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N-Acyl Triazenes as Tunable and Selective Chemodosimeters Toward Cyanide Ion

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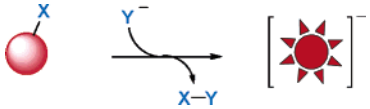

A novel type of chemodosimeters has been developed on the basis of a displacement reaction. *N*-Acyl-triazenes are found to be highly selective and tunable chemodosimeters toward cyanide. When *N*-acetyl-triazene **1a** was titrated with various anions ($^{-}$CN, F^{-}, Cl^{-}, AcO^{-}, $H_2PO_4^{-}$, $^{-}$SCN, ClO_4^{-}, and HSO_4^{-}) in acetonitrile, significant absorption changes (from colorless to deep purple) resulted in the cases of $^{-}$CN and F^{-}, and small changes in the cases of AcO^{-} and $H_2PO_4^{-}$. *N*-Isopropanoyl-triazene **1b** showed significant response only toward $^{-}$CN, weaker response toward F^{-}, and little response toward other anions in acetonitrile. Both of the triazenes **1a** and **1b** responded only to $^{-}$CN in methanol−water, because of the analyte's strong nucleophilicity toward the acyl group and weak hydrogen-bonding ability as compared to other anions examined. The *N*-acyl-triazenes can be used for the naked eye detection of cyanide.

Introduction

Molecular recognition and detection of specific analytes have been subjects of intense research with multiple disciplines. For the recognition of analytes, molecular interactions such as electrostatic interactions, hydrogen bonding, and coordinative bonding have been widely used. A variety of artificial recognition and detection systems developed to date thus contain charged or neutral recognition motifs based on organic or organometallic ligands that provide these molecular interactions.[1] A different type of molecular interactions used for the recognition of analytes involves reversible or irreversible covalent-bond formation between a recognition system and an analyte. This type of "reaction-based" recognition mode enables the recognition system with some characteristic features such as analyte-specific response and little or reduced competition from the aqueous media, which are highly desirable features for an efficient recognition and detection system.[2] The reversible covalent-bonding mode can be found in ionophores such as trifluoroacetophenone-based ones, which have been employed as recognition components of the ion-selective electrodes used for the detection of carbonates and amines.[3] The recognition mode based on irreversible reactions is commonly used in chemodosimeters. Recently, we introduced a novel anion recognition motif based on the trifluoroacetophenone ionophore

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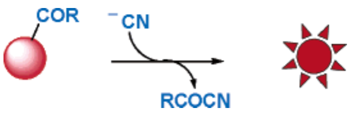


FIGURE 1. A schematic diagram for the displacement approach to new chemodosimeters.

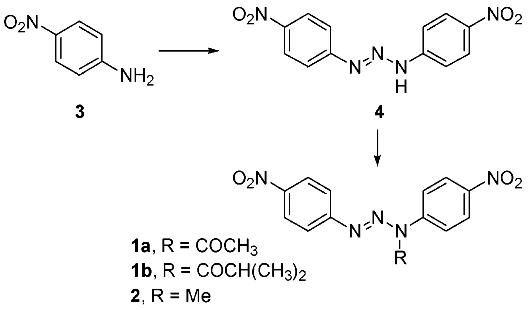
that recognizes anions through reversible adduct formation.[4] The new binding motif has a strong affinity toward cyanide, because of the analyte's strong affinity toward the trifluoroacetyl carbonyl carbon. The strong affinity of cyanide toward the carbonyl carbon suggests that an acylated chromophore may be developed as a chemodosimeter that is selective toward the highly toxic anion. Several other unique probes for cyanide are known, which are mostly based on cyanide addition reactions to boronic acid complexes,[5] squaraine derivatives,[6] pyrylium derivatives,[7] and benzooxazine derivatives.[8] These sensing methods are based on reversible covalent bond formation. Also, a few examples are known for an irreversible approach, that is, cyanide detection by chemodosimeters, which are based on the coordination of cyanide to metal complexes.[9] Herein, we wish to report a simple and tunable chemodosimeter system for cyanide, which is based on an organic displacement reaction, rather than the addition reactions. This displacement approach is based on the strong affinity of cyanide toward an *N*-acyl carbonyl carbon.[4a] Recently, chemosensors based on intramolecular displacement reactions have been developed for the detection of chemical warfare agents such as phosphonic acid halides.[10]

Results and Discussion

Design and Synthesis. Our approach to a new type of cyanide chemodosimeters is depicted in Figure 1.

