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A Highly Sensitive Luminescent Dye@MOF Composite for Probing Different Volatile Organic Compounds

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The probing of volatile organic compounds (VOCs) is critical and challenging in biotechnology and environmental monitoring. Incorporation of luminescent moieties into metal–organic frameworks (MOFs) has produced many unique luminescent sensors for probing different VOCs. The emissions of most MOF sensors are based mainly on the single transitions of luminescent moieties, so the luminescence readouts are only predominant for some special VOCs. We use a natural amino acid derivative as the luminescent moiety to result in a lamellar coordination polymer, and further embed luminescent dye molecules in the crystal matrix to result in a luminescent dye@MOF sensor. The composite sensor exhibits excellent sensitivity for decoding different VOCs with clearly differentiable fluorescence emission by tuning the energy transfer efficiency from the organic ligand to the dye moieties. The composite luminescent sensor is self-calibrated, and much more stable and instantaneous than other more widely explored luminescent sensors.

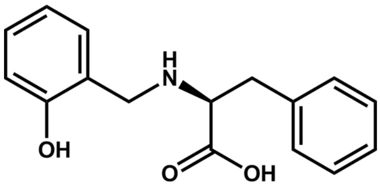
Introduction

Most volatile organic compounds (VOCs) are poisonous and harmful substances. The development of highly sensitive and fast-response probing sensors for the detection of VOCs is highly desirable for reducing the discharge of VOCs and monitoring the content of VOCs, and the choice of sensor materials is central to achieving highly efficient probing of VOCs.[1] Recent work has proved that fluorescence probing based on the sensor–VOC interactions is a powerful detection method.[2] The challenge is how to improve the sensitivity of fluorescence sensors for probing different VOCs, especially for those VOCs with similar chemical and physical properties, such as homologue and isomeride VOCs.

Metal–organic frameworks (MOFs) are a class of functional materials that are self-assembled from organic linkers connecting with metal ions/clusters.[3] By rational design and functionalization of the constituent moieties, applications of MOFs have been realized in many fields.[4–8] Taking the solvent-dependent optical properties of luminescent moieties, MOFs have been used as probing sensors for the detection of many VOCs.[9,10] MOF sensors have the distinct advantages of fast response, high sensitivity, and noninvasive operation. The shortcoming is the excitation and emission energy transfers in MOFs, which are processed mainly in the single-constituent moieties, resulting in luminescence readouts that are only predominant to some special VOCs through close contact with the luminescent moieties. Our strategy is to introduce second luminescent moieties in MOFs as reference emission centers, to improve the luminescent sensitivity of MOF sensors.[11] If the emission bands of the organic ligands match the excitation bands of the second luminescent moieties in MOFs, the sensitivity of MOF sensors can be improved significantly in terms of the probing of different VOCs by tuning the energy transfer efficiency from the first to the second luminescent moieties. Herein, we report the synthesis, characterizations, and applications of a highly sensitive luminescent dye@MOF composite for probing different VOCs with fast response and excellent selectivity.

Results and Discussion

Attracted by the special biological activity and the selective substrate-binding ability of the natural amino acids, we have used them as building synthons for the construction of homochiral MOFs.[12] To tune the luminescent property and improve the bridging ability, we have modified the amino acid L-phenylalanine with 2-hydroxybenzaldehyde to result in a chiral ligand (*S*)-2-(2-hydroxybenzylamino)-3-phenylpropanoic acid (H_2**L**) (Scheme 1). The reaction between Zn^{2+} and H_2**L** resulted in a layered homochiral MOF [Zn_2**L**$_2$]·H_2O (**1**), which is insoluble in water and in common organic solvents such as MeOH,



Scheme 1. (*S*)-2-(2-hydroxybenzylamino)-3-phenylpropanoic acid (H_2**L**).

