p-Dimethylaminobenzamide as an ICT dual fluorescent neutral receptor for anions under proton coupled electron transfer sensing mechanism

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Abstract

The intramolecular charge transfer (ICT) dual fluorescence of p-dimethylaminobenzamide (DMABA) in acetonitrile was found to show highly sensitive response to HSO 4- over several other anions such as H 2 PO 4-, AcO - and ClO 4-. In the presence of bisulfate anion the dual fluorescence intensity ratio and the total intensity of DMABA decreased while the dual emission band positions remained unchanged. Absorption titration indicated that a 1:1 hydrogen bonding complex was formed between bisulfate anion and DMABA, which gave a binding constant of 2.02 × 10^4 mol^-1 l that is two orders of magnitude higher than those for other anions. The obvious isotopic effect observed in the fluorescence quenching [K_{SV}(HSO_4^-)/K_{SV}(DSO_4^-) = 1.63] suggests that the hydrogen atom moving is an important reaction coordinate. It was assumed that the dual fluorescence response was due to proton coupled electron transfer mediated by hydrogen bonds within the 1:1 HSO_4^- -DMABA hydrogen-bonding complex. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

With increasing understanding of the important roles that anions play in life and environmental sciences, interests in anion recognition and sensing have become increasingly intensive [1–5]. A great number of anion receptors have been reported under the basic construction strategy of employing hydrogen bonding [6–10], electrostatic interaction [11,12], and metal–ligand coordination [13,14]. Developing hydrogen bonding based anion receptors appears particularly attractive, since recent investigations have shown that hydrogen bonds could work as efficient bridges [15–19] to mediate electron transfer between hydrogen-bonded species and initiate the so-called proton coupled electron transfer (PCET) [17–21] that occurs because of the proton transfer within the hydrogen bonds. It was therefore considered that if the hydrogen-bonding group was connected to an electron donor or an acceptor it would be possible to construct a receptor with PCET sensing mechanism. Upon PCET a direct communication between the sensing species and the receptor was
established, which would lead to sensitive signal response. In this case hydrogen bonds play the roles of both recognition and mediating electron transfer.

We decided to construct such anion receptors by attaching hydrogen-bonding moiety to N,N-
        dimethylaniline (DMA) to form the DMABN-like intramolecular charge transfer (ICT) dual fluorescent receptors [22], since the receptors themselves have the emissive ICT state that would allow for direct probing of the excited-state reaction by following the change in the CT emission and, in particular, establishing ratiometric assay by taking the dual fluorescence intensity ratio. Amide group has been shown to be an important hydrogen-bonding element in designing anion receptors such as amide derivatives of tripodal tris-2-aminoethylamines [23], calixarenes [24], calixpyrroles [25], and metal–ligand complexes [26]. As the amide group is also an electron-accepting group, our first attempt was to connect it to DMA to construct a neutral amide-based anion receptor, p-dimethylaminobenzamide (DMABA, Scheme 1), that has been shown to emit the ICT dual fluorescence [22,27]. In the absence of anions, DMABA emits dual fluorescence characteristic of the occurrence of the excited-state intramolecular charge transfer [22]. Whereas in the presence of the anions that hydrogen bond to the amide moiety, the ICT dual fluorescence might vary because of the opening of the PCET channel and/or the change in the electron-withdrawing ability of the electron acceptor, thereby allowing for anion fluorescence sensing.

In this Letter we report anion sensing by using the ICT dual fluorescent receptor DMABA (Scheme 1) in which the amide moiety was a part of the electron acceptor. It should be pointed out that dual fluorescent DMA derivatives have been reported as fluorescent receptors for cations based on metal/crown-ether binding interactions [28–30]. We observed that in acetonitrile (ACN) the ICT dual fluorescence of DMABA as well as its absorption showed sensitive response to HSO₄⁻ over several other anions such as H₂PO₄⁻, AcO⁻, and ClO₄⁻. It was assumed that the response was due to a proton coupled electron transfer via hydrogen bonds between HSO₄⁻ anion and DMABA.

