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A highly selective PET-based chemosensor for instant detecting of Zn^{2+}†

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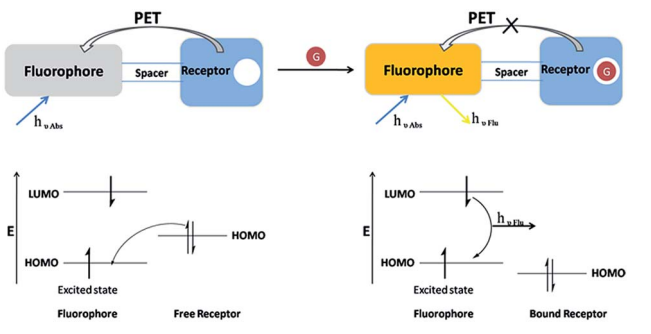
A simple Zn^{2+}-selective chemosensor system based on acylhydrazone was designed and synthesized, which could detect Zn^{2+} ions in aqueous solution with high selectivity and sensitivity over a wide pH range by the mechanism of photo-induced electron transfer (PET). The obvious color changes and pronounced OFF-ON-type fluorescent signaling behavior can be seen by the naked eye. The detection limit of **L2** for Zn^{2+} ion was as low as 0.13 μM. In addition, **L2**–Zn^{2+} complex can be used as an ON-OFF chemosensor candidate for Cu^{2+}, as the Zn^{2+}-induced emission can be quenched upon addition of Cu^{2+}. Moreover, test strips for Zn^{2+} based on **L2** were also fabricated, which could be used as a convenient and efficient test kit for instantly detecting Zn^{2+} in aqueous solution.

Introduction

One of the most active fields of supermolecular chemistry is the design and synthesis of chemosensors with high selectivity and sensitivity for heavy or transition metal ions.[1] The zinc ion (Zn^{2+}), as the second most abundant transition metal essential for human health, has drawn considerable interest due to its broad biological functions, including modulation of catalytic activity of hundreds of specific enzymes, regulation of gene transcription, and involvement in brain pathology.[2] Abnormal concentrations of Zn^{2+} are known to be closely related to several diseases, including chronic diarrhea, growth failure, immune deficiency, and Alzheimer's disease.[3] In addition, with the development of modern industry, the environmental pollution caused by transition metals like Zn^{2+} has become more serious and poses a threat to human health and the environment.[4] Therefore, the accurate measurement of Zn^{2+} concentrations in either the clinical setting or for environmental monitoring is of great importance.

Fluorescence emission spectrometry has emerged as one of the most popular methods for specific measurements because of its high sensitivity, simplicity, and real time monitoring without complicated pretreatment.[5] To date, a variety of fluorescent chemosensors for Zn^{2+} have been reported pertaining to the signaling mechanisms of photoinduced electron transfer (PET),[6] metal-ligand charge transfer (MLCT),[7] intramolecular charge transfer (ICT),[8] excimer/exciplex formation,[9] fluorescence resonance energy transfer (FRET),[10] and excited-state intermolecular proton transfer (ESIPT).[11] Of all possible detection mechanisms, photoinduced electron transfer (PET) appears to be the most elegant, sensitive, and effective way to report the presence of metal ions. A PET fluorescent probe usually consists of two structural units: the receptor unit and the fluorophore unit, the receptor unit is used for specifically recognizing the target ion, which usually contains N, O and S atoms as chelator for ions, and the fluorophore unit is used for translating the host-guest recognition into fluorescence signal, which often contain pyrene, cyanine, naphthalimide, fluorescein, rhodamine, coumarin, quinolone and BODIPY groups to provide a wide emission.[12] Scheme 1 shows the mechanism of PET progress, in the unbound dark state of these systems, the receptor unit efficiently quenches the excited state of the fluorophore unit. This is normally achieved through electron transfer processes that take place between the lone pair electrons of the recognition groups and the relevant orbitals of the fluorophore that are involved in the optical absorption and emission processes. The same lone pair electrons also bind the



Scheme 1 Mechanism and a generalized energy diagram of PET-based sensing.

