

Fluorescence of the 1,4-Benzoquinone Radical Anion

Andrew R. Cook,* Larry A. Curtiss,* and John R. Miller*

Contribution from the Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439Received January 27, 1997[Ⓢ]

Abstract: Information about excited states of radical ions can enable their use as powerful oxidizing and reducing agents capable of driving chemical reactions. This article presents the first measurements of fluorescence from an excited state of the radical anion of 1,4-benzoquinone (BQ⁻), and the first report of a fluorescence quantum yield from any radical anion. BQ⁻ was observed in both a 77 K 2-methyltetrahydrofuran matrix and a room temperature isooctane solution. The low fluorescence quantum yield, $\varphi_f = 0.003$, and the presence of a 0.5 eV red shift of the emission band edge (593 nm) from the absorption band edge (475 nm) imply that the lowest energy transition in BQ⁻, which is the source of the weak fluorescence, is formally forbidden. This conclusion is supported by both semiempirical and ab initio molecular orbital calculations. In addition, we determined the excited state lifetime of BQ⁻ at 77 K to be 63 ns, with an excited state absorption spectrum peaking at 415 nm.

Introduction

Radical ions have been extensively studied.^{1–5} Optical absorption spectra of many are well-known, and have been the subject of a compilation by Shida.⁶ Given reasonable lifetimes, the excited states of radical ions could be used as powerful reductants and oxidants for driving chemical reactions. Unfortunately, little is known about what happens when radical ions absorb light, although there are reports of luminescence or excited state chemistry resulting from a few families of radical ions,^{7–16} and reports of fluorescence quantum yields for some cations.¹⁰ Radical anions of quinones are common intermediates in natural^{17–21} and synthetic,^{17–20,22,23} photochemical energy storage; however, the roles of their excited states have been largely unrecognized and unexplored.

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We report here the first observation of fluorescence from an excited state of the 1,4-benzoquinone radical anion (BQ⁻) at both 77 and 293 K. The experiments give the fluorescence spectrum, quantum yield, and lifetime and show that the transition is forbidden, a finding corroborated by molecular orbital calculations.

Experimental Section

For low-temperature work, authentic samples of BQ⁻ were prepared by γ -irradiation of degassed 77 K 2-methyltetrahydrofuran (MTHF) glasses containing from 1×10^{-3} to 2.8×10^{-2} M BQ. Prior to use, MTHF was purified by passing an alumina column followed by distillation from sodium and benzophenone. BQ was sublimed. Typical radiation exposures lasted 3 h, delivering a controlled total dose of 0.2 to 1.0 Mrad, depending on the distance samples were placed from the cobalt-60 source. The irradiated samples were subsequently exposed to >600-nm light, which removed trapped electrons and increased the yield of BQ⁻. This technique resulted in ca. 5×10^{-5} to 1×10^{-3} M concentrations of BQ⁻. Radical ions are stable in such matrices at least for many days. Spectra were collected with a Spex Fluorolog spectrofluorimeter, with a custom sample holder designed to position the sample reproducibly for accurate quantum yield measurements. Narrow-band interference filters were used in the excitation beam to reduce scattered light passed by the excitation monochromator. Lifetime measurements were made by using a subpicosecond laser excitation source and a flashlamp/transient digitizer probe with a time resolution on the order of 1 ns.

Room temperature measurements were carried out at Argonne's 20 MeV electron Linac facility, described in detail elsewhere.²⁴ Solutions of sublimed BQ in distilled isooctane were irradiated with a 30 ps electron pulse to generate a roughly 2×10^{-6} M concentration of reduced quinone in a mixture of excited and ground electronic states. The resulting dynamics were probed with up to 100 ps time resolution by using a flashlamp/transient digitizer probe for absorption data and the transient digitizer alone for emission data.

