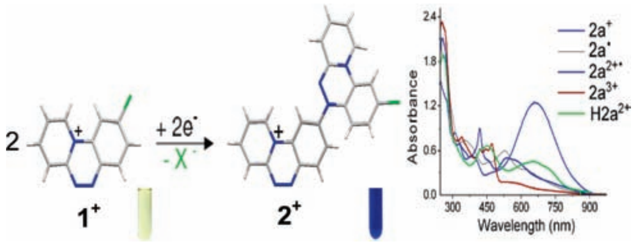
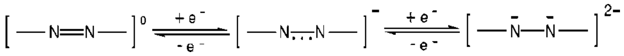
ABSTRACT



Two novel organic azo-dyes (2^+) that feature an intense intramolecular charge transfer transition with end absorption reaching into the NIR region are introduced. Syntheses of these compounds were achieved by an unusual redox-driven C−N bond fusion of the tricyclo azo-aromatic compounds (1^+). The compounds show reversible electro- as well as proton chromism. The results have generated further scope of research in the area of designed syntheses of functional azoaromatics.

Azo-aromatic compounds have been studied extensively over the years owing to their versatile optical and redox properties. Low-lying vacant azo-centered π^* molecular orbitals in azo-aromatic compounds are responsible for their long wavelength transitions[1] and nonlinear optical properties.[2] The π^* MO of these may also be directly populated[3] by one or two electrons, chemically or electrochemically. The resulting two-step redox system (Scheme 1) contains a radical anion[4] as an intermediate and a 1,2-disubstituted hydrazido(2-) species[5] as a fully reduced form. Thus di- and polymeric compounds that contain azo functions in variable oxidation states may be anticipated to constitute charge transfer molecules with absorption in the red wavelength region. Redox-active compounds that absorb intensely in the long wavelength region attract considerable attention as functional materials.

Scheme 1. Successive Azo Reduction



In this communication we introduce two novel examples of donor−acceptor molecules containing azo functions in two different oxidation states. The compounds are bright blue (λ_{max} near 640 nm) with large molar extinction coefficients (>18,000 M^{-1} cm^{-1}) and undergo multiple electron transfer

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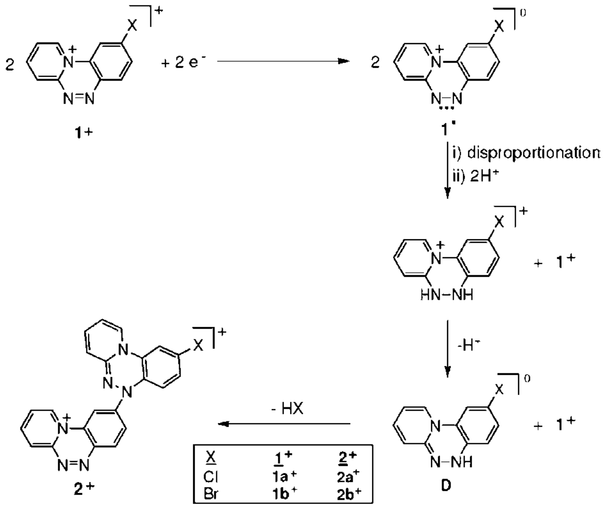
reversibly at low potentials. These are obtained as stable crystalline materials from a novel one-pot redox-driven C−N bond fusion[6] reaction (Scheme 2) of heterocyclic azoaromatics (**1**$^+$) that was recently reported[7] by us. The level of oxidation states of the donor and acceptor units in these compounds differ by two units. As far as we are aware, examples of such azo-organic dyes are not available in the literature. The most closely related dimers are the aryl/saturated hydrocarbon bridged bis-hydrazines[8] and their corresponding radial cations reported by Nelsen et al.

Scheme 2. Synthetic Reaction



The 6-Cl(Br)-substituted yellow compounds **1a**$^+$ and **1b**$^+$ upon electrochemical one electron reduction in water produced the intense blue monocations **2a**$^+$ and **2b**$^+$, respectively. Notably this transformation does not occur in dry acetonitrile. The neutral radical compound **1a**$^{\bullet}$ is stable in dry solvent and showed characteristic single line EPR. It may thus be concluded that a proton source is essential for the reference transformation. Subsequently, we found that chemical reduction of an aqueous solution of **1**$^+$ by the use of aqueous sodium dithionite also produced **2**$^+$ in high yields (ca. 80%). These were isolated as their perchlorate or chloride salts. The mechanism of the reaction remains unresolved as yet. However, one of the most plausible mechanisms is depicted in Scheme 2. The reaction is initiated by one electron reduction of the triazinium cation. The triazene radical, thus produced, undergoes rapid disproportionation in aqueous medium to produce a tricyclo nuleophilic intermediate [**D**], which on subsequent reaction with **1**$^+$ produces the cationic dimer **2**$^+$ with the elimination of HX. Further propagation of the fusion reaction via X substitution in **2**$^+$ was not possible due to nonlability of X bonded to the reduced tricyclo moiety in **2**$^+$. Thus reduction of the azo chromophore is the primary prerequisite for the above dimerization reaction. Interestingly, catalytic hydrogenation of **1a**$^+$ in methanol on 10% Pd/C also produced **2a**$^+$, confirming our above proposition further. The intermediate [**D**] appears to be highly reactive and combines instantaneously (see below) with the unreacted **1a**$^+$ to form **2a**$^+$. Thermodynamic feasibility for the formation of **2a**$^+$ is assessed on the basis of the calculated enthalpy for each step. The overall reaction is found to be highly exothermic, which includes one electron reduction of **1a**$^+$ as well as disproportionation[9] of the ensuing triazene radical. In the last step, formation of the cationic dimer **2a**$^+$ is also found to be favored with a heat of formation of −24.7 kcal/mol.

