Luminescence ethylenediamine sensor based on terbium complexes entrapment

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A B S T R A C T

Ethylenediamine, as important chemical raw materials and fine chemical intermediates, has been widely applied in various industries. Detection of Ethylenediamine is highly desirable for a number of chemical industries due to its potential threat to human health. Chemical sensing bears an advantage over the traditional analysis method (liquid chromatography) owing to its sensing ability of visual inspection (such as the change in color, luminescence etc). Herein we report a new and solid luminescent material by encapsulating of terbium-acetylacetonate complexes within the cavities of Y type zeolite displaying obvious changes in luminescence colors triggered by solvent vapors, with excellent selectivity for En vapor.

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1. Introduction

Ethylenediamine (En), as important chemical raw materials and fine chemical intermediates, has been widely applied in various industries, such as papermaking [1], medicine [2], and petro-chemicals [3,4] etc. However, En vapor can cause serious health concerns through skin contact and inhalation [5,6]. Hence in order to prevent any possible harm, the spillage of En should be detected efficiently. The traditional detection method (such as liquid chromatography) for En vapor requires specialized instruments and professional and technical personnel etc, [7] which limits its extensive application in sensing field. Therefore, a simple, fast, and reliable analysis method is an urgent need. Luminescence sensing bears obvious advantages over the traditional analysis method because a luminescence sensor can detect an analyte through visual inspection method (such as the change in color, luminescence etc) [8]. However, so far, the luminescence sensors for En vapor have been rarely reported. We recently developed such luminescence sensor by hosting Eu^{3+}-β-diketonate complexes within channels of nanozeolite L (NZL), which show rapid luminescence response and high selectivity for small basic aliphatic amines (like Et$_3$N) [9]. The mechanism behind this is that the decrease of the proton strength in NZL channels [10–13]. Yet, such single-emission sensor is susceptible by variation of several factors such as the sensor concentration, excitation power, and the drifts of the optoelectronic systems such as lamps [14,15]. To overcome these drawbacks, our group develop a luminescence platform based on the entrapment of Eu^{3+} and Tb^{3+} co-doped lanthanide complexes within NZL channels, bringing about the categorization of amine solvents according to pKa value and representing excellent fingerprint correlation between amine solvents with larger pKa value and emission intensity ratio (I_{Eu}/I_{Tb}) by means of control of Ligand-to-Metal and Metal-to-Metal Energy Transfer [16]. Such a luminescence sensor is remarkable for probing amine vapor because it did not require any additional calibration. Unfortunately, these developments have no ability to distinguish En vapor from numerous pollutants. Herein we report a new and solid luminescent material through encapsulating of terbium-acetylacetonate complexes within the cavities of Y type zeolite (ZY), which display excellent selectivity for En vapor.

2. Results and discussion

The Tb(acac$_n$)@ZY composites were prepared via "ship-in-a-bottle" method (see the Experimental Section for more details) [17]. As we all know, the pore entrances of ZY have a diameter of approximately 0.74 nm and the diameter of the supercage is about 1.2 nm [18]. Whereas the ligand acac have a largest diameter of 0.61 nm (<0.74 nm, as shown in Fig. S1), therefore they can be inserted into ZY pores under the experimental conditions and

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luminescent lanthanide complexes $Tb(acac_n)$ can be in-situ formed in the pores of ZY. The Tb^{3+} and acac concentration in the pores of ZY were determined to be 0.86/u.c. and to be 1.54/u.c., which are analysed through the back titration of the supernatant using eth-ylenediamine tetraacetic acid (EDTA) and by elementary analysis respectively. The ZY crystals used in this study have average diameter of 500 nm as revealed by the SEM images (Fig. S2a), which also displays highly crystalline by the XRD pattern (Fig. S3a) matching well with the previous report [19]. After encapsulating $Tb(acac_n)$ within the ZY channels, the morphology and size of ZY has no obvious changes (Fig. S2b) and their crystallinity remains unchanged (Fig. S3b).