Results and Discussion

A. Low Temperature. Irradiated samples of BQ were optically excited at 456.7 ± 0.5 nm. This is near the peak of

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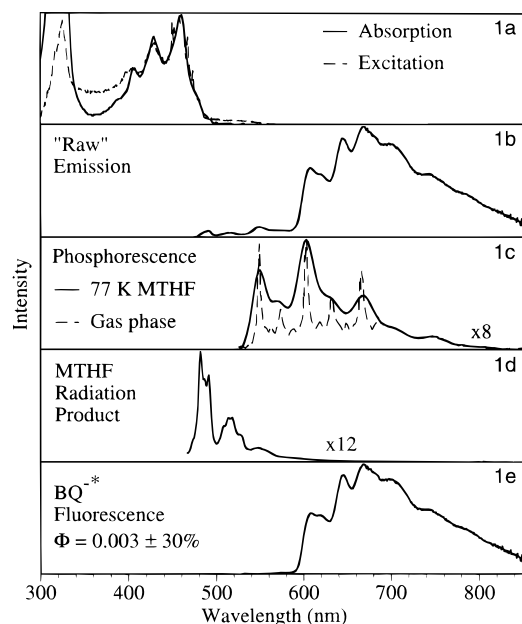


Figure 1. Absorption (from Shida⁶) and excitation ($\lambda_f = 643$ nm) spectra of BQ^- in 77 K MTHF glass are compared in part a. The raw emission spectrum in part b was recorded after optical excitation at 456.7 nm ($\epsilon \sim 9.4 \times 10^3$ M⁻¹ cm⁻¹). BQ^- phosphorescence is compared to a gas-phase spectrum recorded by Itoh²⁵ that has been red shifted by 16 nm in part c. The BQ^- fluorescence spectrum in part e was obtained by subtracting the contributions of BQ^- phosphorescence and the unidentified radiation product spectrum in part d from the spectrum in part b.

the excitation spectrum of BQ^- , which is shown in Figure 1a along with the absorption spectrum reproduced from Shida.⁶ The total emission spectrum is shown in Figure 1b. To obtain the fluorescence spectrum of BQ^- shown in Figure 1e, contributions from two other sources of emission were subtracted. The first and largest is phosphorescence of neutral BQ, measured in an identical sample without irradiation. Its spectrum is shown in Figure 1c along with the gas-phase spectrum reported by Itoh.²⁵ In Figure 1c, Itoh's data has been shifted 16 nm to lower energy for the comparison. The red shift of the present data is easily understood in terms of solvent stabilization of the excited state. The integrated phosphorescence quantum yield, ϕ_P , is $(3.8 \pm 0.2) \times 10^{-3}$. The relative contribution from phosphorescence increases with neutral BQ concentration in a manner consistent with competing absorption by BQ ($\epsilon = 16$ M⁻¹ cm⁻¹) and BQ^- ($\epsilon = 9.4 \times 10^3$ M⁻¹ cm⁻¹) at the 456.7-nm excitation wavelength. The second additional source of emission is an unidentified radiation product, measured in irradiated samples without BQ (Figure 1d). It is not known whether this emission, which occurs only in irradiated samples, is from a radiation-produced product of the solvent itself or an impurity in the solvent or the quartz sample tube. The experimental procedure described above led to a consistent BQ^- fluorescence spectrum over a range of BQ concentration (1×10^{-3} to 2.8×10^{-2} M) and a range of dose which produced 5×10^{-5} to 1×10^{-3} M BQ^- .

Fluorescence of BQ^- has not been reported previously, perhaps due to its relatively small quantum yield, determined here to be $(3 \pm 1) \times 10^{-3}$ from integration relative to known standards. The shape of the fluorescence spectrum does not "mirror" that of the absorption spectrum, and it is substantially red-shifted, having an apparent origin at 593 nm and an initial peak at 607 nm, suggesting that the principal absorption and

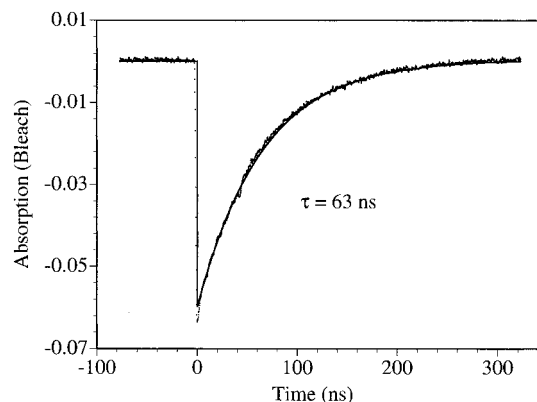


Figure 2. Transient absorption bleach (points) at 460 nm of BQ^- when excited at 395 nm. The single exponential fit (solid line) is an excellent match to the data, giving a 63 ± 3 ns excited state lifetime.

