# Optical Chemosensors Based on Transmetalation of Salen-Based Schiff Base Complexes

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S *Supporting Information*

ABSTRACT: We report our systematic studies of novel, simple, selective, and sensitive optical (both colorimetric and fluorescent) chemosensors for detecting Al^{3+} based on transmetalation reactions (metal displacement or exchange reactions) of a series of K(I), Ca(II), Zn(II), Cu(II), and Pt(II) complexes containing different ligands of salen-based Schiff bases. Both the chemical structure of the salen ligand and the identity of the central metal ion have a tremendous impact on the sensing performance, which is mainly determined by the stability constant of the complex. Moreover, the selectivities of the salen-complex-based chemosensors are much better than those of the corresponding free salen ligands because of the shielding function of the filled-in metal ion in the complex. Therefore, the present work potentially provides a new and simple way to design optical probes via complex-based transmetalation reactions.
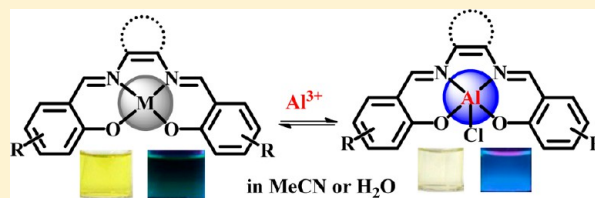
INTRODUCTION

The design and synthesis of optical (both colorimetric and fluorescent) molecular probes have generated great interest in a variety of scientific communities because these detection methods are cost-effective, rapid, and facile and are applicable as analytical tools in the environmental, medical, and biochemical fields as well as in industry.[1] In general, a typical optical molecular probe (chemosensor or chemodosimeter) contains a receptor/ligand unit with/without a signaling unit (Scheme 1a). The receptor/ligand unit can bind with the metal ion with a concomitant change in one or more properties of the system, such as color (colorimetric probes) or fluorescence (fluorescence probes), that arise from the complexation, hydrolysis/substitution, or oxidation/ring transformation. In order to achieve high selectivity, the receptor/ligand is required to have the strongest affinity with the metal ion of interest. Usually, however, it is difficult to meet such a requirement because the receptor/ligand affinities for different metal ions cannot be anticipated in a straightforward manner, and thus, a lot of effort has to be spent on the design and synthesis of tailored receptors/ligands with different chemical structures.

Transmetalation reactions, in which one organometallic complex transfers its organic group to the metal of interest to furnish a thermodynamically more stable structure, have proved to be extremely valuable tools in organometallic synthesis,[2] catalysts,[3] nanomaterials,[4] metal–organic frameworks,[5] and so on. Recently, transmetalation reactions by the other name of metal displacement or exchange reactions have been used in optical chemosensors (Scheme 1b).[6] To date, there are only a limited number of examples of organometallic complexes that have been used to detect metal ions via transmetalation reactions. For example, Cd(II)/Cu²⁺ [i.e., a Cd(II) complex for detecting Cu²⁺ ions],[6a] Cu(II)/Hg²⁺,[6b] Zn(II)/Hg²⁺,[6c] Zn(II)/

Scheme 1. Different Approaches to Optical Molecular Probes for Detecting Metal Ions
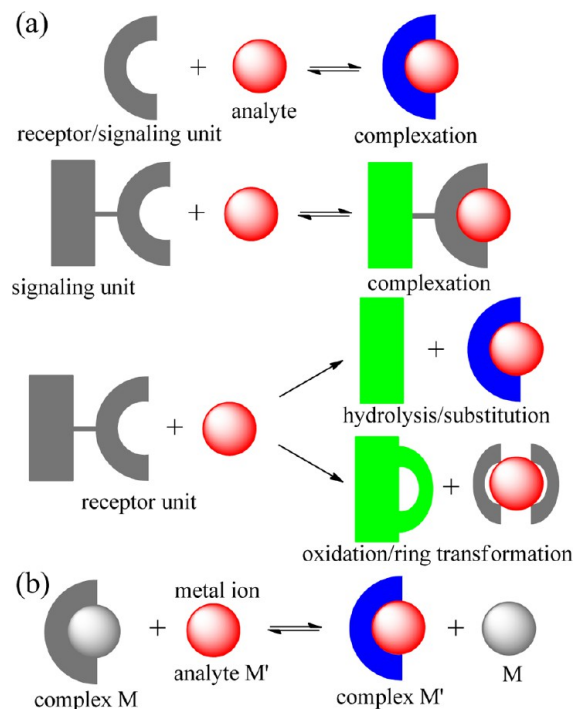
Cu^{2+},[6d,h] $Zn(II)/Cd^{2+}$,[6e] $Cd(II)/Zn^{2+}$,[6f,k] $Mn(II)/Zn^{2+}$,[6g] Cu-(II)/Zn²⁺,[6i] Cu(II)/Cr³⁺,[6j] and Zn(II)/Al³⁺ [6l] sensing systems have been demonstrated. Unlike most of the well-developed
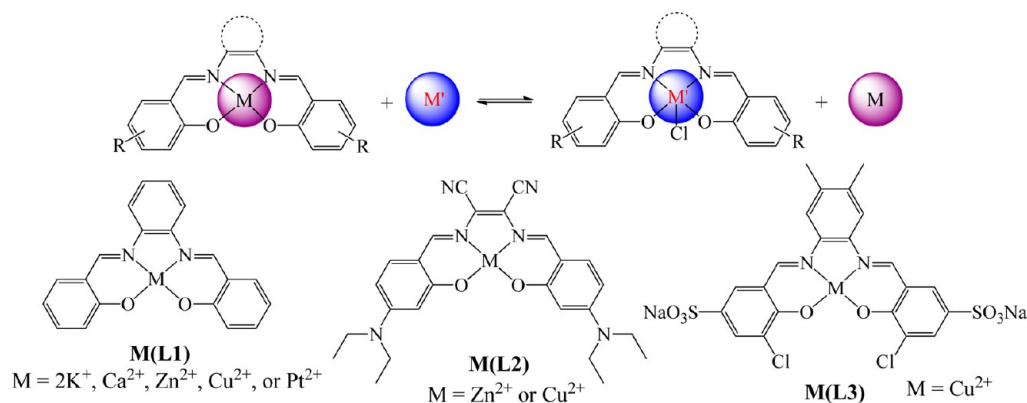
Scheme 2. Present Approach for Detecting Al^{3+} and Chemical Structures of the Salen Complexes Used in This Work

