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Synthesis and photophysical investigation of (BTHN) Schiff base as off-on Cd²⁺ fluorescent chemosensor and its live cell imaging



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A Schiff base, 1-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]methyl-naphthalen-2-ol (BTHN) have been synthesized by the condensation of 2-hydrazinobenzothiazole and 2-hydroxy-1-naphthaldehyde. Structure of BTHN has been determined with the help of spectroscopic techniques and elemental analysis. Photophysical parameters of the BTHN were studied in the different solvents of varying polarity. The photophysical parameter were largely affected by the varying polarity and absorption as well as emission spectra showed strong bathochromic shift. Further, interactions of the BTHN dye with metal ions were also explored by spectrofluorimetry and BTHN found to be an excellent off-on chemosensor for Cd²⁺ in DMF-H₂O solution. The molecular coordination complex between BTHN with Cd²⁺ is 1:1, confirmed by Benesi-Hildebrand and Job-plot method. In addition, the BTHN has been effectively employed for the fluorescence imaging of cadmium ions in the living cells.

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1. Introduction

Azomethine dye commonly known as molecule containing with HC=N group and represent by the general formula R_1 -CH=N- R_2 [1]. It is produced by the equimolar ratio of primary amine with ketone or aldehyde; react to each other under specific conditions, like acidic or basic catalyst or heat, with instantaneous elimination of the water molecule [2]. It is generally known as Schiff base on the name of great scientist Hugo Schiff in 1864 [3]. Generally, Schiff bases are solid and crystalline, which are unconvincingly basic in nature [4]. Importance of these molecules is mainly due to their structural relationship with natural biological substances and comparatively simple method of the synthesis as well as synthetic litheness that permit the propose of suitable structure properties [5]. It is most extensively used synthetic organic molecule. They are used as dyes, pigments [6], catalysts, as polymer stabilizers and precursor for the synthesis of different heterocyclic compounds such as thiazolidinone, azetidinone, formazans, thiazole and arylacetamide [7]. Nitrogen atom of the Schiff base have lone

* Corresponding author. E-mail addresses: sakhan.manuu@gmail.com, sahmad_phd@yahoo.co.in (S.A. Khan). pair of electrons so it can coordinate with the different metals to make various metal complexes. Donor-acceptor chromophores $(D-\pi-A)$ are referred as push-pull chromophores having an electron donating group such as OH. OR. N-CH₃ linked with electron accepting group or heterocyclic moiety such as CN, CO, NO₂, pyridine, pyrazoline and benzothiazole through the pi bond conjugated system [8]. Such type of chromophores transfers the charge from electron donating group to electron acceptor group through π -bond conjugations, reduce the energy gap between HOMO-LOMO and subsequently chromophore shows red shift in absorption and fluorescence spectrum due to ICT $(D-\pi-A)$ [9]. These chromophores have been comprehensively used for numerous optical applications like organic light emitting diodes [10], sensor for the investigation of cancer cells and various hazardous metal ions [11–17], photorefractive polymers. Phtophysical and physical properties of the $(D-\pi-A)$ chromophore can be improved by the modification of donor or acceptor group and increasing the pi-bond conjugation system between donor and acceptor group [18]. In the recent years, fluorescence chemosensors have been remunerated much consideration to detect metal ions because of their selective and sensitive character when mixed with metal ion. Such sensor based on fluorescence intensity and wavelength of the emission has numerous advantages like simple method and instantaneous response [19]. Therefore, various effective metal ion sensors have been developed. In this paper, we have described the synthesis of novel highly florescence Schiff base as florescent sensor for Cd^{2+} metal ion.

