# Electron-transfer Fluorescence Quenching of Radical Ions *
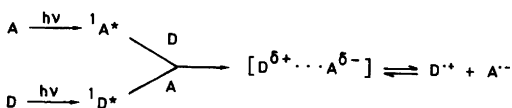
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The radical anions of anthraquinone and 9,10-dicyanoanthracene and the radical cation of thianthrene fluoresce in oxygen-free fluid solution at room temperature. The fluorescence of the radical anions is quenched by added electron acceptors, while the fluorescence of the cation is quenched by added electron donors. The fluorescence quenching is treated in terms of an electron-transfer mechanism. The results agree with Marcus' theory and Weller's equation *only* if very large solvent and/or bond reorganization energies (20–30 kcal/mol) are introduced.
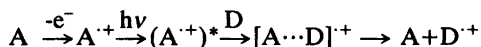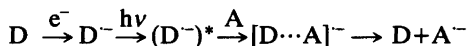
Since the pioneering work of Weller and coworkers,[1] fluorescence quenching *via* electron-transfer mechanisms has been a subject of great interest among photochemists and photophysicists.[2-5] Most work in this field has been centered around electron-transfer to or from the singlet excited state of fluorescing aromatic molecules in the presence of electron donors (D) or acceptors (A), respectively. Thus, the reaction is accompanied by fluorescence quenching of the light absorbing molecule.[1]

The produced radical ions may back-transfer the electron to reform A and D or may go on producing new products. In the presence of oxygen, photooxygenations may occur.[2,6]

$$A \xrightarrow{h\nu} {}^1A^*$$
$$D \xrightarrow{h\nu} {}^1D^*$$
$${}^1A^* + D \text{ (or } {}^1D^* + A) \longrightarrow [D^{\delta+}\cdots A^{\delta-}] \rightleftharpoons D^{\cdot+} + A^{\cdot-}$$

We have previously studied electron-transfer from photoexcited ion radicals [7] and have recently been interested in using ion radicals as light absorbing species in photogalvanic cells. For this purpose we have investigated the fluorescence quenching of molecules that are themselves radical ions which were produced electrochemically.
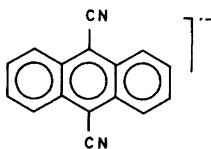
$$D \xrightarrow{e^-} D^{\cdot-} \xrightarrow{h\nu} (D^{\cdot-})^* \xrightarrow{A} [D\cdots A]^{\cdot-} \rightarrow D + A^{\cdot-}$$

$$A \xrightarrow{-e^-} A^{\cdot+} \xrightarrow{h\nu} (A^{\cdot+})^* \xrightarrow{D} [A\cdots D]^{\cdot+} \rightarrow A + D^{\cdot+}$$

The radical ions chosen for this study are the anthraquinone radical anion ($Aq^{\cdot-}$), the 9,10-dicyanoanthracene radical anion ($DCA^{\cdot-}$), and the thianthrene radical cation ($Ta^{\cdot+}$). The radical anion of benzonitrile ($BzN^{\cdot-}$) has been studied briefly.
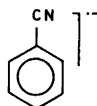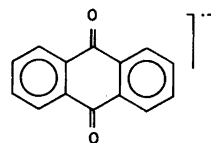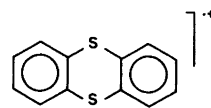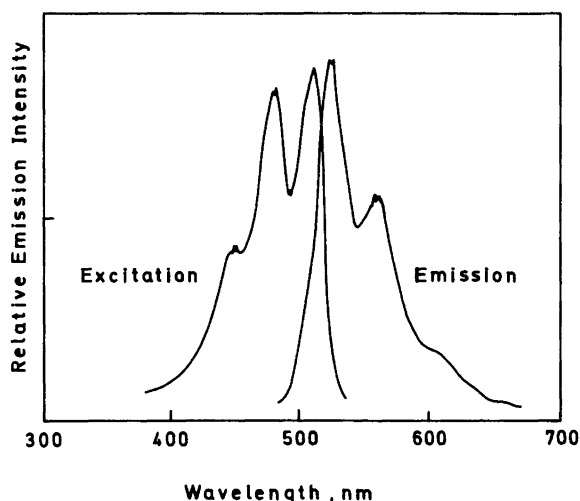


