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ARTICLE TYPE

Quinoline benzimidazole-conjugate for the highly selective detection of Zn(II) by dual colorimetric and fluorescent turn-on responses

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A quinoline benzimidazole-conjugate (**QBC**) has been synthesized for the highly selective detection of Zn(II) both by colorimetry and fluorimetry. Probe **QBC** senses Zn^{2+} over other cations as fluorescence 'off–on' behaviour in HEPES-buffered CH_3CN/H_2O (1:1, v/v, pH = 7.0) solution. A possible mechanism is proposed based on the inhibition of PET and intramolecular restricted torsional rotation through the C-C single bond between the quinoline benzimidazole-conjugate. The Chemosensor is utilized to detect Zn^{2+} in much real sample analysis.

1. Introduction

The development of colorimetric and fluorescent chemosensors for the selective and sensitive detection of chemically and biologically significant metal ions continues to be an area of ever increasing research activity [1]. Zinc ion is an important divalent metal cation in biological system and essential for the human body within sub-nM to ~ 0.3 mM concentration level. It plays a critical role in DNA synthesis, metalloenzyme regulation [2,3] and neurophysiology. While most Zn^{2+} ions are bound to proteins, the disruption of mobile Zn^{2+} is associated with a number of diseases including the formation of β-amyloid related to Alzheimer's disease, ischaemia, epilepsy, and Parkinson's disease [4,5]. Although, zinc ion is helpful for the growth of young children, its deficiency as a nutrient, is a severe threat in many countries [6]. Nevertheless, it is important to monitor the presence of zinc quantitatively and qualitatively in food, biological, and environmental samples. However, the detection of zinc has always been challenging because of the absence of characteristic d-d electronic transition and the absence of redox activity caused by its closed-shell $3d^{10}$ electronic configuration. The exact role of Zn^{2+} can either be structural or functional in biological systems, which are yet to be explored beyond uncertainties [7].

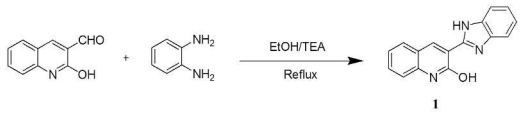
Owing to the importance of Zn^{2+} in biological systems, numerous fluorescent Zn^{2+} sensors based on fluorophores such as quinoline [8], naphthalimide [9], bipyridyl [10], bodipy [11], fluorescein [12], rhodamine [13], pyrene [14], benzoxazole [15], coumarin [16], and other chromophores [17] have been reported. Among these, quinoline is one of the promising classes of fluorophore as it forms strong binding with metals and also reduces the molecular size by rigidification which becomes an important parameter to be used in probing the metal ions in biological systems [18]. In general, the fluorescent properties of quinoline become quenched when substituted with amine due to photoinduced electron transfer (PET) processes. However, suppression of PET by the coordination between Zn^{2+} and amine would enhance the fluorescence, which in fact has been explored as a successful pathway for turn-on fluorescence sensing mechanism. Sensors that contain the quinoline group include those with amide amine ethers [19], hydroxyl quinolines [20, 21], borondipyrromethane [22], fluorescein [23] and spiropyrans [24]. Nevertheless, the detection of zinc metal ion *via* dual chromogenic and fluorescence 'off-on' signalling mechanism has been less explored [25-28]. As a consequence, the development of an efficient Zn^{2+}- ion selective chromogenic and fluorescent sensor becomes important for the fundamental understanding about the role of Zn^{2+} in biological systems. Herein, we report the synthesis and ion recognition properties of a quinoline benzimidazole-conjugate **(QBC)**, which exhibits highly sensitive and selective recognition of Zn^{2+} ion both by colorimetry and fluorimetry with a remarkable fluorescence turn-on response in a semi-aqueous media.

2. Results and discussion

QBC is designed in such a way that the quinoline moiety acts as a fluorophore which is directly linked to the benzimidazole scaffold. The nitrogen atoms and the hydroxyl group present in the benzimidazole and quinoline respectively, acts as receptor units for binding with the Zn^{2+} ion. Their complexation behavior and a possible mechanism are proposed based on the UV-visible absorption and fluorescence spectral studies wherein the carbon-carbon single bond rotation between the quinoline and the benzimidazole moieties becomes arrested during the metal complexation which eventually increases π–conjugation between the two rings thereby enhances the molar absorptivity and emission intensity.

