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A novel pyrazole biscoumarin based chemosensors for the selective detection of Cu^{2+} and Zn^{2+} ions

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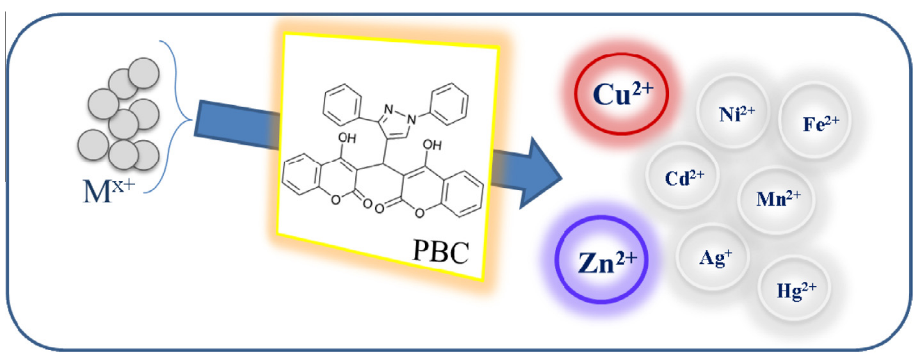
HIGHLIGHTS

- A novel chemosensor based on pyrazole biscoumarin molecule (PBC) was described.
- PBC chemosenses selectively Cu^{2+} and Zn^{2+} visible by naked eye.
- No spectral changes even in the presence of other common metal ions.
- The binding ratio PBC to Cu^{2+} and Zn^{2+} as 1:1 and 2:1 respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel chemosensor based on pyrazole biscoumarin molecule "4-hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(1,3-diphenyl-1H-pyrazol-4-yl)methyl)-2H-chromen-2-one" (PBC) was synthesized by a simple method. The chemosensing properties of PBC towards transition metal ions like Cu^{2+} and Zn^{2+} by naked eye, UV–Visible and fluorescence spectroscopic methods were described. The PBC solution with Cu^{2+} and Zn^{2+} ion showed brown and blue colour respectively. The UV–Visible spectra of PBC with Cu^{2+} and Zn^{2+} ions exposed their corresponding absorption maxima. Further, the Job's plot method confirmed the 1:1 and 2:1 stoichiometry of the complex formation between the PBC with Cu^{2+} and Zn^{2+} ions respectively. The fluorescence enhancement of PBC on binding with Cu^{2+} and Zn^{2+} is due to the inhibition of photo induced electron transfer mechanism.

Introduction

Chemosensors have been placing a vital role in the bio-medicinal science, analytical chemistry and environmental chemistry [1]. Chemosensors provide an accurate and low-cost detection of anions, enzymes and toxic heavy metal ions with high selectivity and sensitivity [2]. In this regard, many organic compounds have been synthesized and are being used as an effective chemosensors.

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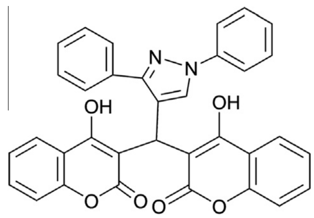

Fig. 1. Structure of the receptor (PBC).

In particular, coumarin derivatives have been showing many advantages including less toxicity, excellent light stability, high fluorescent quantum yield and large stoke shift [3–5]. Various anions and cations such as CN^-, F^-, CH_3COO^-, $P_2O_7^{4-}$ etc., and Hg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+} etc., were effectively sensed by using these coumarin derivatives [6–16]. Furthermore, two or more ions have also been sensed simultaneously by coumarin derivatives [17–20].

Zinc and copper are respectively the second and third most abundant transition metal ion in our human body and are acting as an essential cofactor in many biological processes [21]. The emerging importance of Cu^{2+} and Zn^{2+} in neurological signalling [22,23] and some proposed functions in biological systems have generated an urgent demand for the development of Cu^{2+} and Zn^{2+} specific molecular probes [24–27]. Many Cu^{2+} and Zn^{2+} fluorescent sensors have been reported in the literature exhibiting high selectivity and sensitivity over other biologically essential metal ions in specific concentration ranges [28–31]. For instance, coumarin derivatives are used in manufacturing chromophore, aroma compounds, and certain pharmaceutical derivatives [32–34].

We have recently reported the synthesis of pyrazole based coumarin moieties using FeTUD-1 as heterogeneous solid acid catalyst [35]. To extend their applications, in this work, we have examined the chemosensing property of synthesized pyrazolylbiscoumarin compound (PBC, see Fig. 1). The spectral studies like UV–Visible and fluorescence analysis are also investigated.

