Experimental and computational investigation of highly selective dual-channel chemosensor for Al(III) and Zn(II) ions: construction of logic gates

SAMBAMOORTHY SANTHI^b, SUBBIAH AMALA^b and SABEEL M BASHEER^{a,*}

^aDepartment of Chemistry, University of Calicut, Malappuram, Kerala 673 635, India

^bPG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli, Tamil Nadu 620 002, India

E-mail: sabeelmb@gmail.com

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Abstract. The N,N'-Bis(salicylidene)-2-hydroxy-phenylmethanedi-amine (BSHPMD) was synthesized and characterized by IR, UV-Vis and ¹H NMR spectroscopic techniques. The single crystal X-ray diffraction studies reveal that the compound had a monoclinic crystal system with C2/c space group. The cation recognizing profile of the receptor BSHPMD was explored by UV-Vis and fluorescence spectroscopic methods. The receptor was found to recognize selectively Al³⁺ and Zn²⁺ ions over a panel of other metal ions such as Na⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Sr²⁺, Cd²⁺, Ba²⁺, Hg²⁺ and Pb²⁺. The Job's plot analysis reveals that BSHPMD binds with Al³⁺ and Zn²⁺ in 1:1 stoichiometry ratio. The binding constants of the receptor for Al³⁺ and Zn²⁺ were 2.13×10^3 and $16.23 \times 10^3 \text{ M}^{-1}$, respectively. The detection limit for Al³⁺ and Zn²⁺ is 10.04×10^{-8} and $4.98 \times 10^{-8} \text{ M}$, respectively. The NMR titration and IR titration studies reveal the sensing mechanism of BSHPMD. The multi-ion detection of BSHPMD is used to construct NAND and OR molecular logic gates. Hirshfeld surface analysis based on DFT method with 3-21G as basis set is used to calculate various intermolecular interactions. Fingerprint plots are made to find out the percentage of different types of interactions.

Keywords. Chemosensor; XRD; deformation density; molecular logic gate.

1. Introduction

A chemosensor may be defined as a sensory receptor or chemical indicator that transduces a chemical signal to an action potential indicative of the presence of an analyte.¹ If the colour, emission property or redox potential of the receptor changes upon binding with the analyte, then the receptor is defined as a sensor.² The fabrication of a chemosensor which is highly cost-effective as well as of peerless and inimitable quality has become inevitable since ions are found widespread in almost all fields such as medicine, industries and also in environment.³

Literature survey revealed that Schiff bases act as chemosensors for many anions and cations.⁴⁻⁷ The multi-ion detection using single molecule is very

limited.⁸ Such type of sensors could overcome the difficulties encountered with loading multiple indicators and also finds application in the development of logic gates.⁹ Schiff base may also find application in bio-imaging¹⁰ and water quality assignments.¹¹

In the Earth's crust, aluminium is the most abundant (8.3% by mass) metallic element and the third most abundant of all elements (after oxygen and silicon). The element aluminium is intertwined with our day-to-day activities. The wider use of the said metal in kitchen wares, soft drink cans, in the pharmaceutical industry and also in food packing materials has exposed us to aluminium absorption resulting in slow accumulation of aluminium in various human organs leading to skeletal mineralization.¹² The augmentation of aluminium in human bodies retards numerous

*For correspondence

enzyme activities thereby hampering iron metabolism.¹³ Besides, aluminum affects the lives of aquatic animals such as fish and invertebrates by causing osmoregulatory failure in them.¹⁴ Nerve fibre degeneration also can be ascribed to the adverse effect of aluminium where memory process gets affected, leading to the Alzheimer's and Parkinson's diseases.¹⁵ Zinc, which is *sine qua non* for various biological functions in humans is good when taken in limited quantity; but excessive intake is baleful and counterproductive resulting in many disorders.

In the present study, a Schiff base namely N, N'-Bis(salicylidene)-2-hydroxy-phenylmethanediamine (BSHPMD) was prepared by making some modifications in the literature method and well characterized. The structure of BSHPMD was established by single-crystal XRD study, Hirshfeld surfaces and fingerprint analysis. The chemosensing property of the Schiff base receptor was analysed by UV-Vis and fluorescence spectroscopic methods and it was found to act as a sensor selectively for Al^{3+} and Zn^{2+} ions over a number of other metal ions. The ^1H -NMR and IR studies confirm the deprotonation, revealing the sensing mechanism. The sensing action of the receptor was established as reversible by titration with Na_2EDTA .

