

Dual-emission Tb-based MOF induced by ESPT for ratiometric ammonia sensing

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Materials.

Terbium(III) acetate hydrate [Tb(OAc)₃·xH₂O], 2,5-dihydroxyterephthalic acid (H₄dobdc) were purchased from Energy Chemical (Shanghai, China). N,N-dimethylformamide (DMF), ethanol, ammonia were purchased from Sinopharm Chemical Reagent Co., Ltd. Pure water was purchased from Shenyang Wahaha Group Co., Ltd. All chemicals used in this study were of analytical grade and used without further purification.

Characterization.

Single-crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The scanning electron microscopy (SEM) images were obtained by Hitachi SU8010 field emission SEM operating at primary electron energy of 15 kV. X-ray diffraction (XRD) patterns were collected on Shimadzu XRD-6000 instrument equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of 5° - 50° at room temperature. Fourier transform infrared spectra (FT-IR) were recorded using a Bruker VERTEX 70 with KBr pellets. Thermogravimetric analysis (TGA) was performed on a thermobalance (TGA-2050, TA Instruments) under nitrogen from room temperature to 1000 °C with a heating rate of 10 °C/min. The fluorescence spectra were obtained through fluorescence spectrophotometer (Hitachi F4600) equipped with a 150 W xenon lamp as the excitation source. XPS The compositions of the materials were analyzed through quantitative X-ray photoelectron spectroscopy (AXIS SUPRA). The binding energy of C 1s peak at 284.8 eV is used as the reference calibration.

TD-DFT calculations.

This complex structure of ammonia adsorbed on 2,5-Dihydroxyterephthalic acid (H_4dobdc) molecule was optimized with dispersion corrected density functional theory (DFT-D3) at the PBE0-D3/def2-SVP level using Gaussian program. The SMD (Solvation Model Based on Density) [10.1021/jp810292n] implicit solvent model was used to describe the solvation effect. From the Kasha's rule, the fluorescence spectrum is usually related to the radiation transition of the first singlet excited state (S_1). In order to simulate the emission spectrum of molecule DHTA-NH₃ in solvent environment, the molecular geometry at S_1 excited state was then optimized at the PBE0/def2-SVP level with the time-dependent density functional theory (TDDFT) method.

Synthesis of Tb-DOBDC.

Tb(OAc)₃·xH₂O and 2,5-dihydroxyterephthalic acid (H₄dobdc) were respectively dissolved in a ternary mixture of water, ethanol and DMF in a volume ratio of 1:1:15 with concentration of 0.02 mol·L⁻¹. In a glass culture dish with a diameter of 6 cm, added 1 mL of distilled water to 3 mL of H₄dobdc solution and stirred evenly, and then slowly dropped 3 mL Tb(OAc)₃·xH₂O solution into the above mixed solution and shaken well while adding. Tb-DOBDC was prepared by standing at room temperature for 24 h, and washing with ethanol for 3 times, filtering and naturally drying.

Crystal Structure Determinations.

Single-crystal X-ray diffraction data of Tb-DOBDC were collected on a Bruker APEX-II CCD diffractometer at 173 K with a graphite-monochromatic Mo K α radiation ($\lambda=0.71073$ Å). The structures were solved by direct method with the SHELXS-97 structure solution program and refined by full-matrix least-squares techniques on F² with the SHELXL-2014 refinement package. The detailed crystallographic data, the structure refinement parameters and the important bond lengths/bond angles are provided in Table S1-S3. Cambridge Crystallographic Data Centre (CCDC) No 2262522 contains the supplementary crystallographic data for Tb-DOBDC.