2. Experiment

2.1. Chemicals

All the reagents and chemicals have been procured from Sigma-Aldrich Chemical Pvt. Ltd., and used without additional decontamination. All the solvents used for spectral studies of the BTHN were of spectroscopic grade. Metal salt used to prepare the stock solution of metal ions were CuCl₂.2H₂O, SrCl₂.6H₂O, SnCl₂.2H₂O, CdCl₂.2H₂O, CoCl₂.6H₂O, CrCl₃.6H₂O, MnCl₂.4H₂O, ZnCl₂, and AgNO₃. 2-Hydrazinyl benzothiazole was prepared by the reported method as mentioned in Scheme 1. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel 60 F254 pre-coated aluminum sheets (Merck). Column chromatography have been employed for the purification of reaction products [20].

2.2. Instruments

Stuart Scientific Co. Ltd. melting point apparatus was used to determine the melting-point (m.p.) of prepared α , β -unsaturated ketone, in open capillary tubes. ¹H NMR (600 MHz) and ¹³C NMR (125 MHz) spectrum of the BTHN was recorded on Bruker spectrometer in deuterated DMSO. Perkin-Elmer 100 FT-IR spectrometer was used to record IR spectra of BTHN. UV-visible and fluorescence spectra of the BTHN in various solvents were recorded with Shimadzu Uv-16550PC UV/Vis and Shimadzu RF 5301PC respectively.

2.3. Preparation of 1-(2-benzothiazol-2-yl-hydrazono) methyl naphthalene-2-ol(BTHN)

BTHN was prepared by the condensation reaction of 2-hydroxy napthaldehyde with 2-hydrazinobenzothiazole. Briefly, a mixture of

2-hydroxy napthaldehyde (200 mg, 1.10 mmol) and 2-hydrazinobenzothiazole (190 mg, 1.10 mmol) in EtOH was reflexed for 3 h. After completion of the reaction, the reaction mixture was allowed to stand overnight. The solid thus obtained was filtered, dried in air and recrystallised in chloroform and ethanol (8:2) (Scheme 1) [21].

Yellow color; yields: 87.93%; FT-IR: 3432 (O-H), 3035 (C-H), 2924 (C-H), 1608 (C=Caromatic), 1578 (C=N), 1135 (C-N), ¹HNMR (600 MHz, DMSO- d_6 , ppm); 12.08 (s, 1H, C-OH), 11.12 (s, 1H, NH), 10.08 (s, 1H, CH_{Azomethine}), 8.51 (d, 1H, CH_{Aromatic}, J = 7.8 Hz), 8.31 (d, 1H, CH_{Aromatic}, J = 7.2 Hz), 8.20 (d, 1H, CH_{Aromatic}, J = 7.2 Hz), 7.89 (d, 1H, CH_{Aromatic}, J = 7.8 Hz), 7.36 (dd, 1H, CH_{Aromatic}, J = 7.8 Hz), 7.36 (dd, 1H, CH_{Aromatic}, J = 7.2 Hz), 7.36 (dd, 1H, CH_{Aromatic}, J = 7.2 Hz), 7.36 (dd, 1H, CH_{Aromatic}, J = 5.6 Hz); ¹³C NMR (125 MHz, DMSO- d_6): 166.98, 158.12 (C=N), 133.05, 131.76, 130.06, 128.76, 128.13, 126.90, 124.12, 123.52, 122.54, 118.65, 110.15; ESI-MS (m/z): 318 [M-H]⁻; Anal. Calc. for C₁₈H₁₃N₃OS: C, 67.69, H, 4.10, N, 13.16. Found C, 67.53, H, 4.03, N, 13.11.

3. Result and discussion

3.1. Chemistry

The Schiff base BTHN was produced by the condensation of 2hydrazinobenzothiazole with 2-hydroxy-1-naphthaldehyde (Scheme 1). The structure of the synthesized heterocyclic Schiff Base (BTHN) was established by FT-IR, ¹H NMR, ¹³C NMR, elemental, and mass spectral analysis. FT-IR spectrum of BTHN gave absorption band at 1578 cm⁻¹ and 1135 cm⁻¹ owing to presence of conjugated C=N and conjugated C-N functional group, respectively and simultaneous disappearance of peak at 3412 cm⁻¹ for NH₂ group of reactant amine indicated the formation of heterocyclic Schiff Base (BTHN).

