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A Bis-Quinoline Appended Azobenzene Based Naked Eye Sensor for Selective Detection of Cd^{2+} Ion

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Abstract A new azobenzene chromophore (AZQU), appended with a bis-quinoline unit as a turn-on chemosensor for selective detection of Cd^{2+} ions, has been designed and synthesized. The fluorescent receptor AZQU has an excellent selectivity and sensitivity towards Cd^{2+} ions over other metal ions in CH_3CN:H_2O (80:20, v/v) solution. AZQU is red colored and non-fluorescent in the absence of Cd^{2+} ions, but upon addition of Cd^{2+} ions it turns colorless with appreciable fluorescence. This “off–on” type signaling behavior is attributed to the CHEF (chelation-enhanced fluorescence) effect of the quinoline unit and the change in color from red to yellow occurs by an ICT process with Cd^{2+}. The association constant for AZQU + Cd^{2+} was calculated to be 1.68×10^5 L·mol^{-1} with binding in the 1:1 stoichiometric ratio.

Keywords Azobenzene · Chemosensor · 8-Hydroxyquinoline · Naked eye sensor

1 Introduction

Metal cations play a major role in many biological and environmental processes. The qualitative and quantitative determinations of metal ion present in biological and environmental systems are of current interest in the field of supramolecular chemistry [1–3]. Recently, numerous chemosensors have been developed by various research groups to selectively detect and determine the cation with a variety of sensing mechanisms [4–6]. Transition metals such as Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+} and Cd^{2+} are essential in various

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biological systems at the allowed levels of concentration suggested by WHO. However, excessive concentration of such metals may leads to acute and chronic toxicity to all living organism [7]. Of these transition metals, cadmium is extremely toxic and carcinogenic in nature. Cadmium effluents are mainly discharged from steel processing and paint industries and prolonged exposure to cadmium leads to liver, kidney and cardiovascular diseases and, most importantly, cancer risk to humans [8]. Hence, recognition and detection of Cd^{2+} is of great interest since it is highly toxic to all living organisms. Very few colorimetric as well as fluorometric chemosensors for Cd^{2+} have been reported so far [9, 10]. Therefore, detection of Cd^{2+} in biological and environmental concern has attracted a lot of attention of the research community. There are numerous methods known for cation detection in biological and environmental samples. But, recently the most familiar technique is by analyzing modulation in fluorescence and absorption signals which ensure high sensitivity and ease of use that can be well read by the naked eye without acquiring any sophisticated analytical instrumentation [11, 12].

There is great demand for the design and synthesis of specific colorimetric and fluorometric sensors for selective detection of toxic metal ion in the environment. The design of such optical probes typically involves selective construction of a binding unit in a chromophore that allows the binding event, while in turn the photo-physical behavior of the chromophore results in easily measurable colorimetric or fluorimetric responses [13]. Moreover, there are only a few reports on the combination of an azobenzene sensing unit with another fluorophore. Cheng et al. [14] reported synthesis of azobenzene coupled with a pyrene molecule that selectively detects Hg^{2+} both colorimetrically and fluorometrically. Similarly, Das et al. [15] constructed a molecule with two phthalimide moieties connected to the tertiary amine part of the azobenzene chromophore that selectively detects Nd^{3+} ions both colorimetrically as well as fluorometrically.

Based on the reported literature, the present sensor was designed and synthesized with 8-hydroxy quinoline appended azobenzene chemosensor for selective sensing of Cd^{2+} ions in aqueous medium. 8-Hydroxyquinoline is a well-known fluorophore that chelates metal ions like Hg^{2+}, Zn^{2+} and Al^{3+} because of its electron rich N atom in the 8-position on the pyridine ring and O atom of phenol group, which tend to coordinate with these metal ions [16–19]. In our previous works, coupling of the azobenzene chemosensor with electron rich bis-triazole and bis-pyridine units to identify a chemosensing property with Cu^{2+} ion was investigated by the naked eye detection method. However, it lacks a detection limit even at lower concentrations [20, 21]. Hence, the fluoro-ionophore in the receptor molecule has been constructed. Coupling of the 8-hydroxyquinoline fluorophore with non-fluorescent azobenzene has hitherto not been reported for selective chemosensors. The azobenzene-based chemosensor has attracted considerable attention from fundamental and applied points of view, attributed to its ease of synthesis and ability to tune its spectral properties by substituting a desired functionality.

2 Experimental

2.1 Materials and Techniques

All the chemicals for synthesis were purchased from commercial suppliers and used without further purification. Perchlorate salts of Na^{+}, K^{+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Al^{3+} were purchased from Alfa Aesar, 8-hydroxyquinoline was purchased from

Sigma Aldrich, India. Aniline, 2-chloroethanol, potassium carbonate, potassium iodide, phosphorus oxychloride and sodium hydroxide were purchased from Merck, India and used as received. All the reagent-grade solvents were purified by reported procedures and freshly distilled prior to use [22]. Thin layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA).

