# Stability of Pyridiniumylquinones to Aqueous Media: The Formation of Pyridinium−Oxy Zwitterionic Quinones

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The stability of perpyridiniumyl- and halopyridiniumylbenzoquinones was investigated. Reactions of *p*-chloranil and *p*-fluoranil with pyridines, followed by hydrolysis under mild conditions, gave 2,3-dihalo-5-oxy-6-(pyridinium-1′-yl)-1,4-benzoquinones **1** and 2,5-dioxy-3,6-bis(pyridinium-1′-yl)-1,4-benzoquinone **2**. Using the $H_0$ technique, the aqueous p$K_a$'s for two of these pyridinium−oxy zwitterions were determined to be −3 for 2,5-bis(4′-*tert*-butylpyridinium-1′-yl)-3,6-dioxy-1,4-benzoquinone (**2**) and −2 for 2,3-dichloro-5-oxy-6-(4′-*tert*-butylpyridinium-1′-yl)-1,4-benzoquinone (**1a**). In addition, it was found that a pyridinium-substituted anthraquinone, 1-[4′-(dimethylamino)-pyridinium-1′-yl]anthraquinone (**3**), is quite stable toward hydrolysis conditions and shows two reversible reductions at $E_{1/2} = -0.69$ and −1.10 V vs SCE.

In 1986, the first bispyridiniumyl- and tetrakispyridiniumylbenzoquinones were reported. They were produced by the reaction of *p*-chloranil with *N*-(trimethylsilyl)-4-(dimethylamino)pyridinium triflate (TMS-DMAP) in $CH_2Cl_2$.[1] It was noted that the reduction potentials for the perpyridiniumylquinone, +0.73 (first) and +0.16 V (second), had significantly increased from those of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), +0.51 and −0.30 V.[2] The structure of the perpyridiniumylquinone was confirmed by X-ray crystallography.[3] Many pyridinium compounds have been found to be stable to temperatures above 200 °C, and the positive moieties greatly increase the solubility of these compounds in polar solvents,[4] where oxidations tend to proceed more quickly.[5] Given the increased reduction potential of the pyridiniumquinones and the nature of the solubility of pyridinium compounds, this new class of quinones might lead to superior oxidizing reagents. In addition, the increased steric bulk should deter the formation of Diels−Alder side products, and the pyridine ring offers a new means for attachment to other systems. The potential success of this new class of quinones will depend, in part, on the stability of these quinones toward atmospheric conditions and their reactivity toward protic functional groups.[6]

Quinones have found wide uses, from oxidizing reagents for sensitive molecules to electron transfer agents in photosynthesis. Benzoquinones such as DDQ have found a variety of uses as oxidizing reagents due to their tendency not to react with halide, alkoxy, acyl, or carboxy functional groups.[7,8] Quinone oxidants are inexpensive and tend to avoid many problems that other oxidizing reagents have, such as poor selectivity and numerous side reactions. In addition to the aromatization of conjugated dienes, benzoquinones such as DDQ and *o*-chloranil have been used to oxidize allylic[9−12] and benzylic[13−15] alcohols to ketones and aldehydes.

During our investigation into the formation of various pyridiniumylquinones, we have isolated a series of zwitterionic quinones in which the positive charge of the pyridinium moiety is countered by an adjacent negatively charged oxygen. These compounds are soluble in aqueous solutions when the pH is low enough to protonate the oxygen, giving a pyridinium salt. Upon increasing the pH, the resulting zwitterion precipitates out of solution. This offers a means of purification without decomposition.

In the hope of finding a pyridinium-substituted quinone system that is stable toward hydrolysis conditions, we have prepared the first pyridiniumylanthraquinone and investigated its stability and electrochemistry.