A "latent" chromogenic moiety with an acyl group (−COR) may comprise a new type of chemodosimeters for cyanide, because cyanide has strong affinity toward the acyl group and thus the attack of cyanide to the acyl group may trigger the latent chromogenic moiety into an "active" state. To realize this scenario, we need a chromophore that is latent in the acylated form but active in the deacylated state. A number of chromophores may satisfy this condition if the deacylated state maintains its anionic state, in which state usually a significant change in the absorption wavelength from its neutral form is expected. Compounds belonging to this category may be found among indicator dyes of phenol derivatives.[11] We have briefly examined an azophenol compound as the chromophore. Although the result was positive, the absorption change was not satisfactory to our expectation. Thus, we converted our attention to the *N*-acylated triazene system **1**, which can be readily prepared from the corresponding triazene **4**,[12] which, in turn, was prepared from *p*-nitroaniline through a diazonium coupling reaction (Scheme 1). Such acylated triazenes have been used as acylating agents for amines in the literature.

SCHEME 1. Synthesis of Triazenes 1 and Reference Compound 2



Detection Studies. We have evaluated the reaction-dependent absorption change of the acetylated triazene **1a** toward cyanide. A solution of triazene **1a** itself in organic solvents such as acetonitrile and ethyl acetate is almost colorless under a dilute concentration (0.017 mM), exhibiting an absorption band at $\lambda_{max} = 306$ and a very weak one at $\lambda_{max} = 407$ nm in CH_3CN. When triazene **1a** in acetonitrile was treated with cyanide as its tetrabutylammonium salt at room temperature, the intensity of both of the absorption bands increased with an appearance of a new band at $\lambda_{max} = 565$ nm, which showed a large change, giving a deep purple solution. The color change occurred within minutes and became saturated upon addition of an equimolar amount of cyanide, which indicates that the color change is due to the displacement reaction. Other anions such as F^-, Cl^-, ^-SCN, AcO^-, $H_2PO_4^-$, ClO_4^-, and HSO_4^- were also examined, and only F^-, AcO^-, and $H_2PO_4^-$ showed color changes. A strong color similar to the case of ^-CN was observed in the case of F^-, while a weak color was observed in other cases. The absorption spectra collected for each of the anions are shown in Figure 2,[13] which is clearly in accordance with the color changes.

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(13) The UV−vis titrations do not show clear isobestic points, indicating different absorption species are involved other than the two species (compound **1a** and its deacylated anionic species) from the displacement process. A minor peak ($\lambda_{max} = 407$ nm) appeared in addition to the major absorption peaks (**1a**, $\lambda_{max} = 306$ nm; its deacylated species/anionic form of **4**, $\lambda_{max} = 565$ nm). The minor peak is assigned to the absorption from triazene **4** (Figure S6). The appearance of triazene **4** during the titration is likely due to the water residue present in the solvent and compounds.

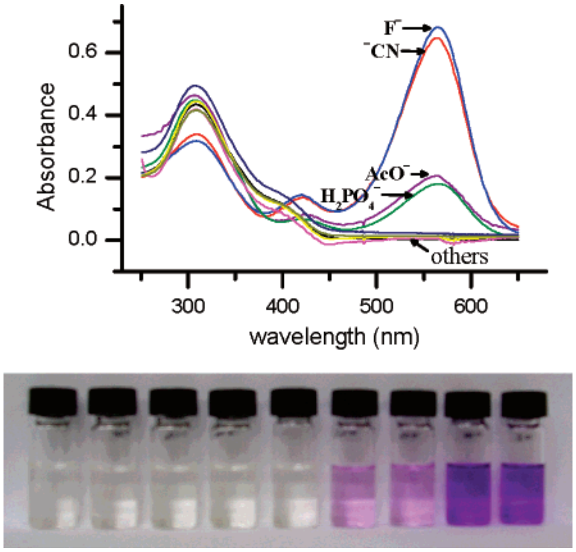
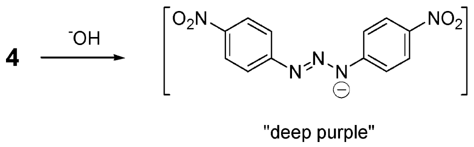


