Unusual Red Shift of the Sensor While Detecting the Presence of Cd^{2+} in Aqueous Environment

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ABSTRACT: A norbornene derived 8-hydroxyquinoline (**N8HQ**) is designed and synthesized. A "turn-on" ratiometric fluorescent response is observed for Cd^{2+} in aqueous solution upon binding with **N8HQ** with a characteristic huge red shift of 164 nm. A lowest detection limit of 1.6 nM of Cd^{2+} is achieved in the presence of other heavy metals.

**KEYWORDS:** *sensor, fluorescence, cadmium, PET, DFT,* **N8HQ**
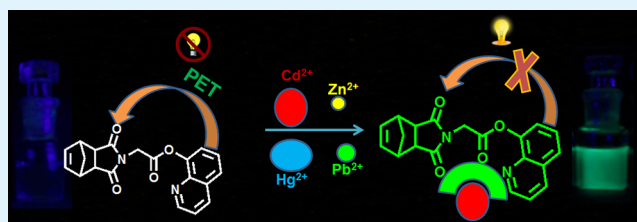
INTRODUCTION

Selective chemosensors are always on demand for the detection of heavy metal ions that are extremely toxic to the environment.[1−3] Until now they have mostly been for mercury,[2,4,5] copper,[6,7] and lead ions.[8,9] Cadmium is also one of the toxic elements in earth and is being used largely in industry, military affairs, agriculture and metallurgy. Cadmium is exposed to society excessively and it causes toxic effects on human health. So developing a selective chemosensor for the detection of cadmium ions is a great challenge in the field of research.[10,11] Significant efforts have been made in this area[12−14] and the researchers have come up with a lot of innovative methods mainly focusing on colorimetric and fluorescence chemosensors.[15−23] Among these, fluorescence sensing[24,25] is a very simple and effective mechanism in metal sensor field due to its high sensitivity and selectivity.[26−29] There are few reports on fluorescent based sensor systems for cadmium but they lack in sensitivity and selectivity. So the key challenge here for the researchers is to come up with one that works effectively in aqueous media and also selectively detects the cadmium in the presence of metals like Hg^{2+}, Pb^{2+}, Cu^{2+} especially Zn^{2+}.[30−35] Being in the same group in the periodic table cadmium and zinc possess similar chemical properties. Hence, they provide same spectral changes while binding with sensor molecules. So it is desirable to make a new sensor system that detects cadmium more effectively without any interference of zinc. Here we report a norbornene derived 8-hydroxyquinoline (**N8HQ**) molecule as ratiometric turn-on sensor system for cadmium with high selectivity and sensitivity in aqueous environment. 8-hydroxyquinoline has been frequently used as fluorophore for the construction of sensors for different metal ions.[18−20] However, its effective "turn-on" response in organic solvent and low specificity to Cd^{2+} has restricted its application in quantitative detection. In this work, Cd^{2+}-induced emission with red shift (164 nm) for **N8HQ** in

methanol−water system suggests that photo induced electron transfer (PET) between 8-hydroxyquinoline and norbornene motif[36] is responsible for the unusual red shift. Because of this, a lowest detection limit of 1.6 nM is achieved from this simple but unique design.

EXPERIMENTAL SECTION

First we synthesized norbornene functionalized acid using *cis*-5-norbornene-endo-2, 3-dicarboxylic anhydride and glycine.[37] 8-hydroxyquinoline was coupled to norbornene functionalized acid by simple DCC coupling (Scheme 1) and the formation of **N8HQ** was confirmed by NMR spectroscopy (see Figures S1 and S2 in the Supporting Information). From ^{1}H NMR spectroscopy, presence of signals at 6.02−6.06 ppm were corresponding to norbornene olefinic bonds and signals at aromatic region were due to 8-hydroxyquinoline.

Scheme 1. Schematic Representation of Synthesis of N8HQ and Its Polymer PN8HQ

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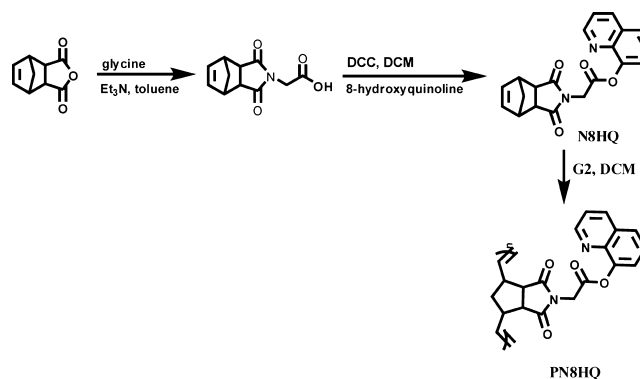
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^{13}C NMR spectroscopy, CHN analysis, and mass spectroscopy further confirmed the formation of **N8HQ**.