2. Experimental

2.1 Materials and methods

Chemicals used for carrying out this work were purchased from Sigma Aldrich chemicals, India and used as received. All the solvents used were of analytical grade. The various metal ion solutions were prepared from the respective chloride salts except for lead (lead acetate). The ^1H -NMR spectrum was recorded at room temperature on an FT-NMR spectrometer (500 MHz) (Bruker Avance III 500) in DMSO-d_6 . IR spectrum was recorded in KBr medium using FT-IR spectrometer (model: Perkin Elmer Spectrum-1) at 298K. The UV-Vis spectrum of the receptor was taken in the Shimadzu UV Spectrophotometer (UV-1800) in methanol medium. The fluorescence measurements were carried out in a quartz cell, in a Jasco Spectrofluorometer (FP-8200). The IR spectral

titration studies were carried out in ATR mode with methanol as solvent.

2.2 X-ray crystallography

Data collection: Bruker AXS kappa APEX2 CCD Diffractometer, temperature 296(2) K, $\text{MoK}\alpha$ radiation ($\lambda = 71073\text{\AA}$) graphite monochromator, cell refinement using APEX2/SAINT, data reduction with SAINT/XPREF, structure solved by SIR92,¹⁶ structure refinement done using SHELXL-2014/7, molecular graphics done by ORTEP 3¹⁷ and mercury¹⁸ and experimental absorption process with SADABS.

2.3 Synthesis of Schiff base receptor

A mixture of ammonium acetate (1 mole) and salicylaldehyde (1 mole) in ethanol was heated to a temperature of 50°C and then shaken well in an airtight container until the solid mass was obtained. It was filtered and then washed with water followed by ether. The single crystal suitable for X-ray studies was obtained on slow evaporation of the compound in an equimolar solution mixture of ethanol and acetonitrile. In the literature method,¹⁹ the condensation was performed in the presence of Et_3N . We have executed the condensation without Et_3N and accomplished with high yield and good purity. Yield: 98% M.p. 165°C ; m.w(g/mol): 346.37; IR (Solid state, cm^{-1}): $\nu(\text{O-H})$ 3247; $\nu(\text{C=N})$ 1625; $\nu(\text{C-O})$ 1251; $\nu(\text{C-H})$ 752; ^1H NMR (In DMSO-d_6 , ppm): δ 13.18(s,H); δ 9.92(s,H); δ 8.81(s,H); δ 6.36–7.57(m,H) (Scheme 1).

3. Results and Discussion

3.1 Spectral characterization of BSHPMD

The synthesized compound was characterized by various analytical and spectroscopic techniques. The IR spectrum (Figure S1, Supplementary Information) of BSHPMD shows a broadband at 3247 cm^{-1} , which indicates the presence of the phenolic $-\text{OH}$ group involved in intramolecular hydrogen bonding.²⁰ There is a sharp and strong absorption band at 752 cm^{-1} , corresponding to aromatic C–H bending mode, supporting the view

Scheme 1. N,N'-Bis(salicylidene)-2-hydroxy-phenylmethanediamine (BSHPMD).

Figure 1. ORTEP view of BSHPMD.

that the compound is aromatic.²¹ The presence of imine group ($-\text{C}=\text{N}-$) is confirmed by the strong band at 1625 cm^{-1} .²² In ^1H NMR spectrum (Figure S2, Supplementary Information), the multiplet extending from δ 6.87 to 7.57 ppm corresponds to the thirteen protons of three phenyl rings of the receptor.²³ The peak at δ 6.35 ppm corresponds to the C–H proton, which is attached to the two imine nitrogen. The phenolic protons ^aH and ^bH which are in similar environment appear at δ 13.18 ppm. The phenolic proton H^c , which is under an entirely different chemical environment appears at δ 8.81 ppm.²⁴ The azomethine protons appear at δ 9.92 ppm.²⁵ The absorption spectrum of BSHPMD shows well-defined bands at 260, 318 and 400 nm in methanol medium. The band at 260 nm is due to $\pi - \pi^*$ transitions of the aromatic part of BSHPMD. Whereas, the band at 318 nm is assigned to $n - \pi^*$ transition associated with the azomethine linkage.²⁶ The longer wavelength band at 400 nm is due to intramolecular charge transfer transitions.

