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View Article Online DOI: 10.1039/C7NJ01186E

Highly sensitive and selective fluorescent sensor for copper(II) based on salicylaldehyde Schiff-base derivatives with aggregation induced emission and mechanoluminescence

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Keywords:

Salicylaldehyde Schiff-base, Aggregation induced emission, Cu2+ detection, Mechanofluorochromism

Abstract

Three new Schiff-base derivatives with aggregation-induced emission (AIE) characteristics have been designed and successfully synthesized. Their photophysical properties in solution, aqueous suspension and solid states were investigated systematically. Three compounds showed obvious ${}^{1}\pi$ - π * transition mixed with intramolecular charge transfer (ICT) properties in UV-vis spectra, which were evidenced by spectral analysis and theoretical calculations. The compounds exhibited evident AIE characteristic with relatively high fluorescence quantum yield in the solid state ($\Phi_{\rm F}$ =15%-21%). Moreover, the morphologies and sizes of particles in water/CH₃CN solutions were studied using a transmission scanning electron microscope (TEM) and dynamic light scattering (DLS). The crystallographic data for A3 suggests that the existence of intramolecular hydrogen bonding interactions restricted intramolecular rotation. Interestingly, A3 showed fluorescence turn-on sensing towards Cu²⁺ via chelation enhanced fluorescence in a CH₃CN-H₂O (4 : 1, v/v) solution. It has fast response time and a linear range of 0-20 μ M for Cu²⁺ ions with a detection limit of 2.3 ×10⁻⁷ mol L⁻¹. In addition, A3 also exhibits a piezofluorochromic response.

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1. Introduction

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Copper ions, the third most abundant metal ions, play significant roles in various biological processes, and their homeostasis are critical for the metabolism and development of living organisms.¹ However, unregulated concentration of Cu²⁺ ions will cause critical health and ecological issues.²⁻³ For example, excess intake of Cu²⁺ ions can lead to serious diseases including Alzheimer's, Parkinson's, Menke's and Wilson's diseases.⁴⁻⁵ On the other hand, deficiency of copper causes growth failure and deterioration of the nervous system.⁶ Copper is also a significant metal pollutant due to its widespread use in life science, medicine, chemistry and biotechnology. Therefore, the determination of copper ions in various samples has been an important topic in the area of environmental protection and healthy life.

Compared with other techniques, the fluorescent chemosensors have attracted great attention due to their great advantages including the high selectivity, sensitivity, specificity, low detection limit and real-time monitoring with fast response.⁷⁻⁸ Up to now, many fluorescent probes for Cu²⁺ have been reported and even extended to applications in biological and environmental fields.⁹⁻²⁰ Nevertheless, some fluorescent molecules have a tendency towards aggregation and become weakly or even non emissive. Such notorious phenomenon is called "aggregation-caused quenching" (ACQ), which greatly limits the applications as efficient fluorescent chemosensors. Aggregation-induced emission (AIE) materials that can solve the problem of ACQ have been paid great attention since their discovery in 2001. The AIE-active materials offer a unique platform for scientists to construct fluorescent sensors. To date, a large variety of AIE-active fluorescent sensors have been developed and utilized as biosensors.²¹⁻²³

It is well known that Schiff-base has advantages of relatively simple synthetic procedures and easily coordinating with metal ions.²⁴⁻²⁵ Moreover, a number of fluorescence sensors based on Schiff-base derivatives bearing AIE/AIEE behavior have been reported.²⁶⁻²⁹ Recently, a few AIE Schiff-base derivatives were used as fluorescent sensors for Cu²⁺ ions.³⁰⁻³³ Herein, we synthesized three new Schiff-base derivatives modified by different electron-donating and electron-withdrawing group (A1 to A3), such as carbazole, fluoren and naphthalimide, which were adopted as terminal substituents. In addition, the molecules are large conjugated systems with twisted skeleton conformations that may show good AIE performance. Their spectroscopic properties in solution, AIE behavior and the utility as

fluorescent sensor for Cu^{2+} were investigated. The results display that all compounds exhibit remarkable AIE property with yellow to red fluorescence emission and **A3** was proved to be a Cu^{2+} fluorescent sensor, whereas **A1** and **A2** showed inferior selectivity to Cu^{2+} . **A3** showed fast response of fluorescence sensing towards Cu^{2+} in a CH₃CN-H₂O (4 : 1, v/v) solution. It has a linear range of 0-20 μ M for Cu^{2+} ions with a detection limit of 2.3 ×10⁻⁷ mol L⁻¹. In addition, **A3** also exhibited an obvious piezofluorochromic response. Such mechanochromism was reversible upon the treatment of grinding and fuming with CH₂Cl₂. The powder XRD studies showed that the mechanofluorochromic nature is generated through crystalline-amorphous phase transformation under the stimulus of external force.