BzN·⁻          Aq·⁻

DCA·⁻          Ta·⁺

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*Fig. 1.* Corrected fluorescence excitation and emission spectra of DCA$^{\cdot-}$ $10^{-5}$ M in oxygen-free MeCN at room temperature.

## RESULTS

*Fluorescence data.* The radical ions investigated in this study all exhibited strong fluorescence in oxygen-free solutions at room temperature. Table 1 contains the emission maxima of several radical ions in various solvents. Fig. 1 shows, as an example, the corrected fluorescence emission and excitation spectra of DCA$^{\cdot-}$ in MeCN. The emission spectrum is quite similar in structure to the fluorescence spectrum of DCA, but red-shifted about 100 nm. For all the compounds studied, the fluorescence excitation spectra were in good agreement with the corresponding absorption spectra. The excitation energies ($\Delta E_{o,o}$, Table 2) could be estimated from the wavelength of the overlap between the fluorescence excitation and emission spectra.

The fluorescence lifetimes ($\tau$, Table 2) were determined by single photon counting[8] (see Experimental). The lifetime of Aq$^{\cdot-}$ in DMF was measured in three different laboratories which resulted in excellent mutual agreement.

*Fluorescence quenching and electrochemical considerations.* The emission of the radical anions and cations in oxygen-free solutions were quenched by a wide variety of electron acceptors and donors, respectively (Tables 3–5). In each case, the quenching followed the well-known Stern-Volmer equation,[9]

$$I_o/I_Q = 1 + k_q \tau [Q] \qquad (1)$$

where $I_o$ and $I_Q$ are the relative fluorescence intensities in the absence and presence of quencher (Q), $k_q$ is the bimolecular quenching rate constant and $\tau$ is the fluorescence lifetime. For

*Table 1.* Maxima in nm of corrected fluorescence spectra of radical ions.[a]

| Solvent | Aq$^{\cdot-}$ | DCA$^{\cdot-}$ | BzN$^{\cdot-}$ | Ta$^{\cdot+}$ |
|---|---|---|---|---|
| DMF[b] | 575 | 525, 560 | 505 | [d] |
| MeCN | [d] | 530, 560 | [d] | [d] |
| Toluene | 470 | [d] | [d] | [d] |
| CH$_2$Cl$_2$[c] | [d] | [d] | [d] | 580 |

[a] In fluid solutions at room temperature. [b] Dimethylformamide. [c] Solvent mixture of methylene chloride, trifluoroacetic anhydride and trifluoroacetic acid (45:5:1, v/v). [d] Not investigated.

*Table 2.* Fluorescence data of radical ions[a].

| Fluorescer | Solvent | $\Delta E_{o,o}$[b] eV | $\tau$[c] ns |
|---|---|---|---|
| Aq$^{\cdot-}$ | DMF | 2.21 | 13.7 |
| DCA$^{\cdot-}$ | DMF | 2.38 | 13.5 |
| BzN$^{\cdot-}$ | DMF | 2.56 | [d] |
| Ta$^{\cdot+}$ | CH$_2$Cl$_2$[e] | 2.18 | 4.7 |

[a] In oxygen-free solution at room temperature. [b] Excitation energy. [c] Fluorescence lifetime. [d] Not determined. [e] See footnote c of Table 1.

