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Full Length Article

Dendrimeric tweezers for recognition of fluorogenic Co^{2+}, Mg^{2+} and chromogenic Fe^{2+}

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ABSTRACT

Dendrimers are the attractive candidature for the formation of metal complexes capable of performing varied application, owing to the presence of multiple terminal groups on the exterior of the molecule has received tremendous attention. Herein, we have synthesized novel dendritic macromolecule (N′E,N‴E,N″″E,N‴″″E)-3,3′,3″,3‴-(ethane-1,2-diylbis(azanetriyle))tetrakis(N′-(2-hydroxybenzyllidene)propanehydrazide) chemosensor **L** and its metal complexes. In the present study the application in the optical sensing for chromogenic Fe^{2+} and fluorogenic Co^{2+} and Mg^{2+}cation is reported. The dendrimeric chemosensor **L** and its metal complexes are investigated with the help of FTIR spectroscopy, Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR), FT Raman Microspectroscopy, fluorescence and UV–visible spectroscopy. Thermal properties are studied using thermal gravimetric analysis.

1. Introduction

Dendrimers are three dimensional scaffolds, which show the wide range of application in various fields such as nanotechnology, supramolecular chemistry, material science, additives, automobile parts, drug delivery, surface coatings, due to their converging reactive functional groups on interior or terminal side of the molecules [1-3].

Poly (amidoamine) [PAMAM] dendrimer with methyl ester terminated at the external surfaces termed half-generation (G= n.5) is used to form metal complexes by modification of terminal groups with different metal ion [4,5]. Terminal groups present in the dendrimer can alter the chemical nature of the dendrimer. The synthesis of new cation binding agents is an important area of current research interest due to the growing awareness of the environmental, clinical importance of cations and transition metals are great biological and chemical importance for the welfare of society [6–9]. For the detection and extraction of transition metal ions a huge plethora of chemosensors have developed, playing an important role in environment remediation [8,10]. Fluorescence spectroscopy an analytical technique is attractive and sensitive (parts per billion/trillion concentration studies), due to inexpensive, sensitive and ease to perform for detection of metal ion is very popular [11–22].

Cobalt is a transition series metal ion with biological relevance, an essential element for life in trace amounts. However, excessive cobalt dose has caused “beer drinkers cardiomyopathy” [28]. Fe^{2+} ion shows varied biological importance for the production of hemoglobin. However, excess of iron accelerates mitochondrial decay causing free radical damage to healthy tissue [29]. Mg^{2+} ions are essential to all cells animals as well as plants, essential to the functioning of numerous enzymes in humans, in green leaf chlorophyll which is a magnesium-centered porphyrin complex used for photosynthesis [33].

Lots of literature for the synthesis of azine metal complexes having chromogenic as well as fluorogenic properties, sensitive to change their optical properties is reported [13,23–26,34–51].

In the present work, we described the designing and fabrication of a novel dendrimer (N′E,N‴E,N″″E,N‴″″E)-3,3′,3″,3‴-(ethane-1,2-diylbis(azanetriyle))tetrakis(N′-(2-hydroxybenzyllidene)propanehydrazide) (chemosensor **L**). The chemosensor **L** with one core along with two side tweezers [52-53] of dendrimeric arms grab the metal cation forming metal complex. With the addition of aqueous solution of Fe^{2+} ion to synthesized chemosensor **L** (dendrimer), visual color change is detected. The fluorescence of chemosensor **L**.Mg^{2+} shows change in fluorescence, however remarked enhancement is observed in Co^{2+} metal ion.