Table 1. Photophysical Data for the Salen Ligands and Complexes at Room Temperature

	medium	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm	Φ_F
L2	MeCN	374 (1.12×10^4); 433 (1.01×10^4); 564 (4.63×10^4)	606	0.80
L3	H$_2$O	318 (1.20×10^4); 377 (7.81×10^3)	436	0.45
L1	MeCN	335 (1.06×10^4); 414 (1.69×10^3)	458	0.21
Cu(L2)	MeCN	381 (1.48×10^4); 434 (7.53×10^3); 571 (1.73×10^4)	$-^a$	–
Zn(L2)	MeCN	381 (1.97×10^4); 431 (9.36×10^3); 579 (2.66×10^4)	613	0.67
Al(L1)	MeCN	315 (7.45×10^4); 330 (7.34×10^4)	455	0.63
Cu(L1)	MeCN	305 (2.34×10^4); 419 (1.75×10^4)	–	–
Zn(L1)	MeCN	292 (2.08×10^4); 395 (1.71×10^4)	497	0.42
Pt(L1)	MeCN	357 (3.25×10^3); 373 (3.50×10^4); 452 (8.73×10^3); 521 (8.66×10^3)	604	0.23
Ca(L1)	MeCN	330 (1.96×10^4); 365 (1.13×10^4)	485	0.068
K(L1)	MeCN	335 (2.17×10^4); 355 (1.40×10^4)	501	0.073
Cu(L3)	H$_2$O	304 (9.64×10^3); 349 (1.27×10^4)	–	–

^{a}Nonemissive.

sensing systems operating via direct metal−ligand interactions between the receptor/ligand and the metal ion of interest, sensing via transmetalation reactions might provide a distinct improvement in selectivity due to the shielding function of the filled-in metal ion.[6j] Furthermore, with the same ligand, complexes containing different central metal ions theoretically may exhibit different sensing performances, which provides another way to design chemosensors. Nevertheless, in the literature there is still a scarcity of reports on systematic studies of the effects of the chemical structure of the ligand and the identity of the central metal ion on the sensing performance via transmetalation reactions, and most of sensing systems based on transmetalation reactions show emission quenching, which is not very efficient because signal quenching is not as sensitive as signal enhancement.

N,N'-Bis(salicylidene)ethylenediamine (salen) ligands, a particular class of tetradentate [O^N^N^O] chelating bis-Schiff base ligands containing two covalent and two coordinate-covalent sites in a planar array (Scheme 2), can coordinate to many metal ions. Because of their easy preparation, reasonable stabilities, biological activities, and rich photophysical properties, salen ligands and their associated metal complexes have attracted much attention in many fields, including catalysts,[7] DNA cleavage,[8] optical materials,[9] magnetic materials,[9c,10] supramolecular materials,[11] cell imaging,[12] and organic light-emitting diodes.[13] Moreover, salen ligands usually containing a π-conjugated tetradentate chelating system can coordinate to various metal ions, resulting in changes in the optical properties that can report on the interaction between the ligands and metal ions, and thus, they are widely used as optical probes for

many metal ions, such as Zn^{2+},[14] Mg^{2+},[15] Cu^{2+},[14c,16] Al^{3+},[16c,17] La^{3+},[18] and Pt^{2+}.[19b] Optical probes for F$^-$ [20] and pH[16d] based on salen ligands have also been demonstrated. In the past few years, advanced synthetic methodology for Ca(II), Ba(II), Sr(II), Ni(II), Pd(II), Mn(II), and Ln(III) salen complexes by means of transmetalation reactions of Zn(II) salen complexes has been developed.[2b,d−i] The origin of this reactivity is found in the fact that the Zn(II) salen unit is kinetically labile, making it an excellent starting point for the introduction of various other metal ions by means of transmetalation.[2g]

Our previous work focused on the synthesis and photophysical properties of salen ligands for sensing applications.[16b−d,19b] For the purpose of detecting metal ions, however, the biggest challenge is the selectivity of salen ligands because they can act as tetradentate chelating agents to coordinate with many metal ions and form stable complexes. As examples, Zn^{2+}, Mg^{2+}, and Al^{3+} might lead to enhanced fluorescence of salen ligands, but Cu^{2+}, Ni^{2+}, Co^{2+}, and Pd^{2+} might quench the fluorescence. In order to solve the problem of selectivity, in the present work we systematically prepared and studied a series of K(I), Ca(II), Zn(II), Cu(II), and Pt(II) salen complexes (Scheme 2) for detecting Al^{3+} by emission enhancement via transmetalation reactions in an organic solvent (MeCN) or pure water. For these salen complexes, both the chemical structure of the salen ligand and the identity of the central metal ion have a strong impact on the sensing performance. Moreover, the sensitivity of complex-based chemosensors is much better than that of the corresponding free ligands.
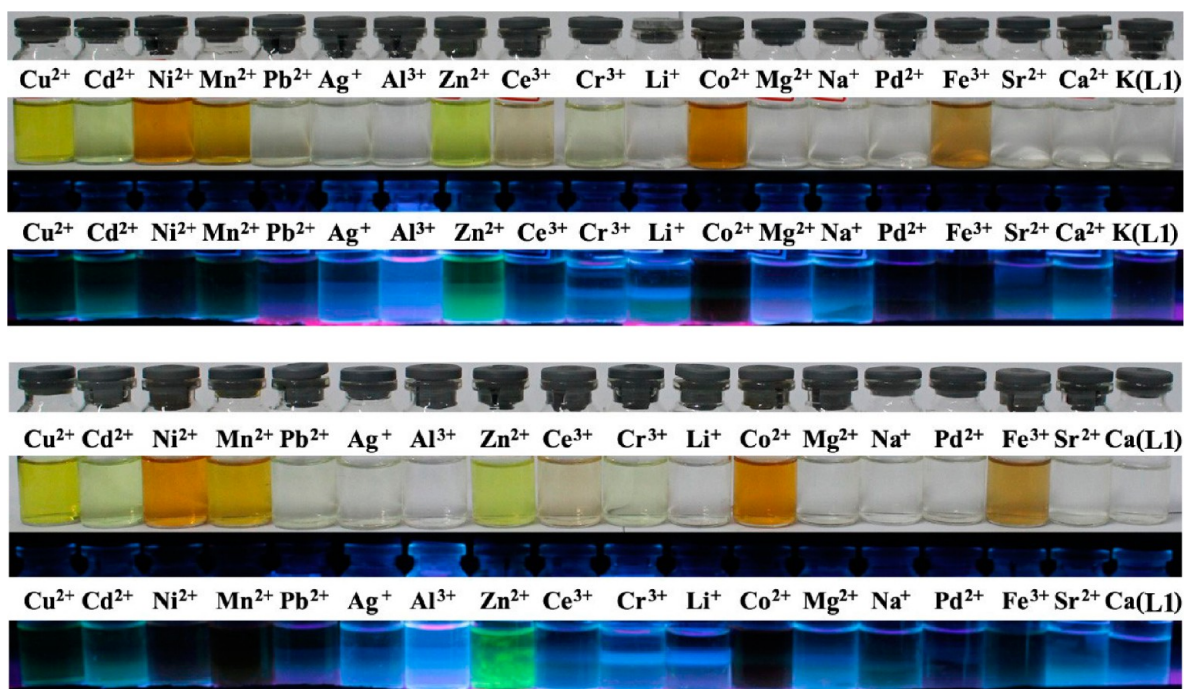
Figure 1. Photographs [(top) under sunlight; (bottom) under 360 nm UV light] of **K(L1)** and **Ca(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN) upon the addition of 2 equiv of different metal ions.