■ RESULTS AND DISCUSSION

After the complete characterization, emission properties of **N8HQ** were explored. Absorbance and fluorescence spectrum of **N8HQ** were recorded in methanol−water (1:1) system (see Figures S3 and S4 in the Supporting Inforamtion). Absorbance spectrum of **N8HQ** exhibited three bands at 288 nm, 300 and 313 nm. Fluorescence emission spectra were measured in methanol−water (1:1) with λ_{ex}: 310 nm. Free **N8HQ** showed weak emissions at 346 and 372 nm. The observed weak emission of **N8HQ** was attributed to the N lone electron pairs in the molecule that were involved in a radiationless process via the nπ* state.[18]

The metal chelating ability of **N8HQ** was studied by adding it in methanol−water solvent system to the metal salts in water. Interestingly, ratiometric behavior was observed only with Cd^{2+}.

While titrating **N8HQ** with Cd^{2+}, the absorbance at 288, 300, and 313 nm decreased linearly with increasing amount of Cd^{2+} (0 to 2 equivalent), whereas two new peaks appeared gradually at 335 and 373 nm with an isosbestic point at 326 nm (Figure 1a). The absorbance increased linearly and remained unchanged after 1 equivalent addition of Cd^{2+}. A plot of absorbance of **N8HQ** at 373 nm verses $[Cd^{2+}]$ showed linear behavior initially and then remained constantly. This prompted us to propose a 1:1 binding between **N8HQ** & Cd^{2+}.

Next, the emission properties of **N8HQ** were explored with gradual addition of Cd^{2+} (0 to 2 equiv.) by exciting the solution at 310 nm. The intensity at 346 and 372 nm decreased gradually with the appearance of a new peak at 536 nm. A red shift of 164 nm was observed from 372 to 536 nm accompanied with an isoemissive point at 450 nm (Figure 1b). The quantum yield of **N8HQ**-Cd^{2+} complex was found to be 0.31 as measured by taking quinine sulfate as standard. To understand this unusual red shift, the three major mechanisms of fluorescence signal transduction such as intermolecular charge transfer (ICT),[21−23,26,27] fluorescence resonance energy transfer (FRET)[38−40] and photoinduced electron transfer (PET)[16,18,27,28] were explored. The possibility of FRET was ruled out as there was no donor and acceptor separately in our design.[39] So the ICT mechanism was explored initially. But the lowest unoccupied molecular orbital (LUMO) on amide portion of norbornene was much higher in energy than quinoline LUMO (see the Supporting Information, Table S1). Because of this, the possibility for the internal charge transfer was less favorable. Finally the possibility of the PET mechanism was proposed. In general, PET mechanism was proposed for the systems where it could only change the fluorescence intensity.[28] In those systems, the sensor molecule would have an receptor (binding site) and a fluorophore. During the event of metal binding, the sensor molecule would show a fluorescence enhancement due to PET. But in our design, there was no separate binding site and fluorophore. After binding to cadmium, we strongly believed that the whole molecule itself involved in the emission process. Because of this, a huge red shift was observed. We hypothesized that the huge red shift was due to (i) the prevention of nonradiative relaxation pathways of N- lone electron pairs in the molecule by Cd^{2+} binding and (ii) photoinduced electron transfer (PET) between 8-hydroxyquinoline and norbornene motif (Figure 2a).
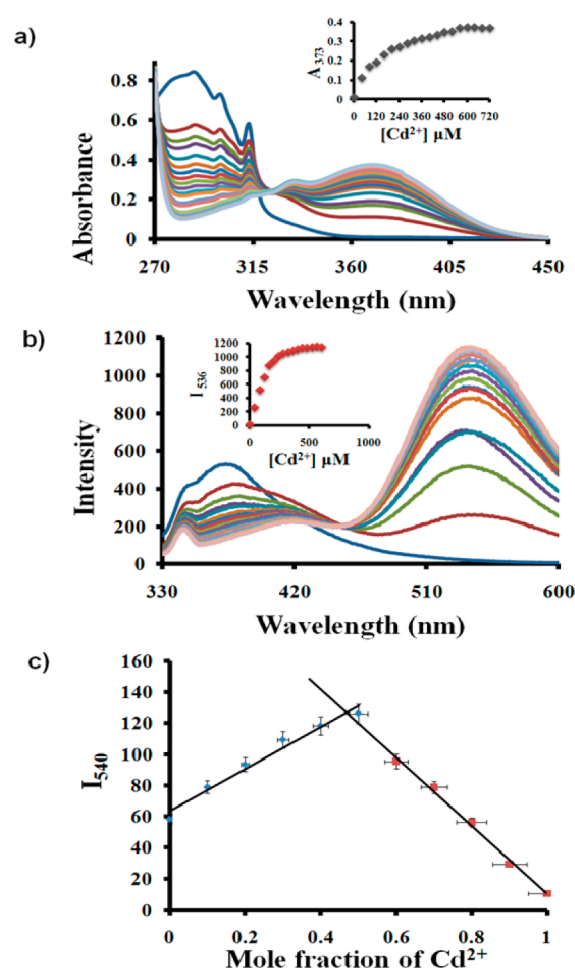