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metal ions and protons to the recognition group. Therefore, upon binding, the lone pair of the recognition group becomes engaged in the newly formed bond and can no longer serve as an efficient quencher for the fluorophore.[13]

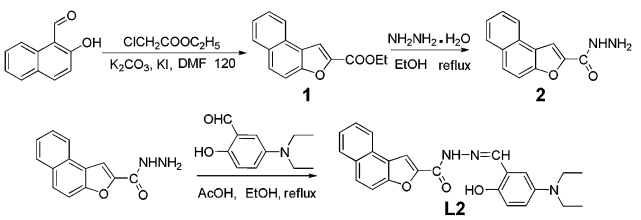
Our research group has a longstanding interest in molecular recognition.[14] Herein, we report a acylhydrazone-based Zn^{2+} chemosensor (compound **L2**) as a new advance in Zn^{2+} recognition, which was synthesized by the reaction route as show in Scheme 2. Our design is based on the well-known fluorescent mechanism of photoinduced electron transfer for Zn^{2+} recognition: First, we chose the acylhydrazone group as the receptor for coordinating with Zn^{2+} (based on the strong coordination ability of N atoms toward the Zn^{2+} ion).[15] On the other hand, the naphthalofuran group as the signaling moiety is attached to the recognition moiety with a PET progress from N atom (nonfluorescent). The addition of Zn^{2+} could inhibit the PET progress, which may lead to a "turn on" fluorescent response. We are very gratifying to see that the results go as we expect, sensor **L2** could allow selectively recognition of Zn^{2+} in aqueous solution. The detection limit for Zn^{2+} ion was as low as 0.13 μM. In addition, **L2**–Zn^{2+} displays an "OFF-ON-OFF" type signaling behavior for Cu^{2+}, because Cu^{2+} can displace Zn^{2+} to form a **L2**–Cu^{2+} complex.[16] In this regard, the complex **L2**–Zn^{2+} can be considered as a good ON-OFF chemosensor candidate for Cu^{2+}.

Results and discussion

The synthesis of chemosensor **L2** is outlined in Scheme 2. It was characterized by ^{1}H NMR, ^{13}C NMR, IR and ESI-MS (Fig. S5, S9 and S10†).

A solution of probe **L2** (20 μM) exhibits an absorption maximum at 390 nm at room temperature in an aqueous solution (0.01 M HEPES buffer, pH 7.24, 80% DMSO). However, an obviously red shift take place (from 390 nm to 423 nm) upon treatment with 20 equivalents of $Zn(ClO_4)_2$ (Fig. 1). And the color of **L2** changes from flavescent to deep yellow after addition of Zn^{2+}.

In order to investigate the binding properties of the receptor **L2** towards Zn^{2+} ion, the UV-vis titration of **L2** (20 μM) with Zn^{2+} ion in the solution of DMSO–H_2O (0.01 M HEPES buffer, pH = 7.24, 80% DMSO) was carried out. The absorption spectral variation of **L2** upon the gradual addition of Zn^{2+} ion is shown in Fig. 2. Upon the gradual addition of Zn^{2+} ion (0–2.8 equiv.), the absorption band centered at 423 nm gradually increase at the expense of the absorbance at 390 nm. Two isosbestic points at 339, 408 nm can be observed. Besides, while the amount of



Scheme 2 Synthetic procedures of sensor **L2**.

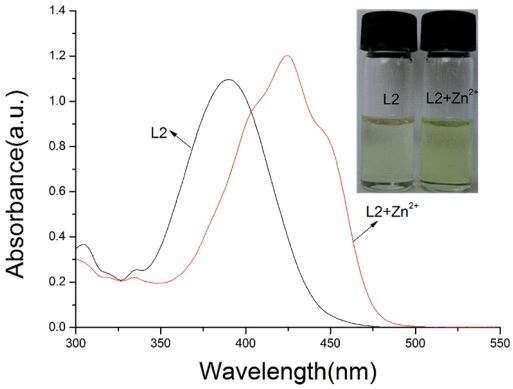


Fig. 1 UV-vis spectra change of **L2** (20 μM) upon addition of 20 equiv. of Zn^{2+} in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24). Inset: color changes of **L2** after addition of Zn^{2+}.