2. Experimental

DMABA was synthesized by isomerizing p-dimethylaminobenzadoxime in the presence of nickel acetate tetrahydrate as described by Field et al. [31], and purified by recrystallization from absolute ethanol. The tetrabutylammonium salts of the tested anions were obtained by reaction of the corresponding conjugate acids of the anions with tetrabutylammonium hydroxide and were purified by recrystallization from ethyl acetate. n-Bu₄N⁺ DSO₄⁻ was prepared from an exchange reaction between n-Bu₄N⁺ HSO₄⁻ and D₂O. All solvents were further purified and checked to have no fluorescent impurity.

Corrected fluorescence spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer using excitation wavelength of 300 nm. Both excitation and emission monochromators' slits were 5 nm and the spectral scan rate was 240 nm min⁻¹. Absorption spectra were recorded on Beckman DU-7400 absorption spectrophotometer using 1-cm quartz cell. ¹H NMR titrations were carried out in DMSO-d₆ on a Varian Unity⁺ 500 MHz NMR spectrometer using TMS as the internal standard.

3. Results and discussion

DMABA has been reported to emit dual fluorescence characteristic of the excited-state intramolecular charge transfer [27]. We investigated the fluorescence spectra of DMABA in ACN in the absence and presence of anions such as HSO₄⁻, H₂PO₄⁻, AcO⁻, and ClO₄⁻. We observed the ICT dual fluorescence of DMABA in ACN at 360 and 484 nm, which could be readily assigned to the LE and the ICT states, respectively, with a total
quantum yield of 0.0365. In the presence of HSO$_4^-$ anion down to $10^{-5}$ mol l$^{-1}$ the ICT dual fluorescence experienced substantial variations whereas the other anions hardly induced any changes in the emission spectra. Fig. 1 shows the fluorescence spectra of DMABA in ACN with varying concentrations of bisulfate anion. The presence of HSO$_4^-$ led to quenching of the dual emission but no changes occurred in the LE and ICT band positions. The fluorescence quenching was found to obey Stern–Volmer equation (inset in Fig. 1), and the quenching constant $K_{SV}$ was calculated to be $1.60 \times 10^4$ mol$^{-1}$ l. The $K_{SV}$ values of other anions were similarly obtained as 110(H$_2$PO$_4^-$), 70(AcO$^-$), and 130 mol$^{-1}$ l (ClO$_4^-$), respectively, which are substantially lower than that of HSO$_4^-$, indicating a highly selective response towards HSO$_4^-$.

We found that a dramatic decrease in the CT to LE fluorescence intensity ratio, $I_{CT}/I_{LE}$, occurred in the presence of HSO$_4^-$, whereas the presence of other anions exerted much less influence on the intensity ratio (Fig. 2), similar to the high selectivity for HSO$_4^-$ observed in the total fluorescence quenching. This observation confirmed that the $I_{CT}/I_{LE}$ ratio could indeed serve as a ratiometric index for anion fluorescence sensing. As no change in the LE and CT band positions was noted (Fig. 1), the variations in the dual fluorescence intensity ratio in the presence of bisulfate anion would not result from change in the electron-withdrawing ability of the acceptor [22,27]. Instead, it is likely due to change in the excited-stated reaction coordinate, otherwise the intensity ratio would have remained unchanged.

Although it is not unreasonable to assume that the formation of hydrogen bonds of DMABA with these anions could be the origin of the spectral response, the response order shown in Fig. 2 was also noted to follow the acidity order of the anions, for example, the $pK_a$ of HSO$_4^-$ is 1.91 and that of H$_2$PO$_4^-$ is 7.21 in aqueous solution [32]. Comparative experiments were thus carried out by addition of up to 100 equivalents of oxalic acid ($pK_a = 1.34$) or chloroacetic acid ($pK_a = 2.86$) into the acetonitrile solution of DMABA. Hardly
any change was observed in the fluorescence and absorption spectra. This means that the spectral response towards the anions is not due to the protonization of DMABA, which was also supported by the NMR titrations in which no shift in the methyl proton NMR signal ($\delta_{2.96}$ ppm, DMSO-$d_6$) was found in the presence of bisulfate anion.

