Fluorescent detection of multiple ions by two related chemosensors: structural elucidations and logic gate applications†

Vijay Kumar,‡ Pramod Kumar‡ and Rajeev Gupta*

Two related chemosensors L1 and L2 display selective detection of multiple ions (Cu²⁺, Al³⁺, Cd²⁺ and S²⁻) as a result of minor variation of functional groups. Both chemosensors offer identical pyrrole-2-carboxamide fragments; however, they differ by the presence of either an ester (L1) or an acid group (L2) at a remote arene ring. While L1 shows selectivity towards the Cu²⁺ ion L2 is highly selective for Al³⁺ and Cd²⁺ cations as well as S²⁻ anion. A combination of studies (Stern–Volmer plots, detection limits and Benesi–Hildebrand fittings) displays the notable sensing abilities of both chemosensors. Both chemosensors were utilized to develop logic gate-based applications by considering multiple detection of assorted ions. Structural studies provide vital details about the mode of binding between chemosensors and cations. Simple synthesis, multi-stimuli response, fast response, solution visualization, and practical detection methods (filter paper strips and polystyrene films) suggest excellent sensing potentials of both chemosensors.

Introduction

Development of strategies for the detection of multiple ions has received considerable attention due to significance in biological, environmental, and chemical assays.¹ Detection of multiple ions by a single probe is not only cost-effective and time-saving but is also desirable for one-pot assays.² Moreover, probes capable of detecting multiple ions have been effectively used for the development of memory devices and molecular logic gates.³ In this direction, molecular logic gates with proper input and output history are appropriate for such memory devices.⁴ However, progress is still in its infancy and hence multiple inputs/outputs based logic operations are required with better safety level and multiple inputs.⁵ Notably, inputs and outputs critically depend on the functional groups being offered by a probe and/or a chemosensor.⁶

It is well known that both cations and anions are required in various biological processes while both their excess as well as deficiency may have detrimental effects.⁷ For example, essential Cu²⁺ ion can cause serious complications due to its excess.⁸ Accumulation of aluminum induces several health hazards such as Alzheimer’s and Parkinson’s diseases while it can also damage the nervous system.⁹ Contamination of cadmium in environment causes serious environmental and health problems, including lung, prostatic, and renal cancers.¹⁰ Similarly, high level of several anions such as sulfide can cause irritation of mucous membrane, and may lead to unconsciousness and respiratory paralysis, Alzheimer’s disease, Down’s syndrome and liver cirrhosis.¹¹ Therefore, detection of several such cations and anions is important due to their momentous effect both on human health and environment.¹²,¹³

Synthetic chemosensors have been developed for the individual detection of Cu²⁺,¹⁴ Al³⁺,¹⁵ Cd²⁺,¹⁶ and S²⁻ ions.¹⁷,¹⁸ However, detection of multiple ions by a single chemosensor has been a major challenge.¹⁹,²⁰ Martinez-Manez and co-workers have reported detection of multiple ions based on a single chemosensor in its different forms.²¹ On the other hand, Schmittel and co-workers have achieved technique-dependent selective detection of multiple ions.²² However,
The development of a single chemosensor, capable of detecting multiple ions, still remains a difficult task. Herein, we present two closely related chemosensors L1 and L2 with adept detection abilities for multiple ions (Cu$^{2+}$, Al$^{3+}$, Cd$^{2+}$ and S$^{2-}$). These chemosensors include biphenyl moiety as the fluorophore while pyrrole-2-carboxamide and carboxylic acid groups serve as the ion interacting sites (Scheme 1).