Column chromatography was performed on silica gel (60–120 mesh). FT-IR spectra were recorded with an IR spectrometer (Perkin–Elmer) using KBr pellets. Elemental analysis was performed on a Perkin–Elmer 240 instrument. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 and 500 MHz spectrometers using tetramethylsilane (TMS) as an internal reference. Electron spray mass spectra (ESI–MS) were carried out on a Bruker MaXis 10138 HRMS instrument. UV–Vis spectra were recorded at room temperature using a Shimadzu UV-1650PC spectrophotometer. Fluorescence spectra were recorded at room temperature using a Perkin Elmer LS-45 Fluorescence spectrometer.

2.2 General Procedures of Spectral Detection

All experiments were carried out in acetonitrile/water (80/20, v/v) solution. Stock solutions (0.1 $\mathrm{mmol{\cdot}L^{-1}}$) of the receptor AZQU were prepared in acetonitrile: water (80:20, v/v) mixture. The absorption and fluorescence spectra were measured using 5 $\mu\mathrm{mol{\cdot}L^{-1}}$ AZQU in aqueous solution with varying concentrations of metal cations.

2.3 General Procedure for the Synthesis of Compounds

2.3.1 Synthesis of 2,2′-(Phenylazanediyl)diethanol (1)

In a three-necked round-bottomed flask, equipped with a stirrer, dropping funnel, and a reflux condenser topped by a calcium chloride tube, was placed 15.83 g of potassium carbonate (128.4 mmol) in dry acetone (100 mL). To a stirred mixture 2 g of aniline (21.4 mmol), 6.91 g of 2-chloroethanol (85.9 mmol) was added dropwise with stirring and then the solution was refluxed for 3 days with a catalytic amount of potassium iodide. Then, the reaction mixture was filtered. The solvent was removed using a rotary evaporator; the crude product was subjected to column chromatography using ethyl acetate: hexane (2:8) as solvent mixture to obtain 4 g (63 %) of a colorless white solid as product. FT-IR (KBr, $\mathrm{cm^{-1}}$) υ: 3392 (O–H), 3052, 3024 (C–H), 2942, 2878 (CH_2), and 1605 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.24 (m, 2H, Ar–H), 6.73 (d, $J = 6.9$ Hz, 2H, Ar–H), 6.68 (dd, $J = 8.4$ Hz, 1H, Ar–H), 4.12 (s, 2H, –OH), 3.78 (t, $J = 4.8$ Hz, 4H, –O–Me), and 3.52 (t, $J = 4.8$ Hz, 4H, –CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$: Me_4Si) δ (ppm): 147.86, 129.31, 116.83, 112.55, 60.72, and 55.40.

Analysis Calculated for $C_{10}H_{15}NO_2$:C, 66.27; H, 8.34; N, 7.73; found C, 66.25; H, 8.30; N, 7.71.

2.3.2 Synthesis of N,N-Bis(2-chloroethyl)aniline (2)

2,2′-(Phenylazanediyl)diethanol (2.0 g, 11 mmol) in phosphorus oxychloride (25 mL) was refluxed for 6 h and the hot reaction mixture was poured with stirring into crushed ice. The reaction mixture was extracted with ethyl acetate and washed with 10 % sodium bicarbonate solution. The combined organic layer was dried, filtered and the solvent was removed by a rotary evaporator; the crude product was subjected to column chromatography using hexane as eluent to obtain 2.1 g (92 %) of an off white solid as product. FT-IR (KBr, cm^{-1}) υ: 2973 (C–H), 1602 (C=C), 1169 (C–N), and 748 (C–Cl). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.12 (m, 2H, Ar–H), 6.68 (d, $J = 6.9$ Hz, 2H, Ar–H), 6.67 (dd, $J = 8.4$ Hz, 1H, Ar–H), 3.90 (t, $J = 3.3$ Hz, 4H, $–CH_2–$), and 3.76 (t, $J = 3.3$ Hz, 4H, $–CH_2–$); ^{13}C NMR (100 MHz, $CDCl_3$: Me_4Si) δ (ppm): 149.14, 128.49, 121.80, 111.41, 77.77, 77.35, 76.92, 56.09, 56.07, 42.94, and 42.87.

Analysis Calculated for $C_{10}H_{13}Cl_2N$:C, 55.06; H, 6.01; N, 6.42; found C, 54.98; H, 5.98; N, 6.39.

