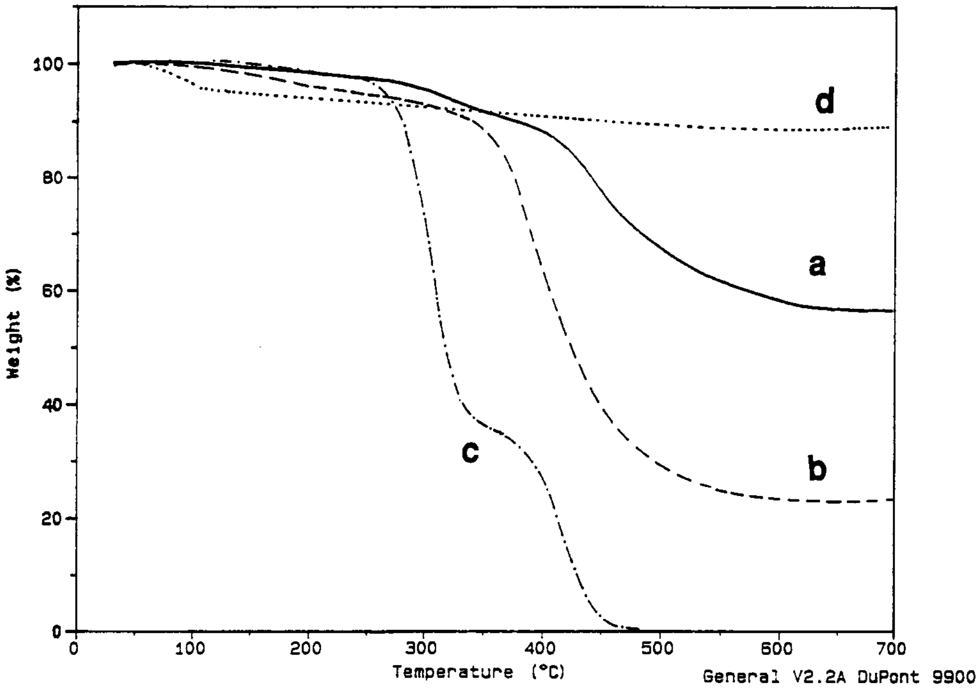

Figure 2. TGA thermograms of (a) the hybrid material derived from the hydrosilyated poly(allyl methacrylate) (39% by mole, based on the repeat unit) and TEOS (61% by mole), (b) hydrosilylated poly(allyl methacrylate), (c) poly(allyl methacrylate), $\bar{M}_n$ = 4360, and (d) a pure SiO_2 sol–gel glass derived from TEOS. The heating process for the TGA runs was performed at a rate of 20 °C/min in a nitrogen atmosphere.

H_2O) resulted from the further hydrolysis and polycondensation.

For a typical example, TEOS (8.6 mmol), distilled water (13.2 mmol), and HCl (0.086 mL of 10 M aqueous solution) were added simultaneously to a solution of freshly prepared poly(triethoxysilylpropyl methacrylate) (5.5 mmol, based on the repeat unit) in 10 mL of dry THF at room temperature in an argon atmosphere with magnetic stirring. After stirring at room temperature for 24 h, the homogeneous and viscous solution was poured into a glass beaker (4.0-cm diameter), which was then covered with a paraffin film having a number of holes made with a syringe needle for the evaporation of the volatiles. After this stood at room temperature for 25 days, a polyacrylate–SiO_2 glass was obtained (Figure 1). Both FTIR (C=O, 1735; C–H, 2950; Si–O, 1100 cm^{-1}) and elemental analysis demonstrated the presence of the polyacrylate components in the SiO_2 network.

The material were further characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Figure 2a, the hybrid material has a major weight loss at ca. 415 °C, which is assigned to a decomposition of the polyacrylate components in the hybrid material. This decomposition temperature is higher than those of poly(triethoxypropyl methacrylate) (Figure 2b) and poly(allyl methacrylate) (Figure 2c). At ca. 700 °C, the weight loss is ca. 42% for the hybrid material (Figure 2a), which is comparable to the calculated value of 45% organic content assuming that the residue at ca. 700 °C consists of only SiO_2. A sol–gel glass derived from TEOS alone under the same conditions retained ca. 90% of it original weight upon heating to 700 °C (Figure 2d). In the differential scanning calorimetry analysis of the hybrid material, no well-defined glass transition for the polyacrylate component was observed, suggesting a good dispersion of the polymer chains in the glass network.[3] The preliminary Izod tests demonstrated that the hybrid materials are tougher than the pure SiO_2 sol–gel glass. Further investigation is in progress to characterize these hybrid materials by Raman and ^{29}Si NMR spectroscopies, small-angle X-ray scattering, and electron microscopy, etc., and to study the mechanical and optical properties of these materials. In addition, further work is being conducted to synthesize the hybrid materials from the polyacrylates with higher molecular weights and telechelic PMMA with triethoxysilyl end groups.