**Results and discussion**

**Synthesis and characterization of L1 and L2**

Chemosensor L1 was synthesized by the coupling of pyrrole-2-carboxylic acid with methyl-4-amino-[1,1-biphenyl]-4-carboxylate whereas L2 was obtained by the base-assisted hydrolysis of L1. FTIR spectrum shows two N–H stretches at 3405 and 3326 cm$^{-1}$ for L1 and 3334 and 3284 cm$^{-1}$ for L2 (Fig. S1 and S2, ESI†). Such stretches have been assigned to the presence of pyrrole-NH and amide-NH resonances.\[^{27}\] Similarly, proton NMR spectrum of L1 displays two signals for two different N–H groups at 9.82 and 11.69 ppm. On the other hand, L2 exhibits two such signals at 9.85 and 11.67 ppm whereas a broad feature at 12.90 ppm corresponds to –COOH group (Fig. S3–S6, ESI†). The ESI$^+$ mass spectra of chemosensors L1 and L2 display [L + H]$^+$ molecular ion peaks at 321.1237 and 307.1079, respectively (Fig. S7 and S8, ESI†). Chemosensor L2 crystallized in P2$_1$/c space group and its molecular structure is shown in Scheme 1b. The crystal structure displays that the biphenyl and pyrrole rings exist in the same plane while pyrrole-N and carboxamide-O groups are nicely positioned on the same side to potentially chelate a metal ion.

**Detection of Cu$^{2+}$, Al$^{3+}$, Cd$^{2+}$ and S$^{2-}$ ions**

The UV-Vis spectra of chemosensors L1 and L2 in CH$_3$OH display intense peaks at 312 nm (44 240 mol$^{-1}$ cm$^{-1}$) and 307 nm (41 050 mol$^{-1}$ cm$^{-1}$) (Fig. S9, ESI†). Such features are assigned to π–π* transitions within these chemosensors. Both L1 and L2 show intense emission at 418 nm upon excitation at 320 nm in CH$_3$OH. We evaluated the effect of addition of alkali (Na$^+$, K$^+$), alkaline (Mg$^{2+}$, Ca$^{2+}$), transition (Cr$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Mn$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, Ag$^+$, Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$) and post-transition (Al$^{3+}$, Pb$^{2+}$) metal ions on the emission spectra of L1 and L2. Notably, addition of five equivalents (100 μM) of assorted metal ions to L1 (20 μM) did not cause appreciable change. However, addition of Cu$^{2+}$ ion resulted in considerable quenching in the emission intensity when compared to other metal ions (Fig. 1). Interestingly, in case of L2, Al$^{3+}$ triggers enhancement with moderate red shift (Δλ = 3 nm) whereas Cd$^{2+}$ caused notable quenching in the emission with considerable blue shift (Δλ = 25 nm) (Fig. 1).

As probe L2 showed emission enhancement in presence of Al$^{3+}$ ion, hence, we measured the fluorescence spectra of L2 in absence as well as in presence of Al$^{3+}$ ion in different combinations of CH$_3$OH and H$_2$O (CH$_3$OH/H$_2$O; 100 : 0, 75 : 25, 50 : 50, 25 : 75, 10 : 90, 1 : 99). Fig. S10† shows that increasing water percentage quenches the emission of L2. Similarly, detection of Al$^{3+}$ ion by chemosensor L2 was also higher in CH$_3$OH when compared to a MeOH–H$_2$O mixture (Fig. S11†). In light of these observations, sensing studies were only performed in CH$_3$OH and not in 100% H$_2$O or HEPES buffer.

The change in the fluorescence intensity of L1 and L2 was investigated by the successive addition of Cu$^{2+}$, Al$^{3+}$ and Cd$^{2+}$ ions (Fig. 2 and 3a). Importantly, Cu$^{2+}$ ion shows quenching without wavelength shift whereas Al$^{3+}$ and Cd$^{2+}$ ions respectively exhibited enhancement and quenching with wavelength shift. To measure the extent of binding, Stern–Volmer constants ($K_{S/V}$)\[^{28}\] detection limits\[^{30}\] and binding constants ($K_b$)\[^{39}\] were calculated using fluorescence spectral titrations. The Stern–Volmer constants were found to be 9.33 × 10$^3$ M$^{-1}$ and 5.95 × 10$^4$ M$^{-1}$ for Cu$^{2+}$ and Cd$^{2+}$ ions, respectively (Fig. S12† and Table 1). The binding constants $K_b$ (M$^{-1}$) were found to be 1.61 × 10$^3$, 3.72 × 10$^3$ and 1.24 × 10$^4$ for Cu$^{2+}$, Al$^{3+}$ and Cd$^{2+}$ ions, respectively (Fig. 3b and Table 1).\[^{30}\]