Reactions:

Synthesis of chemosensor **L** (Fig. 1)(Scheme 1)

2. Experimental

2.1. Materials

All commercial grade reagents are procured and used without further purification. −0.05 G PAMAM is synthesized and purified

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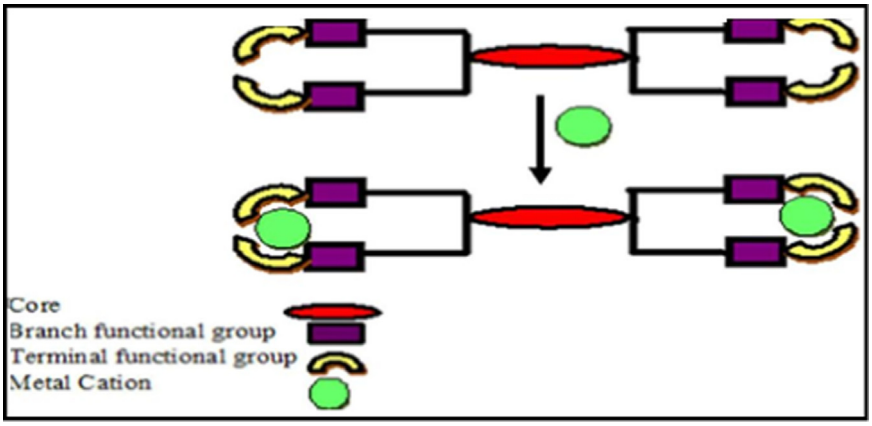

Fig. 1. Diagrammatic reaction illustration.

according to literature method [2]. For UV–visible and fluorescence study all the metal cations were added as their nitrates, chlorides and sulfates. For analytical studies, a stock solution of metal salts (1 mM) and receptor (0.1 mM) was prepared in water and Acetonitrile (MeCN) solvent system respectively.

2.1.1. Characterization

The absorption spectra were recorded on Shimadzu made UV-2450 Spectrophotometer. Fluorescence studies were carried out on a HORIBA JOBIN YVON, Fluoromax-4 Spectro fluorometer. The structural determinations were carried out by using FT-IR, ^{1}H NMR, ^{13}C NMR and LC–MS spectroscopic techniques. FT-IR spectra were recorded on the Perkin Elmer spectrum one Ltd., Singapore Spectrophotometer, by uniformly mixing the sample with KBr. ^{1}H NMR spectrum was recorded in $CDCl_3$ as a solvent with BRUKER ADVANCE II 400 Spectrometer with tetramethylsilane (TMS) as an internal reference standard. Mass spectra were recorded under ESI (+ve) mode, on WATERS, Q-TOF MICROMASS (LC–MS). The thermal gravimetric analysis were recorded on Perkin Elmer 4000 TGA.

2.2. Synthesis of chemosensor

2.2.1. Synthesis of –0.5 G of PAMAM

Synthesized as reported in literature [2]

2.2.2. Synthesis of chemosensor L

Reaction I – Addition of one mole of –0.5 G of PAMAM (12.54 g, 3.0 mmol) with four moles of hydrazine hydrate (6.0074 g, 12.0 mmol) without solvent stirring for 4 h at R.T.

Reaction II (chemosensor L)-Compound **I** is condensed with four moles of o-hydroxybenzaldehyde (14.65 g, 12.0 mmol) in ethanol (50 ml) with refluxing for 4 h. The filtrate is evaporated with the help of the vacuum Rota evaporator. After evaporation viscous compound obtained is washed with hexane.

Yield – 92%.

Solubility: DMSO, ethanol, methanol, chloroform, acetonitrile and DMF solvents.

IR of KBr: υmax/cm^{-1}=3508 cm^{-1} (O–H stretching), 3191 cm^{-1} (N–H stretching), 2840 cm^{-1} (C–H aliphatic, stretching), 1672 cm^{-1} (C=O amide, stretching), 1553 cm^{-1} (C=C aromatic, stretching), 1472 cm^{-1} (C–C aromatic stretching), 1377 cm^{-1} (C=N stretching), 1266 cm^{-1} (C–O aromatic, stretching).

