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Reusable Schiff base functionalized silica as a multi-purpose nanoprobe for fluorogenic recognition, quantification and extraction of Zn^{2+} ions

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ABSTRACT

Nowadays, sole recognition of targeted species is not sufficient to quantify or recover it from environmental samples. Therefore, current challenge in the management of crucial species is to improve or design sensing probes which are able to recognize, quantify as well as recover it from various assays. Herein, a Schiff base chemosensor **SB** has been modulated to **SB-Silt** after incorporating hydrolysable units for its covalent grafting on silica surfaces. Interestingly, despite fluorogenic insensitivity of **SB** towards metallic species, **SB-Silt** was found to be highly efficient for the recognition and quantification of Zn^{2+} ions. Furthermore, functionalization of nanosilica with **SB-Silt** produced a multi-functional nanoprobe **SB@SNPs** for monitoring Zn^{2+} ions. The ‘turn ON' fluorescence emission in **SB-Silt** and **SB@SNPs** (at 437 nm and 457 nm, respectively) in the presence of Zn^{2+} ions enabled the detection upto 6.8 nM and 0.17 μM (LODs), respectively. The maximum adsorption capacity (Q_m) of **SB@SNPs** for Zn^{2+} ions was determined to be 167.2 mg g^{-1}. Moreover, the **SB-Silt-Zn**$^{2+}$ conjugate (formed by the interaction of **SB-Silt** and Zn^{2+} ions) exhibited a complete quenching of fluorescence (at 437 nm) accompanied with continuous red shifting of emission wavelength to 517 nm in the presence of hydrogen phosphate (upto 4 equiv.). Overall, the developed material is highly efficient, sensitive, selective, reusable and easily separable, and hence can be used as a multifunctional nanoprobe.

1. Introduction

Zinc (one of the biologically essential metals) exhibits a crucial role in numerous pathophysiological processes comprising gene transcription, cell apoptosis, regulation of metalloenzymes, neuronal signal transmission, and DNA binding/recognition [1–6]. Inadequate zinc homeostasis in human beings causes various diseases (like Alzheimer's disease, cancer, epilepsy), inhibits cell growth and division, and reduces immunity. Thus, it is used as a supplement in most of the health care products and medicines [7–11]. Besides, zinc and its compounds play vital role in industrial processes; for instance, zinc is widely used in the catalysis of numerous chemical reactions, production of die-castings, galvanizing mechanisms, and alloy manufacturing; zinc oxide is important component in the production of paints, rubber, cosmetics, pharmaceuticals, textiles, soaps, batteries and electrical equipments; and zinc sulphide is used in the production of luminous paints, fluorescent lights, and screens [12].

Nowadays, development of appropriate recycling strategies is of utmost importance to minimize the environmental hazards and reduce the cost of commercial applications. Basically, management strategies comprise three fundamental elements; recognition (qualitative analysis), quantification, and extraction of target from various matrices. Therefore, efforts in this direction are growing day by day to achieve selective recognition, efficient extraction, and highly sensitive quantification methods. In particular, optical chemosensors based upon organic fluorophores (like 1,10-phenanthroline [13,14], quinoline [15–24], fluorescein [25–28], benzazole [29], coumarin [30,31], indole [32], and some Schiff base molecules [33–41]) have been markedly investigated for the recognition of Zn^{2+} ions. Likewise, organo-functionalized nanomaterials (such as magnetic or non-magnetic silica surfaces functionalized with quinoline [15,17,19–24], rhodamine B [40], anthranone [42], acenaphthalenequinone/quinoline [43]) have also been established as fluorescent probes for recognition purposes. Furthermore, inorganic adsorbents (mesoporous silica) and organic-inorganic hybrid

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materials (i.e. silica surfaces decorated with mercaptopropyl- [44], aminopropyl/propylethylene-diamine/propyldiethylenetriamine [45], benzophenone-4-aminobenzoylhydrazone [46], 4,4′-diaminodiphenylether/4,4′-diamino-diphenylsulfonesalicylaldehyde moieties [47]) have been fabricated to extract zinc ions from various assays. However, the limiting feature of these probes is their inability to work for all the three elements because they are specific either in recognition or quantification or extraction. Till date, a single system with covalently grafted quinoline receptor on magnetic fibrous silica material (Fe_3O_4@SiO_2@KCC-1) is known for the determination, adsorption, and removal of Zn^{2+} ions [23]. Therefore, aiming to produce a three-in-one probe, we fabricated a single material capable of accomplishing multiple tasks.

