A Convenient Synthesis and Spectroscopic Characterization of *N,N*-Bis(2-propenyl)-2,7-diazapyrenium Quaternary Salts

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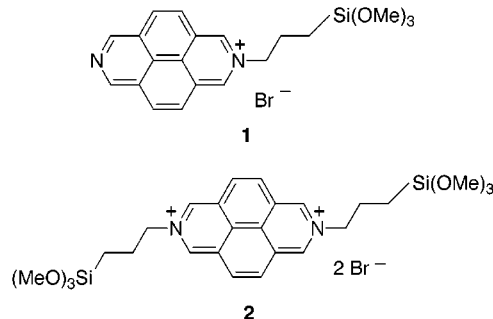*Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65409*

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N,N-Bis(2-propenyl)-2,7-diazapyrenium salts are synthesized in good yield from the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with allylamine, followed by LiAlH$_4$ reduction and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The nature of the counteranion depends on the solvent system used for recrystallization of the crude product from the final DDQ-oxidation step. X-ray analysis shows that if recrystallization is carried out in boiling CH$_3$OH/H$_2$O (1:1, v/v), the counteranion in the resulting deep-red crystals is always the alkoxy anion of 2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone, whether the final DDQ oxidation ends with addition of HClO$_4$ or HCl; on the other hand, if recrystallization is carried out with anhydrous acetonitrile, the product is *N,N*-bis(2-propenyl)-2,7-diazapyrenium diperchlorate or dichloride depending on whether the DDQ oxidation is followed by addition of concd HClO$_4$ or concd HCl, respectively. Importantly, if the DDQ oxidation is quenched with HBr, Br$^-$ is oxidized to Br$_2$ by unreacted DDQ, and the resulting product is *N,N*-bis(2,3-dibromopropyl)-2,7-diazapyrenium dibromide. Comparative absorption and time-resolved emission studies provide evidence for possible dimerization of *N,N*-bis(2-propenyl)-2,7-diazapyrenium diperchlorate in CH$_3$CN.

Introduction

2,7-Diazapyrenium dications combine luminescence properties similar to those of pyrene, redox properties and photoactivity similar to those of viologens, and intercalation properties very similar to those encountered in nucleic acid intercalators.[1–5] In this context, A. J. Blacker et al.[6] have proposed 2,7-diazapyrenium dications as attractive subunits for incorporation into macrocyclic structures to make photo- and electroactive receptors. N. D. Lilienthal et al. have demonstrated that *N,N*-dimethyl-2,7-diazapyrenium dication can function as a redox-dependent receptor for aromatic carboxylates; it was proposed further that, due to water solubility, that dication could be potentially useful for electrochemical sensors for nonactivated aromatics in water.[7] More recently, Leventis et al. published that *N*-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (**1**)[8] can covalently bond to the framework of silica aerogels,[9] and the derived luminescent material has shown sensitivity to oxygen. The same authors proposed that the correspond-

ing dicationic salt, namely, *N,N*-bis(3-trimethoxysilylpropyl)-2,7-diazapyrenium dibromide (**2**), having two possible points of attachment onto a sol–gel framework, would be expected to retain an alignment imposed by an externally applied force field during gelation.[10–13]

On the basis of reports for the synthesis of analogous systems,[14] an attractive method for the synthesis of **2** would be through addition of trimethoxysilane to *N,N*-bis(2-propenyl)-2,7-diazapyrenium bromide using Speir's catalyst (H$_2$PtCl$_6$).[15]

The synthesis of *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication can potentially be carried out by diquaternization of 2,7-diazapyrene. However, traditional methods for the synthesis of 2,7-diazapyrene involve oxidation

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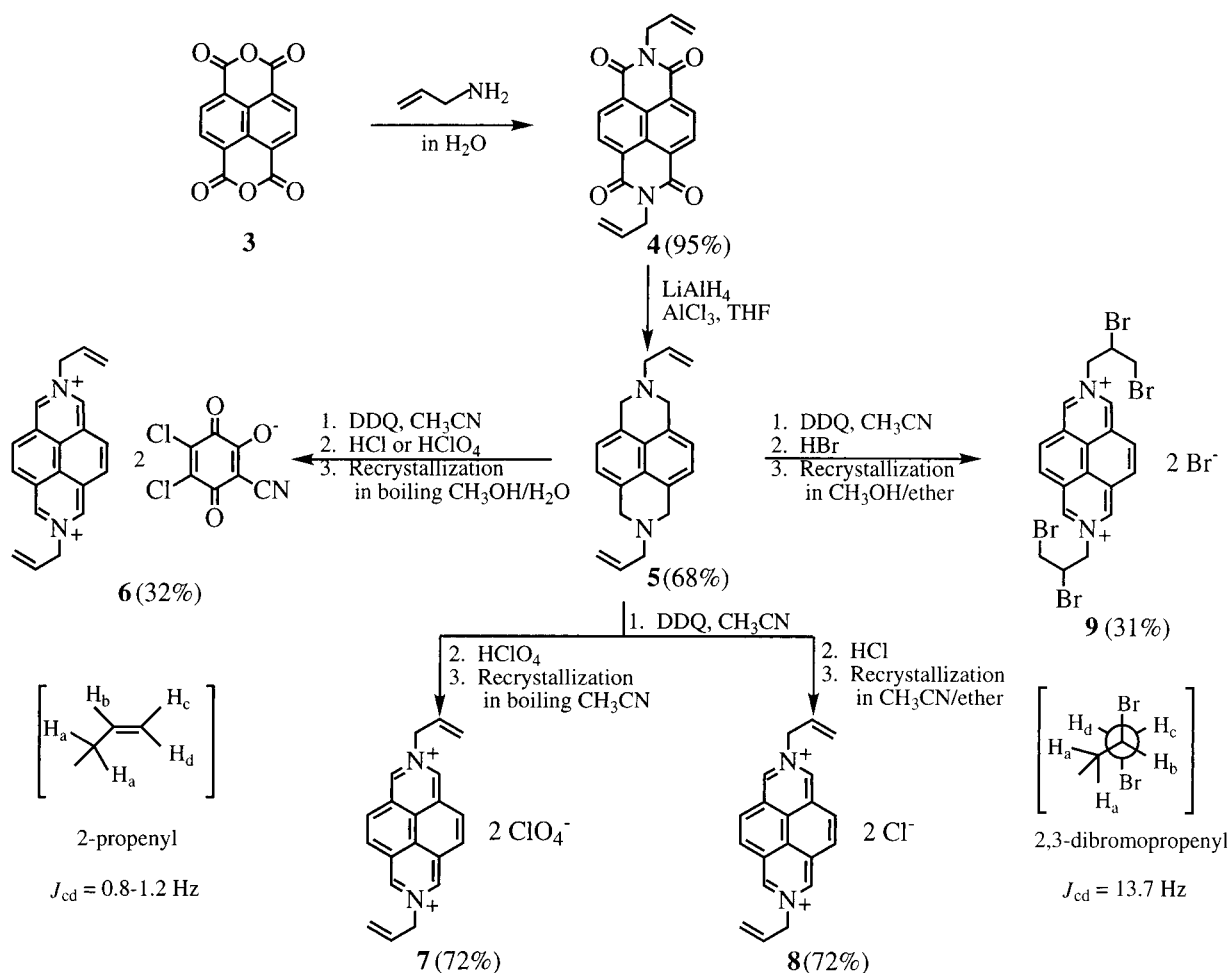
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Scheme 1