■ RESULTS AND DISCUSSION

Synthesis and Features of the Ligands and Complexes. Compared with other well-known robust tetradentate porphyrin ligands and complexes,[21] salen ligands and complexes exhibit reasonable stabilities, and thus, they might be more suitable for sensing applications via transmetalation reactions. In order to investigate the effects of the structure of the salen ligand on the sensing performance, three types of salen ligands, *N,N'*-bis(salicylidene)-1,2-phenylenediamine (**L1**), *N,N'*-bis(4-diethylamino-2-hydroxybenzylidene)-1,2-dicyano-1,2-ethenediamine (**L2**), and *N,N'*-bis(3-chloro-5-sulfonatosalicylidene)-4,5-dimethyl-1,2-phenylenediamine disodium salt (**L3**) (Scheme 2), were prepared according to our previous reports.[16b−d,19b] The UV/vis absorption and emission spectral data for all of the salen ligands are listed in Table 1, and the spectra are shown in Figure S1 in the Supporting Information. **L1** and **L3** containing similar π-conjugated 1,2-phenylenediamine bridges had relatively intense absorption bands centered at 320−350 nm, which are assigned to the π → π* transition involving molecular orbitals essentially localized on the C=N group and the benzene ring. The lower-intensity absorption bands in the 380−420 nm region are assigned to the n → π* transition involving molecular orbitals of the C=N chromophore and the benzene ring.[16b,c] Moreover, **L1** (λ_{em} = 458 nm) and **L3** (λ_{em} = 436 nm) emitted a broad blue fluorescence band, mostly attributed to π → π* transition, with fluorescence quantum yields (Φ_F) of 0.21 (in MeCN) and 0.45 (in water), respectively. With the sulfonate groups, **L3** had good stability and solubility in water and was fully studied in our previous report.[16b] It is noteworthy that **L2** containing a donor−acceptor (D−A) system had strong absorption (λ_{abs} = 564 nm) and saturated red fluorescence (λ_{em} = 606 nm) with a high Φ_F of 0.80 in MeCN.[16c,d]

In order to investigate the effect of the central metal ion on the sensing performance, K(I), Ca(II), Zn(II), Al(III), Cu(II),

and Pt(II) salen complexes were synthesized by direct complexation between the corresponding metal ion and ligand. Moreover, **Al(L1)** could also be prepared by transmetalation reactions based on **K(L1)**, **Ca(L1)**, **Zn(L1)**, and **Cu(L1)**. The photophysical properties of these salen complexes are also listed in Table 1, and their absorption and emission spectra are shown in Figure S2 in the Supporting Information. Unlike **K(L1)** (λ_{em} = 501 nm, Φ_F = 0.073), **Ca(L1)** (λ_{em} = 485 nm, Φ_F = 0.068), **Zn(L1)** (λ_{em} = 497 nm, Φ_F = 0.42), and **Al(L1)** (λ_{em} = 455 nm, Φ_F = 0.63), which exhibit similar fluorescence spectra as the free ligand **L1**, **Pt(L1)** had a long emission decay lifetime in the microsecond time region[13k,19] and a large Stokes shift between the absorption band (λ_{abs} = 521 nm) and the emission band (λ_{em} = 604 nm). For **Pt(L1)** in degassed MeCN, Φ_F = 0.23, and the fluorescence was efficiently quenched in air-saturated MeCN (Φ_F = 0.033). All of these phenomena revealed that the nature of the emission from **Pt(L1)** is phosphorescence rather than fluorescence. **Cu(L1)** was nonemissive, since it is well-known that the paramagnetic Cu^{2+} center has a pronounced quenching effect on fluorescent ligands. Among these **L1**-based complexes, **Al(L1)** had the highest Φ_F of 0.63, which might be due to the much stronger Lewis acidic character of Al^{3+}.[22] This leads to a more ionic Al−O(salicylidene) bond and thereby reinforces the propensity for a quinoid-type resonance structure that enhances the light absorption (molar extinction coefficient ε = 7.34 × 10^4 dm^3 mol^{-1} cm^{-1} at 330 nm) and emission ability for the Al(III) complex.

Chemosensors Based on M(L1). At first, **K(L1)** (Figure 1 and Figures S3−S5 in the Supporting Information) and **Ca(L1)** (Figures 1 and 2 and Figures S6 and S7 in the Supporting Information) were used as chemosensors. These two complexes exhibited similar sensing performances, and thus **Ca(L1)** is used as an example to describe their sensing behaviors. The colorimetric analysis of **Ca(L1)** in MeCN toward various metal ions, including Na$^+$, Li$^+$, Ag$^+$, Zn^{2+}, Mg^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+},
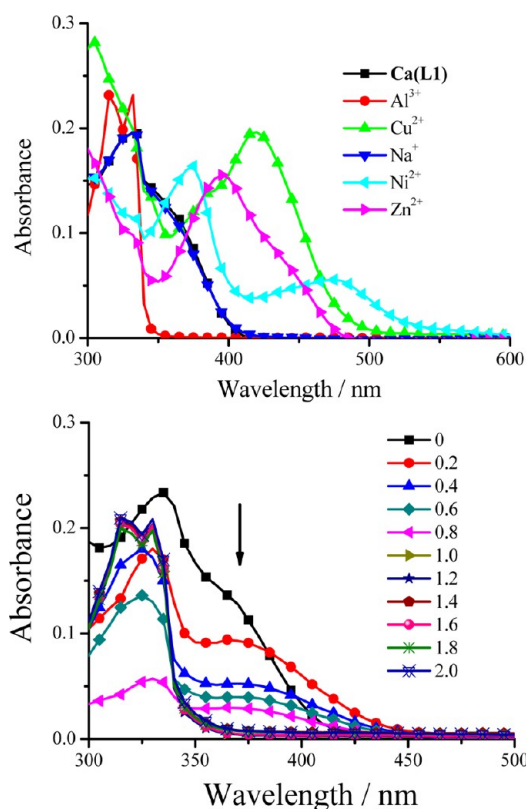
Figure 2. Absorption spectra of **Ca(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN) upon the addition of 2 equiv of different metal ions (top) and different equivalents of Al^{3+} (bottom).

Figure 3. Emission spectra of **Ca(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 320 nm) upon the addition of different equivalents of Al^{3+}.

Co^{2+}, Ni^{2+}, Cd^{2+}, Sr^{2+}, Fe^{3+}, Al^{3+}, Ce^{3+}, Cr^{3+}, and Pd^{2+}, was studied. The color changes of solutions were visualized by the naked eye (Figure 1), and the optical responses were studied by UV/vis absorption spectroscopy (Figure 2). As monitored by the naked eye, the addition of 2 equiv of some transition-metal ions, such as Cu^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, and Ni^{2+}, to the colorless solution of **Ca(L1)** led to a yellow color change, while adding some other metal ions, such as Al^{3+}, Mg^{2+}, Sr^{2+}, Na^{+}, and Li^{+}, did not show any detectable color changes. However, drastic changes were found by UV/vis absorption spectroscopy (Figure 2), indicating that Ca^{2+} in **Ca(L1)** was displaced by many other metal ions. Obviously, adding Al^{3+} resulted in no absorption at wavelengths above 350 nm. The absorption of **Ca(L1)** exhibited a gradual reduction upon the addition of 0–1.0 equiv of Al^{3+} and saturation upon the addition of 1.0–2.0 equiv of Al^{3+} (Figure 2 and Figure S6 in the Supporting Information). Good linearity was established (correlation coefficient R^2 = 0.996). Job plot studies revealed 1:1 stoichiometry for the complex **Al(L1)** formed between **L1** and Al^{3+}, which was also confirmed by the pure product of **Al(L1)** isolated from this transmetalation reaction.

