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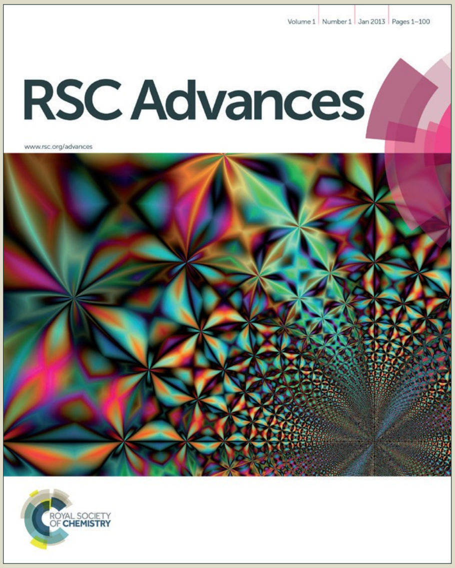

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ARTICLE

Europium (III) β-Diketone Complex as Portable Luminescent Chemosensor for Naked Eye Cu^{2+} Detection and Recyclable On–Off–On Vapor Response

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Fangyi Cao [a], Zheng Yuan [a], Junhua Liu [a], Jun Ling*[a]

A novel Eu^{3+} complex coordinated by polymers with β-diketone pendant groups (Eu^{3+}-PDKMA) has been synthesized for Cu^{2+} cation and acid-base vapor detections. Its sensitive and selective response of Cu^{2+} is confirmed by fluorescence quenching of characteristic emission of Eu^{3+} at 612 nm wavelength. The fluorescence intensity of Eu^{3+}-PDKMA obeys linear relationship at the presence of Cu^{2+} with the concentration in the order of 10^{-7} mol/L. The detection limit of Cu^{2+} is as low as 2.0×10^{-8} mol/L at natural pH, which makes Eu^{3+}-PDKMA an excellent luminescent sensor. Portable strips containing Eu^{3+}-PDKMA can be easily prepared to detect Cu^{2+} in aqueous solution. Moreover, the same strips can also be used to recognize and sense acidic and basic environments by naked eye. The red emission can be switched “off” and “on” when the strips contact acid and base vapors, respectively. The produced strips exhibit relatively fast response time less than 10 s, and good reusability over 10 times. The Eu^{3+}-PDKMA materials are promising in biological and environmental applications.

Introduction

Detection of metal ions has been attracting increasing attention due to the concern of human health, environmental issue and industrial process.[1, 2] Among these metal ions, copper is the third most abundant essential trace element for growth in human body.[3] However, Cu^{2+} cation has toxic and persistent characteristics.[4-6] The sensitive sensing and accurate monitoring of Cu^{2+} in environment is very important.

Although present detecting methods based on atomic absorption emission spectroscopy, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), can directly determine trace Cu^{2+} and reach sub-ng/mL limit,[7-10] the expensive equipment and time-consuming pretreatment hold back their wide and routine applications. Direct fluorescent detection of Cu^{2+} using a chromophore sensor becomes a practical and economical method because most of the methods are highly selective, sensitive, fast responsive, simple, and capable for on-line and on-the-spot monitoring.[11-13] Recently, many sensors with strong fluorescence have been designed to recognize Cu^{2+} by means of fluorescent change.[13-18] Among them, probes with europium (III) cation (Eu^{3+}) complexes possess well-defined photophysical properties in terms of narrow and highly structured emission bands with large Stokes shift.[19-22] Moreover, Eu^{3+} complexes are valuable alternative sensor for conventional dyes because Eu^{3+} complexes cannot be quenched by O_2, which makes the detection possible in non-degassed solution.[17] These advantages make Eu^{3+} complexes attractive sensor for the fluorescent detection of Cu^{2+} cation.