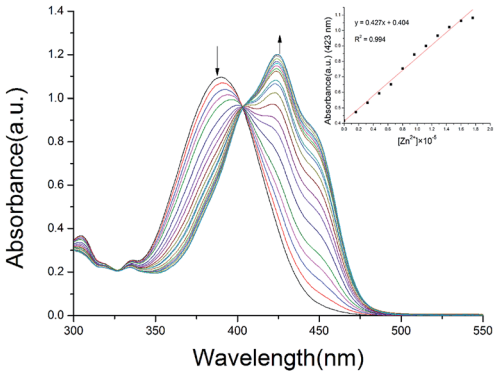


Fig. 2 UV-vis spectra of **L2** (20 μM) in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24) upon adding of an increasing concentration of Zn^{2+} from 0 to 2.4 equiv. Inset: the plot of Zn^{2+} concentration *versus* absorbance at 423 nm.

Zn^{2+} ion is beyond 1.0 equiv., the absorbance at 423 nm tends to saturation, which reveals the possible formation of a 1 : 1 complex between **L2** and Zn^{2+} (Fig. S1†). The result obtained from a Job's plot by UV-vis spectra supports the formation of a 1 : 1 **L2**–Zn^{2+} complex (Fig. S2†). The plot of Zn^{2+} concentration *versus* absorbance at 423 nm analysis of these changes gave a binding constant of 4.69×10^6 (R^2: 0.994). Nice fittings supported the 1 : 1 binding stoichiometry, see Fig. 1 inset.[17]

The fluorescence spectral properties of receptor **L2** with Zn^{2+} are also examined, compound **L2** alone displays a very weak fluorescence emission band at 508 nm when it was excited at 423 nm. The board weak emission is likely due to the extended π-electronic structure, but the lone pair electrons present on the nitrogen atom of acylhydrazone unit result in the photoinduced electron transfer (PET) that quenches the fluorescence. When 20 equivalents of Zn^{2+} was added to the solution of **L2** (0.01 M HEPES buffer, pH 7.24, 80% DMSO), it led to a prominent fluorescence enhancement, (Fig.S3†) Other cations, such as Hg^{2+}, Fe^{3+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, and Mg^{2+}, are completely nonresponsive (Fig. 3). The selectivity of Zn^{2+} over other ions, especially Cd^{2+}, is important because

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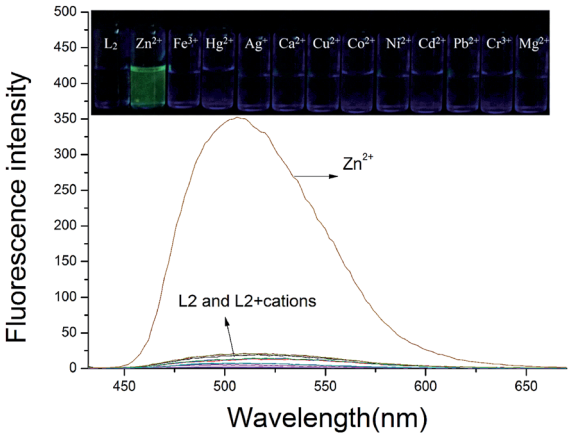

Fig. 3 Fluorescence spectra response of **L2** (20 μM) upon addition of different ions (20 equiv.) in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24), (λ_{ex} = 423 nm). Inset: photograph of **L2** (20 μM) upon adding 20 equiv. of ions, which was taken under a UV-lamp (365 nm).

many reported Zn^{2+} sensors suffer from deleterious interference of other ions. These results suggested that sensor **L2** displays a Zn^{2+}-selective "OFF-ON" fluorescent signaling behavior. The reaction process completed as soon as the addition of Zn^{2+}, implying that sensor **L2** could be used for real-time detection of Zn^{2+}. The reason of the obvious fluorescence enhancement at 508 nm lies in the following two aspects: Firstly, it operates *via* PET, a process that often induces chelation enhanced fluorescence (CHEF). When Zn^{2+} ion coordinates with the nitrogen atoms of the acylhydrazone moiety, the lone pair electrons on the nitrogen atom no longer serve the PET process, which leads to an enhancement of the emission (Scheme 1). Secondly, the coordination of Zn^{2+} and **L2** can enhance the planarity and rigidity, which can also reduce the nonradiative decay of the excited state and lead to the pronounced fluorescence enhancement.