The fluorescence intensity at 455 nm exhibited a gradual increase upon the addition of 0–1 equiv of Al^{3+} and saturation upon the addition of 1.0–2.0 equiv of Al^{3+} to the solution of **Ca(L1)** (Figure 3), revealing a 1:1 stoichiometry of the complex formed between **L1** and Al^{3+} ions, which is consistent with the former absorption result. Good linearity of the fluorescence intensity as a function of the Al^{3+} concentration between 0 and 1.0×10^{-5} mol dm^{-3} was established (R^2 = 0.986; Figure S7 in the Supporting Information). The limit of detection (LOD), based on the definition by IUPAC [LOD =
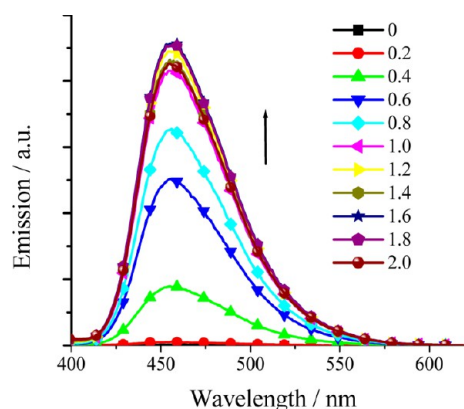
$3S_b/m$, where S_b is the standard deviation of the blank measurements and m is the sensitivity of the method (a change in the percent inhibition divided by the change in concentration near the detection limit)], was found to be 0.95 ppb from 10 blank solutions.

The selectivity behavior, that is, the relative probe response for the metal ion of interest over other metal ions present in solution, is obviously one of the most important characteristics of a probe. For **Ca(L1)**, the selectivity of fluorescence detection is better than that of colorimetric detection, as shown in Figure 4. Adding many other metal ions led to little or no enhancement of the emission intensity at 455 nm, but when Al^{3+} was added, the emission intensity at 455 nm increased about 100-fold, indicating that **Ca(L1)** has good selectivity to detect Al^{3+}. In addition, competition experiments were also performed in the presence of **Ca(L1)** and 2 equiv of Al^{3+} mixed with 2 equiv of the other metal ions to explore the practical applicability of **Ca(L1)** as an Al^{3+}-selective fluorescence chemosensor. The fluorescence intensities of solutions containing both Al^{3+} and the other metal ions showed no obvious variation compared with those containing Al^{3+} only. The combined results revealed that **Ca(L1)** can be used to detect Al^{3+} with minimum interference from other metal ions and is a good fluorescence chemosensor for detection of Al^{3+}. It should be noted that adding Zn^{2+}, Cu^{2+}, or Al^{3+} to a solution of **Ca(L1)** resulted in some obvious changes in both absorption and emission spectra. The resultant new absorption and emission spectra were similar to those of **Zn(L1)**, **Cu(L1)**, and **Al(L1)**, respectively, indicating that Ca^{2+} in **Ca(L1)** might be displaced by Zn^{2+}, Cu^{2+}, and Al^{3+}.

Unlike **K(L1)** and **Ca(L1)**, **Zn(L1)** in MeCN had much stronger absorption beyond 400 nm, resulting in a yellow color (Figure 5). Moreover, **Zn(L1)**-type complexes usually have rich photophysical properties, and thus, they have been used in sensing applications but not via transmetalation reactions.[23] Upon the addition of 2 equiv of many other metal ions to the solution of **Zn(L1)**, only Al^{3+} led to no absorption at wavelengths above 350 nm and a drastic color change from yellow to colorless (Figure S8 in the Supporting Information), indicating that **Zn(L1)** has a much better selectivity than **Ca(L1)** via colorimetric detection. The absorption of **Zn(L1)** exhibited a gradual reduction upon the addition of 0–1.0 equiv of Al^{3+} and saturation upon the addition of 1.0–2.0 equiv of Al^{3+} (Figure S9 in the Supporting Information).
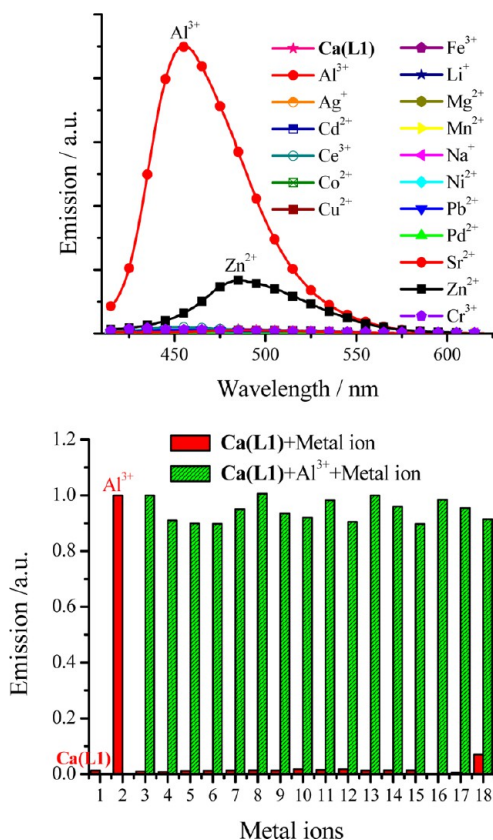
Figure 4. (top) Emission spectra of **Ca(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 320 nm) upon the addition of 2 equiv of different metal ions. (bottom) Selectivity of **Ca(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN, emission excited at 320 nm and measured at 455 nm) toward 2.0 equiv of Al^{3+} and other metal ions: 1, **Ca(L1)**; 2, Al^{3+}; 3, Ag^{+}; 4, Cd^{2+}; 5, Ce^{3+}; 6, Co^{2+}; 7, Cr^{2+}; 8, Cu^{2+}; 9, Fe^{3+}; 10, Li^{+}; 11, Mg^{2+}; 12, Mn^{2+}; 13, Na^{+}; 14, Ni^{2+}; 15, Pb^{2+}; 16, Pd^{2+}; 17, Sr^{2+}; 18, Zn^{2+}).