*Table 3.* Fluorescence quenching of Aq$^{-}$.[a]

| Quencher | $k_q$[b] $10^9$ M$^{-1}$s$^{-1}$ | $E^o_{A/A^-}$[c] V *vs.* SCE | $\Delta G^d$ kcal/mol |
|---|---|---|---|
| 1 Acridine | 13.9 | −1.63[e] | −33.4 |
| 2 Benzophenone | 12.0 | −1.77[e] | −30.2 |
| 3 1-Naphthonitrile | 11.0 | −1.90[e] | −27.2 |
| 4 2-Chloroquinoline | 13.6 | −1.92[f] | −26.8 |
| 5 3-Cyanopyridine | 4.89 | −2.03[e] | −24.2 |
| 6 1-Bromonaphthalene | 2.70 | −2.13[f] | −21.9 |
| 7 1-Chloronaphthalene | 1.61 | −2.19[f] | −20.5 |
| 8 Benzonitrile | 0.708 | −2.23[e] | −18.2 |
| 9 3-Bromopyridine | 0.562 | −2.29[f] | −17.3 |
| 10 3-Chloropyridine | 0.095 | −2.39[f] | −15.9 |
| 11 2-Chloropyridine | 0.102 | −2.40[f] | −15.7 |
| 12 Bromobenzene | 0.036 | −2.44[f] | −14.8 |

[a] In oxygen-free DMF at room temperature. [b] Slope of Stern-Volmer plot (eqn. (1)) divided by lifetime (Table 2). [c] Reduction potential. [d] Calculated from eqn. (2). [e] This study; determined by cyclic voltammetry, see Experimental. [f] Determined by kinetic analysis of homogeneous redox catalysis of electronic reductions. Data from Andrieux, C. P., Blocman, C., Dumas-Bouchiat, J.-M. and Savéant, J. M. *J. Am. Chem. Soc.* **101** (1979) 3431; Andrieux, C. P., Blocman, C., Dumas-Bouchiat, J.-M., M'Halla, F. and Savéant, J. M. *Ibid.* **102** (1980) 3806.

*Table 4.* Fluorescence quenching of DCA$^{-}$.[a]

| Quencher | $k_q$[b] $10^9$ M$^{-1}$s$^{-1}$ | $E^o_{A/A^-}$[c] V *vs.* SCE | $\Delta G^d$ kcal/mol |
|---|---|---|---|
| 1 Acridine | 15.8 | −1.63[e] | −38.1 |
| 2 Benzophenone | 11.0 | −1.77[e] | −34.8 |
| 3 1-Naphthonitrile | 9.48 | −1.90[e] | −31.8 |
| 4 2-Chloroquinoline | 4.59 | −1.92[f] | −31.4 |
| 5 3-Cyanopyridine | 4.44 | −2.03[e] | −28.8 |
| 6 1-Bromonaphthalene | 0.370 | −2.13[f] | −26.5 |
| 7 1-Chloronaphthalene | 0.059 | −2.19[f] | −25.1 |
| 8 Benzonitrile | 0.022 | −2.23[e] | −24.2 |
| 9 3-Bromopyridine | 0.022 | −2.29[f] | −22.8 |
| 10 2-Bromopyridine | 0.0023 | −2.30[f] | −22.6 |

[a–f] See footnotes *a–f* of Table 3.

*Table 5.* Fluorescence quenching of Ta$^{+}$.[a]

| Quencher | $k_q$[b] $10^9$ M$^{-1}$s$^{-1}$ | $E^o_{D^+/D}$[c] V *vs.* SCE | $\Delta G^d$ kcal/mol |
|---|---|---|---|
| 1 Pyrene | 7.23 | −1.36[e] | −46.8 |
| 2 Acenaphthene | 6.11 | −1.52[f] | −43.1 |
| 3 Hexamethylbenzene | 5.32 | −1.61[e] | −41.0 |
| 4 Anisole | 1.38 | −1.76[f] | −37.6 |
| 5 Naphthalene | 0.957 | −1.84[e] | −35.7 |
| 6 Thiophene | 0.140 | −2.03[f] | −31.4 |
| 7 Toluene | 0.149 | −2.37[e] | −23.5 |