Acknowledgment is made to the Office of Sponsored Research Projects, Drexel University, for the support of this research. We also thank Eastman Kodak Co. for a grant in support of the synthesis of polyacrylates. Many useful suggestions from Dr. Robert O. Hutchins are gratefully acknowledged.

Registry No. SiO_2, 60676-86-0; 2-propenoic acid, 79-10-7.

Near-Infrared Dyes. An Air-Stable Radical Anion

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Dyes that absorb in the near-infrared region (NIR, 0.8–2.0 μm) have received limited attention.[1] NIR optical phenomena are of importance, however. Fiber optic transmission in silica is best performed at 1.3 or 1.55 μm, inexpensive semiconductor lasers operate throughout the NIR, and there is an interest in NIR dyes for optical storage.[2]

Recently, we described several anion radicals that absorb NIR light.[3,4] These ions are composed from two or more

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[1] Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

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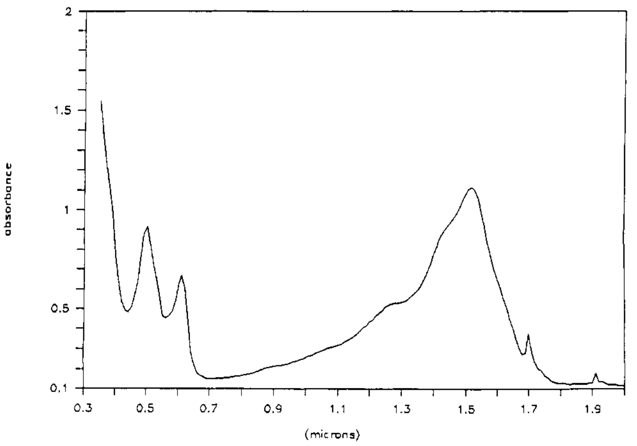
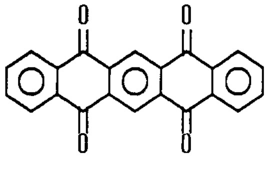


Figure 1. Vis–NIR spectrum of **2**$^{\bullet-}$$\mathrm{Bu_4N^+}$ (7×10^{-5} M), 1-cm cell.

electrophores and are formally mixed-valence species. With use of solutions, anion radicals with intense, narrow bands throughout the 0.8–1.9-μm range have been documented. For materials chemistry these examples are of only theoretical interest because they react with oxygen. We now report an anion radical with very long wavelength absorption that is quite stable in air. It has been characterized in solution and in the form of salts, which are conductive and show electronic transitions in the IR as well as the NIR.

Our previous studies revealed the NIR properties of **1**$^{\bullet-}$ and similar diquinone anions.[3] On the basis of the work of Hunig and co-workers, we proposed that **2**$^{\bullet-}$ would be



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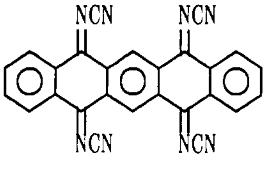

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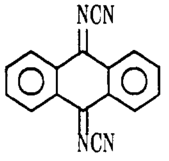

3

an air-stable[5] NIR absorber. Compound **2** was prepared by reaction of **1** with bis(trimethylsilyl)carbodiimide in $\mathrm{CH_2Cl_2(TiCl_4)}$.[5a] The product was purified by recrystallization from *o*-dichlorobenzene and was characterized by NMR, IR, UV–vis, and high-resolution mass spectrometry. Compound **3** was prepared similarly. Cyclic voltammetry on **2** using DMF, 0.1 M $\mathrm{Bu_4NBF_4}$ at 20–1000 mV s^{-1} showed four reversible one-electron couples ($\Delta E_p = 60$ mV, $i_p^a \simeq i_p^c$, E_p independent of sweep rate). Estimated from the center of each pair of anodic/cathodic peaks, $E° = 0.10$, −0.15, −0.91, −1.11 V (SCE). The first $E°$ can be compared to that for the couples **1**/**1**$^{\bullet-}$ (−0.42 V)[3] and **3**/**3**$^{\bullet-}$ (−0.05 V). The extremely positive potential for forming **2**$^{\bullet-}$ indicates that it can be air stable and, indeed, a DMF solution exposed to air for a month was unoxidized.[6]