^{1}H NMR (400 MHz, $CDCl_3$, TMS, s=singlet, d=doublet, t=triplet, h=heptet, m=multiplet): (δ, ppm)= 1.18–3.52(m, 20 H, CH_2); 6.92–7.96(m, 16 H, Ar–H); 8.16(s,4 H, CH); 9.80(s, 4 H, NH); 11.24 (s, 4 H, –OH).

^{13}C NMR (75 MHz, $CDCl_3$)=32.85, 50.28, 58.12, 116.75, 117.55, 119.88, 120.71, 131.25, 131.65, 133.75, 137.01, 158.06, 169.87.

LC–MS (TOF MS ES+) for $C_{42}H_{48}N_{10}O_8$ (m/z), 821 $[M+1]^+$.

2.2.3. Synthesis of L.M(II) complex:

Chemosensor **L.Co(II)** Synthesized by reaction of one mole of Ligand (1.0 g, 1.21 mmol) in 50 ml DMSO with two mole of cobalt chloride (0.57 g, 2.4 mmol) in 5 ml water with stirring and refluxing for 2 h. The precipitation was collected by filtration and dried in a vacuum. Further it is washed with water, then ethanol followed by petroleum ether.

Yield 86%.

Solubility: DMSO, acetonitrile and DMF solvents.

IR of KBr: υ_{max}/cm^{-1}=3402 cm^{-1}(N–H stretching), 2847 cm^{-1} (C–H aliphatic stretching), 1678 cm^{-1} (C=O amide stretching), 1605 cm^{-1} (C=C aromatic stretching), 1461 cm^{-1} (C–C aromatic stretching), 1383 cm^{-1} (C=N stretching) 1211 cm^{-1} (C–O aromatic, stretching), 451 cm^{-1} (Co–N stretching), 575 cm^{-1} (Co–O stretching).

LC–MS (TOF MS ES+) for $C_{42}H_{44}Cl_2Co_2N_{10}O_8$ (*m/z*), 1067 $[M+H_2O+2Na]^+$

L.Fe(II) Synthesized by reaction of one mole of Ligand (1.0 g, 1.21 mmol) in 50 ml DMSO with two mole of ferrous sulfate (0.67 g, 2.4 mmol) in 5 ml water with vigorous stirring and refluxing for 2 h. The precipitation was collected by filtration and dried in a vacuum. Further it is washed with water, then ethanol followed by petroleum ether.

Yield 82%.

Solubility: DMSO, acetonitrile and DMF solvents.

IR of KBr: υ_{max}/cm^{-1}=3477 cm^{-1} (N–H streching), 2777 cm^{-1} (C–H aliphatic stretching), 1670 cm^{-1} (C=O amide stretching), 1596 cm^{-1} (C=C aromatic stretching), 1452 cm^{-1} (C–C aromatic Stretching), 1383 cm^{-1} (C=N stretching), 1209 cm^{-1} (C–O aromatic, stretching), 447 cm^{-1} (Fe–N stretching), 526 cm^{-1} (Fe–O stretching).

LC–MS (TOF MS ES+) for $C_{42}H_{52}Fe_2N_{10}O_{12}$ (*m/z*), 1049 $[M+4H_2O+2Na+2H]^+$

L.Mg(II) Synthesized by reaction of one mole of Ligand (1.0 g, 1.21 mmol) in 20 ml ethanol with two mole of magnesium sulfate (0.60 g, 2.4 mmol) in 5 ml water with stirring and refluxing for 2 h. The precipitation was collected by filtration and dried in a vacuum. Further it is washed with water, then ethanol followed by petroleum ether.

Yield 78%.

Solubility: DMSO, acetonitrile and DMF solvents.

IR of KBr: υ_{max}/cm^{-1}=3183 cm^{-1} (N–H stretching), 2837 cm^{-1} (C–H aliphatic stretching), 1671 cm^{-1} (C=O amide stretching), 1553 cm^{-1} (C=C aromatic stretching), 1465 cm^{-1} (C–C aromatic