An elegant one step synthetic protocol for the synthesis of the receptor quinoline benzimidazole-conjugate **(QBC)** is

shown in Scheme 1. Briefly, the reaction between 3-formyl-2-hydroxyquinoline [29] and o-phenylenediamine in Ethanol/TEA afforded the crude **QBC** which is then purified by recrystallization in DMF. The sensor was well characterized by the ^{1}H, ^{13}C NMR and mass spectral analysis (Fig. S1-S3). UV-visible and fluorescence spectroscopic techniques were used to evaluate the selectivity and sensitivity of **QBC** towards the metal ions of biological and environmental significance such as Na^{+}, K^{+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zr^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^{+}. The metal ion titrations were carried out by adding the known concentration of various metal salts in CH_3CN/H_2O (1:1 (v/v), HEPES=50 mM, pH=7.0) to a fixed concentration of **QBC** in the same solvent.



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Scheme 1. Synthesis of chemosensor QBC

The UV-visible absorption spectrum of **QBC** in CH_3CN/H_2O (1:1 (v/v), HEPES=50 mM, pH=7.0) show two intense bands with absorption maximum at 213 and 372 nm (Fig. 1 & S4). Addition of Zn^{2+} to the sensor **QBC** solution induces a significant enhancement in the absorption bands at 213 and 372, which eventually led to the colour change from pale yellow to intense yellow colour as shown in Figure 1. Further addition of different metal cations including Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, alkali and alkaline earth metal ions to **QBC** under the identical conditions does not yield any notable spectral and colour changes. This implies that Zn^{2+} can coordinate with **QBC** with exclusive selectivity and sensitivity and the change in colour allows the Zn^{2+} ion detection by the naked eye even without any spectroscopic techniques. The smaller red-shifted maxima of both high-energy and low-energy absorption ca. 12-15 nm suggests the possibility of enhanced π-conjugation within the sensor unit owing to the coordination of Zn^{2+} ions. To further understand the absorption behavior of the probe **QBC** and **QBC**–Zn^{2+} complex, we have carried out DFT calculations using Gaussian 03 program [30]. The initial geometries were optimized at B3LYP/6-31G level of theory and are given in Fig. S5-S8. The calculated absorption spectra of **QBC** shows three major transitions at 228, 261 and 333 nm. The oscillator strength of the peak at 264 and 330 nm increased after the coordination of QBC with Zn^{2+} ion. It can also be understood from the optimized geometries that the quinoline and benzimidazole moieties of **QBC** were not in a coplanar configuration and the dihedral angle of C=C-C-N of quinoline and benzimidazole ring was calculated for **QBC** to be 143.44. However upon Zn^{2+} coordination the dihedral angle becomes 154.22, and the **QBC**-Zn^{2+} complex was found to be in near coplanar configuration, which eventually enhances the π-conjugation pathway. Further, the charges on the N atom of **QBC**–Zn^{2+} complex is calculated to be -0.642 which is comparatively smaller than that of free **QBC** i.e. -0.792. This feature is ascribed to the involvement of nitrogen in the coordination of Zn^{2+} ion.

As can be seen from Fig. 2, the absorbance at 213 and 372 nm of **QBC** gradually increases with the increase in the concentration of Zn^{2+} ion till 70 equivalents (Fig. S9). Generally, transition metal cations with an open shell d-orbital often quench the fluorescence due to the electron or energy

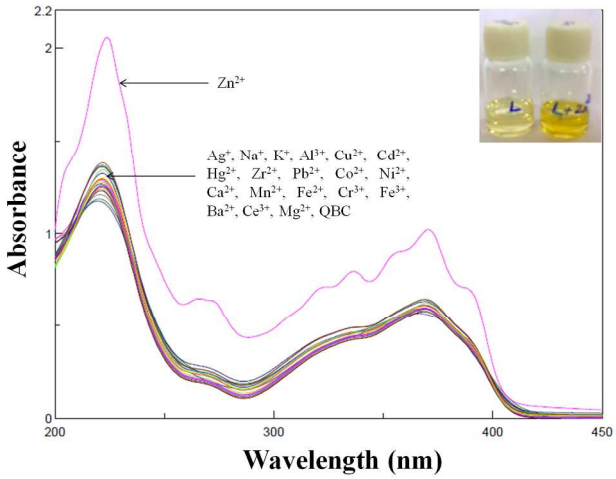


Fig. 1. Absorption changes of **QBC** (4 x 10^{-6} M) solution (CH_3CN-H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.0) in the presence of Zn^{2+}- metal ions (100 equiv.).