emission bands do not arise from the same state. These facts lead us to believe that absorption into the lowest energy excited state is formally forbidden, and that the observed lowest energy absorption peak at 458 nm produces a higher energy excited state, followed by rapid internal conversion to the weakly fluorescing state. This is consistent with previous electron transfer results in our laboratory that suggested the presence of lower energy quinone radical anion excited states²⁶⁻²⁸ than one would expect from absorption spectra. This conclusion is additionally reinforced by the appearance of a weak tail in the range of 500–550 nm present in the absorption and, more prominently, in the excitation spectra of BQ^- seen in Figure 1a. This tail may be the result of an absorption band with an origin near 593 nm, which becomes only very weakly allowed due to vibronic mixing with symmetry-breaking vibrations and possibly intensity borrowing from the strong band at 458 nm.

The lifetime of the lowest energy BQ^- excited state was found to be 63 ± 3 ns. This was determined by optically exciting matrix-isolated BQ^- with a 395-nm subpicosecond laser pulse, and following the recovery of the ground state absorption, seen in Figure 2. This radical ion excited state is surprisingly long lived. A simplistic understanding can be obtained by considering the effect of the "allowedness" of the transition on the radiative lifetime, expressed in terms of fluorescence quantum yield and molar extinction coefficient:²⁹ $\tau_0 = \phi_f 10^{-4} / \epsilon_{\max}$. An excited state lifetime of only 30 ps would be estimated from the measured fluorescence quantum yield $\phi_f = 0.003$ and the extinction coefficient $\epsilon_{\max} = 9.4 \times 10^3$ M⁻¹ cm⁻¹ for the allowed absorption band of BQ^- at 458 nm. The observed fluorescence lifetime of 63 ns would be consistent with $\epsilon_{\max} \approx 5$ M⁻¹ cm⁻¹, which is too weak to be observed in the present experiments. An absorption of this magnitude could be consistent with an extrapolation of the weak "tail" on the absorption and excitation spectra of BQ^- .

The long lifetime of the excited state BQ^-^* has important implications on its ability to participate in chemical reactions. While in many known natural and synthetic systems that employ quinones as electron acceptors the excited state may not play a large role, one can envision cases where it could be used for driving useful chemistry. It is well-known that BQ is a good electron acceptor, having a reduction potential on the order of

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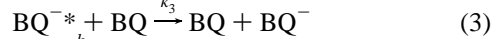
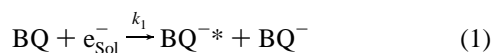
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-0.5 V vs SCE in polar aprotic solvents.^{30,31} From the fluorescence band edge at 593 nm, we can estimate that the excited state of BQ⁻ is a better reducing agent by 2.1 eV. This places its reduction potential near -2.6 V vs SCE, making BQ^{-*} a powerful electron donor, capable of acting as a chromophore in a wide variety of systems, as will be discussed in detail later.

B. Room Temperature. Fluorescence of BQ^{-*} has also been observed in room temperature linac experiments. Solvated electrons formed in isooctane by pulse radiolysis were captured by BQ to predominantly produce excited states of BQ⁻, the decay of which was then monitored by both fluorescence and the growth of BQ⁻ ground state absorption. The absorbance data require that at least 80% of BQ⁻ is formed in the excited state. This observation can be understood in view of the energetics of electron capture. From electron transfer equilibria in tetramethylsilane³² and differences in conduction band energies³³ the free energy of the solvated electron in isooctane is about 0.58 eV above that of biphenyl⁻, while the reduction potential of biphenyl (-2.58 v vs SCE) is close to that estimated above for BQ^{-*}. Therefore, reaction of the solvated electron with BQ is about 0.58 eV exoergic for production of BQ^{-*}, and about 2.7 eV exoergic for production of BQ⁻. Direct formation of the ground state is likely to be retarded due to the greater than 2.7 eV driving force, placing it well within the Marcus inverted regime, as was observed by Jonah and Meisel³⁴ for reactions of hydrated electrons with Ru(bpy)₃³⁺.

