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ARTICLE TYPE

Selective fluorescence sensing of Mg²⁺ ions by Schiff base chemosensor: Effect of diamine structural rigidity and solvent

P. S. Hariharan and Savarimuthu Philip Anthony*

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Highly selective strong turn-on fluorescence for Mg²⁺ ($\Phi = 0.03$ to 0.57) was realized with simple Salen based Schiff base chemosensor (1a) using dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) as solvent. Importantly, Ca²⁺ that often interferes in the Mg²⁺ fluorescence sensing did not show any significant influence on the selectivity. The fluorescence sensing of Mg²⁺ is highly solvent as well as amine structure dependent. It was observed fluorescence sensing of Mg²⁺ only by 1,2-phenylenediamine condensed Schiff bases in DMF or DMSO. Different substituents (1b-e) on the salicylaldehyde unit were synthesized and explored the effect of substitution on Mg²⁺ sensing and selectivity. Except 1c, other chemosensors showed selective fluorescence sensing Mg²⁺ in DMF/DMSO. Interestingly, 1a-e (except 1c) exhibited selective strong turn-on fluorescence for Fe³⁺ ($\lambda_{\text{max}} = 462$ nm, $\Phi = 0.421$) in different solvents (DMSO, DMF, THF, CH₃CN) after 1 h. The concentration dependent studies showed linear enhancement of fluorescence intensity for Mg²⁺ with the detection limit of 10⁻⁷ M. The practical applications of the chemosensor for selective sensing of Mg²⁺ in real samples such as pond, tap, river and ground water have also been demonstrated.

Introduction

Magnesium ion (Mg²⁺) is one of the most abundant divalent cations in cells and plays pivotal roles in many cellular processes, such as enzyme-driven biochemical reactions, proliferation of cells, and stabilization of DNA conformation.¹ The estimated total concentration of Mg²⁺ in mammalian cells varies between 14 and 20 mM, the majority of it bound to ATP and a lesser extent to proteins, phospholipids, and various phosphometabolites.² Mg²⁺ is also involved in many pathological processes, such as congestive heart failure, lung cancer, and muscle dysfunction.³ In contrast, high levels of Mg²⁺ are contribute to a number of age-related and neuronal diseases ranging from hypertension to Alzheimer's disease.⁴ The mechanisms by which Mg²⁺ concentration is regulated at the cellular level and the effects in human health has also been poorly understood due to the scarcity of efficient chemical tools for the study of this ion. As a result, the sensing of Mg²⁺ has generated increasing interest in the areas of chemical and biological sciences. Many analytical methods have been developed for the detection of Mg²⁺, including atomic absorption, ion-selective electrodes (ISEs), and NMR in the past few years.⁵ However, optical methods that track changes of fluorescence or absorption arisen from the Mg²⁺ induced perturbation of the chromophore, is best suitable for Mg²⁺ detection in biological systems.

Particularly, molecular chemosensors have drawn significant attention in recent years due to its convenience, real-time response, high sensitivity, selectivity, versatility and relatively simple handling.⁶ Coumarin based diketone or β -keto acid

derivatives are the highly explored fluorescent sensors for selective detection of Mg²⁺ ions as well as molecular imaging of local changes in intracellular Mg²⁺ concentration.⁷ Yu et al showed Na⁺ triggered coumarin based Salen fluorescence sensor for Mg²⁺.⁸ Crown ether derivatives,⁹ polymer based ligands¹⁰ and nanoparticles,¹¹ have also been successfully employed for selective detection of Mg²⁺ ions. However, most of these chemosensor molecules require intricate synthetic methodologies and hence are relatively difficult to prepare. The major issues with many of the reported chemosensors for Mg²⁺ is their low selectivity against Zn²⁺ and Ca²⁺. The similar chemical properties of Mg²⁺ and Ca²⁺ make it difficult for chemosensor to distinguish them.¹² Hence it is still interesting and of importance to design a highly selective and sensitive fluorescent sensor that can recognize Mg²⁺ without the interference from other metal ions.

