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A Novel Colorimetric and Fluorescent Chemosensor for Anions Involving PET and ICT Pathways

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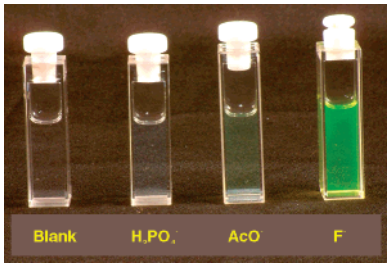
ABSTRACT



A novel colorimetric and fluorescent chemosensor ADDTU-1 bearing dual receptor sites, which shows specific optical signaling for AcO^-, $H_2PO_4^-$, and F^- over other anions and dual response toward AcO^- and F^- via PET and ICT mechanisms, is described.

Anions play a fundamental role in a wide range of chemical and biological processes, and numerous efforts have been devoted to the development of abiotic receptors for anionic species.[1] Anion recognition in biological systems is very often achieved via hydrogen bonding by highly preorganized proteins with sterically well-defined complex sites in the interior of proteins.[2] Macrocyclic hosts with preorganized binding sites can chemically mimic the complex properties of such receptor proteins for anions.[3] The sensors based on anion-induced changes in fluorescence appear particularly attractive because they offer the potential for high sensitivity at low analyte concentration.[4] Many fluorescence anion sensors utilizing photoinduced electron transfer (PET),[5] intramolecular charge transfer (ICT),[6] excited-state proton

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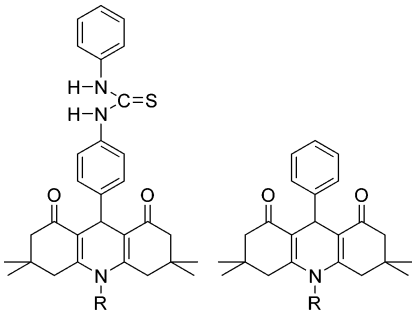
Scheme 1. Structures of ADD Dyes



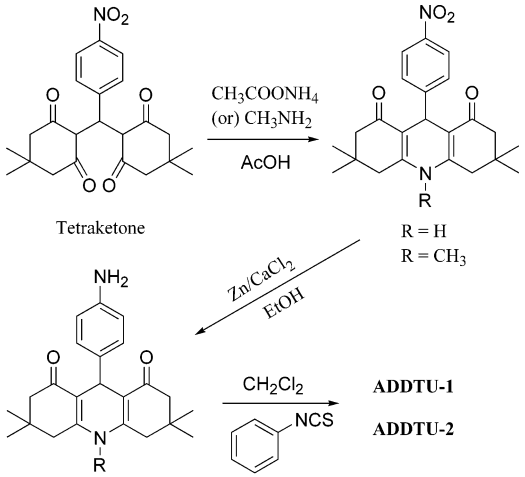
ADDTU-1: R = H
ADDTU-2: R = CH_3

ADD-1: R = H
ADD-2: R = CH_3

transfer,[7] excimer/exciplex formation,[5e,f] competitive binding,[8] and metal-to-ligand charge transfer[9] mechanisms have been developed. We are particularly interested in developing fluorescent chemosensors where the ion recognition takes place at the receptor sites with concomitant changes in the photophysical properties of a acridinedione (ADD) fluorophore by modulation of PET and ICT processes.[10] ADD dyes have been reported as a new class of laser dyes with lasing efficiency comparable to that of coumarin-102.[11] Interestingly, these dyes have been shown to mimic the NADH analogues to a greater extent because of their tricyclic structure, which is capable of protecting the enamine moiety.[12] The photophysical and photochemical properties of ADD dyes in solution and PMMA matrix were extensively studied.[13] In this paper, we report the fluorescent chemosensor ADDTU-1 with two different anion receptor sites operated by both PET and ICT mechanisms. This molecule exhibits excellent specificity toward AcO^-, $H_2PO_4^-$, and F^- over other anions and shows dual response toward AcO^- and F^-, which is the first of its kind (Scheme 1).

The synthesis of ADDTU derivatives is outlined in Scheme 2. Refluxing a mixture of nitroacridinedione with Zn and $CaCl_2$ (catalytic amount) in ethanol afforded the aminoacridinedione (AADD) derivatives. An equimolar mixture

Scheme 2



AADD-1 : R = H
AADD-2 : R = CH_3

of aminoacridinedione and phenyl isothiocyanate in dichloromethane, on stirring at room temperature, afforded the thiourea derivatives (ADDTU).