In the ¹H NMR spectrum of the BTHN, the characteristic singlet for azomethine at δ 12.8 ppm inferred the condensation of aldehyde and amino group. Ten aromatic protons of the BTHN are in the usual range of δ 8.46- δ 6.97 ppm. BTHN structure was further supported by the ¹³C NMR spectrum and the azomethine carbon appeared at 158.12 ppm



Scheme 1. Synthesis of BTHN

Table 1

Photophysical parameters and fluorescence quantum yields of BTHN in various solvents.

Solvent	Δf	E_T^N	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	$\lambda_{em}(nm)$	ϵ M $^{-1}$ cm $^{-1}$	f	μ_{12} Debye	$\Delta \overline{\nu}_{st}$ (cm ⁻¹)	Φ_f
DMSO	0.263	0.441	45.1	390	510	33,950	0.81	8.11	6034	0.32
DMF	0.274	0.404	43.8	389	507	32,920	0.78	8.01	5983	0.28
EtOH	0.288	0.654	51.9	377	474	31,100	0.67	7.31	5428	0.10
MeOH	0.308	0.762	55.4	379	484	26,730	0.61	6.99	5724	0.23
t-BuOH	0.264	0.506	50.2	381	486	26,080	0.59	6.90	5670	0.33
PrOH	0.280	0.520	49.2	380	478	22,400	0.48	6.21	5395	0.40
CHCl ₃	0.148	0.259	39.1	382	486	28,850	0.64	7.19	5602	0.09
CH_2Cl_2	0.218	0.472	41.1	383	488	24,890	0.55	6.67	5612	0.11
CH₃CN	0.305	0.164	45.6	381	479	26,460	0.56	6.68	5370	0.08
Dioxane	0.028	0.210	36.0	380	478	27,200	0.57	6.77	5307	0.07
THF	0.208	0.006	35.1	379	474	25,200	053	6.51	5288	0.12
n-Heptane	0.0002	0.0002	31.1	377	473	21,560	0.45	5.99	5249	0.05

while other aromatic carbons signals in the range of δ 133.05- δ 110.15 ppm. In the mass spectrum (ESI-MS), *m*/*z* 318 molecular ion peak further established the formation of BTHN.

3.2. Physicochemical properties of the BTHN

The UV-visible absorption spectra of the heterocyclic azomethine derivative, BTHN, were recorded in different protic and aprotic solvents with varying polarity viz. methanol (MeOH), ethanol (EtOH), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), tetrahydrofuran (THF), acetonitrile (CH₃CN), chloroform (CHCl₃), dichloromethane (CH₂Cl₂), n-Heptane and 1,4-dioxane. Broad absorption band was observed for the heterocyclic azomethine derivative, BTHN, in different solvents. As evident from Table 1, with increase in the solvent polarity (n-Heptane to DMSO), absorption maxima (λ_{max}) of the BTHN exhibited a red shift of 13 nm. This behavior may be attributed to intermolecular charge transfer (ICT) during transition from electron rich hydroxy (OH) group [22]. The molar absorption coefficient also increased with increase in polarity of the solvent (Table 1). On the similar line, the emission spectra showed bathochromic shift of 37 nm with the change in polarity of the solvent from non-polar (for n-Heptane, $\lambda_{em} =$ 473 nm) to polar (for DMSO, $\lambda_{em} = 510$ nm) Fig. 1. The red shift resultant of photoinduced intramolecular charge transfer (PICT) by intramolcular electron transfer from hydroxy (OH) group to the thiazole group at excited state [23].

The absorption energy (Ea) and emission energy (E_f) of the heterocyclic Schiff base showed a linear relationship with Dimroth empirical polarity parameters $E_T(30)$ of the different solvents as presented in Fig. 2 [24].



Fig. 1. Fluorescence spectra of 1×10^{-5} M of BTHN in various solvents.

The linear relation between different polarities of the solvents and energies $(E_a \otimes E_f)$ has been assimilated by the given equations.