Figure 1. (a) Absorbance spectra of **N8HQ** upon titration with Cd^{2+} in in MeOH-H_2O (1:1). Inset, titration curve based on absorbance at 373 nm. (b) Emission spectra of **N8HQ** $(4 \times 10^{-4}$ M$)$ in MeOH-H_2O (1:1) with gradual addition of Cd^{2+} $(4 \times 10^{-4}$ M$)$. Inset: titration curve based on emission at 540 nm. λ_{ex}: 310 nm. (c) Job's plot showing 1:1 binding stoichiometry between **N8HQ** and Cd^{2+} in MeOH-H_2O (1:1).

While titrating with Cd^{2+}, it was observed that fluorescence intensity at 536 nm increased linearly and remained constant after addition of 1 equiv. of Cd^{2+}. This supported our hypothesis for a 1:1 binding stoichiometry between **N8HQ** and Cd^{2+}. To determine the stoichiometry between **N8HQ** and Cd^{2+}, a method of continuous variation, i.e., Job's method, was followed.[41] Results confirmed our prediction of a 1:1 binding of Cd^{2+} to **N8HQ** (Figure 1c). The apparent dissociation constant of **N8HQ**-Cd^{2+} was calculated to be 50 μM (see Figure S14 in the Supporting Information).[27]

To explore the metal ion binding sites of **N8HQ**, we carried out density functional theory (DFT) calculation[36] without Cd^{2+} at the B3LYP/6-31G(d) level using the Gaussian 09 package (see Figure S12 in the Supporting Information). Structure optimization with Cd^{2+} was done for two proposed structures, **I** and **II** (see Figure S13 in the Supporting Information). In proposed structure **I**, the coordination of Cd through carboxylate oxygen while in the case of **II**, the coordination was through norbornene anhydride oxygen. It could be seen from the optimized structure that a Cd^{2+} ion suitably fit between the nitrogen of 8-hydroxyquinoline (see Table S2 in the Supporting Information). Also, the bond length in the case
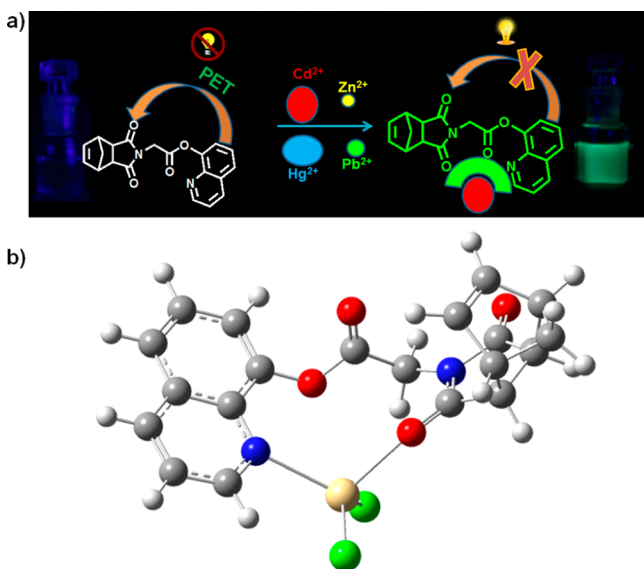
Figure 2. (a) Cartoon representation for the proposed binding site and PET; (b) calculated energy minimized structure of **N8HQ** with proposed binding sites for CdCl$_2$.

