



Radical cations from diarylamino-substituted fluorenones

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ABSTRACT

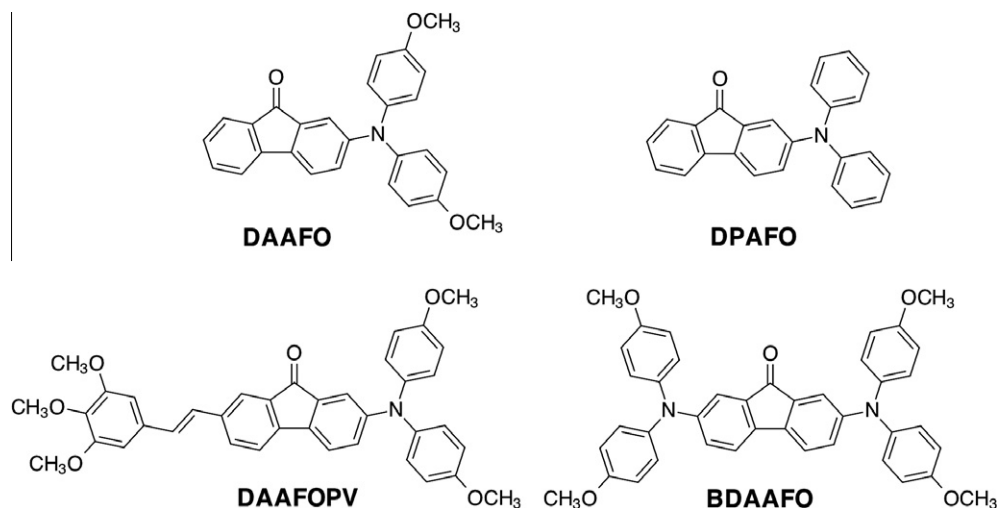
Chemical oxidation of diarylamino-substituted fluorenones gives highly persistent radical cations, some of which can be stored in the solid state for months. Solution UV–vis–NIR spectra show strong monoradical cation absorption bands in the 750–1700 nm range, with minimum energy about 0.73 eV. 2,7-Bis(dianisylamino)fluorenone exhibits strong absorptions at 1670 (monocation) and 873 nm (dication). Fast intervalence electron transfer behavior between amine sites in the monocation is indicated by EPR spectroscopic and absorption spectral Hush analyses.

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Introduction

Conjugated aminium radical cations are of much interest as organic electronic materials. They can be spin-bearing building blocks in molecule based magnetic materials and polymers,¹ and

as charge carriers in organic batteries² and conducting polymers.³ They also play important roles in photovoltaic charge pair generation,⁴ typically as donor materials. Simpler model triarylaminium radical cations thus are useful models for the behavior of more complex electro-active materials.



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Triarylammonium cations tend to be very deeply colored, due in part to their strong conjugation. When structural connectivity allows direct π -resonance to the radical cation site, the resulting absorption bands can be energetically tuned. Adding triarylamine sites in direct π -resonance with a radical cation site can give intervalence charge transfer (IVCT) that pushes the band gap transition well into the near infrared (NIR) region.⁵ Comparison of the IVCT behavior gives insight about the ease of electron hopping through a π -conjugated linker or polymer, shows whether or not the radical cation and neutral triarylamine sites are strongly coupled, and shows how conjugative IVCT radical to amine coupling varies with linker types and lengths.^{5,6}

In this Letter, we describe the absorption and electron paramagnetic resonance (EPR) spectra obtained from oxidation of the diarylamine substituted fluorenones DAAFO, DPAFO, DAAFOPV, and BDAAFO. The latter two systems were investigated to test the effects of extending through-conjugation across the fluorenone unit, with BDAAFO providing linkage for intervalence transfer behavior in the radical cation. Although electronic properties have been investigated for fluorenes linked to diarylamines,⁷ to our knowledge this has not been done for electron deficient fluorenones attached to diarylamines. This study shows that fluorenones yield highly persistent triarylammonium cations, and are effective IVCT linkers.

Experimental

Starting materials

The neutral amines used in this study were made and identified using literature procedures.⁸ Purities of the compounds were established by HPLC.

Electrochemistry and oxidation procedures

Redox potentials were obtained by cyclic voltammetry using platinum auxiliary and working electrodes with an Ag/AgCl reference electrode (in acetonitrile). All measurements were done in dry acetonitrile with 0.1 M tetrabutylammonium hexafluoro-phosphate as a supporting electrolyte, using analyte concentrations of about 10 mM. Ferrocene oxidation under these conditions was used as an external voltage standard.