Table S1 Crystal data and structure refinement for Tb-DOBDC

Empirical formula	C ₁₈ H ₂₀ N ₂ O ₁₁ Tb
Formula weight	672.39
Temperature	173 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.4819(7) Å b = 10.9273(7) Å c = 12.5634(7) Å α = 104.646(4)° β = 108.134(4)° γ = 97.016(5)°
Volume	1291.14(14) Å ³
Z	2
Mu(mm ⁻¹)	2.805
Density (calculated)	1.729 g/m ³
F(000)	670.0
Theta range for data collection	3.03 to 25.10°
Index ranges	-12 ≤ h ≤ 12 -12 ≤ k ≤ 12 -14 ≤ l ≤ 14
Reflections collected	12784
Independent reflections	4474 [R(int) = 0.0187]
Completeness to theta=25.10°	98.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4474 / 0 / 373
Goodness-of-fit on F ²	1.139
Final R indices [I > 2σ(I)]	R1 = 0.0190, wR2 = 0.0466
R indices (all data)	R1 = 0.00207, wR2 = 0.0479
Extinction coefficient	n/a

Table S2 Selected bond lengths (Å) for Tb-DOBDC

Tb1-O1	2.3347(18)
Tb1-O3	2.575(2)
Tb1-O4	2.3788(19)
Tb1-O6	2.3105(19)
Tb1-O7	2.421(2)
Tb1-O8	2.3895(18)
Tb1-O10	2.3854(19)
Tb1-O12	2.378(2)
Tb1-C6	2.844(3)

Table S3 Selected bond angles (°) for Tb-DOBDC

O3-Tb1-O1	151.43(6)
O4-Tb1-O1	126.62(7)
O7-Tb1-O1	73.99(7)
O8-Tb1-O1	78.78(7)
O10-Tb1-O1	145.89(7)
O12-Tb1-O1	78.18(7)
C6-Tb1-O1	163.29(7)
C6-Tb1-O3	26.62(7)
O3-Tb1-O4	68.50(6)
O7-Tb1-O4	141.16(7)
O8-Tb1-O4	77.94(7)
O10-Tb1-O4	77.84(7)
C6-Tb1-O4	70.08(7)
O1-Tb1-O6	77.23(7)
O3-Tb1-O6	131.24(6)
O4-Tb1-O6	76.03(7)
O7-Tb1-O6	78.27(8)
O8-Tb1-O6	122.30(7)
O10-Tb1-O6	88.49(7)
O12-Tb1-O6	145.88(7)
C6-Tb1-O6	109.79(7)
O3-Tb1-O7	110.22(7)
C6-Tb1-O7	92.27(8)
O3-Tb1-O8	81.99(6)
O7-Tb1-O8	140.87(7)
C6-Tb1-O8	108.05(8)
O3-Tb1-O10	52.67(6)
O7-Tb1-O10	72.84(7)
O8-Tb1-O10	133.89(7)
C6-Tb1-O10	26.11(8)
O3-Tb1-O12	76.52(7)
O4-Tb1-O12	138.07(7)
O7-Tb1-O12	72.44(8)
O8-Tb1-O12	74.89(7)
O10-Tb1-O12	99.02(7)
C6-Tb1-O12	88.76(8)

Fluorescence properties

The well-dispersed and stable Tb-DOBDC suspension was generated by diffusing 5 mg Tb-DOBDC powder in 50 mL DMF and ultrasound treatment for 40 min. For fluorescence experiments, ammonia was diluted with water in order to detect lower concentrations. Different volumes of ammonia were added to 3 mL of Tb-DOBDC suspension in quartz cuvette to prepare a series of concentrations of ammonia for fluorescence testing. The concentrations of ammonia were calculated according to by equation (1).

$$C = \frac{1000 \times \rho \times \omega \times V}{3 \times 10^{-3} \times M} \quad (1)$$

Where C = concentration of ammonia, ρ = density of ammonia (0.91 g cm^{-3}), ω = 25% (mass fraction of ammonia), V = volume of ammonia added, and M = molecular weight (17 g mol^{-1}).

For the sensing experiments toward various interferences, the various interferences (acetone, methylbenzene, n-hexane, dichloromethane, trichloromethane, acetonitrile) with a concentration of 0.1 mM were added to the Tb-DOBDC solution respectively. And then mixed with 0.1 mM ammonia to record the corresponding emission spectra.

The emission spectra for the samples in range of 350-700 nm under single excitation at 313 nm were determined by a Hitachi F4600 fluorescence spectrometer.