3.2 Crystal structure of BSHPMD

The single crystal X-ray diffraction studies on the ligand further confirm the proposed structure. The CCDC deposit number for the crystal structure is 1429891. An ORTEP view of the ligand with the atom-numbering scheme is shown in Figure 1. The crystallographic data are shown in Table 1 and the bond angles and bond distances are shown in Table 2. The existence of a hydrogen bond between the phenolic hydrogen and azomethine nitrogen is confirmed and the data for the hydrogen bonding are presented in Table 3. A crystal with dimensions of $0.300 \times 0.250 \times 0.200\text{ mm}^3$ was used for X-ray data collection. The compound

crystallised in monoclinic lattice having C2/c space group with $a = 17.2077(8)\text{ \AA}$, $b = 12.3043(5)\text{ \AA}$, $c = 18.1985(12)\text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 112.650(2)^\circ$ and $Z = 8$. The torsion angle between C(6)–C(7)–N(1)–C(8) is $178.63(16)^\circ$ and the angle between C(16)–C(15)–N(2)–C(8) is $175.72(15)^\circ$ confirmed the Schiff base formation. The C(7)–N(1) distance is $1.270(2)\text{ \AA}$ and the distance between C(15)–N(2) is $1.280(2)\text{ \AA}$. In the Schiff base ligand C(7)–N(1)–C(8) bond angle is $121.96(15)^\circ$ and C(15)–N(2)–C(8) bond angle is $120.73(14)^\circ$. The crystal packing and the hydrogen bond network of Schiff base ligand are depicted in Figure 2.

3.3 Metal ion detection studies

To ascertain the metal ion sensing property, the receptor was subjected to absorption and emission studies in methanol medium at a concentration of $1 \times 10^{-4}\text{ M}$. The metal ion concentration was maintained at $3 \times 10^{-3}\text{ M}$.

3.3a UV-Vis spectral studies: The receptor was allowed to interact with two equivalents of various metal ions such as Na^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sr^{2+} , Cd^{2+} , Ba^{2+} , Hg^{2+} , Pb^{2+} and Al^{3+} . A significant change in absorption behaviour of the receptor was observed only in the presence of Al^{3+} and Zn^{2+} ions. In the absence of metal ions, the receptor exhibited three absorption bands at 260, 318 and 400 nm. The interaction with Al^{3+} was exemplified by the appearance of a new band at 352 nm with a concomitant disappearance of the bands at 318 and 400 nm. Likewise, the interaction between the receptor and Zn^{2+} was authenticated by the blue shift of the band at 400 nm to an extent of 39 nm (Figure 3). The addition of other metal ions resulted in no significant spectral changes, thus proving the selective sensing property of the receptor towards Al^{3+} and Zn^{2+} ions.

The coordinating potentiality of the receptor was further scrutinized by UV-Vis titration experiments involving the gradual addition of 0.2 to 2 equivalent of $3 \times 10^{-3}\text{ M}$ solutions of Al^{3+} and Zn^{2+} to a solution of the receptor. The incremental addition of Al^{3+} resulted in a decrease in the absorbance of the bands at 318 and 400 nm and there is the appearance of a new band at 350 nm. The sequential addition of Zn^{2+} to the receptor showed a small redshift along with an increase in the absorbance of the band at 318 nm. In addition, for the band at 400 nm, a blue shift was observed to an extent of 39 nm with an obvious isosbestic point at 379 nm. The deviations in the absorbance of the new band occurring during the addition of respective ions were depicted in the inset plot. The variations in the absorption may be due to the complex formation between the receptor and

Table 1. Crystal data and structure refinement for BSHPMD.

