



Designed benzimidazolium salts: Modulation of fluorescence response towards metal cations in pure aqueous media



Amita Krishan Lal, Marilyn Daisy Milton*

Department of Chemistry, University of Delhi, Delhi 110007, India

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ABSTRACT

Design and synthesis of two new benzimidazolium salts based PET sensors of the type 'receptor₁-spacer₁-fluorophore-spacer₂-receptor₂' is described. Alteration in one of the receptor arm modulates the emission intensity as well as the fluorescence response towards different metal ions. The ligand with morpholine receptor arm exhibits good selectivity for sensing Cr(III), Ba(II) and Fe(III) by 'turn-ON' PET mechanism in pure aqueous media. ¹H NMR studies confirmed the interaction of the morpholine nitrogen with metal ion. However, the ligand with piperidine receptor arm acted as 'turn-OFF' sensor for Fe(III) in pure aqueous media.

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1. Introduction

The use of fluorescent probes for sensing metal ions, anions and other biologically relevant species has attracted a great deal of attention in the past few years due to their selectivity, sensitivity and precision [1–4]. The PET (photoinduced electron transfer) phenomenon has been the subject of considerable interest in design of fluorescent probes [5,6]. The combination of fluorophore with the receptor through the spacer group constitutes the basic PET scaffold. The 'receptor-spacer-fluorophore-spacer-receptor' type models enhance the PET phenomenon statistically as the PET process can take place with either of the two or both the receptors [7–10]. Also, the PET phenomenon is strongly dependent on the position and the availability of the lone pairs of electrons on the receptors. Therefore, the modification in the receptor arm modulates the fluorescence response of the designed molecules [11].

Biological importance of trivalent form of chromium and iron is due to their involvement in many biochemical processes at cellular level [12–14]. Chromium plays an important role in carbohydrate and lipid metabolism. Iron is involved in many metabolic and electron transfer electron processes of the cell [3,15]. Similarly, barium may cause severe health hazards, depending upon the dose of the barium compounds ingested [16,17]. So, there is great necessity

attached to the development of selective chemosensors for these metal ions. Moreover, development of sensors which can work in pure aqueous solution is a challenging task due to the poor solubility of sensors in water. Iron and chromium are known to be the most efficient fluorescent quenchers due to their paramagnetic nature. Thus, the design of 'turn-ON' fluorescent probes for chromium and iron is a difficult task and needs attention [18–24].

Benzimidazolium salts have been used as receptors in anion sensing [25–29] due to the ionic hydrogen bonding between acidic proton of the benzimidazolium ring and anion. However, recently they have also been employed as metal ion sensors [30,31]. As part of our research work on the design and synthesis of water-soluble benzimidazolium salts and their application as fluorescent probes for metal ions [31], we have designed novel and highly water-soluble benzimidazolium salts (Fig. 1). The ligand design consists of benzimidazolium fluorophore unit attached to a pyridine ring through a methylene spacer (Spacer 1) on one side and linked to a morpholine (2) or piperidinium (3) ring through an ethylene spacer (Spacer 2) on the other side of the benzimidazole ring. In 2, the nitrogen atom of both pyridine and morpholine can act as receptors by transferring lone pair of electrons to the benzimidazolium ring by PET mechanism. However, in 3, due to the masking of lone pair of electrons on piperidine nitrogen, the possibility of piperidine acting as a receptor in PET process is removed. Hence 2, has two receptor arms while, 3 has only one receptor arm. Thus it would be interesting to see the effect of statistical enhancement of PET process on modulation of fluorescence response. Also, we reasoned that binding of metal ions to these PET sensors (2, 3) may cause enhancement of fluorescence due to the hindrance in the PET pathway.

* Corresponding author. Tel.: +91 11 27667794 140.

E-mail address: mdmilton@chemistry.du.ac.in (M.D. Milton).

