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Fluorescence Response of a 4-Trifluoroacetylaminophthalimide to Iodide Ions upon 254 nm Irradiation in MeCN

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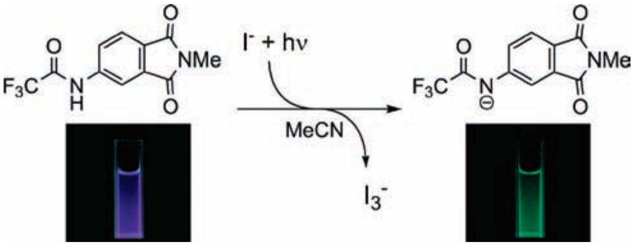
ABSTRACT



The title trifluoroacetylaminophthalimide derivative produced a violet fluorescence (λ^{FL}_{max} 392 nm) in MeCN, and it displayed a green emission (λ^{FL}_{max} 506 nm) after irradiation at 254 nm in the presence of iodide ions. The corresponding amidate ion of the trifluoroacetamide was identified as the green fluorescence emitter. The deprotonation reaction may be caused by proton-abstracting solvated electrons generated by a photochemical charge−transfer-to-solvent process from I^- to MeCN.

Fluorometric and colorimetric probes for anions have attracted much attention in the field of chemosensors.[1] Among such anionic species, halide ions are important analytes from biological and environmental aspects. Namely, iodide is of particular significance in biological activities such as the thyroid gland function.[2] Thus, it would be of significance to construct an iodide-specific probe. Although a number of halide-ion sensing probes have been proposed,[3] much less effort has been addressed toward developing iodide-selective sensors,[4] namely, fluorescent ones.[5] Jang[5a] and Kang,[5b] respectively, reported a tripodal receptor and an imidazolium-based sensor which displayed fluorescence quenching by the addition of I^-. Carbazole-containing polymers were reported to show colorimetric and fluorimetric responses to iodide.[6] Also, photoinduced electron-transfer fluorescence quenching by iodide[7] has been used for discriminating halide ions.[8]

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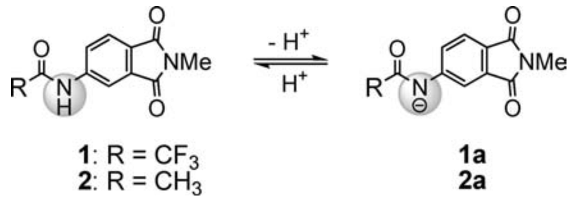
During our fluorescence studies of aminonaphthalimides, we have found that the trifluoroacetylation of the amino group markedly modifies the fluorescence properties of the naphthalimide derivatives by proton dissociation equilibrium of the amide part.[9] Therefore, it is also expected that the trifluoroacetylation of amino-substituted aromatic carbonyl compounds, e.g., aminophthalimide, which displays an intramolecular charge-transfer (ICT) fluorescence, enhances the acidity of the amide proton and, as a result, effectively modulates the ICT fluorescence character through proton dissociation (Scheme 1).[9,10]

Scheme 1. Modification of Electronic Properties of **1** and **2**



In the present study, we have investigated the fluorescence behavior of the title trifluoroacetamide **1** in the presence of halide ions in MeCN, namely, under photoirradiation conditions at 254 nm, and now describe its fluorescence response to halide ions which was caused by the enhanced acidity of the amide part. The trifluoroacetamide **1** displayed an unexpected response to I^- to afford the amidate ion **1a** due to the 254 nm irradiation.

Figure 1 shows the absorption and fluorescence spectra of the trifluoroacetamide **1** in the presence of 5 equiv of halide ions. Cl^-, Br^-, and I^- displayed no appreciable change in the absorption profile. These halide ions only slightly affected the fluorescence properties of the trifluoroacetamide **1** (Figure 1b). These facts indicate that the halide ions, Cl^-, Br^-, and I^-, did not significantly interact with the trifluoroacetamide **1** in both the ground and excited states. In contrast, upon the addition of F^-, the trifluoroacetamide **1** displayed remarkably red-shifted new absorption ($\lambda^{ABS}{}_{max}$ 381 nm) and fluorescence emission ($\lambda^{FL}{}_{max}$ 506 nm) bands. Since it has been reported that the basic F^- ion can effectively abstract the acidic proton[3e] of a 4-benzoylamidophthalimide derivative,[10b] the red-shifted absorption and fluorescence bands of the trifluoroacetamide **1** were assigned to the amidate ion **1a**. Formation of the amidate ion **1a** was further confirmed by addition of DBU to **1** (Figure S2, Supporting Information). The fluorescence quantum yield Φ_F was determined to be 0.20 for **1** and 0.41 for **1a**, thus the amidate ion **1a** fluoresced more efficiently than the amide form **1**.