The ease of synthesis coupled with tailorability, good biological activities, strong photophysical properties and coordination ability with metal ions has made Schiff bases as one of the most widely explored molecular chemosensors for selective sensing of metal ions.¹³ Particularly, Salen based π -conjugated tetradentate [O⁻N⁻N⁻O] chelating ligands have been widely employed for selective sensing of various metal ions such as Zn²⁺, Cu²⁺, Al³⁺, La³⁺, and Pt²⁺. The interaction of organic ligands with metal ions and resultant solid state structural organization are highly influenced by solvent, temperature, anions and pH.¹⁴ A subtle change of organic ligand structure or solvent resulted in completely different molecular organization and properties.^{14b,c} Herein, we report the highly selective fluorescence sensing of Mg²⁺ ions by simple 1,2-

phenylenediamine based Salen Schiff base chemosensor (1a-e) in DMF or DMSO. The chemosensor did not show fluorescence turn-on for Mg^{2+} other than DMF and DMSO solvent. Chemosensors with different substituent was prepared and studied their role on Mg^{2+} sensing and selectivity. Importantly, Ca^{2+} that often interferes in the Mg^{2+} fluorescence sensing did not show any significant influence on the selectivity. The linear enhancement of fluorescence with concentration of Mg^{2+} was observed. The chemosensors showed the detection limit of 10^{-7} M. The practical application of the chemosensor in selective sensing of Mg^{2+} in real samples such as pond, tap, and ground water have also been demonstrated.

Experimental Section

1,2-phenylenediamine, ethylene diamine, (\pm)-trans-1,2-diaminocyclohexane (99 %), salicylaldehyde, 2-hydroxy-4-methoxy benzaldehyde, 2-hydroxy-4-diethylamino benzaldehyde, 2, 4-dihydroxy benzaldehyde and 2-hydroxynaphthaldehyde was obtained from sigma-Aldrich. The spectroscopic grade solvents were obtained from Merck India. All chemicals are used as received. The metal ion solutions used for the fluorescence sensor experiments were prepared using Mill-Q water. The chemosensors were dissolved in organic solvents (DMF, DMSO, acetonitrile, methanol, tetrahydrofuran (THF)). Absorption and fluorescence spectra were recorded using Perking Elmer Lambda 1050 and Jasco fluorescence spectrometer-FP-8200 instruments.

General synthesis of 1a-e

Schiff bases were prepared according to the reported procedure.¹⁵ Typically, aldehyde (2.2mmol, salicylaldehyde or 4-methoxysalicylaldehyde, 4-diethylamino-2-hydroxy benzaldehyde or 2, 4-dihydroxy benzaldehyde) was dissolved in ethanol (30 ml) and stirred at room temperature. To this solution, 1,2-phenylenediamine (1mmol) in ethanol (5 ml) was added in drop-wise under stirring. The immediate appearance of yellow colour indicates the formation of Schiff bases. The solution was allowed stir for another 6 h at room temperature that produced yellow to light yellow coloured precipitates. The formed precipitate was filtered and washed with ethanol and dried under vacuum.

1a (N, N'-bis(salicylidine)-O-phenylenediamine): Yield = 87 %. m.p. 160-162 °C. ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm) 12.95 (s, 2H (OH)), 8.94 (s, 2H (CH=N)), 7.66-7.68 (d, 2H (aromatic)), 7.40-7.48 (m, 6H (aromatic)), 6.95-7.00 (m, 4H (aromatic)). ¹³C NMR (200 MHz, *d*₆-DMSO, δ ppm) 166.61, 160.54, 146.41, 133.50, 132.44, 130.24, 126.50, 122.70, 117.64, 116.96. $C_{20}H_{16}N_2O_2$ (316.12): calcd. C 75.93, H 5.10, N 8.86; found C 75.57, H 5.31, N 8.67. m/z (LC-MS) 317.00 (M+H).

1b (N, N'-bis(4-methoxy salicylidine)-O-phenylenediamine): Yield = 85 %. m.p. 174-176 °C. ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm) 13.525 (s, 2H (OH)), 8.83 (s, 2H (CH=N)), 7.53-7.55 (d, 2H (aromatic)), 7.41-7.44 (m, 2H (aromatic)), 7.34-7.37 (m, 2H (aromatic)), 6.53-6.56 (d, 2H (aromatic)), 6.48 (s, 2H (aromatic)), 3.80 (s, 6H (OCH₃)). ¹³C NMR (200 MHz, *d*₆-DMSO, δ ppm) 168.12, 166.76, 162.53, 144.50, 134.74, 133.94, 128.50, 118.80, 116.31, 55.84. $C_{22}H_{20}N_2O_4$ (376.14): calcd. C 70.20, H 5.36, N 7.44; found C 70.11, H 5.23, N 7.52. m/z (LC-MS) 377.00 (M+H).