2.3.3 Synthesis of N,N-Bis(2-chloroethyl)-4-((4-nitrophenyl)diazenyl)aniline (3)

The diazonium salt of 4-nitroaniline was prepared by adding an aqueous solution of sodium nitrite (0.414 g, 6 mmol) drop wise into a solution of 4-nitroaniline (0.7 g, 5 mmol) dissolved in a $HCl{:}H_2O$ mixture. The mixture was stirred at 0 °C for 30 min. The diazonium salt solution was added drop wise into a solution containing 1.1 g of N,N-bis(2-chloroethyl) aniline, 240 mg (6 mmol) of sodium hydroxide in a small amount of water and 15 mL of THF; immediately afterwards the color of the solution turned to dark red and a precipitate of azo compound formed. Then, the mixture was stirred for few hours and it was poured into an excess amount of ice cold water. The precipitate was collected by a filtering funnel and repeatedly washed with water. The crude product was subjected to column chromatography using a solvent mixture of (1:10) ethyl acetate and hexane to obtain as dark red needles with yield of 85 % (1.1 g). FT-IR (KBr, cm^{-1}) υ: 2992 (C–H), 1605 (–C=C–), 1510, 1350 ($–NO_2$), 1178 (C–N), and 743 (C–Cl). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 8.21 (d, $J = 8$ Hz, 2H, Ar–H), 8.14 (d, $J = 8$ Hz, 2H, Ar–H), 7.96 (d, 2H, $J = 8$ Hz, Ar–H), 6.98 (d, $J = 8$ Hz, 2H, Ar–H), 4.04 (t, $J = 8$ Hz, 4H, $–CH_2–$), and 3.82 (t, $J = 8$ Hz, 4H, $–CH_2–$); ^{13}C NMR (100 MHz, $CDCl_3$: Me_4Si) δ (ppm): 155.35, 149.14, 148.52, 145.19, 125.89, 123.24, 121.80, 112.66, 56.09, and 40.88.

Analysis Calculated for $C_{16}H_{16}Cl_2N_4O_2$:C, 52.33; H, 4.39; N, 15.26; found C, 52.31; H, 4.36; N, 15.19.

2.3.4 Synthesis of 4–9(4-Nitrophenyl)diazenyl)-N,N-bis(2-(quinolin-8-yloxy)ethyl)aniline (AZQU)

In a 250 mL three-neck round-bottom flask was placed 100 mL of dry acetone. Then, 8-hydroxyquinoline (2.69 mmol, 2 g), K_2CO_3 (10.8 mmol, 1.48 g) and a small amount of KI were added under a nitrogen atmosphere. N,N-Bis(2-chloroethyl)-4-((4-nitrophenyl)-diazenyl)aniline (**3**) was added drop wise over an hour in the addition funnel containing 20 mL of acetone and the mixture was stirred for 24 h at 80 °C under a nitrogen atmosphere. After completion of the reaction (which was monitored by TLC), the reaction mixture was filtered through a filtering funnel and concentrated under reduced pressure, The resulting crude product was purified by silica gel column chromatography using hexane/EtOAc to obtain a dark red solid (1.47 g, 67 %). FT-IR (KBr, cm^{-1}) υ: 3004, 2942 (C–H), 1640 (–C=N–), 1448 (–N=N–), and 1376 (NO_2). ^1H NMR (500 MHz, $CDCl_3$, Me_4Si) δ (ppm): 8.88 (d, $J = 4.2$ Hz, 2H, Ar–H), 8.36 (d, $J = 9.0$ Hz, 2H, Ar–H), 8.14 (d, $J = 8.3$ Hz, 2H, Ar–H), 7.94 (d, $J = 8.9$ Hz, 2H, Ar–H), 7.45–7.35 (m, 6H, Ar–H), 7.12–6.99 (m, 6H, Ar–H), 4.62 (t, $J = 6.3$ Hz, 4H, $–CH_2–$), and 4.31 (t, $J = 6.3$ Hz, 4H, –OMe–).^{13}C NMR (125 MHz, $CDCl_3$: Me_4Si) δ (ppm): 156.16, 151.87, 150.15, 149.00, 144.45, 140.71, 134.82, 129.65, 129.20, 127.92, 127.00, 126.63, 123.85, 121.01, 118.98, 105.97, 66.94, and 59.80.

Analysis Calculated for $C_{34}H_{28}N_6O_4$:C, 69.85; H, 4.83; N, 14.38; found C, 69.79; H, 4.80; N, 14.35. ESI–MS (*m/z*): calculated for $C_{34}H_{28}N_6O_4$ $[M + H]^+$: 584.22, found: 584.15.

3 Results and Discussion

The general synthetic routes to prepare the bis-quinoline appended azobenzene receptor AZQU are summarized in Scheme 1. Briefly, the synthesis of 2,2′-(phenylazanediyl)diethanol (**1**) was achieved by reaction of aniline with 2-chloroethanol in refluxing acetone, catalyzed by basic K_2CO_3 and a small pinch of KI as reactivity enhancer with a 63 % yield. N,N-bis(2-chloroethyl) aniline (**2**) was prepared by refluxing with excess of $POCl_3$ for 24 h with 92 % yield. Then it was condensed with diazotized nitroaniline in the presence of sodium acetate to get N,N-bis(2-chloroethyl)-4-((4-nitrophenyl)diazenyl)aniline (**3**) with 85 % yield. Finally, the receptor AZQU was prepared with good yield by using precursor **3** with 8-hydroxyquinoline in the presence of K_2CO_3/KI as catalyst. The synthesized AZQU was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra.