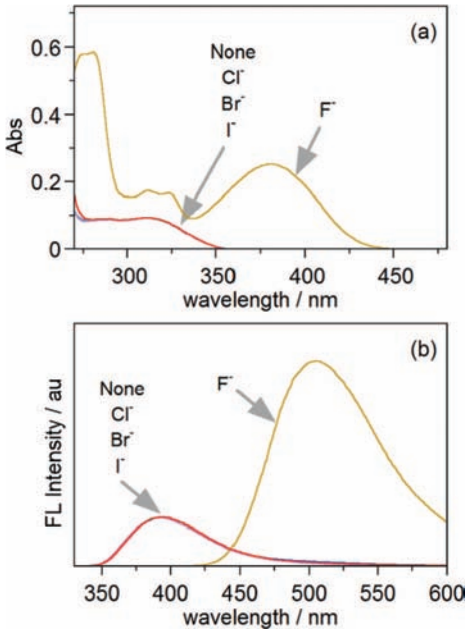


Figure 1. (a) Electronic absorption and (b) fluorescence (λ_{ex} 320 nm) spectra of **1** (3.50×10^{-5} M) in the presence of halide ions (1.75×10^{-4} M, as tetrabutylammonium) in MeCN.

In Figure 2, the absorption and fluorescence spectra of the trifluoroacetamide **1**, observed after irradiation at 254 nm for 20 s, are shown. In the presence of Cl^-, Br^-, or F^-, no appreciable change in the spectra was observed by the irradiation (cf. Figure 1). In contrast, for the photoreaction mixture of a **1**$-I^-$ system, it is remarkable that new absorption peaks appeared at around 285 and 365 nm (Figure

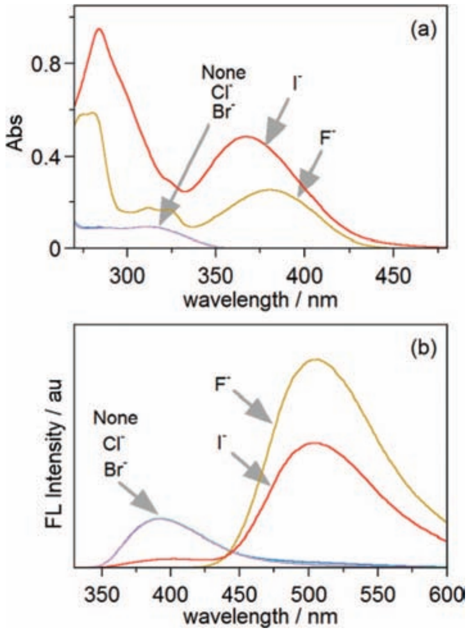


Figure 2. (a) Electronic absorption and (b) fluorescence (λ_{ex} 320 nm) spectra of **1** (3.50×10^{-5} M) in the presence of halide ions (1.75×10^{-4} M, as tetrabutylammonium) observed after irradiation at 254 nm for 20 s in MeCN.

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2a). In the fluorescence spectrum of the mixture, the emission band of the trifluoroacetamide **1** (λ^{FL}_{max} 392 nm) decreased, and a new long-wavelength fluorescence band (λ^{FL}_{max} 506 nm) appeared (Figure 2b). Thus, only for the **1**−I$^-$ system, the absorption and fluorescence properties were significantly modified by the 254 nm photoirradiation. Upon irradiation, the color of the photoreaction mixture turned from colorless to yellow, and the fluorescence changed from violet to green.

To determine the green-fluorescence emitter in the photoreaction mixture of the **1**−I$^-$ system, the excitation spectrum of the 506 nm emission band was observed. As shown in Figure 3, the excitation profile of the 506 nm emission band of the photolysate was essentially identical to that of the absorption of the amidate ion **1a**. Moreover, the fluorescence emission band of the photoreaction mixture of the **1**−I$^-$ system (λ^{FL}_{max} 506 nm) was identical to that of the amidate ion **1a** (Figures 1b, 2b, and S2). Therefore, the 506 nm emitting species in the photoreaction mixture of the **1**−I$^-$ system was assigned to the amidate ion **1a**. The formation of the amidate ion **1a** was also investigated by ^{1}H NMR spectroscopy, and the results are shown in Figure S3.