The detection of Cu$^{2+}$, Al$^{3+}$ and Cd$^{2+}$ ions by the photosensitive chemosensors L1 and L2 was also investigated by the UV-Vis spectral titrations. The intense peak at $\lambda_{max} = 312$ nm (44 240 mol$^{-1}$ cm$^{-1}$) for L1 (20 μM, CH$_3$OH) was redshifted by 4 nm in presence of Cu$^{2+}$ ion (0–100 μM). The observation of two isosbestic points at 288 and 330 nm suggests...
the formation of a new species (Fig. 4a). Chemosensor L2 (20 
µM, CH3OH) displays an intense peak at λmax = 307 nm (41 050 
mlcm⁻¹) which was red-shifted to 317 nm (Δλ = 12 nm) on 
addition of Al³⁺ ion (0–100 µM). The isosbestic points at 260 nm 
and 315 nm point towards the generation of a new species 
(Fig. 4b). The switch-on behavior of chemosensor L2 in presence 
of Al³⁺ ion was clearly noted under the UV light (Fig. 4b, inset).

Similarly, chemosensor L2 (20 µM, CH3OH) showed a red shift 
of 5 nm on addition of Cd²⁺ ion (0–100 µM) with isosbestic points 
at 250 nm and 310 nm (Fig. S14†). Benesi–Hildebrand fitting of 
UV-visible spectral titrations provided the binding constants (Kb = 10³ M⁻¹) of 0.77, 10.1 and 7.3 for Cu²⁺, Al³⁺ and 
Cd²⁺ ions, respectively (Fig. S15† and Table 1).21

Fig. 4 (a) Change in absorption spectra of chemosensor L1 (20 µM) 
after addition of different concentrations of Cu²⁺ ion (0–100 µM). (b) 
Change in absorption spectra of chemosensor L2 (20 µM) with Al³⁺ ion 
(0–100 µM); inset: color change of a CH3OH solution of L2 in absence 
(a1, b1) and in presence of Al³⁺ ion (a2, b2) under visible and UV light, 
respectively.

Table 1 Stern–Volmer constants (Ksv), detection limits and binding 
constants (Kb) for chemosensors L1 and L2 with Cu²⁺, Al³⁺, Cd²⁺ and 
S²⁻ ions

<table>
<thead>
<tr>
<th>Species</th>
<th>Ksv (M⁻¹)</th>
<th>Detection limit (µM)</th>
<th>Fluorescence</th>
<th>UV-visible</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 + Cu²⁺</td>
<td>9.33 × 10³</td>
<td>1.39</td>
<td>1.61 × 10⁴</td>
<td>0.77 × 10⁴</td>
</tr>
<tr>
<td>L2 + Al³⁺</td>
<td>—</td>
<td>0.55</td>
<td>3.72 × 10⁴</td>
<td>1.01 × 10⁴</td>
</tr>
<tr>
<td>L2 + Cd²⁺</td>
<td>5.95 × 10⁴</td>
<td>1.02</td>
<td>1.24 × 10⁵</td>
<td>0.73 × 10⁵</td>
</tr>
<tr>
<td>L2 + S²⁻</td>
<td>4.21 × 10⁶</td>
<td>0.01657</td>
<td>1.25 × 10⁶</td>
<td>1.49 × 10⁶</td>
</tr>
</tbody>
</table>