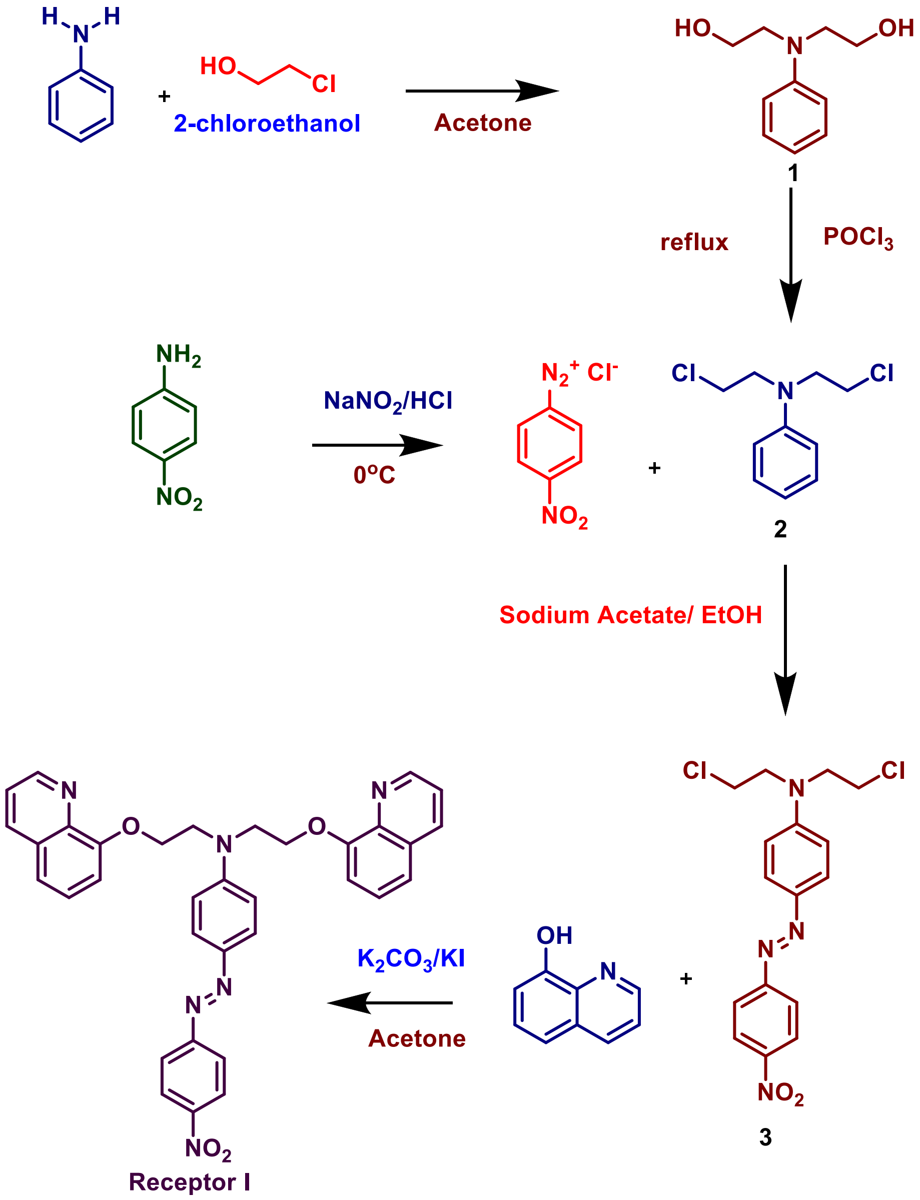
3.1 Colorimetric Investigation

The free receptor AZQU formed a red color solution in acetonitrile/water medium and with the addition of cadmium ion the red color suddenly turned pale yellow. No significant color change was observed on the addition of other studied metal ions (Fig. 1). This feature shows that the receptor AZQU acts as a naked eye sensor for the cadmium ions.

3.2 Photophysical Studies of Receptor AZQU

The photophysical behavior of receptor AZQU were investigated with several metal cations: Na^+, Al^{3+}, K^+, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} as their perchlorate salts in CH_3CN/H_2O (80:20, v/v) by using UV–Vis measurement and fluorescence measurement at pH 7.2 (HEPES buffer). The absorption spectrum of AZQU alone has absorption maxima at 287 and 466 nm. The absorption at 466 nm is assigned to $n - \pi^*$ transition of the azobenzene chromophore by their strong push–pull effect from donor nitrogen to the acceptor $–NO_2$ group [23, 24]. Absorption at 287 nm is assigned to a $\pi - \pi^*$ transition of the alkylated 8-hydroxy quinoline. Figure 2 shows the absorption spectral changes of receptor AZQU in CH_3CN/H_2O (80:20, v/v) upon addition of various competitive metal ions. The UV–Vis spectra of AZQU clearly shows the formation of a new absorption band centered at 322 nm in the presence of five equivalents of Cd^{2+} ion, with a distinct color change from red to pale yellow. However, no appreciable spectral changes were observed upon addition of competitive metal cations, which indicates that the selectivity of the receptor AZQU for Cd^{2+} ion over other competitive cations is high enough.

