



# Novel symmetric diimine-Schiff bases and asymmetric triimine-Schiff bases as chemosensors for the detection of various metal ions



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## ABSTRACT

In this study, two symmetric diimine-Schiff bases (**D<sub>1</sub>**, **D<sub>2</sub>**) containing nitro group were synthesized by a simple one-pot condensation of 4-nitro-o-phenylenediamine with substituted-salicylaldehyde (5-Cl, 5-CH<sub>3</sub>) in 1:2 ratio. After the selective reduction of nitro group to amino group by using sodium dithionite and forming the new imine bond by adding substituted-salicylaldehyde or 2-hydroxy-1-naphthaldehyde, four asymmetric triimine-Schiff bases (**T<sub>1s</sub>**, **T<sub>1n</sub>**, **T<sub>2s</sub>**, and **T<sub>2n</sub>**) were obtained. Results of the newly synthesized compounds established by elemental analyses, FT-IR, UV–vis, 2D NMR (HMQC), <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and TOF-mass spectroscopic experiments were consistent with their chemical structures. The tautomeric equilibria were also studied. The sensor properties of all Schiff bases were examined upon addition of the metal ions, such as Cr<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Pb<sup>2+</sup>. The interactions between receptors and ions are easily monitored by UV–vis method. The receptor **D<sub>2</sub>** showed colour changes from yellow to intense deep orange colour for Cu<sup>2+</sup>, a orange colour for Co<sup>2+</sup> and dark yellow colour for other ions. Although metal ions caused no change in colour of **T<sub>2s</sub>**, the main absorption band of receptor shifted from 351 nm to 343–372 nm **T<sub>2n</sub>** underwent colour changes from yellow to light yellow on gradual addition of Fe<sup>3+</sup>.

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## 1. Introduction

The designing and synthesis of new organic molecules with colorimetric or fluorescent chemosensor, which is eco-friendly, non-harmful and highly sensitive and selective towards metals, are currently of great attention. Many organic sensors have been developed to detect metal ions such as Mn<sup>2+</sup> [1], Fe<sup>2+</sup> [2], Co<sup>2+</sup> [3], Ni<sup>2+</sup> [4], Cu<sup>2+</sup> [5], Zn<sup>2+</sup> [6], Hg<sup>2+</sup> [7], Al<sup>3+</sup> [8], and Pb<sup>2+</sup> [9] in aqueous media.

Schiff bases, having an azomethine group (–C=N–), and diimine (bis-) Schiff bases, having two azomethine group (–C=N–), are among the most important ligands used in modern coordination chemistry due to their well-known coordinative capability. These Schiff bases and their complexes have wide application in different areas of electrochemistry [10], catalysis [11], solid phase extraction of metal ions and separation processes [12,13], and various types of polymerization [14]. They are also found to exhibit a broad range of biological activities, containing antibacterial [15],

antifungal [16], antimalarial [17], antiproliferative [18], anti-inflammatory [19], antiviral [20], antipyretic [21], antitumor [22], and antioxidant [23]. Moreover, they are becoming important in the corrosion inhibitors [24], highly selective polymer membrane electrodes [25], optical sensors [26], and biological probes [27].

Symmetrical bis-Schiff bases of the type R–N=CH–Ar–CH=N–R or R–CH=N–Ar–N=CH–R are prepared by the condensation reaction of primary amines with active carbonyl groups of dialdehydes in 2:1 M ratio and the reaction of diamines with aldehydes or ketones in 1:2 M ratio. But, asymmetric diimine Schiff bases of the type R–N=CH–Ar–N=CH–R can not be synthesized directly. At this stage, my particular interest was focused on the synthesis of these Schiff bases with a new two step method [28], which is based on the conversion of the nitro group into the amino group.

Aromatic nitro compounds can be reduced to the corresponding derivatives such as nitroso, N-arylhydroxylamine, amine and also azoxy-arene, azo-arene and hydrazo-arene with varieties of methods, catalytic and non-catalytic. For example, catalytic transfer hydrogenation by palladium, platinum on carbon [29]; metal hydrides (lithium tetrahydroaluminate, lithium borohydride, sodium tetrahydroborate, etc.) [30]; Bechamp reduction by iron metal [31];

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stannous chloride dihydrate [32], Birch reduction by using sodium, potassium, lithium, and samarium metals in alcohol [33]; Zinin reduction by sulfide, hydrosulfide, polysulfides [34]; Wolff-Kishner reduction by hydrazine [35]; and carbon catalyzed reduction [36]. However, many of these methods require either expensive equipment, compressed hydrogen gas, heavy metal catalysts, acidic conditions, high temperatures or pressure. Some of them have disadvantage of formation of metal sludge that is difficult to filter and the risk of reducing other groups.

Nitroarenes including reducible substituents such as acid, phenol, halogen, etc. are also chemoselectively reduced to amines in good yields by using sodium dithionite (sodium hydrosulfite) [37]. Sodium dithionite is stable at temperatures below 50 °C. It is readily soluble in water, but it has the poor solubility in organic solvents.

In this work, it has been aimed to obtain new colorimetric chemosensors for selective detection of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  ions in aqueous media. Therefore, the symmetric diimine Schiff bases of the type  $\text{R}-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{R}$  in quantitative yields have been synthesized by condensation of 4-nitro-*o*-phenylenediamine with two equivalents of (5-Cl/CH<sub>3</sub>)-salicylaldehyde. Then, the nitro group of these Schiff bases has been reduced to the amino group by using sodium dithionite, and formed the new imine bond by adding aldehyde without isolation the corresponding amino compound. So, a new novel series of two symmetric tetradentate Schiff bases and four asymmetric hexadentate Schiff bases, which having more binding nature towards metal ions, have been prepared as chemosensor. The investigation of phenol-imine keto-amine tautomerism in all Schiff bases has been also noted by spectroscopic methods.