1c (N, N'-bis(4-diethylamino salicylidine)-O-phenylenediamine): Yield = 80 %. m.p. 141-143 °C. ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm) 13.58 (s, 2H (OH)), 8.61 (s, 2H (CH=N)), 7.51-7.52 (d, 2H (aromatic)), 7.42-7.45 (m, 2H (aromatic)), 7.30-7.33 (m, 2H (aromatic)), 6.51-6.54 (d, 2H (aromatic)), 6.34 (s, 2H (aromatic)), 3.31-3.37 (q, 8H), 1.05-1.10 (t, 12H). ¹³C NMR (200 MHz, *d*₆-DMSO, δ ppm) 163.45, 162.19, 155.12, 144.45, 134.22, 133.00, 128.92, 122.78, 117.78, 116.78, 43.73, 12.53. $C_{28}H_{34}N_4O_2$ (458.27): calcd. C 73.33, H 7.47, N 12.22; found C 73.42, H 7.30, N 12.41. m/z (LC-MS) 459.20 (M+H).

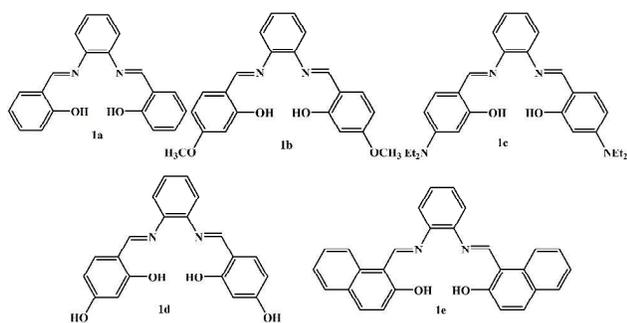
1d (N, N'-bis(4-hydroxy salicylidine)-O-phenylenediamine): Yield = 80 %. m.p. 266-269 °C (decomp.). ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm) 13.40 (s, 2H (OH)), 10.30 (s, 2H (OH)), 8.75 (s, 2H (CH=N)), 7.42-7.44 (d, 2H (aromatic)), 7.37-7.39 (m, 2H (aromatic)), 7.30-7.33 (m, 2H (aromatic)), 6.37-6.40 (d, 2H (aromatic)), 6.28 (s, 2H (aromatic)). ¹³C NMR (200 MHz, *d*₆-DMSO, δ ppm) 164.88, 163.42, 161.87, 145.85, 133.33, 128.26, 122.32, 116.23, 115.90. $C_{20}H_{16}N_2O_4$ (348.11): calcd. C 68.96, H 4.63, N 8.04; found C 68.80, H 4.45, N 8.20. m/z (LC-MS) 349.00 (M+H).

1e (N, N'-bis(2-hydroxy naphthalidine)-O-phenylenediamine): Yield = 80 %. m.p. 284-287 °C (decomp.). ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm) 15.13 (s, 2H (OH)), 9.70 (s, 2H (CH=N)), 8.53-8.55 (d, 2H (aromatic)), 7.96-7.98 (d, 2H (aromatic)), 7.82-7.84 (d, 4H (aromatic)), 7.53-7.58 (t, 2H (aromatic)), 7.44-7.46 (t, 2H (aromatic)), 7.36-7.40 (t, 2H (aromatic)), 7.08 (s, 2H (aromatic)). ¹³C NMR (200 MHz, *d*₆-DMSO, δ ppm) 166.74, 162.51, 147.90, 135.22, 134.40, 133.74, 133.02, 128.89, 127.78, 124.62, 122.86, 122.12, 118.88, 114.90. $C_{28}H_{20}N_2O_2$ (416.15): calcd. C 80.75, H 4.84, N 6.73; found C 80.55, H 5.11, N 6.80. m/z (LC-MS) 417.00 (M+H).

Result and Discussion

Schiff base chemosensors, 1a-e, were synthesized by quite straightforward condensation reaction between primary amine and an aldehyde precursor in ethanol solution at room temperature (Scheme 1,S1). The fluorescence responses of chemosensor 1a-e for various metal ions such as such as, Mg^{2+} , Ca^{2+} , Cr^{3+} , Al^{3+} , Fe^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} have been investigated in DMF, DMSO, acetonitrile, methanol and THF. The chemosensors and metal ions were dissolved in organic solvents (DMF, DMSO, acetonitrile and Ethanol) and water, respectively.

