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Selective fluorescence sensing of Mg^{2+} ions by Schiff base chemosensor: effect of diamine structural rigidity and solvent†

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Highly selective strong turn-on fluorescence for Mg^{2+} (Φ = 0.03 to 0.57) was realized with a simple Salen based Schiff base chemosensor (**1a**) using dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) as solvent. Importantly, Ca^{2+} that often interferes in the Mg^{2+} fluorescence sensing did not show any significant influence on the selectivity. The fluorescence sensing of Mg^{2+} is highly solvent as well as amine structure dependent. Fluorescence sensing of Mg^{2+} only by 1,2-phenylenediamine condensed Schiff bases in DMF or DMSO was observed. Different substituents (**1b–e**) on the salicylaldehyde unit were synthesized and we explored the effect of substitution on Mg^{2+} sensing and selectivity. Except **1c**, other chemosensors showed selective fluorescence sensing of Mg^{2+} in DMF/DMSO. Interestingly, **1a–e** (except **1c**) exhibited selective strong turn-on fluorescence for Fe^{3+} (λ_{max} = 462 nm, Φ = 0.421) in different solvents (DMSO, DMF, THF, CH_3CN) after 1 h. The concentration dependent studies showed linear enhancement of fluorescence intensity for Mg^{2+} with the detection limit of 10^{-7} M. The practical applications of the chemosensor for selective sensing of Mg^{2+} in real samples such as pond, tap, river and ground water have also been demonstrated.

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Introduction

Magnesium ions (Mg^{2+}) are among the most abundant divalent cations in cells and play 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 Mg^{2+} in mammalian cells varies between 14 and 20 mM, the majority of it bound to ATP and a smaller amount to proteins, phospholipids, and various phosphometabolites.[2] Mg^{2+} is also involved in many pathological processes, such as congestive heart failure, lung cancer, and muscle dysfunction.[3] In contrast, high levels of Mg^{2+} are contribute to a number of age-related and neuronal diseases ranging from hypertension to Alzheimer's disease.[4] The mechanisms by which Mg^{2+} 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 Mg^{2+} has generated increasing interest in the areas of chemical and biological sciences. Many analytical methods have been developed for the detection of Mg^{2+}, 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 Mg^{2+} induced perturbation of the chromophore, is best suitable for Mg^{2+} 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 Mg^{2+} ions as well as molecular imaging of local changes in intracellular Mg^{2+} concentration.[7] Dong *et al.* showed Na^+ triggered coumarin based Salen fluorescence sensor for Mg^{2+}.[8] Crown ether derivatives,[9] polymer based ligands[10] and nanoparticles,[11] have also been successfully employed for selective detection of Mg^{2+} 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 Mg^{2+} is their low selectivity against Zn^{2+} and Ca^{2+}. The similar chemical properties of Mg^{2+} and Ca^{2+} 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 Mg^{2+} 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

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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 Zn^{2+}, Cu^{2+}, Al^{3+}, La^{3+}, and Pt^{2+}. 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 Mg^{2+} 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, (±)-*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 (2.2 mmol, 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 (1 mmol) 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. ^{1}H 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)). ^{13}C NMR (200 MHz, d6-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. ^{1}H 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)). ^{13}C 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).

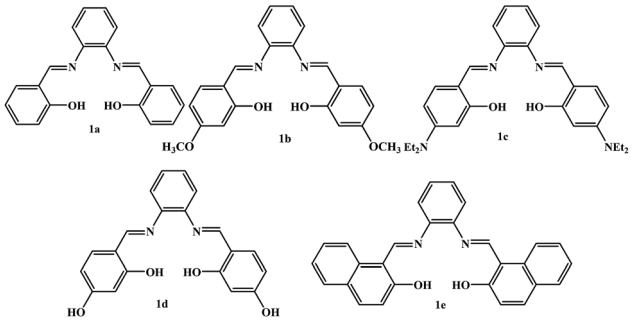
1c (*N*,*N*′-bis (4-diethylamino salicylidine)-*O*-phenylenediamine). Yield = 80%. m.p. 141–143 °C. ^{1}H NMR (400 MHz, d_6-DMSO, δ ppm) 13.58 (s, 2H (OH)), 8.61 (s, 2H (CH=N)), 7.51–7.52 (d, 2H (aromatic)), 7.42–7.45 (m, 2H (aromatic)), 7.30–7.33 (m, 2H (aromatic)), 6.51–6.54 (d, 2H (aromatic)), 6.34 (s, 2H (aromatic)), 3.31–3.37 (q, 8H), 1.05–1.10 (t, 12H). ^{13}C 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.). ^{1}H 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)). ^{13}C 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.). ^{1}H 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)). ^{13}C 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