For fluorescence detection, **Zn(L1)** had a bit worse sensing performance than **Ca(L1)** when monitored by the naked eye, since **Zn(L1)** itself emitted much stronger green emission (Figure 5). Addition of some metal ions, such as Cu^{2+}, Ni^{2+}, and Fe^{3+}, led to efficient quenching of the emission of **Zn(L1)**, while on the other hand, addition of some other metal ions, such as Al^{3+}, Sr^{2+}, and Cr^{3+}, resulted in blue emission. This also revealed that Zn^{2+} in **Zn(L1)** was partly or fully displaced by these metal ions. When monitored by a fluorescence spectrophotometer, however, **Zn(L1)** exhibited good selectivity

to Al^{3+} similar to that of **Ca(L1)** (Figure 6 and Figure S10 in the Supporting Information). The fluorescence intensity at 455
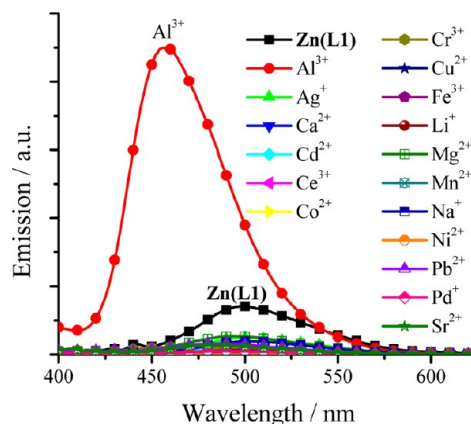

Figure 6. Emission spectra of **Zn(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 320 nm) upon the addition of 2 equiv of different metal ions.

nm exhibited a gradual increase upon the addition of 0−1 equiv of Al^{3+} and saturation upon the addition of 1.0−2.0 equiv of Al^{3+} to the solution of **Zn(L1)** (Figures S11 and S12 in the Supporting Information). Good linearity of the fluorescence intensity as a function of the Al^{3+} concentration between 0 and 1.0×10^{-5} mol dm^{-3} was established ($R^2 = 0.980$), and the LOD was 1.16 ppb.

Contrary to **K(L1)**, **Ca(L1)**, and **Zn(L1)**, **Cu(L1)** exhibited a deep-yellow color and was nonemissive in MeCN (Figure 7). Upon the addition of 2 equiv of many other metal ions to the solution of **Cu(L1)**, only Al^{3+} gave an obvious color change from deep yellow to colorless when monitored by the naked eye, indicating that **Cu(L1)** is an excellent, simple, and rapid colorimetric receptor for sensing of Al^{3+}. The absorption spectra (Figure 8) further confirmed that except for another strong Lewis acid, Fe^{3+}, the addition of many other metal ions to the solution of **Cu(L1)** had little effect on the absorption spectrum, which revealed that Cu^{2+} in **Cu(L1)** might be displaced only by Al^{3+} and Fe^{3+}. This was also verified by the emission spectra (Figure 8). When Al^{3+} was added, the emission intensity at 455 nm increased over 10000-fold, but no emission was observed upon the addition of any other metal ions, including Fe^{3+} (like Cu^{2+}, paramagnetic Fe^{3+} as the central ion has a pronounced quenching effect on fluorescent ligands). Obviously, for **Cu(L1)**, both colorimetric detection and
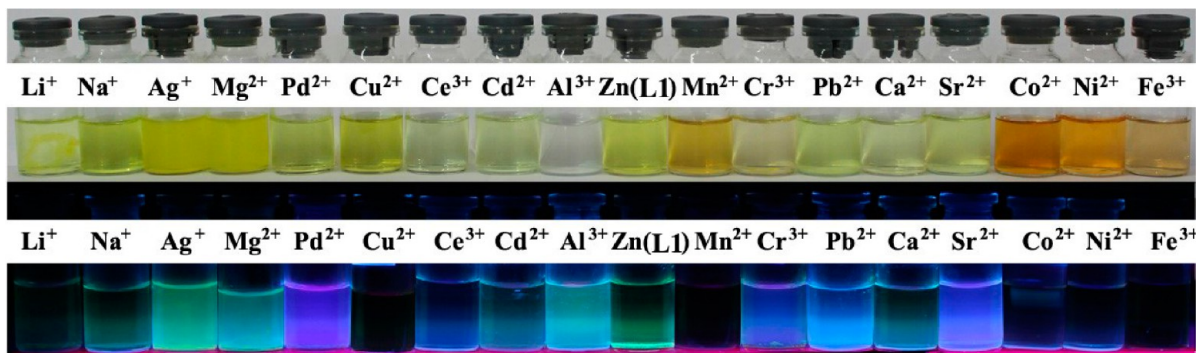

Figure 5. Photographs [(top) under sunlight; (bottom) under 360 nm UV light] of **Zn(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN) treated with 2 equiv of different metal ions.
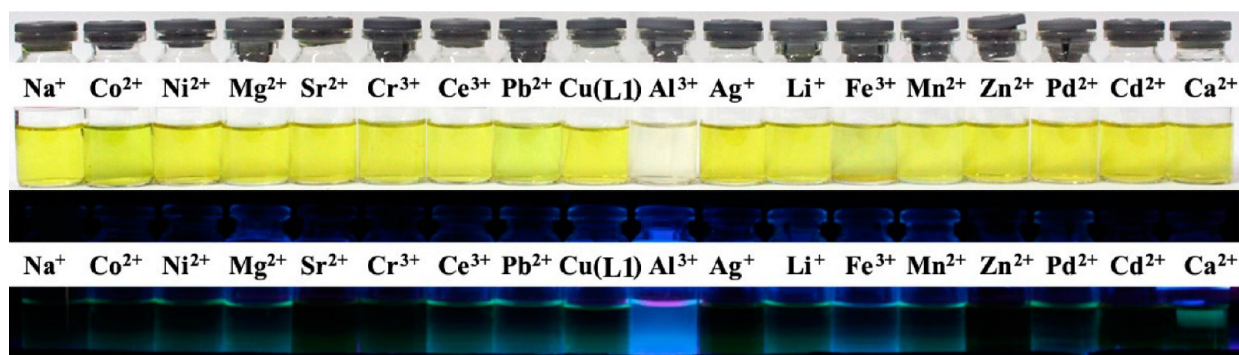
Figure 7. Photographs [(top) under sunlight; (bottom) under 360 nm UV light] of **Cu(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN) treated with 2 equiv of different metal ions.
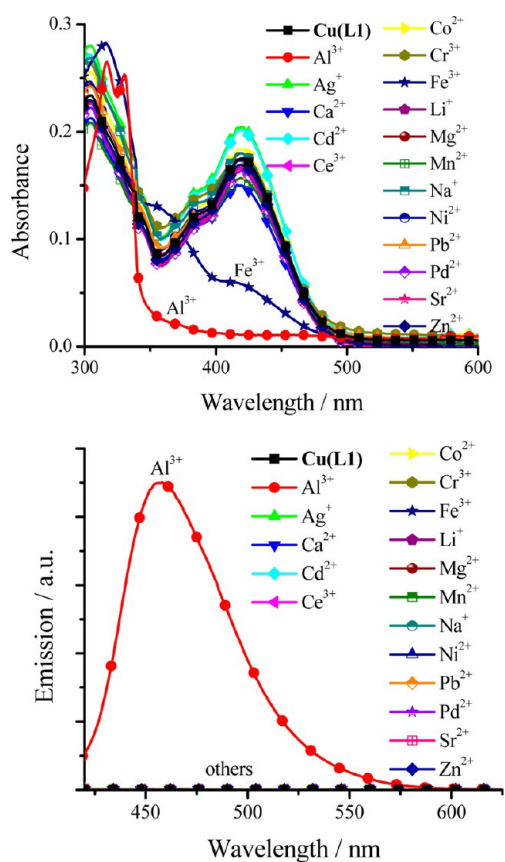