1a showed weak fluorescence in DMF ($\lambda_{max} = 499$ nm, $\Phi = 0.0092$). Addition of Mg^{2+} ions into 1a lead to the strong enhancement of fluorescence without altering the fluorescence λ_{max} ($\Phi = 0.1787$, Fig. 1). Importantly, other metal ions with 1a did not show any significant fluorescence enhancements. It is noted that Ca^{2+} addition showed only a small enhancement in the fluorescence intensity. Absorption studies of 1a with Mg^{2+} in DMF revealed distinct changes that suggest the formation of coordination complex between Mg^{2+} and 1a (Fig. 2). 1a in DMF showed a strong absorption at 270 nm and 330 nm. The former is assigned to $\pi-\pi^*$ transition involving the molecular orbitals of imine. As scheme 2 describes, 1a exist in equilibrium between the two configurations (Normal and Tautomer) due to excited state intramolecular proton transfer (ESIPT).¹⁶ The absorption at 330 nm could be assigned to the transition of O=C-C=C-(NH) in



Scheme 1. Molecular structures of Schiff base chemosensors.

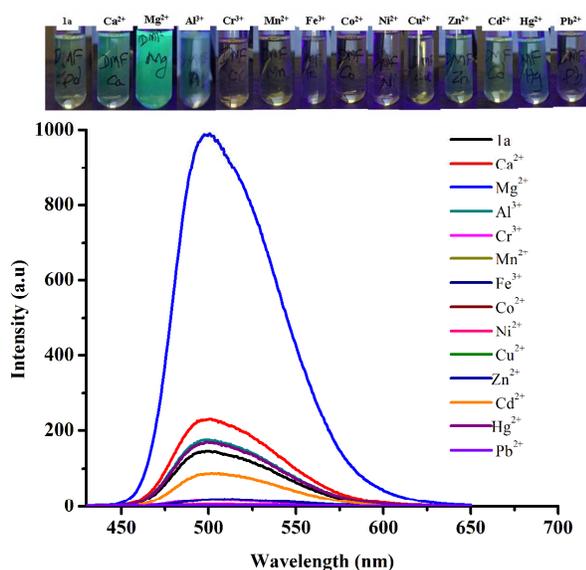
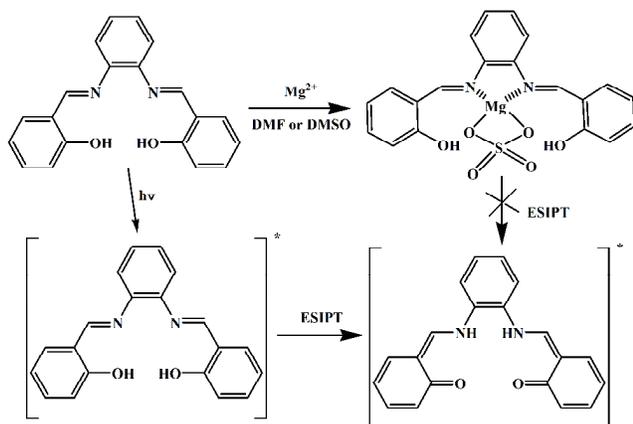


Figure 1. Digital and fluorescence spectra of 1a in DMF with different metal ions.



Scheme 2. Mg-complex structure with 1a and Tautomer formation by ESIPT.

Tautomer. Addition of Mg^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Cr^{3+} , Mn^{2+} , Co^{2+} and Ni^{2+} reduced the intensity at 330 nm since the metal coordination prevents the ESIPT and Tautomer formation (Scheme 2). The metal coordination with imine nitrogen that

increase the electron withdrawing property of imine leads to the strong absorption at longer wavelength (380 nm to 440 nm).¹⁷ Mg^{2+} with 1a in DMF showed a strong red shifted absorption at 396 nm. 1a exhibited similar strong selective turn-on fluorescence with higher intensity for Mg^{2+} in DMSO (Table 1).

