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A photochromic phenoxyquinone based cyanide ion sensor

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ABSTRACT

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Photochromic materials undergo structural changes that interconvert two distinct isomeric forms upon irradiation at specific wavelengths.^{1–3} Owing to their light driven molecular switching properties, photochromic compounds have been incorporated into many intriguing systems, including molecular switches, optical memory devices, holographic gratings, and drug delivery vesicles.^{4–19} Because of these wide ranging applications, various photochromic molecules, such as azobenzenes, spiropyrans, phenoxyquinones, and bisthienylethenes have been developed.

Among the many photochromic compounds described to date, phenoxyquinone derivatives are unique in several ways.²⁰⁻²⁴ First, these molecules participate in a photoinduced reversible phenyl group migration process. For example, the 'trans'-quinone form of 1-phenoxy-5.12-naphthacenequinone (1) undergoes photochemical rearrangement to form the '*ana*'-guinone form upon irradiation with UV light (Scheme 1a). The reverse conversion of the 'ana'quinone to 'trans'-quinone form occurs readily upon irradiation with visible light. Second, unlike azobenzene or spiropyran derivatives, phenoxyquinones display negligible thermal interconversion of these forms at room temperature. Third, phenoxyquinone derivatives usually show an excellent resistance to fatigue. For example, it has been reported that the photochemical rearrangement process can be repeated 500 times without decomposition of the materials.²⁴ Lastly, the 'ana'-quinone form of phenoxyquinones is known to undergo nucleophilic substitution reactions with amines to form amine-quinone adducts (Scheme 1b).²⁴

Close inspection of the structure of the photochemically generated '*ana*'-quinone form indicates that it contains two electrophilic sites at carbons a and b (Scheme 1a). Nucleophilic

We have developed a new chemosensor system for cyanide ion that is based on a photochromic material. We observed that addition of cyanide anion to a UV irradiated solution of a phenoxynaphthacenequinone derivative brought about a significant change in the absorption spectra that enabled detection of cyanide ion in a selective and sensitive manner. A carbanion intermediate was shown to be responsible for the long wavelength absorption band (630–940 nm) that is generated by cyanide addition.

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addition to carbon (a) would form an adduct like **3** (Scheme 1b). Similarly, the carbon center (b) should also be reactive toward nucleophiles. A survey of the literature suggests that only amine–quinone adducts, arising from reaction at carbon (a), have been prepared thus far from the photochemically generated 'ana'-quinone form.²⁴

We felt that it would be intriguing to investigate the reactivity of the photochemically produced '*ana*'-quinone form toward other



Scheme 1. (a) Photoinduced isomerization of 1-phenoxy-5,12-naphthacenequinone, (b) structure of an amine–quinone adduct, (c) structure of a phenoxyquinone derivative investigated in this study.



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nucleophiles, such as cyanide, acetate, and iodide anions since covalent adduct formation would be expected to promote changes in the electronic absorption or emission properties of the quinone chromophore. Furthermore, if the spectral changes are sensitive and specific to the type of nucleophile used, phenoxyquinones would serve as selective chemosensors for anions. Although



Figure 1. (a) UV-visible absorption spectra of an acetonitrile solution containing 0.1 mM of the phenoxyquinone **4** upon irradiation with 365 nm UV light (1 mW/ cm²). (b) Absorption spectra of 365 nm UV-irradiated (20 min, 1 mW/cm²) acetonitrile solutions (0.1 mM) of the phenoxyquinone **4** after addition of CN⁻, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, H₂PO₄⁻, and AcO⁻ (10 molar equiv to **4**). The spectra were obtained 30 s after addition of the anions. The inset shows photographs of a cyanide anion-treated vial containing photoirradiated **4**. (c) Plot of absorbance at 885 nm as a function of cyanide ion concentration. The inset contains a plot of the absorption ratio vs cyanide anion concentration in the micromolar range.

numerous probe molecules have been described, those that serve as photochromism-based chemosensors are exceptionally rare. Until recently, we²⁵ and others²⁶ were the only groups that have investigated photochromic spiropyran-based cyanide ion chemosensors.²⁷

In Figure 1 are shown the UV-visible absorption spectral changes that occur upon UV-irradiation (365 nm) of an acetonitrile solution (0.1 mM) containing 6-(4'-ethylphenoxy)-5,12-naphthacenequinone 4. The spectral changes show that characteristic peaks in the 400-550 nm region, corresponding to the 'ana'quinone form of the phenoxynaphthacenequinone, increase (Fig. 1a) with increased irradiation time. In order to investigate the possible use of the photochemically generated 'ana'-quinone form as a chemosensor, various anions, including CN⁻, F⁻, Cl⁻, Br ⁻, I⁻, NO₃⁻, H₂PO₄⁻, and AcO⁻, with *n*-Bu₄N⁺ as a common countercation were added to the UV irradiated solution of 4. As displayed in Figure 1b. addition of cvanide anion to the UV irradiated phenoxyquinone **4** results in the generation of a broad absorption peak in the 630-940 nm (visible and infrared) region. This spectral change can be detected even when the cyanide anion concentration is as low as 18.7 µM (Fig. 1c). The detection limit was found to be 5.26 μ M when a lower concentration (0.05 mM) of 4 was used (Fig. S5, Supplementary data). Fluoride anion addition also results in formation of the broad peak while addition of other anions, including Cl⁻, Br⁻, I⁻, NO₃⁻, H₂PO₄⁻, does not. Importantly, the magnitude of the increase in absorption in the visible-infrared region promoted by fluoride is much lower than that generated by cyanide addition. In addition, the color of the irradiated acetonitrile solution of 4 was found to change from yellow to pale brown when cyanide anion is added (Fig. 1b inset). It should be noted that a solution containing unirradiated phenoxyquinone 4 does not undergo any spectral changes in the presence of the anions tested including cyanide (Fig. S1, Supplementary data). This observation demonstrates that the spectral change observed originates from a



Figure 2. Absorption spectral changes of an acetonitrile solution containing 365 nm irradiated (20 min, 1 mW/cm²) **4** (0.1 mM) and cyanide anion (10 molar equiv to **4**) upon standing in the dark. Spectra were obtained 30 s after addition of cyanide anion. The inset contains absorption spectra before (red) and immediately after (blue) addition of TFA (1 equiv to cyanide anion used).