transfer processes between the metal cations and fluorophores, providing a very fast and efficient nonradiative decay pathway of the excited states. However, it is expected that metal ions such as Zn^{2+} with close shell d-orbitals do not induce any, new low-energy, metal-centered excited states so that the possibility of additional excited state deactivation pathway can be overruled [31].

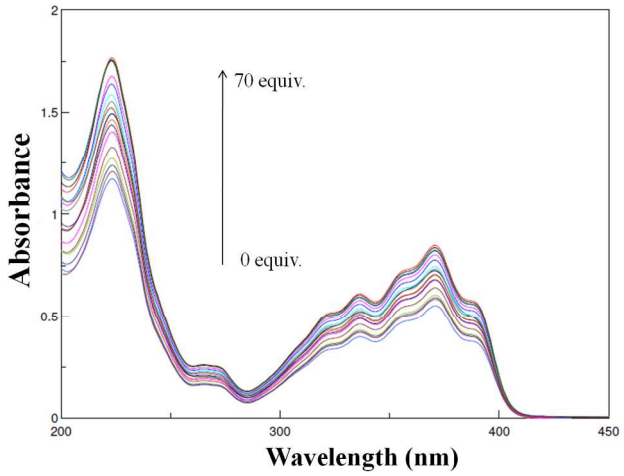


Fig. 2. Changes of absorption intensity of **QBC** (4 x 10^{-6} M) solution (CH_3CN-H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.0) upon addition of different amount of Zn^{2+} (0-70 equiv.).

The metal ion recognition capability of **QBC** was systematically carried out for a variety of metal ions using the fluorescence technique. The fluorescence spectrum of **QBC** (4 μM) exhibited a weak, single emission band at ca. 425 nm at ambient temperature. This is due to intramolecular photoinduced electron transfer (PET) process and the unrestricted torsional rotation between the C-C single bond which covalently links the quinoline and the benzimidazole units. Figure 3 shows the fluorescence spectra (λ_{ex} = 380 nm) of **QBC** (4 μM) measured in CH_3CN/H_2O (1:1 (v/v), HEPES=50 mM, pH=7.0) with different metal ions (100 equiv). Only the addition of Zn^{2+} (100 equiv.) causes a prominent emission enhancement with an intense yellowish-green fluorescence with the emission maxima at 425

nm. In contrast, addition of other cations (Na^+, K^+, Al^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zr^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^+) to **QBC**, under identical conditions show almost no or little fluorescence enhancement. This indicates that **QBC** has a selective emission enhancement toward Zn^{2+} probably by a) inhibiting the photoinduced electron transfer process between quinolone benzimidazole-conjugate and or b) by restricting the rotation of C–C single bond that connects quinoline and benzimidazole ring.

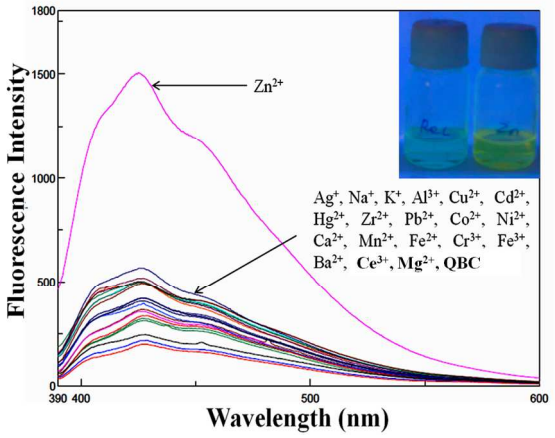


Fig. 3. Fluorescence changes of **QBC** (4 x 10^{-6} M) solution (CH_3CN-H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 380 nm)