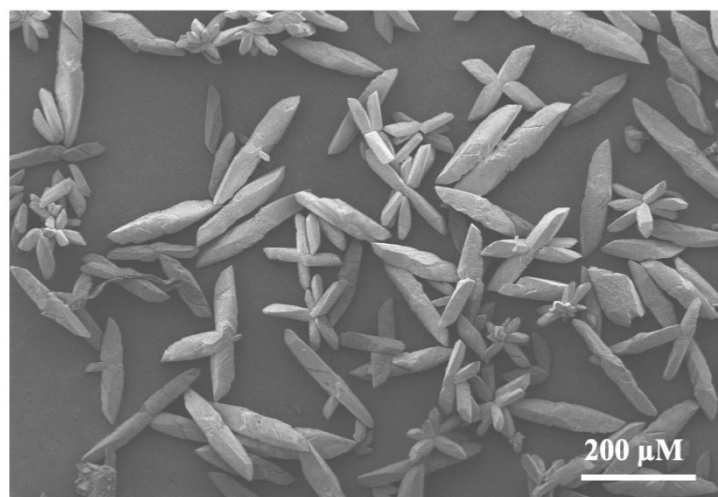


Fig. S1 The scanning electron microscopy (SEM) image of Tb-DOBDC.

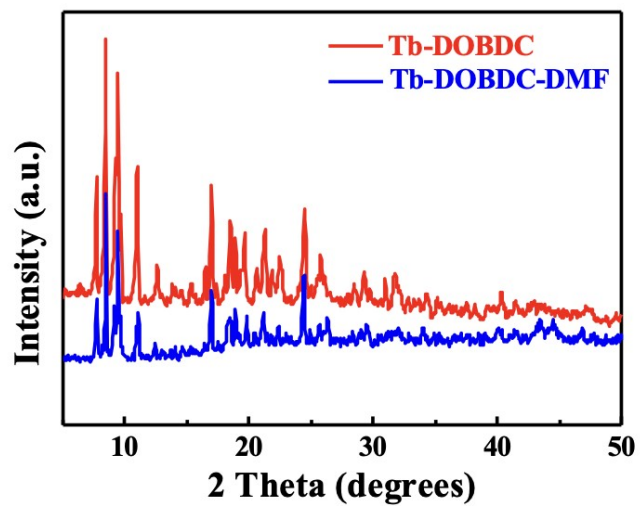


Fig. S2 The PXRD patterns of Tb-DOBDC sample and after immersion in DMF solvent.

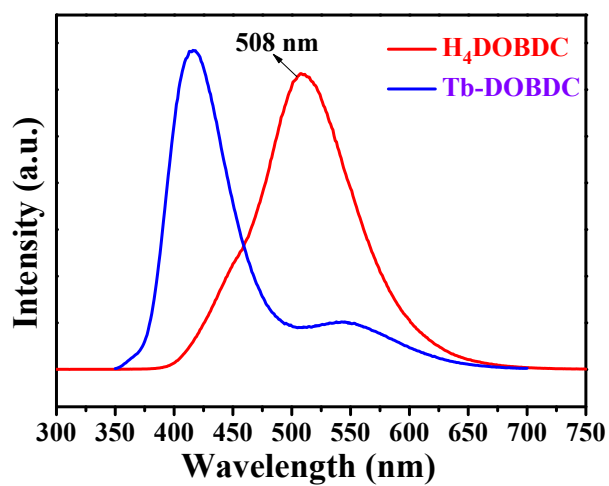


Fig. S3 The fluorescence emission spectra of organic ligand (H₄dobdc) and as-synthesized Tb-DOBDC.