Scheme 1 Molecular structures of Schiff base chemosensors.

organic solvents (DMF, DMSO, acetonitrile and ethanol) and water, respectively.

1a showed weak fluorescence in DMF (λ_{max} = 499 nm, Φ = 0.0092). Addition of Mg^{2+} ions into **1a** lead to the strong enhancement of fluorescence without altering the fluorescence λ_{max} (Φ = 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 π–π* 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).

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

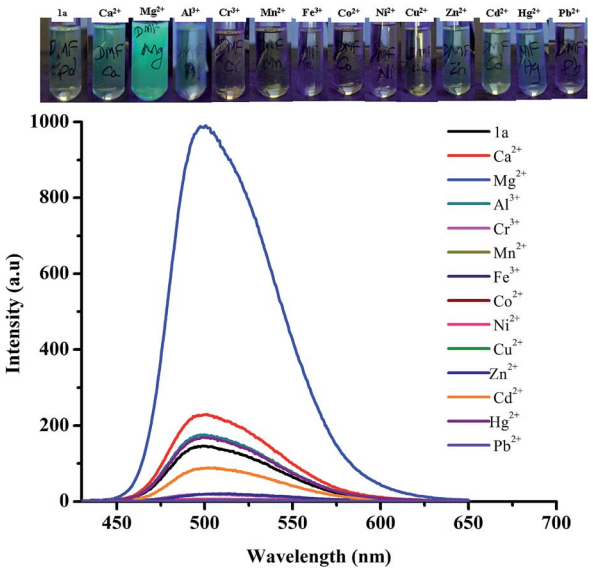


Fig. 1 Digital and fluorescence spectra of **1a** in DMF with different metal ions.

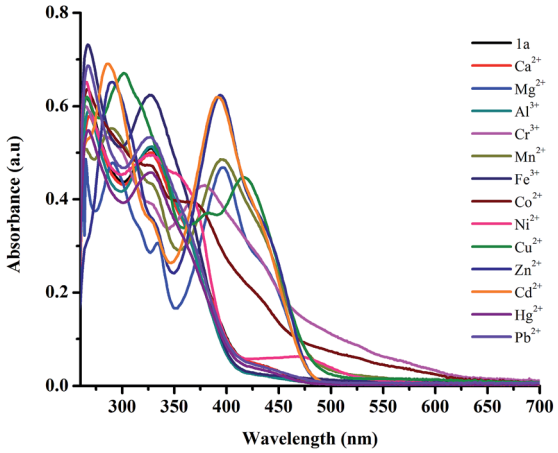
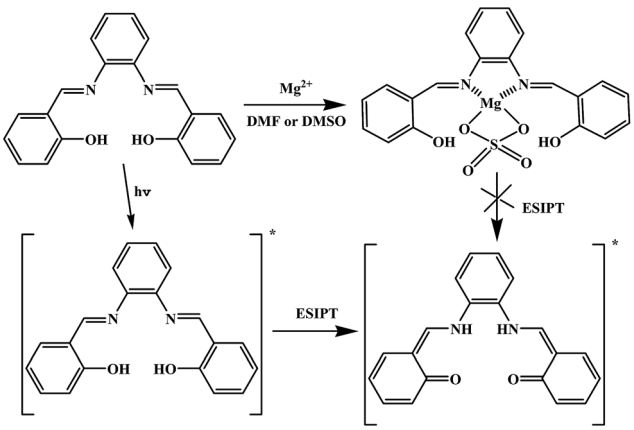


Fig. 2 Absorption spectra of **1a** in DMF.