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EtOH, THF, DMF, and so on. The formula was established on the basis of single-crystal X-ray diffraction, thermogravimetric analysis (TGA), and elemental analysis. The bulk purity of the as-synthesized sample was confirmed by powder X-ray diffraction (PXRD).

Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the nonsymmetric triclinic space group *P*1. The asymmetric unit of **1** contains two Zn^{II} cations, two **L** ligands, and one lattice water molecule. The carboxylate group of **L** forms a bidentate bridge with two Zn^{II} cations, and the deprotonated phenol group μ_2-bridges two Zn centers. As shown in Figure 1 a, the Zn cation is coordinated with two carboxyl oxygen atoms from two **L** ligands, two phenol oxygen atoms, and one amino group. The five-coordinated Zn^{II} cations are coupled by two phenol oxygen atoms to form a binuclear unit {Zn$_2$}. This {Zn$_2$} is further connected with four neighboring {Zn$_2$} units by carboxylate groups to extend into a 2D lamellar network propagated in the *ab* plane (Figure 1 b). The lattice water molecules are imbedded in the void space. There is no significant interaction between the layered networks except for the van der Waals contacts (Figure 1 c).

The lamellae in compound **1** are connected by van der Waals interactions, so this provides an opportunity for us to tune the luminescent property by encapsulating luminescent dye moieties in the crystal matrix. Molecules of Rhodamine B dye can be imbedded easily in the as-synthesized sample (named Rho@**1**) if Rhodamine B is added into the reaction mixture during the synthesis of **1**, as observed by the naked eye (Figure 2). Analysis by UV/Vis absorption spectroscopy shows that there is 0.047 wt% imbedded Rhodamine B in Rho@**1**. The PXRD pattern of Rho@**1** suggests that the main network structure is basically same as that of **1**. Because compound **1** is nonporous, as suggested by the single-crystal structure and N_2 sorption experiments, the loaded dye molecules should be included in the MOF crystal matrix. The slight shifts in the diffraction peak positions suggest that the networks are flexible and tunable depending on the imbedded substance molecules. Notably, Rho@**1** is very stable, and the included Rhodamine B molecules did not leak out upon immersion of Rho@**1** in different solvents such as EtOH, CH_3CN, DMF, and water, as monitored by UV/Vis absorption spectroscopy. If Rhodamine B is imbedded in the crystal matrix of Rho@**1**, the second luminescent transition from the dye can be generated readily, in addition to the original one in **1**. The above properties of Rho@**1** are beneficial for its application in the sensing of different VOCs.