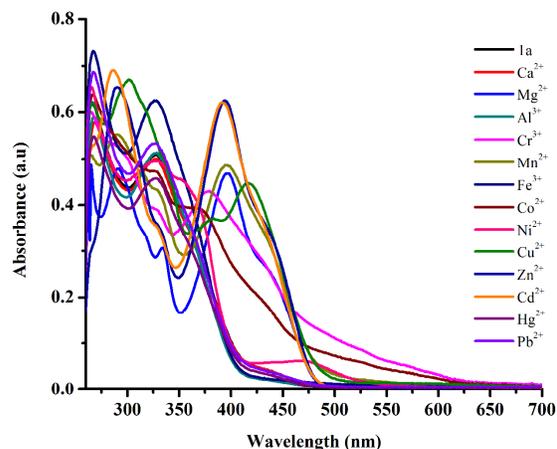


Figure 2. Absorption spectra of 1a in DMF.

Table 1. Quantum yield (Φ) of 1a-1e and with Mg^{2+} and Fe^{3+} in different solvents. Quinine sulfate in 0.5 M H_2SO_4 was used as reference.

Compound	Φ_{DMF}	Φ_{DMSO}	$\Phi_{\text{CH}_3\text{CN}}$	Φ_{THF}
1a	0.0092	0.021	-	-
1b	0.0083	0.019	-	-
1d	0.015	0.034	-	-
1e	0.003	0.007	-	-
1a- Mg^{2+}	0.1787 ^a	0.3603 ^a	-	-
1b- Mg^{2+}	0.1811 ^a	0.4194 ^a	-	-
1d- Mg^{2+}	0.1861 ^a	0.5767 ^a	-	-
1e- Mg^{2+}	0.025 ^a	0.088 ^a	-	-
1a- Fe^{3+}	0.1318 ^b	0.421 ^b	0.353 ^b	0.431 ^b
1b- Fe^{3+}	0.0942 ^b	0.406 ^b	0.092 ^b	0.316 ^b
1d- Fe^{3+}	0.021 ^b	0.193 ^b	0.073 ^b	0.174 ^b
1e- Fe^{3+}	0.041 ^b	0.073 ^b	0.035 ^b	0.122 ^b

a = measured immediately, b = measured after 1 h.

The strong enhancement of fluorescence upon Mg^{2+} coordination is due to the restriction of C=N isomerisation and rigidification of fluorophore structure.¹⁸ It is noted that 1a showed strong turn-on fluorescence as well as absorption changes for

Mg²⁺ either in DMF or DMSO. Other solvents such as acetonitrile, methanol and THF did not show any turn-on fluorescence for Mg²⁺. Absorption studies also showed that Mg²⁺ did not show any changes in other solvents with 1a (Fig. S1). This suggests that both DMF and DMSO facilitate the formation of stable Mg²⁺ coordination complex with 1a by involving the coordination. The possible structure of the Mg²⁺ complex with 1a is shown in Scheme 2. The concentration dependent studies of 1a with Mg²⁺ are shown in figure 3a. A steady fluorescence enhancement was observed with 1a in DMF (10⁻⁷ M) up to the addition of 1 equivalent of Mg²⁺ (10⁻⁷ M). These results suggest the formation of 1:1 coordination complex between 1a and Mg²⁺. It is noted that most of the reported Mg²⁺ chemosensor showed only micromolar (10⁻⁶ M) detection limit.⁸⁻¹¹ The selectivity studies of 1a for Mg²⁺ in presence of other metal ions revealed that Ca²⁺, Al³⁺, Cd²⁺ and Hg²⁺ had negligible interference. But no turn-on fluorescence was observed for Mg²⁺ in presence of Zn²⁺. Transition metal ions (Cr³⁺, Fe³⁺, Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) showed strong influence on the Mg²⁺ selectivity that could be due to the stronger coordination with 1a (Fig. 3b).