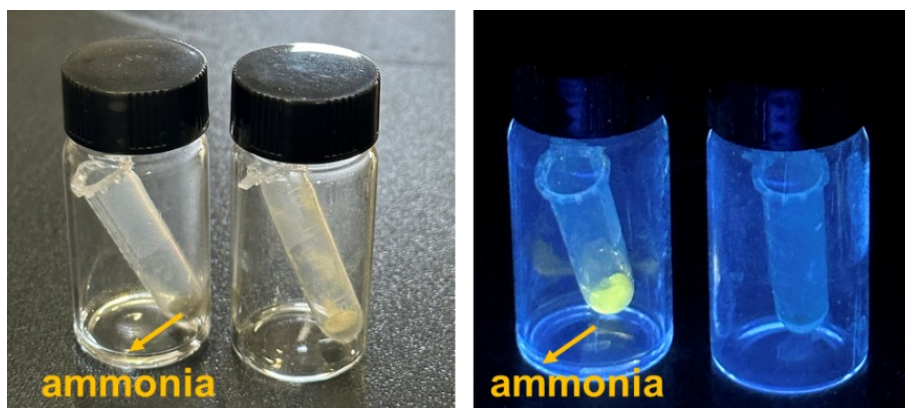


Fig. S4. The digital photographs of Tb-DOBDC and after adding ammonia under normal light photos (left) and the ultraviolet irradiation (right).

When exposed to ultraviolet light, the Tb-DOBDC with ammonia vapor showed yellow-green light, while the Tb-DOBDC without ammonia vapor atmosphere had a slight blue light, which was consistent with the fluorescence detection results. During the experiment, it was found that after the solid Tb-DOBDC was put into ammonia vapor for a few seconds, it gave off a yellow-green light under ultraviolet irradiation. When the Tb-DOBDC is exposed to air for a few seconds, it returns to its original state under ultraviolet light. Repeat the operation four times can be restored to the original state. This indicates that Tb-DOBDC has excellent repeatability in ammonia detection, and the response time and recovery time are within a few seconds.

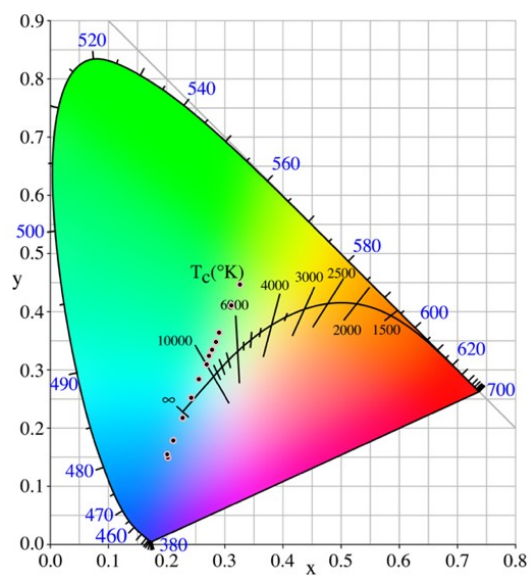


Fig. S5 CIE chromaticity coordinates of Tb-DOBDC in the concentration range of 1-300 μ M ammonia.

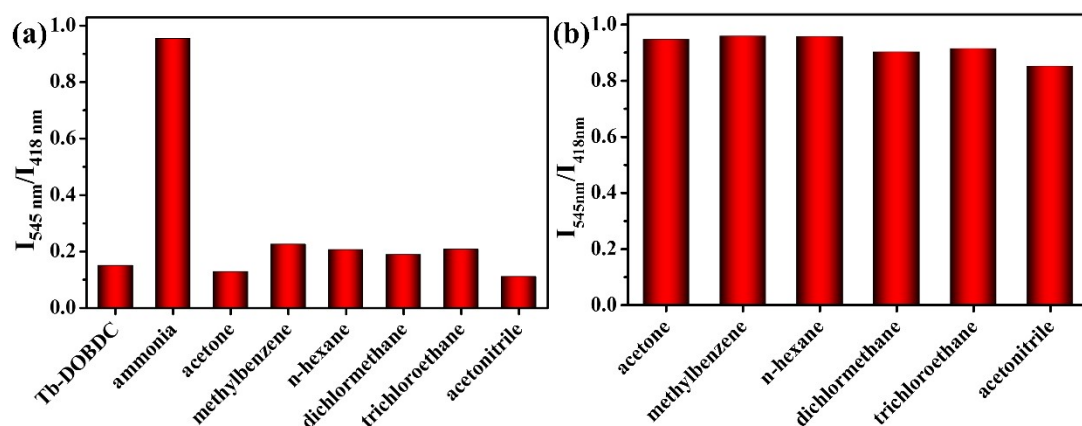


Fig. S6 (a) Selectivity sensing ability of Tb-DOBDC toward various typical interferents, (b) anti-interference sensing ability of Tb-DOBDC.

