Communication

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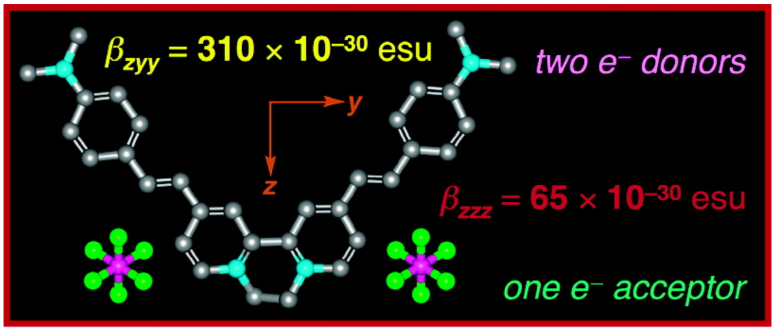

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Molecular Salts with Diquat-Based Electron Acceptors for Nonlinear Optics

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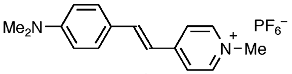
Organic nonlinear optical (NLO) materials show great promise for uses in optoelectronics and photonics.[1] Compounds studied in this context include various salts, for example, *trans*-4′-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST).[2] Most molecules with large quadratic NLO responses, characterized by first hyperpolarizabilities β, contain polarizable π-systems with electron donor (D) and acceptor (A) substituents.[1] The linear optical spectra of such chromophores show intense $\pi(D) \rightarrow \pi^*(A)$ intramolecular charge-transfer (ICT) absorptions. Synthetically accessible pyridinium rings act as powerful A units in stilbazolium and related compounds.

Most quadratic NLO chromophores have simple D−π−A structures in which β is dominated by one tensor component, but multidimensional species (e.g., 2D dipoles)[3] have recently attracted interest. Such compounds offer potential advantages over 1D chromophores, including increased β without undesirable visible transparency losses. Furthermore, C_{2v} molecules with large off-diagonal β components are attractive for electro-optic applications and for phase-matched second harmonic generation. Since very few charged 2D dipolar chromophores are known,[3d,f] we have prepared such compounds based on the familiar stilbazolium template by using "diquat" (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium, DQ^{2+}) units. The introduction of 2D chromophores into salts offers extensive possibilities for "crystal engineering" of noncentrosymmetric materials suitable for bulk NLO effects.



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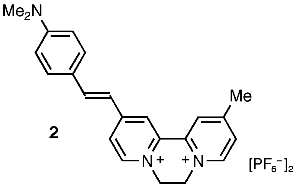

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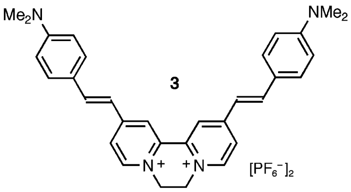

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Knoevenagel condensations of $[2,11\text{-}Me_2DQ^{2+}]Br_2$[4] with 4-(dimethylamino)benzaldehyde afford the new cations in salts **2** and **3** (full synthetic details will be published elsewhere). A compound related to **3**, but with $-NEt(C_2H_4OH)$ instead of $-NMe_2$ groups, has been investigated as a two-photon absorber, with a view to potential applications in upconversion lasing or optical limiting.[5] However, no other related DQ^{2+} derivatives have been prepared or studied to our knowledge.

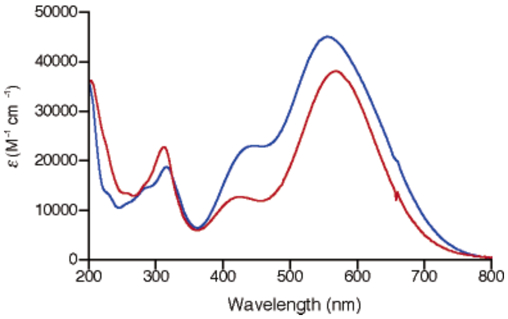

Figure 1. UV−visible absorption spectra of **2** (red) and **3** (blue) at 295 K in MeCN.