of 1,3,6,8-tetrahydro-*N,N*-dimethyl-2,7-diazapyrene with either Se or 10% Pd/C in high-temperature melts.[16,17] Both methods are cumbersome, but the selenium method can be hazardous.[16] Also, the oxidation with 10% Pd/C is low yield (23%).[17] For the synthesis of *N,N*-dimethyl-2,7-diazapyrenium dication, the above procedures have been circumvented by a direct but low-yield (20%) oxidation of 1,3,6,8-tetrahydro-*N,N*-dimethyl-2,7-diazapyrene with mercuric acetate in boiling glacial acetic acid.[16,18] The latter method, however, lacks generality. For instance, the oxidation of 1,3,6,8-tetrahydro-*N,N*-bis(2-propenyl)-2,7-diazapyrene (**5**) cannot be carried out in the presence of mercuric acetate because the latter could be added across the double bonds of the allyl groups.

In this paper, we report an alternative simple procedure where **5** can be oxidized directly with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature to the *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication in good yield.

Results and Discussion

Scheme 1 summarizes the route for the synthesis of various salts containing the *N,N*-bis(2-propenyl)-2,7-

diazapyrenium dication. The first step involves preparation of *N,N*-bis(2-propenyl)-1,4,5,8-naphthalenetetra-carboxylic diimide (**4**) from the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride (**3**) with allylamine at room temperature for 6 h. This step comprises a simplifying modification of Hünig's procedure where 1,4,5,8-naphthalenetetracarboxylic acid was converted first into the tetrakis(*N*-methylammonium) salt by evaporation of its solution in aqueous methylamine.[16] Subsequently, that salt was heated in 1-methylpyrrolidone for 1 h at 150−203 °C to give *N,N*-dimethyl-1,4,5,8-naphthalenetetracarboxylic diimide in 89% yield. Here, we found that the direct reaction of **3** with allylamine in water proceeds quantitatively to an insoluble precipitate of analytically pure **4** in excellent yield (95%). The second step involves AlCl$_3$-catalyzed reduction of **4** with LiAlH$_4$ to yield 1,3,6,8-tetrahydro-*N,N*-bis(2-propenyl)-2,7-diazapyrene (**5**), which was isolated by Soxhlet extraction and recrystallized from CHCl$_3$/hexane (68%). The targeted *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication (in compounds **6**−**8**) was synthesized by oxidation of **5** with DDQ in anhydrous CH$_3$CN at room temperature for 10 h, followed by addition of concentrated acid carrying the intended anion for the diazapyrenium salt. For example, if the reaction ends with addition of concd HClO$_4$, and the crude product is recrystallized from boiling anhydrous acetonitrile, pale-yellow *N,N*-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (**7**) is obtained in good yield (72%). Similarly, if the reaction ends with addition of concd HCl, yellow *N,N*-bis(2-propenyl)-2,7-diazapyre-

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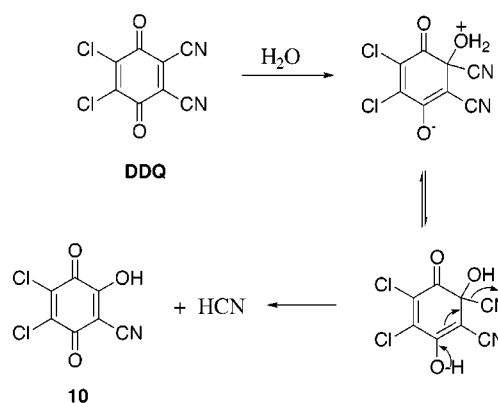(17) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273−6283.