The neutral amines were oxidized by two procedures. For the precipitation protocol, roughly 30 μ M of amine was dissolved in toluene and treated with SbCl₅ to give a very dark, powdery precipitate that could be isolated by filtration, and stored under ambient

conditions for months. Re-dissolution of these precipitates in dichloromethane readily yielded the characteristic colors of the aminium cation species.

For a solution oxidation protocol, the amine was dissolved in dry dichloromethane and directly treated with oxidants such as SbCl₅, AgSbF₆, Pb(OAc)₄, or dissolved in acetonitrile for oxidation with CuClO₄.

Spectroscopy

UV-vis spectra were obtained using both the solution oxidation protocols described above, or by re-dissolving the solid phase aminium cation salts obtained from the precipitation oxidation protocol. Molar absorptivities given for the oxidized species assume 100% conversion of neutral triarylamine precursors, and so are minimum values.

EPR spectra were obtained at room temperature by the solution oxidation protocol, or by re-dissolving products from the precipitation oxidation protocol. Hyperfine coupling constants were obtained by spectral simulation, and *g*-values obtained for spectra were calibrated using a frequency counter and an E-036TM teslameter on a Bruker Elexsys E-500 spectrometer.

Results and Discussion

Mono(diarylmino)fluorenone oxidations

DAAFO and DAAFOPV have lower oxidation potentials than DPAFO (Fig. 1, Table 1), consistent with the decreased donor

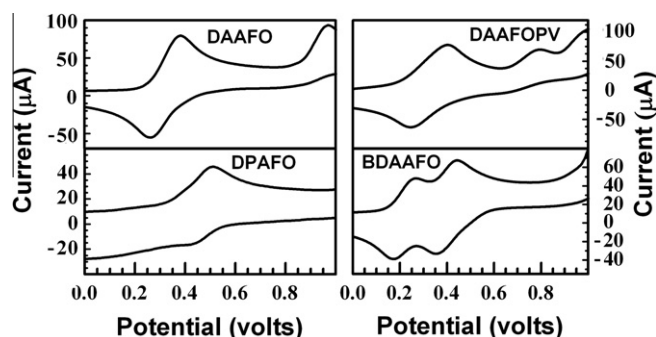


Figure 1. Cyclic voltammograms showing the amine oxidation region. Potentials are referenced to the ferrocene/ferrocenium redox standard reaction in dry acetonitrile.

Table 1
Spectral and electrochemical characteristics of radical cations and dications

Compound	Oxidized absorption, nm [eV] ($\log_{10} \epsilon$) ^a	Computed Transition, ([eV], (oscillator strength)) ^b	Oxidation $E_{1/2}$ (mV) to Cation ^c	HOMO Energy (eV) Observed (Computed) ^d	Oxidized EPR spectrum Hyperfine (<i>g</i> -value) ^e
DAAFO	777 [1.60] (4.41)	[1.57] (<i>f</i> = 0.24) [1.77] (<i>f</i> = 0.22)	320	−5.03 (−5.03)	8.6 gauss [1 N] (2.0033)
DPAFO	823 [1.51] (4.86)	[1.54] (<i>f</i> = 0.26) [1.66] (<i>f</i> = 0.03)	460	−5.12 (−5.35)	5.8 gauss [1 N], (2.0028) ^f
DAAFOPV	1036 [1.20] (4.02) 747 [1.66] (4.32)	[0.77] (<i>f</i> = 0.65) [1.52] (<i>f</i> = 0.02)	326	−4.98 (−4.95)	≤8 gauss [1 N] (2.0033)
BDAAFO	1670 [0.74] (4.44) ^g 873 [1.42] (4.88) ^h 699 [1.77] (4.46) ^h	[0.83] (<i>f</i> = 0.59) [1.21] (<i>f</i> = 1.38) ^h [1.79] (<i>f</i> = 0.16) ^h [1.80] (<i>f</i> = 0.25) ^h	220 400	−4.95 (−4.73)	4.7 gauss [2 N] (2.0032)

^a Band maximum; $\epsilon = \text{M}^{-1} \text{cm}^{-1}$.

^b B3LYP/6-31G(d,p) computed transition energy, oscillator strength for radical cations, and BDAAFO singlet dication.

^c Cyclic voltammetric half-wave potential vs ferrocene/ferrocenium standard (acetonitrile).

^d E(HOMO) from Ref⁸ using onset of first oxidation feature; computed E(HOMO) from B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) calculations in this work.

^e Solution X-band spectrum (~9.6 GHz) in dichloromethane.

^f Large linewidth spectrum (unresolved hfc?).

^g Monocation.

^h Dication.

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