To investigate the binding behavior, a UV–visible titration experiment was performed, During titration, the concentration of AZQU was kept constant at 5 $\mu mol \cdot L^{-1}$ and the moles of Cd^{2+} were varied from 0.25 to 5 $\mu mol \cdot L^{-1}$. Titration of the receptor AZQU with increasing concentrations of Cd^{2+} revealed that the intensity of the absorption band at 287 nm decreased and a new red-shifted absorption band at 322 nm gradually appeared, accompanied by three clear isobestic points at 256, 295 and 383 nm, respectively,



Scheme 1 Synthetic route for receptor AZQU

indicating that AZQU complexes with Cd^{2+} (Fig. 3). The absorption maximum attains saturation at 322 nm with addition of 5 $\mu mol \cdot L^{-1}$ of Cd^{2+} and also a gradual decrease in the absorption band at 466 nm reveals that azobenzene takes part in coordination.

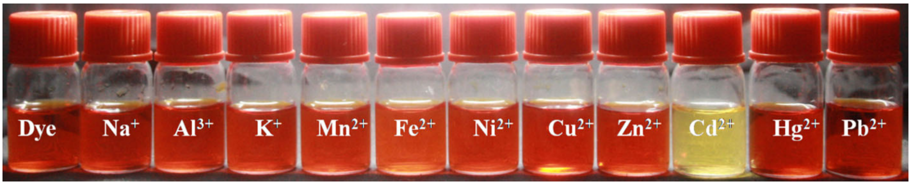


Fig. 1 Pictures of receptor I (100 μmol·L^{-1}) upon addition of various metal ions (five equivalents) in CH_3CN/H_2O (80/20, v/v)

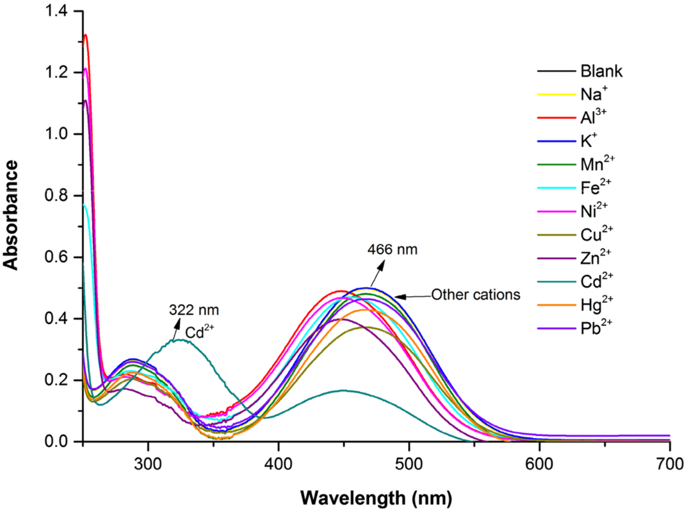


Fig. 2 UV–Vis absorption spectra of receptor AZQU [1 × 10^{-5} mol·L^{-1} in CH_3CN/H_2O (80:20, v/v)] in the presence of different cations (five equivalents)

3.3 Fluorescence Spectroscopic Studies

Emission spectroscopic studies were carried out to prove the effectiveness of receptor AZQU as a fluorescent probe for the detection of Cd^{2+}. The fluorescence ability of AZQU with various metal ions was investigated to examine the selectivity of the receptor by exciting at 322 nm and its emission was monitored from 350 to 600 nm. The fluorescence spectra of AZQU with different metal cations are shown in Fig. 4. Free AZQU is ascribed to a weak fluorescence at 400 nm upon excitation at 322 nm in CH_3CN/H_2O (80:20, v/v) because the electron rich oxygen atom of the quinoline unit quenches the fluorescence behavior of 8-hydroxyquinoline by an effective PET process. Upon the addition of Cd^{2+} ions to the solution of AZQU, the fluorescence is appreciably enhanced at 400 nm ($\phi = 0.18$). The fluorescence enhancement of AZQU with Cd^{2+} ion may be attributed by the chelation-enhanced fluorescence (CHEF) mechanism of 8-hydroxyquinoline in CH_3CN/H_2O (80:20, v/v). Titration of AZQU with increasing concentration of Cd^{2+} ion revealed that the fluorescent intensity increases linearly with the concentration of Cd^{2+} as shown in Fig. 5. Addition of competing metal ions in large excess does not produce any substantial changes in fluorescence intensity. Hence, the receptor is specific for Cd^{2+} only.