The anion-binding ability of ADDTU-1 and its analogues (ADDTU-2, ADD-1, and ADD-2) with the anions F^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, AcO^-, $H_2PO_4^-$, and BF_4^- (as their tetrabutylammounium salts) in acetonitrile were investigated using UV−vis, steady-state, and time-resolved emission techniques. The absorption and emission spectra of ADDTU-1 in acetonitrile display a maximum at 360 and 420 nm, respectively, which are assigned to the ICT from the ring nitrogen to ring carbonyl oxygen center within the ADD moiety.

No significant change was observed in the longer wavelength absorption band of ADDTU-1 (16 μM) even after the addition of AcO^- (<0.2 mM) and F^- (<0.4 mM) in acetonitrile. This indicates that there is no interaction between these anions and ADD moiety within this concentration range in the ground state. On the other hand, the corresponding fluorescence spectra showed fluorescence quenching in the presence of AcO^- and F^- as depicted in Figures 1 and 2, respectively. The hydrogen-bonding interaction of these anions with thiourea (TU) brings out a decrease in the oxidation potential of TU receptor which triggers the PET from TU to the relatively electron deficient ADD moiety,[5b,5c] and this causes the fluorescence to be "Switched off". To further confirm the hydrogen bonding interactions between the AcO^- and TU moiety, we also carried out ^1H NMR titration experiments in $CDCl_3$ + DMSO-d_6. In the presence of 25 equiv of AcO^-, the complete disappearance of the amide −NH proton signal was observed similar to that of the earlier investigation.[14]

Addition of F^- beyond 0.4 mM to ADDTU-1 shows a color change which is perceptible to the naked eye, from

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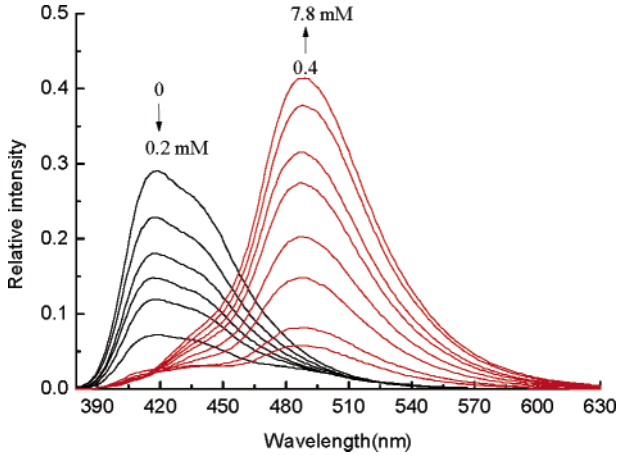

Figure 1. Emission spectra of ADDTU-1 (16 μM) in acetonitrile upon titration with AcO^- (0 → 7.8 mM); λ_{exc} = 370 nm.

colorless to an intense fluorescent green. In particular, titration spectra of fluoride anion are found to show a new peak in both absorption and emission spectra in acetonitrile. This new longer wavelength absorption (460 nm) and emission (500 nm) beyond 0.4 mM of F^- is due to the deprotonation of the ADD amino hydrogen with associated enhancement in the push−pull character of the ICT transition, which is reflected in the new red shifted absorption and emission. A similar result with OH^- ion confirms the deprotonation of ADD amino hydrogen providing evidence for the above observation.

The addition of AcO^- beyond 0.2 mM to ADDTU-1 in acetonitrile shows a red shift of 13 nm (360 to 373 nm) along with a clear isosbestic point at 370 nm in the absorption spectrum. The red shift has resulted because of the hydrogen-bonding interaction of AcO^- with the amino hydrogen of the ADD moiety. However, the fluorescence spectrum presented in Figure 1 shows the formation of a new emission band at 490 nm beyond 0.2 mM of AcO^-.