Figure 8. (top) Absorption spectra and (bottom) emission spectra (excited at 320 nm) of **Cu(L1)** (1.0×10^{-5} mol dm^{-3} in MeCN) upon the addition of 2 equiv of different metal ions.

fluorescence detection had an excellent selectivity for Al^{3+}, as shown in Figure 7. The fluorescence intensity at 455 nm exhibited a gradual increase upon the addition of 0−1 equiv of Al^{3+} and saturation upon the addition of 1.0−2.0 equiv of Al^{3+} to the solution of **Cu(L1)** (Figures S13 and S14 in the Supporting Information). Good linearity of the fluorescence intensity as a function of the Al^{3+} concentration between 0 and 1.0×10^{-5} mol dm^{-3} was established ($R^2 = 0.989$), and the LOD was 0.92 ppb. To the best of our knowledge, this LOD makes **Cu(L1)** one of the most sensitive fluorescence probes for detecting Al^{3+}, indicating that **Cu(L1)** is suitable to be used as highly sensitive Al^{3+} optical chemosensor.[24]

Among these salen complexes, only **Pt(L1)** is phosphorescent, and thus, it might be used as a phosphorescence probe.

Compared with traditional fluorescence probes, phosphorescence probes offer several important advantages, including longer lifetimes of emission, larger Stokes shifts, and richer excited states.[1c] Unexpectedly, however, upon the addition of many other metal ions to a solution of **Pt(L1)**, no transmetalation reaction was observed (Figures S15 and S16 in the Supporting Information) in 2 h at room temperature. It is interesting that complexation between Pt^{2+} and salen ligands is usually difficult because of the lack of suitable Pt(II) precursors, and thus, long reaction times and heating are needed. However, once the Pt(II) salen complexes with square-planar geometry are formed, the tetradentate character of the salen ligands provides high stability of the Pt(II) salen complexes.[8b,13c,k]

Chemosensors Based on M(L2). Unlike **L1**, **L2** containing a D−π−A−π−D system has strong absorption at $\lambda_{abs} = 564$ nm and saturated red fluorescence at $\lambda_{em} = 606$ nm with a high fluorescence quantum yield of up to 0.80 in MeCN. This is advantageous for rapid ratiometric detection by the naked eye and for bioapplications because there is no need for a high-energy excitation wavelength in the UV, blue, or green region and less absorption and autofluorescence from proteins. A recent example revealed that the phosphorescence ($\lambda_{em} = 764$ nm and $\Phi_P = 0.095$) of the complex of Pt(II) with **L2** can be red-shifted into the near-infrared region.[25] As expected, **Zn(L2)** itself exhibited a deep-purple color, but adding 2 equiv of many other metal ions to the solution of **Zn(L2)** led to color changes (Figure 9). For example, the color of the solution changed to bright red and blue after the addition of Al^{3+} and Co^{2+}, respectively. However, the absorption spectra (Figure S17 in the Supporting Information) revealed that **Zn(L2)** has poor selectivity and sensitivity to Al^{3+} because the **L2** ligand of **Zn(L2)** has a stronger absorption in the visible region than **L1**, with the result that different central metal ions have little effect on the absorption of **L2**-based complexes.

Contrary to **Zn(L2)**, **Cu(L2)** is nonemissive in MeCN. Upon the addition of 2 equiv of many other metal ions, even Al^{3+}, to a solution of **Cu(L2)**, the color showed little change (Figure 9 and Figure S19 in the Supporting Information). However, when monitored by a fluorescence spectrophotometer, only Al^{3+} led to strong red emission, as shown in Figures 9 and 10, indicating that **Cu(L2)** might potentially be used as a fluorescence probe for detection of Al^{3+}.

Chemosensor Based on M(L3). For metal ion probes, the preferred working conditions are aqueous media, and thus, water-soluble sulfonato salen ligand **L3** and complex **Cu(L3)** were prepared for sensing applications. Our recent work has
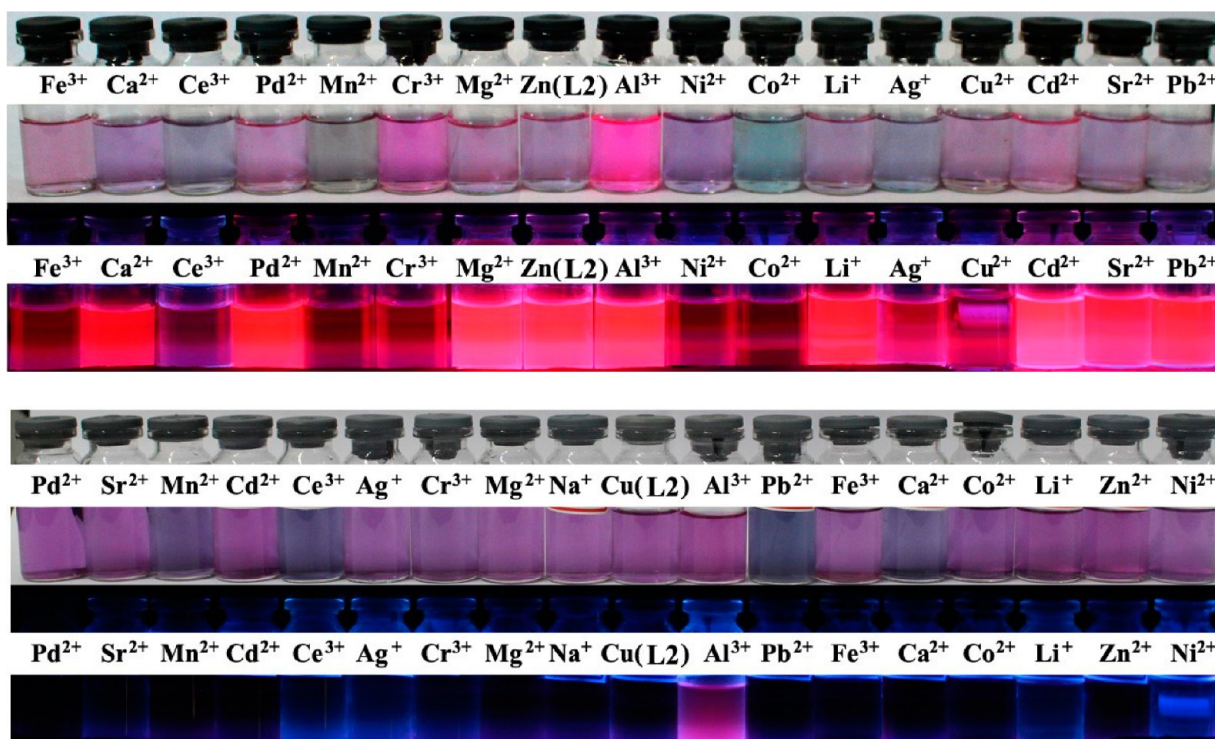
Figure 9. Photographs [(top) under sunlight; (bottom) under 360 nm UV light] of **Zn(L2)** and **Cu(L2)** (1.0×10^{-5} mol dm^{-3} in MeCN) treated with 2 equiv of different metal ions.
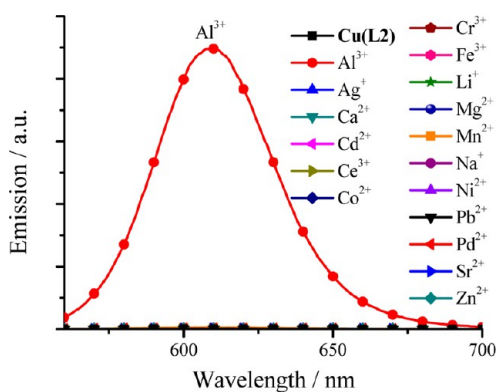