2. Experimental

2.1 Reagents

All solvents and reagents for synthesis were purchased from Aldrich and Energy Chemical Regent Co. Ltd. Unless otherwise noted, all materials used in this work were commercially available without any further purification. HPLC grade absolute acetonitrile and distilled deionized water were used throughout the experiment. Silica gel (200–300 mesh) used for chromatography was purchased from Sinopharm Chemical Reagent Co. Ltd. TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm and 365 nm. Stock solutions of **A1-A3** (5.0×10⁻⁴ M) were prepared in spectroscopy grade acetonitrile. Stock solutions (0.01 M) were prepared by FeCl₃·6H₂O, AlCl₃·6H₂O, CoCl₂·2H₂O, Pb(NO₃)₂, CuSO₄·5H₂O, NiSO₄·6H₂O, CdCl₂, AgNO₃, MnCl₂·4H₂O, Zn(NO₃)₂·6H₂O, BaCl₂·2H₂O and CrCl₃·6H₂O in deionized water.

2.2 Synthesis and Characterization

All of the target compounds were characterized by proton and carbon nuclear magnetic resonance spectroscopy (¹H NMR, ¹³C NMR) and matrix-assisted laser desorption/ ionization time of flight mass spectrometry (MALDI-TOF). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were collected using CDCl₃ as the solvent. ¹H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s=singlet, d=doublet, t=triplet, m=multiplet). ¹³C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. Mass spectra were obtained on an autoflex speed MALDI-TOF mass spectrometer. UV-Vis spectra were obtained on U-3310 UV spectrophotometer. Fluorescence spectra

were recorded on a Hitachi-F-4500 fluorescence spectrophotometer. Dynamic light scattering (DLS) experiments were conducted using a NanoPlus-3 dynamic light scattering particle size analyzer. Transmission electron microscopy (TEM) data were obtained on a FEI Tecnai G2 S-Twin. Single crystal X-ray diffraction analyses were carried out on a Rigaku Saturn 724 CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature.

2.3. General synthetic procedure

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Scheme 1. Synthetic route to compounds A1-A3.

General synthetic procedure of compounds A1-A3 is as follows. 1 mmol 4-N,Ndimethylaminoaniline and 1 mmol corresponding salicylaldehyde derivatives (Fig. S1-S3) were added to 20 mL anhydrous ethanol. The mixture was stirred and heated to 80 °C for 4 h. The reaction mixture was allowed to cool to room temperature and concentrated in vacuo. The residue was purified by column chromatography with petroleum/DCM. After dried under reduced pressure, products were obtained in high yields (67-79%).

4-(9-butyl-9H-carbazol-3-yl)-2-(((4-(dimethylamino)phenyl)imino)methyl)phenol (A1). ¹H NMR (CDCl₃, 400 MHz): δ ppm 13.75 (s, 1H), 8.75 (s, 1H), 8.27 (s, 1H), 8.15 (d, J=4 Hz, 1H), 7.68 (d, J=4 Hz, 3H), 7.45 (m, 3H), 7.33 (d, J=4 Hz, 2H), 7.23 (d, J=2 Hz, 1H), 7.11 (d, J=4 Hz, 1H), 6.77 (d, J=4 Hz, 2H), 4.34 (t, J=8 Hz, 2H), 3.01(s, 6H), 1.87 (m, 2H), 1.43 (m, 2H), 0.96 (t, J=8 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ ppm 164.37, 164.17, 161.35, 165.58, 150.16, 146.21, 136.47, 133.38, 132.68, 132.54, 131.17, 130.87, 130.18, 129.36, 128.82, 127.75, 126.82, 123.02, 122.30, 121.56, 119.88, 117.55, 112.68, 40.54, 30.25, 20.42, 13.87. ESI-HRMS: m/z calc. for [C₃₁H₃₁N₃O+H]⁺: 462.25399, found 462.25351. Elemental analysis calculated for C₃₁H₃₁N₃O: C, 80.66; H, 6.77; N, 9.10;

Found: C, 80.67; H, 6.75; N, 9.07.

