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Ratiometric Fluorescent Sensor for Silver Ion and Its Resultant Complex for Iodide Anion in Aqueous Solution

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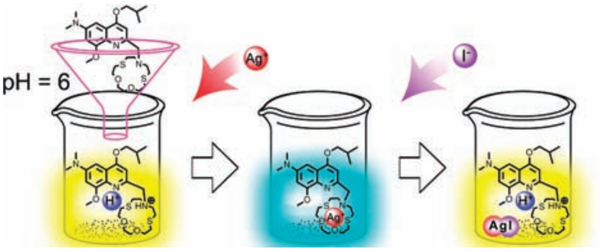
ABSTRACT



In aqueous solution, sensor DQAg can selectively detect Ag^+ based on inhibition of the resonance, demonstrating a large hypsochromic shift of 84 nm and remarkable changes in the ratio ($F_{481\ nm}/F_{565\ nm}$) of the emission intensity (R/R_0 up to 26-fold). Furthermore, the resultant Ag–DQAg also displays a ratiometric and highly selective response to iodide anion over other anions due to the liberation of DQAg from the complex by precipitating AgI.

It is well-known that anions, such as Cl^-, I^-, HCO_3^-, NO_3^-, and PO_4^{3-}, play significant roles in the biological and physical systems. In particular, the iodide anion has been attracting much attention in recent years for its biological activities, such as mental development, growth, and basic metabolism.[1] Hence, iodine deficiency can cause serious diseases.[2] Although adding iodide into food (salt) has been utilized as a routine method to prevent iodine deficiency for years, it is still a public health problem in some countries.[3] On the other hand, increasing amounts of iodine and its derivatives, in particular, its hazardous radioactive isotopes, have been released into the biosphere due to human activities.[4] Therefore, it is strongly desirable to develop reliable analytical techniques for detecting and monitoring iodide levels in drinking water, foods, and environmental samples.

Owing to the features of high sensitivity, facile operation, and real time and online detection, fluorescent sensors have been recognized as powerful tools for monitoring cations, anions, and small molecules.[5] However, only a few iodide anion sensors have been developed so far because of the lack of efficient receptors for the iodide anion, which is

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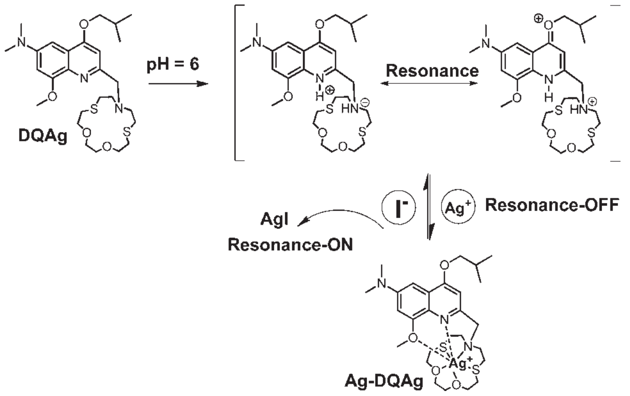
characteristic of large ionic radius, low charge density, and low hydrogen-bonding ability.[6] These notorious properties make it extremely difficult to design sensors for iodide anions. Moreover, most of the hydrogen-binding-based sensors for iodide suffer from the competition of water molecules in aqueous media.

On the other hand, metal-based complexes have successfully developed for sensing anions, such as PPi,[7] CN^-,[8] F^-,[9] and even I^-,[10] in aqueous media, and can afford low limits of detection (LOD) and high sensing abilities via cation–anion cooperative interaction or precipitation.[11] It is well-known that AgX (X is halide) is insoluble in water and has a very low solubility constant (K_{sp}). For instance, the K_{sp} value of AgI is 1.5×10^{-16}.[12] We envisioned that a silver complex or sensor could be utilized for sensing iodide anion through sequestrating Ag^+ from the complex by means of formation of AgI precipitates in aqueous media. This process would liberate sensor from silver complex and consequently induces a significant fluorescence signal output.