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

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).

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 Mg^{2+} either in DMF or DMSO. Other solvents such as acetonitrile, methanol and THF did not show any turn-on fluorescence for Mg^{2+}. Absorption studies also showed that Mg^{2+} did not show any changes in other solvents with **1a** (Fig. S1†). This suggests that both DMF and DMSO facilitate the formation of stable Mg^{2+} coordination complex with **1a** by involving the coordination. The possible structure of the Mg^{2+} complex with **1a** is shown in Scheme 2. The concentration dependent studies of **1a** with Mg^{2+} are shown in Fig. 3a. A steady fluorescence enhancement was observed with **1a** in DMF

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

Compound	$\Phi_{(DMF)}$	Φ_{DMSO}	Φ_{CH3CN}	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.

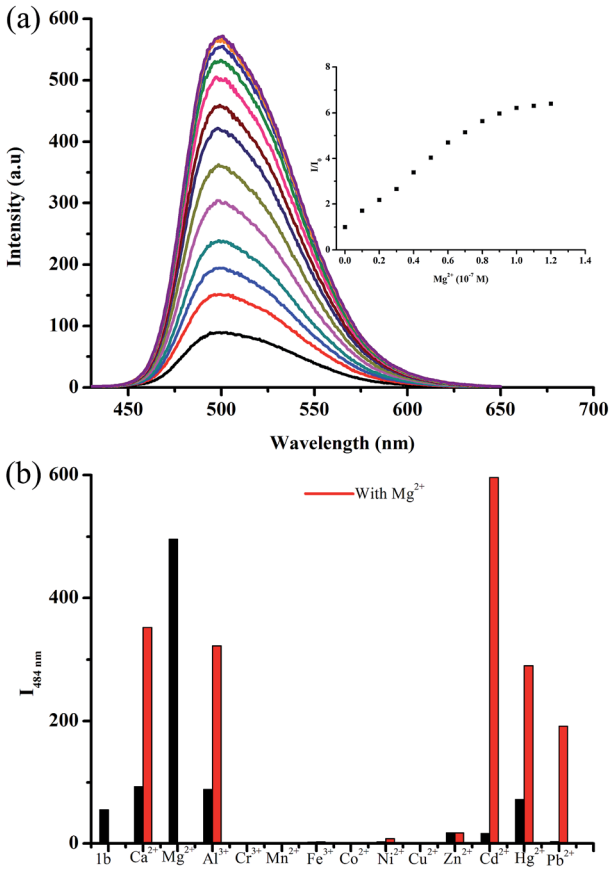


Fig. 3 (a) **1a** (10–6 M in DMF) fluorescence *vs.* concentration of Mg^{2+} (10–6 M in water) and (b) interference studies of other metal ions (mM) on the selectivity of Mg^{2+} (μM).

(10^{-7} M) up to the addition of 1 equivalent of Mg^{2+} (10^{-7} M). These results suggest the formation of 1 : 1 coordination complex between **1a** and Mg^{2+}. It is noted that most of the reported Mg^{2+} chemosensor showed only micromolar (10^{-6} M) detection limit.[8–11] The selectivity studies of **1a** for Mg^{2+} in presence of other metal ions revealed that Ca^{2+}, Al^{3+}, Cd^{2+} and Hg^{2+} had negligible interference. But no turn-on fluorescence was observed for Mg^{2+} in presence of Zn^{2+}. Transition metal ions (Cr^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}) showed strong influence on the Mg^{2+} selectivity that could be due to the stronger coordination with **1a** (Fig. 3b).