## Results and Discussion

**Reaction of Perhalobenzoquinones with Pyridines.** In an attempt to isolate a monopyridiniumyltrihalobenzoquinone, the reactions of various pyridines with both chloranil and fluoranil were investigated. Though the reactions of pyridine, 4-*tert*-butylpyridine, and 4-(dimethylamino)pyridine were studied, for solubility reasons the 4-*tert*-butylpyridine adducts were the easiest to work with and will be discussed here. Chloranil or fluoranil reacts with 1 equiv of 4-*tert*-butylpyridine without exclusion of atmospheric moisture to give dark red crystalline products **1a** and **1b**, respectively. However, if the reaction is carried out under anhydrous conditions, the $^1$H NMR of the crude reaction product

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(1) Weiss, R.; Salomon, N. J.; Miess, G. E.; Roth, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 917.
(2) Peover, M. E. *J. Chem. Soc.* **1962**, 4540.
(3) Bock, H.; Nick, S.; Bats, J. W. *Tetrahedron Lett.* **1992**, *33*, 5941.
(4) Koch, A. S.; Feng, A. S.; Hopkins, T. A.; Streitwieser, A. *J. Org. Chem.* **1993**, *58*, 1409.
(5) Finley, K. T. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons Ltd.: Chichester, UK, 1988; p 684.
(6) Careful reading of ref 1 suggests that the work was carried out under anhydrous conditions.
(7) Hiebert, J. D.; Walker, D. *Chem. Rev.* **1967**, *67*, 153.
(8) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.
(9) Jackman, L. M. In *Advances in Organic Chemistry: Methods and Results*; Raphael, R. A., Taylor, E. C., Wynberg, H., Eds.; Interscience: New York, 1960; Vol. II, p 329.
(10) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.
(11) Becker, H.-D. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley-Interscience: New York, 1974; pp 335−423.
(12) Turner, A. B. In *Synthetic Reagents*; Pizey, J. R., Ed.; Halsted Press (Wiley): New York, 1977; Vol. 3, pp 194−225.
(13) Becker, H.-D.; Björk, A.; Alder, E *J. Org. Chem.* **1980**, *45*, 1596.
(14) Brown, D. R.; Turner, A. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1307.
(15) Ohki, A.; Nishiguchi, T.; Fukuzimi, K. *Tetrahedron* **1979**, *35*, 1737.

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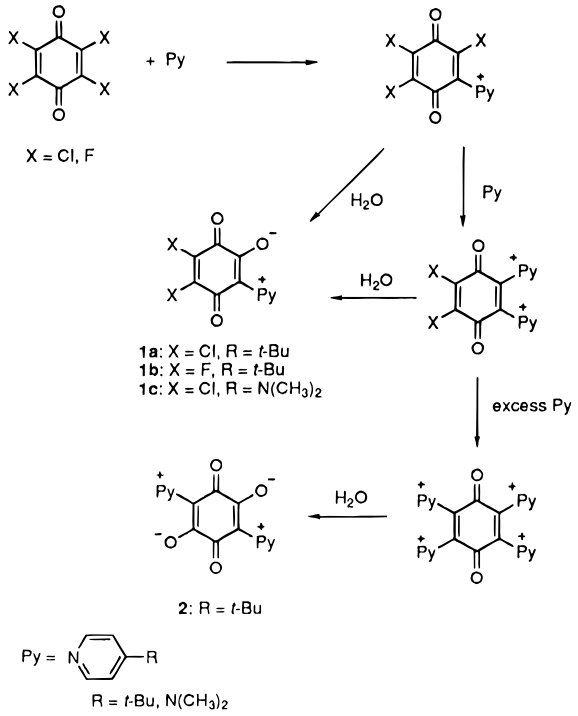
**Scheme 1**