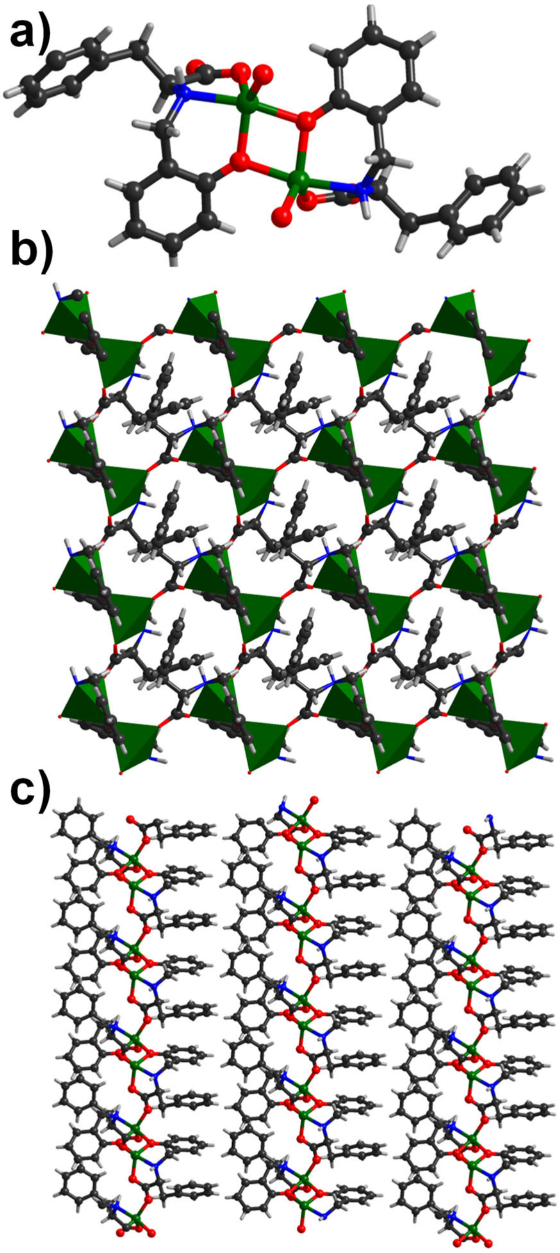

Figure 1. Crystal structure of compound **1**: a) views of the coordination mode of the **L** ligand and the coordination environment of Zn^{II} ion; b) lamellar network of **L** linking up Zn binuclear units as viewed down the *c* axis; and c) packing diagram as viewed down the *a* axis. Color codes: Zn, green; O, red; N, blue; C, deep gray; H, light gray.

The excitation and emission spectra of H_2**L**, **1**, and Rho@**1** were examined in the solid state at room temperature (Figure 3). The free H_2**L** ligand displays an intense and broad band with a maximum at 403 nm in the emission spectrum under 310 nm UV light excitation, which is attributed to the electron transition of the H_2**L** ligand involving a ligand-centered excited state. The light emission peak of **1** shifts to 411 nm upon excitation at 310 nm. The slight redshift of the emission of **L** in **1** is attributed to the deprotonation and coordination of **L** to Zn^{2+} ions.[13] As expected, the dye-encapsulated sample Rho@**1** simultaneously shows both the characteristic emissions of the dye and **L** moieties upon excitation at 310 nm in the solid state at room temperature. The emission bands for the Rhodamine B and **L** moieties in Rho@**1** are around 583 and 416 nm, respectively. To make comparisons, we have measured the emission spectra of Rhodamine B and a thoroughly ground mixture of Rhodamine B and **1** under the same conditions. Rhodamine B does not display any emission, whereas the mechanical mixture mainly presents the emission band of **1** excited at 310 nm in the solid state. These results demonstrate that the dye molecules were encapsulated in the crystal matrix of **1**. Moreover, isolation of the dye molecules by

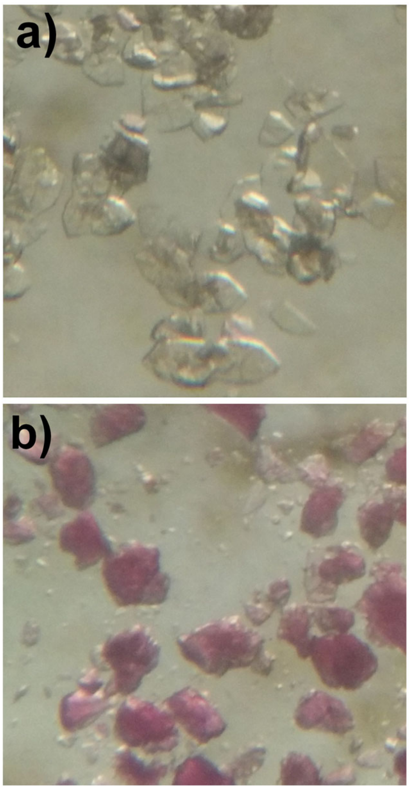

Figure 2. Photo pictures of the crystals of a) compound **1** and b) Rho@**1**.