Herein, we extended the application of **SB** which we recently reported as a chromogenic sensor for iron species [48]. The derivatization of **SB** not only transformed it into a probe for the selective recognition and quantification of Zn^{2+} ions but also provided a hydrolysable site for its incorporation on to silica surface. The covalent grafting of the probe onto silica nanoparticles resulted in the inorganic-organic hybrid silica material capable of acting as a fluorogenic probe for monitoring Zn^{2+} ions. Although, similar fluorescent silica probes have been reported for metal ion recognition (Cr^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}) [49], however, Schiff base functionalized fluorescent silica is reported herein for the first time as a multipurpose probe for Zn^{2+} ions. The use of silica surface, despite toxic metal oxide surfaces, makes the method greener to cope up the environmental issues.

2. Experimental

2.1. Materials and methods

All the reagents namely copper(II) nitrate trihydrate (HPLC Lab Reagents), nickel(II) nitrate (Merck), iron(III) nitrate anhydrous (Thomas Baker), iron(II) sulphate (Loba Chemie), manganese(II) acetate (Sigma–Aldrich), chromium(III) nitrate (Loba Chemie), cobalt(II) nitrate (Loba Chemie), zinc(II) nitrate hexahydrate (HPLC Lab Reagents), lead(II) nitrate (Fischer Scientific), mercuric(II) chloride (Merck), cadmium(II) nitrate tetrahydrate (CDH), tetraethylammonium fluoride (Acros Organics), potassium chloride (Fischer Scientific), potassium bromide (Fischer Scientific), sodium acetate (Qualigens), sodium formate (Loba Chemie), dipotassium hydrogen phosphate (Merck), sodium nitrite (Qualigens), sodium thiocyanate (Merck), sodium tetrafluoroborate (Spectrochem), disodium EDTA (Merck), ethanol absolute (Merck), dichloromethane (Fischer Scientific), polyethyleneglycol (Acros), tetraethylorthosilicate (Acros), 3-isocyanatopropyl(triethoxy)silane (Aldrich), triethanolamine (Merck), ammonia (25%, Sd-fine), diethylenetriamine (Acros), cetyltrimethylammonium bromide (CDH), concentrated hydrochloric acid and concentrated nitric acid (National Chemical) were purchased and used as such. Toluene (Fischer Scientific), diethyl ether (Fischer Scientific), chloroform (Fischer Scientific), and methanol (Finar) were distilled before use and stored over molecular sieves.

2.2. Physical measurements

Infrared spectra were obtained on Thermo scientific NICOLET IS50 FT-IR and Perkin Elmer RX-I FT-IR spectrophotometers. Mass spectral measurements (ESI source with capillary voltage 2500 V) were carried out on a VG Analytical (70-S) spectrometer. The CHN elemental microanalyses were obtained on a FLASH-2000 organic elemental analyzer. Solution NMR (^1H, ^{13}C) spectra were recorded at 25° C on a Bruker Avance II FT NMR (AL 400 MHz) spectrometer. Chemical shifts in ppm are reported relative to tetramethylsilane (TMS). Emission spectra were recorded using a Schimadzu fluorescence spectrophotometer RF-6000 using quartz cells (1 cm). Centrifugation was done using Eppendorf Centrifuge 5804 R. Thermogravimetric analyses were carried out in a dynamic nitrogen atmosphere using a TA Q600 analyzer at a heating rate of 20 K min^{-1}. The micrographs of the fabricated materials were investigated by FESEM Zeiss Ultra Plus and transmission electron microscope (TEM) at 120 kV voltage using a Hitachi (H-7500) instrument.

2.3. Fabrication of materials

2.3.1. Synthesis of Schiff base (SB)

The **SB** was synthesized and characterized as reported in our recent paper [48]. Briefly, diethylenetriamine (0.47 mL, 4.4 mmol) was added to a solution of 2-hydroxy-4-methoxybenzophenone (2.0 g, 8.8 mmol) in 2-propanol (50 mL). The contents were refluxed for 6 h and thereafter, the solvent was removed using rotary evaporator. The resulted yellow oil was kept in the refrigerator for few days, which gave a yellow solid. **M.P.:** 98–100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.85 (t, 4H^{15}, $J = 6.2$ Hz), 3.36 (t, 4H^{14}, $J = 6.2$ Hz), 3.76 (s, 6H^{16}), 6.10 (dd, 2H^5, $^4J = 2.5$ Hz, $^3J = 9.0$ Hz), 6.35 (d, 2H^3, $^3J = 2.5$ Hz), 6.62 (d, 2H^6, $^4J = 9.0$ Hz), 7.19–7.48 (m, 10H$^{9-13}$), 16.24 (s, 2H, Ar–OH).