On–off–on acid-base dependent fluorescence switching of smart luminescent materials has received unprecedented attentions.[23-26] Actually, acid–base gas-responsive fluorescent materials were designed in an effective strategy of tuning intermolecular reactions, for instance, reversible hydrogen bonding.[27, 28] They have applications in sensors and biological assay.[24-26] Some materials have described a rapidly on–off luminescent switch in acidic and basic vapors.[24, 25, 29] From the viewpoint of application in acid-base vapors, polymeric materials have attractive advantages including the ease of fabrication, high mechanical strength, and low cost compared with small molecular complexes. For instance, Higuchi et al. reported a europium-based metallo-supramolecular luminescence sensor for switchable acid-base vapors.[26] They introduced Eu^{3+} complexes into polymer system in order to overcome the poor photo-stability of small molecular Eu^{3+} complexes in water or at high temperature.

Among the reported Eu^{3+} complexes, β-diketone ligands are well-known as a sensitizer of Eu^{3+} cation. Furthermore, β-diketone-coordinated Eu^{3+} complexes can easily dissociate by Cu^{2+} and rapidly respond with acid-base gas. By this approach, β-diketone-coordinated Eu^{3+} complexes are able to act as

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[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, 310027 Hangzhou, China. * Correspondence author: lingjun@zju.edu.cn*

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chemosensor for both Cu^{2+} detection and acid-base vapors response. In this contribution, we polymerize vinyl monomer containing pendant β-diketone functional group via RAFT method, and fabricate dual-responsible chemosensor after coordinating Eu^{3+}. The polymeric chemosensor is exclusively sensitive to Cu^{2+} and acid-base vapors in both solution and solid state. Application of portable test paper is also demonstrated. To the best of our knowledge, this is the first example of both cations and acid-base vapor sensors based on Eu^{3+}-polymer complex.

Experimental

Materials

1-(4-Hydroxyphenyl)-3-phenylpropane-1,3-dione (DIK) and 4-(3-oxo-3-phenylpropanoyl)phenyl methacrylate (DKMA) were prepared according to our previous report.[30] 1-(4-hydroxyphenyl)ethanone (Energy Chemical), methyl benzoate (Sinopharm Chemical Reagent), 2,2'-Azoisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized twice from ethanol. Cumyl dithiobenzoate (CDB) was synthesized as reported.[31] Methacryloylchloride (Mingxing Chemical Co.) was distilled under reduced pressure before use. Eu_2O_3 (99.9%, Beijing Founde Star Science and Technology Co. Ltd.) were transformed to Eu^{3+} through reaction with diluted nitric acid at elevated temperature. Triethylamine (TEA) was distilled over CaH_2 and stored in argon atmosphere at room temperature. Tetrahydrofuran (THF) was refluxed over potassium/benzophenone ketyl prior to use. All other solvents and chemicals were of analytic grade and used as received.

Measurements

Nuclear magnetic resonance spectroscopy (NMR) were recorded on a Bruker Avance III 400 spectrometer (^1H: 400 MHz and ^{13}C: 100 MHz) at room temperature using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Gas chromatography-time of flight mass spectrometry (GC-TOFMS) spectrum was measured by GCT Premier, WATERS. Molecular weights (MWs) and polydispersity index (*Đ*) were determined by size exclusion chromatography (SEC) on a Waters-150C apparatus equipped with Waters Styragel HR3 and HR4 columns and a Waters 2414 refractive index detector. THF was used as the eluent with a flow rate of 1.0 mL/min at 40 °C. Commercial polystyrene samples were used as the MW calibration standards. FT-IR spectra were recorded on Bruker VECTOR 22. The measurements were performed on tablets containing KBr and sample. The absorbance spectra of the polymers and Eu^{3+} hybrid materials were recorded in the range between 3500 and 400 cm^{-1}. UV-Vis spectra were conducted on a UV-2450 UV-Vis spectrophotometer (SHIMADZU). The absorbance and transmittance spectra of the Eu^{3+}-coordinated polymer were recorded in the range from 380 to 680 nm. Photoluminescence (PL) emission spectra of the samples were recorded by using a FluoroMax-4 spectrofluorometer (HORIBA). A UV lamp operating at 365 nm was applied to record the luminescence images of solution samples, films and test paper strips. The elemental analyses were performed on a Vario MICRO cube (Elementar).

Methods

4-(3-Oxo-3-phenylpropanoyl)phenyl methacrylate (DKMA).