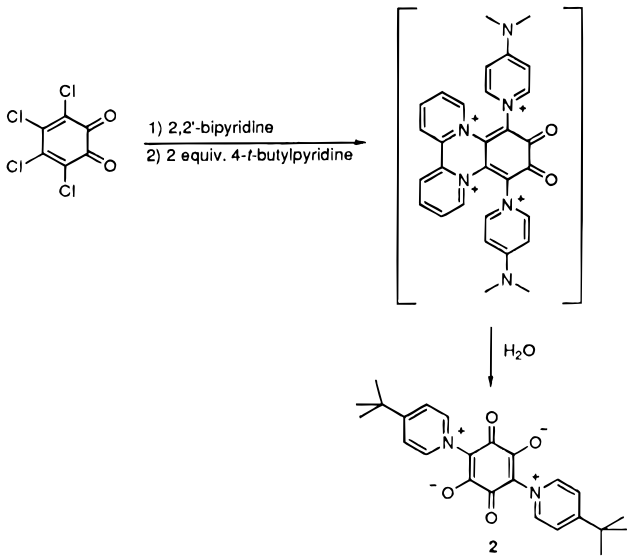



shows an additional pyridinium compound as the major product; this is assumed to be the trihalopyridiniumylquinone. Upon exposure to atmospheric moisture or a protic solvent such as methanol, rapid conversion to **1** was noted (see Scheme 1). This shows that replacement of even one of the halogens for a pyridinium moiety leads to a system that is so electrophilic that the resulting pyridiniumylquinone cannot be worked with outside of an inert atmosphere.

The $^1$H NMR of **1** shows one type of pyridinium, while the proton-decoupled $^{13}$C NMR shows six signals in addition to those of the pyridinium moiety. In the case of **1b**, two of the signals, $\delta$ 145.4 and 141.8, are doublets due to coupling with fluorine, $J$ = 285 and 282 Hz, respectively. It is also noted that one of the carbonyl carbons is split into a doublet, $J$ = 22, while the other is broadened due to coupling from the fluorines on the adjacent carbons. The IR spectrum shows a strong absorbance in the carbonyl region at 1706 cm$^{-1}$ and a very strong absorption at 1580 cm$^{-1}$ that can be attributed to the conjugated enolate of the oxyanion with one of the carbonyls. Elemental analyses are consistent with the proposed structures. The facile hydrolysis indicates that the initially formed 2-pyridiniumyl-3,5,6-trihalo-1,4-benzoquinones are extremely electrophilic at the 3-position.

When the tetrakispyridiniumylbenzoquinone was first prepared under anhydrous conditions and then exposed to moisture, a new compound, which has been assigned as 2,5-bis(4′-*tert*-butylpyridinium-1′-yl)-3,6-dioxy-1,4-benzoquinone (**2**), was isolated (see Scheme 1). Alternatively, if either chloranil or fluoranil is reacted with excess 4-*tert*-butylpyridine in DMSO without precautions to exclude moisture, **2** is formed directly. Analysis of **2** by $^1$H and $^{13}$C NMR shows one type of pyridinium along with two other carbons. It is worth noting that all of the quinone carbons that are bonded to oxygen are equivalent through resonance. The lack of an IR absorbance in the carbonyl region, along with the presence of a strong 1570 cm$^{-1}$ signal, indicates that both carbonyls are conjugated

**Scheme 2**




to an enolate. No chloride was found in the elemental analysis. This reaction was also carried out using pyridine to give an analogous compound.

When 2 equiv of 4-(dimethylamino)pyridine (DMAP) was used, only the monopyridinium-1-yl zwitterion **1c** was formed. When the reaction is monitored by $^1$H NMR, all of the free DMAP is initially consumed. Before the addition of water, <10% of **1c** is observed, and the majority of pyridinium signals correspond to compounds that could not be isolated and are assumed to arise mostly from the precursor to **1c**, along with some higher substituted products. This would indicate that, in the reaction of DMAP, the two pyridinium substituents in the intermediate bispyridiniumylbenzoquinone are 2,3- with respect to each other, as opposed to the normal 2,5-substitution. Since the reaction most probably occurs via an $S_NAr$ mechanism, the electronic effect of placing a pyridinium group on the quinone ring apparently enhances the electrophilicity of the 3-carbon much more than the steric effects deter reaction at this site (see Scheme 1).