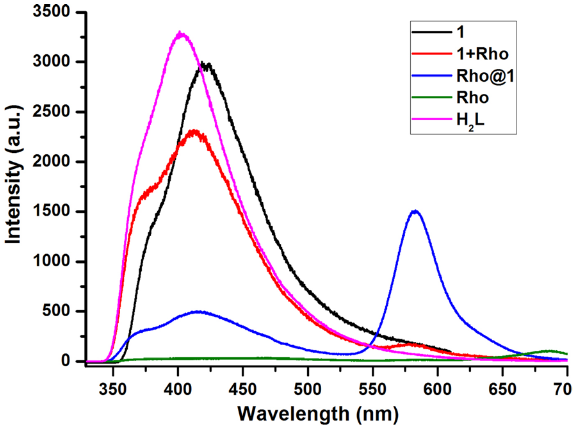

Figure 3. Emission spectra of H_2**L** (pink), **1** (black), Rho@**1** (blue), dye (green), and a thoroughly ground mixture of dye and **1** (red), excited at 310 nm in the solid state at room temperature.

the lamellar networks in Rho@**1** can restrain the nonradiative energy transfer process to prevent fluorescence quenching.[14]

Notably, the emission of the dye is mainly sensitized by the **L** moiety in Rho@**1**. Such a ligand-to-dye energy transfer behavior can be modulated systematically by tuning the excitation energy. Upon increasing the excitation wavelength, the emission intensities of **L** and the dye changed gradually in the luminescence spectra of Rho@**1**. The above results demonstrate that the emission energy of ligand **L** ligand matches well with the excitation energy of the dye in Rho@**1**, which results in efficient ligand-to-dye energy transfer.

The emission energy of the dye is mainly transferred from the **L** moiety through ligand-to-dye energy transfer, so the transmission process might be very sensitive to different VOCs by tuning the energy transfer efficiency between the excited states of **L** and Rhodamine B. We used the ground samples of Rho@**1** to study the luminescent sensitivity for probing different VOCs. Upon immersion of the samples of Rho@**1** in different solvents (MeOH, EtOH, phenol, benzyl alcohol, 1,2-dichlorobenzene, acetonitrile, acetone, THF, and DMF, as shown in Figure 4), these solid samples emit solvent-dependent fluorescence. The emissions of the dye and/or **L** moieties are clearly enhanced and/or quenched by different VOCs. In other words, the emission bands of the **L** and dye moieties are both varia-