The selectivity sensing ability for Tb-DOBDC against various typical interferents has been tested. The various interferences (acetone, methylbenzene, n-hexane, dichlormethane, trichlormethane, acetonitrile) with a concentration of 0.1 mM were added to the Tb-DOBDC solution respectively. As shown in Fig. S6a, Tb-DOBDC demonstrates high selectivity for ammonia, with virtually no effect on interferents. And then mixed with 0.1 mM ammonia to record the changes of fluorescence intensity (Fig. S6b). The ratio fluorescence values ($I_{545\text{nm}}/I_{418\text{nm}}$) of Tb-DOBDC were not significantly different from those of pure ammonia, indicating that Tb-DOBDC has excellent anti-interference performance.

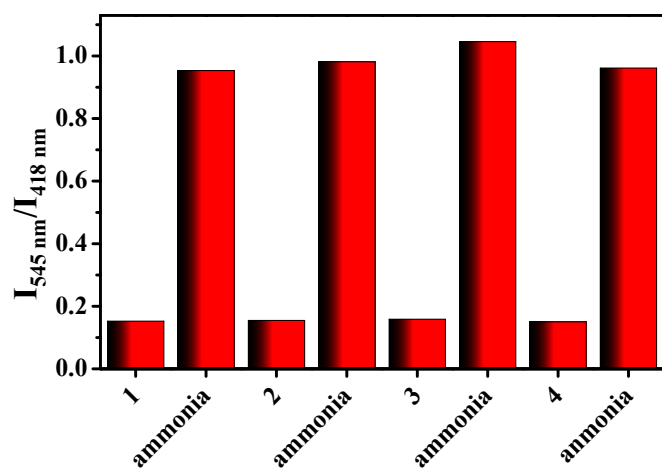


Fig. S7 The reproducibility for Tb-DOBDC in detecting ammonia.

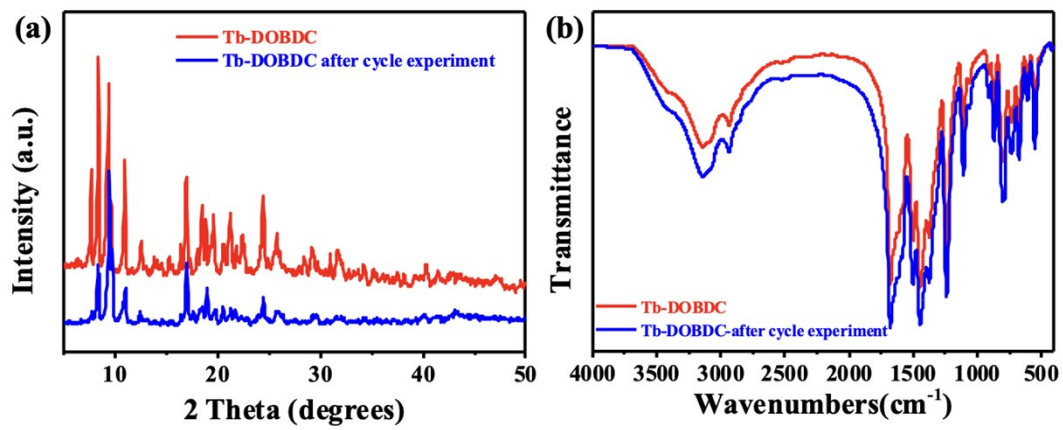


Fig. S8 (a) The XRD and (b) the FT-IR of Tb-DOBDC and Tb-DOBDC after cycle experiment.