When *o*-chloranil was treated with either 4 equiv of 4-*tert*-butylpyridine or 1 equiv of 2,2′-bipyridyl, followed by 2 equiv of 4-*tert*-butylpyridine, **2** was isolated after hydrolysis. This indicates that the first two additions occur at the normal 4- and 5-positions and that, after complete replacement of chloride, hydrolysis also occurs at the carbon 4- and 5-positions. This places the introduced oxygens in conjugation with the carbonyls but avoids direct interaction of the two negative charges with each other (see Scheme 2).

**Acidity Measurements of 1a and 2.** At ambient temperatures, both **1** and **2** are sparingly soluble in water and concd HCl but are quite soluble in concd $H_2SO_4$. The corresponding $\lambda_{max}$ in the visible spectrum of **2** was 380 nm in concd $H_2SO_4$, 458 nm in 2 M $H_2SO_4$, and 449 nm in water. The small decrease in $\lambda_{max}$ on going from 2 M $H_2SO_4$ to $H_2O$ is most likely a solvent effect. The extinction coefficients for the visible absorption in concd $H_2SO_4$ and water are virtually identical. An interesting feature of this change in $\lambda_{max}$ is that, as the concentration of hydronium ion is increased, the $\lambda_{max}$ gradually shifts from 458 to 380 nm. However, there is never a point when both signals can be observed. The greatest decrease in $\lambda_{max}$ occurs over a relatively narrow range from

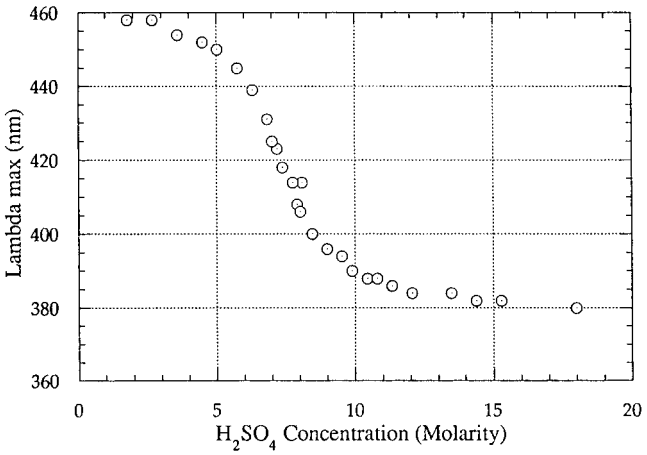



**Figure 1.** Plot of $\lambda_{max}$ vs concentration of sulfuric acid for **2**.

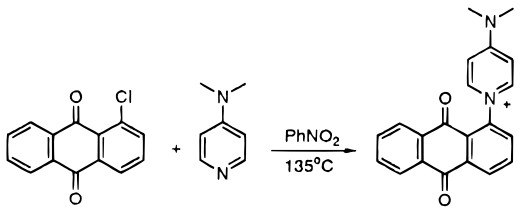
6 to 9 M $H_2SO_4$. The solubility behavior is consistent with the assumption that this change in $\lambda_{max}$ is due to the protonation of the oxy groups. When a concentrated solution of **2** in concd $H_2SO_4$ is diluted with water to give an 8 M solution, **2** starts to precipitate out of solution due to the lack of net charge. It is most likely that the monoprotonated species exist in concd $H_2SO_4$, and upon dilution, the dizwitterionic species predominates. A plot of the change in $\lambda_{max}$ versus concentration of $H_2SO_4$ should give a reasonable estimate of the p$K_a$, as previously described by Streitwieser et al.[16] (see Figure 1).

Twenty-seven points were taken, giving a point of inflection at approximately 6.9 M $H_2SO_4$, which corresponds to 49% $H_2SO_4$ by weight. Using the $H_0$ scale constructed by Ryabova et al.,[17] this corresponds to an $H_0$ value of −3.3, and a p$K_a$ of approximately −3.