The luminescent data of $Tb(acac_n)@ZY$ were recorded and shown in Fig. S4. The excitation spectrum monitored at 544 nm ($^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}) displays a broad band with two components centered at 270 nm and 317 nm, which can be attributed to the absorption of the ligand acac, while the band at 365 nm is very weak due to a low absorption coefficient (black line in Fig. S4). Excitation into the broad absorption at 317 nm leads to the emission spectrum consisting of four sharp lines at 490, 544, 584, and 620 nm, which is ascribed to the $^5D_4 \rightarrow {}^7F_J$ ($J = 6,5,4,3$) transition (blue line in Fig. S4). It is dominated by the $^5D_4 \rightarrow {}^7F_5$ line at 544 nm, which is responsible for the green light when illumi-nated with a UV lamp (302 nm) shown in Fig. 1a. The emission intensity is somehow sensitive to the vapors of various solvents as

Fig. 1. a) Digital photographs of $Tb(acac_n)@ZY$ upon contact with various solvent va-pors for 10 min under near UV irradiation at 365 nm. (ethylenediamine: En, triethyl-amine: Et_3N, n-butylamine: n-$BuNH_2$, aniline: Ani, Methyl methacrylate: MMA, Acetonitrile: MeCN, Ethanol: EtOH, Dichloromethane: CH_2Cl_2; b) Emission spectra of $Tb(acac_n)@ZY$ before (black line) and after exposure to En (red line), Propanediamine (green line), Et_3N (blue line), MMA (cyan line), and EtOH (magenta line), MeCN (olive line), Acetone (orange line) and CH_2Cl_2 (Gray line) excited at 302 nm. Inset: Increase for Tb^{3+} emission intensity at 544 nm upon exposure to various solvents vapors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shown in Fig. 1b, although the emitting colors remain unchanged (Fig. 1a). All the solvents except CH_2Cl_2 can lead to luminescence enhancement of $Tb(acac)_n@ZY$, and this enhancement caused by En vapor is the most remarkable. Surprisingly, the totally different situation can be observed when $Tb(acac)_n@ZY$ is illuminated with a UV lamp (365 nm). The emitting color of $Tb(acac)_n@ZY$ changes from weak green to bright blue (Fig. 2) for En vapor, whereas most of solvents give weak green light with different brightness levels (Fig. 2). The observed emission colors match well with the calcu-lated chromaticity coordinates according to the 1931 Commission Internationaled' Eclairage (CIE) chromaticity diagram. As shown in Fig. 3, En corresponds to the chromaticity coordinate (0.21, 0.22), while other solvents range from (0.26, 0.33) to (0.31, 0.49). There-fore, such a luminescent material displays excellent selectivity for En vapor, taking an important step forward to the detection of En.