Table 1. UV−Visible and Electrochemical Data at 295 K in MeCN

salt	λ_{max}[a] (nm)	E_{max}[a] (eV)	ϵ_{max}[a] (M^{-1} cm^{-1})	E, V vs Ag–AgCl (ΔE_p, mV)[b] E_{pa}[c]	 E_{pc} or $E_{1/2}$[d]	 $E_{1/2}$[e]
1[f]	470	2.64	42800	0.94	−1.11	
	270	4.59	11100			
2	572	2.17	38000	0.98	−0.41 (100)	−0.82 (90)
	426	2.91	12700			
	314	3.95	22700			
3	560	2.21	45100	0.98	−0.42 (90)	−0.77 (80)
	442	2.80	12100			
	318	3.90	18700			

[a] Solutions ca. 10^{-5} M. [b] Solutions ca. 10^{-3} M in analyte and 0.1 M in $[N(^nBu)_4]PF_6$ at a glassy carbon working electrode with a scan rate of 200 mV s^{-1}. Ferrocene internal reference $E_{1/2} = 0.46$ V, $\Delta E_p = 90$ mV. [c] For first irreversible $-C_6H_4\text{-}4\text{-}NMe_2^{+/0}$ oxidation. [d] For irreversible $Mepy^{+/0}$ or reversible $DQ^{2+/+}$ reduction. [e] For reversible $DQ^{+/0}$ reduction. [f] Taken from ref 6.

The UV−visible absorption spectra of **2** and **3** in acetonitrile (Table 1) show intense low energy bands, ascribed to $\pi(-C_6H_4\text{-}4\text{-}NMe_2) \rightarrow \pi^*(DQ^{2+})$ ICTs, with high energy shoulders (Figure 1). Weaker $\pi \rightarrow \pi^*$ bands are also observed in the UV region. The main ICT bands are red-shifted by ca. 0.45 eV when compared with that of **1** (which contains the cation of DAST), indicating that the DQ^{2+} unit is a much stronger electron acceptor than a *N*-methylpyridinium ($Mepy^+$) group. The cyclic voltammograms of **2** (Figure 2) and **3** show completely irreversible processes assigned to oxidation of the $-C_6H_4\text{-}4\text{-}NMe_2$ groups and reversible DQ^{2+}-based reductions (Table 1). The oxidation and first reduction processes of **2** and **3** occur at identical potentials, while the second reduction is ca. 50 mV more positive for **3**. In contrast, **1** displays only irreversible redox chemistry.[6a] The E_{pa} values show that the $-C_6H_4\text{-}4\text{-}NMe_2$ unit is slightly easier to oxidize in **1** as opposed to **2** and **3**, while the very low E_{pc} for **1** shows that the $Mepy^+$ group is much harder to reduce than a DQ^{2+} unit. Both of these observations corroborate the stronger electron-accepting ability of the latter indicated by the ICT data.

Data from Stark (electroabsorption) spectroscopic studies on **2** and **3** in butyronitrile glasses at 77 K are shown in Table 2. In contrast to the room temperature situation, the visible absorption spectrum of **2** shows only a single Gaussian-shaped band with no

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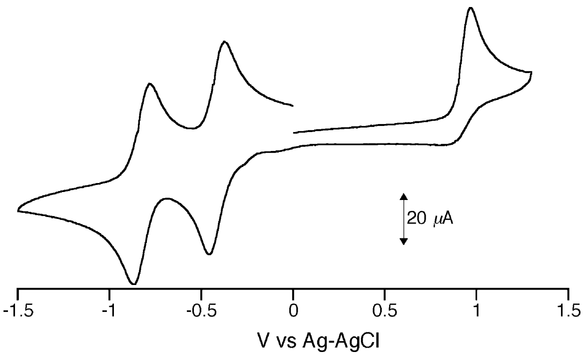

Figure 2. Cyclic voltammogram of **2** at 295 K in MeCN.

Table 2. UV−Visible and Stark Spectroscopic Data at 77 K in PrCN

salt	λ_{max} (nm)	E_{max} (eV)	μ_{12}[a] (D)	$\Delta\mu_{12}$[b] (D)	$\Delta\mu_{ab}$[c] (D)	β_0[d] (10^{-30} esu)
1[e]	480	2.58	9.1	16.3	24.4	236
2	563	2.20	7.7	20.6	25.8	297
3-G1[f]	564	2.20	11.0	23.6	32.2	688
3-G2[f]	437	2.84	7.1	25.7	29.4	188

[a] Transition dipole moment derived from $|\mu_{12}| = [f_{os}/(1.08 \times 10^{-5}E_{max})]^{1/2}$ (f_{os} = oscillator strength). [b] Dipole moment change derived from $f_{int}\Delta\mu_{12}$ using $f_{int} = 1.33$. [c] Diabatic dipole moment change derived from $\Delta\mu_{ab}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2$. [d] Derived from $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{max})^2$ (perturbation series convention;[8] error ca. ±20%). [e] Taken from ref 6b. [f] G# indicates the Gaussian curve to which the data belong.