Figure 10. Emission spectra of **Cu(L2)** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 540 nm) upon the addition of 2 equiv of different metal ions.
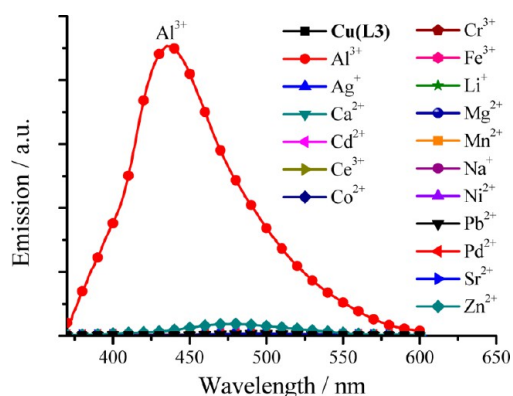

Figure 11. Emission spectra of **Cu(L3)** (1.0×10^{-5} mol dm^{-3} in H$_2$O, excited at 350 nm) upon the addition of 2 equiv of different metal ions.

demonstrated that sulfonate groups on salen ligands can ensure good stability and solubility in water without affecting their excited-state properties.[16b] As expected, like **Cu(L1)**, **Cu(L3)** exhibited good performance for sensing of Al^{3+} in aqueous media (Figure 11 and Figure S20 in the Supporting Information).

Possible Sensing Mechanism. The selectivities of the salen complexes are much better than those of the free salen ligands (Figure S21 in the Supporting Information) because free salen ligands acting as tetradentate chelating agents can coordinate with many metal ions to form stable complexes.[16b−d,19] It is our hypothesis that the fluorescence enhancement of **M(L1)**, **M(L2)**, and **M(L3)** (M = K$^+$, Ca^{2+}, Zn^{2+}, Cu^{2+}) in the presence of Al^{3+} is due to the displacement of M by Al^{3+}. In theory, the stability constants for complex formation (*K*) play a key role in determining the direction and yield of the transmetalation reaction. The stability constants of **K(L1)**,

Ca(L1), **Zn(L1)**, **Cu(L1)**, and **Al(L1)** were found to be 6.4×10^4, 9.5×10^4, 6.5×10^5, 8.1×10^6, and 1.9×10^8 dm^3 mol^{-1}, respectively. These values were obtained by fitting the absorbance versus metal ion molar ratio data to a 1:1 [2:1 for **K(L1)**] binding model using a nonlinear least-squares curve-fitting program (Figures S22−S26 in the Supporting Information). The values of the stability constants increase in the order $K_{K(L1)} \approx K_{Ca(L1)} < K_{Zn(L1)} < K_{Cu(L1)} < K_{Al(L1)}$, which is roughly consistent with the Irving−Williams stability series[26] and the experimental results discussed above. This was also confirmed by the reaction times. At room temperature, Al^{3+} needed less than half an hour to replace K$^+$ and Ca^{2+} in **K(L1)** and **Ca(L1)**, respectively, but about 1 and 2 h were required for **Zn(L1)** and **Cu(L1)**, respectively. Moreover, the absorption and emission spectra of **Al(L1)** remained unchanged upon the addition of many other metal ions (Figures S27 and S28,

respectively, in the Supporting Information), which matched well with the interference experiments (Figure 4 and Figure S10 in the Supporting Information) and indicated that **Al(L1)** has the highest stability constant and subsequently the lowest interference from other metal ions.

Influence of the Anion. It is well-known that the counteranion plays an important role in the preparation of organometallic complexes and in metal-catalyzed reactions. Of course, the counteranion also has a strong effect on the sensing performance, especially for Al(III) complexes, since the Al(III) probably coordinates with the counteranion. We used three Al(III) salts, including $AlCl_3$, $Al_2(SO_4)_3$, and $Al(NO_3)_3$, to examine the effect of the counteranion on the sensing performance of **Cu(L1)**. At room temperature in MeCN, it took about 2 and 8 h to complete the transmetalation reactions for $AlCl_3$ and $Al_2(SO_4)_3$, respectively, but for $Al(NO_3)_3$, no such blue emission was observed even after 1 day. Thus, $AlCl_3$ was used in the sensing applications.

CONCLUSIONS

We have systematically synthesized and studied the photophysical properties and sensing applications of a series of complexes of salen-type Schiff base ligands with K(I), Ca(II), Zn(II), Cu(II), and Pt(II). Most of these complexes have good sensitivity and selectivity for detecting Al^{3+} via transmetalation reactions in MeCN and water, and thus, they can potentially be used as simple and rapid colorimetric and turn-on fluorescence chemosensors for Al^{3+}. Both the chemical structure of the salen ligand and the identity of the central metal ion have a tremendous impact on the sensing performance. Since the values of the stability constants increase in the order $K_{K(L1)} \approx K_{Ca(L1)} < K_{Zn(L1)} < K_{Cu(L1)} < K_{Al(L1)}$ and also since **Cu(L1)** and **Al(L1)** are nonemissive and highly emissive, respectively, **Cu(L1)** exhibits the best sensing performance for detecting Al^{3+}. Moreover, the selectivities of the salen complexes are much better than those of the corresponding free salen ligands because of the shielding function of the filled-in metal ion. We believe that this novel kind of complex-based probe based on transmetalation reactions will provide a new paradigm in the design of optical probes.

EXPERIMENTAL SECTION

Materials and Instrumentation. All reagents were purchased from commercial suppliers and used without further purification. UV/vis absorption spectra were recorded using a UV 765 spectrophotometer with quartz cuvettes of 1 cm path length. Fluorescence spectra were obtained using an F-7000 Fluorescence spectrophotometer (Hitachi) at room temperature. The slit width was 5.0 nm for both excitation and emission. The photon multiplier voltage was 400 V. All the salen ligands were prepared according to our previous reports.[16b−d,19b] K(L1),[27] Ca(L1),[28] Zn(L1),[13d] Cu(L1),[29] Al(L1),[30] Pt(L1),[13c,k] Zn(L2), Cu(L2),[31] and Cu(L3)[32] were synthesized according to the previous reported methods.