Experimental

Materials and methods

Copper bromide, zinc bromide and acetonitrile (HPLC grade) were obtained from Merck. Millipore water was used for preparation of the respective solutions. The UV–Vis spectra was analysed on a Shimadzu UV-160 spectrophotometer with 5.0 cm quartz cell. The photoluminescence analysis was recorded using JASCO FP-5600 instrument with 1.0 cm quartz cell.

Preparation of PBC

In a 50 mL round bottom flask, pyrazole aldehyde (1,3-diphenyl-1H-pyrazole-4-carbaldehyde) (1 mmol) and 4-hydroxycoumarin (2 mmol), ethanol (5 mL) as a solvent and mesoporous FeTUD-1 (60 mg) as a catalyst were taken for the synthesis (Fig. 2) [35]. The reaction temperature was maintained at 80 °C for 4 h. Thin-layer chromatography (TLC) was used to examine the progress of the reaction. The spectral studies of the isolated product confirmed its structure formation (4-hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(1,3-diphenyl-1H-pyrazol-4-yl)methyl)-2H-chromen-2-one; colourless solid; M.pt: 222 °C; FTIR ν_{max} (KBr): 3434, 3056, 2025, 1654, 1619, 1110, 906, 759, 694, 469 cm^{-1}; ^1H NMR: 6.42 (1H, s), 6.98 (1H, t, J = 7–7.5), 7.08 (2H, t, J = 7–8), 7.25–7.30 (5H, m), 7.43–7.49 (4H, m), 7.55 (2H, t, J = 8), 7.81 (2H, d, J = 8), 7.87 (2H, d, J = 8.5), 8.35 (1H, s), 10.79 (2H, bs); ^{13}C NMR: 29.1, 104.6, 116.2, 117.9, 118.2, 120.1, 120.4, 124.1, 124.2, 126.2, 127.5, 127.8, 127.8, 128.2, 129.5, 129.9, 130.1, 130.5, 132.2, 134.0, 140.0, 151.4, 152.4, 164.6, 164.9; GC–MS m/z: 554 (M^+); Anal.cald for $C_{34}H_{22}N_2O_6$: C, 73.64; H, 4.00; N, 5.05. Anal.found: C, 73.58; H, 3.92; N, 5.02).

Preparation of PBC and metal ion solutions

0.05 M PBC solution was prepared by dissolving 0.6925 g of PBC with acetonitrile in a 25 mL volumetric flask. Similarly, the 0.01 M Cu^{2+} and Zn^{2+} stock solutions were prepared by dissolving respective bromide salts in a 5 mL volumetric flask containing acetonitrile.

Spectrophotometric procedure

Prior to the spectrophotometric studies, the sample solutions were magnetically stirred for 1 min and scanned in the spectrometer. This process was repeated until the change in fluorescence intensity became insignificant. The binding constants (K_a) for cations were derived from plots of change in fluorescence intensity relative to baseline (F/F_0) vs. [cation]. The UV–Vis and emission titrations of PBC with metal ions were performed. The titrations were carried out by addition of microlitre (μL) amounts of solutions of the cations in acetonitrile. A slit width of 5 nm and excitation wavelength of 300 nm were used for emission titration.

Results and discussion

Pristine solution of PBC in acetonitrile gave pale yellow colour. However, the addition of Cu^{2+} and Zn^{2+} ions in PBC-acetonitrile solution yielded brown and blue colour respectively. The PBC compound showed the UV absorption band centered at 260 nm. The absorption band clearly red shifted to 312 nm and 394 nm while adding Cu^{2+} and Zn^{2+} ion (Fig. 3) respectively. With the increasing of metal ion concentration, gradual increase in the absorbance intensity of these peaks are observed (Fig. 4). Coumarin are well-known to show good affinity for Cu^{2+} and Zn^{2+}, the binding of copper and zinc ion always leads to spectral changes due to the formation of a complex [8,10]. Though, significant changes of the absorption spectrum with the addition of Zn^{2+}, Cu^{2+} was observed,

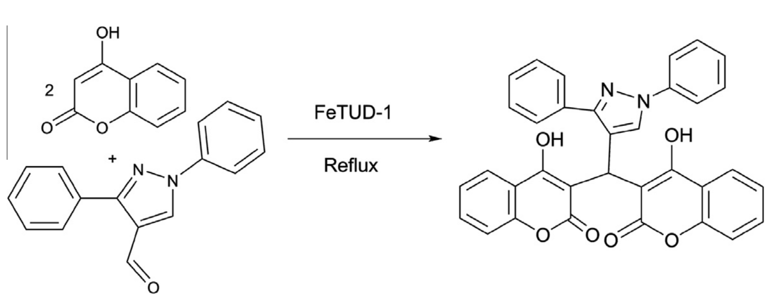

Fig. 2. Synthesis scheme of the PBC.