## 2. Experimental

### 2.1. Materials and reagents

All chemicals used were of the analytical reagent grade and of highest purity available. They included 4-nitro-*o*-phenylenediamine (Merck), 5-chloro-salicylaldehyde (Aldrich), 5-methyl-salicylaldehyde (Aldrich), 2-hydroxy-1-naphthaldehyde (Aldrich), sodium dithionite (Aldrich),  $\text{Pb}(\text{NO}_3)_2$  (Aldrich),  $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Panreac Applichem),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (Carlo Erba),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Aldrich),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Merck). Organic solvents used included absolute ethyl alcohol (Sigma-Aldrich), diethylether (Riedel-de-Haen), dimethylsulfoxide (DMSO) (Merck), dimethylformamide (DMF) (Riedel-de-Haen), methanol (Merck), chloroform (Aldrich) and toluene (Riedel-de-Haen). These solvents were spectroscopic pure.

### 2.2. Instrumentation

Melting points were determined on Barnstead Electrothermal BI 9200. Elemental analysis was performed on LECO CHNS-932 analyzer. IR spectra in the 4000–400  $\text{cm}^{-1}$  range were measured using KBr discs on a Mattson 1000 FTIR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance DPX FT-NMR spectrometer operating at 400 MHz (DMSO-*d*<sub>6</sub> as solvent, TMS as internal standard). 2D NMR (HMQC) were obtained on a Bruker Ultrashield 300 MHz. The high resolution mass spectra were performed on a Waters Lct Premier XE oa-TOF Mass spectrometer. UV–visible absorption spectra were obtained using Shimadzu UV–1800 UV–Vis spectrophotometer.

#### 2.2.1. Absorption measurements of all Schiff bases

UV–vis spectra were measured in DMSO for (**D**<sub>1</sub>, **D**<sub>2</sub>, **T**<sub>1s</sub> and **T**<sub>2s</sub>),

and in various solvents (DMSO, methanol, chloroform and toluene) for (**T**<sub>1n</sub> and **T**<sub>2n</sub>) with 0.01 mM concentration over the wavelength range 270–600 nm at room temperature. Changes in the wavelength of the maximum absorption ( $\lambda_{\text{max}}$ ) were also investigated in pure solvents, acidic and basic media for (**T**<sub>1n</sub> and **T**<sub>2n</sub>). 0.2 mL trifluoroacetic acid and 0.2 mL triethylamine were added to the solutions (5 mL) in all polar and non-polar solvents to provide the acidic and basic media, respectively.

### 2.3. Colorimetric chemosensor

#### 2.3.1. Evaluation of sensitivity

To investigate the sensing properties of the diimine-Schiff base **D**<sub>2</sub> and triimine-Schiff bases **T**<sub>2s</sub> and **T**<sub>2n</sub>, the metal ions  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  for complexation with receptor were used. A stock solution of the metal ions (1 mM) was prepared in distilled water, and it was diluted to 0.1 mM in water. A stock solution of receptors (0.1 mM) was prepared in DMF. In selectivity experiments, the test samples were prepared by placing 2 mL of metal cation solution (0.1 mM) into 2 mL solution (0.1 mM) of ligand. After mixing them, UV–vis spectra were taken at room temperature in the wavelength interval of 270–900 nm, in steps of 1 nm using a 1-cm-thick quartz cell. For comparison of the effect of time on the stability of Schiff bases and the interaction of Schiff bases with ions, UV–vis spectra were also recorded 4 days later.

#### 2.3.2. UV–vis titration

In titration experiments, each time a 1 mL DMF solution of receptor (0.1 mM) was filled in test tube, and then increasing volumes (1–10 mL) of aqueous solution of the metal ion (0.1 mM) were added into tube. After mixing these samples, UV–vis spectra were taken at room temperature in the wavelength interval of 270–900 nm.

#### 2.3.3. Job plot measurements

In this study, the total concentration (0.1 mM) and total volume (10 mL) of the receptor and metal ion were kept constant, and changing the molar ratio of receptor from 0.1 to 1.0.

### 2.4. Synthesis

#### 2.4.1. Synthesis of the symmetric diimine-Schiff bases (**D**<sub>1</sub> and **D**<sub>2</sub>)

A solution of 4-nitro-*o*-phenylenediamine (0.153 g; 1 mmol) in 20 mL ethanol was added slowly and dropwise into a solution of substituted-salicylaldehyde (5-Cl, 5-CH<sub>3</sub>) (2 mmol) and the mixture was stirred. The resultant solution was heated on an electromagnetic stirring apparatus to reflux for 3 h. A yellow colored precipitate was filtered, washed with EtOH, recrystallized from EtOH, then dried in air.

#### 2.4.2. Synthesis of the asymmetric triimine-Schiff bases (**T**<sub>1s</sub>, **T**<sub>2s</sub>, **T**<sub>1n</sub> and **T**<sub>2n</sub>)

Asymmetric triimines were prepared with a new two step method:

##### D<sub>1</sub> derivatives (**T**<sub>1s</sub> and **T**<sub>1n</sub>)

1 mmol (0.430 g) of **D**<sub>1</sub> was dissolved in ethanol-water mixture (60:60 mL) at 70 °C. 5 mmol (0.8707 g) of solid sodium dithionite was slowly added to the solution as small solid pieces over one hour and stirred for one hour at 45 °C for finishing the reducing process. Thus, amino derivative of **D**<sub>1</sub> was formed in the solution. 1 mmol of appropriate aldehyde (5-methyl-salicylaldehyde and 2-hydroxy-1-naphthaldehyde) in 30 mL ethanol was added to this solution dropwise during the period of an hour with stirring. The mixture

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