CCDC number	1429891	
Empirical formula	C ₂₁ H ₁₈ N ₂ O ₃	
Formula weight	346.37	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.2077(8) Å b = 12.3043(5) Å c = 18.1985(12) Å	$\alpha = 90^\circ$ $\beta = 112.650(2)^\circ$ $\gamma = 90^\circ$
Volume	3556.0(3) Å ³	
Z	8	
Density (calculated)	1.294 Mg/m ³	
Absorption coefficient	0.088 mm ⁻¹	
F(000)	1456	
Crystal size	0.300 × 0.250 × 0.200 mm ³	
Theta range for data collection	2.094 to 24.998°	
Index ranges	−20 ≤ h ≤ 20, −14 ≤ k ≤ 14, −21 ≤ l ≤ 21	
Reflections collected	22251	
Independent reflections	3142 [R(int) = 0.0199]	
Completeness to theta = 24.998°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.990 and 0.968	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3142 / 0 / 235	
Goodness-of-fit on F ²	1.146	
Final R indices [I > 2sigma(I)]	R1 = 0.0419, wR2 = 0.0997	
R indices (all data)	R1 = 0.0565, wR2 = 0.1176	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.245 and −0.203 e.Å ⁻³	

Table 2. Selected bond distances(Å) and bond angles(°) for BSHPMD.

C(1)–O(3) 1.351(2)	N(1)–C(7)–C(6)	122.31(17)
C(14)–O(2) 1.358(2)	N(1)–C(7)–H(7)	118.8 122.31(17)
C(15)–N(2) 1.280(2)	N(1)–C(8)–N(2)	113.28(14)
C(21)–O(1) 1.337(2)	N(1)–C(15)–C(16)	121.24(16)
O(1)–H(1A) 0.8200	N(2)–C(15)–H(15)	119.4
O(2)–H(2A) 0.8200	O(1)–C(21)–C(20)	120.08(17)
O(3)–H(3A) 0.8200	C(7)–N(1)–C(8)	121.96(15)
C(15)–N(2)–C(8)		120.73(14)

Table 3. Hydrogen bonds for BSHPMD [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	< (DHA)
C(15)–H(15)...O(3)#1	0.93	2.62	3.541(2)	173.0
O(1)–H(1A)...N(2)	0.82	1.78	2.5231(18)	149.1
O(2)–H(2A)...O(1)#2	0.82	1.86	2.6797(18)	176.7
O(3)–H(3A)...N(1)	0.82	1.89	2.616(2)	147.0

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, -y+3/2, -z+1$; #2 $-x+1/2, y+1/2, -z+1/2$.

the metal ion, paving the way for the ligand to metal charge transfer transitions.²⁷ The binding constants of Al³⁺ and Zn²⁺ ions with receptor are determined using

Benesi–Hildebrand plot, as 2.13×10^3 and $16.23 \times 10^3 \text{ M}^{-1}$ respectively, which is indicative of a firm coordination of Al³⁺/Zn²⁺ ions with the receptor.^{28,29}

Figure 2. Packing view of BSHPMD.

Figure 3. (a) UV-Vis titration of receptor BSHPMD (1×10^{-4} M) with Al^{3+} (3×10^{-3} M); Inset: Variation of absorbance at 364 nm in the presence of Al^{3+} ; (b) UV-Vis titration of receptor (1×10^{-4} M) with Zn^{2+} (3×10^{-3} M); Inset: Variation of absorbance at 375 nm in the presence of Zn^{2+} , where [R] is the concentration of receptor BSHPMD. Optical path length = 1.

3.3b Fluorescence spectral studies: The fluorescence spectrum of the receptor BSHPMD recorded by keeping the excitation wavelength at 260 nm, showed emission at 450 nm. The changes in the emission behaviour of the receptor upon addition of 2 equivalent of various metal ions are depicted in Figure 4. A conspicuous augmentation in the fluorescence intensity of the receptor band at 450 nm, 18-fold in the case of Al^{3+} and 95-fold in the case Zn^{2+} on the addition of 2 equivalents was striking to the eye. Whereas the addition of other metal ions such as Na^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Sr^{2+} , Cd^{2+} , Ba^{2+} , Hg^{2+}

and Pb^{2+} did not trigger any noticeable change in fluorescence intensity. The above enhancement in fluorescence intensity may be attributed to the complex formation between the metal ion and the receptor. The formed complex may be a rigid chelate system leading to chelation-enhanced fluorescence effect (CHEF).^{30,31} The CHEF effect diminished the PET process in the ligand. The binding mode of the receptor with Al^{3+} and Zn^{2+} was ascertained by gradual addition (0.2 to 2 equivalent) of the latter to the former. In both cases, the intensity of the emission peak at 450 nm (λ_{max}) was gradually enhanced (Figure 5a and 5b). A small blue

shift was also observed in the case of titration with Al^{3+} ions. The results indubitably revealed that the receptor BSHPMMD could serve as a good fluorescent probe for Al^{3+} and Zn^{2+} ions in methanol solution.