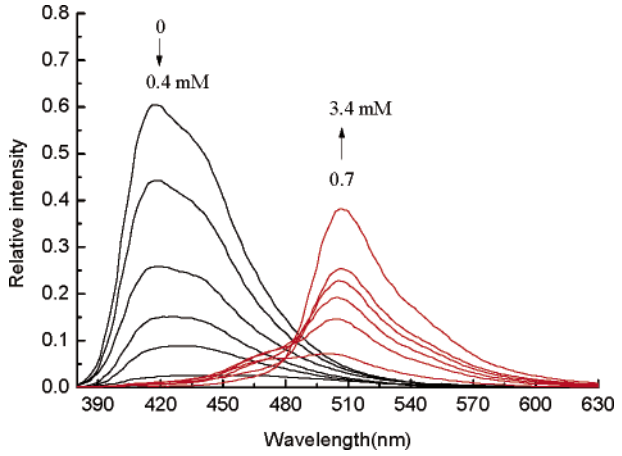

Figure 2. Emission spectra of ADDTU-1 (16 μM) in acetonitrile upon titration with F^- (0 → 3.4 mM); λ_{exc} = 363 nm.

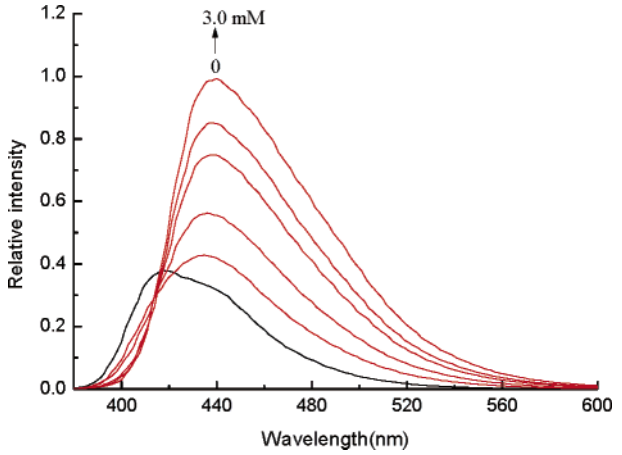

Figure 3. Fluorescence enhancement of ADDTU-1 (16 μM) in the presence of $H_2PO_4^-$ (0 → 3.0 mM) in acetonitrile; λ_{exc} = 363 nm.

On the other hand, the addition of $H_2PO_4^-$ to the ADDTU-1 in acetonitrile leads to a red shift (360−376 nm) in the absorption spectrum with an isosbestic point at 363 nm as witnessed in the case of AcO^- (>0.2 mM). Figure 3 shows the fluorescence spectra of ADDTU-1 as a function of $H_2PO_4^-$ concentration. Increase in the concentration of $H_2PO_4^-$ caused an enhancement in the fluorescence intensity along with 20 nm red shift in the emission maximum.

The anion hydrogen bonding with the donor or acceptor moiety changes the photophysical properties of ICT fluorophore due to its effect on the efficiency of charge transfer. Addition of AcO^- (beyond 0.2 mM) and $H_2PO_4^-$ to ADDTU-1 in acetonitrile brings in hydrogen-bonding interaction with the ADD amino hydrogen, thereby increasing the electron density in the donor group (ADD amino group). This increase in charge density results in the red shift of the absorption and emission together with an increase in the fluorescence intensity. The different optical signal response obtained for AcO^- and $H_2PO_4^-$(490 and 440 nm) is due to the difference in the charge density and size of the anions. On the other hand, no such changes were observed upon the addition of Br^-, Cl^-, I^-, HSO_4^-, ClO_4^-, and BF_4^- to ADDTU-1 in acetonitrile.

Evidence for 1:1 complex formation is provided by linear relationship obtained in the Benesi−Hildebrand plot.[15] The binding constant was obtained from the variation in the fluorescence intensity at the appropriate wavelength [AcO^- (419 nm); F^- (419 nm); $H_2PO_4^-$ (440 nm)] by plotting the ratio of $1/(I_0 - I)$ against [anion]$^{-1}$. The binding constants for ADDTU-1 with AcO^-, F^-, and $H_2PO_4^-$ (1:1) were determined to be 17 400, 16 275, and 380 M^{-1}, respectively, and the same for the 1:2 complex formation between ADDTU-1 and AcO^- (490 nm) was determined to be 13.56 M^{-1}.