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nium dichloride (**8**) is obtained also in good yield (72%). It should be emphasized, however, that if the DDQ oxidation is carried out in anhydrous methanol instead of acetonitrile, followed by addition of concd HClO$_4$ and recrystallization from CH$_3$CN, **7** is produced at a much lower yield (~12%). The low yield of **7** is probably due to the competing reaction of DDQ with methanol to give 2-cyano-5,6-dichloro-3-methoxy-1,4-benzoquinone.[19] Finally, if the DDQ oxidation ends with addition of concd HBr, Br$^-$ is oxidized to Br$_2$ by DDQ remaining in the reaction mixture,[20-22] and the resulting product is the yellow *N,N*-bis(2,3-dibromopropyl)-2,7-diazapyrenium dibromide (**9**). The ^{1}H NMR spectrum of **9** includes a coupling constant, J_{cd} = 13.7 Hz, which indicates that the geminal protons H$_c$ and H$_d$ are diastereotopic (Scheme 1). The unambiguous assignment of H$_c$ and H$_d$ was based on [1]H−^{13}C NMR correlation. In comparison, the coupling constant, J_{cd}, corresponding to the geminal vinylic protons H$_c$ and H$_d$ of the propenyl group ranges from 0.8 Hz (compounds **7** and **8**) to 1.2 Hz (compound **6**). The composition of dibromide **9** was confirmed by elemental analysis (Experimental Section).

Importantly, it was also found that the nature of the counterion depends not only on the chemical identity of the concentrated acid added to the DDQ reaction mixture, but more so on the solvent system used for recrystallization of the crude product from the DDQ oxidation. Specifically, if recrystallization is carried out with CH$_3$-OH/H$_2$O (1:1, v/v, reflux 1 h), the counterion in the resulting deep-red crystals is the alkoxy anion of 2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone (**6**; Scheme 1), whether the DDQ reaction ends with addition of concd HClO$_4$ or concd HCl. This unexpected counterion has been observed before in the reaction of DDQ with amidopyridines[23] and 1,10-phenanthroline.[24] DDQ is a powerful oxidizing agent frequently employed in synthetic procedures,[22,25,26] and is normally used under rigorously anhydrous conditions. In this context, it was first noted by Thiele and Gunther, almost a century ago, that DDQ in aqueous EtOH produces a red-colored solution.[27] Recently, the deep-red crystalline product was isolated from such a solution and characterized as the 2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone (**10**).[28] Scheme 2 illustrates the formation of **10** via a Michael addition of H$_2$O to DDQ followed by elimination of HCN.[28] It seems that the solubility of **6** in H$_2$O/CH$_3$OH is lower than the solubility of the corresponding perchlorate **7** or chloride **8**; thereby, **6** precipitates preferentially during recrystallization.

Formation of **6** was unexpected, and both its elemental analysis and the ^{13}C NMR spectra were perplexing and

Scheme 2

difficult to interpret, initially. It became possible, however, to identify its chemical composition by single-crystal X-ray diffraction analysis.[29] An ORTEP plot and a packing diagram of **6** are shown in Figures 1 and 2, respectively. The 2,7-diazapyrenium dications form two almost parallel stacks with a shallow angle between them (172°) and a 3.512 Å interplanar distance (Figure 2). The alkoxy anions of **10** also form two separate stacks with the same angle between them (172°). The counteranion and the 2,7-diazapyrenium stacks are not parallel, forming an angle of 133°.

In contrast, the X-ray crystal structure of the diperchlorate salt **7** is different.[30] An ORTEP plot and a packing diagram of **7** are shown in Figures 3 and 4, respectively. The 2,7-diazapyrenium moieties of **7** form two stacks in a herringbone type of structure, with an angle between them equal to 111° and a 3.94 Å interplanar distance (Figure 4A). The two ClO$_4^-$ ions per 2,7-diazapyrenium dication are placed between the planes of the dications (Figure 4B).

The electronic absorption spectra of *N,N*-bis(2-propenyl)-2,7-diazapyrenium dications **6**, **7**, and **8** are compared in Figure 5. The spectra of **6** and **8** are essentially identical, retaining the features expected for the *N,N*-dimethyl-2,7-diazapyrenium dication.[2] Compound **6** exhibits an additional broad maximum at 477 nm (ϵ 3200 M^{-1} cm^{-1}; 1600 M^{-1} cm^{-1} for each red counteranion), assigned to the alkoxy anion of **10** (lit. 476.5 nm, ϵ 1400 M^{-1} cm^{-1}).[28,31] In contrast, the spectrum of **7** is markedly different: the absorption features are strongly blue shifted and broader, to the point of losing their vibronic resolution. Dramatic blue shifting in the absorption spectrum is a phenomenon usually associated with ground-state stabilization through aggregation (e.g., dimerization, etc.).[32,33] Electrostatic supramolecular ag-

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(20) The redox potentials ($E°$) in volts vs SCE for the one-electron reduction of DDQ, of Br$_2$ to Br$^-$, and of Cl$_2$ to Cl$^-$ are 1.0 (in EtOH), 0.846 (in H$_2$O), and 1.117 (in H$_2$O), respectively.[21,22] These values show that DDQ can oxidize Br$^-$ to Br$_2$ but not Cl$^-$ to Cl$_2$.

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(29) X-ray data for compound **6**: crystal dimensions 0.40 × 0.25 × 0.10 mm; deep-red needles; empirical formula C$_{17}$H$_9$Cl$_2$N$_2$O$_3$; formula weight 360.16; crystal system monoclinic; lattice parameters a = 7.2126(9) Å, b = 18.245(2) Å, c = 11.4827(14) Å, α = 90°, β = 99.706-(2)°, γ = 90°; space group *P2$_1$/n*; V = 1489.4(3) Å^3; Z = 4; D_{calcd} = 1.606 g/cm^3; λ (Å) = 0.710 70; T = 173 ± 2 K.