DIK (5.0 g, 20.4 mmol) was dissolved in 50 mL dry THF followed by adding TEA (3.4 mL, 25.1 mmol). A 10 mL THF solution of methacryloylchloride (2.37 mL, 24.5 mmol) was added dropwise at 0 °C, then the reaction was carried out for 30 min followed by another 8 h at room temperature. A dilute ammonium chloride aqueous solution was added. After stirred for 15 min, the mixture was concentrated and the THF was evaporated. After that, aqueous phase was extracted 3 times with ethyl acetate, and washed by 1 mol/L HCl, saturated sodium bicarbonate and brines successively. The organic layer was dried by anhydrous sodium sulfate and the solution was evaporated. The residue was purified by column chromatography (1/10 EtOAc/Hexanes), recrystallized and dried in vacuum at 30 °C. DKMA was obtained as white crystal (5.35 g, yield = 88%).

Poly[4-(3-oxo-3-phenylpropanoyl)phenyl methacrylate] (PDKMA).

PDKMA was synthesized via RAFT polymerization using CDB as chain transfer agent (CTA) and AIBN as initiator. In a typical homo-polymerization, DKMA (1.70 g, 5.52 mmol), CDB (17.99 mg, 0.066 mmol), and AIBN (2.71 mg, 0.017 mmol) were dissolved in 5.5 mL anisole to form a crimson transparent solution. The monomer concentration was 1.0 mol/L. After deoxygenated by bubbling Ar for 30 min, the flask was sealed and immersed into a preheated oil bath at 70 °C to start the polymerization. After a predetermined time, the reaction mixture was cooled to room temperature and the product was precipitated from cold diethyl ether. PDKMA was obtained by centrifugation and dried in vacuum at 35 °C for 24 h (1.34 g, yield = 78.2%).

Solution of Eu^{3+}-coordinated PDKMA complex.

Eu^{3+}-chelated polymer complexes solution was prepared by mixing the $Eu(NO_3)_3·6H_2O$ with PDKMA in alkaline THF solution while the molar ratio of [Eu]:[PDKMA]:[C_2H_5ONa] was 1:3:3. In a typical chelation process, Eu^{3+} hybrid complex was manufactured in 4 mL THF at initial concentrations of 6.25 mg/mL PDKMA in a spawn bottle. After 1 mL of $Eu(NO_3)_3$ in THF containing 12.06 mg $Eu(NO_3)_3·6H_2O$ was added with continuous stirring, 5.2 mg C_2H_5ONa was added at room temperature. The mixture was allowed for 2 h vigorous stirring. Homogeneous Eu^{3+} hybrid complex solution was obtained by passing a filter with 0.45μm pores.

Test paper of Eu^{3+} hybrid PDKMA.

Paper-based strips containing Eu^{3+}-coordinated polymer complex (PEP-strips) were prepared by simply immersion of filter paper in Eu^{3+}-PDKMA solution and then dried. In brief, as-prepared homogeneous Eu^{3+}-PDKMA solution was put into a round glass tray with a plastic cover, and 30 pieces of Whatman filter paper sheets (50 × 10 mm) were immersed into the solution for 10 min and air-dried for approximately

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half an hour. They were dried in vacuum at 30 °C for 2 h. The above was repeated two more times. Finally, the test paper strips were stored in air-tight bags.

Copper (II) cation detection in solution.

To evaluate the selectivity of Eu^{3+}-PDKMA complex on Cu^{2+} detection, the quenching ability of other metal ions on the fluorescence of Eu^{3+}-PDKMA complex were also examined. A 20 μL THF solution of Eu^{3+}-PDKMA solution (5 mg/mL) was added into 2 mL aqueous solutions of Mg^{2+}, Ca^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Al^{3+}, Cr^{3+} and Pb^{2+}, respectively. The concentrations of the metal ions were set as 2.0×10^{-5} mol/L. The muddy mixture was ultrasonic oscillating for 1 min at room temperature, and then fluorescence intensity were measured by spectrometers.

A mixture solvent of THF and deionized water with the volume ratio of 9:1 was used in the measurement of Cu^{2+} sensing ability of Eu^{3+}-PDKMA complex. A 20 μL THF solution of Eu^{3+}-PDKMA (5 mg/mL) was added to 2 mL THF/H_2O solvent in quartz cuvette. 2 μL Cu^{2+} aqueous solutions with different concentrations were added, ultrasonic oscillated for 1 min, and examined by fluorescence photometer directly.