Figure 3. Image of Solutions of **N8HQ**-metal complexes of various metal ions in MeOH-H$_2$O (1:1) taken under UV lamp (top). Demonstration of the Cd^{2+} sensing in water by polymer (**PN8HQ**) coated paper strip (bottom left). **PN8HQ** film on quartz slide after dipping into cadmium solution exposed under UV lamp (bottom right).

of structure **II** was shorter than structure **I**. The observed lower in energy (11.4 kcal/mol) of structure **II** than **I** also strongly favored the cadmium coordination to norbornene anhydride oxygen. Finally the proposed 1:1 structure (Figure 2b) was supported by mass spectroscopy. It was seen that **N8HQ** alone showed a mass peak at 349. After addition of cadmium, **N8HQ**-Cd^{2+} peak was obtained at 461, whereas **N8HQ**-CdCl$_2$ was observed at 531 (see Figures S10 and S11 in the Supporting Information).

The specificity of the sensor molecule **N8HQ** toward Cd^{2+} was also determined. Equal amounts (1 equiv.) of various metal ions Hg^{2+}, Pb^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}, Na$^+$, Mg^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+} were added separately to **N8HQ** in methanol−water (1:1) and fluorescence spectra were recorded. Only Cd^{2+} induced a significant characteristic red shift (see Figure S5 in the Supporting Information). Plot of intensity ratio (I$_{536}$/I$_{372}$) against different metal ions indicated none of them other than Cd^{2+} induced a red shift accompanied with enhancement in fluorescence (Figure 4a). The concentration of other metal ions was ten times greater than that of Cd^{2+} ions. The fluorescence enhancement with Cd^{2+} was almost four times greater than with Zn^{2+}. Among other metals, Fe^{2+} quenched the fluorescence of **N8HQ**. When all the metal solutions of **N8HQ** were irradiated with a hand-held UV light, Cd^{2+} showed a bright green emission and could be distinguished visually (Figure 3). These results demonstrated the selectivity behavior of **N8HQ**, especially between Zn^{2+} and Cd^{2+}. The binding sites of **N8HQ** suitably fit for only cadmium in presence of other metal ions and emits bright green emission as shown in Figure 2a. Selectivity of **N8HQ** to Cd^{2+} among various anions also confirmed by fluorescence spectroscopy (see Figure S8 in the Supporting Information). A lowest detection limit of 1.6 nM Cd^{2+} for **N8HQ** was determined through fluorescence titration experiment (see Figure S6 in the Supporting Information). Finally, the reversibility behavior of the molecule **N8HQ** was also tested. EDTA was used as metal chelator. With the addition of EDTA to **N8HQ**-Cd^{2+} complex, fluorescence emission was completely turned off and the emissions were similar to the free **N8HQ**. Again with addition of Cd^{2+} a red
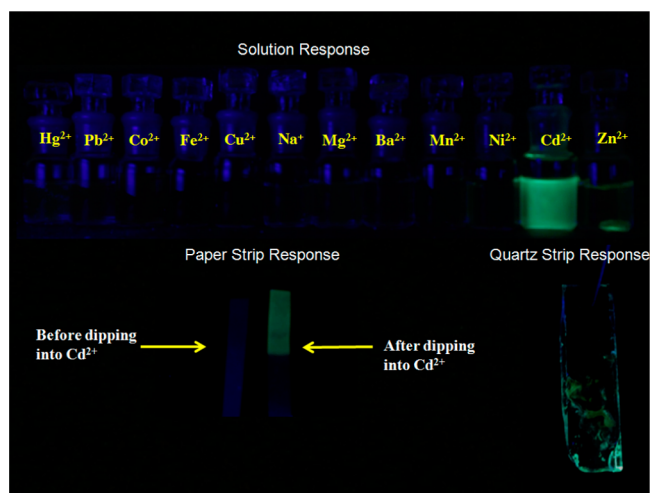
shift of 164 nm with fluorescence enhancement was observed (see Figure S7 in the Supporting Information). This was tested up to five cycles. These findings indicated that **N8HQ** acts as a reversible sensor molecule.

