



Triphenylamine based reactive coloro/fluorimetric chemosensors: Structural isomerism and solvent dependent sensitivity and selectivity



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ABSTRACT

Triphenyl amine based chemosensors, 2-(((2-(9H-carbazol-9-yl)phenyl)imino)methyl)-5-(diphenylamino)phenol (**ortho-CPDP**) and 2-(((4-(9H-carbazol-9-yl)phenyl)imino)methyl)-5-(diphenylamino)phenol (**para-CPDP**), showed solvent and isomerism dependent selective coloro/fluorimetric sensing of multiple metal ions (Fe³⁺, Al³⁺ and Zn²⁺) with distinguishable responses. In CH₃CN, **ortho** and **para-CPDP** selectively produced yellow color upon addition of Al³⁺ and Fe³⁺ that was slowly disappeared. The yellow color of **ortho** and **para-CPDP** in DMF was decolorised selectively by adding Al³⁺ and Fe³⁺. Both **ortho** and **para-CPDP** in CH₃CN showed nearly similar rate of decolorization for Fe³⁺ and Al³⁺. However, the rate of decolorization of **ortho** and **para-CPDP** in DMF was different for Fe³⁺ (10 μM, 8 min) and Al³⁺ (5 × 10⁻⁴ M, 40 min) ions. The limit of detection of **para-CPDP** for Fe³⁺ is 10 μM and Al³⁺ 500 μM. The mechanistic studies revealed the imine hydrolysis of **ortho** and **para-CPDP** in presence of Lewis acidic Fe³⁺ and Al³⁺. The reactivity based sensing lead to high selectivity for Al³⁺ and Fe³⁺ ions. Further, **para-CPDP** exhibited selective fluorescence turn-on for Zn²⁺ in DMF (λ_{max} = 513 nm) and detection limit of 6.0 μM. Thus, reactive chemosensors, **ortho** and **para-CPDP**, exhibited selective and distinguishable colorimetric sensing of Fe³⁺ and Al³⁺ ions and isomerism and solvent dependent fluorescence sensing of Zn²⁺.

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1. Introduction

Molecular chemosensors particularly that exhibit selective colorimetric and fluorescence response upon interacting heavy transition metal ions have received significant attention over the years because of their potential applications in monitoring as well as understanding the role of metal ions in biological and environmental process [1–3]. The structure controlled selectivity and synthetic tailorability of chemosensors together with other advantages such as cost effectiveness, real time monitoring, rapid and naked-eye detectable response makes them interesting materials both in academic research as well as industry [4–16]. For example, organic molecular chemosensors tailored with metal interacting crown ethers, pyridines and quinolines have been reported for selective sensing of different metal ions depend on the functionality [17–19]. Schiff bases, one of the most widely used chemosensors due to facile synthesis, good photophysical and strong metal coordination via bidentate chelating functionality, exhibited selective colorimetric as well as fluorescence response towards different metal ions depends on the molecular structure [20–27]. The change of solvent and substituent in salicylaldehyde salicylhydrazone chemosensor lead to tunable fluorescence sensing of Mg²⁺ and Zn²⁺ [28]. Selective and

clearly distinguishable color for Zn²⁺ and Cd²⁺ was observed using 2-aminobenzamide based carbazole fluorophore [29]. Imidazole based julolidine chemosensor showed selective sensing of different metal ions in different solvents [30].

The coordination induced color/fluorescence modulation was the most common method reported for selective sensing of metal ions by molecular chemosensors. However, this method often encountered strong interference from other metal ions that could form more stable coordination complex. On the other hand, the reaction based chemosensors offered unique selectivity for a particular metal ion due to irreversible structural transformation. The unique reactivity of cyanide ions towards various organic functional groups has been successfully employed to develop ratiometric colorimetric as well as fluorescence probes [31–32]. However, the reaction based chemosensors for metal ions especially for Fe³⁺ and Al³⁺ are rarely reported. The Lewis acidic property of Fe³⁺ and Al³⁺ induces selective color and fluorescence change in pyridine functionalized perylenediimide [33]. The deprotection of acetals in imidazole derivative by Fe³⁺ leads to selective fluorescence red shift [34]. The solution color and fluorescence of rhodamine based chemosensors were selectively modulated via opening spiroactam by Fe³⁺ and Al³⁺ ions [35–36].