[a] In oxygen-free CH$_2$Cl$_2$/trifluoroacetic anhydride/trifluoroacetic acid (45:5:1) at room temperature. [b] Slope of Stern-Volmer plot (eqn. (1)) divided by lifetime (Table 2). [c] Voltammetric half-wave oxidation potential. [d] Calculated from eqn. (3). [e] Data from Eberson, L. *Adv. Phys. Org. Chem.* **18** (1982) 79, Table 9. [f] Data from Eberson, L. *Private communication.*

each fluorescer-quencher pair, five suitable concentrations of Q were used. Data treatment according to eqn. (1) gave correlation coefficients generally >0.999. All quenching runs were performed twice and in all cases the data could be reproduced.

The slopes ($k_q$ $\tau$) and the lifetimes (Table 2) allowed for determination of the quenching rate constants, $k_q$ (Tables 3–5).

The free energy change ($\Delta G$) involved in an electron-transfer process from an excited donor radical anion to a neutral acceptor is given by eqn. (2),[1,10]

$$\Delta G(\text{kcal/mol}) = 23.06(E^{\circ}_{D/D^-} - E^{\circ}_{A/A^-} - \Delta E_{o,o}) \qquad (2)$$

where $E^{\circ}_{D/D^-}$ is the reversible electrode potential of the fluorescer couple D/D$^-$, $E^{\circ}_{A/A^-}$ the reversible electrode potential of the acceptor couple, and $\Delta E_{o,o}$ is the excitation energy defined above. By cyclic voltammetry (CV) we found $E^{\circ}_{Aq/Aq^-}$ =–0.87 V vs. SCE and $E^{\circ}_{DCA/DCA^-}$ =–0.89 V vs. SCE; both redox systems show reversible behavior in CV. Electrode potentials for the neutral acceptors are given in Tables 3 and 4.

Similarly, $\Delta G$ for quenching of an excited acceptor radical cation (A$^{\cdot+}$)* by neutral donors is given by eqn. (3),[1,10]

$$\Delta G(\text{kcal/mol}) = 23.06(-E^{\circ}_{A^{\cdot+}/A} + E^{\circ}_{D^{\cdot+}/D} - \Delta E_{o,o}) \qquad (3)$$

where $E^{\circ}_{A^{\cdot+}/A}$ is the reversible electrode potential of the fluorescer couple A$^{\cdot+}$/A and $E^{\circ}_{D^{\cdot+}/D}$ that of

the donor couple. CV gave $E^{\circ}_{Ta^{\cdot+}/Ta}$=1.21 V vs. SCE. Electrode potentials for the neutral donors are given in Table 5.

Values of $k_q$ measured by fluorescence quenching (eqn. (1)) and $\Delta G$ values calculated from eqn. (2) or (3) (Tables 3–5) have been used to construct Weller plots [1] for the fluorescence quenching of radical ions, see Figs. 2–4.

*Miscellaneous.* In order to test for exciplex formation as a possible mechanism in the fluorescence quenching, we have looked for exciplex emission from Aq$^-$ quenched by BzN in non-polar as well as polar solvents. Aq dissolved in toluene was reduced by sodium amalgam and enough BzN was added under nitrogen to quench >90 % of the Aq$^-$ fluorescence. The emission spectrum was scanned at highest spectrofluorimeter sensitivity in the region 500–800 nm. No exciplex emission, however, could be detected. A similar experiment using DMF as solvent gave likewise a negative result. A combined electron- and energy-transfer process,

$$(Aq^-)^* + BzN \rightarrow Aq + (BzN^-)^*$$
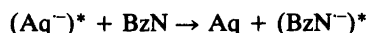
which would be expected to give rise to emission from BzN$^-$ (see Table 1) is unlikely, since the process is endothermic. No such emission could be detected.