4-(9,9-dibutyl-9H-fluoren-2-yl)-2-(((4-(dimethylamino)phenyl)imino)methyl)phenol (**A2**). ¹H NMR (CDCl₃, 400 MHz): δ ppm 13.84 (s, 1H), 8.75 (s, 1H), 7.74 (q, J_1 =4 Hz, J_2 =2 Hz, 2H), 7.65 (d, J =2 Hz, 2H), 7.55 (d, J =4 Hz, 1H), 7.52 (s, 1H),7.30-7.36 (m, 5H), 7.11 (d, J =4 Hz, 1H), 7.11 (d, J =4 Hz, 1H), 6.77 (d, J =4 Hz, 2H), 3.02(s, 6H), 2.01 (t, J =8 Hz, 4H), 1.02-1.07 (m, 4H), 0.64-0.70 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ ppm 160.40, 160.34, 157.53, 157.17, 151.48, 150.88, 150.01, 143.39, 140.84, 140.43, 139.96, 139.31, 137.47, 137.00, 132.58, 130.90, 129.88, 126.93, 126.79, 125.37, 122.89, 122.27, 120.56, 119.87, 119.65, 117.49, 112.77, 55.08, 40.61, 40.29, 26.01, 23.10, 13.89. ESI-HRMS: m/z calc. for $[C_{36}H_{40}N_2O+H]^+$: 517.32134, found 517.32080. Elemental analysis calculated for $C_{36}H_{40}N_2O$: C, 83.68; H, 7.80; N, 5.42; Found: C, 83.65; H, 7.83; N, 5.44.

2-butyl-6-(3-(((4-(dimethylamino)phenyl)imino)methyl)-4-hydroxyphenyl)-1H-benzo[de]isoqui noline-1,3(2H)-dione (**A3**). ¹H NMR (CDCl₃, 400 MHz): δ ppm 14.10 (s, 1H), 8.70 (s, 1H), 8.64 (d, *J* =4 Hz, 2H), 8.32 (d, *J*=4 Hz, 1H), 7.72 (t, *J*=8 Hz, 2H), 7.50 (s, 1H), 7.47 (d, *J*=4 Hz, 1H), 7.18 (d, *J* =4 Hz, 1H), 6.76 (d, *J*=4 Hz, 2H), 4.22 (t, *J*=8 Hz, 2H), 3.02(s, 6H), 1.71-1.75 (m, 2H), 1.45-150 (m, 2H), 1.00 (t, *J*=8 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ ppm 159.84, 157.77, 149.96, 140.94, 139.69, 137.17, 133.18, 131.62, 131.07, 129.99, 125.78, 124.73, 122.25, 120.41, 119.92, 118.85, 118.29, 117.42, 112.80, 108.85, 42.92, 40.62, 31.19, 20.60, 13.91. ESI-HRMS: m/z calc. for [C₃₁H₂₉N₃O₃+H]⁺: 492.22817, found 492.22803. Elemental analysis calculated for C₃₁H₂₉N₃O₃: C, 75.74; H, 5.95; N, 8.55; Found: C, 75.77; H, 5.93; N, 8.52.