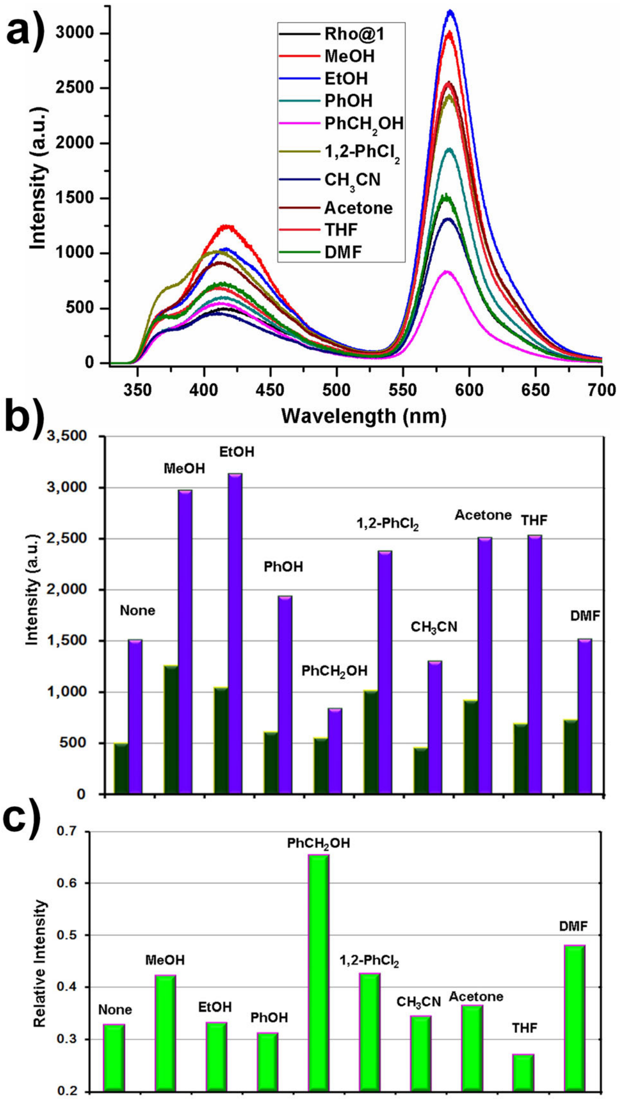

Figure 4. a) Photoluminescence spectra of Rho@**1** in the presence of different VOCs excited at 310 nm in the solid state at room temperature. b) Emission peak heights of **L** (left column) and dye (right column) moieties, and c) emission peak height ratios of **L** to dye moieties in the photoluminescence spectra of Rho@**1** after addition of different VOCs excited at 310 nm in the solid state at room temperature.

bles that are dependent on the environmental VOCs, that is, Rho@**1** emits solvent-dependent light colors by tuning the energy transfer from the ligand to the dye moieties in Rho@**1**. Moreover, the distinguishabilities of the luminescence readouts can be improved by monitoring the relative emission peak heights of the **L** to the dye moieties in the luminescence spectra of Rho@**1** (Figure 4c). These results demonstrate that introduction of the luminescence reference of dye moieties in MOFs can increase the probing sensitivity in the detection of different VOCs by self-referencing the emission peak heights of different luminescent moieties in the photoluminescence spectra. The composite material Rho@**1** is nonporous, so these solvents should mainly be in contact with the solid surface.

We also used Rho@**1** to probe different organic sulfides such as thiol and thioether molecules. As shown in Figure 5, these smelly and poisonous substances can be differentiated easily by monitoring the relative emission height ratios of the **L** to the dye moieties. Upon mixing the samples of Rho@**1** with different amines, as shown in Figure 6, the dye emission is also fully quenched by the different amine substances. In other words, the energy transfer from the ligand to dye moieties in Rho@**1** might be cut off by these amines. It is interesting that these amine molecules have different effects on the emission of the **L** moieties, which can be differentiated easily by monitoring the emission intensities. Even though different nitroaromatic molecules exhibit significant quenching effects on the emissions of both **L** and dye in Rho@**1**, they can also be differentiated easily by monitoring the emission intensities in the luminescence spectra owing to their different quenching effects (Figure 7). The high sensitivity of Rho@**1** is further proved by probing nitrobenzene in ethanol. Even though the concentration of nitrobenzene is lowered to 0.01 wt%, the emission quenching effect is still clear (Figure 8). Moreover, the luminescence emission can also be almost fully quenched upon exposure of Rho@**1** to nitrobenzene vapor. The Rho@**1** composite luminescent sensor is very stable, and the luminescence emission can be regenerated by heating at 60 °C for 10 min. The recovered solid sample can be reused for ten cycles with retained high sensitivity in the probing of nitrobenzene.

Conclusion

In summary, we have synthesized a luminescent lamellar coordination polymer, and further developed a dye@MOF composite luminescent sensor to realize the detection of different VOCs by monitoring the emissions of different moieties in the luminescence spectra. The luminescent dye@MOF composite exhibits excellent sensitivity and distinguishability in probing different VOCs. The relative emission intensity of **L** versus the dye moieties is variable for different solvent molecules in the luminescence spectra of Rho@**1**. It is interesting that the internal reference strategy has overcome the drawback of traditional MOF sensors based on single emission transitions. There are numerous MOFs and dyes for the construction of luminescent dye@MOF sensors, so we believe that the internal reference strategy is a very promising approach for the development of highly sensitive composite sensors.