## DISCUSSION

Figs. 2–4 show that our data on fluorescence quenching of radical ions do not fit Weller's curve for electron-transfer fluorescence quenching.[1]
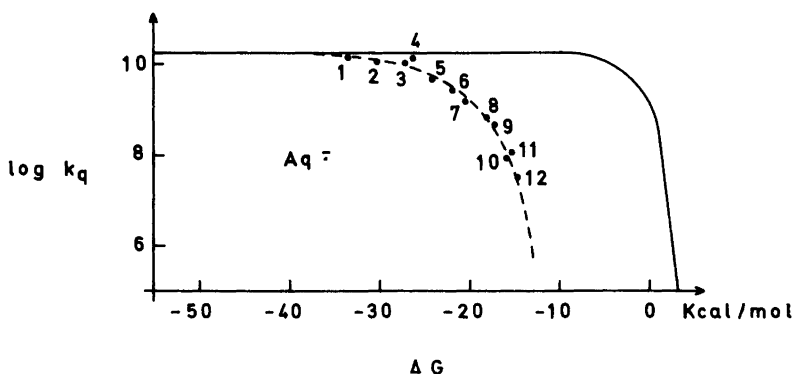


*Fig. 2.* Fluorescence quenching plot of Aq$^-$ in DMF. Quencher numbers refer to Table 3. Solid line calculated by Rehm and Weller for an electron-transfer quenching mechanism.[1]
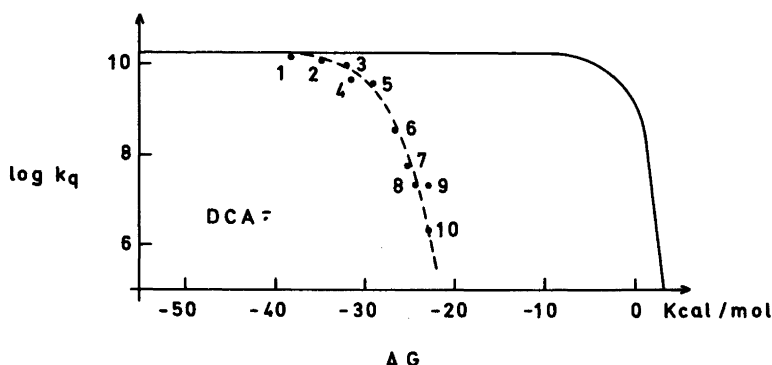
Fig. 3. Fluorescence quenching plot of DCA$^-$ in DMF. Quencher numbers refer to Table 4. Solid line: See Fig. 2.

Although our curves are similar in shape to Weller's curve, they are shifted some 20–30 kcal/mol, far outside the range of reasonable experimental error. Numerous experimental works on electron-transfer fluorescence quenching of neutral molecules,[1–6] including our own, have verified Weller's curve. It is therefore surprising to us to see this large discrepancy.

There might be several ways to explain our data on radical ions. Perhaps fluorescence quenching of these ions does not follow an electron-transfer mechanism. An *energy*-transfer mechanism, however, is not likely (see above), and the fact that our curves *in shape* are similar to Weller's curve certainly indicates some type of charge-transfer mechanism.

An electron-transfer mechanism involving an exciplex may be considered. The intermediacy of an exciplex formed *via* a nonrelaxed charge-transfer state has recently been suggested by Kramer *et al.* in the fluorescence quenching of the cationic dye oxonine.[5a] Exciplexes, however, are generally formed in cases where a stabilization of the excited fluorescer is obtained.[11] Thus, formation of an exciplex from an excited fluorescer and a quencher is an exothermic process. Short-lived exciplexes could therefore be involved in systems where the observed $k_q$ is diffusion-controlled. In order to explain our present results by formation of exciplexes, these would have to be formed also in cases where $k_q$ is several orders of magnitude less than diffusion-controlled. Why would the excited radical-ion/ quencher pair pass through a higher lying energy state (endothermic exciplex formation) when simple electron-transfer according to eqn. (2) or (3) is highly exothermic? Attempts to detect emission from an exciplex failed (see above).
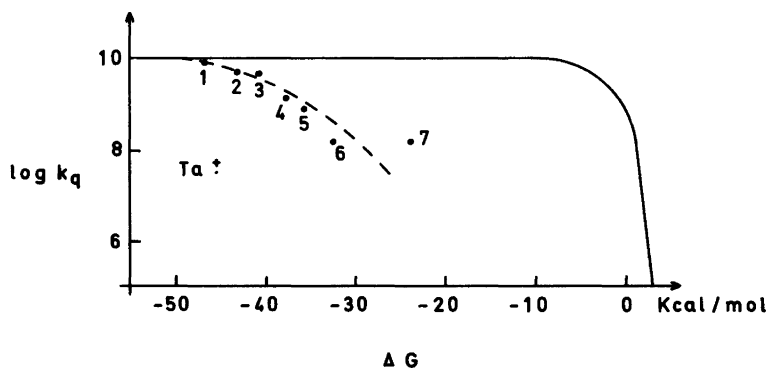