Likewise, **1** was found to display similar solubility and UV/vis absorption properties. In concentrated sulfuric acid, the visible $\lambda_{max}$ of **1a** was found to be 388 nm. As the concentration of $H_2SO_4$ was gradually decreased, a gradual increase in the $\lambda_{max}$ to 472 nm resulted. The point of inflection was found to occur at 5.0 M $H_2SO_4$, corresponding to an $H_0$ of −2.4, and a p$K_a$ of approximately −2.

**Preparation and Characterization of Pyridiniumylanthraquinone 3.** The main problem with benzoquinones is the ease with which nucleophiles add to the ring. We are currently investigating the reactions of pyridines with 2-chloro-1,4-benzoquinone and 2,5-dichloro-1,4-benzoquinone, but these products appear to be unstable toward moisture. Since they are not aromatic in the strictest sense and addition to α,β-unsaturated carbonyls is quite facile, we decided to investigate the reaction of pyridines with 1-chloroanthraquinone. Since the anthraquinone must break aromaticity in order for substitution to occur, it is not nearly as reactive as the benzoquinones. When 1-chloroanthraquinone is heated with DMAP in nitrobenzene at 135 °C for 92 h, a yellow solid starts to form on the walls of the flask. Removal of most of the nitrobenzene and dilution with a nonpolar aromatic solvent such as benzene gives a brownish yellow solid. After exchange of the counterions for tetrafluoroborate and recrystallization from 95% ethanol, yellow needles were obtained in a 45% yield (see Scheme 3). The $^1$H NMR shows one type of pyridine ring shifted downfield from that of DMAP, along with a complex aromatic region comprised of seven other hydrogens. The $^{13}$C NMR shows 18 signals, consistent with one pyridinium ring and the anthraquinone. The two carbonyl carbons fall very close together at $\delta$ 182.6 and 182.4, indicating that the pyridinium substituent is electron-withdrawing primarily by induction. Furthermore, the IR spectrum shows two carbonyl signals at 1674 and 1651 cm$^{-1}$, and elemental analysis is consistent with the proposed structure.

**Scheme 3**




**3**

Worth noting is the considerable stability of this pyridiniumylanthraquinone toward water and heat: it does not start to decompose until 255 °C. While the pyridiniumquinones are sensitive to even atmospheric moisture, the pyridiniumylanthraquinone can be taken up in boiling water with no signs of decomposition, making it possible to work with under atmospheric and aqueous conditions.

The electrochemistry of **1a**, **2**, and **3** was investigated by cyclic voltammetry. Ferrocene was added after obtaining reduction potentials of the samples under investigation, and the oxidation at $E_{1/2} = 0.42$ V was used as an internal standard. Compound **1a** failed to show a typical reversible two-electron reduction. Three irreversible reductions at −0.62, −1.25, and −1.85 eV were observed. Compound **2** shows neither of the quinone reductions when scanning out to −2.5 V in acetonitrile or to −1.0 V in concd $H_2SO_4$, where the oxyanions should be protonated. An irreversible reduction of the pyridinium ring is seen at −1.78 V, which is in the same region as for other pyridinium reductions.[4] Apparently, the oxyanions in conjugation with the quinone ring significantly alter the nature of the quinone ring so as to render it useless as an oxidation reagent. However, **3** shows two reversible reductions at $E_{1/2} = -0.65$ and −1.06 V, with no noted sign of reduction of the pyridinium moiety.

## Conclusion

Pyridiniumylquinones containing a suitable leaving group such as halide or another pyridinium moiety readily undergo hydrolysis to give very stable pyridinium−oxy quinone zwitterions. The delocalized negative charge severely alters the nature of the quinone ring, thus rendering it useless as a reducing agent, even in strongly acidic media, where the oxygen is protonated. We conclude that pyridiniumylbenzoquinones are ill-suited as potential oxidizing reagents in any reaction where moisture is not rigorously excluded in the handling of the material.