(30) X-ray data for compound **7**: crystal dimensions 0.35 × 0.30 × 0.15 mm; pale yellow needles; empirical formula C$_{20}$H$_{18}$Cl$_2$N$_2$O$_8$; formula weight 485.26; crystal system monoclinic; lattice parameters a = 8.1977(6) Å, b = 10.3261(7) Å, c = 12.1523(8) Å, α = 90°, β = 93.3440(10)°, γ = 90°; space group *P2$_1$/n*; V = 1026.94(12) Å^3; Z = 2; D_{calcd} = 1.569 g/cm^3; λ (Å) = 0.710 70; T = 173 ± 2 K.

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(32) Refer for instance to the case of methylene blue.[14a,33]

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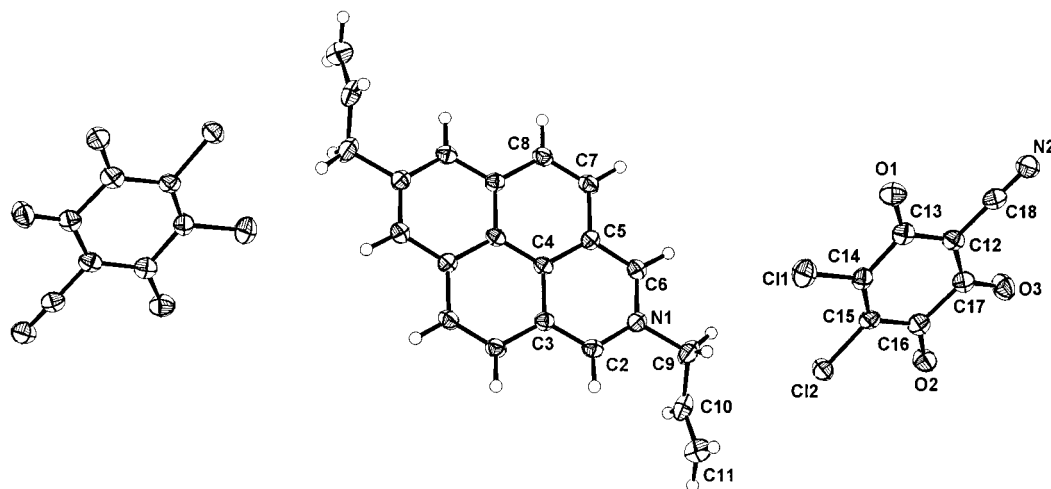
Figure 1. ORTEP plot of *N,N*-bis(2-propenyl)-2,7-diazapyrenium bis(2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone alkoxide) (**6**). Thermal ellipsoids are drawn at the 50% probability level.
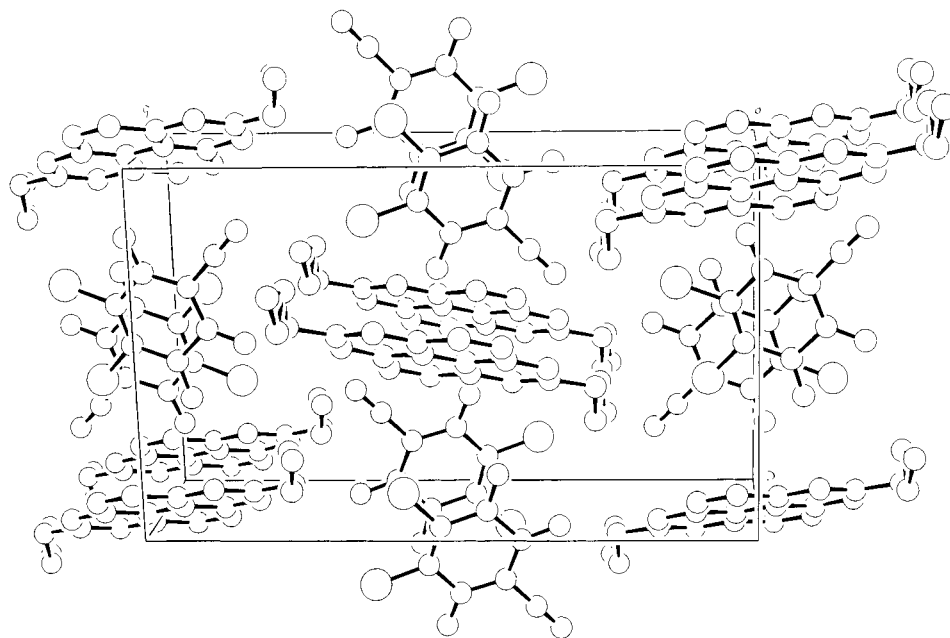
Figure 2. Packing diagram for *N,N*-bis(2-propenyl)-2,7-diazapyrenium bis(2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone alkoxide) (**6**), projection down the α axis.