The presence of N–H groups both from pyrrole and amide 
ioieties suggested that chemosensors L1 and L2 may also offer 
anion sensing abilities. Therefore, we investigated the effect of 
following anions on the emission of chemosensors L1 and L2: SCN⁻, SO₄²⁻, 
SO₂⁻, S²⁻, SO₃²⁻, PO₄³⁻, CH₃COO⁻, CO₃⁻, HCO₃⁻, CI⁻, Br⁻, I⁻, NO₃⁻, NO₂⁻ and PO₄³⁻. In case of L1 (20 µM), 
ddition of 1.2 equivalents (24 µM) of any anion did not cause 
detectable change. Importantly, in case of L2 (20 µM), addition 
of S²⁻ ion resulted in significant quenching in the emission 
spectrum with a blue shift (Δλ = 7 nm) (Fig. S16† and 5a). The 
change in fluorescence intensity of L2 was then investigated by 
the successive addition of S²⁻ ion (Fig. 5b and S17af). The 
Stern–Volmer constant (Ksv) was found to be 4.21 × 10⁶ M⁻¹ 
suggesting a strong quenching by S²⁻ ion (Fig. S17bf and Table 1).22 A high detection limit of 16.57 nM and a high binding 
constant (Kb = 10⁶ M⁻¹) of 1.25 × 10⁶ were observed for S²⁻ ion.23,24 
(Fig. S18† and Table 1). Detection of S²⁻ ion by chemosensor L2 
as was also investigated by the UV-visible titration in CH3OH. The 
intense peak at 307 nm (20 µM) was found to blue shift (Δλ = 4 
mm) after the addition of S²⁻ ion (0–30 µM) (Fig. 5c). Benesi– 
Hildebrand fitting of the UV-visible spectral titration data 
provided Kb of 1.49 × 10⁷ M⁻¹ (Fig. S19† and Table 1).

Selectivity studies
A good chemosensor should not only offer high sensitivity and 
fast response time but also high degree of selectivity for an 
analyte from a mixture. Therefore, selectivity was investigated 
by performing competitive binding studies of L1 towards Cu²⁺ 
and L2 towards Al³⁺ as well as Cd³⁺ ion in presence of other ions. 
As shown in Fig. 6a, no significant change in the emission 
intensity of chemosensor L1 (20 µM) towards Cu²⁺ ion was 
observed in presence of following metal ions (100 µM): Na⁺, K⁺, 
Mg²⁺, Ca²⁺, Al³⁺, Cr³⁺, Co²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Mn³⁺, Zn²⁺, 
Ag⁺, Pb²⁺, Hg²⁺, Pd²⁺, Cd²⁺. Similarly, no remarkable change in 
the emission intensity of L2 (20 µM) in presence of Al³⁺ ion 
was observed upon addition of (100 µM) of other metal ions. As 
expected, however, Cd²⁺ ion showed considerable quenching 
(Fig. 6b). The selectivity was also investigated for S²⁻ ion in

Fig. 5 (a) Bar diagram exhibiting change in emission intensity in 
CH3OH at 418 nm of chemosensors L1 (20 µM, red pillars) and L2 (20 
µM, green pillars) in presence of 1.2 equivalents of different anions (24 
µM). (b) Change in emission spectra of L2 (20 µM) on exposure to S²⁻ 
ion (0–24 µM) in CH3OH. (c) Change in absorption spectra of 
chemosensor L2 (20 µM) with different concentrations of S²⁻ ion (0–30 
µM).

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was observed upon addition of (100 µM) of other metal ions. As 
expected, however, Cd²⁺ ion showed considerable quenching 
(Fig. 6b). The selectivity was also investigated for S²⁻ ion in
gate in which Al\(^{3+}\) line goes into a YES gate as compared to Cd\(^{2+}\) and S\(^{2-}\)

Al\(^{3+}\) ion is more dominating as compared to S\(^{2-}\) ion below the threshold values was allocated as above the threshold values is assigned as output with the threshold value of 200 (Fig. 8). The emission change in emission intensity of L2 at 418 nm was selected as the other anions: L2 + anions (blue pillars); and L2 + anions + S\(^{2-}\) (pink pillars).