To probe the sensing mechanism of $Tb(acac_n)@ZY$ for En vapor, we measured luminescence data of $Tb^{3+}(acac_n)@ZY$ before and after treated with En vapor. As we discussed above, the excitation spectrum has a weak absorption band at 365 nm (black line in Fig. S4), which can explain why $Tb(acac_n)@ZY$ exhibits weak green emission when illuminated with a 365 nm UV lamp (Fig. 2). The emission spectrum of $Tb(acac_n)@ZY$ excited at 365 nm shows four characteristic peaks of Tb^{3+} at 490, 544, 584, and 620 nm (red line in Fig. S4). Interestingly, upon exposure to En vapor, a broad band centered at 415 nm emerged in the emission spectrum of $Tb(acac_n)$ @ZY and the emission intensity of $^5D_4$ for $Tb(acac_n)@ZY$ had an obvious increase (red line in Fig. S5). What was the reason for the occurrence of the broad band at 415 nm? The luminescence data of $(acac_n)@ZY$ were also analysed to find an answer to this question. As shown in Fig. S5 (magenta line), no obvious band can be detected in the emission spectrum of $(acac_n)@ZY$. However, after treatment with En vapor, $(acac_n)@ZY$ displays a broad emission band at 415 nm using an excitation wavelength of 365 nm (blue line in Fig. S5). Moreover, the emission intensity of the broad band at 415 nm for $(acac_n)@ZY@En$ is approximately equivalent to that for $Tb(acac_n)@ZY@En$ (Fig. S5), implying that this broad band is mainly caused by a definite interaction with the ligand acac constructed by the En molecules, which can be supported by the FTIR spectra (Fig. S6). Fig. S6a and Fig. S6b show the FTIR spectra of $(acac_n)@ZY$ before and after treatment with En vapor, respectively. In com-parison to $(acac_n)@ZY$ (Fig. S6a), upon treatment with En vapor, we can observe the generation of additional intense bands at about 1586 cm^{-1}, 1484 cm^{-1}, 1387 cm^{-1} and 1327 cm^{-1} assigned to the C=N and C–N stretching, which is probably resulting from the interaction between the $-NH_2$ group of En and the $-C=O$ group of acac molecules. Apart from this, Fig. S6a has identical absorption peaks with Fig. S6b. The intense peak at 1026 cm^{-1} can account for $v_{as}(T-O)$ stretching vibration (T = Si^{4+} or Al^{3+}) [20] and the broad band at 3430 cm^{-1} is due to the stretching modes of water mole-cules [12]. The absorption band near 1634 cm^{-1} can be considered to be a superposition of the bending vibrations of lattice water molecules (and surface silanol groups) and the C=O stretching vibrations of acac. Furthermore, owing to the occurrence of the broad band at 415 nm, we speculate that the reaction product may possess conjugate structure [21] and the possible structure (pos-sessing two conjugated groups) is displayed in Fig. S7. The occur-rence of the above reaction may be attributed to that the size of the possible product structure is roughly 1.12 nm (<1.2 nm [18], shown in Fig. S8) and the structural features of En (such as the small steric hindrance and two amino group) is favourable to the aforemen-tioned reaction. Subsequently, we discussed the emission intensity enhancement of $^5D_4$ for $Tb(acac_n)@ZY$ treated with En vapor. Upon exposed to En vapor, the excitation spectrum of $Tb(acac_n)@ZY$ displays an enhanced and broadening band ranging from 250 nm to 370 nm (Fig. S9a). In thi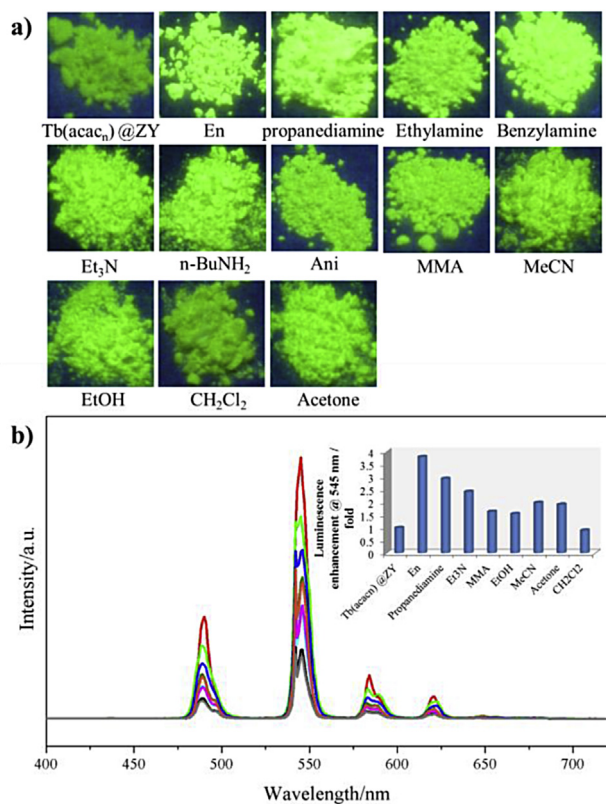s case, the absorption intensity at 365 nm