Measurements of the Fluorescence Quantum Yield (Φ_F). Φ_F was measured by the optical dilute method with a standard of quinine sulfate ($\Phi_r = 0.55$ for quinine in 0.05 mol dm^{-3} sulfuric acid). The values were calculated as $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, where the subscripts s and r refer to the sample and the reference standard solution, respectively, n is the refractive index of the solvent, D is the integrated intensity, and B is the excitation intensity. Values of B were calculated as $B = 1 − 10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length ($L = 1$ cm in all cases). The refractive indices of the solvents at room temperature were taken from standard sources. Errors for the Φ_F values ($\pm10\%$) were estimated.

Measurements of Metal Ion Sensing. Metal ion titration experiments were started with 6 mL of a solution of the salen complex of known concentration (1.0×10^{-5} mol dm^{-3} in MeCN or water). For the titration, a 1.0×10^{-2} mol dm^{-3} solution of the metal nitrate salt (or $AlCl_3$ for Al^{3+}) in H_2O was added by a microsyringe. For the water reactions and sensing applications, the pH was about 6−7. For the competition experiments, Al^{3+} and one other metal ion were added to the solution simultaneously. All types of absorption and fluorescence measurements were monitored at least 2 h after the addition of the metal salt to the salen complex solution at room temperature.

Synthesis of Zn(L1). A mixture of **L1** (316 mg, 1 mmol) and zinc acetate (263 mg, 1.2 mmol) in 40 mL of ethanol was refluxed at 78 °C for 3 h. After the reaction was complete, the product was collected by filtration as a yellow solid (84% yield) after the mixture was cooled to room temperature. ^{1}H NMR (DMSO-d_6): δ 9.02 (s, 2H); 7.91 (m, 2H); 7.41 (m, 4H); 7.24 (m, 2H); 6.71 (d, 2H); 6.52 (t, 2H). MS (FAB): m/z 379.0. Anal. Calcd (Found): C, 63.26 (63.11); H, 3.72 (3.73); N, 7.38 (7.36).

Synthesis of Cu(L1). Salicylaldehyde (1.1 mL, 10 mmol) was added to 25 mL of an ethanol solution of o-phenylenediamine (540 mg, 5 mmol) with stirring. To the resulting mixture, an ethanolic solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (1.00 g, 5 mmol) was added dropwise. This was stirred continuously for 3 h. Gradually, the color of the solution changed to deep blue. A yellowish-brown compound precipitated out and was filtered off (90% yield). Because of its highly insoluble nature, no single crystals suitable for X-ray diffraction were obtained. Anal. Calcd (Found): C, 63.57 (63.38); N, 7.41 (7.38); H, 3.73 (3.72). MS (ESI): m/z 395.9 (M + H)$^+$.

Synthesis of K(L1). A mixture of **L1** (316 mg, 1 mmol) and potassium acetate (216 mg, 2.2 mmol) in 25 mL of ethanol was refluxed at 78 °C for 1 h. After the reaction was complete, the product was collected by filtration as an orange solid (86% yield) after the mixture cooled to room temperature. ^{1}H NMR (DMSO-d_6): δ 8.92 (s, 2H); 7.87 (m, 2H); 7.41 (m, 4H); 7.28 (m, 2H); 6.79 (d, 2H); 6.42 (t, 2H). Anal. Calcd (Found): C, 61.20 (61.19); N, 7.14 (7.12); H, 3.59 (3.58).

Synthesis of Al(L1). A mixture of **L1** (316 mg, 1 mmol) and aluminum chloride (133 mg, 1 mmol) in 100 mL of CH_3CN was refluxed at 78 °C for 12 h. After the reaction was complete, an impurity was filtered off, and the precipitate was washed with water and CH_3CN, dried, and recrystallized with CH_3CN (80% yield). ^{1}H NMR (DMSO-d_6): δ 8.81 (s, 2H); 8.41 (m, 2H); 7.31 (m, 4H); 7.27 (m, 2H); 6.81 (d, 2H); 6.62 (t, 2H). Anal. Calcd (Found) for $C_{20}H_{14}AlClN_2O_2 \cdot 2H_2O$: C, 58.19 (58.11); N, 6.79 (6.81); H, 4.40 (4.41).

Synthesis of Zn(L2). A mixture of 4-(diethylamino)salicylaldehyde (386 mg, 2 mmol) and diaminomalonitrile (108 mg, 1 mmol) in 50 mL of hot absolute ethanol was added to $Zn(CH_3COO)_2 \cdot 2H_2O$ (219 mg, 1 mmol) in 150 mL of hot absolute ethanol, and the resulting mixture was stirred for 2 days at 70 °C. The resulting red mixture was filtered hot and cooled in a freezer, which led to the appearance of dark-blue crystals (78% yield). Anal. Calcd (Found): C, 59.21 (59.37); H, 6.03 (6.01); N, 14.80 (14.76). ^{1}H NMR (in CDCl$_3$): δ 1.14 (t, 12H); 3.26 (q, 8H); 5.61 (s, 2H); 5.99 (d, 2H); 6.80 (d, 2H); 8.04 (s, 2H).

Synthesis of Cu(L2). A mixture of 4-(diethylamino)salicylaldehyde (386 mg, 2 mmol) and diaminomalonitrile (108 mg, 1 mmol) in 50 mL of hot absolute ethanol was added to $Cu(CH_3COO)_2 \cdot H_2O$ (200 mg, 1 mmol) in 100 mL of hot absolute ethanol at 70 °C. Golden-yellow crystals were kept growing for a few days, filtered, and washed with ethanol (65% yield). Anal. Calcd (Found): C, 60.04 (59.88); H, 5.43 (5.42); N, 16.16 (16.11).

Transmetalation Reaction. A 100 mL CH_3CN solution of **Cu(L1)** (316 mg, 1 mmol) was added to a round-bottom flask, and then 10 mL of an aqueous solution containing aluminum chloride (133 mg, 1 mmol) was added dropwise to the solution of **Cu(L1)**. The mixture solution was stirred for 3 h at 78 °C. After the reaction was complete, an impurity was filtered off, and the precipitate **Al(L1)** was washed with water and CH_3CN, dried, and recrystallized with CH_3CN

(78% yield). ^{1}H NMR (DMSO-d_6): δ 8.81 (s, 2H); 8.41 (m, 2H); 7.31 (m, 4H); 7.27 (m, 2H); 6.81 (d, 2H); 6.62 (t, 2H). Anal. Calcd (Found) for $C_{20}H_{14}AlClN_2O_2·2H_2O$: C, 58.19 (58.11); N, 6.79 (6.82); H, 4.40 (4.41).

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Absorption and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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