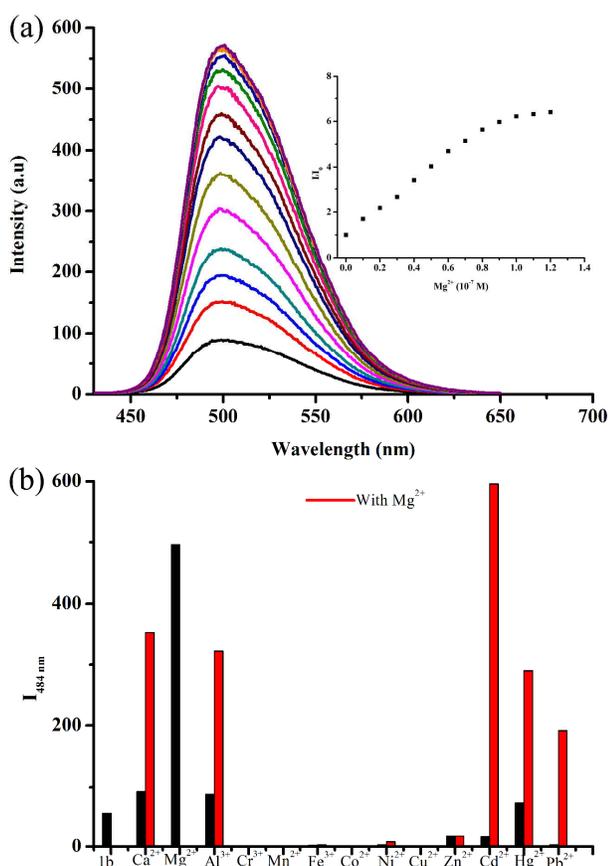


Figure 3. (a) 1a (10⁻⁶ M in DMF) fluorescence Vs concentration of Mg²⁺ (10⁻⁶ M in water) and (b) interference studies of other metal ions (mM) on the selectivity of Mg²⁺ (μM).

In order to study the effect of substitutional change on the selectivity and sensitivity of Mg²⁺, chemosensor 1b-e was synthesized (Scheme 1). Except 1c, other three chemosensors exhibited highly selective strong turn-on fluorescence for Mg²⁺ in DMF and DMSO (Fig. 4, S2). Surprisingly 1c did not show turn-on fluorescence for any metal ions in explored solvents. 1b

showed a weak broad fluorescence with two peaks (480 nm and 504 nm). Addition of Mg²⁺ showed 10 fold fluorescence enhancements with a small red shift λ_{max} (480 nm to 484 nm, Fig. 4a). 1d chemosensor exhibited weak and two clear fluorescence peaks at 520 nm and 547 nm. Addition of Mg²⁺ increases the fluorescence by 4 fold without affecting the fluorescence λ_{max} (Fig. 4b). 1e chemosensor showed 30 fold fluorescence enhancements selectively for Mg²⁺ ions in DMF (Fig. S2). The quantum yield measurements revealed strong fluorescence for chemosensors with Mg²⁺ in DMSO compared to DMF (Table 1). Among the chemosensors, 1e with Mg²⁺ exhibited weak fluorescence both in DMF and DMSO and 1d with Mg²⁺ exhibited strong fluorescence in DMSO. The concentration dependent studies of 1b, 1d, 1e also showed steady enhancement of fluorescence up to the addition of 1 equivalent of Mg²⁺ (Fig. S3). However, the detection limit of Mg²⁺ was differed for 1e. 1a, 1b and 1d showed selective detection of Mg²⁺ up to the level of 10⁻⁷ M. But 1e showed selective turn-on fluorescence only for the addition of 10⁻⁴ M Mg²⁺. The selectivity studies of 1b, 1d and 1e for Mg²⁺ showed that Ca²⁺, a strong competitor with Mg²⁺, had little interference on the selectivity with all chemosensor in DMF (Fig. 5, S4). The transition metal ions had strong interference (no fluorescence turn-on) on the selectivity of Mg²⁺ that is due to the strong coordination character of these metal ions.