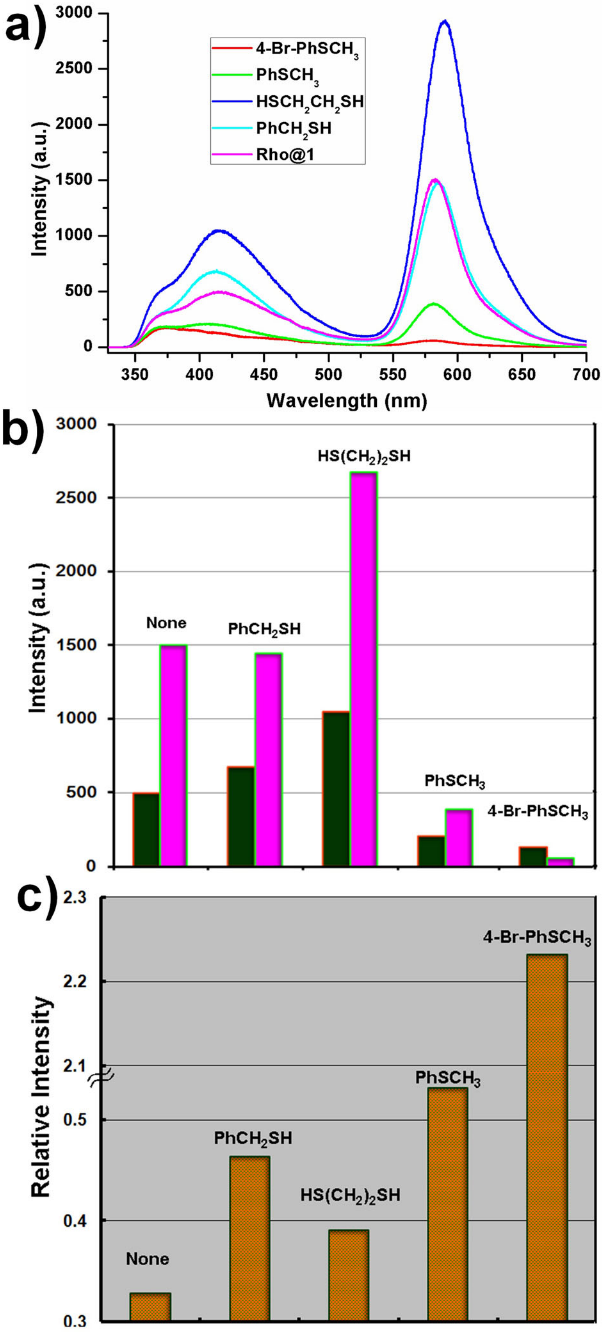

Figure 5. a) Photoluminescence spectra of Rho@**1** in the presence of different thiol and thioether molecules excited at 310 nm in the solid state at room temperature. b) Emission peak heights of **L** (left column) and dye (right column) moieties, and c) the emission peak height ratios of **L** to dye moieties in the photoluminescence spectra of Rho@**1** after addition of different thiol and thioether molecules excited at 310 nm in the solid state at room temperature.

Experimental Section

Materials and measurements

All the chemicals were obtained from commercial sources and were used without further purification. Elemental analyses were performed with a ThermoFinnigan Flash EA 1112 elementary analyzer. FTIR spectra were recorded from KBr pellets on a FTS-40

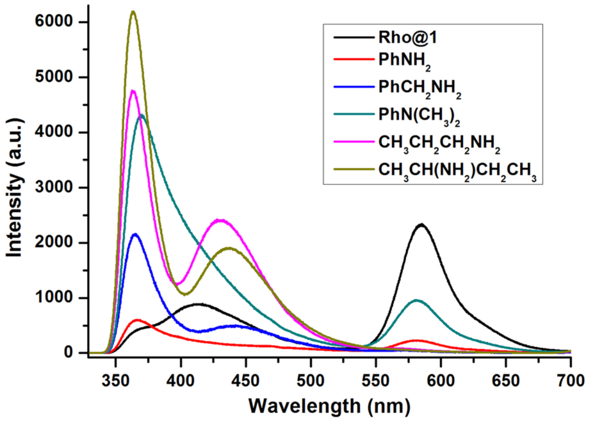

Figure 6. Photoluminescence spectra of Rho@**1** in the presence of different amine molecules excited at 310 nm in the solid state at room temperature.