Copper (II) cation detection by PEP-strips.

Paper strips containing Eu^{3+}-PDKMA (PEP-strips) were simply immersed into aqueous solutions of different metal ions for approximately 45s under ambient condition. The ions included Mg^{2+}, Ca^{2+}, Fe^{3+}, Fe^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, and Cr^{3+}. The PEP-strips were dried under a warm air stream and then examined by naked eye under a standard UV lamp with 365 nm excitation light.

Acid–base gas switching test by PEP-strips and Eu^{3+}-PDKMA film.

A PEP-strip was exposed to acidic vapor of HCl gas and basic ammonia vapor consecutively in a hood. Each time the strip was kept for about 10 s. The PEP-strip was examined by naked eye under a standard UV lamp (365 nm). We also made a Eu^{3+} hybrid PDKMA film on a quartz plate by spin coating. The polymer film also underwent the acid-base vapors switching from HCl and ammonia vapors. The corresponding fluorescence spectra were recorded for each cycle.

Results and Discussion

Polymerizations and characterizations of PDKMA

The β-diketone-containing monomer, i.e. DKMA, is prepared from aldol reaction and followed by esterification with methacrylic chloride. The overall yield can reach 74%. DKMA has been fully characterized by ^1H NMR and ^{13}C NMR (Figures 1A, S1 and S2 in ESI†). The characteristic signals of methacrylate protons (H^b and H^a) are observed at 6.39, 5.80 and 2.08 ppm. The singlet signals of enol protons (H^d and H^e at 16.87 and 6.84 ppm) and methyne protons (H^c at 4.62 ppm) present equilibrium between enol and ketone forms with the molar ratio of 96.0:4.0. Meanwhile, high resolution mass spectrum confirms the composition of DKMA (calculated: 308.1049 g/mol, found: 308.1048 g/mol).

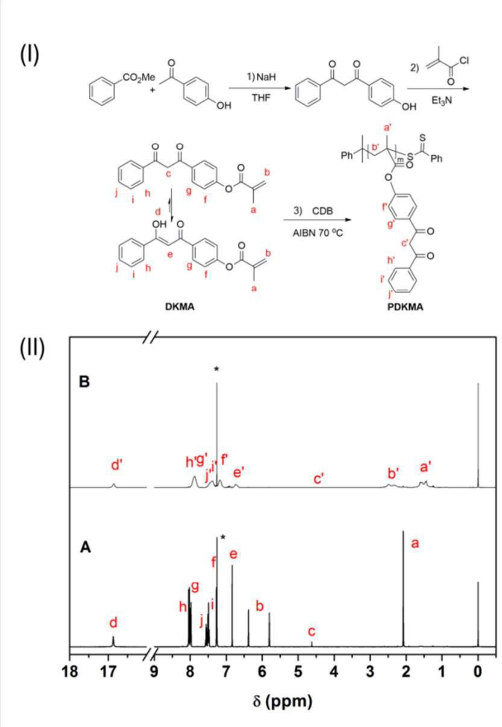

Figure 1. (I) Synthesis of PDKMA. (II) ^1H NMR spectra of DKMA (A) and $PDKMA_{67}$ (B) with assignments. *: residue $CHCl_3$ in solvent $CDCl_3$.

Well-defined PDKMAs with different chain lengths are synthesized by RAFT polymerization. MWs measured by SEC, ^1H NMR and ^{13}C NMR spectroscopy (Table 1 and Figures 1, S3 and S4 in ESI†) agree well with the corresponding theoretical values indicating well-controlled RAFT polymerizations. As shown in Figures 1B and S3, the ratio of enol/ketone in $PDKMA_{67}$ is calculated as 94.6:5.4 by the integrals of proton signals at 16.87 and 4.50 ppm, which indicates that the equilibrium is not changed after polymerization. The protons of aromatic rings ($H^{f', g', h', i', j'}$ at 7.86-7.18 ppm) and backbone ($H^{b', a'}$ between 2.44 and 1.43 ppm) of $PDKMA_{67}$ are observed and carefully assigned. The C, H and N percentages of obtained homo-polymers are determined by elemental analysis consistent with the theoretical values. As a typical result of $PDKMA_{67}$, C, H and N percentages are 73.09%, 5.45% and 0%, respectively, and the calculated values for $PDKMA_{67}$ are 73.96%, 5.25% and 0%.