To further explore its practical applicability, the interference of other metal ions in the presence of Zn^{2+} on **QBC** was studied. Figure 4 displays the fluorescence emission enhancement upon addition of Zn^{2+} to **QBC**, which are in fact not affected by the addition of other cations. These findings indicate that **QBC** detects Zn^{2+} selectively and the presence of other metal ions does not interfere with the detection of Zn^{2+} ions. Although this chemosensor did not overcome the influence, it is worth mentioning that many Zn^{2+} chemosensors suffer from low selectivity over Cd^{2+}. However, this chemosensor eliminated the problem by inhibition of PET mechanism between quinoline benzimidazole-conjugates. This indicates that **QBC** coordinates with Zn^{2+} more strongly, as is observed for quinoline benzimidazole-linkage.

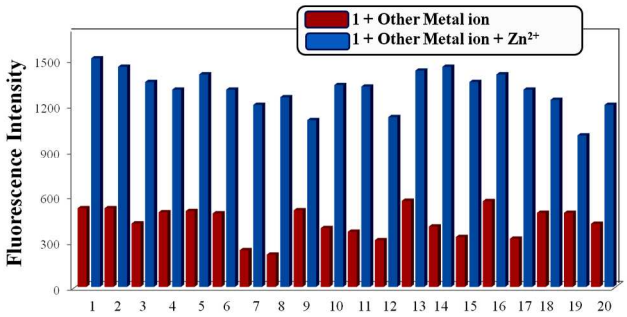


Fig. 4. Metal ions competition analysis of **QBC** (4 x 10^{-6} M) in CH_3CN/H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.0. The red bars represent the fluorescence emission of **QBC** and 100 equiv. of other metal ions. The blue bars represent the fluorescence changes that occur upon addition of 100 equiv. of other metal ions to the solution containing **QBC** and Zn^{2+} (100 equiv.). 1. **QBC**, 2. Na^+, 3. K^+, 4. Al^{3+}, 5. Cu^{2+}, 6. Cd^{2+}, 7. Hg^{2+}, 8. Zr^{2+}, 9. Pb^{2+}, 10. Co^{2+}, 11. Ni^{2+}, 12. Ca^{2+}, 13. Mn^{2+}, 14. Cr^{3+}, 15. Ba^{2+}, 16. Ce^{3+}, 17. Mg^{2+}, 18. Fe^{2+}, 19. Fe^{3+}, 20. Ag^+.

Figure 5 shows the fluorescence titration spectra of **QBC** with the gradual increasing concentration of Zn^{2+} added. Stepwise, gradual addition of the Zn^{2+} to **QBC** led to an emission enhancement in the fluorescence intensity and becomes saturated when 75 equivalents of Zn^{2+} was added (Fig. S10). The Job's continuous variation method is utilized to find out the stoichiometry between the Zinc chloride and **QBC**. As can be seen from Figure 6, the maximum value was found at the mole fraction 0.52, which is indicative of the 1:1 binding stoichiometry between **QBC** and Zn^{2+} [32].

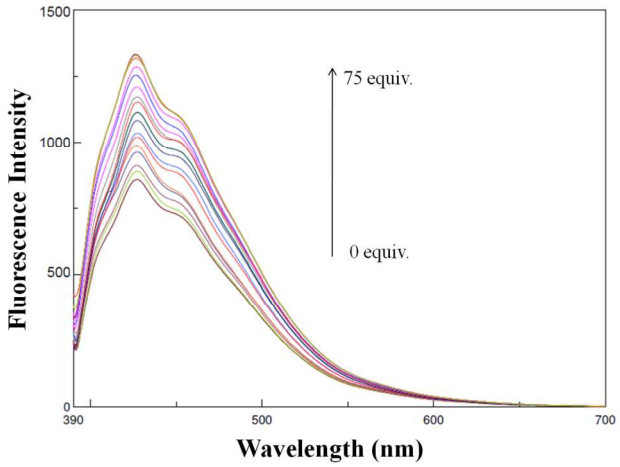


Fig. 5. Changes of fluorescence intensity of **QBC** (4 x 10^{-6} M) solution (CH_3CN-H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.0) upon addition of different amount of Zn^{2+} (0-75 equiv. excited at 380 nm) emission = 425 nm.