gregates occupy a near energy continuum in shallow potential wells, thus explaining the broadening of the absorption features of the diazapyrenium moiety in **7**. By providing the energy to promote a molecule to the excited state, the stabilizing interactions in the aggregates should disappear, producing identical excited states from all three compounds **6**, **7**, and **8**.[34,35] Indeed, that is confirmed by the emission spectra of **6**, **7**, and **8**, which are identical, with identical excited-state lifetimes, ~10 ns (Figure 6, inset). Having two positive charges each, the *N,N*-bis(2-propenyl)-2,7-diazapyrenium moieties experience strong electrostatic repulsions. Therefore, it is rather difficult to explain aggregation by simple π-system interactions (i.e., attrac-

tive forces between induced dipoles and quadrupoles). It is speculated thereof that dimerization in solution is mediated by a negatively charged ClO_4^- held between two diazapyrenium moieties. There are indications that ClO_4^- promotes electrostatic aggregate formation.[36] However, due to the larger size of the alkoxy anion of **10** and the smaller size of Cl^- in comparison with ClO_4^-, similar aggregates in solutions of **6** are weak, while aggregates of **8** would require closer proximity of the diazapyrenium moieties, thus becoming unstable due to strong electrostatic repulsions. The X-ray data of **6** and **7** (Figures 2 and 4B) show that ClO_4^- can be accommodated between the 2,7-diazapyrenium dications, while anions of **10** are not, thus supporting this hypothesis.

(34) We follow logic parallel to the one used for the interpretation of the absorption and emission spectra of biphenyl/fluorene and 2,2′-bipyridine/4,5-diazafluorene, respectively.[35]

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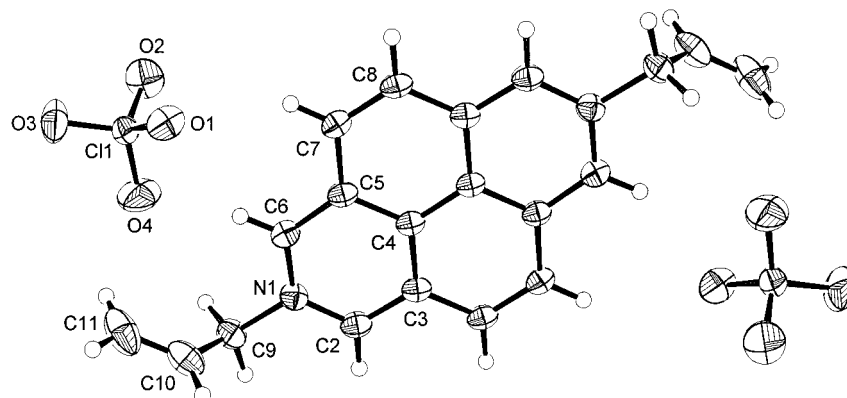
Figure 3. ORTEP plot of *N,N*-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (**7**). Thermal ellipsoids are drawn at the 50% probability level.
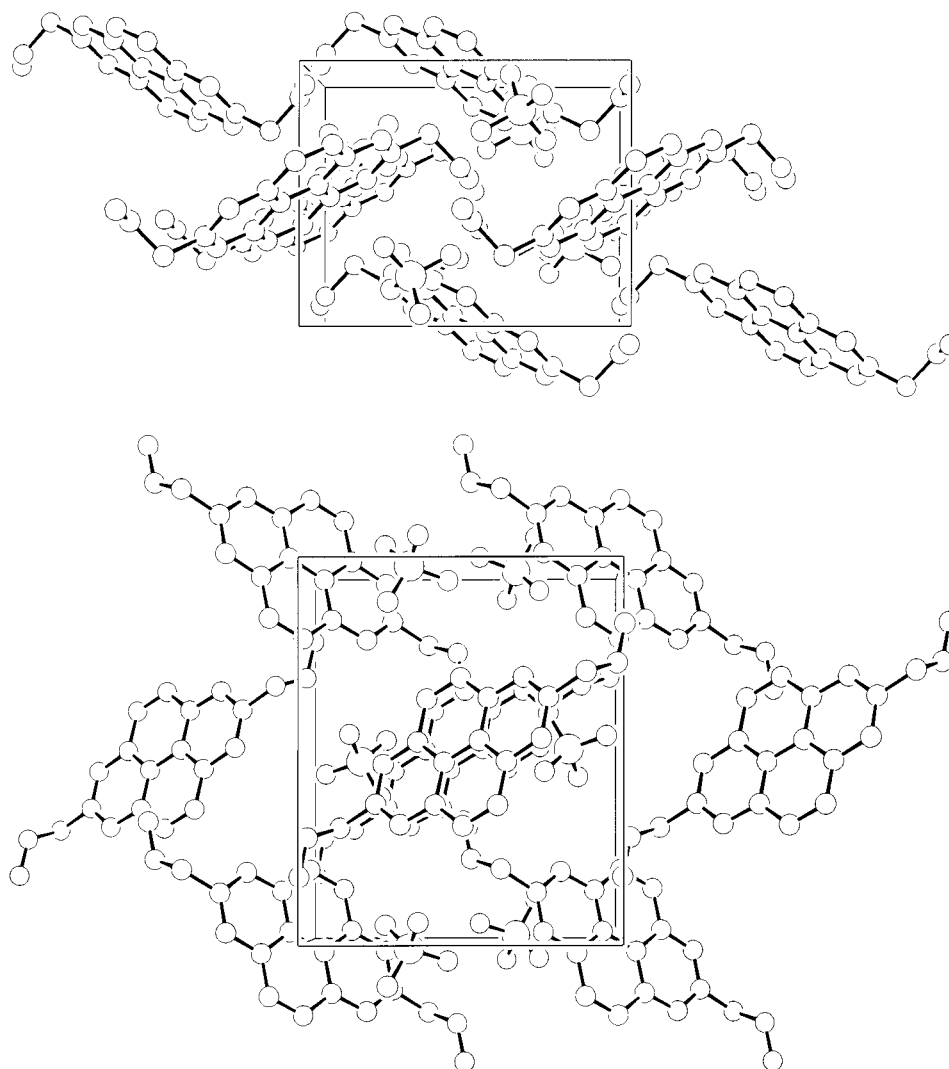

Figure 4. Packing diagram for *N,N*-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (**7**). (A, top) projection down the *c* axis; (B, bottom) projection down the *a* axis.