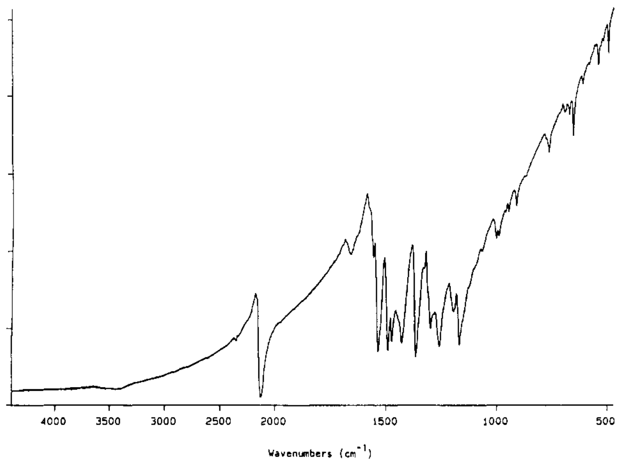

Figure 2. IR spectrum of **2**$^{\bullet-}$K in KBr.

The NIR spectrum of **2**$^{\bullet-}$ prepared coulometrically in DMF, 0.1 M $\mathrm{Bu_4NBF_4}$ shows an intense absorption at 1520 nm ($\epsilon = 15\,000$) as well as bands below 600 nm (Figure 1). The NIR band shape shows vibrational structure similar to that observed for **1**$^{\bullet-}$ and like **1**$^{\bullet-}$ and **2**$^{\bullet-}$ showed only a very small shift when the solvent was changed from DMF to *o*-dichlorobenzene. On this basis it is suggested that this long-wavelength absorption is due to a $\pi^*-\pi^*$ transition. The λ_{max} for **2**$^{\bullet-}$ in DMF can be compared to that for **1**$^{\bullet-}$ (1335 nm[3]) and **3**$^{\bullet-}$ (904 nm), showing the importance of two electrophores for the observation of bands beyond 1 μm.

Polycrystalline samples of **2**$^{\bullet-}$M$^+$, e.g., M = $\mathrm{Bu_4N}$, K, Na, are readily prepared.[7] When redissolved in DMF, the three salts have identical vis–NIR spectra. Not surprisingly, the NIR spectra of the solids are different from those in solution. Measured as KBr or NaCl pellets, each salt showed a broad band near 1.2 μm and a broad, presumably charge transfer band at longer wavelength. This band extended into the IR (Figure 2). The IR spectra have other unusual features, including the Fano bands at 2150 and 1600 cm^{-1}, due to the coupling of the C≡N and C=N vibrations with the electronic transitions.[8] It is expected from these spectra that **2**$^{\bullet-}$M$^+$ will be conductors,[9] and indeed pressed pellets show $\sigma \simeq 0.5$, 0.05 S cm^{-1} for **2**$^{\bullet-}$Na$^+$ and **2**$^{\bullet-}$K$^+$, respectively, at room temperature. The conductivity and IR of the salts are unchanged in air over several months. These salts are unusual in that high conductivity is observed even though there is no charge transfer to the countercation.

Because of the ease of preparation of these ions and the possibility for manipulating the molecular structure,[3] it should be possible to vary the "color" of the NIR dyes over a wide range, maintain the stability, and prepare interesting materials.

Acknowledgment. This work was supported by NSF and ONR. Initial experiments were performed by S. Rak. Kent Mann assisted with the NIR spectra.

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[5] (a) Aumuller, A.; Hunig, S. *Liebigs. Ann. Chem.* **1986**, 142. (b) *Ibid.*, p 165. (c) Hunig, S.; Aumuller, A.; Erk, P.; Meixner, H. *Synth. Met.* **1988**, *27*, B181.

[6] On standing in DMF, **2**$^{\bullet-}$$\mathrm{Bu_4N^+}$ forms some **2**$^{2-}$. Compound **2** in DMF slowly forms some **2**$^{\bullet-}$.

[7] **2** (0.10 g) was reduced in a two-compartment cell containing 100 mL of DMF (0.10 M $\mathrm{NaBF_4}$, $\mathrm{KBF_4}$, or $\mathrm{Bu_4NBF_4}$) with Pt electrodes. Na$^+$**2**$^{\bullet-}$ and K$^+$**2**$^{\bullet-}$ were filtered off as solids and washed with DMF. $\mathrm{Bu_4N^+}$**2**$^{\bullet-}$ was precipitated with acetonitrile, filtered, and washed with acetonitrile. $\mathrm{Bu_4N^+}$**2**$^{\bullet-}$ was further purified by recrystallization from DMF.

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