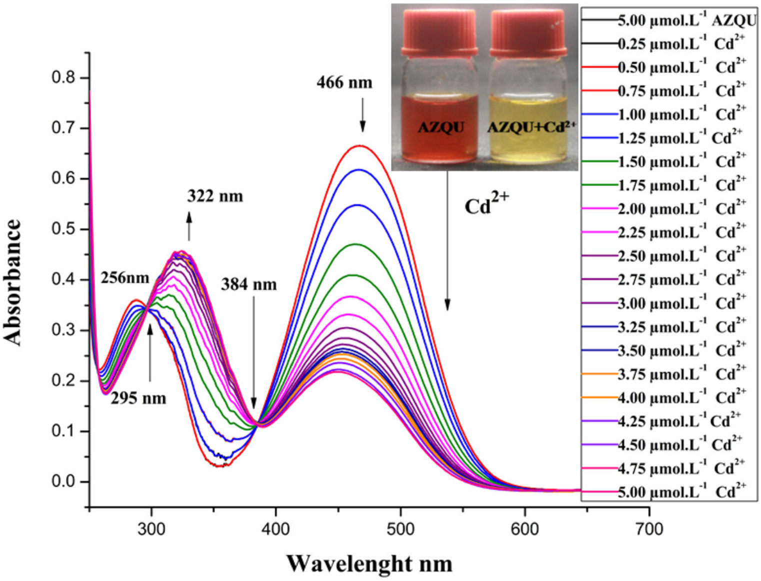


Fig. 3 UV–Vis absorption spectra of receptor AZQU with increasing concentration of Cd^{2+} (0–100 μmol·L^{-1}) in CH_3CN/H_2O (80:20, v/v)

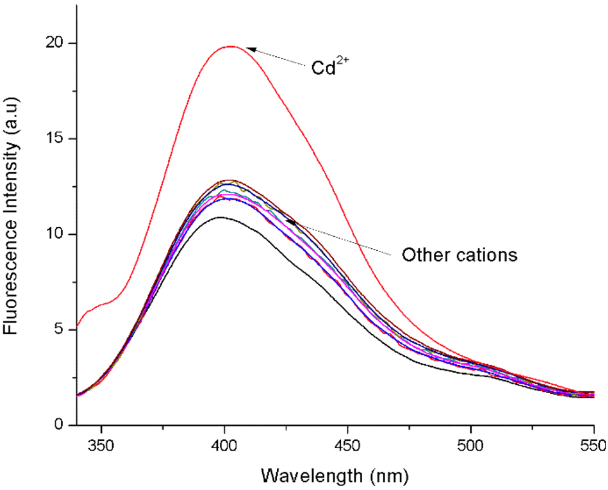


Fig. 4 Fluorescence spectra of receptor AZQU (100 μmol·L^{-1}) upon addition of various metal ions (five equivalents) in CH_3CN/H_2O (80/20, v/v)

We further conducted competition experiments using solutions containing Cd^{2+} and all the other anions. As can be seen, these competitive species did not lead to any significant absorption or fluorescence changes of AZQU, because the azo chromophore does not involve a deprotonation process.

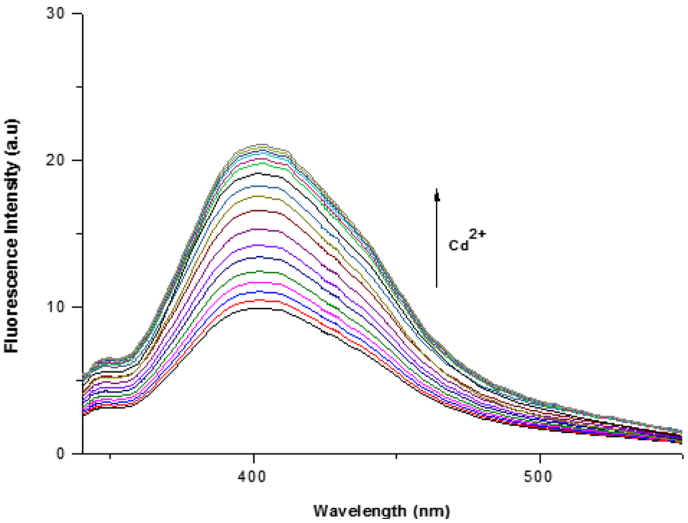


Fig. 5 Fluorescence spectra of receptor AZQU with increasing concentration of Cd^{2+} ion (0–100 μmol·L^{-1}) in CH_3CN/H_2O (80:20, v/v)