Figure 3, parts a and b shows scans of growing absorption at 460 nm and decaying emission at 650 nm, both of which reflect conversion of the excited state to ground state BQ⁻. The kinetics in this system can be understood with the following simplified scheme, which also includes values determined for the rate constants k_1 - k_3 :



$$k_1 = (2.1 \pm 0.4) \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2 = (8 + 8, -3) \times 10^6 \text{ s}^{-1}$$

$$k_3 = (3.0 \times 1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

The rate constant k_1 for the reaction of solvated electrons in isooctane with BQ was determined by using the average of previously reported values of k_1 for biphenyl in isooctane of 1.1 and $1.5 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$,^{35,36} and measurements of competition for solvated electrons in mixtures of biphenyl and BQ which gave a ratio of $k_1(\text{BQ})/k_1(\text{biphenyl}) = 1.65 \pm 0.2$. The very high electron capture rate constants on the order of $10^{13} \text{ M}^{-1} \text{ s}^{-1}$ are attributed to an unusually high electron mobility in isooctane.^{35,37} In Figure 3a, the growth of absorbance at 460 nm, where the BQ⁻ ground state is the principal absorbing

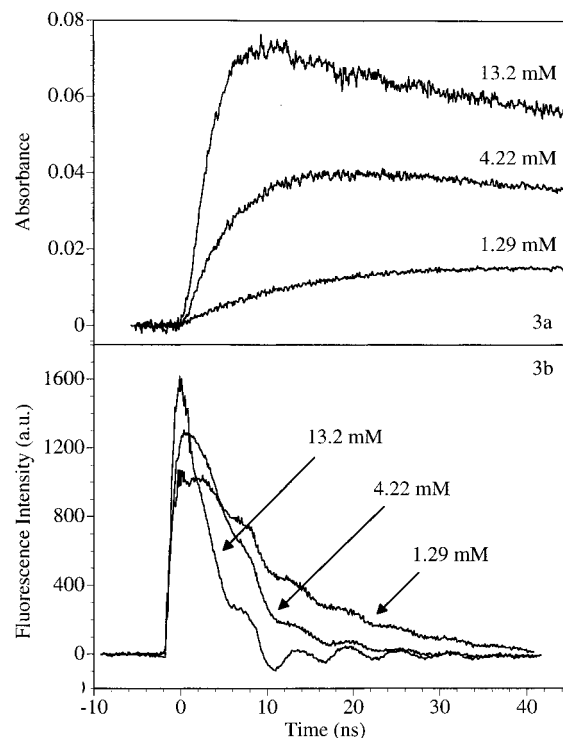


Figure 3. Pulse radiolysis of BQ in isooctane showing BQ^{-*} formation, decay, and fluorescence at room temperature. BQ^{-*} is formed directly by rapid (<0.1 ns) capture of electrons from the electron pulse, leading to the gradual rise in absorbance at 460 nm (a) and the prompt rise and gradual decay of BQ^{-*} fluorescence at 650 nm (b). In part b the data show distortions due to rings in the detector.

species, is due to the sum of intramolecular excited state decay and pseudo-first-order bimolecular excited state electron transfer, with rate constants k_2 and $k_3[\text{BQ}]$, respectively. Similarly, the decay seen in the emission data shown in Figure 3b is also due to the sum of both rates. The "step" rise seen in Figure 3b is a manifestation of the rapid electron capture rate forming BQ^{-*}, which occurs faster than 100 ps at all BQ concentrations studied. At longer times, BQ⁻ is lost both by recombination with solvent cations formed by the initial linac pulse and by reactions with other radicals formed from solvent cations. To fit the data, the complex kinetics of this relatively slow process was approximately described with a rate constant k_4 , and the distortions of the data due to detector response were included by iterative deconvolution.

