



# A new Schiff-base as fluorescent chemosensor for selective detection of Cr<sup>3+</sup>: An experimental and theoretical study

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## ABSTRACT

A novel Schiff base fluorescent sensor N,N'-bis(salicylidene)-2,6-bis(4-aminophenyl)-4-phenylpyridine (**P3**) was synthesized through condensation of 2,6-bis(4-aminophenyl)-4-phenylpyridine and 2-hydroxybenzaldehyde. The obtained results from fluorescence analysis revealed that by excess of Cr<sup>3+</sup> to **P3**, a remarkable increase was observed in the fluorescent intensity of the Schiff base at 663 nm with the ratio of CH<sub>3</sub>CN/H<sub>2</sub>O (95/5%), even though the other cations would likely have no impact on the fluorescence intensity. The cause of this trend might be ascribed to the formation of a 1:1 stoichiometric **P3**-Cr<sup>3+</sup> complex, confirmed by Job's plot, which is resulted in preventing the photo-induced electron transfer (PET) process. From fluorescence titration, the association constant *K*<sub>a</sub> was gained 2.28 × 10<sup>5</sup> M<sup>-1</sup> and the limit of detection (LOD) was determined to be 1.3 × 10<sup>-7</sup> M. Furthermore, the optimized structure together with the electronic spectra of the proposed complex was determined by DFT and TDDFT calculations.

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## 1. Introduction

The synthesis and development of new fluorescent chemosensors with the goal of detecting the heavy and transition metal ions are attractive and promising, whereas their use is growing fast in several research areas such as supramolecular chemistry, organic chemistry, drug delivery, biological chemistry and environmental chemistry.<sup>1,2</sup> Among these compounds, N-heterocycles are considerable attention toward chemosensors due to their high selectivity and sensitivity and also most important moieties in medicinal chemistry.<sup>3–5</sup> To tackle the environmental and medical challenges, a significant effort has been devoted in designing small-molecule fluorescent organic issues for chromium (Cr<sup>3+</sup>) ion sensing. This vital ion, as an essential nutrient, plays a major role in the metabolism of carbohydrates, lipids, proteins, and nucleic acids in human body.<sup>6</sup> Another most important reason for enhancing the

risk factors connected with diabetes and cardiovascular disease is concerned to insufficient dietary intake of chromium ion.<sup>7</sup>

On the other hand, chromium is recognized as a noxious pollutant, omitted through various industrial and agricultural activities, that it can definitely be detrimental for both environment and human health.<sup>8</sup> Despite the biological and environmental benefits of Cr<sup>3+</sup>, few reports regarding fluorescent detection of Cr<sup>3+</sup> are available.<sup>9–14</sup> A diversity of electron transition mechanisms, for example, chelation enhanced fluorescence (CHEF), intermolecular charge transfer (ICT), fluorescence resonance energy transfer (FRET), metal to ligand charge transfer (MLCT), photoinduced electron transfer (PET), photoinduced proton transfer (PPT), excited state intermolecular proton transfer (ESIPT), chelation-enhanced fluorescence (CHEF) effect, and C=N isomerization has been considered for developing fluorescent chemosensors.<sup>15–20</sup> Among the mentioned mechanisms, PET process has been used as a sensing tool in which the electron transfer directly occurs between the fluorophore (signaling unit) and the receptor (“switch” of the fluorescence intensity).<sup>21–23</sup> The receptor unit can be connected chemically to fluorophore with absorption of shorter wavelength, where the PET efficiently happens between donor-acceptor probes.<sup>24–26</sup> In this regard, the electron-donating Schiff base

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ligand, can be considered as a receptor unit to absorb short wavelength light through forming chelate complex with the metal ions. Due to paramagnetic property of  $\text{Cr}^{3+}$  ion and the deficiency of a selective multi-chelating ligand, the appropriate fluorescent turn-on chemosensors to monitor intracellular  $\text{Cr}^{3+}$  are still under developed.<sup>27</sup> With this approach, we report a new chemosensor, *N,N'*-bis(salicylidene)-2,6-bis(4-aminophenyl)-4-phenylpyridine (**P3**) for  $\text{Cr}^{3+}$  that was prepared by condensing 2,6-bis(4-aminophenyl)-4-phenylpyridine with 2-hydroxybenzaldehyde (Scheme 1). Upon addition of  $\text{Cr}^{3+}$ , **P3** shows a large fluorescence enhancement because of the formation of a 1:1 **P3**- $\text{Cr}^{3+}$  complex that inhibits photo-induced electron transfer (PET) process. The other metal ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Bi}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  have almost no influence on the fluorescence.

To get more insight related to the electronic structures of **P3** and **P3**- $\text{Cr}^{3+}$  complex, density functional theory (DFT) calculations were carried out on the plausible structures of the molecules. Moreover, time dependent density functional theory (TDDFT) was used as an accurate method for finding the excited state energies and UV–Vis absorption spectra of **P3** and **P3**- $\text{Cr}^{3+}$  complex.