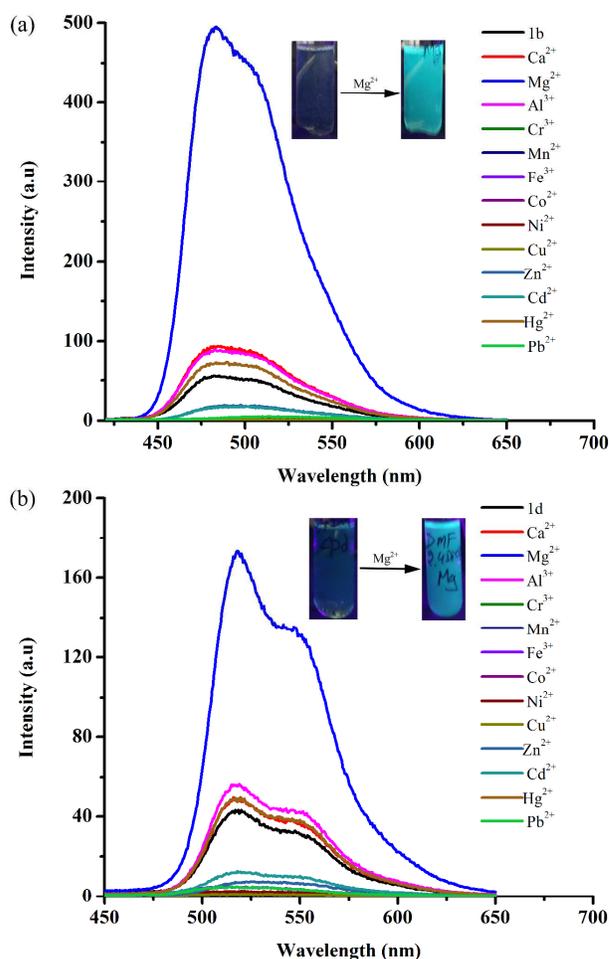


Figure 4. (a) 1b and (b) 1d fluorescence spectra with different metal ions in DMF.

The selective fluorescence sensing of Mg^{2+} by 1a-e is highly solvent dependent. Similarly, Mg^{2+} fluorescence sensing also depends on the structure of amine moiety in the chemosensor (Scheme S2). For example, use of ethylene diamine or cyclohexane diamine instead of ortho-phenylenediamine did not show any fluorescence sensing for Mg^{2+} in any solvents including DMF or DMSO. Instead, the ethylene or cyclohexane diamine based Schiff base chemosensor showed highly selective turn-on fluorescence for Zn^{2+} ions (Fig. S5-8). These results indicate that along with solvent the structural rigidity amine also plays a role in the formation of Mg^{2+} coordination complex. The practical applicability of 1a for selective sensing of Mg^{2+} ion in different samples such as river, ground, pond and tap water have also been demonstrated. Mg^{2+} was dissolved in different water (10^{-6} M) and addition of 100 μ l into 1a in DMF (10^{-6} M) clearly showed the strong bluish green fluorescence (Fig. 6).

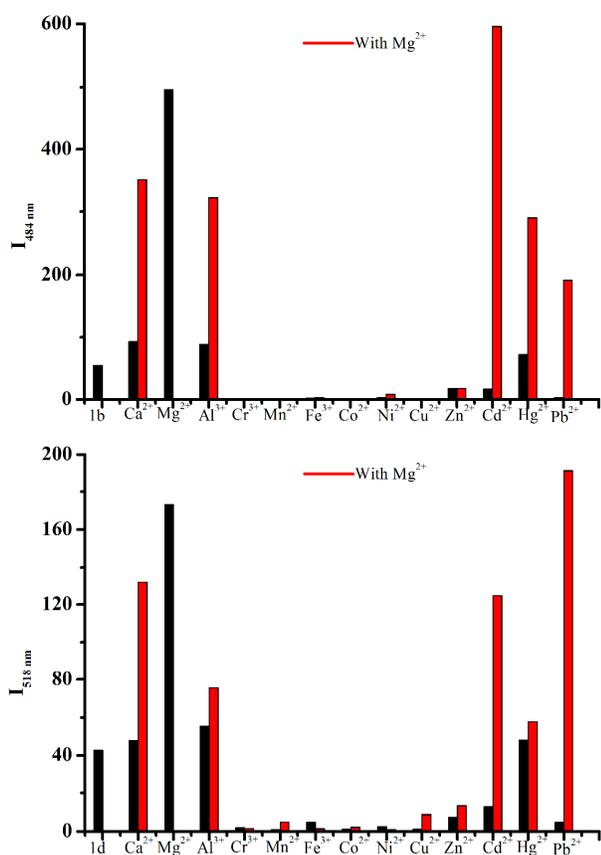
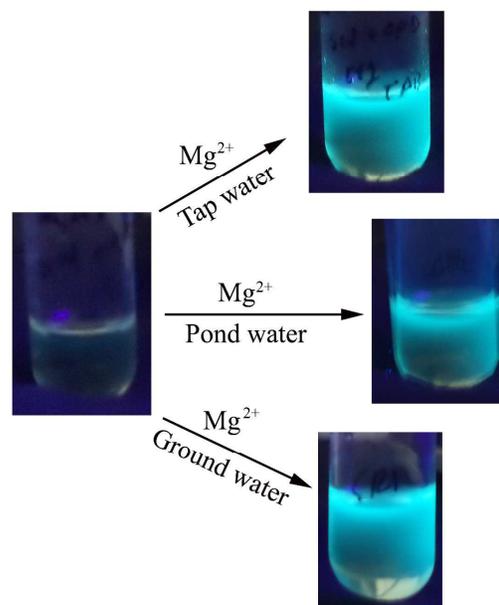


Figure 5. Mg^{2+} interference studies of (1b) and (b) 1d in presence of other metal cations in DMF.