 $E_a = 76.33 - 0.010 \times E_T(30) \tag{1}$

$$E_f = 66.95 - 0.072 \times E_T(30) \tag{2}$$

3.3. Determination of transition dipole-moments and stokes shift

The physico-chemical parameters, viz. Stokes shift, transition dipole moment, oscillator strength in the solvents of varying polarity have been determined for the heterocyclic azomethine derivative, BTHN. The change in dipole-moment between ground state and excited state $(\Delta \mu = \mu_e - \mu_g)$ in different solvents for the heterocyclic azomethine BTHN, was determined.

The various physicochemical parameters of the heterocyclic azomethine, BTHN, in different solvents could be determined by using Lipert-Mataga equation [25].

$$\Delta \overline{v}_{st} = v_{abs} - v_{em} = \frac{2\Delta\mu^2}{hca^3} \Delta f + Const$$
(3)

Where, $(\Delta \overline{v}_{st})$ is the Stokes shift, a is the Onsager cavity radius, c is the velocity of the light, h is the Plank's constant and Δf is the orientation polarizability.



Fig. 2. Plot of energy of absorption (E_a) and emission (E_f) versus $E_T(30)$ of different solvents.



Fig. 3. Plot of Δf versus stokes shift.

The orientation polarizability (Δf) of the solvent is given by the following equation [26].

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\eta^2 - 1}{2\eta^2 + 1} \tag{4}$$

where ϵ is solvent dielectric constant and η is the refractive index of the solvent.

The linear correlation between orientation polarizabilty (Δf) and Stokes shift (Δv_{st}) (Fig. 3) indicated that Stokes shift is dependent on the solvent polarity or polarizabilty.

Using Lippert-Matga Eq. (3) and dipole moment of the ground (μ_g) and excited state (μ_e) , the Onsager cavity radius (a) for the heterocyclic azomethine BTHN was obtained by the following relation [27,28].

$$a = \left(\frac{3M}{4N\pi d}\right)^{1/3} \tag{5}$$

Where, M is Molar mass, N is Avigadro number and d is density of BTHN. The change in dipole moments ($\Delta\mu$), calculated from the plot of Stokes shift versus polarizability, for the azomethine BTHN was found to be 0.23 Debye. This increase in dipole moment indicated the



Fig. 4. Plot of ϕ_f versus $E_T(30)$ of the different solvents.



Fig. 5. Emission spectra of 1.0×10^{-5} mol dm $^{-5}$ of BTHN upon addition of 5.0×10^{-5} M Cu $^{2+}$, Sr $^{2+}$, Sn $^{2+}$, Cd $^{2+}$, Co $^{2+}$, Cr $^{3+}$, Mn $^{2+}$, Zn $^{2+}$ and Ag $^+$ in DMF/ water (9:1, v/v).

intaramolecular charge transfer character and photoinduced ICT led to creation of stronger dipole that resulted into enhanced interaction with surrounding solvent medium to produce solvent reformation.

The transition dipole moments of the heterocyclic azomethine BTHN in different solvents have been calculated using following Eq. (6).

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} E_{\text{max}}} \tag{6}$$

Where, f is oscillator strength and E_{max} is energy of absorption maximum.

The tabulted transition dipole moments (Table 1) revealed the increase in dipole-moments with increasing solvent polarity.

The oscillator strength of heterocyclic azomethine BTHN in the solvents have been calculated by the following Eq. (7) [29].

$$f = 4.32 \times 10^{-9} \int \varepsilon(\overline{\nu}) d\overline{\nu} \tag{7}$$

Where, ε is molar absorption coefficient and $\overline{\nu}$ is wavenumber (cm⁻¹). From Table 1, it is clear that oscillator strength (*f*) of BTHN is directly correlated to polarity of solvent.



Fig. 6. Emission of BTHN in presence of different metal ions.



Fig. 7. Competitive experiments in the BTHN + Cd^{2+} system with interfering metal ion. [BTHN] = 1 × 10⁻⁵ M, [Cd^{2+1} = 5 × 10⁻⁵ M, and [M^{n+1}] = 5 × 10⁻⁵ M, excited at 370 nm.