3. Results and discussion

3.1. Synthesis of A1-A3

The synthetic routes for Schiff-base derivatives were shown in Scheme 1. Compounds 3, 4 and 5 were synthesized according to the literatures.³⁴⁻³⁶ Firstly, compound 2 was prepared by compound 1 and bis(pinacolato)diboron in the presence of 1,1'-[bis(diphenylphosphino)]ferrocene palladium(II) dichloride and potassium acetate in anhydrous 1,4-dioxane with a yield of 82%.³⁷ Then S1-S3 were obtained *via* suzuki reaction between compounds 2 and 3(4,5) catalyzed by tetrakispalladium in relatively high yields (81% for S1, 88% for S2 and 83 % for S3). Finally, S1-S3 were allowed to react

with 4-N,N-dimethylaminoaniline in dry EtOH to give corresponding Schiff-base derivatives(A1-A3), respectively. A1-A3 are soluble in CH_2Cl_2 , $CHCl_3$, toluene and DMSO, but show poor solubility in alcohols (such as methanol and ethanol) and aliphatic hydrocarbon solvents (such as cyclohexane and n-hexane) at room temperature. All target molecules were purified by column chromatography on silica gel, and unambiguously characterized by ¹H and ¹³C NMR, MALDI-TOF mass spectrometry.

3.2. UV-vis absorption and fluorescent emission spectra in solutions

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Fig. 1 (a) UV-vis absorption spectra and (b) normalized emission spectra of A1, A2 and A3 in CH₃CN at a concentration of 1×10^{-5} M. The excitation wavelength was 397 nm for A1, 390 nm for A2, 350 nm for A3.

The UV-vis absorption and fluorescent emission spectra of A1, A2 and A3 in CH₃CN solution are presented in Fig. 1, and their optical characteristics are summarized in Table 1. In Fig. 1a, it is clear that A1 exhibited two main absorption bands located at 281 nm and 395 nm. The absorption band at 281 nm could be attributed to the 1π - π * transition of the conjugated π -system due to large molar extinction coefficients, while the absorption band at 395 nm is corresponded to the 1π - π * transition and the intramolecular charge transfer (ICT) transitions, which is in line with the salicylaldehyde derivatives reported previously.³⁸⁻⁴⁰ For A2, three absorption bands are observed around 283 nm, 318 nm and 393 nm, whose assignment is similar with A1. Only one absorption band at 390 nm for A3 could be seen, which could be attributable to 1π - π * transition mixed ICT transition and bigger molar extinction coefficients of A3 than those of A1 and A2. Furthermore, minor solvatochromic effect of the major absorption bands and positive solvatochromic effect of the low-energy bands (Fig. S4-S6) support the 1π - π * and ¹ICT assignments for these compounds. The 1π - π */¹ICT transition assignment of the lowest energy absorption band is also supported by the density functional theory (DFT) calculations, which will be discussed in the following section.

Normalized emission spectra of compounds A1, A2 and A3 in CH₃CN at a concentration of 1×10^{-5} M are illustrated in Fig. 1b. The emission properties of these compounds are influenced significantly by the different aryl substituents and excitation of three compounds at room temperature results in blue to orange luminescence. The emission of A1 and A2 bearing electron-donating components with the low quantum yields ($\Phi_{\rm F}$ =0.01 and 0.007) in CH₃CN solution is bathochromic shift compared with that of A3 containing electron-withdrawing substituent. Furthermore, the emission characteristics of compounds A1, A2 and A3 in a variety of solvents were investigated at room temperature in Fig. 2. The emission of A1 had less dependence on the solvent polarity, suggesting that weak ICT occurred. A similar outcome for compounds A2 was observed in Fig.S7. However, the fluorescence spectra of A3 displayed two emission peaks in nonpolar solvent. Long-wavelength emission was quenched with increasing the polarity of solvents, which indicates its emission state originating from ICT state, whereas the short-wavelength emission peak could be assigned as the $^1\pi$ - π * of naphthalimides group.



Fig. 2 Normalized emission spectra of A1 (a) and A3 (b) in different solvents $(1 \times 10^{-5} \text{ M})$.

Table 1. Photophysical data for A1, A2 and A3

Compd.	$\lambda (nm)^{a}$	$\varepsilon_{\rm max}(10 \ {}^{4}{\rm L} \cdot {\rm mol}^{-1} \cdot {\rm cm}^{-1})$	$\lambda_{\max}(nm)$	Φ	$E_{\rm g}/{\rm eV}$
				solution/powder	
A1	281,356,395	5.8,2.5,2.8	^a 586/ ^b 597	0.01/0.21	3.46
A2	283,318,393	3.2,3.8,2.6	^a 573/ ^b 591	0.007/0.19	3.62
A3	389	3.3	^a 439/ ^b 574	0.002/0.15	3.68



^aRecorded in 1×10⁻⁵ M CH₃CN solution at R.T. ^b Recorded powder at R.T. ^cCalculated using DFT at the B3LYP/6-31G* level.