PDKMAs with MWs ranging from 12.8 to 16.3 kDa and moderate polydispersity indices ($Đ \leq 1.30$) are obtained by varying the feed ratio of [DKMA]/[CDB] (Table 1 and Figure S4). The symmetrical and mono-modal peaks indicate that polymerization showed satisfactory results in both reactivity and dispersity. We keep monomer conversions applicable (45-85%) for better polymerization control.

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Table 1. RAFT homo-polymerization of DKMA in anisole at 70 °C.

Sample	[DKMA]/[CDB]/[AIBN]$^{a)}$	Time (h)	Conv. (%)	$DP^{b)}$	$M_{n,\text{ NMR.}}$$^{c)}$ (kDa)	$M_{n,\text{SEC}}$$^{d)}$ (kDa)	$Đ^{d)}$
1	300/3/1	10.0	69	69	21.5	16.3	1.30
2	333/4/1	6.5$^{e)}$	81	67	20.9	15.3	1.25
3	300/3/1	7.5	49.5	50	15.7	12.8	1.30

a) Molar ratio in feed. The concentration of DKMA is 0.5 mol/L. b) Degree of polymerization (*DP*) was calculated by *(*[DKMA]/[CDB]*)* × *Conversion*. c) Determined by ^{1}H NMR according to trioxymethylene as internal reference, $M_{n,NMR}$ = MW_{monomer} × *(*[DKMA]/[CDB]*)* × *Conversion* + MW_{CDB}. d) Determined from SEC in THF. e) The concentration of DKMA is 1.0 mol/L.

Eu^{3+} coordination with PDKMA

The coordination of Eu^{3+} with PDKMA is supported by FT-IR analysis. Figure S5 in ESI† shows an example of PDKMA$_{67}$ and the corresponding Eu^{3+} complex. Strong absorbent bands at 1600 and 1495 cm^{-1} in PDKMA$_{67}$ attribute to the stretching vibrations of C=O and C=C (enol isomer) in β-diketone side groups, respectively.[32] Their red shifts to 1595 and 1475 cm^{-1} in Eu^{3+}-PDKMA$_{67}$ complex evidence the coordination of carbonyl group to Eu^{3+}.[33]

UV and fluorescence of Eu^{3+} Chelated PDKMA Complex.

The UV-Vis absorption spectra of PDKAM with and without Eu^{3+} in THF are shown in Figure S6 ESI†. In a typical UV-Vis profile of PDKMA$_{67}$, a broad absorption band is observed between 300 and 420 nm with maximum of 340 nm. With the increasing concentration of Eu^{3+}, the π-π* transition bands centered on the β-diketone moiety experience a red shift of ca. 10-15 nm compared with that of free β-diketone chromophore, indicating an electronic interaction between the light-absorbing aryl β-diketone and the light-emitting Eu^{3+} center.[34] Photoluminescent spectra of Eu^{3+}-polymer in aqueous solution consist of two groups of emission peaks after being excited at 350 nm.[30, 35-38] The first group from 400 to 550 nm contains the emission bands originated from π-π* transitions of ligand in PDKMA. The second one is composed of typical narrow-band Eu^{3+} luminescence in the region of 570-680 nm at 579 (J = 0), 590 (J = 1), 612 (J = 2) and 650 (J = 3) nm (antenna effect), which are originated from Eu^{3+} ions corresponding to $^5D_0 \rightarrow {}^7F_J$ *f-f* transitions (Figure S7 in ESI†).[39] When the concentration of PDKMA$_{67}$ reaches 0.05 mg/mL, the luminescence of Eu^{3+} is the largest. After that, the intensity of Eu^{3+} photoluminescence decreases quickly due to the precipitation of hydrophobic PDKMA$_{67}$. Therefore, we choose 0.05 mg/mL as the standard concentration of PDKMA$_{67}$ for subsequent analysis.