Conclusions

We have described a new three-step facile route to the *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication, from commercially available 1,4,5,8-naphthalenetetra-carboxylic dianhydride. Our method is general and can be used for the synthesis of any *N,N*-dialkyl-2,7-diazapyrenium dication, without having to synthesize first the 2,7-diazapyrene. Unexpectedly, it was discovered that *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication shows a special affinity toward the alkoxy anion of 2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone, which is produced from unreacted DDQ and water during recrystallization. It was found further that if the DDQ oxidation is quenched with HBr, Br⁻ is oxidized to Br_2 by the DDQ excess, and the resulting product is
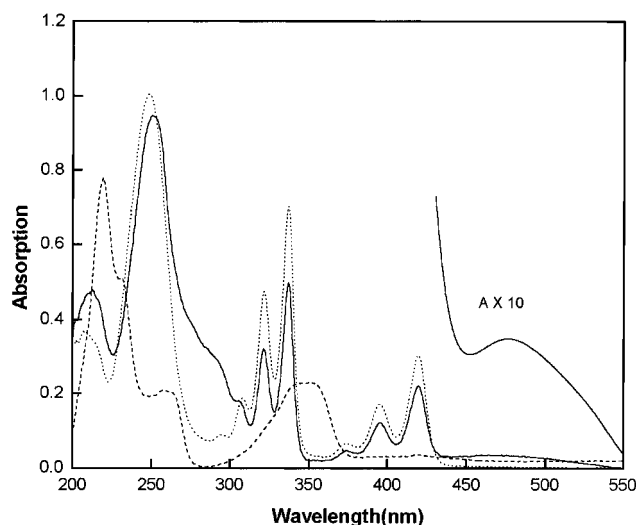
Figure 5. UV–vis absorption spectra of **6** in CH$_3$CN (—), **7** in CH$_3$CN (- - -), and **8** in CH$_3$CN/MeOH, 9:1, v/v (...) ([**6**] = 1.041×10^{-5} M, [**7**] = 1.278×10^{-5} M, [**8**] = 3.809×10^{-5} M). The expanded *A*-scale shows the absorption of the alkoxy anion of **10** in **6**.
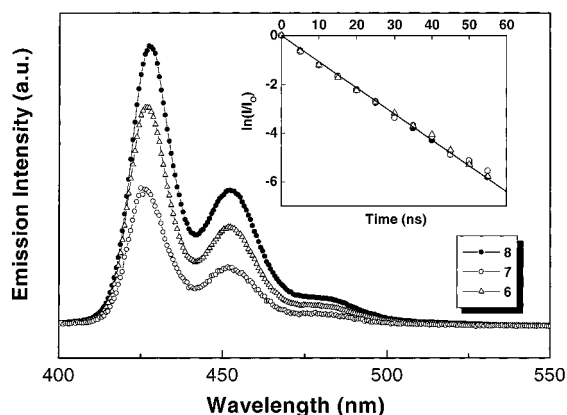

Figure 6. Emission spectra (λ_{ex} = 337.1 nm) of **6** (in CH$_3$-CN), **7** (in CH$_3$CN), and **8** (in CH$_3$CN/MeOH, 9:1, v/v) ([**6**] = 1.166×10^{-5} M, [**7**] = 1.813×10^{-5} M, [**8**] = 2.577×10^{-5} M). Inset: Time-resolved emission intensity for calculation of the emission lifetimes. (The emission decays from all three compounds **6**–**8** coincide.)

N,N-bis(2,3-dibromopropyl)-2,7-diazapyrenium dibromide.

Hydrosilylation of the strongly photoluminescent *N,N*-bis(2-propenyl)-2,7-diazapyrenium dication and investigation of the corresponding hydrosilylated product as a dopant of sol–gel-derived materials for sensor applications are currently under way in our laboratory.

Experimental Section

General Methods. Elemental analyses were performed by Oneida Research Services, Inc. X-ray crystallography was performed at the University of Missouri–Columbia. Time-resolved emission data were obtained with samples in freeze–pump–thaw degassed and flame-sealed ampules using a system composed of an ORIEL pulsed N$_2$ laser model 79111 (5 ns), a Spectrograph model 77480, and an InstaSpecV image intensifier/CCD detector using a Stanford Research Systems, Inc. four-channel delay/pulse generator model DG535. Excited-state lifetimes were determined by curve fitting using the Origin 5.0 software package on a Pentium PC. Melting points were uncorrected. Starting materials and solvents were pur-

chased from Aldrich or Fisher and used as received unless otherwise stated.

***N,N*-Bis(2-propenyl)-1,4,5,8-naphthalenetetracarboxylic Diimide (4).** Naphthalenetetracarboxylic dianhydride (**3**), (12.5 g, 46.6 mmol) was dissolved in a stirred aqueous solution of allylamine (500 mL, 40% v/v) under nitrogen. The new solution was stirred at room temperature for 6 h under nitrogen. During this time, analytically pure diimide **4** precipitated as an off-white product, which was filtered, washed with distilled water, and dried under vacuum: yield 15.3 g (95%); mp ~266 °C; ^{1}H NMR (TFA/CDCl$_3$, 500 MHz) δ 3.57 (4H, d, J_{ab} = 5.8 Hz, H$_a$), 4.01 (2H, dd, J_{cd} = 0.98, J_{bc} = 10.3 Hz, H$_c$), 4.11 (2H, dd, J_{cd} = 0.98, J_{bd} = 17.2 Hz, H$_d$), 4.74 (2H, ddt, J_{ab} = 5.8 Hz, J_{bc} = 10.3 Hz, J_{bd} = 17.2 Hz, H$_b$), 7.52 (4H, s, ArH); ^{13}C NMR (TFA/CDCl$_3$, 125 MHz) 44.1, 119.0, 126.9, 127.2, 130.3, 132.7, 164.7 (NC=O). Anal. Calcd for C$_{20}$H$_{14}$N$_2$O$_4$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.10; H, 4.08; N, 8.07.