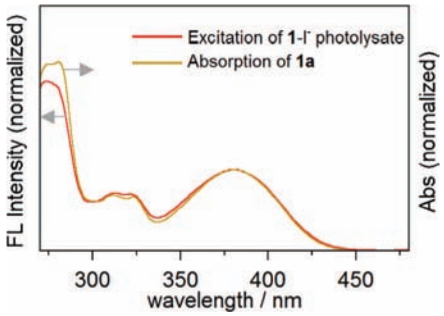

Figure 3. Excitation spectrum of the emission band (λ^{FL}_{max} 506 nm) of the photoreaction mixture of trifluoroacetamide **1** and I$^-$ after irradiation at 254 nm (cf. Figure 2b) and absorption spectrum of the amidate ion **1a** (normalized at 367 nm).

The absorption spectrum of the photoreaction mixture of the **1**−I$^-$ system was different than that of the amidate ion **1a** (Figure 2a), thus an additional photoproduct(s) must be considered to reveal the absorption properties of the photoreaction mixture. I$^-$ ions did not contribute to the absorption spectrum since they displayed no absorption band in the wavelength region >300 nm (Figure S4). It has been reported that I$^-$ underwent photooxidation in MeCN.[11] Among the possible oxidized species of I$^-$, the triiodide, I$_3^-$, has been known to show absorption bands in the wavelength region (λ^{ABS}_{max} 292, 363 nm, Figure S4)[12] similar to that of the photoreaction mixture. It was found that the absorption spectrum observed for the **1**−I$^-$ photoreaction mixture (Figure 2a, curve for I$^-$) was well simulated by the sum of the absorption spectra of the trifluoroacetamide **1**, amidate ion **1a**, and I$_3^-$ (Figure S5). On the basis of the experimentally determined molar extinction coefficients of **1**, **1a**, and I$_3^-$, the photoreaction mixture displaying the absorption curve for I$^-$ in Figure 2a was determind to be an ca. 0.8:2.2:1 mixture of **1**:**1a**:I$_3^-$ (Figure S5). Since the absorption spectrum of a mixture of trifluoroacetamide **1** and I$_3^-$ was the simple sum of these components (data not shown), the possibility that the absorption curve for I$^-$ in Figure 2a was caused by an interaction between **1** and I$_3^-$ can be excluded. Therefore, we concluded that the products for the photolysis of the **1**−I$^-$ system were the amidate ion **1a** and I$_3^-$.

To reveal the significance of the trifluoroacetamide moiety, the photolysis of the acetyl analogue **2** was investigated in the presence of halide ions. In contrast to the case of the trifluoroacetamide **1**, the irradiation at 254 nm displayed a minimal effect on the absorption and fluorescence spectra of the **2**−halide mixtures, even in the presence of I$^-$ (Figures S6 and S7). Thus, no evidence was obtained about the formation of the corresponding amidate ion **2a**. These results are consistent with that reported for a related 4-benzoylamidophthalimide: I$^-$ did not affect its absorption and fluorescence behavior.[10b] The acidity of the amide part is thus considered to be important for the formation of the amidate ion **1a** in the photoreaction. The pK_a value of the trifluoroacetamide **1** in MeCN was determined to be 20 ± 0.1 by titration with triethylamine (pK_a of conjugate acid 18.82).[13] (See Figure S8 for the titration results.) For the acetamide **2**, the addition of DBU (pK_a of conjugate acid 24.34)[13] up to 100 equiv did not result in deprotonation of the acetamide moiety (data not shown). The pK_a value of acetamide **2** is thus several orders of magnitude greater than that of the trifluoroacetamide **1**. Therefore, the strongly electron-withdrawing trifluoroacetyl group played a crucial role in the enhancement of the acidity, thus the formation of the amidate ion **1a**.