Quantum chemical calculation of coordination of Eu^{3+} with PDKMA

In order to further understand the details of chelation between DKMA and Eu^{3+}, a theoretical calculation of Eu^{3+}-DKMA is performed by means of density functional theory (DFT). The calculation details are included in ESI†. Figure 2 illustrates the optimized geometry at B3LYP/6-31G(d,p). Three DKMA repeating units evenly distribute in space around Eu^{3+} and the dihedral angle of two carbonyl (C=O) groups on each DKMA is about 6° in proximity to a plane. All the bond lengths between Eu^{3+} and oxygen atom of C=O group in each DKMA are nearly 2.30 Å indicating a strong coordinating interaction. TD-DFT calculation at B3LYP/6-311+(d,p) level provides the frontier molecular orbitals of excited states. It suggests a 3.44 eV energy gap between HOMO and LUMO. Its corresponding excitation wavelength is 360.8 nm quite close to the experimental value of 350 nm. Thus the chelation between the three DKMA repeating units and Eu^{3+} is proved.

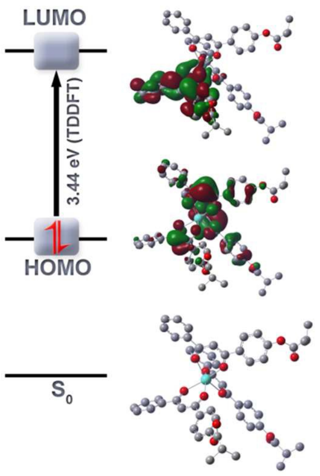

Figure 2. Optimized geometries of chelation of Eu^{3+} with three DKMA repeating units and the frontier molecular orbitals.

Fluorescence of Eu^{3+}-PDKMA in various pH conditions

To explore the stability of Eu^{3+}-PDKMA in aqueous solution, we investigated the luminescent features of Eu^{3+}-PDKMA at

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various pH values. The pH values of the solutions are tuned by adding either HNO_3 or NaOH solutions. The plot of photoluminescence intensity vs. pH over a range between 2.0 and 10.0 shows a non-linear trend with a peak near pH = 7.2-8.2 (Figure S8). The dissociation between Eu^{3+} and diketone in acidic medium quenches chromophore fluorescence. On the contrary, high basic solution also destroys the coordination of Eu^{3+} and diketone to form $Eu(OH)_3$ precipitation and decreases the fluorescent emission.[40] At neutral pH from 6 to 9, Eu^{3+}-PDKMA complexes exhibit good stability and strong light emission. The pH values in all the following metal detection are fixed under neutral condition.

Cu^{2+} detection by Eu^{3+}-PDKMA

Eu^{3+}-PDKMA shows a strong red emission at 612 nm under the excitation light of 350 nm. Cu^{2+}, a typical transition metal cation, can quench its luminescence to make Eu^{3+}-PDKMA a good chemosensor.[41, 42] The fluorescence turn-off switch probably contributes to the reason that Cu^{2+} can replace Eu^{3+} in coordinating β-ketone groups, and quench excitation energy through heavy atom effect.[43] Eu^{3+}-PDKMA solution exhibits very good selectivity for Cu^{2+}. Other common cations including Mg^{2+}, Ca^{2+}, Fe^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+} and Cr^{3+} in 2×10^{-5} mol/L aqueous solution do not quench the luminescence at 612 nm of Eu^{3+}-$PDKMA_{67}$ as shown in Figure 3. The highest quenching intensity is less than 15% while Cu^{2+} and Fe^{3+} show the effect as high as 66.8% and 48.5%, respectively. Fortunately in practice Fe^{3+} can be easily reduced to Fe^{2+} which is negative in the luminescence quench of Eu^{3+}-PDKMA. And thus the interference of Fe^{3+} is not a problem.