1,3,6,8-Tetrahydro-2,7-bis(2-propenyl)-2,7-diazapyrene (5). Tetrahydrofuran (250 mL, dried over LiAlH$_4$) was added to a three-neck round-bottom flask, equipped with a reflux condenser and a magnetic stirring bar. To this flask, cooled in ice, was slowly added AlCl$_3$ (12.2 g, 0.092 mol) under nitrogen. After AlCl$_3$ had been dissolved, LiAlH$_4$ (10.4 g, 0.273 mol) was slowly added into the stirred solution at 0 °C. To the resulting suspension was also added at 0 °C diimide **4** (12.5 g, 0.036 mol), and the reaction mixture turned immediately to red and changed to green after ~10 min. The resulting mixture was stirred at room temperature for 1 h and then refluxed for 3.5 h under nitrogen. At the end of the reaction time, the reaction mixture was cooled to room temperature and poured over ice (~400 g), and the solid was filtered, washed with distilled water, and dried under vacuum (45 °C) overnight. The dry solid was subjected to Soxhlet extraction with CHCl$_3$ (~300 mL). The chloroform solution was concentrated to ~50 mL, and hexane (50 mL) was added. The precipitated product was filtered, washed with a small amount of CHCl$_3$/hexane (1:1), and dried under vacuum overnight: yield 7.05 g (68%); mp ~163 °C dec; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.26 (4H, d, J_{ab} = 6.6 Hz, H$_a$), 3.95 (8H, s, ring CH$_2$), 5.20–5.27 (4H, m, H$_c$ and H$_d$), 6.00 (2H, ddt, J_{ab} = 6.6 Hz, J_{bc} = 10.3 Hz, J_{bd} = 17.0 Hz, H$_b$), 7.12 (4H, s, ArH); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 56.2, 60.3, 117.9, 121.6, 127.7, 131.4, 135.2; UV–vis (CH$_3$CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 229 (40 000), 294 (6500). Anal. Calcd for C$_{20}$H$_{22}$N$_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.41; H, 7.73; N, 9.61.

General Method for the Synthesis of *N,N*-Bis(2-propenyl)-2,7-diazapyrenium Salts 6 and 7. Diamine **5** (0.25 g, 0.86 mmol) was added to anhydrous acetonitrile (50 mL) in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The suspension was stirred under nitrogen and heated to ~40 °C to dissolve the starting material. At that point, heating was stopped and DDQ (0.78 g, 3.44 mmol) was added to the warm solution. The color of the solution changed immediately to red and quickly turned to dark brown. The reaction mixture was stirred for 10 h at room temperature, under nitrogen, followed by the addition of 70% perchloric acid (1.0 mL, 11.6 mmol), which changed the color of the reaction mixture to clear yellow. The reaction mixture was concentrated down to ~20 mL at room temperature under vacuum, followed by the addition of dichloromethane until a yellow precipitate was observed. The resulting crude product was filtered, washed with a small amount of dichloromethane, and dried under vacuum overnight.

***N,N*-Bis(2-propenyl)-2,7-diazapyrenium Bis(2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone alkoxide) (6).** The crude product from above was recrystallized twice in boiling CH$_3$OH/H$_2$O (1:1, v/v) to give deep-red needles: yield 0.20 g (32%); mp > 350 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 5.56 (2H, dd, J_{cd} = 1.2 Hz, J_{bc} = 10.4 Hz, H$_c$), 5.60 (2H, dd, J_{bd} = 17.2 Hz, J_{cd} = 1.2 Hz, H$_d$), 5.76 (4H, d, J_{ab} = 6.0 Hz, H$_a$), 6.34 (2H, ddt, J_{ab} = 6.0 Hz, J_{bc} = 10.4 Hz, J_{bd} = 17.2 Hz, H$_b$), 8.91 (4H, s, ArH), 10.31 (4H, s, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 64.5, 87.7, 118.0, 122.9, 126.2, 129.0, 130.0, 131.4, 136.1, 141.8, 144.6, 171.0, 171.8, 174.2; UV–vis (CH$_3$CN) λ_{max},

nm (ϵ, M^{-1} cm^{-1}) 206 (52 800), 250 (78 600), 305 (10 900) 320 (24 900), 335 (36 300), 372 (3900), 393 (9100), 417 (16 400), 477 (3200); emission (CH_3CN) λ_{max}, nm, 426.8, 451.6; τ, ns, 9.7 $\pm$ 0.1. Anal. Calcd for $C_{34}H_{18}N_4Cl_4O_6$: C, 56.82; H, 2.53; N, 7.80. Found: C, 56.58; H, 2.72; N, 7.81. The structure was confirmed by X-ray analysis (Figures 1 and 2).