Fig. 4. Fluorescence quenching plot of Ta$^{·+}$ in methylene chloride–trifluoroacetic anhydride– trifluoroacetic acid (45:5:1). Quencher numbers refer to Table 5. Solid line: See Fig. 2.

As a possible explanation of our results one might argue that our fluorescers being radical ions are surrounded by a highly organized solvent shell, thus preventing close contact to a quencher molecule. Weller's curve is based upon an empirical equation (eqn. (4))[1]

$$k_q = \frac{2 \times 10^{10}}{1 + 0.25[\exp(\Delta G^{\ne}/RT) + \exp(\Delta G/RT)]} \, M^{-1}s^{-1} \quad (4)$$

where $\Delta G$ is given by eqn. (2) or (3) and $\Delta G^{\ne}$, the activation free enthalpy, was assumed to be a monotonous function of $\Delta G$, eqn. (5):

$$\Delta G^{\ne} = [(\Delta G/2)^2 + (\Delta G_o^{\ne})^2]^{1/2} + \Delta G/2 \quad (5)$$

Here, $\Delta G_o^{\ne}$, the activation free enthalpy at $\Delta G = 0$, was found experimentally to be 2.4 kcal/mol.[1] Based on an outer-sphere, adiabatic electron-transfer theory Marcus [12,13] has derived an equation similar to eqn. (4), but with $\Delta G^{\ne}$

$$\Delta G^{\ne} = \Delta G_o^{\ne} [1 + \Delta G/4\Delta G_o^{\ne}]^2 \quad (6)$$

With $\Delta G_o^{\ne} = 2.4$ kcal/mol both eqns. (5) and (6) together with eqn. (4) are in good agreement with experimental results for electron-transfer fluorescence quenching of neutral molecules when $\Delta G > -15$ kcal/mol. For more exothermic reactions, however, the Marcus relation (eqn. (6)) predicts a drastic decrease in $k_q$ (Marcus' inverted region [1,12,13]). Thus, neither Weller's nor Marcus' equations agree with our experimental data for fluorescence quenching of radical ions, at least with the assumption $\Delta G_o^{\ne} = 2.4$ kcal/mol.

The main contribution to $\Delta G_o^{\ne}$ is a solvent reorganization energy due to electron removal from or addition to the involved molecules, although bond reorganization energies may play some role as well.[12] Eberson has recently argued that the widely accepted value of $\Delta G_o^{\ne} = 2.4$ kcal/mol need not and indeed should not be valid for all electron-transfer reactions.[12,14] Thus, a value of $\Delta G_o^{\ne} = 10$ kcal/mol was found for one-electron reductions of diacyl peroxides.[14a]

As mentioned above, radical ions might be expected to require large solvent reorganization energies in electron transfer reactions, thus resulting in large $\Delta G_o^{\ne}$ values. The fact that each radical ion (Figs. 2–4) gives a separate Weller/Marcus plot even though a variety of quenchers are used, suggests that the solvent reorganization energy of the fluorescing radical ion is more important than that of the quencher. In order to make our data fit Weller's or Marcus' equations, $\Delta G_o^{\ne}$ values of the order of 20–30 kcal/mol are required.