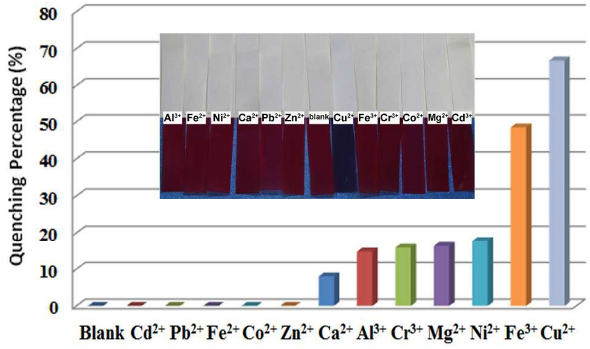

Figure 3. Photoluminescence quenching intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (612 nm) as a function of various cationic species in aqueous solution. Insets: photographs of PEP-strips with different cations under sunlight (top) and UV light of 365 nm (bottom), Blank: deionized water.

The photoluminescent properties of Eu^{3+}-$PDKMA_{67}$ at various Cu^{2+} concentrations in the range between 0 and 2×10^{-5} mol/L in a mixture of THF and water (V_{THF}/ V_{water} = 9/1) are recorded and summarized in Figure 4. With the increase of Cu^{2+} concentration, the characteristic Eu^{3+} emission decreases drastically. To further quantify the turn-off efficiencies, the fluorescence intensities of Eu^{3+}-PDKMA at the presence of Cu^{2+} with various concentrations shows a linear range from 0 to 1×10^{-6} mol/L (In set of Figure 4), where I_0 and I are the luminescent intensities before and after metal ion incorporation, respectively. The detection limit of Cu^{2+} by Eu^{3+}-PDKMA is 2×10^{-8} mol/L when the signal/noise ratio decreases to 5.

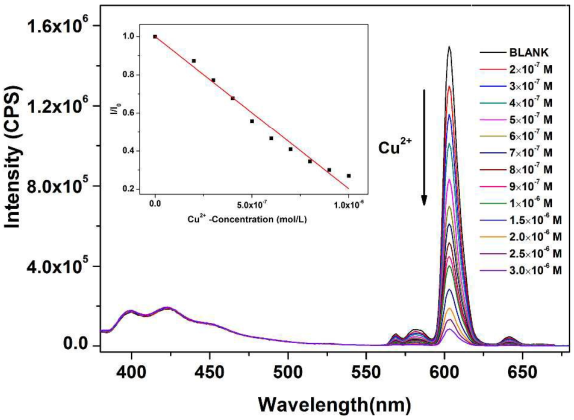

Figure 4. Luminescence spectra of Eu^{3+}-$PDKMA_{67}$ in THF/water solution with different Cu^{2+} concentrations under excitation at 350 nm at 25 °C. Inset: the photoluminescence intensity ratios at 612 nm as a function of various Cu^{2+} concentrations.

Since Eu^{3+}-PDKMA probe is highly sensitive and selective in Cu^{2+} recognition, it provides numerous advantages to fabricate portable test paper or films, such as effective reagent immobilization, simple preparation, versatility, and good mechanical properties.[44, 45] With a simple immerse-and-dry method (see the Experimental section), we develop fluorescence test paper (PEP-strip) for rapid detection of Cu^{2+} in aqueous solution. The inset of Figure 3 shows an obvious emission color change from red to blue by naked eye when the test paper immerses into Cu^{2+} solution with the concentration of 2.0×10^{-5} mol/L. On the contrary, no color change is found for other cations. The response of PEP-strips to Cu^{2+} is fast within 45 s. All the above suggest PEP-strip an excellent candidate for fast and selective Cu^{2+} detection.

Recyclable On–Off–On vapoluminescent sensor.

Luminescent On–Off–On response is based on the coordination of Eu^{3+} with diketone groups assisted by alkali. The classical Eu^{3+} emission is turned on in basic condition. Eu^{3+} dissociates from polymer if the diketone groups are protonated by extra acid, which turns off the red luminescent emission of Eu^{3+} and shows blue emission of diketone itself. This color-tunable mechanism makes Eu^{3+}-PDKMA a vapoluminescent sensor. A video in ESI† illustrates the reversible color change of PEP-strip by the two vapors which is similar with other reported vapoluminescent materials.[24-26]

