

Supporting Information

New imine-linked conjugated mesoporous polymer for turn-on fluorescence detection of Ga³⁺

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Experimental Detail

Chemicals and instrumentation

Unless otherwise specified, all the reagents and chemicals acquired from commercial suppliers and utilized without further purification. The characterization of TM-HB had been performed in detail. Ultrapure water from Milli-Q water purification system was utilized in all the experiments. A Nicolet IS50 Fourier transform infrared spectrometer was used to record the Fourier transform infrared (FT-IR) spectra. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Multilab 2000 system equipped with Al K α radiation. Bruker AVANCE III 400 WB spectrometer was used for ^{13}C CP/MAS NMR in solid state using a magnetic field of 9.39 T with a 4 mm standard bore CPM AS probe head at 297K. A Rigaku Dmax 2200 PC diffractometer was utilized to perform PXRD measurements. Hitachi SU8010 scanning electron microscope (SEM) was used to see the morphology of the TM-HB. The N_2 adsorption and desorption isotherms and pore size distribution were obtained at 77 K with an Autosorb iQ2 adsorptometer. The METTLER-TOLEDO TG/DTA analyzer was utilized for thermogravimetric analysis (TGA). UV-vis absorption spectra data was taken from a Varian Cary 500 Spectrophotometer. Fluorescence spectra was measured on an F-4600 spectrometer (Hitachi, Japan). The fluorescence lifetime analysis was performed on Edinburgh Fluorescence Spectrometer (FLS920P). DFT calculations were performed on Guassian 9.0 software.

Synthesis of TM-HB

The solvents ratio, catalytic amount of acetic acid, concentration, temperature and reaction time played a pivotal role in the novel synthesis of TM-HB conjugated mesoporous polymer, as given in Table S1. A new method had been developed to facile synthesis of TM-HB conjugated mesoporous polymer at room temperature by Schiff-base condensation. In this method, the synthesis of TM-HB conjugated mesoporous polymer was performed at room temperature through the co-condensation of Tris(4-aminophenyl) methane (TM) (0.06 mmol, 17.36 mg) and 5-hydroxy-benzene-1,3-dicarbaldehyde (HB) (0.09 mmol, 13.51 mg) in the Pyrex tube by adding mesitylene (1 mL) and 1,4-dioxane (1 mL) in the mixture by 1:1. AcOH (3 M, 0.2 mL) after 12 minutes of sonication was added and flash frozen in the liquid nitrogen bath for the three pump thaw cycles at 77 K. The liquid nitrogen bath for the three pump thaw cycles were used only to

remove the air from the Pyrex tube. The Schiff base condensation reaction was carried out at room temperature. The tube was immersed in a water tub placed under the shade at room temperature for 72 hours after flame sealing, yielding light pink precipitates. These precipitates were collected by breaking the tube at the neck and soaked for 15 minutes in N,N-dimethylformamide (DMF) and washed with DMF, tetrahydrofuran (THF) and acetone three times to get rid of guest molecules. Afterwards, these precipitates were kept for drying for 12 hours at 90 °C aiming to get rid of the solvent molecules and yielding TM-HB as light pink powder (71%).

Fluorescence Quantum yield

Quantum yield (Q) of TM-HB and TM-HB@Ga³⁺ was measured according to the reported method in the literature³⁶ using quinine sulfate as reference (Q_s = 54 %, 0.01 mol/L H₂SO₄). Following equation is used to calculate the value of quantum yield (Q):

$$Q (\%) = Q_s \times S/S_s \times n^2/n_s^2 \times 100\%$$

Here, “S” and “S_s” are fluorescence peak areas of the conjugated polymer and quinine sulfate respectively, “n” and “n_s” are the refractive indexes of the solvents.

Stock solutions preparation

10.0 mg of TM-HB was evenly dispersed in 200 mL of different solvents under ultrasonic for 30 minutes to get the suspension. The aqueous metal ions stock solutions (20 mM) including Fe²⁺, K⁺, In³⁺, Na⁺, Sr²⁺, Ag⁺, Cd²⁺, Al³⁺, Sn²⁺, Fe³⁺, Mg²⁺, Cr³⁺, As³⁺, Tl³⁺, Co²⁺, Pb²⁺, Hg²⁺, Mn²⁺, Cu²⁺, Ba²⁺, Zn²⁺, Ca²⁺, Ga³⁺, Ni²⁺, and Li⁺ were also prepared from their corresponding salts. During selective experiment, the aforementioned metal ions solutions (30 μL) were separately added to TM-HB suspension (3.0 mL).