The possibility of the dimerization of DMABA in ACN, probably via intermolecular hydrogen bonding, and that the presence of anions disrupts the dimer that leads to change in the dual fluorescence intensity ratio were examined by monitoring the absorption and fluorescence variations as a function of DMABA concentration. Over DMABA concentration range of $5.0 \times 10^{-6}$–$1.0 \times 10^{-4}$ mol l$^{-1}$ no change in the shape of DMABA absorption spectrum was noted and the variation of the maximal absorbance at 298 nm against DMABA concentration exactly obeyed the Lambert–Beer formula with a linear coefficient of 0.9993 ($n = 15$). This means that no substantial intermolecular interaction takes place in DMABA solution of this concentration range. Meanwhile, we found that the total fluorescence intensity varied linearly with DMABA concentration ranging from $2.5 \times 10^{-6}$ to $2.0 \times 10^{-5}$ mol l$^{-1}$ and later on leveled off until the highest examined concentration of $3 \times 10^{-5}$ mol l$^{-1}$, with the CT to LE intensity ratio remaining more or less constant at 3.7. It should be pointed out that in the presence of HSO$_4^-$ the quenching of the total fluorescence of DMABA was accompanied by a decrease in the $I_{CT}/I_{LE}$ ratio (Fig. 2). It was hence concluded that there would be no substantial intermolecular interactions and the quenching of the total fluorescence and the decrease in the CT to LE intensity ratio might not be due to the disruption of the DMABA dimer, if there is any.

Absorption titration clearly demonstrated the formation of 1:1 complex between HSO$_4^-$ and DMABA. Fig. 3 shows the absorption spectra of DMABA in ACN in the presence of varying concentration of HSO$_4^-$. It was observed that bisulfate anion led to decrease in the absorbance at 298 nm ($\varepsilon_{298 \text{ nm}} = 1.93 \times 10^4$ mol$^{-1}$ l cm$^{-1}$) while the appearance of a new absorption band peaked at 345 nm, with distinct isosbestic points at 246 and 328 nm.
The other anions that showed much weaker influence on the fluorescence spectra of DMABA had very weak effect on the absorption spectra either (inset in Fig. 3), indicating that the absorbance of DMABA shows highly selective response towards HSO$_4^-$.

The binding constants ($K_{\text{ass}}$) of the anions with DMABA were calculated by non-linear fitting [33] of the absorbance at 298 nm as a function of anion concentration. The $K_{\text{ass}}$ values were $2.02 \times 10^4$ (HSO$_4^-$), $5.33 \times 10^2$ (H$_2$PO$_4^-$), $2.52 \times 10^2$ (AcO$^-$) and $2.58 \times 10^2$ mol$^{-1}$ l$^{-1}$ (ClO$_4^-$), respectively. Further dilution experiments [34] carried out for DMABA-HSO$_4^-$ system yielded, by following the change in absorbance at 298 nm, a binding constant of $2.44 \times 10^4$ mol$^{-1}$ l$^{-1}$ that is in well agreement with those obtained by fluorescence quenching and absorption titration.