In order to study the effect of substitutional change on the selectivity and sensitivity of Mg^{2+}, chemosensor **1b–e** was synthesized (Scheme 1). Except **1c**, other three chemosensors exhibited highly selective strong turn-on fluorescence for Mg^{2+} 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 Mg^{2+} 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 Mg^{2+} increases the fluorescence by 4 fold without affecting the fluorescence λ_{max} (Fig. 4b). **1e** chemosensor showed 30 fold fluorescence enhancements selectively for Mg^{2+} ions in DMF (Fig. S2†). The quantum yield measurements revealed strong fluorescence for chemosensors with Mg^{2+} in DMSO compared to DMF (Table 1). Among the chemosensors, **1e** with Mg^{2+} exhibited weak fluorescence both in DMF and DMSO and **1d**

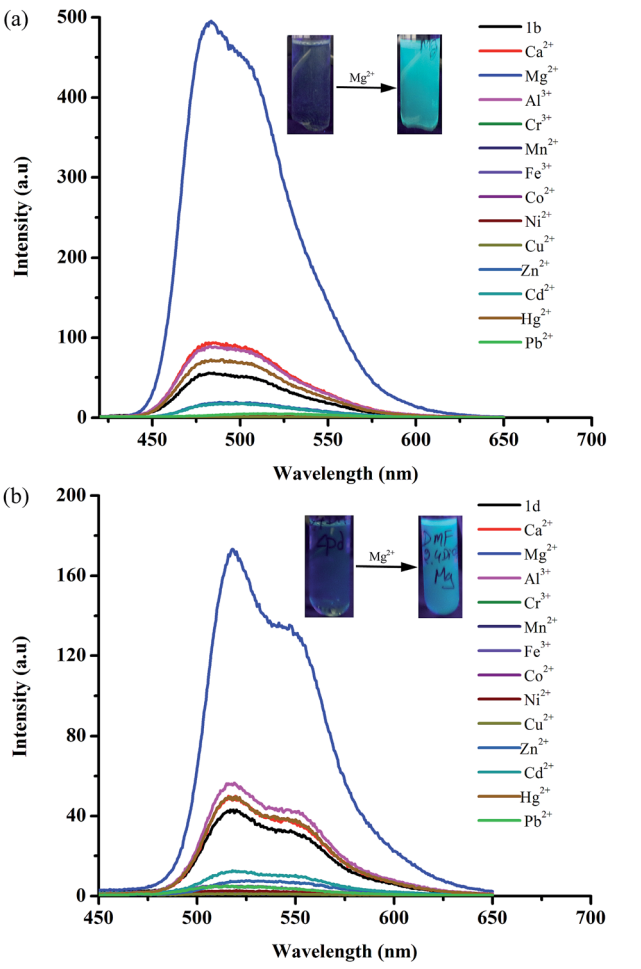


Fig. 4 (a) **1b** and (b) **1d** fluorescence spectra with different metal ions in DMF.

with Mg^{2+} 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 Mg^{2+} (Fig. S3†). However, the detection limit of Mg^{2+} was differed for **1e**. **1a**, **1b** and **1d** showed selective detection of Mg^{2+} up to the level of 10^{-7} M. But 1e showed selective turn-on fluorescence only for the addition of 10^{-4} M Mg^{2+}. The selectivity studies of **1b**, **1d** and **1e** for Mg^{2+} showed that Ca^{2+}, a strong competitor with Mg^{2+}, 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 Mg^{2+} that is due to the strong coordination character of these metal ions.