The pyridiniumylanthraquinones appear to be quite stable toward heat and moisture. Although their reduction potentials are too negative for them to be considered

(16) Koch, A. S.; Waterman, K. C.; Bank, K.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6166.
(17) Ryabova, R. S.; Medvetskaya, I. M.; Vinnik, M. I. *Russ. J. Phys. Chem.* **1966**, *40*, 182 (cited in Rochester, C. *Acidity Functions*; Academic Press: London and New York, 1970; p 26.

as suitable oxidizing reagents, the pyridiniumanthraquinones possess several attributes that indicate their suitability for use in electron transport reactions.[18] These include stability to heat and moisture, the reversible nature of the two-electron reduction, a reduction potential similar to that of ruthenium bipyridine complexes, and the fact that the solubility properties of these compounds can be changed to encompass a wide range of polar solvents by exchange of their counterions.

## Experimental Section

**General.** Unless otherwise indicated, all materials were obtained from commercial suppliers and used without purification. The 4-*tert*-butylpyridine was distilled from KOH and stored over activated molecular sieves. Chloranil was recrystallized twice from acetone. Dry acetonitrile refers to triple distillation from $CaH_2$, followed by $P_2O_5$, and then $K_2CO_3$, unless stated otherwise. Melting points and decomposition points (Pyrex capillary) are uncorrected. $^1$H NMR spectra were determined at 200 or 300 MHz, and $^{13}$C NMR spectra were obtained at 50.327 or 75.477 MHz on an IBM/Bruker WP-2000 SP or Bruker 300 DPX spectrometer. Chemical shifts are reported in ppm, referenced to TMS directly or indirectly by the resonance of the solvent or added acetonitrile, 1.35 ppm. All positive values indicate a downfield shift from TMS. All $^1$H NMR data are tabulated in the following order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and coupling constants in hertz. UV/vis spectra were obtained using a Hewlett Packard 8452 UV/vis diode array spectrophotometer and are reported as $\lambda_{max}$ ($\epsilon$). Infrared spectra were obtained using a Nicolet Magna-IR spectrometer 550 with the OMNIC 1.1 or 1.2 operating program (s, strong; m, medium; w, weak; b, broad; sh, sharp).

Cyclic voltammograms were obtained using a BAS CV-27 cyclic voltammograph equipped with a BAS C-1 B cell stand and a BAS Model RXY recorder. The working electrode was glassy carbon with a Pt wire counter electrode and a Ag/AgCl saturated KCl reference electrode. The supporting electrolyte solution was 0.25 M tetrabutylammonium hexafluorophosphate in dry acetonitrile, and potentials were referenced to ferrocene as an internal standard.

**Formation of 2,3-Dichloro-5-oxy-6-(4′-*tert*-butylpyridinium-1′-yl)-1,4-benzoquinone (1a).** A solution of 500 mg (2.03 mmol) of *p*-chloranil in 400 mL of diethyl ether was prepared with the aid of a Soxhlet extractor. A solution of 1.127 g (8.34 mmol) of 4-*tert*-butylpyridine in 25 mL of ether was added to the stirred solution of *p*-chloranil. After being stirred for 18 h at room temperature, the yellowish orange mixture was filtered via suction and washed three times with ether to give a deliquescent yellow solid that turned orange as it absorbed water. The solid was dissolved in 6 mL of hot methanol to give a red solution. This solution was allowed to sit for 30 days while stoppered, after which the red crystals that had formed were collected via suction filtration, washed with methanol, and dried *in vacuo* to give 355 mg (1.09 mmol) of **1a**, yield 53.6%: $^1$H NMR ($CDCl_3$/TMS) 1.45 (9H, s), 7.84 (2H, d, $J$ = 7.1), 8.51 (2H, d, $J$ = 7.1); $^{13}$C NMR ($CDCl_3$/TMS) 30.17, 36.54, 119.81, 123.99, 135.86, 144.55, 146.02, 163.87, 167.27, 169.66, 175.38; IR (KBr) 1710 (sh, s), 1570 (br, s). Anal. Calcd for $C_{15}H_{13}NCl_2O_3$: C, 55.24; H, 4.02; N, 4.30; Cl, 21.74. Found: C, 55.23; H, 4.06; N, 4.24; Cl, 21.70.