Fig. 6 (a) Selectivity of chemosensor L1 towards Cu\(^{2+}\) ion in presence of other metal ions: L1 + metal ions (blue pillars); and L1 + metal ions + Cu\(^{2+}\) ion (green pillars). (b) Selectivity of chemosensor L2 towards Al\(^{3+}\) ion in presence of other metal ions: L2 + metal ions (green pillars); and L2 + metal ions + Al\(^{3+}\) ion (purple pillars).

Fig. 7 Selectivity of chemosensor L2 towards S\(^{2-}\) ion in presence of other anions: L2 + anions (blue pillars); and L2 + anions + S\(^{2-}\) ion (pink pillars).

Reversibility studies

Reversibility is an important factor for the optimum functioning of a chemosensor.\(^\text{36}\) In case of Cu\(^{2+}\) ion, Na\(_2\)S was used to remove Cu\(^{2+}\) ion to achieve the reversibility.\(^\text{37}\) Fig. 9a shows that Cu\(^{2+}\) ion quenches the fluorescence of L1; however, addition of sulfide ion restores it (ca. 96%). Reversibility cycles were generated for L1 (20 \(\mu\)M) at 418 nm upon successive addition of Cu\(^{2+}\) (100 \(\mu\)M) and S\(^{2-}\) (200 \(\mu\)M) ions (Fig. 9b). Similarly, in order to develop a reversible chemosensor for the detection of Al\(^{3+}\) and Cd\(^{2+}\) ions, K\(_2\)HPO\(_4\) was used to remove Al\(^{3+}\) (red bars) as well as Cd\(^{2+}\) ions (green bars) from L2-Al and L2-Cd systems (Fig. 10a). Reversibility cycles were generated for L2 (20 \(\mu\)M) by the successive addition of Al\(^{3+}\)/Cd\(^{2+}\) ions (100 \(\mu\)M) and K\(_2\)HPO\(_4\) (100 \(\mu\)M) (Fig. 10b and 10b').

As Na\(_2\)S and K\(_2\)HPO\(_4\) can be used for achieving reversibility by respectively removing Cu\(^{2+}\) and Al\(^{3+}/Cd^{2+}\) ions; logic circuits and truth tables for chemosensors have been constructed (IN 1 = Cu\(^{2+}\) and IN 2 = S\(^{2-}\) for L1, IN 1 = Al\(^{3+}\) or Cd\(^{2+}\) and IN 2 = K\(_2\)HPO\(_4\) for L2). The threshold emission values were fixed at 150 (for L1), 200 and 100 (for L2) at 418 nm (OUT) for the detection of Cu\(^{2+}\), Al\(^{3+}\) and Cd\(^{2+}\) ions, respectively (Fig. 9a and 10a). The emission above and below these threshold values were allocated as “ON” and “OFF” for “on” and “off” output signals, respectively.

Fig. 9 (a) Emission outputs of L1 at 418 nm in presence of chemical inputs viz. IN 1 = Cu\(^{2+}\) and IN 2 = S\(^{2-}\) (blue bars) and the corresponding two-input combinational logic circuit; dotted line provides guide to eyes.

(a) Selectivity of chemosensor L1 towards Cu\(^{2+}\) ion in presence of chemical inputs viz. IN 1 = Cu\(^{2+}\) and IN 2 = S\(^{2-}\) (blue bars) and the corresponding two-input combinational logic circuit. (b) Reversibility cycles for L1 (20 \(\mu\)M) at 418 nm upon addition of Cu\(^{2+}\) (100 \(\mu\)M) and subsequent regeneration by the addition of Na\(_2\)S (200 \(\mu\)M); dotted lines provide guide to eyes.

Fig. 8 Emission outputs of L2 at 418 nm in presence of chemical inputs viz. IN 1 = Al\(^{3+}\) and IN 2 = Cd\(^{2+}\) (green bars); IN 1 = Al\(^{3+}\) and IN 2 = S\(^{2-}\) (blue bars) and the corresponding two-input combinational logic circuit; dotted line provides guide to eyes.