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From the viewpoint of device applications, reversibility and response time are the most important factors. Although PEP-strip works well in the color change, we use a Eu^{3+}-PDKMA coated quartz substrate to quantitative examine the reversibility. This film shows bright-red emission excited under a UV lamp at 365 nm after brief exposure with NH_3 and drifted back to the blue emission when treated with HCl gas (the inset of Figure 5). The spectral changes at 612 nm are monitored upon alternating exposure to NH_3 and HCl gases over several NH_3–HCl cycles as shown in Figure 5. The Eu^{3+}-PDKMA$_{67}$ film exhibits good reversibility at least 10 times suggesting that PEP-strip shows a good recyclable Off–On–Off response. In addition, the response time of PEP-strip is also rapid about 10 s. Such a naked eye distinguishable sensor of Eu^{3+}-PDKMA will be of importance in a variety of applications.

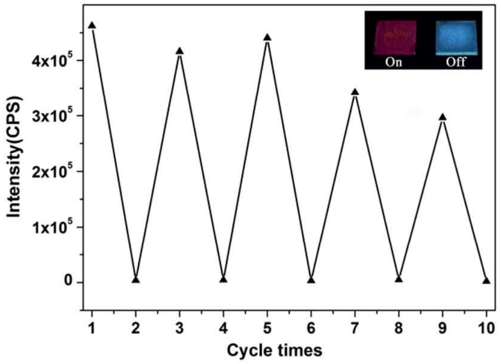

Figure 5. Responses of luminescence intensities at 612 nm of Eu^{3+}-PDKMA$_{67}$ film coated quartz substrate (excitation: 350 nm) during several alternate acid and base vapors exposure cycles. Inset: photo of the Eu^{3+}-PDKMA$_{67}$ film upon short exposure with NH_3 (On) and HCl (Off).

Conclusions

A novel dual-responsible fluorescent sensor for Cu^{2+} and acid-base vapors is prepared. Eu^{3+}-PDKMA exhibits high selectivity and sensitivity in targeting Cu^{2+} cations through the quenching of characteristic Eu^{3+} fluorescence. Meanwhile, the fluorescent intensity of Eu^{3+}-PDKMA shows a good linear correlation to Cu^{2+} in the range 0 to 1×10^{-6} mol/L. Eu^{3+}-PDKMA-containing fluorescence test paper has quick response to Cu^{2+} and acid-base vapors which can be seen directly by naked eye. Eu^{3+}-PDKMA is a novel dual-responsible material for simple and reliable monitoring of Cu^{2+} as well as acid-base vapors. It is promising in the application of pollution control and environmental monitoring.

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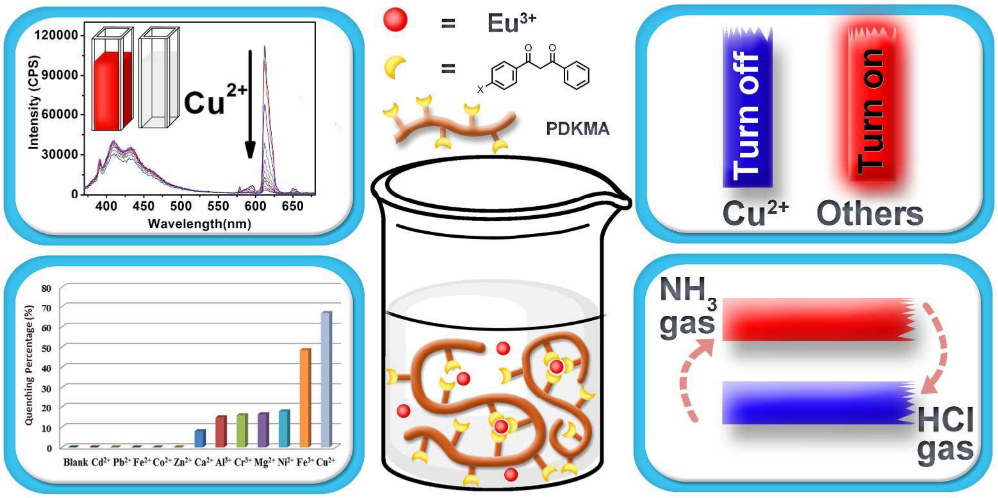

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