The fluorescence titration data obtained with Zn^{2+} (425 nm) is plotted by $1/(I - I_0)$ vs $1/[Zn^{2+}]$ (Fig. 7). On the basis of titration profile, using the non-linear fitting of the titration curve of 1:1 binding model, the association constant (K_a) of **QBC**+Zn^{2+} was computed to be 1.53 x 10^4 M^{-1}, indicating that the probe can detect Zn^{2+} at the micromolar level. The detection limit of **QBC** calculated using the formula 3δ/S [33], where δ is the standard deviation of the blank signal, and S is the slope of the linear calibration plot is to be 1.5 × 10^{-5} M. Indeed, the detection limits of **QBC** towards Zn^{2+} cation are closer (drinking water = 5 mg/L) to the regulation levels set by the US National Environmental Protection Agency (EPA) [34].

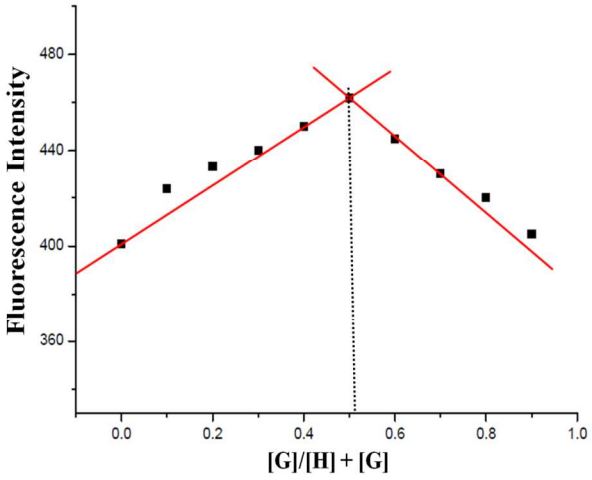


Fig. 6. Job's plot for probe **QBC** in CH_3CN-H_2O (1:1 v/v, HEPES = 50 mM, pH=7.0) solutions.

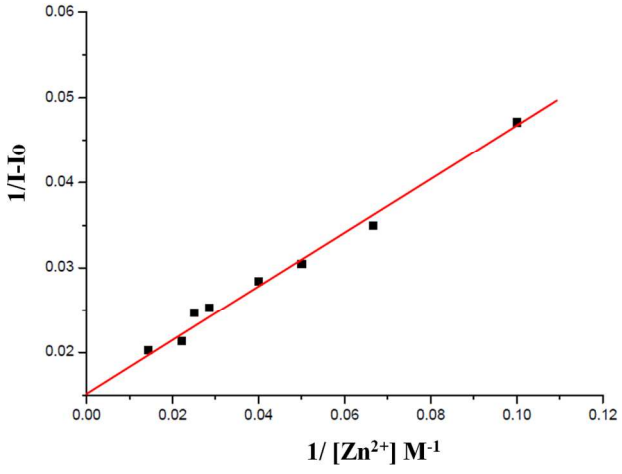


Fig. 7. Benesi–Hildebrand plot (emission 425 nm) of **QBC,** assuming 1:1 stoichiometry for association between **QBC** and Zn^{2+}.

^1H NMR analysis were performed to further support the coordination structures for Zn^{2+} complex with **QBC** in a D_2O/DMSO mixture (1/2 v/v, pH=7.0). Figure 8 shows the partial ^1H NMR spectra of **QBC** measured in a D_2O/DMSO mixture (1/2 v/v, pH=7.0) with and without Zn^{2+} (0-2 equiv). All chemical shifts were identified by ^1H–^1H COSY analysis (Fig. S11-S13). Addition of Zn^{2+} leads to the large downfield shift of the quinoline-benzimidazole protons (H_a, H_b, H_c, H_d, H_f, H_g, H_h, H_i). These changes in the chemical shift value of aromatic protons are due to the decrease in electron density of the quinoline-benzimidazole moieties by the benzimidazole 'C=N' and quinoline 'O' coordination [35]. This indicates that Zn^{2+} is coordinated with the benzimidazole 'C=N' and quinoline 'O' as shown in scheme 2. The SCF calculations for NMR studies also carried out for **QBC** and **QBC**–Zn^{2+} in TMS HF/6-31G(d) GIAO as a reference. The ^1H NMR analysis shows that the aromatic protons (21, 24, 25, 23, 10, 11 and 7) shifts to downfield region after coordination with Zn^{2+} ion which further confirms the experimental evidences (Fig. S14-17).