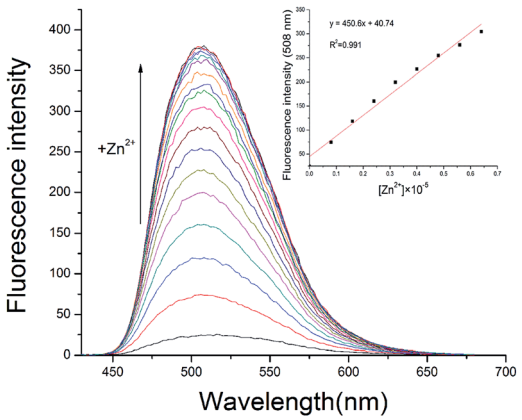

Fig. 4 Fluorescence titration spectra of **L2** (20 μM) in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24) upon adding of an increasing concentration of Zn^{2+} from 0 to 4.0 equiv. (λ_{ex} = 423 nm). Inset: the plot of Zn^{2+} concentration *versus* fluorescence intensity.

The fluorescence titration of receptor **L2** toward Zn^{2+} ion was also carried out. As shown in Fig. 4, free receptor **L2** shows a board weak emission band situated between 450 nm and 625 nm. The fluorescent intensity remarkably increased as the Zn^{2+} concentration increasing from 0 to 4.0 equivalents. It can be also saw clearly form Fig. S4†, while the amount of Zn^{2+} ion is beyond 1.0 equivalents, the emission at 508 nm tends to saturation, which reveals the possible formation of a 1 : 1 between **L2** and Zn^{2+}. Besides, as shown in Fig. 4 inset, there is a good linear (R^2 = 0.991) relationship between the fluorescence intensity at 508 nm and the concentration of Zn^{2+}, which makes a stoichiometric assay of Zn^{2+} ion possible. On the basis of the 1 : 1 stoichiometry and fluorescence titration data, the binding constant of **L2** for Zn^{2+} was calculated to be 7.72×10^6 M^{-1}. In the meantime, the detection limit of the fluorescence spectra changes calculated on the basis of $3S_B/S$ was 0.13 μM for Zn^{2+} ion in aqueous solution.[17]

In order to quantify the complexation ratio between **L2** and Zn^{2+} ion, besides the UV-vis titration and fluorescence titration experiments, the fluorescence Job's plot measurement (Fig. 5) was conducted by varying the concentration of both the receptor and the Zn^{2+} ion with a total concentration of 40 μM. The maximum point appears at the mole fraction of 0.5 which indicates **L2** and Zn^{2+} form a 1 : 1 complex. It was further confirmed by the appearance of a peak at *m*/*z* 503.9 assignable to $[\mathbf{L2} + Zn^{2+} + 2H_2O + H]^+$ (*m*/*z* calcd = 503.4) in the ESI-MS spectrum (Fig. S6†).

The recognition mechanism of the sensor **L2** with Zn^{2+} was investigated by FT-IR spectra (Fig. S8†). In the IR spectra of **L2**, the stretching vibration absorption peaks of O–H, N–H, C=O, and C=N appeared at 3419 cm^{-1}, 3218 cm^{-1}, 1640 cm^{-1}, and 1601 cm^{-1}, respectively. However, when coordinated with Zn^{2+}, the absorption of O–H and N–H shifted upfield, while the stretching vibration absorption peaks of C=O and C=N shifted downfield to 1617 cm^{-1} and 1567 cm^{-1}, which indicated that **L2** coordinated with N, O atoms.

The proposed mechanism was also confirmed by ^1H NMR measurements. ^1H NMR titration displayed the chemical shift changes of **L2** upon the addition of Zn^{2+}, as shown in Fig. 6, sensor **L2** showed two single peaks at 12.23 and 11.25 ppm in

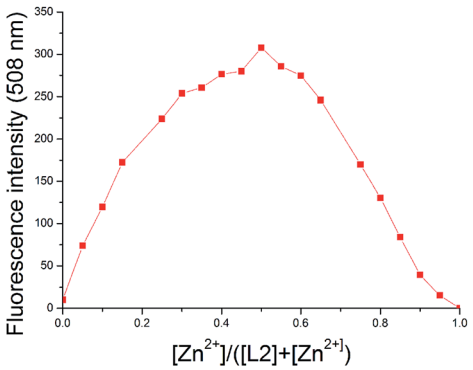

Fig. 5 The Job's plot examined between Zn^{2+} and **L2**, indicating the 1 : 1 stoichiometry, which was carried out by fluorescence spectra, (λ_{ex} = 423 nm).