After the successful demonstration of Cd^{2+} sensing in monomer level, **N8HQ** was polymerized by using Grubbs second generation catalyst to form **PN8HQ** (Scheme 1). ^{1}H NMR spectroscopy confirmed the formation of polymer (see Figure S9 in the Supporting Information). Paper strips were prepared by coating the polymer solution on a filter paper to demonstrate the in-field device application. The green emission was observed from the polymer coated paper strip after dipping into a cadmium chloride solution under a hand-held UV lamp as shown in the Figure 3. The paper strips made of **PN8HQ** showed a turn on response similar to its monomer under the UV lamp (supporting video). Surprisingly, the selectivity of the paper strip as well as quartz slide was very specific to cadmium as shown in Figure 3. Being in the same group in the periodic table cadmium and zinc possess similar chemical properties. Hence, they provide the same spectral changes while binding with most of the sensor molecules reported in the literature. Even in our hand, with our monomer molecule **N8HQ**, a little turn on response was observed. Interestingly, it was observed that zinc did not show any response with paper strips. It was further confirmed by the fluorescence spectroscopy where the **PN8HQ** coated quartz slide was excited at 310 nm. The fluorescence response was observed after dipping the slide in to each metal ion solutions. It was only with cadmium, the quartz slide became green (Figure 3) and showed the fluorescence spectrum (Figure 4b). To best of our knowledge this is the first report that demonstrates the paper strip model that can efficiently sense Cd^{2+} in presence of other metals including Zn^{2+}. Finally, the presence of anions along with cadmium was also tested. It was observed that presence of anions did not stop the turn on response of the sensor molecule (Figure 4c).

■ CONCLUSIONS

In conclusion, we have designed a unique 8-hydroxyquinoline based ratiometric sensor for Cd^{2+}, **N8HQ**, that can detect Cd^{2+}
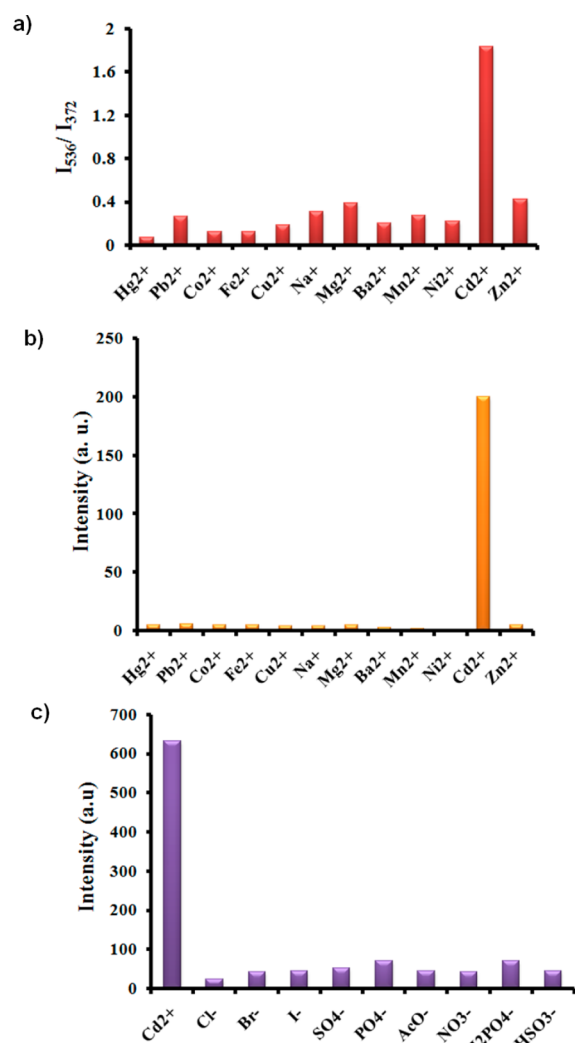
a)

b)

c)

Figure 4. (a) Emission ratio of **N8HQ** at 536 and 372 nm (I_{536}/I_{372}) in the presence of indicated metal ions in MeOH: H_2O (1:1). ex: 310 nm. (b) Fluorescence intensity of **PN8HQ** film on quartz slide in presence of Cd^{2+} and different metal ions. λ_{ex}: 310 nm. (c) Change in fluorescence intensity of **N8HQ** in presence of Cd^{2+} and different anions in MeOH-H_2O (1:1). λ_{ex}: 310 nm.

in nanomolar level in aqueous environment with a large red shift. We hypothesis that the huge red shift is due to the prevention of nonradiative relaxation pathways of N lone electron pairs in the molecule by Cd^{2+} binding. Photoinduced electron transfer (PET) between 8-hydroxyquinoline and norbornene motif is responsible for the unusual red shift. The system behaves reversibly and is able to efficiently distinguish between Zn^{2+} and Cd^{2+}.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Detailed synthesis, characterization, and selected UV and fluorescence data are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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