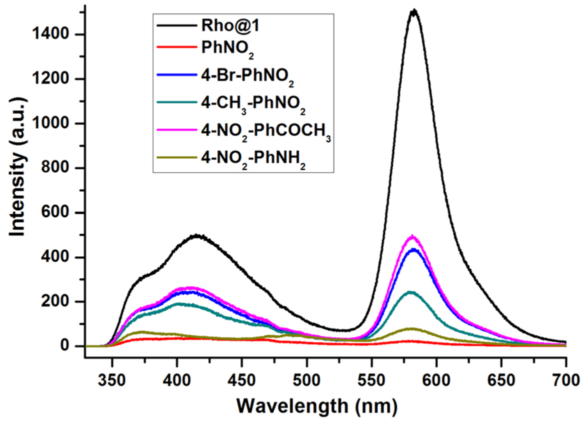

Figure 7. Photoluminescence spectra of Rho@**1** in the presence of different nitroaromatic molecules excited at 310 nm in the solid state at room temperature.

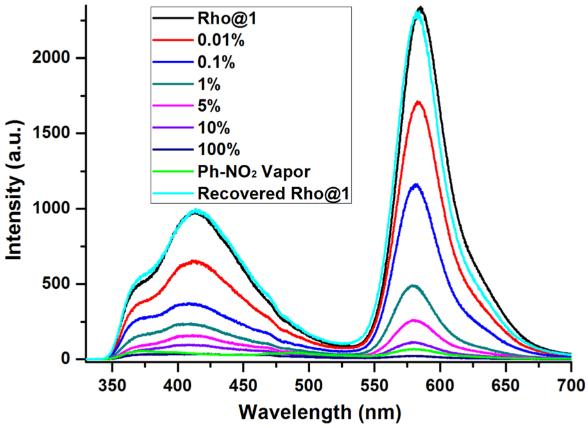

Figure 8. Photoluminescence spectra of Rho@**1** in the presence of nitrobenzene in ethanol with different concentrations and nitrobenzene vapor, excited at 310 nm in the solid state at room temperature.

spectrophotometer in the 4000–400 cm^{-1} region. Thermogravimetric analyses (TGAs) were performed on an SDTQ600 compositional analysis instrument from 30 to 800 °C under a N_2 atmosphere at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a RIGAKU D/MAX 2550/PC with CuK$_\alpha$ radiation (λ = 1.5406 Å). Luminescence spectra of the solid samples were recorded on a Hitachi F4600 fluorescence spectrometer at room temperature. UV/Vis spectra were recorded on a UNICO 2802 spectrophotometer. The ^{1}H NMR spectrum was recorded on a 400 MHz spectrometer in methanol solution, and the chemical shifts were reported relative to internal standard TMS (0 ppm).

Synthesis of (*S*)-2-(2-hydroxybenzylamino)-3-phenylpropanoic acid (H_2L)

A mixture of 2-hydroxybenzaldehyde (121 mg, 1.0 mmol), L-phenylalanine (166 mg, 1.0 mmol), and NaOH (79 mg, 2.0 mmol) in a mixed solvent of water (3 mL) and EtOH (3 mL) was stirred at room temperature for 2 h. Sodium borohydride (76 mg, 20 mmol) was added to the resulting yellow solution under stirring. The reaction mixture was stirred for 1 h at room temperature, then the pH value of the solution was adjusted to 5.0 with 10 % aqueous HCl solution. The resulting white solid was filtered, washed with ethanol and diethyl ether, and recrystallized in water. Yield: 85.3 %; elemental analysis calcd (%) for $C_{15}H_{15}NO_3$: C 70.83, H 6.32, N 5.16; found: C 71.02, H 6.35, N 5.19; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.62–6.40 (m, 9 H), 3.75 (d, *J* = 17.6 Hz, 1 H), 3.33 (s, 2 H), 3.21 (t, *J* = 13.8 Hz, 1 H), 3.08–2.79 ppm (m, 1 H); IR (KBr pellet): $\tilde{\nu}$ = 1654(m), 1596(s), 1460(s), 1390(s), 1357(m), 1334(w), 1272(m), 1256(m), 1190(w), 1131(w), 1111(w), 1083(w), 1031(m), 1003(m), 946(m), 874(m), 826(m), 757(s), 699(s), 669(w), 530(m), 490(w) cm^{-1}.