Micro analytical, positive-ion ESI-mass spectra, together with NMR spectral data (Figures S1−S3, Supporting Information) of the compounds, [**2**]A (A = ClO_4, Cl) convincingly support their formulations. X-ray structure determination of a representative compound, [**2a**]ClO_4 confirms its formation. A molecular view of the cationic compound is shown in Figure 1 (for its ORTEP see Figure S4, Supporting Information).

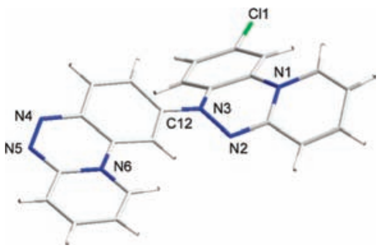


Figure 1. Molecular view of **2a**$^+$.

The most significant observation in this structure is that an essentially planar triazinium unit (acceptor) is bonded to a boat-shaped two electron reduced unit (donor) through a newly formed C(12)−N(3) bond. The N−N length in the acceptor unit indicates a double[10] bond (N(4)−N(5), 1.311(3) Å), whereas that in the reduced unit is a single[11] bond (N(2)−N(3), 1.411(3) Å). The connecting C(12)−N(3) bond is shorter than a single bond, indicating electron delocalization between the two rings.

Cyclic voltammetry (CV) studies (Figure 2) of **2**$^+$ revealed two one electron oxidative waves associated with the formation of the dication radical $\mathbf{2}^{2+\bullet}$ and the trication, $\mathbf{2}^{3+}$, respectively. In addition to the above anodic responses, a

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(9) Electron affinity of **1a**$^+$ is −131.5 kcal/mol, and calculated heat of reaction for disproportionation followed by protonation is −245.6 kcal/mol (B3LYP/6-31G*).

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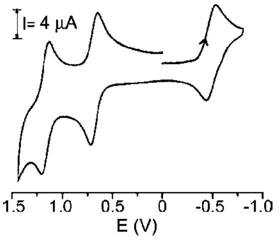

Figure 2. Cyclic voltammogram of **2a**$^{+}$.

reductive response at −0.49 V signifies the formation of a neutral radical, **2**$^{\bullet}$. For comparison, the parent triazinium salt [**1a**]ClO_4 displayed[7] a reductive one electron wave at −0.17 V forming a neutral triazene radical, **1a**$^{\bullet}$.

The electrolytically generated compounds, **2a**$^{2+\bullet}$ and **2a**$^{\bullet}$, each showed a single line sharp EPR spectrum at $g = 2.004$ and 2.006, respectively, characterizing the formation of the free radicals. The trication, **2a**$^{3+}$ is, however, EPR silent as expected (Figures S5−S8, Supporting Information).

To gather further insights into the molecular origin of these redox reactions, we have analyzed the B3LYP/6-31G* optimized geometries of these species.[12] The agreement between the experimental structural parameters and that obtained through DFT calculations for **2a**$^{+}$ are found to be excellent (Table 1). The geometric comparison between **2a**$^{+}$ and the corresponding one electron reduced species, **2a**$^{\bullet}$, reveals an elongation of N(4)−N(5) bond. Further, the spin orbital contours of **2a**$^{\bullet}$ (Figure 3) indicate a relatively larger localization of spin density on N(4). It is therefore concluded that the reduction of **2a**$^{+}$ is predominantly centered at the acceptor part. The oxidation of **2a**$^{+}$, on the other hand, is identified to impart double bond character to the N(3)−N(2) bond.

Table 1. Essential Structural Parameters of Compounds from DFT Calculations[a]

	bond lengths			torsional angle
	N(5)−N(4)	N(3)−N(2)	N(3)−C(12)	N(2)−N(3)−C(12)−C(22)
2a$^{\bullet}$	1.343	1.414	1.409	−18
2a^{+}	1.307 (1.311)	1.406 (1.411)	1.364 (1.372)	−9 (−4)
2a$^{2+\bullet}$	1.277	1.349	1.425	−37
2a^{3+}	1.269	1.297	1.466	−55

[a] Experimental data available for **2a**$^{+}$ is given in parentheses

Spin density of the first oxidized product **2a**$^{2+\bullet}$ is primarily at the N(3)−N(2) bond of the donor unit. The LUMO of the subsequent oxidized species **2a**$^{3+}$ is also found to be localized on the N(3)−N(2) bond (Figure S9, Supporting Information). Moreover, both oxidation and reduction of **2a**$^{+}$ result in out-of-plane geometric disposition of the two rings.