Interestingly, 1a with Fe^{3+} also exhibited selectively strong blue fluorescence ($\lambda_{max} = 462$ nm) in DMF/DMSO but after 1 h (Fig. 7). However, it takes 1 h to produce strong blue fluorescence with Fe^{3+} . 1a- Fe^{3+} fluorescence is completely different from 1a- Mg^{2+} fluorescence. The absorption studies also revealed a clear change in the absorption after 1 h. A new peak appeared at 317 nm along with 330 nm peak. It is noted that the absorption peak of 1a has also been changed from broad to sharp (Fig. S9). It is noted that absorption spectra of 1a and 1a with Mg^{2+} did not show significant variation after one hour. Unlike

Mg^{2+} that showed turn-on fluorescence only in DMSO and DMF, Fe^{3+} addition into 1a as well as 1b, 1d-e exhibited strong blue fluorescence in DMF, DMSO, acetonitrile and THF after 1 h (Fig. S10, Table 1).

Figure 6. Selective sensing of Mg^{2+} by 1a in different water. 1a was



dissolved in DMF (10^{-6} M) and Mg^{2+} (10^{-6} M) was dissolved in different water. 100 μ l of Mg^{2+} was added into 1a-DMF.

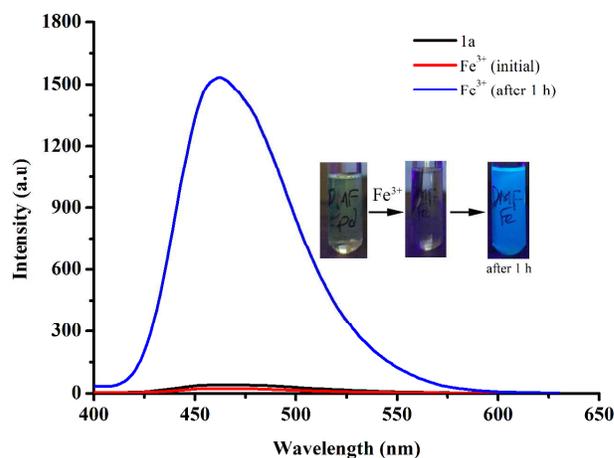


Figure 7. The change of 1a (10^{-6} M in DMF) fluorescence with Fe^{3+} (10^{-6} M in water) with time.

Conclusion

We have demonstrated a highly selective strong turn-on fluorescence for Mg^{2+} ($\Phi = 0.03$ to 0.57) with simple Salen based Schiff base chemosensors using DMF or DMSO as solvent. The solvent and rigidity of the amine structure was found to be critical for fluorescence sensing of Mg^{2+} . The concentration dependent studies showed linear enhancement of fluorescence for Mg^{2+} with the detection limit of 10^{-7} M. Importantly, the chemosensors

displayed good Mg^{2+} selectivity in presence of Ca^{2+} that often interferes in the Mg^{2+} fluorescence sensing. Salen chemosensors with different substitution in the salicylaldehyde unit (1b, 1d-e) also exhibited similar Mg^{2+} fluorescence sensing except small variation in the sensitivity. 1b and 1d showed strong turn-on fluorescence for Mg^{2+} with similar sensitivity whereas 1e exhibited reduced sensitivity (10^{-5} M). Thus simple Salen chemosensor have been effectively used to detect biologically important Mg^{2+} ions by changing the solvent medium. The practical application of the chemosensor in selective sensing of Mg^{2+} in real samples such as pond, tap, and ground water have also been demonstrated.

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Notes and references

School of Chemical & Biotechnology, SASTRA University, Thanjavur-613401, Tamil Nadu, India. Fax: +914362264120; Tel: +914362264101; E-mail: philip@biotech.sastra.edu

† Electronic Supplementary Information (ESI) available: Colorimetric absorption spectra for metal ions and turn-on fluorescence sensing by 1a-d and 2a-d. See DOI: 10.1039/b000000x/

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