Fig. 3 Contour plots of electron density distribution and energy values of HOMO and LUMO for A1-A3.

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To understand nature of the ground electronic state and the low-lying singlet excited electronic state, the density functional theory (DFT) calculations were carried out by Gaussian 09 program using DFT/B3LYP/6-31G* method. Fig. 3 shows the electron density distribution of the HOMO and LUMO for compounds A1, A2 and A3. The π -electrons in the LUMOs for A1, A2 and A3 are mainly localized on the N,N-dimethylaniline part, while their distributions of HOMOs are affected significantly by aryl substituents. The HOMOs are mainly distributed on the N,N-dimethylaniline part and salicylaldimine motifs for A1, and the fluorene and salicylaldimine motifs for A2, as well as the naphthalimide segment for A3. Therefore, the HOMO-LUMO transition dominantly contributing configuration to the S_1 state should be ascribed to ${}^{1}\pi$ - π^* characters with a little of ${}^{1}ICT$ feature for A1 and ${}^{1}\pi$ - π^* / ${}^{1}ICT$ characters for A2, respectively. However, the HOMO-LUMO transition of A3 should be corresponded to ¹ICT characters with some ${}^{1}\pi$ - π^{*} feature. The calculated energy values and relative energy band gaps (Eg) are presented in Fig. 3 and Table 1. The values of HOMO-LUMO gap decrease when salicylaldimine core was introduced by the carbazole or fluorene, causing a slight red shift of the ${}^{1}\pi$ - π */¹ICT band compared with that modified by the naphthalimides substituent. These results are consistent with our analysis of the low-energy absorption in the UV-vis absorption spectra. Moreover, three compounds adopt twisted spatial conformation at their optimized lowest energy states, which prevents close molecular packing in the solid state. Dihedral angles between the terminal electron-donating or withdrawing section and salicylaldimine motifs are 37.2° for A1, 36.8° for A2 and 51.9° for A3, respectively. Therefore, the introduction of different aryl substituents also influences

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molecular packing modes in the solid state and may endow them with AIE behaviors.

To further study the aggregation characteristics of compounds A1, A2 and A3, solid state fluorescence emission spectra were measured. As shown in Fig. 4, the solid fluorescence spectra of A1, A2 and A3 showed emission peaks at 597 nm, 591 nm and 575 nm, respectively. The values of quantum efficiencies (Φ_F) of the solids were determined to be 21%, 19% and 15%, respectively, which are influenced distinctly by the aryl substituents. The relative high Φ_F values make them potential candidates in OLEDs.



Fig. 4 The normalized emission spectra of A1, A2 and A3 as solid powders.

3.3. Aggregation induced emission (AIE) properties

To explore the aggregation-induced emission of A1, A2 and A3, we used anhydrous CH₃CN as good solvent and water as poor solvent, which are commonly used in the study of AIE behavior. The nano-aggregates of A1, A2 and A3 were prepared by the precipitation method, adding water to a CH₃CN solution of the three compounds. The concentration of them in aqueous CH₃CN with different CH₃CN-water ratios was kept at 1×10^{-5} M. As expected, all these compounds present the AIEE and AIE character. As example, the corresponding emission spectra and digital photo of compound A1 in CH₃CN-H₂O mixture solution with different H₂O fractions are shown in Fig. 5. A1 emitted fairly weak orange emission in pure CH₃CN peaked at 589 nm, and the Φ_f was only 0.01. It exhibited variable emission in CH₃CN-water mixture solutions with different water fractions, which directly elucidates the AIE process. When f_w was below 60%, weak orange emission was gradually quenched. However, the compound aggregated and an obvious enhancement of luminescence intensity was observed in the 70% (v/v) CH₃CN-water mixture. The PL intensity in a CH₃CN-water mixture with $f_w = 80\%$ was

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about 21-fold higher than that in pure CH₃CN solution. When f_w reached 90% in CH₃CN-water mixture systems, the PL intensity decreased slightly. The fluorescent images of the solvent mixtures present a clear view demonstrating the AIE effect in Fig. 5b. Similar trends of emission spectra for A2 and A3 in a CH₃CN-water mixture are observed (Fig. S8-S9).