Data collected at different BQ concentrations interpreted with this model indicate that the excited state lifetime of BQ^{-*} is long, but the uncertainties in separating the intra- and intermolecular rates are substantial. From these data the most probable lifetime for BQ^{-*} is ≈ 120 ns, which is about twice as long as the more accurate lifetime in MTHF glass. The rate of intermolecular electron transfer, $k_3 = 3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, is about twice as fast as intermolecular rate constants for electron transfer from biphenyl⁻ to quinones in isooctane, when both are attached to steroid spacers,²⁷ so it is plausible that the k_3 is overestimated and therefore k_2 is underestimated. Similar experiments in THF at 295 K showed that the excited state lifetime was 50 ns or longer, but a precise determination was not possible due to the additional reaction of BQ with radicals produced in the solvent. Excited state lifetimes at room temperature are at least as long as those at low temperature, but whether they are longer is uncertain. A longer lifetime at room temperature than at 77 K might be understandable in terms of the differing solvent environments and temperature. We are

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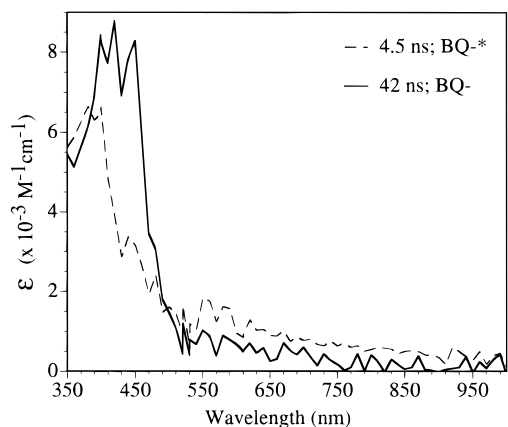


Figure 4. Absorption spectra resulting from pulse radiolysis of 1.1×10^{-3} M BQ in isoctane at room temperature. The spectra at 4.5 and 42 ns after the electron pulse are due principally to BQ^{*-} and BQ^- , respectively.

currently pursuing enhancements of our experimental capabilities that will improve our ability to measure lifetimes at room temperature.

It was also possible to measure the absorption spectrum of BQ^{*-} , as shown in Figure 4. At the lowest concentration of BQ, the bimolecular decay of BQ^{*-} is significantly retarded. Consequently, in the first few nanoseconds after the linac pulse most of the BQ radical anions are formed in their excited state. The 4.5-ns spectrum is therefore assigned principally to BQ^{*-} . It has a broad peak near 415 nm, and no other observed features to the red as far as 1000 nm. The 42-ns spectrum is due principally to ground state BQ^- . This spectrum is in good agreement with the 77 K result shown in Figure 1a. From the spectrum we can assign the BQ^{*-} absorption extinction coefficient at 415 nm to be $(6.5 \pm 2) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

C. Theoretical Calculations. To further support our understanding of the electronic structure of BQ^- , we have carried out molecular orbital calculations at both semiempirical and ab initio levels, which are summarized in Table 1. These calculations support the notion that the lowest energy transition in BQ^- is indeed forbidden. The ground state geometry for BQ^- used in semiempirical calculations was obtained by using the AM1 method, which is known to give good results for the geometries of a wide variety of organic molecules.^{38–40} Electronic transition energies were then calculated by using the ZINDO/S method with configuration interaction (CI), a technique that is specifically parametrized for the reproduction of UV/visible absorption spectra.^{40,41} The ground state geometry of BQ^- used in the ab initio calculations⁴² was obtained at the Hartree–Fock level by using the 6-31G* basis set (HF/6-31G*). At the ab initio level, excitation energies were obtained by using second-order Møller–Plesset perturbation theory with the 6-31G* basis set (MP2/6-31G*). As can be seen in Table 1, semiempirical and ab initio techniques yield results that are

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similar. Both predict that the two lowest energy electronic transitions are symmetry forbidden, involving the promotion of an electron from an oxygen-based n -orbital to a π^* orbital. The experimental data do indicate that fluorescence occurs from a forbidden transition below the allowed absorption bands, but contain insufficient information to substantiate the prediction of a second forbidden transition below the allowed one. The low-energy tails in the absorption and excitation spectra suggest that the lowest transition becomes very weakly allowed due to vibronic coupling, and is the source of the observed weak fluorescence. In the calculations, the third transition is orbitally allowed, and accounts for the BQ^- absorption we observe at 458 nm. The calculations also predict that the lowest energy quartet state is well above the third doublet state, ruling out the possibility that the observed emission is phosphorescence. Though the predicted transition energies are not a perfect match to what we observe in the absorption and fluorescence spectra, they are well within the expected accuracy of molecular orbital calculations.