3.3c Selectivity and competitive studies: In order to manifest the selectivity of the receptor, its recognizing ability was examined in the presence of other metal ions. In the presence of competitive cations, trapping of Al^{3+} and Zn^{2+} ions caused the same fluorescence changes. The receptor was treated with 2.0 equivalent of Al^{3+} in the presence of 2.0 equivalent of all other metal ions. The data clearly suggest that there is no interference of

other metal ions for the sensing of Al^{3+} . Likewise, the selectivity of receptor towards Zn^{2+} in the presence of various other metal ions was proved by nil interference shown by other metal ions for the sensing of Zn^{2+} ions except for Cu^{2+} (Figure S4, Supplementary Information). Thus, the receptor can serve as a selective fluorescent sensor for Al^{3+} and Zn^{2+} .^{32–35}

3.3d Stoichiometry, detection limit and reversibility: Jobs plot studies reveal that the stoichiometry of the complex formed by receptor with Al^{3+} and Zn^{2+} ions was 1:1 (Figures S5 and S6, Supplementary Information).^{36,37} The detection limits for Al^{3+} and Zn^{2+} were 10.04×10^{-8} and 4.98×10^{-8} M respectively (Figures S7 and S8, Supplementary Information).³⁸ The reversibility of the recognition process of receptor was evaluated by adding Na_2EDTA to a mixture of receptor and $\text{Al}^{3+}/\text{Zn}^{2+}$ which resulted in the diminution of the fluorescent intensity at 450 nm, indicating the reappearance of the free receptor (Figure S9, Supplementary Information).^{39,40}

3.3e ^1H NMR titration studies: To explain the binding mode of receptor and metal ions, the ^1H NMR titrations were performed in DMSO-d_6 . In the case of free ligand, both the phenolic protons ^aH and ^bH appeared at δ 13.17 ppm. The addition of 2 equivalents of Zn^{2+} ions leads to the disappearance of the peak at δ 13.17 ppm, which confirms the involvement of the two phenolic groups in coordination with the metal ion in a deprotonated fashion. The other two coordination sites are authenticated by the downfield

Figure 4. Fluorescence spectrum of receptor BSHPMMD (1×10^{-4} M) in presence of 2 equiv. various metal ions (3×10^{-3} M) in CH_3OH solution.

Figure 5. (a) Fluorescence spectrum of receptor BSHPMMD (1×10^{-4} M) with gradual addition of Al^{3+} in CH_3OH solution ($\lambda_{\text{ex}} = 260$ nm); Inset: changes of fluorescence upon addition of Al^{3+} at 450 nm, where $[\text{R}]$ is the concentration of receptor BSHPMMD; (b) Fluorescence spectrum of receptor (1×10^{-4} M) with gradual addition of Zn^{2+} in CH_3OH solution ($\lambda_{\text{ex}} = 260$ nm); Inset: changes of fluorescence upon addition of Zn^{2+} at 450 nm., where $[\text{R}]$ is the concentration of receptor BSHPMMD.

Figure 6. ^1H NMR Spectra of receptor BSHPMD and receptor with Zn^{2+} and Al^{3+} ions.

Figure 7. Cyclic voltammogram of receptor and receptor with Al^{3+} and Zn^{2+} ions, where R is BSHPMD.

shift of azomethine protons' signal from δ 9.92 ppm to δ 9.96 ppm. These observations confirm the chelate formation between the receptor and Zn^{2+} ions (CHEF effect).

In the case of aluminium, the addition of two equivalents of Al^{3+} ion causes the disappearance of the peak at δ 13.17 ppm confirming the coordination involvement of phenolic groups present in A and B rings *via* deprotonated fashion. The disappearance of the peak corresponding to H^c proton in the ligand (δ 8.81 ppm)

confirms the aluminium ion coordinated to the phenolic group in the ring C in a deprotonated fashion. The peak corresponds to azomethine proton shifted to downfield shift (δ 10.05 ppm). The peak at δ 6.35 ppm, which corresponded to the C-H proton in between the two imine nitrogens, was shifted to upfield to δ 5.68 and 5.56 ppm in the presence of Zn^{2+} and Al^{3+} ions respectively. The small variations in the aromatic region are due to the variations in the geometry of the formed complexes. Thus, in the sensing of Al^{3+} , the aluminium ion coordinates to BSHPMD *via* three phenolic oxygen and two imine nitrogen, and form penta coordinated complex.^{41–44} Whereas, in the case of Zn^{2+} ion, tetra coordinated complex was formed. Figure 13 shows the different binding nature of metal ions towards the receptor BSHPMD. Figure 6 shows the ^1H NMR spectra of receptor BSHPMD and receptor in the presence of zinc and aluminium ions.