FIGURE 2. Absorption spectra and color changes when triazene **1a** (0.017 mM) was treated with various analytes (vials from the left: **1a** only, ^-SCN, ClO_4^-, HSO_4^-, Cl^-, $H_2PO_4^-$, AcO^-, F^-, and ^-CN as Bu_4N^+ salts, 0.2 mM) in acetonitrile at 25 °C.

The strong color change in the case of F^- suggests that fluoride also has strong affinity toward the *N*-acetyl group of triazene **1a** in the organic solvent, and thus such a triazene system may be also used for its detection in the presence of other halide anions.

To confirm that the color change results from the displacement of the acyl group in triazene **1a**, we treated *N*-methyl-triazene **3** with the anions under similar conditions. There was a little change in the absorption spectra and no color change. Thus, the color change observed in the case of **1a** should be originated from a deacylated species, that is, the corresponding anion of triazene **4**. The displacement reaction could be followed by NMR titrations (Figure S11). Thus, upon addition of cyanide (as tetrabutylammonium salt) to triazene **1a** in CD_3CN, a new set of peaks immediately appeared along with decreasing peak intensity from **1a**. The change was complete when cyanide was added up to 2.0 mol equiv. At this point, all peaks from **1a** completely disappeared and only the new set of peaks was observed, which could be assigned to the corresponding deacylated species (anionic form of **4**) because there appeared only two doublets at 7.4 and 8.1 ppm. An anionic solution of triazene **4**, generated by treating it with hydroxide, exhibited deep blue, which confirms our reasoning. It should be noted that triazene **4** itself shows little color in acetonitrile.



Because the detection method described above is dependent on the nucleophilic displacement of the *N*-acetyl-triazene, its operation in aqueous media is expected to be little or less dependent on the solvent than those detection methods based on hydrogen bonding. To demonstrate this point, we carried out similar titrations as above in protic solvents. We used a mixed solvent system, MeOH−water (10:1), because *N*-acetyl-triazene **1a** was not soluble in pure water. In this medium, triazene **1a** itself exhibited two absorption bands at $\lambda_{max} = 305$ and 397 nm, showing slightly faint yellow. When triazene **1a** was titrated with cyanide in the protic medium, the absorption band at $\lambda_{max} = 305$ decreased while the band at $\lambda_{max} = 397$ and a new one at $\lambda_{max} = 521$ increased, giving a red-pink solution. In stark contrast to cyanide, triazene **1a** in the protic medium showed little changes in the absorption spectra and hence no color changes toward other anions such as F^-, Cl^-, Br^-, I^-, ^-SCN, ClO_4^-, HSO_4^-, $H_2PO_4^-$, and AcO^- (Figure 3).

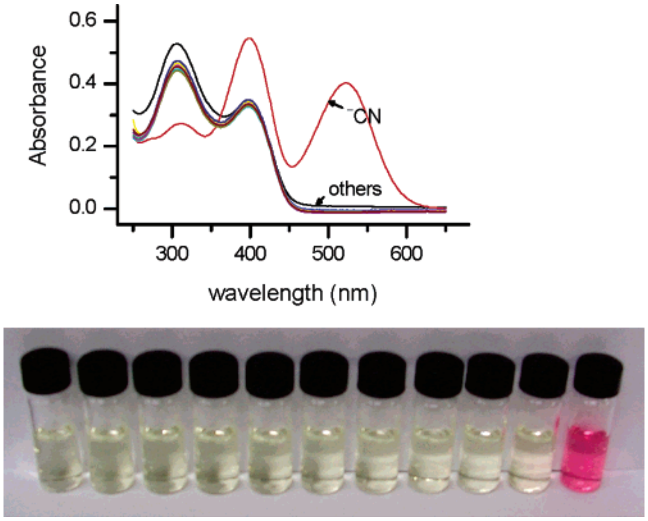


FIGURE 3. Absorption spectra and the corresponding color changes when triazene **1a** (0.017 mM) was treated with various anions (vials from the left: **1a** only, F^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, AcO^-, and ^-CN as Na^+ salts except for K^+F^-; 0.39 mM) in MeOH−water (10:1).