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

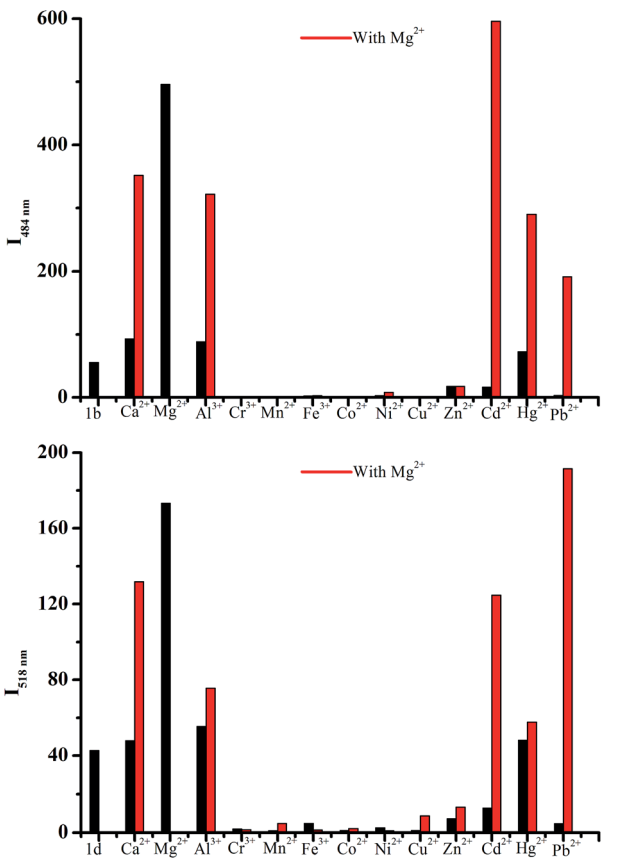


Fig. 5 Mg^{2+} interference studies of **1b** and (b) **1d** in presence of other metal cations in DMF.

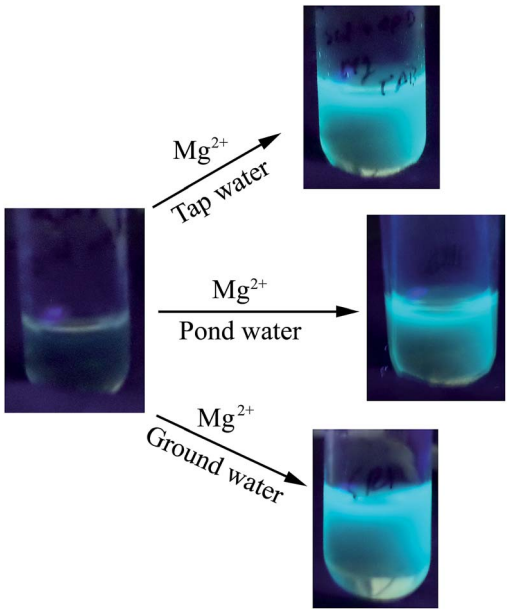


Fig. 6 Selective sensing of Mg^{2+} by **1a** in different water. **1a** was dissolved in DMF (10^{-6} M) and Mg^{2+} (10^{-6} M) was dissolved in different water. 100 mL of Mg^{2+} was added into **1a**-DMF.

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 μl into **1a** in DMF (10^{-6} m) clearly showed the strong bluish green fluorescence (Fig. 6).

Interestingly, **1a** with Fe^{3+} also exhibited selectively strong blue fluorescence (λ_{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**

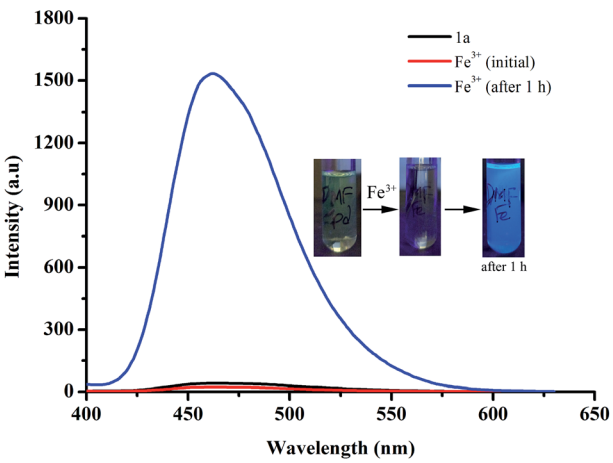


Fig. 7 The change of **1a** (10^{-6} M in DMF) fluorescence with Fe^{3+} (10^{-6} M in water) with time.

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).

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 salycylaldehyde 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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