**Formation of 2,3-Difluoro-5-oxy-6-(4′-*tert*-butylpyridinium-1′-yl)-1,4-benzoquinone (1b).** A solution of 500 mg (2.78 mmol) of *p*-fluoranil in 80 mL of diethyl ether was added dropwise to a stirred solution of 413 mg (3.05 mmol) of 4-*tert*-butylpyridine in 10 mL of ether. After being stirred for 8 h at room temperature, the reddish brown mixture was filtered via suction, washed three times with ether, and dried *in vacuo* to give 544 mg (1.73 mmol) of **1b**, yield 62%, mp > 200 °C dec: $^1$H NMR (acetone-$d_6$) 1.49 (9H, s), 8.18 (2H, d, $J$ = 7.0), 8.64 (2H, d, $J$ = 7.1); $^{13}$C NMR ($CDCl_3$/TMS) 30.1, 36.6, 118.0, 124.0, 141.8 ($J$ = 282), 145.4 ($J$ = 285), 145.8, 163.3, 167.2 ($J$ = 22), 169.6, 176.4 (broadened); IR (KBr) 1706 (sh, s), 1580 (br, s); UV/vis ($H_2SO_4$) 388 (324), 296 (15 800), 260 (12 700), 232 (8600), 202 (14 500). Anal. Calcd for $C_{15}H_{13}NFO_3$: C, 61.43; H, 4.47; N, 4.78. Found: C, 61.15; H, 4.48; N, 4.75.

**Formation of 2,3-Dichloro-5-oxy-6-[4′-(dimethylamino)pyridinium-1′-yl]-1,4-benzoquinone (1c).** A solution of 200 mg (0.813 mmol) of *p*-chloranil in 40 mL of $CH_3CN$ (distilled from $CaH_2$) was added to a stirred solution of 203 mg (1.661 mmol) of DMAP in 20 mL of $CH_3CN$. The resulting dark red solution was stirred for 20 min and then added to 25 mL of boiling methanol with a small amount of water added. After 10 min at reflux, the mixture was allowed to cool slowly to room temperature. The resulting solid was collected via suction filtration and washed with hot MeOH. The resulting deep purple solid was purified by dissolving in the minimum amount of concd HCl and then diluting the solution with $H_2O$ until precipitate formation was no longer observed. The solid was collected via suction filtration, washed with $H_2O$ and then MeOH, and dried *in vacuo* to give 103 mg (3.29 mmol) of **1c**, yield 40%: $^1$H NMR (DCl/MeOH) 3.18 (6H, s), 6.88 (2H, d, $J$ = 7.9), 7.79 (2H, d, $J$ = 7.8); $^{13}$C NMR ($CD_3OD$/HCl) 39.74, 106.95, 119.91, 137.42, 140.47, 141.52, 152.12, 156.05, 173.37, 173.82; IR (KBr pellet) 1703 (s, sh), 1555 (s, br); UV/vis ($CH_3CN$) 500 (1200), 286 (21 000), 216 (19 000).

**Formation of 2,5-Bis(4′-*tert*-butylpyridinium-1′-yl)-3,6-dioxy-1,4-benzoquinone (2)**. A solution of 6.62 g (48.98 mmol) of 4-*tert*-butylpyridine dissolved in 30 mL of DMSO was added to a solution of 2.00 g (8.16 mmol) of *p*-chloranil in 20 mL of DMSO. The resulting solution was stirred for 7 days at room temperature. A muddy brown precipitate developed, and the DMSO was removed via suction filtration. The precipitate was washed with 2-propanol; upon washing, its color went from brown to bright yellow. The resulting pale yellow powder was dried *in vacuo* (2.521 g, 6.20 mmol, 78.0%). The crude product was purified by Soxhlet extraction with THF, 92% recovery.