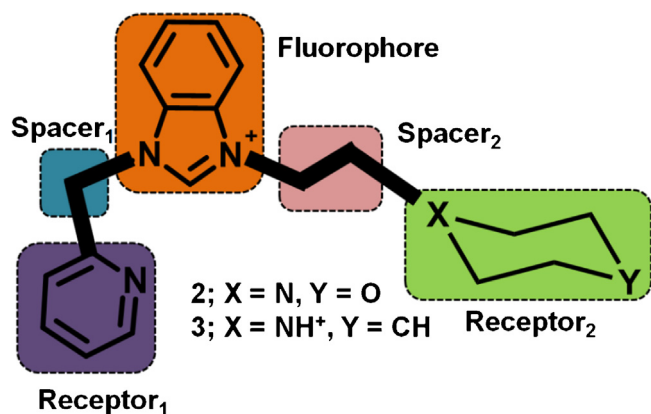


Fig. 1. Design of benzimidazolium salts with 'receptor₁-spacer₁-fluorophore-spacer₂-receptor₂' PET design.

Herein, we wish to report the study of synthesis of new benzimidazolium salts and their application as sensor for chromium (III), barium (II) and iron (III) in pure aqueous medium. It is noteworthy that amongst the various chemosensors developed for chromium (III) [18–21], barium (II) [32,33] and iron (III) [22–24], this is one of the few reports on the use of benzimidazolium salts as 'turn-ON' fluorescent probes [25,29] in pure aqueous media.

2. Experimental

2.1. Reagents and apparatus

IR spectra were recorded on Perkin Elmer (FTIR)-2000 spectrophotometer with KBr pellets. Melting points were recorded on Buchi M-560 and are uncorrected. The ¹H NMR and ¹³C NMR spectra were recorded on JEOL ECX 400P spectrometer at 295 K. The peaks in NMR spectra were further characterized by ¹H–¹H COSY and ¹H–¹³C HETCOR studies. The mass spectra were measured with Bruker maXis impact mass spectrometer. UV–vis spectra were recorded with UV Specord 250 Analytik Jena spectrophotometer at room temperature (200–700 nm) with 1.0 cm optical path. Fluorescence spectra were recorded with Varian CARY Eclipse fluorescence spectrophotometer with excitation and emission slit width of 5 nm. Chemicals were obtained from commercial sources, and were used without further purification. 1-(Pyridin-2-ylmethyl)-1H-benzimidazole (**1**) [34] was synthesized according to literature procedure. The metal salts NaCl, KCl, CaCl₂, MgCl₂·6H₂O, Ba(NO₃)₂, Cu(NO₃)₂, Zn(NO₃)₂·6H₂O, CrCl₃·6H₂O, Pb(NO₃)₂, Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, MnCl₂·4H₂O, Co(NO₃)₂·6H₂O, FeCl₂ and HgCl₂ were received from commercial sources. Crystallographic data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on X'Calibur single crystal X-ray diffractor with a CCD area detector. Empirical correction 'multi-scan' was applied. Compound was crystallized by slow evaporation method using MeOH/CHCl₃. The structure was solved by direct-methods using SIR92 and refined with SHELXL-97 and the refinement (based on F^2 of all data) were performed by full matrix least-squares techniques [35]. Data reduction and refinement were completed using WinGX suite of crystallographic software [36]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were obtained from difference Fourier maps and were included in the final cycles of refinement. CCDC-979506 contains the supplementary crystallographic data. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2. Synthesis

In a Schlenk flask, 5.0 mmol of **1** and 5.0 mmol of alkyl halide (4-(2-chloroethyl)morpholine hydrochloride or 1-(2-chloroethyl)piperidine hydrochloride) were added to 20.0 mL of acetonitrile and refluxed at 80 °C for 40 h under inert atmosphere. The solvent was removed under reduced pressure and the compounds were purified by column chromatography (MeOH:CHCl₃, 20:80) to obtain pure solids.