3.3f IR spectral studies: In IR spectra of free ligand, the band due to $-\text{C}=\text{N}-$ bond appears at 1635 cm^{-1} . While the peak was shifted to an extent of 3 and 15 cm^{-1} in the presence of Al^{3+} and Zn^{2+} ions respectively. The appearance of new bands at 419 and 415 cm^{-1} in the presence of Al^{3+} and Zn^{2+} respectively, corresponding to the metal-nitrogen bond further confirms the coordination of receptor with metal ions. The emergence of new bands in the region of about

Figure 8. Hirshfeld surfaces (a) $dnorm$, (b) de , (c) di , (d) curvedness and (e) shape index.

650 cm^{-1} may be due to the coordination of receptor through its phenolic oxygens. Figure S10 (Supplementary Information) shows the FTIR spectra of receptor and receptor in the presence of zinc and aluminium ions.

3.3g CV studies: The coordination of BSHPMD with Al^{3+} and Zn^{2+} ions was further evidenced by cyclic voltammetry studies. The cyclic voltammogram of receptor exhibits two oxidation peaks ($E_{\text{ox}} = -0.142\text{ V}$ and 0.933 V) and one reduction peak ($E_{\text{red}} = -0.133\text{ V}$).

Figure 9. Fingerprint plots of BSHPMD.

The addition of 2 equivalents of Al^{3+} and Zn^{2+} causes the disappearance of the oxidation peak at $E_{\text{ox}} = 0.933\text{ V}$ and E_{red} value is changed to $-0.614/-1.120\text{ V}$ from -1.133 V . It is observed that there is also a considerable change in the ΔE value of the order of 0.479 and 0.624 V for Al^{3+} and Zn^{2+} respectively. These observations provide additional evidence for complex formation (Figure 7).

3.4 Hirshfeld surface analysis and Fingerprint analysis

Hirshfeld surface analysis technique is exploited for the calculation of intermolecular interactions. Hirshfeld surface of the receptor BSHPMD is portrayed in Figure 8 with respect to various properties such as d_i ,

Figure 10. Pie chart of molecular interactions for BSH-PMD.

de, *dnorm*, shape index and curvedness.⁴⁵ *dnorm* surface highlighted two bright red spots indicating the presence of close contacts in terms of hydrogen bonding, as well as O–H and H–O interactions.⁴⁶ The *di* surfaces exhibited red spots proving the presence of H...O interactions to an extent of 6.4%. The *de* surface showed bright red spots evidencing O...H interactions as dominating ones. The shape index indicated the shape of electron density surface around the molecular interactions. The surfaces in the crystal packing clearly indicate the O–H...C and O–H...O interactions (Figure S11, Supplementary Information). The deformation density of the molecule is calculated as 0.008 a.u. (maximum) and –0.008 a.u. (minimum). A graphical view of the deformation density is shown in Figure S12 (Supplementary Information). The surfaces are calculated using DFT method with 3–21G as a basis set from the crystal data. The 2D fingerprintplots⁴⁷ of the Schiff base BSH-PMD (Figure 9) summaries the pattern of various intermolecular interactions. The O...H interactions and H...O interactions were appearing as spikes in the bottom and top regions. The H...H interactions appeared in the middle region, whereas, H...C, C...H and C...C interactions were present in the top right, left corners and top region respectively. The presence of very weak N...H and H...N interactions were also depicted in the picture. The pie chart delineates the percentage contribution of various types of interactions present in the receptor (Figure 10).