Fig. 5 (a) The fluorescence spectra of A1 in CH_3CN-H_2O mixture solution with different H_2O fractions (vol., 0–90%). (b) Plot of I/I_0 vs. water content of the solvent mixture, where I_0 is the PL intensity in pure CH_3CN solution and the digital photo of A1 in CH_3CN-H_2O mixture solution under irradiation of UV lamp at 365 nm.

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Since the three compounds were hydrophobic, their nanoparticles began to aggregate as the water fraction increased. To further investigate the morphological properties of all compounds in aggregated state, transmission electron microscopy (TEM) and dynamic light scattering (DLS) were used to measure the samples (90% water and 10% CH₃CN, $c = 1.0 \times 10^{-5}$ M). As shown in Fig. 6, spherical aggregates in the CH₃CN-water mixture emerge with the increasing proportion of water for all compounds. Moreover, the average particle diameter determined by DLS data for each compound is 191 nm for A1, 204 nm for A2, 212 nm for A3, respectively. These results reveal the existence of nano-aggregates in high water content. Therefore, we deemed that the weak-emissive nature of the three compounds in CH₃CN-H₂O systems with low f_w might be ascribed to twisted intramolecular charge transfer (TICT) activity that dominates the emission intensity and quenches the light emission.^{41,42} However, the aggregation of particles restricted the intramolecular rotation (RIR) process at high f_w in CH₃CN-water, which facilitated the radiative decay and resulted in an enhanced fluorescence emission.



Fig. 6 TEM images (a-c) and particle size distributions (d-f) of A1–A3 in CH₃CN-water mixtures (1: 9, v/v) at a concentration of 1×10^{-5} M.

3.4 Crystal structure



Fig. 7 (a) Molecular structure and dihedral angle between aromatic rings of A3. (b) Crystal packing mode of A3 by weak π - π interactions.

Crystal structure is important for understanding the optoelectronic properties and molecular packing. Single crystal of compound A3 was obtained by slow evaporation from the ethanol solution at

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room temperature. The relevant crystallographic data are summarized in Table S1-S2. Compound A3 crystallizes in the triclinic system (space group P-1 (2)) and each unit cell contains two molecules. As shown in Fig. 7a, the dihedral angles between the naphthalimide ring (P1) and the middle salicylaldimine ring (P2), and the N,N-dimethylaniline ring (P3) are 58.857° (P1-P2), 3.831° (P2-P3), respectively. It is worth noting that all the atoms except hydrogen are nearly in the same plane in P2 and P3 due to intramolecular OH•••N hydrogen bond, which is consistent with the early report.²⁷ In the packing structure, the **A3** molecules are stacked in an antiparallel fashion (head to tail) through weak π - π interactions between the P1 (*ca.* 3.49 Å and 0.58 Å). The molecules after aggregation restrict the molecular rotation where the enol conformation is favorable in ground state because of intramolecular hydrogen bonding. After excitation, the enol form gets isomerized into keto form and hence results a bright emission .^{43,44} Thus, the emission enhancement of **A3** in solid state/aggregated state is ascribed by restricted intramolecular rotation (RIR). Similarly, the reason for AIE behavior of **A1** and **A2** may be identical with that of **A3**.

3.5 Recognition towards metal ions

The sensor properties of three Schiff-base derivatives for metal ions were evaluated in the CH₃CN-H₂O (4 : 1, v/v) solution. The selectivity of probes A1-A3 towards Cu²⁺ was firstly evaluated by employing the metal salts of Fe³⁺, Al³⁺, Co²⁺, Pd²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Ag⁺, Mn²⁺, Zn²⁺, Ba²⁺and Cr³⁺ through fluorescence spectra. A1 and A2 show enhanced fluorescence with numerous metal ions (Fig. S10-S11), whereas A3 is a specific sensor for Cu²⁺. As shown in Fig. 8a, the emission centered at 463 nm exhibited unconspicuous change on the addition of several kinds of metal ions except in the case of Cu²⁺. Upon the addition of 10 equiv Cu²⁺, the intensity of original emission band remarkably increased within 5 s, which resulted in a significant cyan emission under the 365 nm UV-lamp (Fig. 8c). In contrast, the other metal ions showed minor changes in fluorescence intensity when they were introduced into the solutions of probe. Subsequently, competition experiment was performed by adding 10 μ M Cu²⁺ to the solution of A3 (10 μ M) in the presence of other coexisting metal ions. As shown in Fig. 8b, the PL intensity of A3 in the presence of Cu²⁺ are almost unaffected by the addition of most frequently coexisting metal ions. Namely, the fluorescent response of A3 for Cu²⁺ could be hardly interfered by other cations.