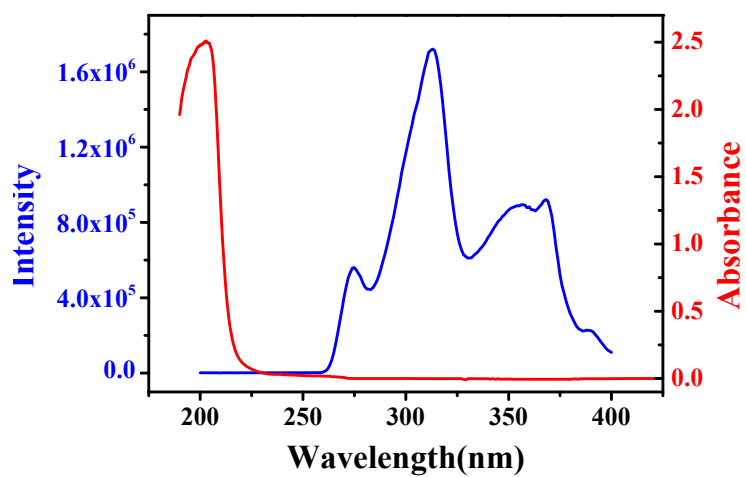


Fig. S9 The absorption spectrum of ammonia (1 mM) and the excitation spectrum of Tb-DOBDC.

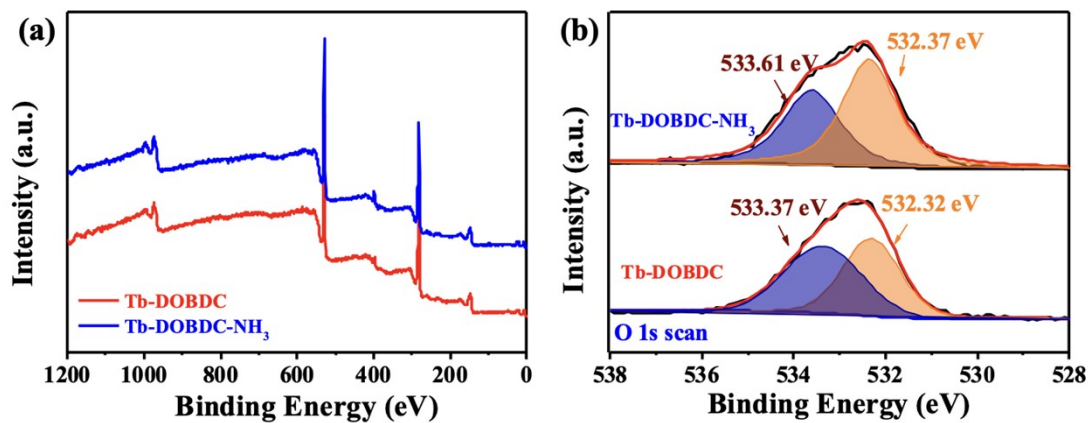


Fig. S10 XPS spectra of original Tb-DOBDC and ammonia-impregnated Tb-DOBDC: (a) XPS full spectrum, (b) Zn 2p spectra.

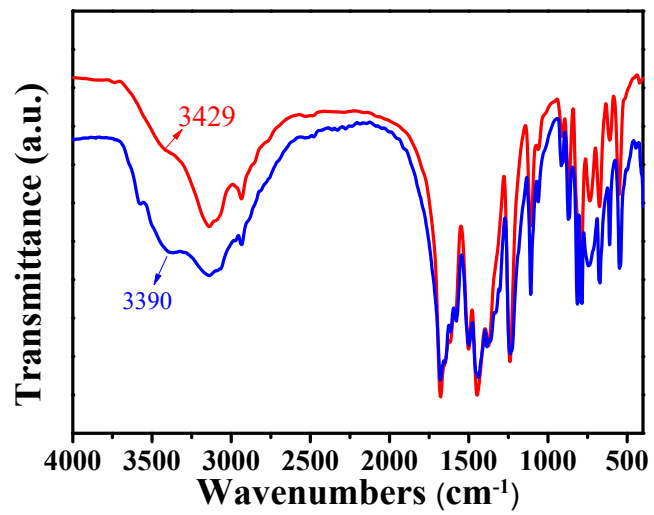


Fig. S11 The FT-IR spectra of Tb-DOBDC and Tb-DOBDC exposed to ammonia.