Figure 3. Structure of CN-adduct 5 and its soluton colors in acid/base condition.



Scheme 2. Proposed mechanism for the formation of the intermediate and CN-adduct 5.

reaction of the 'ana'-quinone form of phenoxyquinone **4**. The cyanide-induced spectral change in the visible and infrared region was observed even in acetonitrile–HEPES buffer (5 mM, pH 7.4) (99:1, v/v) solution with a detection limit of 27.5 μ M (Figs. S6 and S7, Supplementary data).

Observations made in several experiments provided information about the nature of the visible-infrared absorbing substance formed by adding cyanide. First, the substance generated in this process was found to be unstable, as evidenced by the gradual decrease in the intensity of broad peak in the visible-infrared region (Fig. 2). The broad peak disappears completely in 2 h. Second, addition of trifluoroacetic acid to the solution containing the formed substance results in immediate quenching of the absorption peaks in the visible-infrared region (Fig 2, inset).

The results described above clearly indicate that a relatively short-lived, acid sensitive intermediate is formed in the reaction of the photochemically generated 'ana'-quinone form of 4 with cyanide anion. We believed that structural identification of the stable product formed eventually in this process would provide valuable information about the nature of the unstable intermediate produced by cyanide addition. In order to produce a sufficient quantity of the final reaction product, a preparative scale photochemical reaction of phenoxyquinone 4 was conducted in an acetonitrile solution containing cyanide anion (10 equiv to **4**). Thin layer chromatographic (TLC) analysis of the crude mixture showed that the process generates a single product, which can be isolated by using silica gel column chromatography (see Supplementary data). Interestingly, data gained from ¹H NMR, IR (Fig. S2, Supplementary data) and mass spectroscopic analyses showed that the product formed in the reaction of the photochemically generated 'ana'quinone form of 4 with cyanide anion is 6,12-dihydroxytetracene-5,11-dicarbonitrile 5 (Fig. 3).

An acetonitrile solution of the CN-adduct **5** is yellow and it undergoes a yellow-to-purple color transition upon addition of base (Fig. 3), a change that is likely a result of base-promoted deprotonation of the phenolic hydroxyl groups. Addition of acid to the basic solution of **5** results in regeneration of the yellow color, confirming that color change is reversible. Monitoring of these color transitions by using UV-visible spectroscopy reveals that the CN-adduct **5** and the deprotonated form **6** have maximum absorption wavelengths at 434 nm and 527 nm, respectively (Fig. S3, Supplementary data).

The mechanisms for formation of the long wavelength absorbing intermediate and the CN-adduct **5** are worthy of comment. It is apparent that irradiation of the '*trans*'-quinone form of phenoxyquinone **4** promotes an excited state aryl group migration reaction to generate the '*ana*'-quinone form **7** (Scheme 2). Nucleophilic addition of cyanide anion to one of the highly electrophilic carbons in **7** then produces the phenolate intermediate **8**. Tautomerization by way of a 1,4-proton shift yields the carbanion **9** that is believed to be the intermediate which absorbs light in the visible-infrared region. Addition of a second cyanide anion to **9** involves displacement of a *p*-ethylphenolate anion to form **10**, which likely exists as tautomer **6** under basic conditions.

An analogy for this pathway is found in the work of Happ et al. who reported that *N*-methylacridium ion **11** forms the cynide adduct 12 through a nucleophilic addition reaction (Scheme 3).²⁸ Interestingly, these workers observed that a solution of **12** in the presence of excess cvanide anion displays broad absorption bands in the 530–600 nm region. Based on the results of additional experiments, they concluded the long wavelength absorption band was a consequence of the formation of the carbanion intermediate 13. These observations support the assignment of carbanion 9 (Scheme 2) as the transient intermediate formed by cyanide addition to 7. In addition, rapid quenching of the broad absorption peak upon addition of acid serves as further support for this proposal (Fig. 2, inset). Importantly, Happ et al. reported that carbanion 13 is highly reactive toward molecular oxygen, a phenomenon we observed with the long wavelength absorbing intermediate 9, which disappears more rapidly in an oxygen purged solution than in solutions that are either unpurged or purged with nitrogen (Fig. S4, Supplementary data). Tae and coworkers also reported an acridium ion based colorimetric cyanide anion sensor.²⁶

In conclusion, this study has led to the development of a new chemosensor system for cyanide ion that is based on a photochromic material. Specifically, addition of cyanide anion to a UV irradiated solution of phenoxynaphthacene quinone **4** brings about a significant change in the absorption spectra that enables detection of cyanide



Scheme 3. Mechanism of the formation of Happ's carbanion 13.

ion in a selective and sensitive manner. Intermediate **9** was shown to be responsible for the long wavelength absorption band that is generated by cyanide addition. Considering the fact that only few examples of photochromism-based chemosensor exist, the results described above represent an important contribution to the ever widening chemosensor research area.

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Supplementary data

Supplementary data (experimental procedures, ¹H NMR spectra, IR spectrum, and additional experimental data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.02.105.

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