Triphenylamine, a non-planar propeller shaped optoelectronic molecule, has been widely employed for developing molecules for fluorescent and optoelectronic applications including sensors and dye-

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sensitized solar cells [37–38]. We have recently explored the role of conformational flexibility of amine in triphenylamine based Schiff base sensors on the fluorescence and colorimetric sensing [39–40]. Herein, we report the synthesis of new isomeric triphenylamine based Schiff base chemosensors, **ortho-CPDP** and **para-CPDP** (Scheme 1) and solvent and isomeric structure dependent selective and distinguishable sensing of multiple metal ions (Fe^{3+} , Al^{3+} and Zn^{2+}). **ortho** and **para-CPDP** in CH_3CN exhibited selective appearance of yellow color for Fe^{3+} and Al^{3+} ions that was slowly disappeared. In contrast, the yellow color of **ortho** and **para-CPDP** in DMF was decolourised selectively by the addition of Fe^{3+} and Al^{3+} ions. Although, both **ortho** and **para-CPDP** in CH_3CN showed nearly similar rate of color disappearance for Fe^{3+} and Al^{3+} ions, the rate of color disappearance drastically varied in DMF. Fe^{3+} ions decolorize **para-CPDP**-DMF yellow color in 10 min whereas higher concentration and time are required for Al^{3+} . The yellow color of **ortho-CPDP** in DMF was decolourized by Fe^{3+} in 90 min and Al^{3+} takes more than 4 h. The interference studies demonstrated high selectivity of **ortho** and **para-CPDP** for Fe^{3+} and Al^{3+} ions over other common metal cations due to reactivity based sensing. Both **ortho** and **para-CPDP** undergo imine hydrolysis in presence of Lewis acidic Fe^{3+} and Al^{3+} and transformed to corresponding amine and aldehyde. Interestingly, isomeric chemosensor **para-CPDP** exhibited selective fluorescence turn-on for Zn^{2+} in DMF. The concentration dependent and NMR studies indicated the formation of 1:2 coordination complex of Zn^{2+} with ligand 2 in DMF. Thus, **ortho** and **para-CPDP**, simple Schiff base chemosensors, exhibited selective and distinguishable colorimetric sensing of Fe^{3+} and Al^{3+} ions and isomeric and solvent dependent fluorescence sensing of Zn^{2+} .

2. Experimental Sections

2.1. Materials

4-Fluoronitrobenzene, 2-Fluoronitrobenzene, NaH (60%), 3-OMe triphenylamine, carbazole (95%), POCl_3 , Pd/C and NaBH_4 obtained from Sigma-Aldrich and used as received. Carbazole was recrystallized from ethyl acetate and then dried in vacuum before used for any reaction. Solvents were obtained from Merck India. 3-OH-TPA aldehyde was synthesized as reported in our previous work [39]. The metal ion solutions used for the coloro/fluorometric sensor experiments were prepared in Mill-Q water. The chemosensors were dissolved in acetonitrile (CH_3CN) or dimethylformamide (DMF). The colorimetric sensor studies were performed by adding aqueous solution of metal ions (10^{-3} M) into CH_3CN /DMF solution of **ortho** and **para-CPDP**. Acetate of Zn^{2+} , Cd^{2+} , Cu^{2+} , Cr^{2+} and chlorides of Ca^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Hg^{2+} , nitrates of Al^{3+} , Pb^{2+} and $\text{Mg}(\text{SO}_4)_2$ and Ferrous ammonium sulphate (FAS) were dissolved in aqueous medium. ^1H and ^{13}C NMR spectra were measured on a Bruker 300 MHz AVANCE-II. UV-Vis spectra were recorded using Perking Elmer Lambda 1050. Fluorescence spectra were recorded on Jasco fluorescence spectrometer FP-8200 instruments. Single crystals of **ortho-CPDP** coated with paratone-N oil and diffraction data was measured at 100 K with synchrotron radiation ($\lambda = 0.62998$ Å) on an ADSC Quantum-210 detector at 2D SMC with a

silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. Colorimetric and fluorescence sensor studies were performed by adding aqueous solution metal cations (10^{-3} M) into CH_3CN /DMF solution of **ortho** and **para-CPDP** (10^{-4} M) in a test tube. The color/fluorescence change was observed by naked-eye and hand held UV lamp. UV-Visible spectra were recorded by transferring the solution into a cuvette. The concentration dependent studies were performed by adding metal cations (μL) directly into the 2.5 mL cuvette that contains 2 mL of chemosensor.