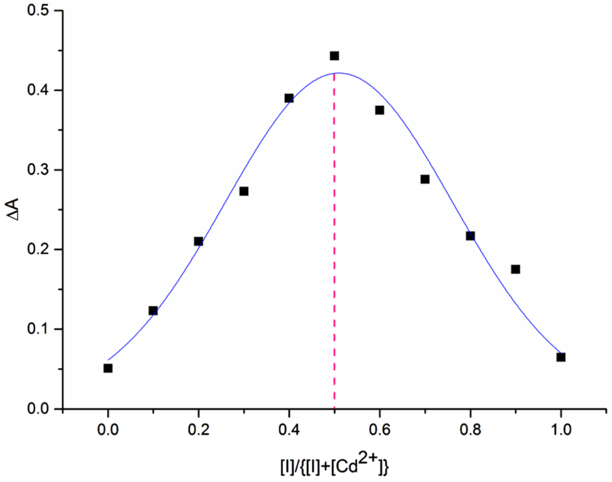


Fig. 6 Job's plot of a 1:1 complex for receptor AZQU and Cd^{2+} in CH_3CN/H_2O

Stoichiometric analysis of the complex between receptor AZQU and Cd^{2+} was performed by means of continuous variation by using Job's method [25] where the absorption of complex at 322 nm was plotted against mole fraction of AZQU under the condition of an invariant total concentration (Fig. 6). Job's plot depicts a maximum absorption center at 0.5 mol fraction of Cd^{2+}, further supporting 1:1 complex formation between AZQU and Cd^{2+}. From UV–Vis absorption measurements, the association constant (K_a) of Cd^{2+} complex with AZQU was calculated using the Benesi–Hildebrand (B–H) equation [26] and it was found to be $K_a = 1.68 \times 10^5$ L·mol^{-1} (Fig. 7).

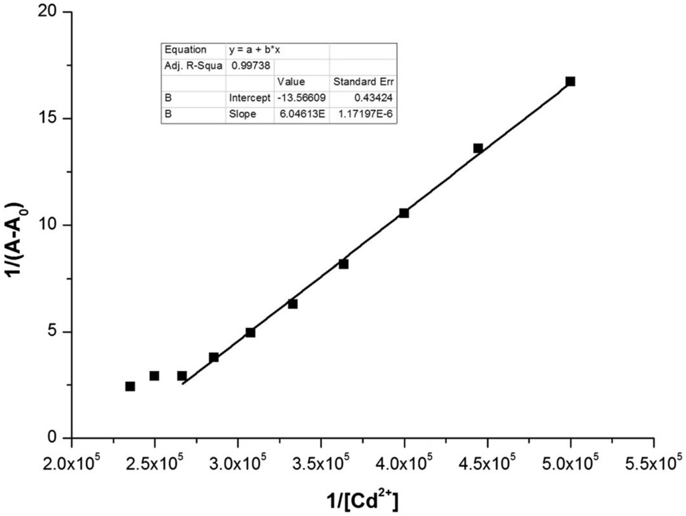


Fig. 7 Benesi-Hildebrand plot for complexation of receptor AZQU with Cd^{2+}

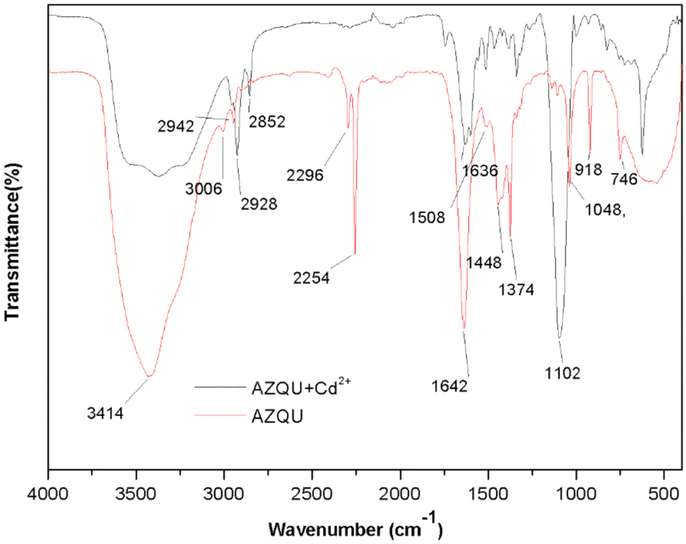


Fig. 8 FT-IR spectra of receptor AZQU with Cd^{2+} ion

3.4 FT-IR and ^{1}H-NMR Spectroscopic Studies for Receptor AZQU

The detailed complexation behavior of receptor AZQU with Cd^{2+}, studied by FT-IR and ^{1}H-NMR, was performed by adding different equivalent of Cd^{2+} to AZQU. Coordination sites of receptor AZQU with Cd^{2+} were identified by IR spectra in the region around 1000–3000 cm^{-1}. In the IR spectra (Fig. 8), the stretching frequency of C=N in the quinoline ring appears at 1642 cm^{-1}, but coordination with Cd^{2+} results in a shift from