Table 3. Results of Theoretical Calculations

parent salt	E_{max}[a] (eV)	μ_{12} (D)	$\Delta\mu_{12}$ (D)	contributions[b]	β_0[c] (10^{-30} esu)	β_0[d,e]
1[f]	2.65	11.5	13.9	$H \rightarrow L$ (68%)	150	186
2	1.42	6.8	25.7	$H \rightarrow L$ (68%)	440	318
	2.66	11.5	7.9	$H \rightarrow L + 1$ (43%) $H - 1 \rightarrow L + 1$ (18%)		
3	1.70	10.9	10.6	$H \rightarrow L$ (75%)	375	411
	1.82	3.9	10.5	$H - 1 \rightarrow L$ (67%) $H \rightarrow L + 1$ (25%)		
	2.56	6.5	8.5	$H - 1 \rightarrow L + 1$ (74%) $H \rightarrow L + 2$ (14%)		
	2.65	6.2	11.3	$H - 1 \rightarrow L + 2$ (42%) $H \rightarrow L + 1$ (42%)		
	2.73	7.6	14.0	$H \rightarrow L + 2$ (78%)		
	2.92	9.6	10.5	$H - 1 \rightarrow L + 2$ (50%) $H \rightarrow L + 1$ (17%)		

[a] Transitions below 3 eV are shown. [b] H = HOMO; L = LUMO; only contributions above 10% are included. [c] FF-derived total value. [d] CPHF-derived total value. [e] HF/LanL2DZ model chemistry. [f] Taken from ref 9.

shoulder, and both this and the Stark spectrum were fit satisfactorily using a single Gaussian. However, the 77 K absorption spectrum of **3** shows two resolved but overlapped bands and was, hence, modeled with two Gaussians. This approach gave a satisfactory fit to the Stark data, yielding two $\Delta\mu_{12}$ values. Application of the two-state model[7] affords estimated static first hyperpolarizabilities β_0. The following conclusions emerge from the data in Table 2. (i) Moving from the well-studied chromophore in **1** to its DQ^{2+} analogue in **2** causes E_{max} and μ_{12} to decrease, while $\Delta\mu_{12}$ and β_0 increase; (ii) the lower energy ICT transition in **3** has an especially large β_0 which is associated with increases in μ_{12} and $\Delta\mu_{12}$ when compared with **1** and **2**; (iii) the β_0 values of **3** are large in comparison with those of other 2D dipolar C_{2v} chromophores.[3]

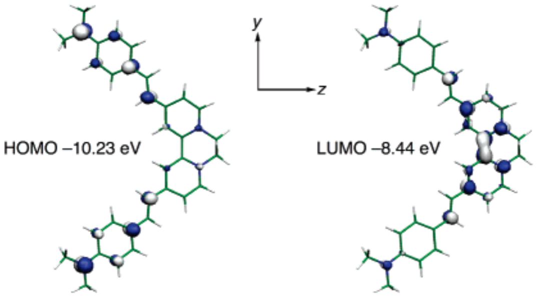

Figure 3. TD-DFT 0.05 contour plots of the MOs involved in the lowest energy transition of the cation in salt **3**.

Collected in Table 3 are the results of MO calculations on the cations in **1**−**3**; time-dependent density functional theory (TD-DFT) was used to study electronic transitions, and β values were derived at DFT level by using the finite field (FF) method and also via the coupled perturbed Hartree−Fock method (CPHF). Figure 3 shows the HOMO and LUMO for **3**.

For both **1** and **2**, the lowest energy transition is polarized essentially parallel to $\Delta\mu_{12}$, and the NLO response arises mostly from the β_{zzz} component, with a large increase predicted on moving from **1** to **2**. The calculations on **3** suggest a more complex picture than is apparent experimentally, with TD-DFT predicting six transitions below 3 eV. Those at 1.82, 2.65, and 2.92 eV have *A* symmetry (*z*-polarized) and contribute to β_{zzz}, while those at 1.70, 2.56, and 2.73 eV have *B* symmetry (*y*-polarized) and contribute to β_{zyy}. The dominant contribution to β is expected to arise from the lowest energy transition with the larger μ_{12}, indicating that the off-diagonal component β_{zyy} is larger than β_{zzz}. In fact, the derived values of β_{zyy} and β_{zzz} (10^{-30} esu) are 310 and 65 (FF-DFT), and 277 and 133 (CPHF), respectively.

In summary, we have prepared and studied novel diquat-containing NLO chromophores, allowing the incorporation of 2D dipoles into salt materials. Further studies will address in more detail the properties of these and related compounds.

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Supporting Information Available: Complete ref 6; analytical data for **2** and **3**; further experimental and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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