With this goal in mind, we designed a new fluorescent sensor for Ag^+ by incorporating Ag^+-selective receptor azacrown[N,S,O] to the 4-isobutoxy-6-(dimethylamino)-8-methoxyquinaldine fluorophore (Scheme 1). We expected that this senor could be protonated in acidic or neutral aqueous media. This facilitates the formation of the resonance charge transfer between the quinolinium and oxonium electronic structures, consequently stabilizing its protonated species as we observed for DQCd1.[13] Both absorption and emission spectra of the protonated species exhibit a bathochromic effect in comparison with the neutral form. The coordination of silver ion with the pronotanted DQAg would lead to the deprotonation of DQAg and consequently generates a significant ratio signal output through Ag^+-induced inhibition of the resonance. Moreover, the sequestration of Ag^+ in means of precipitating insoluble AgI is able to liberate the sensor from the silver complex. Thus, this will switch on the resonance process and revive the ratio signal outputs. Herein, we disclose the versatility of DQAg as an excellent ratiometric fluorescent sensor not only for detecting Ag^+ in aqueous solution but also for detecting I^- by utilizing its Ag^+ complex.

Scheme 1. Proposed Binding Processes



The 4-isobutoxy-6-(dimethylamino)-8-methoxyquinaldine fluorophore recently reported by us[13] was oxidized to generate its carbaldehyde derivative. This was further coupled with an azacrown moiety to efficiently afford DQAg, which was characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectra analysis (see the Supporting Information).

At first, we measured the emission intensity and absorption of DQAg against pH in the range of 1.5 to 11 (Figure S2, Supporting Information). Three apparent pK_a values were obtained to be 7.38, 6.42, and 2.97 from the fluorescence spectra. The very similar values of 7.51, 6.38, and 3.08 were also extracted from UV/vis spectra. We infer the most basic tertiary nitrogen atom would be the first protonated site for the pK_{a1} value of 7.38, whereas $pK_{a2} = 6.42$ and $pK_{a3} = 2.97$ can be assigned to the quinolinic and dimethylamino nitrogen atom, respectively. Notably, this observation was different from the reported sensor, DQCd1,[13] in which the DPA moiety and quinolinic nitrogen form a proton binding pocket and exhibits a combined pK_a value ($pK_{a1} = 7.31$). In contrast, this is not the case for DQAg because the large steric hindrance of the azacrown moiety prevents the formation of such a proton binding pocket. Therefore, two separated pK_a values were obtained for the quinolinic and tertiary nitrogen atoms. These data also indicate that the protonation of quinolinic site needs a weak acidic media. Thus, a MES buffer solution (20 mM MES, pH = 6.0) was prepared for photophysical measurements in this context.

As shown in Figure 1, DQAg exhibits a broad band from 400 to 450 nm. Upon addition of Ag^+ (0–1.5 mol equiv),

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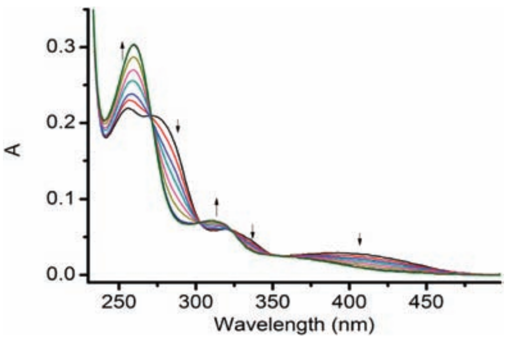

Figure 1. UV/vis spectra of DQAg (10 μM) titrated with Ag^+(0 − 15 μM) in MES buffer (20 mM MES, pH = 6.0).

this band decreases gradually, accompanying clear isosbestic points at 353, 324, 304, and 270 nm, indicating that the quinolinic nitrogen got involved in coordination with Ag^+. Moreover, the absorbances remain constant in the presence of more than one equiv Ag^+, suggesting the formation of 1:1 complex between DQAg and silver ion, which was further confirmed by the appearance of a peak at m/z 644.1758 (calcd for 644.1740) assignable to $[DQAg + Ag]^+$ in the HRMS-ESI spectrum (Figure S1).