Synthesis of $[Zn_2L_2]\cdot H_2O$ (1)

H_2**L** (54 mg, 0.2 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (60 mg, 0.2 mmol) were thoroughly dissolved in a mixed solvent of EtOH (5 mL) and DMF (3 mL). An aqueous solution of NaOH (0.3 mL, 0.05 mol L^{-1}) was added dropwise to the solution under stirring. The resulting mixture was heated at 65 °C for three days. Colorless crystals of **1** were isolated by filtration, washed with EtOH, and dried in air. Yield: 76 %; elemental analysis calcd (%) for $C_{32}H_{32}N_2O_7Zn_2$: C 56.13, H 4.71, N 4.09; found: C 55.86, H 4.75, N 4.13; IR (KBr pellet): $\tilde{\nu}$ = 1655(m), 1598(s), 1582(s), 1486(s), 1451(s), 1414(m), 1382(w), 1276(s), 1095(w), 1053(w), 875(m), 752(s), 700(s), 595(m), 551(m) cm^{-1}.

X-ray crystal data collection and structure determination

The unit cell determination and data collection for the crystal of compound **1** were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic enhanced ultra Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[15] The structure of compound **1** was solved by direct methods and refined by full-matrix least-squares methods with the SHELX-97 program package.[16] All nonhydrogen atoms were located successfully from Fourier maps. H atoms were generated geometrically. Crystal data for compound **1**: $C_{32}H_{32}N_2O_7Zn_2$, M_w = 687.34, triclinic, space group *P*1, a = 7.3268(6) Å, b = 7.3295(6) Å, c = 14.0539(11) Å, α = 102.897(7)°, β = 91.286(6)°, γ = 92.116(7)°, V = 734.8(1) Å^3, Z = 1, T = 293 K, ρ_{calcd} = 1.553 g cm^{-3}, μ = 2.443 mm^{-1}, F(000) = 354, 4634 reflections, 3229 independent reflections, R_{int} = 0.0288, $R_1[I > 2\sigma(I)]$ = 0.0396, wR_2 = 0.0962, GOF = 1.199, Flack parameter = −0.02(4).

CCDC 1451760 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: dyes · luminescence · metal–organic frameworks · sensors · volatile organic compounds

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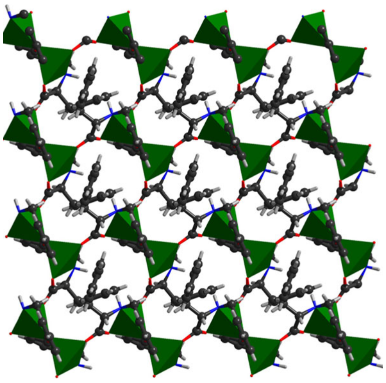
Metal–organic framework sensor: We report an interesting layered coordination network based on the derivative of the natural amino acid L-phenylalanine and zinc ions, which can embed Rhodamine B dye to result in a luminescent sensor of Rho@MOF composite, which can detect different volatile organic compounds with clearly differentiable and unique luminescence readouts by tuning the ligand-to-dye energy transfer (see figure).



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A Highly Sensitive Luminescent Dye@MOF Composite for Probing Different Volatile Organic Compounds