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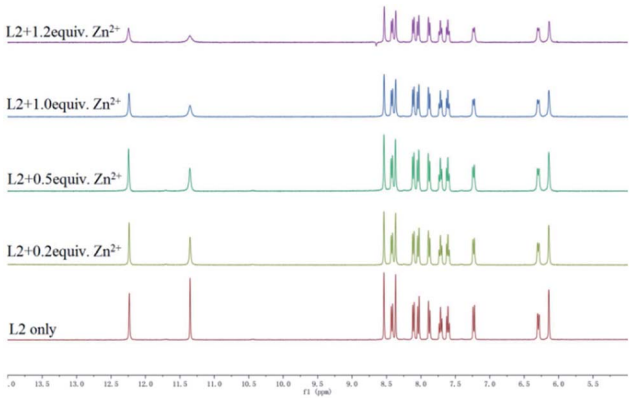
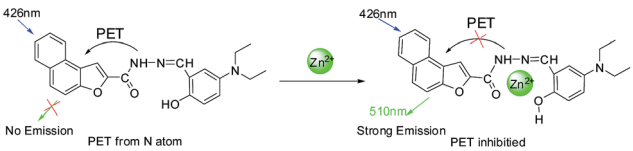


Fig. 6 Partial ^{1}H NMR spectra of **L2** (2 mM, DMSO-d_6) and in the presence of varying amounts of Zn^{2+}.

DMSO-d_6, we confirmed that which correspond to the protons of –NH– and –OH, respectively. During the titration, the concentration of **L2** was kept constant and a gradual increase was brought in the concentration of Zn^{2+} to vary the mole ratio from 0 to 1.2 equiv. With the addition of Zn^{2+}, both the singlet signals of –NH– and –OH protons were broadened, but no obvious shift, this phenomenon indicated that **L2** coordinated with N, O atoms, while no chemical reaction occurred between them. Based on these reasons, we proposed the following signaling mechanism for detection Zn^{2+} (Scheme 3). **L2** alone showed no emission at 500 nm, when Zn^{2+} ion coordinates with the nitrogen atoms of the acylhydrazone unit, the lone pair electrons of nitrogen atom no longer serve the PET process, that leads to an enhancement of the emission.

The effects of pH on the fluorescence of the free compound **L2** and its complex **L2**–Zn^{2+} are shown in Fig. 7. Over the pH range we tested, compound **L2** alone was not sensitive to pH. However, the fluorescence intensity of **L2**–Zn^{2+} displayed a strong pH dependence, as illustrated by its fluorescence intensity at 508 nm. An intense and stable fluorescence of **L2**–Zn^{2+} in the pH range 6.0–12.0 warrants the binding of **L2** with Zn^{2+} occurred effectively between pH from 6 to 12.

The competition experiments were also measured by addition of 20 equivalents of Zn^{2+} to the solution of **L2** in the presence of 20 equivalents of other metal ions, such as, Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+} and Mg^{2+}. Results of our studies revealed that all potentially competitive metal cations (except Cu^{2+}) exerted no or little influence on the fluorescence detection of Zn^{2+} in aqueous buffer solutions, as show in Fig. 8. The good news is that the addition of S^{2-} can mask the influence of Cu^{2+} effectively (Fig. S9†). In order to understand the strong quenching behavior of Cu^{2+}, we have measured the change in emission intensity of **L2**–Zn^{2+} with addition 20 equiv. of Cu^{2+} ion. The emission intensity of **L2**–Zn^{2+} at 508 nm quenched (Fig. 9) due to the paramagnetic properties of Cu^{2+}, indicating that Cu^{2+} can displace Zn^{2+} to form a **L2**–Cu^{2+}



Scheme 3 Proposed sensing mechanism.

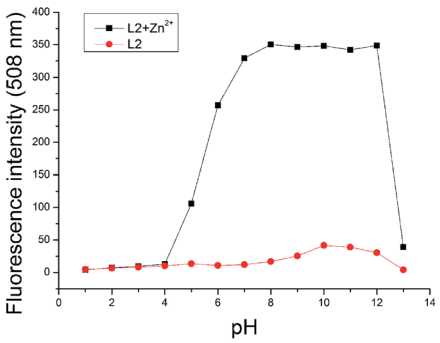


Fig. 7 Effect of pH on the fluorescence spectra of **L2** (20 μM) in response to Zn^{2+} (20 equiv.) in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES) solution.