The results indicate that the displacement of the *N*-acetyl carbonyl group from triazene **1a** with the anions except for cyanide is greatly influenced by protic solvents. The large solvent effect should be mostly due to H-bonding in nature. Anions such as F^-, AcO^-, and $H_2PO_4^-$ should interact with the aqueous medium through H-bonding, and this solvation leads to a decrease in their nucleophilicity toward the carbonyl group. This reduced nucleophilicity resulted in the poor deacylation reaction, and hence no color change occurred. In contrast, cyanide has much weaker H-bonding ability in comparison with F^-, AcO^-, and $H_2PO_4^-$ but has stronger carbonyl carbon affinity that is required for the displacement reaction. Thus, only cyanide displaces the *N*-acyl group of triazene **1a** and gives the dramatic color change. The results clearly demonstrate that a highly selective detection system for an analyte can be developed on the basis of a specific chemical reaction, this time, via the displacement reaction of an *N*-acyl group by cyanide.

An apparent advantage of our approach is that we may modulate the displacement reaction by changing the *N*-acyl group. To this end, we have prepared the *N*-isopropanoyl-triazene **1b** and evaluated its response toward the anions under similar conditions. First, we examined the four reactive anions (^-CN, F^-, AcO^-, and $H_2PO_4^-$) that gave significant absorption changes in the case of *N*-acetyl-triazene **1a** in acetonitrile. As shown in Figure 4, triazene **1b** only responded to ^-CN and F^-. Furthermore, F^- that gave an absorption change similar to that of ^-CN in the case of **la** exhibited significantly diminished absorption in acetonitrile. Such differences resulted in a dramatic color change in the case of ^-CN, from colorless to bright purple, whereas a small change in the case of F^-, to faint pink. Thus,

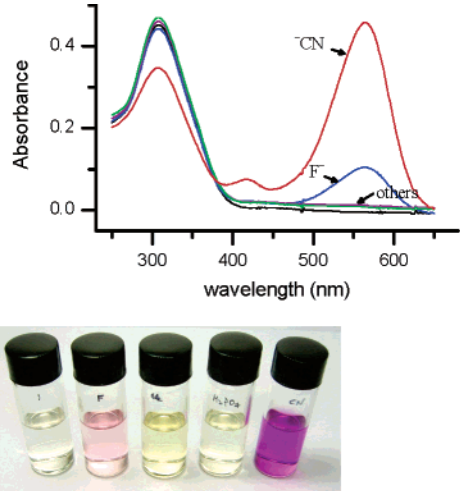


FIGURE 4. Absorption spectra and corresponding color changes when triazene **1b** (0.017 mM) was treated with selected anions (vials from the left: **1b** only, F^-, AcO^-, $H_2PO_4^-$, and ^-CN as Bu_4N^+ salts; 1.15 equiv) in CH_3CN.

FIGURE 5. A two-phase detection experiment with triazene **1a (**0.5 mM) in the presence of a phase-transfer catalyst ($Bu_4N^+Br^-$, 0.1 M) in CH_2Cl_2-Tris buffer (pH 8.6, 1.0 mM) with selected anions (from the left: 0.5 mL of **1a** only, NaCN, NaOAc, NaH_2PO_4, and KF).

by changing the *N*-acyl group from *N*-acetyl to *N*-isopropanoyl, the nucleophilic displacement reaction is modulated, plausibly by steric reasons, resulting in a highly selective detection pattern toward the competing anions even in the organic medium. A plot of $(A - A_{min})/(A_{max} - A_{min})$ versus $[^-CN]/[\mathbf{1b}]$ gave a linear relationship, which suggests that the new detection system may be potentially useful for the quantification of cyanide with up to an about 10 μM detection limit in a sample solution.

The detection ability of triazene **1b** toward the anions in MeOH−water (10:1) was also evaluated. As in the case of its *N*-acetyl analogue **1a**, triazene **1b** also showed specific reactivity toward cyanide among the tested anions under the conditions. This time, similar absorption changes were also observed, albeit less dramatic as compared to the case of **1a**.