2.2. Synthesis of 9-(2-Nitrophenyl)-9H-Carbazole and 9-(4-Nitrophenyl)-9H-Carbazole

A solution of carbazole (1.0 eq) in CH_3CN was treated with sodium hydride (60%, 3 eq) and stirred for 1 h at room temperature. Then 2-/4-fluoronitrobenzene (1.5 eq) was added drop-wise for over 30 min and the resultant solution was stirred at room temperature for 3 h. After concentrating under reduced pressure, the reaction mixture was dumped into water with vigorous stirring at room temperature. The yellow precipitate was filtered, washed with water and dried under vacuum. Yield = 95%.

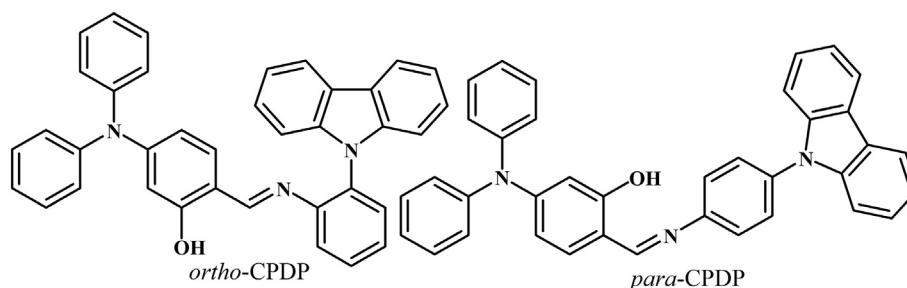
2.3. Synthesis of 2-(9H-Carbazol-9-yl) Aniline and 4-(9H-Carbazol-9-yl)Aniline

9-(2-nitrophenyl)-9H-carbazole/9-(4-nitrophenyl)-9H-carbazole (1 eq) was dissolved in 5 mL of dry methanol and catalytic amount of 1% Pd/C was added in ice-cold condition under vigorous stirring. NaBH_4 (2 eq.) was added in portion-wise over a period of 30 min into reaction solution at ice-cold condition. The reaction mixture was brought to room temperature and stirred for another 2 h. Then Pd/C was filtered off and solvent was evaporated using rota-vapour. The residue was extracted with ethyl acetate and the extract was washed with brine solution and dried over Na_2SO_4 . Finally, the evaporation of ethyl acetate using rota-vapour produced white coloured solid as product. Yield: 68%.

2.4. Synthesis of 2-(((2-(9H-carbazol-9-yl)phenyl)imino)methyl)-5-(diphenylamino)phenol (ortho-CPDP) and 2-(((4-(9H-carbazol-9-yl)phenyl)imino)methyl)-5-(diphenylamino)phenol (para-CPDP)

A methanol solution of 3-OH TPA aldehyde (1.1 mmol) was added drop-wise into the methanol solution of 2-(9H-carbazol-9-yl) aniline/4-(9H-carbazol-9-yl) aniline (1 mmol) under stirring at room temperature. Then the reaction mixture was refluxed for overnight. The Schiff base product was precipitated upon cooling the reaction mixture to room temperature. The precipitate was filtered, washed with methanol and dried under vacuum.

ortho-CPDP: Yield = 85%. ^1H NMR (300 MHz, CDCl_3 , ppm) δ 11.65 (s, 1H (OH)), 8.38 (s, 1H (imine)), 8.12 (d, $J = 7.5$ Hz, 2H), 7.59–7.49 (m, 2H), 7.45–7.41 (m, 2H), 7.39–7.34 (m, 2H), 7.27 (s, 1H), 7.25–7.21 (m, 5H), 7.16 (d, $J = 8.1$ Hz, 2H), 7.09–7.02 (m, 6H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.36 (dd, $J = 2.1, 8.7$ Hz, 1H), 6.18 (d, $J = 2.1$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ 162.1, 162.1, 152.6, 147.4, 146.3, 141.2, 133.1,



Scheme 1. Molecular structures of reactive chemosensor **ortho** and **para-CPDP**.

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