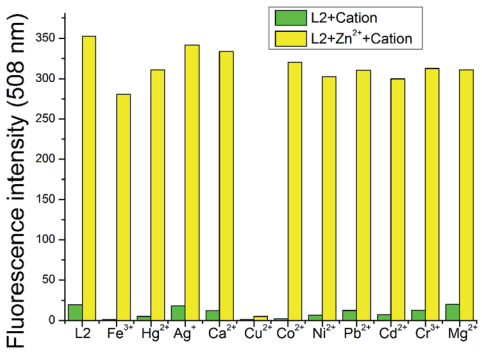


Fig. 8 Fluorescence spectra response of **L2** (20 μM) in the presence of 20 equiv. of various ions containing 20 equiv. of Zn^{2+} in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24), (λ_{ex} = 423 nm).

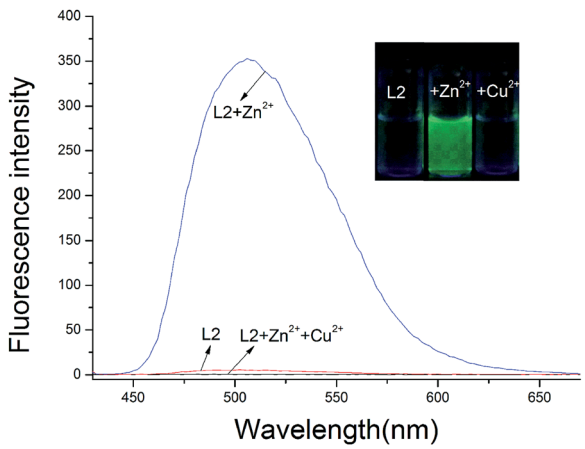


Fig. 9 Fluorescence spectra of **L2** (20 μM) in the presence of Zn^{2+} or Zn^{2+} and Cu^{2+} in DMSO–H_2O (8 : 2, v/v, containing 0.01 M HEPES, pH = 7.24), (λ_{ex} = 423 nm). Inset: Photograph of **L2** (20 μM), **L2**+ Zn^{2+} (20 equiv.) and **L2**–Zn^{2+} + Cu^{2+} (20 equiv.), which was taken under a UV-lamp (365 nm).

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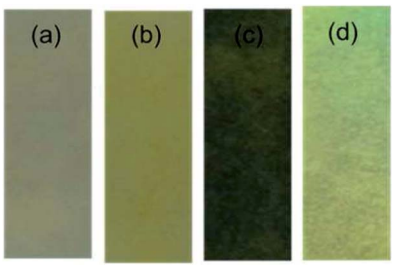

Fig. 10 Photographs of test strips (a: only **L2**; b: **L2** + Zn^{2+}; c: only **L2**; d: **L2** + Zn^{2+}.), (c) and (d) was taken under a UV-lamp (365 nm).

complex. Which was confirmed by the appearance of a peak at *m*/*z* 463.1 assignable to $[\mathbf{L2} + Cu^{2+}]^+$ (*m*/*z* calcd = 463.5) in the ESI-MS spectrum (Fig. S7†). In this regard, the complex **L2**–Zn^{2+} can be considered as a good ON-OFF chemosensor candidate for Cu^{2+}.[15]

To investigate the practical application of chemosensor **L2**, test strips were prepared by immersing filter papers into a aqueous solution of **L2** (0.001 M) and then drying in air. The test strips containing **L2** were utilized to sense Zn^{2+}. As shown in Fig. 10, when Zn^{2+} solution was added on the test kits, the obvious color change can be observed and the fluorescence turn on response can be saw under UV irradiation (λ_{ex} = 365 nm). Therefore, the test strips could conveniently detect Zn^{2+} in solution.