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high-resolution ESI-MS spectrum of L1–Cu displayed molecular ion peak at \( m/\ell \) 475.9728 attributed to \([\text{[L1–H]} + \text{Cu}^{2+} + 2\text{Cl}^{-} + \text{Na}^+ + \text{H}^+]\) (Fig. S24†). The solution molar conductance of L1–Cu compound displayed non-conducting nature.42 Collectively, these studies suggest a 1 : 1 stoichiometry between L1 and Cu\(^{2+}\) ion forming a L1–Cu compound as displayed in Scheme 2.

Finally, blue colored plate-shaped crystals were obtained by the slow evaporation of a CH\(_2\)OH/CH\(_3\)CN solution of [L1–Cu] compound. The partial molecular structure however shows a bis-chelated composition, [Cu(L1)\(_3\)] \((\text{Fig. 11).}^41\) The crystal structure shows a distorted square-planar geometry around the Cu(II) ion wherein two deprotonated pyrrole-N and two neutral O-amide atoms constitute the basal plane around the metal ion. We believe that during the crystallization, a thermodynamically stable product, [Cu(L1)\(_3\)], was crystallized which is different from the solution-based species [L1–Cu] responsible of sensing of Cu\(^{2+}\) ion in solution. Nevertheless, crystal structure of [Cu(L1)\(_3\)] clearly illustrates the coordination mode of chemosensor L1 and its strong ligating ability.

On the other hand, FTIR spectra of L2–Al and L2–Cd showed two different N–H signals due to the presence of both pyrrole-NH and amide-NH groups thus suggesting protonated form of L2 (Fig. S25 and S26†). In addition, \( v_{C=O} \) stretches for the carboxylate group exhibited moderate red shift thus suggesting its coordination to the metal ion. The \(^1\)H NMR spectrum of L2 in presence of Al\(^{3+}\) and Cd\(^{2+}\) ions showed disappearance of COO–H signal which was noted at 12.89 ppm in free L2 (Fig. S27†). Therefore, both FTIR and NMR spectral studies confirm the coordination of L2 through the deprotonated carboxylate group in L2–Al and L2–Cd as shown in Scheme 2. The nature of interaction of L2 with Al\(^{3+}\) and Cd\(^{2+}\) ions was also examined by

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**Notes:**

1. This work was supported by the National Natural Science Foundation of China (No. 21171115, 21571183) and the Fundamental Research Funds for the Central Universities (No. 19L106, 19L109).

2. NMR data were collected on a Bruker Avance DRX 800 MHz spectrometer.

3. ESI-MS spectrum of L1–Cu displayed molecular ion peak at \( m/\ell \) 475.9728 attributed to \([\text{[L1–H]} + \text{Cu}^{2+} + 2\text{Cl}^{-} + \text{Na}^+ + \text{H}^+]\). The solution molar conductance of L1–Cu compound displayed non-conducting nature.

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**Fig. 11** Ball and stick representation of the partial crystal structure of [Cu(L1)\(_3\)]. Selected bond distances (Å) and angles (°): Cu1–N2, 1.902; Cu1–O3, 2.014. Selected bond angles (°): O3–Cu1–O3#, 180.0; N2–Cu1–O3, 84.4; N2–Cu1–O3#, 95.6; N2–Cu1–N2, 180.0.
the high-resolution ESI+ mass spectra. Herein, molecular ion peaks were observed at m/z 475.3264 and 531.2752 that were assigned to \([\{L2\text{-}H+Al^{3+}+2NO_3^-+H_2O\}+H^+}\) (Fig. S28†) and \([\{L2\text{-}H+Cd^{2+}+CH_3COO^-+H_2O\}+Na^+}\), respectively (Fig. S29†). The presence of coordinated water in L2–Al and L2–Cd was established by the thermal weight loss (3.4–3.8% for 1\(\text{H}_2\text{O}\)) in the TGA studies (Fig. S30, ESI†).