3.4. Fluorescence quantum yields of the BTHN in different solvents

The fluorescence quantum yield (Φ_f) of the heterocyclic azomethine BTHN was obtained by relative method using Quinine Sulphate as reference dye ($\Phi_r = 0.55$), following equation was used to obtaine the Φ_f value [30].

$$\Phi_f = \Phi_r \, \frac{I \times A_r \times \eta^2}{I_r \times A_r \times \eta_r^2} \tag{8}$$

Where, Φ_f is fluorescence quantum yield of heterocyclic azomethine BTHN, Φ_r is fluorescence quantum yield of Quinine Sulphate (reference), I & I_r is fluorescence intensity of BTHN and reference dye (in DMSO), A & A_r is absorbance of BTHN and reference dye (in DMSO) and η is refractive indices.

The fluorescence spectra of heterocyclic azomethine BTHN was affected by the solvent polarity as indicated by the changes in ϕ_f values (Table 1). This seem to be the result of polarizability, hydrogen bonding with electron donor and electron acceptor group. The plot of ϕ_f versus E_T (30) show that fluorescence quantum yield increased with increase in solvent polarity (Fig. 4) [31]. But positive solvatokinetic effect in strongly polar solvents (like methanol, ethanol) adversely affect the ϕ_f unlike less polar solvent. With increase in solvent polarity, interaction of solvent with BTHN increases and interaction of the hydrogen bonding



Fig. 8. Emission spectra of BTHN (1×10^{-5} M) exposed to various concentration of Cd²⁺ in DMF: water (9:1, ν/ν).



Fig. 9. Inset: Fluorescence titrations cure of BTHN $(1\times 10^{-5}\mbox{ M})$ with Cd^{2+} in aqueous solution.

proton donor solvent and BTHN molecules led to decrease in fluorescence quantum yield (ϕ_f).

3.5. Fluorescent chemosensor of BTHN for metal ion

The sensing behavior of BTHN with different metal ions i.e. Cu^{2+} , Co^{2+} , Sn^{2+} , Sr^{2+} , Zn^{2+} , Cd^{3+} , Cr^{3+} , Mn^{2+} and Ag^{+} in DMF-H₂O (9:1) were examined by emission measurements corresponding to excitation at 380 nm. As shown in the Fig. 5, azomethine BTHN showed weak fluorescence. Upon addition of Cd^{2+} , a substantial augmentation (~9 fold) in fluorescence intensity is observed with the blue shift from 507 nm to 494 nm (Fig. 5). Whereas addition of other metal ion i.e. Cu^{2+} , Co^{2+} , Sn²⁺, Sr²⁺, Zn²⁺, Cr³⁺, Mn²⁺ and Ag⁺ to the azomethine BTHN did not give fluorescence intensity change (Fig. 5) and thus showing excellent selectivity for Cd²⁺. The observed enhancement of the fluorescence intensity and blue shift attributed to the mutual effect of the dissuasion of intramolecular charge transfer (ICT) and chelation-enhanced fluorescence (CHEF) [32]. In addition, the substantial fluorescence change from light yellow to reddish orange could be practically observable by the naked eye under UV-lamp of 365 nm, thus making the azomethine BTHN selective off-on chemosensor for Cd^{2+} .

In order to assess the further selectivity of BTHN for Cd^{2+} , competition experiments of Cd^{2+} in combination with other metal ion were



Fig. 10. Benesi-Hildebrand plot for BTHN (1 \times 10 $^{-5}$ M) at various concentration of Cd $^{2+}$ ion.



Fig. 11. Job's plot, Fluorescence Intensity vs. mole fraction of Cd²⁺ Job's plot.

carried out (Fig. 6). The emission intensity of the BTHN with Cd^{2+} remain almost unchanged when mixed with the other metal ions (Cu^{2+} , Co^{2+} , Sn^{2+} , Sr^{2+} , Zn^{2+} , Cr^{3+} , Mn^{2+} and Ag^+); indicated the selectivity of the azomethine BTHN for the Cd^{2+} over the other metal cations. Hence, BTHN could be employed as a very selective sensor for Cd^{2+} even in the presence of other metal ions (Fig. 7).