N,N-Bis(2-propenyl)-2,7-diazapyrenium Diperchlorate (7). The crude product from above was recrystallized in boiling anhydrous acetonitrile to give pale yellow needles: yield 0.30 g (72%); mp 257 °C dec; ^1H NMR (DMSO-d_6, 400 MHz) δ 5.57 (2H, dd, J_{cd} = 0.80 Hz, J_{bc} = 10.4 Hz, H_c), 5.60 (2H, dd, J_{bd} = 17.2 Hz, J_{cd} = 0.80 Hz, H_d), 5.76 (4H, d, J_{ab} = 6.4 Hz, H_a), 6.34 (2H, ddt, J_{ab} = 6.4 Hz, J_{bc} = 10.4 Hz, J_{bd} = 17.2 Hz, H_b), 8.92 (4H, s, ArH), 10.30 (4H, s, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 64.5, 123.0, 126.3, 129.0, 130.0, 131.5, 141.9; UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 217 (76 200), 231 (46 400), 263 (14 700), 351 (16 800); emission (CH_3CN) λ_{max}, nm, 426.8, 451.6; τ, ns, 9.7 $\pm$ 0.5. Anal. Calcd for $C_{20}H_{18}N_2$-Cl_2O_8: C, 49.50; H, 3.74; N, 5.77. Found: C, 49.35; H, 3.76; N, 5.80. The structure was confirmed by X-ray analysis (Figures 3 and 4).

N,N-Bis(2-propenyl)-2,7-diazapyrenium Dichloride (8). Diamine **5** (0.25 g, 0.86 mmol) in anhydrous acetonitrile (50 mL) was stirred at room temperature, under nitrogen, for 10 h with DDQ (0.78 g, 3.44 mmol) as described above. The reaction mixture was quenched with concentrated HCl (1 mL, 12 mmol), followed by the addition of diethyl ether (5 mL). The resulting yellow precipitate, consisting mainly of the dichloride salt of unreacted diamine **5**, was filtered. To the filtrate was added ether (30 mL), and the resulting new yellow precipitate was filtered, washed with CH_3CN/diethyl ether (1: 1, v/v), and dried under vacuum to give the dichloride **8**: yield 0.22 g (72%); mp 246 °C dec; ^1H NMR (CD_3OD, 400 MHz) δ 5.70 (2H, dd, J_{bc} = 10.3 Hz, J_{cd} = 0.82 Hz, H_c), 5.78 (2H, dd, J_{cd} = 0.82 Hz, J_{bd} = 17.0 Hz, H_d), 5.86 (4H, d, J_{ab} = 6.6 Hz, H_a), 6.44 (2H, ddt, J_{ab} = 6.6 Hz, J_{bc} = 10.3 Hz, J_{bd} = 17.0 Hz, H_b), 8.97 (4H, s, ArH), 10.29 (4H, s, ArH); ^{13}C NMR (CD_3OD, 100 MHz) δ 66.7, 124.8, 128.4, 131.3, 131.4, 131.9, 143.0; UV−vis (CH_3CN/CH_3OH, 9:1, v/v) λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 208 (15 300), 249 (42 800), 295 (3600), 308 (7600), 322 (19 100), 337 (28 100), 375 (2600), 395 (7000), 420 (12 400); emission (CH_3CN/CH_3OH, 9:1, v/v) λ_{max}, nm, 428.1, 452.2, τ, ns, 9.9 $\pm$ 0.3. Anal. Calcd for $C_{20}H_{18}N_2Cl_2$: C, 67.24; H, 5.08; N, 7.84. Found: C, 67.09; H, 5.16; N, 7.77.

N,N-Bis(2,3-dibromopropyl)-2,7-diazapyrenium Dibromide (9). Diamine **5** (0.25 g, 0.86 mmol) in anhydrous acetonitrile (50 mL) was stirred at room temperature, under nitrogen, for 10 h with DDQ (0.78 g, 3.44 mmol) as described above. The reaction mixture was quenched with 48% HBr (2 mL, 17 mmol) and filtered to remove the hydrobromide salt of **5**, and the filtrate was evaporated to dryness under vacuum at room temperature. The resulting solid was dissolved in CH_3-OH at room temperature, and the crude product was precipitated by addition of diethyl ether. The precipitate was filtered and purified further by recrystallization from MeOH/diethyl ether at room temperature to give **9** as a yellow powder: yield 0.20 g (31%); mp 233 °C dec; ^1H NMR (DMSO-d_6, 400 MHz) δ 4.26 (4H, d, J_{ab} = 5.5 Hz, H_a), 5.38 (2H, septet, J_{ab} = 5.5 Hz, J_{bd} = 9.3 Hz, J_{cd} = 13.7 Hz, H_b), 5.47 (2H, dd, J_{bd} = 9.3 Hz, J_{cd} = 13.7 Hz, H_d), 5.83 (2H, dd, J_{bc} = 3.9 Hz, J_{cd} = 13.7 Hz, H_c), 8.99 (4H, s, ArH), 10.49 (4H, s, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz, peak assignment is based on HMQC and DEPT) δ 35.3 (CH_2N^+), 51.2 (CHBr), 66.2 (CH_2Br), 126.6 (Ar =C), 128.8 (Ar =C), 130.3 (Ar =CH), 142.7 (Ar =CH); UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 219 (16 000), 253 (31 600), 298 (2200), 310 (4900), 324 (12 500), 339 (19 000), 378 (1600), 401 (4200), 425 (7500). Anal. Calcd for $C_{20}H_{18}N_2Br_6$: C, 31.36; H, 2.40; N, 3.66. Found: C, 31.30; H, 2.40; N, 3.55.

Supporting Information Available: Tables of X-ray single-crystal structure data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and torsion angles for compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.