Fig. 8 (a) Fluorescence spectra of **A3** in CH₃CN-H₂O (4 : 1, v/v) solution upon adding of 10 equiv. different metal ions. (b) The interference tests of **A3**-Cu²⁺ in CH₃CN-H₂O (4 : 1, v/v) solution. The low bars represent **A3** (1.0×10^{-5} M) with cations (1.0×10^{-5} M) with cations (1.0×10^{-5} M) except for Cu²⁺; the high bars represent **A3** (1.0×10^{-5} M) with cations (1.0×10^{-5} M) upon the subsequent addition of Cu²⁺ (1.0×10^{-5} M). (c) Image of **A3** upon adding of 10 equiv. different metal salts in water solution under excitation of UV light at 365 nm. From left to right: blank, Fe³⁺, Al³⁺, Co²⁺, Pd²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Ag⁺, Mn²⁺, Ba²⁺, Cr³⁺, Zn²⁺.

The quantitative analytical behavior of A3 in CH₃CN-H₂O (4 : 1, v/v) solution for determination of Cu²⁺ was repeated three times and averaged during titration with different concentrations of Cu²⁺ from 0 to 2.2 equivalents (Fig. 9a).⁴⁵ With the concentration of Cu²⁺ increased, the fluorescence intensity of A3 at 463 nm increased steadily. Moreover, an excellent linear relationship was observed between I₄₆₃ and the concentration of Cu²⁺ in the range of 0-20 μ M with a correlation coefficient of R² = 0.9904, which demonstrated the potential utility of A3 in the CH₃CN-H₂O (4:1, v/v) solution for quantitative determination of Cu²⁺. By plotting the PL intensity changes as a function of concentration, the detection limit of A3-Cu²⁺ based on the DL =3 σ /S (σ is the standard deviation of blank measurements, and S is the slope between the fluorescence versus Cu²⁺ concentration) (Fig. 9b), is calculated to be about 2.3 × 10⁻⁷ M, which is much lower than that recommended by WHO in drinking water (30 μ M). Furthermore, to gain an idea for the design of new Cu²⁺ chemosensors, specific features of A3 were compared with some reported Schiff-base chemosensors (Table S3). A3 exhibited appealing analytical features such as relatively wide linear range and low detection limit.



Fig. 9 (a) Fluorescence titration spectra of A3 in the presence of different concentrations of $Cu^{2+}(0-2.2 \text{ equiv.})$ in CH₃CN-H₂O (4 : 1, v/v) solution. (b) Determination of the detection limit based on PL intensity (463 nm) of A3 with Cu^{2+} .

Moreover, in order to explore the interaction and binding mechanism of A3 and Cu^{2+} , the fluorescence spectroscopy and MS spectrum were conducted. The result of the Job's plot experiment showed a 2 : 1 stoichiometry complexation between A3 and Cu^{2+} (Fig. 10a), which was further confirmed by mass spectrometry analysis. The ion mass spectrum indicated that an ion peak at m/z 1044.5134 was assignable to $[A3+Cu^{2+}+H]^+$ (Fig. 10b). Based on the above findings, we propose that the reaction mechanism in this system may proceed through the route depicted in Fig. 10c : Cu^{2+} bonding takes place with nitrogen of imine groups and oxygen of phenolic hydroxyl group.

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Fig. 10 (a) Job's plot of A3 and Cu^{2+} (464 nm). The total concentration of A3 and Cu^{2+} was 1.0×10^{-5} M. The experiments were carried out at room temperature in CH₃CN-H₂O (4 : 1, v/v) solution. (b) MS spectrum of A3 in the presence of Cu^{2+} .(c) Proposed

binding mode of A3 with Cu^{2+} .