Conclusions

In summary, a photo-induced electron transfer based chemosensor (**L2**) for Zn^{2+} was designed and synthesized, which could detect Zn^{2+} ions in aqueous solution with high selectivity and sensitivity at a wide pH range (from 6.0 to 12.0). The colorimetric and ratiometric fluorescent response to Zn^{2+} was realized through the coordination of sensor **L2** with Zn^{2+}, namely, when Zn^{2+} was added to the solution of **L2**, it resulted in an obvious color changes and pronounced OFF-ON-type fluorescent signaling behavior. The detection limit of **L2** for Zn^{2+} ion in aqueous solution was as low as 0.13 μM. In addition, the complex **L2**–Zn^{2+} can be used as an ON-OFF chemosensor candidate for Cu^{2+}, for the Zn^{2+}-induced emission can be quenched upon addition of Cu^{2+}. Moreover, test strips based on **L2** were fabricated, which also exhibited a good selectivity to Zn^{2+} as in solution. We believe the test strips could act as a convenient and efficient Zn^{2+} test kit.

Experimental

Chemicals used for syntheses were commercially available. Solvents for spectral titrations were redistilled DMSO and deionized water.

All reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards) UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

All fluorescence spectroscopy was carried out just after the addition of perchlorate metal salts in DMSO solution, while keeping the ligand concentration constant (2.0×10^{-5} M). The solution of metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}.

Preparation and characterization of L2

The synthesis of chemosensor **L2** is outlined in Scheme 2: 2-hydroxy-1-naphthaldehyde (0.86 g, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol), ethyl chloroacetate (0.72 g, 6 mmol) and KI (0.09 g, 0.6 mmol) were dissolved in appropriate absolute DMF and stirred half an hour at room temperature, respectively. Blended them together and stirred for 4 h at 90 °C, then raised up to 120 °C kept for 9 h, after cooling to room temperature, the solution was dispersed in 200 mL distilled water, and filtered to obtain pale yellow powdery product **1**. After further purification, compound **1** (0.48 g, 2 mmol) was dissolved in 20 mL EtOH, hydrazine monohydrate (0.40 g, 8 mmol) was added and stirred under reflux for 8 h, then dispersed in 100 mL distilled water, and filtered to obtain yellow powdery product **2**. After further purification, compound **2** (0.45 g, 2 mmol), 4-(*N*,*N*-diethylamino) salicylaldehyde (0.42 g, 2.2 mmol) and a catalytic amount of acetic acid (AcOH) were combined in absolute ethanol (40 mL). The solution was stirred under reflux for 6 h. After cooling to room temperature, the yellow precipitate was filtered, washed three times with hot absolute ethanol, then recrystallized with EtOH–DMF to give a luminous yellow powder product **L2** (0.68 g) in 85% yield (m.p. > 300 °C), IR: (KBr, cm^{-1}) ν: 3419 (OH), 3215 (NH), 3080 (HC═N), 3030 (HC═C), 1631 (C═O), 1600 (C═N), 1550 (C═C), 1535 (C═C), 1283 (Ar–O), 1238 (N–N), 1131(C–C). ^1H NMR (DMSO-d_6, 400 MHz): δ 12.23 (1H, s, OH), 11.25 (1H, s, NH), 8.54 (1H, s, N═CH), 8.41–8.43 (1H, d, J = 8, ArH), 8.37 (1H, s, ArH), 8.10–8.12 (H, d, J = 8, ArH), 8.03–8.05 (1H, d, J = 8, ArH), 7.87–7.89(1H, d, J = 8, ArH), 7.70–7.73(1H, t, J = 12, ArH), 7.59–7.62(1H, t, J = 12, ArH), 7.22–7.24 (1H, d, J = 8, ArH), 6.28–6.30 (1H, d, J = 8, ArH), 6.14 (1H, s, ArH), 3.35–3.40 (4H, m, J = 20, CH_2), 1.10–1.13 (6H, t, J = 12, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.87, 158.95, 157.50, 155.68, 155.47, 152.64, 136.75, 135.25, 133.99, 133.52, 132.61, 132.45, 130.58, 128.84, 127.83, 117.63, 115.23, 114.43, 108.93, 102.65, 48.95, 17.68; Anal. calcd for $C_{24}H_{23}N_3O_3$: C 71.61, H 5.72, N 10.44; found C, 7162; H, 5.70; N, 10.47%. ESI-MS calcd for $C_{24}H_{23}N_3O_3$, $[M + H]^+$ = 402.2, found $[M + H]^+$ = 402.2.

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