The time course of the photoreaction of the **1**−I$^-$ mixture was investigated to understand the photoreaction profile (Figure 4). Upon 254 nm irradiation of the **1**−I$^-$mixture, the absorption bands around 285 and 365 nm appeared within 10 s. The product yields for the photolysis are displayed in the inset of Figure 4. The ratio of the photoproducts **1a**:I$_3^-$ was close to 2:1 during the irradiation.

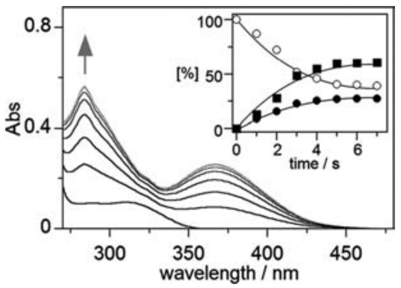

Figure 4. Absorption spectral change for a mixture of trifluoroacetamide **1** (3.50×10^{-5} M) and I$^-$ (1.75×10^{-4} M) during irradiation at 254 nm. The inset shows the time course of the photolysis: **1** (○), **1a** (■), I$_3^-$ (●).

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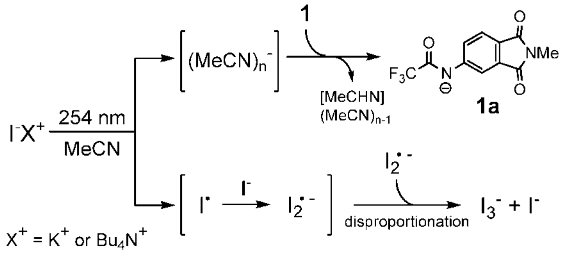
A plausible mechanism for the formation of the amidate ion **1a** by irradiation of the **1**−I^- system is shown in Scheme 2. The photoexcitation of I^- in MeCN causes the formation of the MeCN-solvated electrons $(MeCN)_n^-$ and iodine radicals by a charge−transfer-to-solvent (CTTS) process.[14] It has been reported that the solvated electrons $(MeCN)_n^-$ can extract acidic protons.[15] Thus, the acidic amide proton of the trifluoroacetamide **1** was considered to be effectively extracted by the $(MeCN)_n^-$ to afford the amidate ion **1a**. The iodine radical counterpart was trapped by I^- to form $I_2^{\bullet -}$ which finally afforded I_3^- via a disproportionation process.[16]

Scheme 2. Plausible Mechanism for the Photolysis



The ratio of **1a**:I_3^- is thus expected to be 2:1 according to this mechanism. For the photolysis of the **1**−I^- system, the ratio of the photoproducts **1a**:I_3^- was experimentally observed to be ∼2:1 (Figure 4, inset).

The formation of amidate ion **1a** was also observed for the 254 nm photolysis of the **1**−I^- system in THF for which photoinduced CTTS has been reported.[17] Details of the solvent effects on the photolysis are underway.

In summary, the fluorescence properties of the trifluoroacetamide **1** can be modified by F^- and the combination of I^- and the 254 nm photolysis; F^- deprotonated the amide proton of **1a** resulting in the formation of the amidate ion **1a** in the ground state, while the combination of I^- and the 254 nm irradiation caused the formation of the amidate ion **1a**. Cl^- and Br^- did not affect the optical properties of the trifluoroacetamide **1**. The trifluoroacetamide **1**, thus served as a potential halide ion recognition probe in MeCN. Moreover, it is worth noting that upon the 254 nm photolysis of the **1**−I^- system (for 30 s) the intensity of the 506 nm fluorescence band increased depending on the concentration of I^- (Figure 5). The trifluoroacetamide **1** might be applicable for a quantitative probe for I^-.

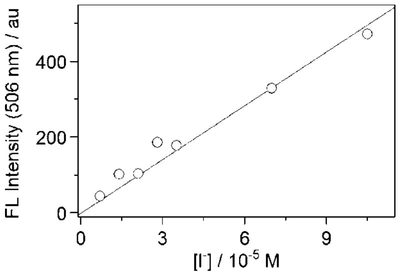


Figure 5. Dependence of fluorescence intensity at 506 nm upon concentration of I^- after 254 nm irradiation (30 s) of the **1**−I^- system ([**1**] 3.50 × 10^{-5} M, λ_{ex} 380 nm).

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Supporting Information Available: Experimental procedures, electronic spectra of **1** and **2**, and ^{1}H NMR spectra of **1** (photolysate and titration results). This material is available free of charge via the Internet at http://pubs.acs.org.

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