2.3.2. Triethoxysilyl derivative of schiff base (SB-Sil)

Briefly, 3-isocyanatopropyltriethoxysilane (0.47 g, 1.90 mmol) in dry chloroform (10 mL) was added to the solution of **SB** (1.0 g, 1.90 mmol) in an inert atmosphere. The contents were stirred and refluxed for 6 h. The solvent was evaporated to get an orange-yellow oil (**SB-Sil**). Yield: 71%, 1.044 g, **FT-IR (cm^{-1}):** 748 (Si—O), 953 (C—C), 1072 (Si-O), 1163 (CH_2O), 1442 (C=C), 1523 (NH), 1592 (C=N, C=O), 2888, 2971 (CH_2), 3060 (—NH), 3363 b (OH). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 0.53 (t, 2H^{19}, $^3J = 8.2$ Hz), 1.21 (t, 9H^{21}, $^3J = 7.0$ Hz), 1.48 (quin, 2H^{18}, $^3J = 8$ Hz), 3.01 (q, 2H^{17}, $^3J = 7.0$ Hz), 3.40 (t, 8H^{14,15}, $^3J = 4$ Hz), 3.78 (s, H^{22}) 3.80 (q 6H^{20}, $^3J = 7.0$ Hz), 4.53 (t, NH, $^3J = 5.5$ Hz), 6.14 (dd, 2H^5, $^4J = 2.5$ Hz, $^3J = 8$ Hz), 6.41 (d, 2H^3, $^4J = 2.5$ Hz), 6.61 (d, 2H^6, $^3J = 8$ Hz), 7.12-7.14 (m, 4H^{9,13}), 7.45-7.50 (m, 6H$^{10-12}$), 15.91 (s, 2H, OH). **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ (ppm); 6.7 (C^{19}), 17.3 (C^{21}), 22.4 (C^{18}), 47.5 (C^{14}), 48.0 (C^{17}), 54.2 (C^{15,22}), 57.4 (C^{20}), 100.7 (C^3), 104.8 (C^5), 111.8 (C^1), 126.4 (C^{10,12}), 127.8 (C^{9,13}), 128.3 (C^{11}), 132.0 (C^6), 132.2 (C^8), 156.3 (C^{16}), 163.0 (C^2), 167.5 (C^4), 173.9 (C^7). **MS**: m/z (relative abundance (%), fragment assigned): 524 (62.5, L)$^+$, 771 (100, M)$^+$, 772 (96.8, M + H)$^+$, 793 (43, M − H + Na)$^+$, 794 (23, M + Na)$^+$. **Elemental analysis:** $C_{42}H_{54}N_4O_8Si$, **Calculated**: C, 65.43; H, 7.06; N, 7.27. **Found**: C, 62.80; H, 6.42; N, 7.05.

2.3.3. Silatranyl derivative of schiff base (SB-Silt)

Further, **SB-Sil** was derivatized to its silatranyl analogue (**SB-Silt**). It was obtained by dissolving triethanolamine (0.19 g, 1.27 mmol) and **SB-Sil** (1.0 g, 1.29 mmol) in dry toluene (40 mL) in a single-necked round bottom flask fitted with the Dean-Stark trap. Then, sodium methoxide (0.070 g, 1.2 mmol) was added and the mixture was refluxed for 6 h. Thereafter, the contents were cooled, filtered under vacuum and toluene was evaporated. The residue was washed with diethyl ether and dried to get a yellow solid. Yield: 82%, 0.83 g, **M.P.:** 182 °C. **FT-IR (cm^{-1}):** 592 ($Si \longleftarrow N$), 702, 767 (Si—O), 1067 (C—O), 1127 (Si—O), 1180 (CH_2O), 1286 (CH_2O), 1374, 1417 (CH), 1464 (C=C), 1548 (NH), 1585 (C=N), 1654 (—CO—NH), 2876, 2915 (CH_2), 3060 (-NH), 3378 b (OH). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 0.35 (t, 2H^{19}, $^3J = 7.6$ Hz), 1.49 (quin, 2H^{18}, $^3J = 7$ Hz), 2.76 (t, 6H^{21}, $^3J = 5.8$ Hz), 3.04 (q, 2H^{17}, $^3J = 6.6$ Hz), 3.39 (s, 8H^{14,15}), 3.72 (t, 6H^{20}, $^3J = 5.8$ Hz), 3.78 (s, 6H^{22}), 4.82 (t, 1H, NH, $^3J = 5.2$ Hz), 6.11 (dd, 2H^5, $^3J = 8.9$ Hz $^4J = 2.5$ Hz), 6.40 (d, 2H^3, $^4J = 2.5$ Hz), 6.61 (d, 2H^6, $^3J = 8.9$ Hz), 7.23-7.27 (m, 4H^{9,13}), 7.45-7.50 (m, 6H$^{10-12}$),