## 2. Experimental

### 2.1. General and reagents

Melting points were measured on an Electrothermal 9100 apparatus. Mass spectra were obtained on an Agilent 5975c spectrometer operating at 70 eV.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were measured with Bruker DRX-400 AVANCE spectrometer at 400.1 and 100.6 MHz, respectively. The UV–Vis spectra were recorded using a

Perkin-Elmer lambda-EZ 201 and a Jasco FP-200 spectra fluorometer was used to obtain fluorescence emission spectra. Fluorescence intensity measurements were performed in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (95/5%) at room temperature.

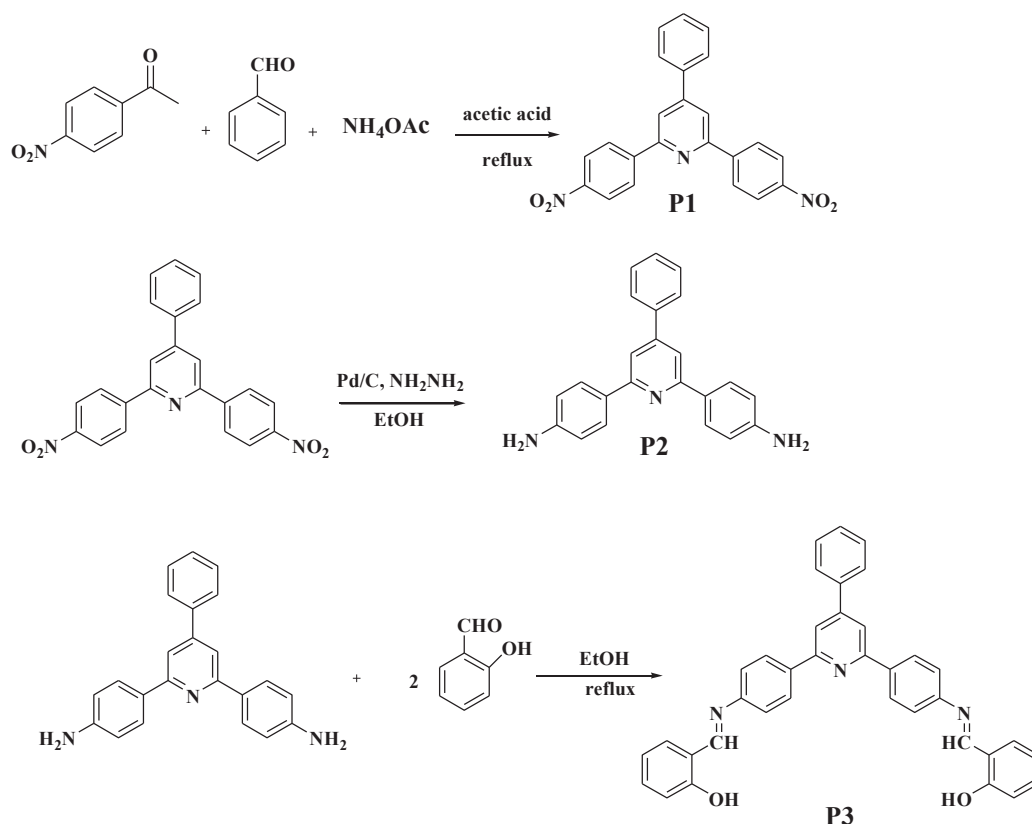
### 2.2. Synthesis

#### 2.2.1. Synthesis of 2,6-bis(4-nitrophenyl)-4-phenylpyridine (**P1**)

A mixture of benzaldehyde (6.4 g, 0.06 mol), *p*-nitroacetophenone (20 g, 0.12 mol), ammonium acetate (60 g), in glacial acetic acid (150 ml) was refluxed for 2 h.<sup>28</sup> After cooling the reaction mixture to room temperature a solid residue was obtained which then filtered and washed with acetic acid (50%) and cold ethanol, respectively. The crude 4-phenyl-2,6-bis(4-nitrophenyl)pyridine (**P1**) was recrystallized from absolute ethanol, and dried under vacuum (Scheme 1). Yield: 66%, mp: 319–321 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 8.43–8.38 (8H, m), 8.07 (2H, s), 7.80–7.77 (m, 2H), 7.63–7.56 (3H, m).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 155.52, 151.39, 148.44, 144.83, 137.90, 129.73, 129.42, 127.94, 127.19, 124.11 and 119.12 (Fig. S1).

#### 2.2.2. Synthesis of 2,6-bis(4-aminophenyl)-4-phenylpyridine (**P2**)

A mixture of 4-phenyl-2,6-bis(4-nitrophenyl)pyridine (13.75 g, 48 mmol) and palladium on carbon 5% (5 g) in ethanol (500 ml) as solvent were prepared in a two-necked round-bottomed flask (500 ml) equipped a dropping funnel. The mixture was warmed up to 50 °C and then hydrazine hydrate 85% (35 ml) in ethanol (50 ml) was added dropwise over a 1.5 h period through the dropping funnel while maintaining the temperature at about 50 °C. The reaction mixture was then refluxed for 2 h and filtered. Upon cooling, the filtrate gave white colored crystals of the 2,6-bis(4-



Scheme 1. The synthetic route of compound **P3**.

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