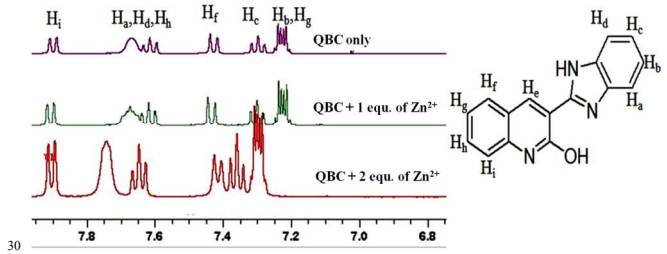
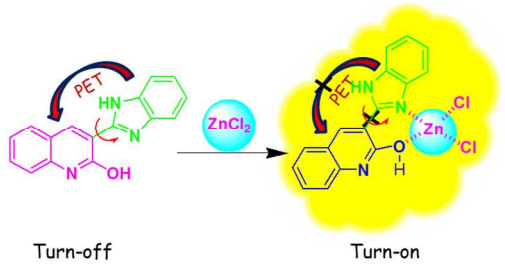


Fig. 8. Partial ^1H-NMR titration spectrum of **QBC** + Zn^{2+}

For an effective chemosensor, the detection at the physiological pH is very important. Hence, the effect of pH of **QBC** in CH_3CN-H_2O (1:1 v/v) was investigated (Fig. S18). The fluorescence emission of **QBC** was stable within the wide pH range. In the presence of Zn^{2+} the fluorescence intensity of **QBC** has been stable between the pH 6-9. However, when the pH is less than 6 the fluorescence intensity decreases due to the protonation of benzimidazole moiety and when the pH is more than 9, the fluorescence intensity again decreases due to the hydrolysis of metal ions. Therefore, the results suggest that **QBC** as an effective chemosensor and is very much suitable for the environmental, clinical and biological applications. The quick time response of **QBC** for the detection of Zn^{2+} in CH_3CN-H_2O (1;1 v/v, HEPES=50 mM, pH=7.0) was performed (Fig. S19). It reveals that the **QBC** can complex with 100 equiv. of Zn^{2+} ion in almost 3 minutes, after which the fluorescence intensity becomes constant without any further changes.

The proposed signalling mechanism of **QBC**, illustrated in scheme 2 is based on the inhibition of PET process and the rigidification of **QBC** through Zn^{2+} ion coordination. The receptor **QBC** exhibit weak fluorescence, owing to the photoinduced electron transfer process from imidazole moiety which is one of the predominant non-radiative relaxation pathways for the excited state molecule. Further, the C–C single bond rotation of the quinoline and benzimidazole moiety would also been responsible for the pronounced non-radiative decay pathway. Addition of divalent metal ion induces the chelation involving the benzimidazole imine 'nitrogen' and the quinoline amide or carbonyl oxygen moieties which would restrict the free C–C rotation and suppresses the non-radiative decay channel through C–C single bond rotation. Further, we have also examined the alternations in the photoinduced electron transfer process upon Zn^{2+} coordination. A close examination of the frontier orbitals calculated using Gaussian 03 programme at B3LYP/6-31G (d,p) level suggests that the highest occupied molecular orbital and lowest unoccupied molecular orbital does not show any significant difference before and after Zn^{2+} coordination (SI, Figure S6 and S8). Hence, the contribution for the fluorescence enhancement is not only limited to the inhibition of photoinduced electron transfer but also due to the rigidification of **QBC** by arresting C-C single bond rotation. Therefore, in addition to colorimetric response, we can also anticipate chelation enhanced fluorescence (CHEF) upon metal ion binding. Thus, the probe **QBC** serves a selective Zn^{2+} sensor by the Fluorescence "turn off-on" process.