3-(2-Morpholinoethyl)-1-(pyridin-2-ylmethyl)-1H-benzimidazolium chloride (2): Yield: 0.505 g (28%); mp: 85.3–87.1 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.03 (s, 1H, NCHN), 8.42 (d, $J = 3.6$ Hz, 1H, py-H6), 8.09 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.93 (d, $J = 7.3$ Hz, 1H, Ar-H), 7.84 (td, $J = 2.2, 8.0$ Hz, 1H, py-H4), 7.64–7.56 (m, 3H, py-H3 and Ar-H), 7.34–7.31 (m, 1H, py-H5), 5.96 (s, 1H, NCH₂-py), 4.66 (t, $J = 5.5$ Hz, 2H, NCH₂CH₂N), 3.43 (t, $J = 4.0$ Hz, 4H, ring methylene), 2.73 (t, $J = 5.5$ Hz, 2H, NCH₂CH₂N), 2.39 (t, $J = 4.0$ Hz, 4H, ring methylene); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 153.2, 149.6, 143.4, 137.5, 131.0, 126.6, 126.5, 126.4, 123.6, 122.7, 113.9, 113.8, 66.1, 55.7, 52.8, 50.7, 43.7; IR (KBr): 3256.6, 1636.7, 1384.5, 1194.7, 1117.7, 872.7, 761.7, 575.5 cm⁻¹; HRMS (ESI): calcd. for C₁₉H₂₃N₄O [M–Cl]⁺: 323.1866. Found: 323.1867.

3-(2-(Piperidin-1-ium-1-yl)ethyl)-1-(pyridin-2-ylmethyl)-1H-benzimidazolium chloride (3): Yield: 0.65 g (33%); mp: 177.2–179.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.59 (s, 1H, NH), 10.21 (s, 1H, NCHN), 8.49 (d, $J = 4.3$ Hz, 1H, py-H6), 8.27 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.94 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.88 (td, $J = 1.4, 8.0$ Hz, 1H, py-H4), 7.71–7.62 (m, 3H, py-H3 and Ar-H), 7.39–7.36 (m, 1H, py-H5), 5.92 (s, 2H, NCH₂-py), 5.14 (br, 2H, NCH₂CH₂N), 3.65 (br, 2H, NCH₂CH₂-piperidine), 3.56 (m, 2H, ring methylene), 2.98 (q, $J = 10.2$ Hz, 2H, ring methylene), 1.90–1.68 (m, 5H, ring methylene), 1.44 (q, $J = 12.2$ Hz, 1H, ring methylene); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 153.5, 150.9, 144.6, 138.0, 131.8, 131.4, 127.3, 127.1, 124.2, 123.4, 114.5, 114.4, 57.9, 53.7, 52.7, 51.5, 41.7, 41.6, 22.6, 21.7; IR (KBr): 3437.2, 3145.4, 3087.9, 2938.6, 2613.5, 2536.7, 2439.2, 1625.9, 1440.1, 1376.1, 1189.6, 1101.3, 1010.2, 773.3, 763.4, 646.0, 623.9, 578.2, 431.6 cm⁻¹; HRMS (ESI): calcd. for C₂₀H₂₅N₄ [M–2Cl–H]⁺: 321.2074. Found: 321.2073.

2.3. Spectrophotometric studies

The stock solution of the benzimidazolium salts were prepared in water at the concentration of 1.0×10^{-3} M and diluted to 1.0×10^{-4} M. The stock solutions of metal salts were prepared in water at the concentration of 0.1 M and were diluted accordingly before experimentation. While examining the sensitivity, selectivity and interaction of probe with metals, 3 mL stock solution was taken and metal salt solution was added accordingly.

3. Results and discussions

3.1. Synthesis and characterization of benzimidazolium salts

3-(2-Morpholinoethyl)-1-(pyridin-2-ylmethyl)-1H-benzimidazolium chloride (**2**) was obtained in 28% yield by refluxing 2-(1H-benzimidazol-1-ylmethyl)pyridine (**1**) [34] with equimolar ratio of 4-(2-chloroethyl)morpholine hydrochloride in acetonitrile (Scheme 1). The identity of **2** was confirmed by various spectroscopic methods. A peak at δ 10.03 ppm was observed in the ¹H NMR spectrum due to benzimidazolium ring C2-H proton. But the absence of downfield peak for morpholinium –NH– proton confirmed the existence of monocationic benzimidazolium salt. The reaction of **1** with 1-(2-chloroethyl)piperidine hydrochloride gave a dicationic species 3-(2-(piperidin-1-ium-1-yl)ethyl)-1-(pyridin-2-ylmethyl)-1H-benzimidazolium chloride (**3**) due to

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