3.5 Logic gate application

The molecular computing is based on chemical reactions that has motivated in the development of molecular

logic devices at the molecular level. The distinct optical behavior of BSH-PMD towards Zn^{2+} and Al^{3+} ions is used to construct a molecular logic gate. For the investigation of their logic behaviors, the threshold values are assigned and then the logic convention is used for their inputs and outputs signals. The input signals are the values of '0' and '1' corresponding to the absence and the presence of $\text{Al}^{3+}/\text{Zn}^{2+}$ ions respectively. Whereas, the absorbance at a given wavelength taken as output, which are the values of 0 and 1 depending on the absorbance value below or above a certain threshold. The investigation was carried out with taking two input signals, such as the presence of Zn^{2+} (In_1) and Al^{3+} (In_2) ions. Figure 11 shows different absorption spectra of BSH-PMD observed with the addition of two inputs (Al^{3+} and Zn^{2+}). In the presence of individual ions (Al^{3+} and Zn^{2+}), the absorbance at 317 nm was retained, whereas in the mixture of Al^{3+} and Zn^{2+} the intensity of the absorbance reduced, which leads to the construction

Figure 11. UV-Vis spectral changes with the addition of individual and mixture of Al^{3+} and Zn^{2+} ions. (Concentration of receptor BSH-PMD = 1×10^{-4} M, Concentration of $\text{Zn}^{2+}/\text{Al}^{3+}$ = 3×10^{-3} M Optical path length = 1).

Truth Table			
Input 1 (Al^{3+})	Input 2 (Zn^{2+})	Output (352 nm)	Output (317 nm)
0	0	0	1
1	0	1	1
0	1	1	1
1	1	1	0

Figure 12. Truth table and schematic representation of OR and NAND gates.

Figure 13. (a) Proposed binding mode of BSHPMD towards Zn²⁺; (b) Proposed binding mode of BSHPMD towards Al³⁺.

of NAND logic gate. The presence of Al³⁺ ion results formation of the new strong absorption peak at 352 nm. The addition of Zn²⁺ and the mixture of Al³⁺ and Zn²⁺ ions also show an increase in absorbance at 352 nm. This can be explained by using OR logic gate. By monitoring the absorption changes of BSHPMD at 317 and 352 nm, the logic gates were constructed. The circuit and the truth table are shown in Figure 12.

3.6 Binding site

On the basis of experimental and computational results, the probable binding mode of the receptor with the metal ions is sketched in Figure 13.

4. Conclusions

The Schiff base N,N'-Bis(salicylidene)-2-hydroxy-phenylmethanedi-amine (BSHPMD) has been synthesized. The structure of receptor BSHPMD has been confirmed from the Single-crystal X-ray diffraction technique. The intermolecular interactions are visualized by a Hirshfeld surface analysis. Fingerprint plots confirm the quantity of interactions present in the receptor molecule. The Schiff base BSHPMD acts as a chemosensor selectively for Al³⁺ and Zn²⁺ ions over a number of other metal ions such as Na⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Sr²⁺, Cd²⁺, Ba²⁺, Hg²⁺ and Pb²⁺. The sensing property of the receptor is assessed by UV-Vis and fluorescence spectroscopic methods. The association constants of the receptor for Al³⁺ and Zn²⁺ ions are determined by the Benesi-Hildebrand plot and

found as 2.13×10^3 and $16.23 \times 10^3 \text{ M}^{-1}$ respectively. The stoichiometry ratio of the receptor BSHPMD with Al³⁺ and Zn²⁺ is found to be 1:1. On the basis of experimental and computational results, the probable binding mode of the receptor with the metal ions is suggested. The recognizing efficiency of the receptor is found to be reversible. It can be concluded that Schiff base receptor BSHPMD prepared from commonly available reagents could act as cost-effective, selective, sensitive and reversible sensor for Al³⁺ and Zn²⁺ ions over many other ions. It could also be used for OR and NAND molecular logic gates.

Supplementary Information (SI)

CCDC: 1429891 contains the supplementary crystallographic data for BSHPMD. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. IR spectra of receptor (Figure S1), ¹H NMR spectra of receptor (Figure S2), UV-Vis spectrum of receptor in presence of 2 equivalent of various metal ions (Figure S3), Selectivity and competitive studies (Figure S4), Job's plots (Figures S5 and S6), Calibration curves for calculating detection limit (Figures S7 and S8), reversibility plot of receptor (Figure S9), IR spectral studies (Figure S10), Hirshfeld surfaces (Figure S11) and deformation density surface (Figure S12) are given in the supplementary information. Supplementary Information is available at www.ias.ac.in/chemsci.

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