The fluorimetric titration of DQAg with Ag^+ was conducted to value the response of DQAg to silver ions. As depicted in Figure 2a, DQAg displays a weak fluorescence emission band centered at 565 nm (λ_{ex} = 405 nm, Φ_0 = 0.05), which originates from the protonated quinoline fluorophore with the resonance effect (Scheme 1). Addition of various concentrations of Ag^+ results in quenching of the emission at 565 nm. Simultaneously, a new emission at 481 nm (Φ_{Ag} = 0.28) with a hypsochromic shift of 84 nm and a distinct isoemission point at 554 nm were observed. The ratio calibration curve ($R = F_{481\ nm}/F_{565\ nm}$) showed a significant increase from 0.19 to 4.99, suggesting DQAg a good ratiometric sensor for Ag^+ in aqueous solution (R/R_0 up to 26). These data confirm our design that Ag^+ is able to displace the proton at the quinolinic site and consequently triggers the inhibition of the resonance.

Subsequently, we evaluated the response of DQAg to other metal ions and found that only 1 equiv of Ag^+ caused a significant ratio signal output (Figure 2b). In contrast, Cr^{3+}, Fe^{3+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, K^+, Mn^{2+}, and Cd^{2+} did not induce remarkable response under otherwise identical conditions. The further selectivity profile for DQAg in metal/silver coexisted systems indicates that other metal ions pose little impact on the $F_{481\ nm}/F_{565\ nm}$ value of silver complex (Figure S3, Supporting Information). The results imply that DQAg

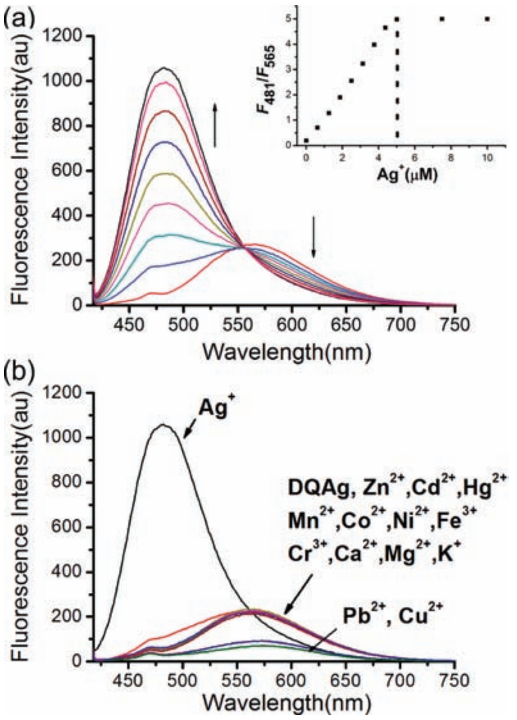

Figure 2. (a) Fluorescence emission spectra of DQAg (5 μM) upon addition of Ag^+ (0−10 μM) in MES buffer. Inset: ratio ($F_{481\ nm}/F_{565\ nm}$) changes as a function of the Ag^+ concentration. (b) Emission spectra DQAg (5 μM) in the presence of various metal ions (5 μM Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+},Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and 1 mM Mg^{2+}, $Ca^{2+}$and K^+) in MES buffer, λ_{ex} = 405 nm.

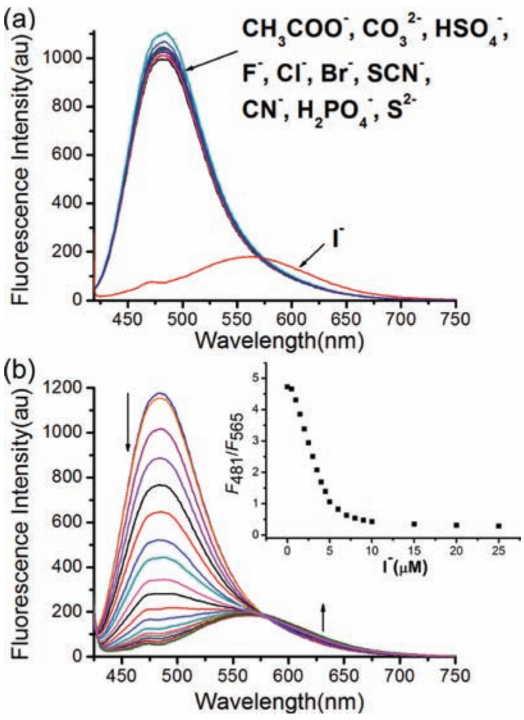

Figure 3. (a) Fluorescence emission spectra of Ag−DQAg (5 μM) in the presence of various anions (10 μM I^-, F^-, Cl^-, Br^-, CO_3^{2-}, HSO_4^-, CN^-, SCN^-, $H_2PO_4^-$ S^{2-}, AcO^-) in MES buffer. (b) Fluorescence emission spectra of Ag−DQAg (5 μM) upon addition of I^- (0−25 μM) in MES buffer. Inset: ratio ($F_{481\ nm}/F_{565\ nm}$) changes as a function of the I^- concentration.

bears the high selectivity for silver ions in the presence of other competitive metal ions.