Scheme 2. Proposed binding mode of **QBC** with Zn^{2+}

The scanning electron micrographs (SEM) of **QBC** and **QBC**+Zn^{2+} are displayed in Fig. 9. The SEM images show the surface topograpy of **QBC** is different from that of the complex **QBC**+Zn^{2+} which further advocates the selectivity of the probe **QBC** towards Zn^{2+}.

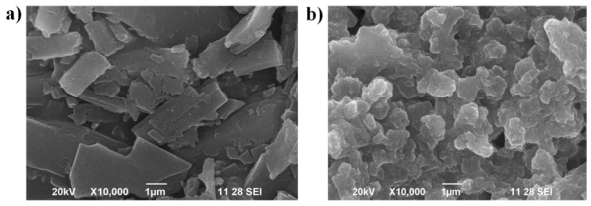


Fig. 9. SEM image of a) receptor **QBC** (b) **QBC** + Zn^{2+} complex.

We have examined the feasibility of **QBC** for the determination of the most abundant Zn^{2+} ion in different samples *via* fluorescence techniques. Five numbers of samples were analysed by this method and these include commercially available tablets, juice extracted from pomegranate and tap water (Table 1). As a result, the quantitative recoveries of non-spiked and spiked samples were satisfactory and confirmed with known standards. This indicates that **QBC** could potentially be used for the determination of Zn^{2+}-ion in real samples without any other co-existing metal ion interferences.

Table 1. Determination of Zn^{2+} in real samples

Sample	Amount of Zn^{2+} present in Blank ppm (AAS)	Zn^{2+}-ion spiked (ppm)	Zn^{2+}-ion found (ppm) (Fluorescence) (Mean ± S.D.)	Recovery (%)
Tablet -1	61.8	0	61.82 ± 0.03	100
Tablet-2	61.0	0	61.04 ± 0.08	100
Pomegranate	0.12	4	4.10 ± 0.15	99
Tap water-1	0.24	6	6.22 ± 0.02	99
Tap water-2	0.36	10	10.35 ± 0.04	99

3. Experimental Section

Synthesis of 3-(*1H*-benzo[*d*]imidazol-2-yl)quinolin-2-ol (QBC)

Appropriate 2-hydroxyquinoline-3-carbaldehyde (0.50 g, 2.89 mmol) was taken in ethanol (20mL) in the presence of triethylamine and refluxed with o-phenylenediamine (0.34 g, 3.17 mmol) for 5 h. The reaction mixture was cooled, and the precipitate was filtered and recrystallized from DMF to give sensor **QBC.** Yellow colour Solid (80% yield). Mp: 252°C; ^{1}H NMR (400 MHz, DMSO-d_6): 12.65 (s, 1H),12.47 (s, 1H), 9.11 (s, 1H), 7.95 (d, 1H), 7.73-7.59 (m, 3H), 7.43 (d, 1H), 7.29 (t, 1H), 7.23-7.18 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) 113.2, 115.7, 118.7, 119.6, 120.4, 122.3, 122.7, 123.1, 129.5, 132, 134.9, 139.1, 139.5, 143.2, 148.1, 161.2 ppm. Elemental analysis: $C_{16}H_{11}N_3O$; calc.; C, 73.55; H, 4.24; N, 16.08%. Found; C, 73.48; H, 4.21; N, 16.02%. LC-MS calcd. for $C_{16}H_{11}N_3O$: $[M^+]$ 261, found $[M^+{+}1]^+$ 262.

Conclusions

In summary, we have synthesized a probe by incorporating quinoline benzimidazole-conjugate which could sense the Zinc (II) ion by optical and fluorescence methods. The metal chelate, comprising the 'benzimidazole nitrogen' and the 'quinoline oxygen' exhibits selective Zn^{2+} binding, causing inhibition of major non-radiative decay pathways like PET process and the rigidization of **QBC** moiety. This phenomenon delivers a visual naked eye detection (pale yellow to intense yellow) and a fluorescence turn-on response for targeting Zn^{2+} under visible light excitation. The probe has potential to detect micromolar levels of zinc in environmental samples.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Quinoline benzimidazole-conjugate for the highly selective detection of Zn(II) by dual colorimetric and fluorescent turn-on responses

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