D. Comparison with Prior Studies. While this is the first report of fluorescence of BQ^- , previous reports describe fluorescence and chemistry from photoexcited, electrochemically generated naphthoquinone and anthraquinone radical anions (NQ^- and AQ^-).^{14–16} However, Breslin and Fox¹³ have recently shown that under the conditions used for electrochemical production of AQ^- , 9,9'-bianthrone dianion, BA^{2-} , produced by reactions in solution subsequent to formation of the radical anions, was in fact the species responsible for the observed fluorescence and subsequent chemistry. For NQ^- the reported ambient temperature absorption spectrum¹⁴ is inconsistent with that published elsewhere in low-temperature matrices,⁶ indicating that the reported fluorescence might be due to a similar radical reaction product. It is therefore not clear whether fluorescence of either AQ^- or NQ^- was observed in the electrochemical experiments. The observations described in this report demonstrate authentic fluorescence for anions of benzoquinone by radiation chemistry techniques both at room temperature and in a low-temperature glass. Unlike electrochemical techniques, these methods produce radicals substantially free from opportunities for subsequent chemistry and from the effects of counterions.

Fujita and co-workers¹¹ reported light-driven electron transfer reactions upon photoexcitation of several radical anions including anthraquinones. Their results clearly indicate photochemistry from radical ions. The excited states could not be directly observed by absorbance or fluorescence,¹¹ but the yields of the electron transfer reactions suggest that these excited states have much shorter lifetimes than that reported here.

E. Use of BQ^{*-} To Study Electron Transfer. We undertook this investigation because little is known about the excited states of radical ions and because long-lived excited states of groups such as benzoquinone could be very valuable in the study of electron transfer rates and their regulation by such factors as energy and distance. It was our intent to enable new types of measurements of ET rates in molecules such as the biphenyl–steroid–quinone molecules used to confirm²⁷ the existence of the Marcus inverted region. These new types of measurements could dramatically extend the time resolution of current pulse radiolysis experiments, while retaining their desirable characteristics including well-known energetics, which are independent of distance and nearly independent of solvent polarity.

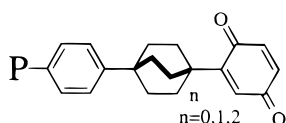
The uses of long-lived radical ion excited states should also extend to the study of natural photosynthesis and to synthetic model systems. Many quinone-containing molecules have been

Table 1. Summary of Semiempirical and ab Initio Molecular Orbital Calculations of Vertical Excitation Energies in the 1,4-Benzoquinone Radical Anion Compare Reasonably To Observed Fluorescence And absorption Band Edges at 593 (2.1 eV) and 475 nm (2.6 eV), Respectively

method	energy (eV)	state symmetry	%	type	comments
ZINDO/S ^a	2.31	² B _{2g} → ² B _{3g}	90.6	n → π	forbidden
	2.36	² B _{2g} → ² B _{2u}	89.8	n → π	forbidden
	2.98	² B _{2g} → ² A _u	99.3	π → π*	allowed
MP2/6-31G* ^b	2.05	² B _{2g} → ² B _{3g}		n → π	forbidden
	2.16	² B _{2g} → ² B _{2u}		n → π	forbidden
	3.24	² B _{2g} → ² A _u		π → π*	allowed

^a 3×3 CI calculation; at the AM1 geometry of the ²B_{2g} ground state. ^b At the HF/6-31G* geometry of the ²B_{2g} ground state.

assembled for study of energy storage by electron transfer.^{20,22,43–61} These references represent a small sampling of the many papers on this type of molecule. In most cases it has not been possible to determine electronic couplings from the rates, which are strongly influenced by Franck–Condon factors of uncertain magnitude. Measurement of a second rate with a very different free energy change could greatly enhance the information obtainable from such molecules. An example is provided by molecules produced by Dervan and co-workers.^{43,62,63} Photoexcitation of their porphyrinquinone (PQ) molecules produce charge separated (P⁺, Q⁻) states.