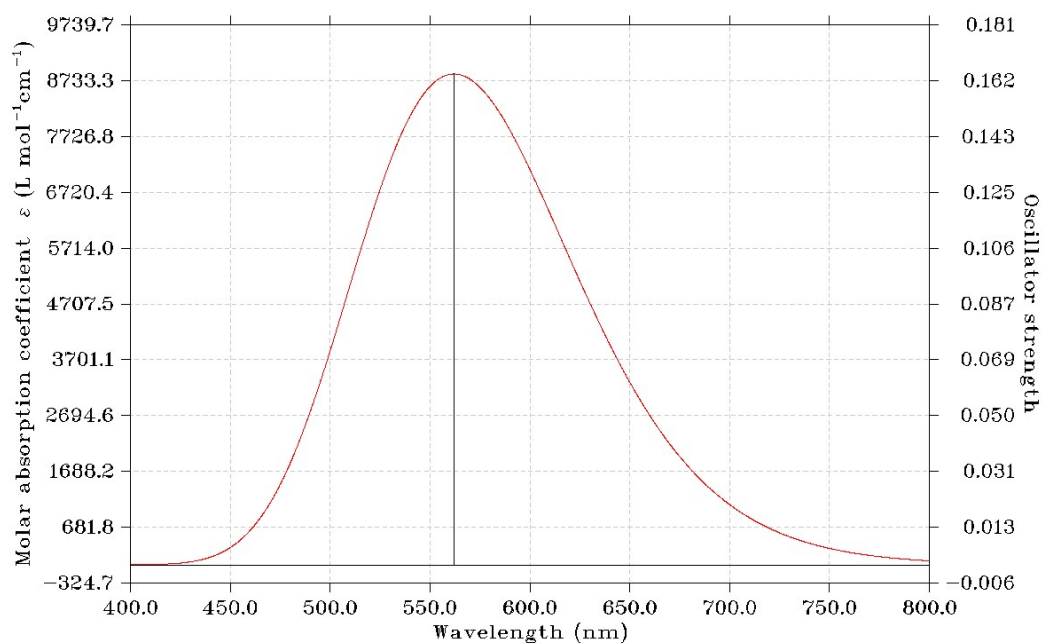


Fig. S12 The calculated emission band obtained by TD-DFT method.

Comparing with the geometry at ground state, there is an obvious proton transfer between phenolic hydroxyl group and ammonia group at S1 excited state. And the photophysical characteristics of the excited states of Tb-DOBDC are also in good agreement with the experimental results.

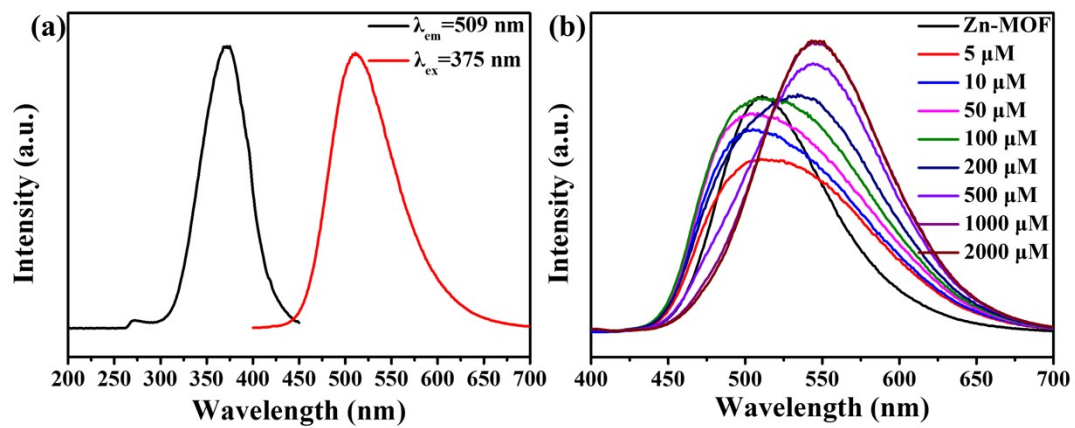


Fig. S13 (a) The excitation and emission spectra of Zn-DOBDC in DMF, (b) The fluorescence emission spectra of Zn-DOBDC suspension upon increase of the concentrations of ammonia at excitation wavelength of 375 nm.