Clearly, much more experimental work is required to test for very large $\Delta G_o^{\ne}$ values. We are presently looking at the contributions to $\Delta G_o^{\ne}$ from bond reorganizations and solvent reorganizations from both the radical ions and the quenchers.

## EXPERIMENTAL

*Spectra.* All emission spectra were recorded on an Aminco SPF-500 Corrected Spectrofluorimeter. Scan-rate: 50 nm/min. Band widths: 2 nm. Oxygen-free solutions were transferred to quartz-cells with four polished sides. Absorption spectra using the same cells were recorded on a Varian Cary Model 219 Spectrophotometer.

*Materials.* DMF was distilled under vacuum and stored over Molecular Sieves 4 A. MeCN was spectrograde (Merck, Uvasol) and used as received. Aq and DCA were recrystallized from ethanol and toluene, respectively, prior to use. Other chemicals were generally highest purity available and used as received.

*Lifetimes.* Fluorescence lifetimes of $Aq^{\cdot-}$. $DCA^{\cdot-}$ and $Ta^{\cdot+}$ were determined by single photon counting.[8] Oxygen-free solutions $10^{-5}$ M in the radical ions were placed in sealed tubes. The lifetime of $Aq^{\cdot-}$ was measured in three different laboratories at New York University (Professor D. I. Schuster), University of California, Los Angeles (Professor V. N. Schumaker) and Max-Planck-Institut, Mülheim, BRD (Professor K. Schaffner). The lifetimes of $DCA^{\cdot-}$ and $Ta^{\cdot+}$ were determined in the Mülheim laboratory.

*Formation of radical ions* was carried out by electrolysis at constant potentials in H-cells.[15] The reference electrode was an Ag/AgI (0.1 M tetrabutylammonium iodide, TBAI) electrode. During reduction an Hg-electrode and a graphite stick were used as cathode and anode, respectively, while oxidation was carried out with Pt-electrodes. The potentiostat (from Tage Juul, Copenhagen, 100 V and 300 V) was adjusted to a potential at the limiting current of the compound ($10^{-5}$ M) to be reduced or oxidized. The solutions were purged with $N_2$ for 15 min prior to and during the reduction or oxidation.

*Redox potentials* were obtained by cyclic voltammetry at a Pt-electrode (oxidations) or Hg-drop (reductions). The reference electrode was an Ag/AgI (0.1 M TBAI) electrode (–0.56 V relative to the standard calomel electrode, SCE). The solvent was dried over anhydrous Alumina and purged with $N_2$ for 20 min prior to use. The supporting electrolyte was TBAI or tetrabutyl-ammonium fluoroborate (TBAFB) at 0.1 M. The potentials were measured at scan rates 40, 60, 80 and 100 v/s. Potentials in this study (see text and Tables 3 to 5) were all reversible. The obtained reduction potential for DCA was in good agreement with a literature value of –0.82 V vs. SCE.[16]

*Fluorescence quenching procedure.* Formation of the fluorescing radical ions and all sample manipulations were carried out in a glove-box which has been flushed overnight with oxygen-free $N_2$. Solutions of the radical ion were pipetted into each of five volumetric flasks (10 ml). Appropriate amounts of a quencher stock solution were added using pipettes and the mixtures were diluted to the 10-ml mark. The flasks were shaken and their contents transferred to five Quartz cuvettes which were then stoppered and removed from the glove-box. The concentration of the fluorescer was $\sim 10^{-6}$ M giving rise to optical densities $\sim 0.05$. The relative emission intensities were determined at the wave-length of maximum emission and the data were analyzed according to eqn. (1) using a least-squares program. In order to check for possible ground-state complexation or reactions the absorption spectrum and the fluorescence excitation and emission spectra were recorded for the solution containing the highest concentration of quencher. These spectra were in all cases analogous to those without added quencher.

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