The hydrogen-bonding interaction between DMABA and HSO$_4^-$ was directly probed by NMR titration in DMSO-$d_6$ that indicated a downfield shift of the NMR signal of the $-NH$ proton of DMABA in the presence of bisulfate anion. The broadening and the overlapping of the NMR signal of the $-NH$ proton with those of the aromatic protons in DMABA in the presence of bisulfate anion, however, made it impossible to determine the binding constant of bisulfate with DMABA. The hydrogen bonding interaction nature was further supported by the effect of protic solvents on the absorption spectrum of DMABA–HSO$_4^-$ complex. We found that, in ACN solution of DMABA and HSO$_4^-$ of 1:4 molar ratio, addition of methanol, ethanol or iso-propanol led to the recovery of the absorption spectrum of DMABA, see Fig. 4, which means the breakdown of the DMABA–HSO$_4^-$ interaction in the presence of hydrogen-bonding solvents. We thus concluded that the formation of the 1:1 hydrogen-bonding complex (Scheme 1) was the origin for the spectral responses towards HSO$_4^-$.

We further found that deutero-bisulfate, DSO$_4^-$, had a substantially lower quenching constant $K_{\text{SV}}$ than that of HSO$_4^-$, with an isotopic ratio $K_{\text{SV}}(\text{HSO}_4^-)/K_{\text{SV}}(\text{DSO}_4^-)$ of 1.63, which suggested
that excited-state proton transfer was an important coordinate for the quenching [15]. The examination of the solvent polarity effect on fluorescence quenching indicated the occurrence of the electron transfer reaction between the hydrogen-bonded species. In much less polar solvent, dichloromethane (CH$_2$Cl$_2$), the absorption spectra of DMABA in the presence of bisulfate of increasing concentration underwent practically the same variation profile as those in ACN, showing isosbestic points at 348 and 260 nm, respectively. The 1:1 complex formation was similarly assumed in CH$_2$Cl$_2$, which was evaluated to have a binding constant $K_{ass}$ of 1.30 $\times$ 10$^4$ mol$^{-1}$ l that is of the same order of the magnitude as that in ACN (2.02 $\times$ 10$^4$ mol$^{-1}$ l). It was found, however, that the dual fluorescence of DMABA in CH$_2$Cl$_2$ was quenched much less efficiently by bisulfate than in ACN, $K_{SV}$ being 4.67 $\times$ 10$^3$ mol$^{-1}$ l in CH$_2$Cl$_2$ compared to 1.60 $\times$ 10$^4$ mol$^{-1}$ l in ACN. This means that an electron transfer quenching is operative, in less polar medium the electron transfer reaction and in turn the fluorescence quenching being suppressed. It was therefore assumed that the substantial fluorescence quenching observed in ACN was due to the excited-state PCET within the 1:1 hydrogen-bonding complex [15–19]. In accordance with this assumption, the CT to LE fluorescence intensity ratio of DMABA in CH$_2$Cl$_2$ in which the PCET was suppressed was found to remain more or less constant at ca.0.9, instead of decreasing in ACN, with the introduction of bisulfate. This implied that a sufficient PCET in the excited state led to the decrease of the CT to LE fluorescence intensity ratio.

4. Conclusion

A simple ICT dual fluorescent neutral receptor DMABA was found to be a good chemosensor for anions with total fluorescence intensity, dual fluorescence intensity ratio, and absorbance being the sensing indexes. The sensing was highly selective
for HSO$_4^-$ over H$_2$PO$_4^-$, AcO$^-$ and ClO$_4^-$. We showed that it was the formation of the 1:1 hydrogen-bonding complex between DMABA and HSO$_4^-$ that resulted in changes in the dual fluorescence intensity ratio and the total intensity because of an excited-state proton coupled electron transfer within the complex. It deserves to point out that the dual fluorescence intensity ratio serving as the sensing index allows for a ratio-metric assay for anions [8,30], which makes the sensing not subject to the fluctuation in the excitation source that has been suffered in total intensity sensing mode. We thus established a new hydrogen-bonding based sensing system for anions by using the ICT dual fluorescence under the proton coupled electron transfer mechanism. Further work would be carried out to clarify the ICT photophysics in the presence of PCET channel that guides the designing of new ICT dual fluorescent receptors and the applications of the PCET sensing mechanism to the more sophisticatedly designed receptors for improved anion sensing performance.

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