Finally, we have carried out a two-phase detection experiment by using triazene **1a** in dichloromethane−water in the presence of a phase-transfer catalyst. Once again, the system showed a complete selectivity toward cyanide with an accompanying color change to purple (Figure 5).

It should be noted that a sample containing cyanide requires a basic condition; otherwise, a dangerous gaseous HCN ($pK_a = 9.31$) generates. An aqueous solution containing cyanide is weakly basic (pH = 8.15 for 0.1 mM solution at 25 °C). Therefore, the above two-phase experiment demonstrates that our system is effective for cyanide detection in a practical pH range.

In summary, we have demonstrated that a novel type of chemodosimeters can be developed on the basis of an analyte-specific displacement reaction. We have developed *N*-acyl-triazenes as highly selective and tunable chemodosimeters toward cyanide by taking the advantage of the cyanide's strong affinity toward the acyl carbonyl carbon. The *N*-acetyl-triazene **1a** exhibited large absorption changes toward ^-CN and F^-, and small changes toward AcO^- and $H_2PO_4^-$ in acetonitrile among various anions examined. In contrast, triazene **1a** responded only toward ^-CN in MeOH−water (10:1), which was explained by the analyte's strong nucleophilicity and weak hydrogen-bonding ability as compared to other anions. The triazene **1b**, which has an *N*-isopropanoyl group instead of *N*-acetyl, showed significant response only toward ^-CN, weaker response toward F^-, and little response toward other anions in acetonitrile. The triazene **1b** also responded only toward ^-CN in the protic solvent system among other anions examined. A two-phase experiment in the presence of a phase-transfer catalyst suggests that the simple chemodosimeter system may be potentially useful for a simple naked eye detection of cyanide in a real sample. A further study on the development of chemosensors/chemodosimeters based on analyte-specific reactions is underway.

Experimental Section

1,3-Bis(4-nitrophenyl)triazene (4). *p*-Nitroaniline **3** (138 mg, 1 mmol) was dissolved in 1 mL of warm concentrated hydrochloric acid. The flask was placed in an ice-salt bath and cooled to 0 °C while being stirred vigorously. A cold solution of isoamyl nitrite (134 μL, 1.0 mmol) was slowly added. **3** (138 mg, 1.0 mmol) was dissolved in a solution of NaOH (40 mg, 1.0 mmol) in 3 mL of methanol and cooled in an ice-bath. To the resulting solution of **3** was slowly added the diazotized solution with stirring. After being stirred overnight, the yellow precipitate was filtered with water and dried in vacuo; 260 mg (91%); mp 230−231 °C (dec) (lit. 230−232 °C, dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.5 (br s, 1H), 8.2 (d, 4H), 7.5 (d, 4H); MS (70 eV, EI) *m/z* (rel intensity) 287.05 (M^+, 0.6%), 150.07 (53.0%), 138.05 (22.5%), 122.08 (100%), 91.91 (63.0%), 74.92 (81.8%); HRMS *m/z* calcd for $C_{12}H_9N_5O_4$ $[M]^+$ 287.0655; *m/z* found 287.0656.

3-Acetyl-1,3-bis(4-nitrophenyl)triazene (1a). To a solution of triazene **4** (287 mg, 1.0 mmol) in CH_2Cl_2 were added triethylamine (303 mg, 3.0 mmol), followed by acetyl chloride (0.20 mL, 2.8 mmol) under an argon atmosphere, and the resulting mixture was stirred for 48 h. The reaction mixture was treated with 10% aq HCl (10 mL) and diluted with ethyl acetate. The crude reaction mixture was purified by column chromatography to give a yellow solid **1a** (248 mg, 75%); mp 150−151 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.4 (d, $J = 8.9$ Hz, 2H), 8.3 (d, $J = 9.0$ Hz, 2H), 7.7 (d, $J = 9.0$ Hz, 2H), 7.4 (d, $J = 8.9$ Hz, 2H), 2.8 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 152.3, 148.3, 148.2, 141.0, 130.4, 125.1, 124.9, 123.1, 23.0; MS (EI) *m/z* (rel intensity) 329 (M^+, 0.05%), 150 (79%), 138 (13%), 122 (100%), 92 (37%), 75 (55%); HRMS *m/z* calcd for $C_{14}H_{11}N_5O_5$ $[M]^+$ 329.0760; *m/z* found 329.0754.