Interestingly, when L2–Cd was crystallized from DMSO–CH\(_3\)OH, a new compound L2–Cd\(^\#\) was obtained that was structurally characterized. The asymmetric unit of L2–Cd\(^\#\) displays two L2, one Cd\(\text{[n]}\) ion, and two Cd-coordinated DMSO molecules. The crystal structure of L2–Cd\(^\#\), shown in Fig. 12, exhibits that a Cd\(\text{[n]}\) ion is coordinated to two O-carboxylate and two O-amine atoms from two different chemosensor L2 in addition to two DMSO molecules. As a result, two chemosensors L2 hold two Cd\(\text{[n]}\) ions to generate a large metallacycle. Such metallacycles are further extended via Cd–O_\text{amide} bonds to generate a double chain structure. It is suggested that the solution-based species, L2–Cd, slowly reorganizes to form a thermodynamically stable product, L2–Cd\(^\#\). Importantly, crystal structure of L2–Cd\(^\#\) proves our assumption that chemosensor L2 coordinates preferentially through its O-carboxylate end and not through pyrrole-N part. Interestingly, the proton NMR titration of chemosensor L2 with 0, 0.5, 1.0, 1.5 and 2.0 equiv of Na\(_2\)S showed changes in the solution-based species, L2–Cd\(^\#\), shown in Fig. 12, and recognition for the sulfoxide group.

The proton NMR titration of chemosensor L2 with 0–2 equivalents (0, 0.5, 1.0, 1.5 and 2.0) of Na\(_2\)S showed changes in the biphenyl ring protons (Fig. S31†). In addition, a new signal was observed at –3.34 ppm that has been assigned to the HS\(^-\) species (Fig. S32†). Such an experiment suggests that the interaction of S\(^2-\) ion with the carboxylic acid group of L2 potentially generates HS\(^-\) species and anionic carboxylate group. Importantly, no change in the emission of L1 (having ester group) in presence of Na\(_2\)S was observed at 3.34 ppm that has been assigned to the HS\(^-\) ion strongly support the role of free carboxylic acid in its sensing. In the high-resolution ESI-MS spectrum of [L2–S], a peak was observed in the negative mode with m/z 341.0679 that corresponded to \([\{L2+HS^-+H^+\}+H^+]\) (Fig. S33†). Collectively, these experiments suggest that the recognition of S\(^2-\) ion is due to its ability to abstract a proton from COO–H group of the chemosensor L2. Literature has suggested similar mode of interaction and recognition for the sulfide ion.45

**Monitoring of Al\(^{3+}\) ion in different systems**

In literature, most of the Al-sensors only operate in a solvent, thus, limiting the practical applications.46 However, straight-forward and cost-effective detection of Al\(^{3+}\) ion is important for the practical applications. Therefore, “turn-on” sensing of Al\(^{3+}\) ion and its reversibility using K\(_2\)HPO\(_4\) provided us an attractive and cost-effective detection opportunity. Towards such a goal, we fabricated filter-paper test strips as well as polystyrene films for the detection of Al\(^{3+}\) ion. Fig. 13x exhibits that the presence of Al\(^{3+}\) ion in CH\(_3\)OH enhances the emission of L2 while addition of K\(_2\)HPO\(_4\) quenches the emission. For the monitoring of Al\(^{3+}\) ion, filter-paper test strips were prepared by immersing filter-paper strips in a CH\(_3\)OH solution of L2 followed by air drying.47 Such test strips successfully detected Al\(^{3+}\) ion by dipping them directly into either CH\(_3\)OH or even water solution of Al\(\text{[III]}\) salt (Fig. 13y). Importantly, if such strips were exposed to an aqueous solution of K\(_2\)HPO\(_4\); the original emission of L2 can be retrieved thus providing reversibility. We also attempted to detect Al\(^{3+}\) ion using thin polystyrene films. Such thin films were prepared by doping L2 during the synthesis of polystyrene films \(^{29-40}\) and demonstrated attractive detection of Al\(^{3+}\) ion as well as its reversibility using a solution of K\(_2\)HPO\(_4\) (Fig. 13z). Both such detection methods suggest potential monitoring of Al\(^{3+}\) ion under environmental as well as industrial conditions.