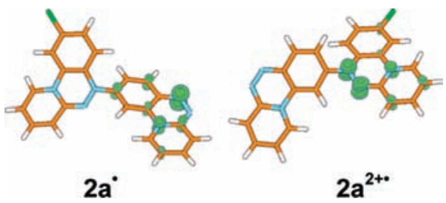

Figure 3. DFT calculated spin orbitals of the compounds **2a**$^{\bullet}$ and **2a**$^{2+\bullet}$.

The intense blue color of the parent compound, **2a**$^{+}$, upon electrolyses faded considerably along with blue shift (electrochromic effect) of the transition bands (Figure 4). The analyses of frontier MOs of **2a**$^{+}$ indicate that the HOMO and HOMO−1 are localized on the donor triazinium, while the unoccupied orbitals such as LUMO and LUMO+1 are localized primarily on the acceptor unit. On the basis of values of the oscillator strength predicted using TD-DFT, the most intense transition at 634 nm for the compound **2a**$^{+}$ is ascribed to the excitation from HOMO to LUMO.[13]

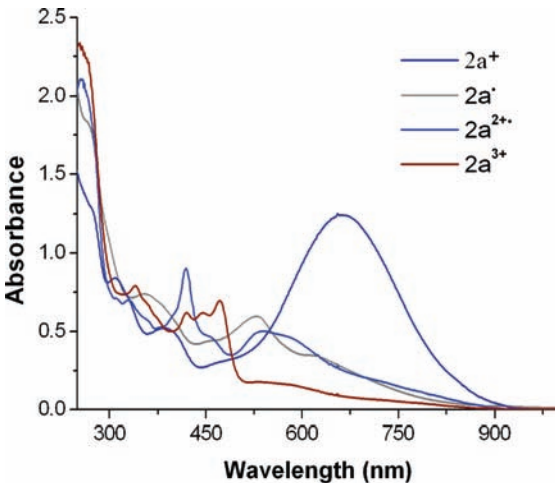

Figure 4. UV−vis spectra of **2**$^{\bullet}$, **2**$^{+}$, **2**$^{2+\bullet}$, and **2**$^{3+}$.

Moreover, upon addition of H^{+} to a solution of the compound [**2a**]$^{+}$ in MeOH−H_2O (1:1 v/v), the intense blue color became light yellowish green, which is attributed to protonation of N2 resulting in loss of conjugation with the C5 atom.[14] The effect of H^{+} in the above spectral change is reversible with a sharp isosbestic point at 510 nm (Figure 5).

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(12) All electronic structure calculations were performed using Gaussian 03: Frisch, M. J. et al., *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004 (see Supporting Information for full citation). All stationary points are characterized by frequency calculations on the optimized geometries.

(13) Frontier molecular orbitals of **2a**$^{+}$ as well as list of computed vertical excitations of **2a**$^{\bullet}$, **2a**$^{+}$, **2a**$^{2+\bullet}$, **2a**$^{3+}$, and **1a**$^{+}$ are given in Supporting Information.

(14) An increase in N(2)−C(5) distance from 1.309 to 1.409 Å is noticed upon protonation of **2a**$^{+}$ (see Supporting Information).

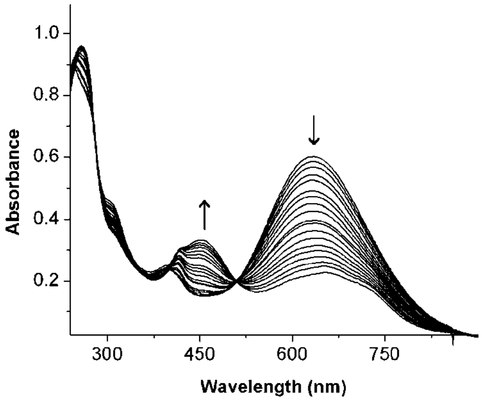

Figure 5. UV−vis spectral change of **2a**$^+$ as a function of [H$^+$].

In summary, we have introduced a redox-driven one-pot synthesis of two novel azoaromatic dyes that feature intense intramolecular charge transfer bands with end absorption reaching into the NIR region. These compounds show appealing optoelectronic and redox properties. The applications of these azo dyes as functional materials[15] are under scrutiny.

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Supporting Information Available: X-ray crystallographic table of [**2a**]ClO_4, TD-DFT calculations results, relevant figures as noted in the text, and experimental and computational details This material is available free of charge via the Internet at http://pubs.acs.org.

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