The PL spectra of A3 were recorded in CH_3CN -buffer mixture (1:9, v/v) with different pH solution (pH=1-14) (Fig. S12). The emission spectra at lower pH (1-10) showed a very weak PL intensity, whereas PL enhancement was observed with pH>10 because the phenolic group can be deprotonated and form the phenoxide ion.

3.6 Mechanofluorochromic properties



Fig. 11 (a) Normalized fluorescent spectra of A3 in different solid-states: original, grinding and fuming ($\lambda_{ex} = 400$ nm). (b) Photo of A3 color changes after grinding and fuming stimuli under UV light at 365 nm. (c) Cycle numbers for reversible grinding-fuming. (d) Powder X-ray diffraction patterns of the corresponding samples.

The mechanochromic materials with tunable emission have attracted considerable attention due to their potential applications as sensors, security inks, optical recording and memory devices.⁴⁶⁻⁴⁸ The twisted conformations of the molecules may generate mechanofluorochromic properties for them. Therefore, we scratched three compounds with a metal spatula directly. Pristine sample of **A3** exhibited mechanochromic luminescent behavior in response to external stimuli (Fig. 11). When the sample was

ground or scratched, its yellow emission band located at 573 nm turned dramatically orange-red emission (ca. 594 nm) with the maximum emission red-shifted by *ca.* 21 nm. Furthermore, the grinding solid was exposed to CH_2Cl_2 vapor at room temperature and the fluorescence color of the grinding state was almost converted to the original color. The grinding-fuming processes can be performed reversibly many times. The red-shift observed in the ground solid powder may be attributed to conformation planarity in the molecular packing process. Grinding gave relatively large effect on the quantum yield (Φ_{PL}) at room temperature (the pristine sample: $\Phi_{PL} = 0.15$; the ground sample: $\Phi_{PL} = 0.07$), which indicates that A3 molecules may enhance the intermolecular π - π interactions.

To further study the mechanochromic and vapochromic properties of **A3** in the initial and ground states, powder X-ray diffraction (PXRD) measurements in different solid states were performed. As shown in Fig. 11d, the initial sample of **A3** exhibited several sharp and strong peaks, indicating that the packing of molecules is in a well-ordered mode. In contrast, many diffraction peaks in the ground sample weakened or disappeared, which indicates that the ordered structure has been destroyed and amorphous structure formed after grinding. Then the diffraction pattern of the fumed sample is similar to that of the initial sample in terms of the intensity and shape of diffraction peaks, which implies that molecules are repacked in the well-ordered mode. Therefore, phase transformation between crystal and amorphous states under external grinding induces a significant mechanochromic behavior.

Conclusion

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In summary, we successfully synthesized three new Schiff-base derivatives with aggregation-induced emission (AIE) characteristics. All compounds exhibited evident AIE characteristic with high fluorescence quantum yield in the solid state. The crystallographic data for A3 indicated that the existence of intramolecular hydrogen bonding interactions restricted intramolecular rotation. In a CH_3CN-H_2O (4:1, v/v) solution, A3 showed highly sensitive and selective fluorescent response for Cu^{2+} , which could be applied to various industrial and environmental monitoring fields. More importantly, A3 also exhibited reversible mechanochromic luminescence with mechanical stress-induced spectral shift of 21 nm. It has been confirmed that the transformation between the crystalline and amorphous states is responsible for the reversible mechanofluorochromic behavior upon external stimuli. The present study provides valuable information for designing materials with AIE,

View Article Online DOI: 10.1039/C7NJ01186E

Cu²⁺ sensor and mechanofluorochromic properties based on Schiff-base.

Acknowledgements

This work was supported by Research Fund for the Doctoral Program of Jinling Institute of Technology (jit-2012-27), Natural Science Foundation of Jiangsu Province (BK20130095), and the 'Qing Lan' Project Foundation of Jiangsu Province. The authors declare that we have no potential conflict of interest.

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The present study provides valuable information for designing materials with AIE, Cu^{2+} sensor and MFC properties based on Schiff-base.