Quantitative separation of the effects of electronic coupling and Franck–Condon factors is difficult even with extensive temperature and solvent dependence data. Photoexcitation of (P⁺, Q⁻) could produce (P⁺, Q^{-*}) which would subsequently

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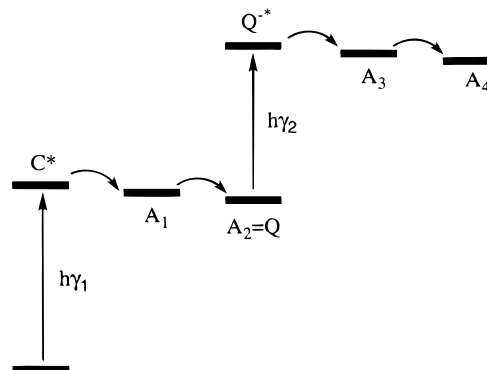


Figure 5. Moderately long lived excited states of quinone radical anions can be used to implement a “Z-Scheme” that mimics nature, in which two photons are sequentially absorbed leading to a very long lived and highly energetic charge separated state.

drive the electron back to the porphyrin in a highly-exoergic electron transfer step that is likely to have Franck–Condon factors of the order of unity. This would make it possible to make better and more direct measurements of electronic couplings. It might also be possible to examine the competition between moderately exoergic back reactions of P⁺, Q^{-*} to produce the lowest or higher excited states, with highly exoergic back reaction to produce the ground state.

Excited states of radical ions could also make possible convenient construction of molecular systems to implement “Z-schemes” related to those used by green plants to obtain large redox energies, as is exemplified in Figure 5. Two photons are sequentially absorbed to store an amount of redox energy larger than that of either photon, and to substantially enhance the charge separated state lifetime. An excited state of an initial chromophore (C*) such as a porphyrin rapidly transfers an electron down a chain of electron acceptors A₁ and A₂, where A₂ is a quinone. Subsequent photoexcitation of the quinone radical anion leads to a long enough lived excited state to further efficiently transfer the electron down an additional chain of acceptors A₃ and A₄, yielding a very long lived and highly energetic charge separated state. Such a scheme is dependent on the existence of an excited state having a substantial lifetime.

Excited states of quinone radical anions may also provide insights into natural photosynthesis, which has been extensively studied in bacterial photosynthetic reaction centers.^{64–67} Such reaction centers from many species contain the redox chain B₂, B_H, Q_A, Q_B where B = bacteriochlorophyll, H = pheophytin, and Q_A and Q_B are quinone derivatives. Important unanswered

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questions about the operation of these reaction centers concern the electron transfers from H^- to Q_A and the weakly-exoergic electron transfer step from Q_A^- to Q_B . The nature of these steps might be elucidated by observations of substantially exoergic ET reactions of Q^{-*} , either to drive electrons back to H or rapidly between Q_A and Q_B .

Conclusions

The radical anion of 1,4-benzoquinone, which is ubiquitously present in both artificial and natural systems for photochemical energy storage, has an excited state with 2.1 eV of energy and a lifetime of 63 ns at 77 K, and perhaps longer in a nonpolar solvent at room temperature. Fluorescence is observed both at 77 K and room temperature. The fluorescence quantum yield,

measured to be 3×10^{-3} at 77 K, appears to be the first quantum yield reported for any radical ion. The long lifetime and relatively low quantum yield indicate the forbidden nature of the transition, as do the absorption and fluorescence spectra and corroborating molecular orbital calculations. These results have important implications for the possibility of using excited states of radical ions for driving chemical reactions, including electron transfer, as the highly energetic (-2.6 eV vs SCE) excited state BQ^{-*} is long enough lived to drive useful chemistry.

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