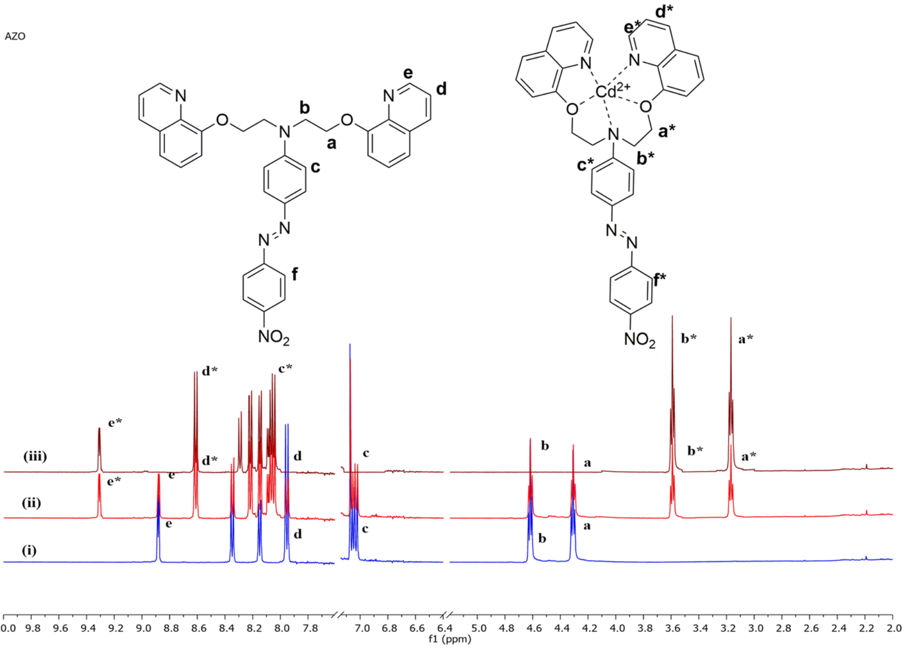
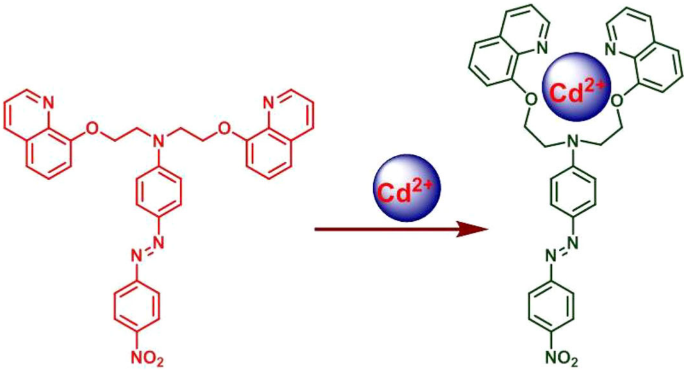


Fig. 9 Partial ^{1}H-NMR in CH_3CN-d_3: (*i*) receptor AZQU only, (*ii*) receptor AZQU + 0.5 equivalents of Cd^{2+} and (*iii*) receptor AZQU + 1 equivalent of Cd^{2+}



Scheme 2 Proposed binding mode of receptor AZQU with Cd^{2+}

1642 to 1636 cm^{-1} ascribed to electron transfer from the electron rich quinoline nitrogen to the Cd^{2+} ion, which clearly gives information about coordination of the Cd^{2+} ion with AZQU.

To further elucidate the precise coordination site of receptor AZQU for Cd^{2+}, ^{1}H-NMR spectra were measured. Figure 9 shows the stacked plots of ^{1}H-NMR spectra of AZQU (10 mmol·L^{-1}) in the absence and also in the presence of various equivalents of Cd^{2+}. Before addition of Cd^{2+}, all individual proton signals of AZQU were assigned. Upon complexation with 0.5 equivalents of Cd^{2+}, there is a significant upfield shift in the aliphatic methyl proton of receptor, from 4.31 ppm (a) and 4.62 ppm (b) to 3.17 ppm (a*) and 3.59 ppm (b*), respectively, indicating the oxygen atom of methoxy group is strongly bonded with Cd^{2+} ions. Similarly, the proton adjacent to the quinoline nitrogen undergoes a downfield shift from 8.88 ppm (e) to 9.30 ppm (e*) due to change in the electron density of quinoline by coordination with Cd^{2+} (Scheme 2).

The tertiary nitrogen of the azo chromophore also participated in coordination with Cd^{2+}. This can be identified because the ortho proton (c) of aniline shifts from 7.04 ppm (c) to 8.06 ppm (c*). This gives prominent results about electron density of the tertiary amine being transferred to the lower electron density of Cd^{2+} ions [27, 28].

4 Conclusions

In conclusion, a new bis-quinoline appended azobenzene receptor AZQU has been successfully synthesized and its dual mode in sensing with Cd^{2+} was studied by colorimetric as well as fluorimetric techniques. Upon additions of Cd^{2+} there is a color change from red to pale yellow due to hindrance of ICT mechanisms in the azo chromophore, which can be identified by the naked eye and by an increase in fluorescence due to the CHEF effect by the two quinoline moieties. Similarly, fluorescence sensors could be further developed and modified for detection of cations in living cells.

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