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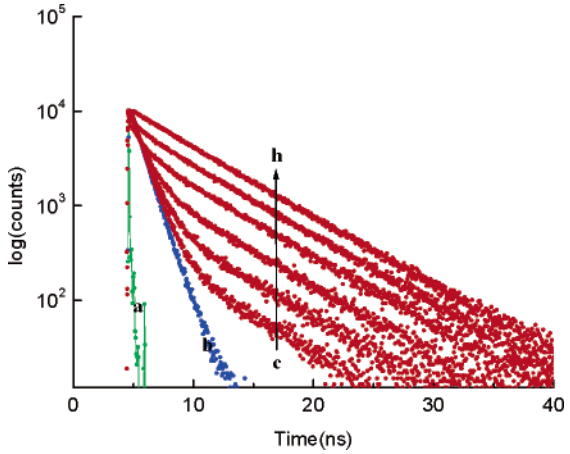

Figure 4. Fluorescence decay profiles of ADDTU-1(16 μM) at different concentrations of AcO^- in acetonitrile; $\lambda_{exc} = 375$ nm and $\lambda_{em} = 490$ nm: (a) laser profile; (b) ADDTU-1 alone; (c) 0.02; (d) 0.03; (e) 0.07; (f) 0.17; (g) 0.42; (h) 5.50 mM of AcO^-.

We have also carried out a blank experiment with ADD-2 (where both the receptor sites are absent) for all the anions in acetonitrile. In this case we did not observe any change in the absorption and emission spectra. This result indicates that the fluorescence signaling of ADDTU-1 is not caused directly by the interaction of the ADD group and the added anions. Similar studies were also carried out using ADDTU-2 (the methyl group in the ADD ring blocks the ICT pathway), which showed fluorescence quenching in the presence of AcO^-, F^-, and $H_2PO_4^-$, but it is insensitive toward other anions. The fact that TU is the only receptor available for anions in chemosensor ADDTU-2 indicates that the anion hydrogen-bonding interaction with TU results in the fluorescence quenching by PET mode of action. In ADD-1, absence of TU receptor (blocks the PET mechanism) results in the normal ICT pathway sensing action by the hydrogen-bonding interactions of the anions with the amino nitrogen in the 10th position. The specific optical signaling of ADD-1 is due to the formation of new distinct ICT emitting states in the presence of AcO^- (490 nm), $H_2PO_4^-$ (440 nm), and a deprotonated state in the presence of F^- (510 nm) over other anions.

The complexation between anions and ADDTU-1 has also been investigated by the time-resolved fluorescence technique. Figure 4 presents the fluorescence decay of ADDTU-1 at different concentrations of AcO^-. In the absence of anion, ADDTU-1 exhibited a single-exponential lifetime ($\tau = 1.04 \pm 0.03$ ns) in acetonitrile, whereas in the presence of anions, the fluorescence decay of ADDTU-1 is biexponential. This suggests that there are two distinct species, consisting of anion bound or deprotonated form [AcO^- (5.81 $\pm$ 0.03 ns), $H_2PO_4^-$ (4.13 $\pm$ 0.03 ns), and F^- (6.20$\pm$ 0.03 ns)] and free ADDTU-1. The shorter component amplitude decreases gradually in the presence of anions and the new longer component amplitude increases. We observe single exponential decay with longer lifetime component only on complete complex formation between the anion and ADDTU-1.

We conclude that the chemosensor ADDTU-1 has two different anion receptor sites which play a key role in specific and dual optical output in anion sensing. At low concentrations of AcO^- and F^-, selective binding with the TU moiety of ADDTU-1, results in the fluorescence quenching by PET mechanism. Higher concentrations of F^- and AcO^- leads to a new CT state emission which is due to the deprotonation and hydrogen bonding interaction with the amino hydrogen of ADD moiety, respectively. The sensing action for $H_2PO_4^-$ ion occurs through the hydrogen bonding interaction with ADD amino hydrogen, which result in the fluorescence enhancement. This observation is first of its kind where both PET and ICT processes lead to different optical output within the same molecule.

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Supporting Information Available: Experimental procedures and characterization for compounds ADDTU-1 and ADDTU-2, UV−vis spectra of receptor ADDTU-1with different anions, color change, ^{1}H NMR spectra, Benesi−Hildebrand plot, 3D contour plot and binding mode of anions with ADDTU-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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