**Formation of 2 via Reaction with 2,2′-Bipyridyl and 4-*tert*-Butylpyridine.** A solution of 1.00 g (4.07 mmol) of *o*-chloranil in 5 mL of dry acetonitrile was added to a solution of 0.635 g (4.07 mmol) of 2,2′-bipyridyl in 5 mL of dry acetonitrile. All additions were carried out under argon, via syringe. The reaction mixture was stirred at reflux for 1 h and then allowed to cool to room temperature, and a solution of 1.10 g (8.14 mmol) of 4-*tert*-butylpyridine in dry acetonitrile under argon was added with stirring. After 6.5 h, the orange-yellow solid was collected via suction filtration and dried *in vacuo* to give 546 mg of yellow solid, which was purified by Soxhlet extraction using THF, 20.3% recovery, yield 7%: $^1$H NMR ($CDCl_3$/TMS) 1.43 (9H, s), 7.78 (2H, d, $J$ = 7.2), 8.63 (2H, d, $J$ = 7.1); $^{13}$C NMR ($CD_3OD$/HCl) 30.26, 37.90, 120.84, 126.16, 147.60, 167.67, 173.91; IR (KBr pellet) 1570 (s, sh); UV/vis ($H_2O$) 446 (317), 316 (23 900), 228 (25 000). Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89; Cl, 0.0. Found: C, 70.30; H, 6.55; N, 6.81; Cl, 0.0.

**Preparation of 1-[4′-(Dimethylamino)pyridinium-1′-yl]-anthraquinone (3).** A 1.015 g (8.31 mmol) portion of DMAP was added to a solution of 2.00 g (8.24 mmol) of 1-chloroanthraquinone dissolved in 50 mL of warm nitrobenzene. The mixture was stirred at 135 °C for 92 h. The amount of nitrobenzene was reduced to 15 mL by vacuum distillation, and 60 mL of benzene was added to aid in precipitation of the pyridinium salt. The resulting brownish yellow solid was collected via suction filtration and then rinsed three times with benzene and once with ether. The solid was taken up in boiling $H_2O$, filtered, allowed to cool, and then washed three times with $CHCl_3$. The aqueous fraction was treated with an excess of saturated $NaBF_4$, and the resulting precipitate was collected and rinsed three times with $H_2O$, yielding 2.093 g (5.03 mmol) of **3**, which was recrystallized from 95% ethanol, 74% recovery, overall yield 45%: $^1$H NMR (acetone-$d_6$) 3.49 (6H, s), 7.30 (2H, d, $J$ = 7.9), 7.96 (2H, overlapping signals),

(18) For reviews see: Juris, A.; Barigelletti, S.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 92 and references therein.

8.13 and 8.20 (3H, overlapping signals), 8.29 (1H, m), 8.41 (2H, d, $J = 7.9$), 8.60 (1H, dd, $J = 7.6, 1.5$); $^{13}$C NMR (acetone-$d_6$) 40.6, 108.3, 127.6, 127.9, 128.6, 130.5, 133.3, 134.8, 135.2, 135.6, 135.7, 136.1, 136.2, 141.5, 143.4, 157.9, 182.4, 182.6; IR (KBr pellet) 1674, 1651; UV/vis ($CH_3CN$) 340 (shoulder), 296 (25 000), 274 (25 000), 254 (37 000). Anal. Calcd for $C_{22}H_{17}N_2O_2BF_4$: C, 60.61; H, 4.12; N, 6.73 Found: C, 60.87; H, 4.18; N, 6.80.

**Acidity Measurements.** The procedures for measuring the p$K_a$ of **1a** and **2** were essentially the same. For example, a 13.2 mM stock solution of **1a** was prepared using concd $H_2SO_4$ and diluted with water/$H_2SO_4$ mixtures to give 13 solutions of 2.64, 0.66, or 1.32 mM, in which the concentration of **1a** varied from 12.6 to 0.9 M in $H_2SO_4$. Each solution was titrated in triplicate to a phenolphthalein end point using a 0.1016 M NaOH standardized solution.

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