To understand the mechanism of the complexation of BTHN with Cd^{2+} ion, fluorescence titration experiments upon stepwise addition of Cd^{2+} ions (0.1 to 0.9×10^{-4} M) were conducted and resulted into approximately 9 fold enhancement in emission intensity accompnied by blue shift (Fig. 8). The shift exhibited good linear response ($R^2 = 0.98$) as shown in Fig. 9, and BTHN was revealed to be a discriminating turn on fluorescent chemosensor for Cd^{2+} metal ion.

Stoichiometry ratio and association constant between the BTHN and Cd²⁺ metal ion have been investigated using the Benesi-Hildebrand method and the equation as following [33,34].

$$\frac{1}{F^{o}-F'} = \frac{1}{F^{o}-F'} + \frac{1}{K_{app}} \times \frac{1}{(F^{o}-F')\left[Cd^{2+}\right]}$$
(9)

As shown in the Fig. 10 for the plot between the $1/(F-F_0)$ vs $1/Cd^{2+}$, the linearity of the plot indicated that stoichiometry ratio for the coordination of BTHN and Cd^{2+} is 1:1 and the BTHN- Cd^{2+} association constant was calculated from the fluorescence titration of BTHN with Cd^{2+} and found to be 1.17×10^4 M⁻¹.

Stoichiometry ratio between the BTHN and Cd^{2+} was further confirmed by the Job plot method [35]. The fluorescence intensity was recorded by varying the mole fraction of Cd^{2+} as mentioned in the Fig. 11. Maximum fluorescence emission intensity was observed when the mole fraction of Cd^{2+} was 0.5, indicating the BTHN and Cd^{2+} coordination possibility as 1:1. Emission enhancement mechanism of BTHN in presence of Cd^{2+} may be possibility of the formation of coordination bond between nitrogen atom of the azomethine and hydroxyl group with Cd^{2+} metal ion.

To utilize the present sensor for the detection of Cd(II) ions in living cells, fluorescence imaging experiments were carried out. HeLa cells were cultured in DMEM medium, the cells were incubated with the probe BTHN (5 μ M) for 30 min. After the incubation, HeLa cells were washed thrice with the HEPES buffer to remove the extracellular probe and the cells were examined under the fluorescence microscope. The probe BTHN treated cells showed very weak fluorescence. Then the BTHN incubated cells were treated with Cd(II) solution (25 μ M) for 10 min (Fig. 12). Then the cells were imaged through the fluorescence microscope, the intracellular region of the cells showed bright fluorescence, suggesting the practical utility of the probe for live cell imaging.



Fig. 12. Imaging of Cd(II) ions in Living HeLa cells. (a), (c) Fluorescence images of Probe BTHN treated cells and Bright field images of Probe treated cells respectively. (b), (d) Fluorescence images of BTHN and BTHN with cadmium ions treated cells respectively.

The bright field images of the cells clearly suggesting that the cells are viable throughout the experimental conditions.

4. Conclusion

A simple Schiff base BTHN was produced by the condensation of 2hydrazinobenzothiazole and 2-hydroxy-1-naphthaldehyde and the structure was established. Physicochemical parameters of the BTHN were investigated in different solvents with varying polarity and found that polarity of the solvent strongly affected the physicochemical parameters. In addition, BTHN displayed excellent selectivity as turn-on sensor for Cd²⁺ metal ion even in the presence of other competing metal ions. The molecular coordination complex between BTHN with Cd²⁺ was found to be 1:1, confirmed by Benesi-Hildebrand and Jobplot method. Further, the live cell imaging experiments for the detection of Cd(II) ions in HeLa cells augment the utility of the probe BTHN for intracellular imaging of cadmium ions.

Declaration of Competing Interest

None.

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