**Conclusions**

This report illustrated a simple strategy of developing effective chemosensors for the detection of multiple ions by simply changing the remote functional group. In two related chemosensors, carboxylic acid group was found responsible for the detection of Al\(^{3+}\), Cd\(^{2+}\), and S\(^2-\) ions whereas a pyrrolecarboxamide fragment was needed for the recognition of Cu\(^{2+}\) ion.

![Image](Image 14x290 to 26x354)

![Image](Image 49x146 to 285x283)

![Image](Image 310x627 to 546x729)

![Image](Image 23132 | RSC Adv., 2017, 7, 23127–23135)

![Image](Image 23132 | RSC Adv., 2017, 7, 23127–23135)

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![Image](Image 23132 | RSC Adv., 2017, 7, 23127–23135)
Utilizing multiple detection abilities of two chemosensors, different logic gates were developed. The “turn on” sensing of Al\(^{3+}\) ion helped us in developing filter-paper strips as well as polystyrene films based detection strategies. Facile synthesis and multi-stimuli response offered by the present chemosensors may offer potential detection applications.

**Experimental section**

The discussion about the Stern–Volmer constants \((K_{SV})\), detection limits, binding constants \((K_b)\) and X-ray crystallography as well as figures for the characterization of L1, L2, L1–Cu, L2–Al, L2–Cd and L2–S can be found in the ESI.

**Materials and physical measurements**

The analytical grade commercially available reagents were used without furtherpurifications. Stock solutions (10 mM) of cations and anions were prepared in methanol. HPLC grade solvents were used for the UV-Vis and fluorescence spectral measurements and spectra were recorded with a 1.0 cm path length cuvette at ambient temperature. Elemental analysis data were obtained by the Elemental Analysen Systeme GmbH Vario EL-III instrument. The \(^1\)H and \(^13\)C NMR spectra recorded with a JEOL 400 MHz instrument. The FTIR spectra (ZnSe ATR) were recorded with a Perkin-Elmer Spectrum-Two spectrometer. The absorption spectra were recorded with a Perkin-Elmer Lambda-25 spectrophotometer. Fluorescence spectral studies were performed with a Cary Eclipse fluorescence spectrometer. ESI-MS mass spectra were measured with an Agilent Q-TOF LC-MS mass spectrometer.

**Synthesis of L1 (methyl 4'-[1H-pyrrole-2-carboxamido][1,1' biphényl]-4-carboxylic acid)**

Pyrrole-2-carboxylic acid (1.0 g, 0.0090 mol) and methyl-4 amino-[1,1'-biphényl]-4-carboxylate (2 g, 0.0090 mol) in 25 mL of pyridine were refluxed for 30 min at 120 °C. P(OPh)\(_3\) (3.348 g, 0.0108 mol) was added drop-wise to the aforementioned reaction mixture. The reaction mixture was then stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice-cold water that caused precipitation of the product, which was filtered, washed with water followed by ethanol and dried under vacuum. Yield: 2.2 g (73%).

**Syntheses of L2 (4'-[1H-pyrrole-2-carboxamido][1,1' biphényl]-4-carboxylic acid)**

1 g of L1 was dissolved in 10 mL mixture of THF/water (3:1) followed by the addition of a saturated aqueous NaOH solution (5 mL). The said mixture was stirred at room temperature for 8 h. The progress of the reaction was monitored by the thin layer chromatography. After the complete hydrolysis, the reaction mixture was neutralized by the drop-wise addition of 1 N HCl. Subsequently, THF was evaporated under the reduced pressure that caused precipitation of a product. The product was filtered, washed with water and dried under vacuum. Single crystals of L2 were grown by the slow evaporation of a DMSO/H\(_2\)O solution. Yield: 0.827 g (93%).

**Notes and references**

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