3-Isobutanoyl-1,3-bis(4-nitrophenyl)triazene (1b). This was prepared similarly as above starting from **4** after purification by column chromatography (hexane:EtOAc, 8:1) in 67% yield as an orange solid: mp 132−134 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.4 (d, $J = 9.6$ Hz, 2H), 8.3 (d, $J = 8.8$ Hz, 2H), 7.6 (d, $J = 8.8$ Hz, 2H), 7.3 (d, $J = 8.7$ Hz, 2H), 3.8 (m, 1H), 1.4 (s, 3H), 1.4 (s, 3H); ^{13}C NMR 178.5, 151.9, 147.5, 140.8, 129.7, 124.5, 124.1, 122.4, 32.3, 18.6; HRMS *m/z* calcd for $C_{16}H_{15}N_5O_5$ $[M]^+$ 357.1073; *m/z* found $[M + H]^+$ 358.1167.

3-Methyl-1,3-bis(4-nitrophenyl)triazene (2). Powdered NaOH (40 mg, 1.0 mmol) and MeI (456 mg, 3.2 mmol) were added to the solution of a triazene **4** (287 mg, 1.0 mmol) in MeOH and heated under reflux for 1 h. Next, another portion of MeI (456 mg, 3.2 mmol) was added at room temperature and the reaction mixture was stirred, until the starting triazene disappeared as followed by TLC. The reaction mixture was kept at 0 °C for 1−2 h. The product was filtered off and washed with MeOH (2 × 3 mL); yellow solid (163.9 mg, 78%); mp 229−230 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.3 (d, 4H), 7.7 (d, $J = 8.9$ Hz, 2H), 7.6 (d, $J = 9.1$ Hz, 2H), 3.8 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 148.7, 146.2, 143.3, 124.9, 124.5, 121.7, 115.9, 32.0; MS (70 eV, EI) *m*/*z* (rel intensity) 301.03 (M^+, 100%), 273.07 (24.0%), 267.30 (23.0%); HRMS *m*/*z* calcd for $C_{13}H_{11}N_5O_4$ $[M]^+$ 301.0811; *m*/*z* found 301.0807.

Titrations in Acetonitrile. Deionized water and a spectroscopic grade of MeOH and CH_3CN were used as the solvent for UV−vis titrations. The titrations were carried out in 10-mm quartz cuvettes at 25 °C. Stock solutions of anions (6.0 mM) were prepared by dissolving their Na^+ or Bu_4N^+ salts in the specified solvents. To a solution of triazene **1a** in acetonitrile (0.52 mM, 0.1 mL) in a cuvette was added the analyte dissolved in acetonitrile (as Bu_4N^+ salt, 6.0 mM, 0.10 mL, 11.5 equiv). The final volume was adjusted to 3.0 mL by adding the solvent, which results in 0.017 mM of triazene and 0.20 mM of the analyte.

Titrations in MeOH−Water. To a solution of triazene **1a** (0.52 mM, 0.1 mL) in a cuvette were added the anions (as Na^+ salts except for K^+F^-, 6.0 mM, 0.20 mL) in MeOH−water (10:1). The final volume was adjusted to 3.0 mL by adding MeOH−water (10:1), which results in 0.017 mM of the triazene and 0.39 mM of the analyte.

Two-Phase Experiments. Each stock solution of the anions (30 mM, as Na^+ salts except for K^+F^-) was prepared in 1.0 mM Tris buffer (pH 8.6). A stock solution of triazene **1a** was prepared in dichloromethane (30 mM). The detection was carried out by placing the probe solution (0.05 mL), the anion solution (0.05 mL), and the phase-transfer catalyst solution (0.1 mL, 1.0 M $Bu_4N^+Br^-$) into a vial, which was diluted with the Tris buffer solution to give a final volume of 1.5 mL. Vigorous stirring and subsequent standing resulted in the phase separation.

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Supporting Information Available: All other UV−vis absorption and titration data not shown in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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