With these data in hand, we believe that DQAg is an excellent ratiometric sensor for Ag^+ in aqueous solution with high affinity and no interference from other cations. On the other hand, the halide anions have strong tendency to form AgX precipitates in the presence of Ag^+. This process could be used to sequestrate Ag^+ from the resultant Ag–DQAg complex and consequently reverts the resonance of quinoline platform in the protonated DQAg, displaying a reversed ratio signal output. Therefore, we further determined the fluorimetric response of Ag–DQAg (DQAg/Ag^+ = 1:1) to various anions in the MES buffer (20 mM MES, pH = 6.0). As shown in Figure 3a, F^-, Cl^-, Br^-, CO_3^{2-}, HSO_4^-, CN^-, SCN^-, $H_2PO_4^-$, S^{2-}, and AcO^- give little or poor responses, while only I^- generates a significant fluorescence response.

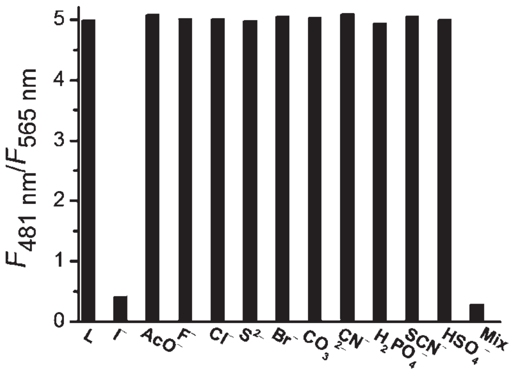

Figure 4. Emission ratio ($F_{481\ nm}/F_{565\ nm}$) of Ag–DQAg (5 μM) in MES buffer induced by indicated anions. The final concentration for I^-, AcO^-, F^-, Cl^-, S^{2-}, Br^-, CO_3^{2-}, CN^-, $H_2PO_4^-$, SCN^-, and HSO_4^- is 10 μM. L = Ag–DQAg. Mix = a mixed solution containing all the tested anions.

As indicated in Figure 3b, gradual addition of I^- (0–5 equiv) into Ag–DQAg solutions induced a dramatic deactivation of the fluorescence emission at 481 nm and a simultaneous revival of the emission at 565 nm. The relevant ratio ($R = F_{481\ nm}/F_{565\ nm}$) calibration exhibited a significant decrease and almost reverted to the initial value of the apoligand DQAg after 2.0 equiv of I^- was added. These data indicate that Ag^+ was removed from the coordination center of Ag–DQAg by the competitive binding with I^-. From the fluorimetric titration curve, we have estimated the detection limit of Ag–DQAg for I^- to be 7.16×10^{-6} M (0.9 ppm based on ratio calibration, Figure S6, Supporting Information), which reveals a high sensitivity for the analysis of iodide by using the Ag–DQAg complex. Furthermore, the presence of other indicated anions does not evidently interfere with the response to I^- in MES buffer (Figure 4). Thus, the Ag–DQAg complex can also afford a high selectivity for I^- over common cations and anions in aqueous solution.

In summary, we designed a new fluorescent sensor for Ag^+ based on cation-induced inhibition of the resonance process. It provides ratiometric measurements for Ag^+ with high sensitivity and selectivity in aqueous solution. We also present that its resultant silver complex (Ag–DQAg) can be an excellent sensory system for detecting I^- in aqueous solution by sequestrating Ag^+ from the Ag–DQAg complex. The approach utilizing a metal-based complex for anions is feasible and efficacious and allows one to design new ratiometric sensors for other anions with high sensitivity in aqueous solutions.

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Supporting Information Available. Synthetic procedures, characterization of DQAg, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.