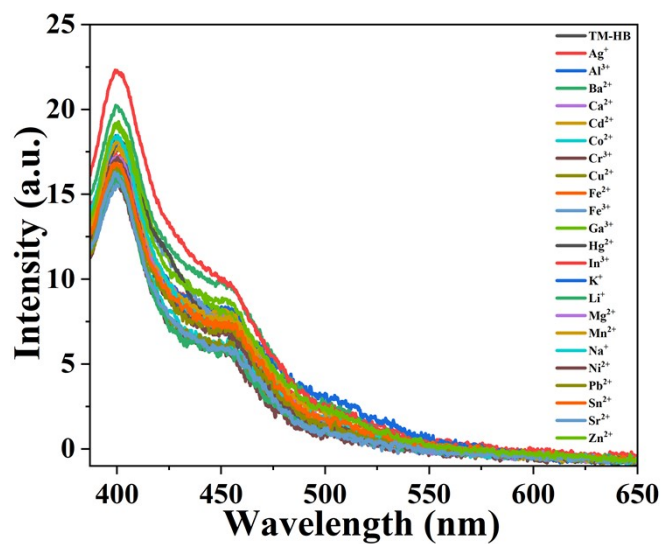


Figure S1. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in methanol upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 367 \text{ nm}$)

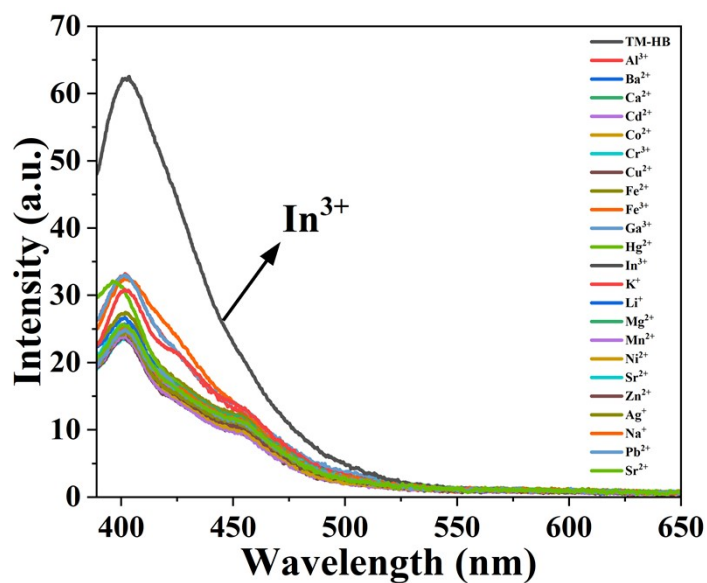


Figure S2. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in ethanol upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 369 \text{ nm}$)

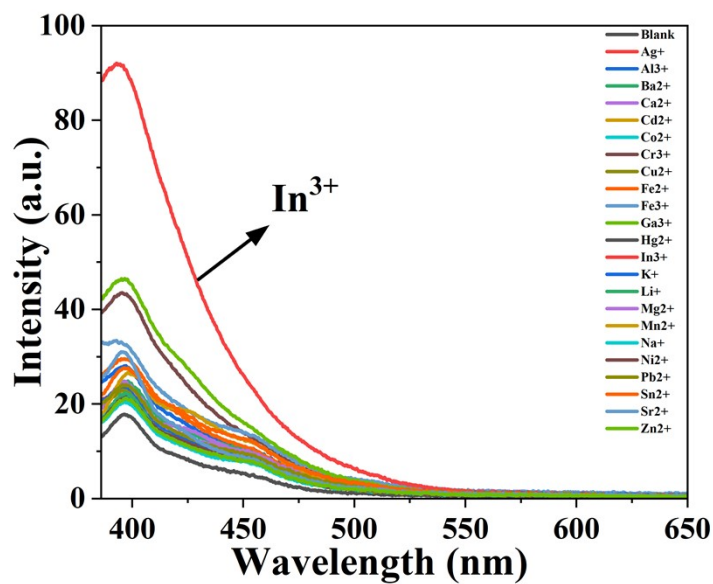


Figure S3. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in 1,4-dioxane upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 366 \text{ nm}$)

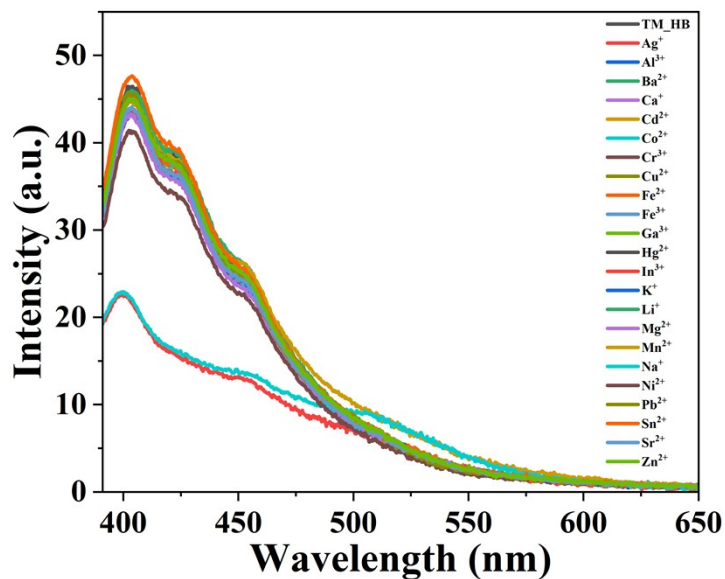


Figure S4. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in DMF upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 371 \text{ nm}$)

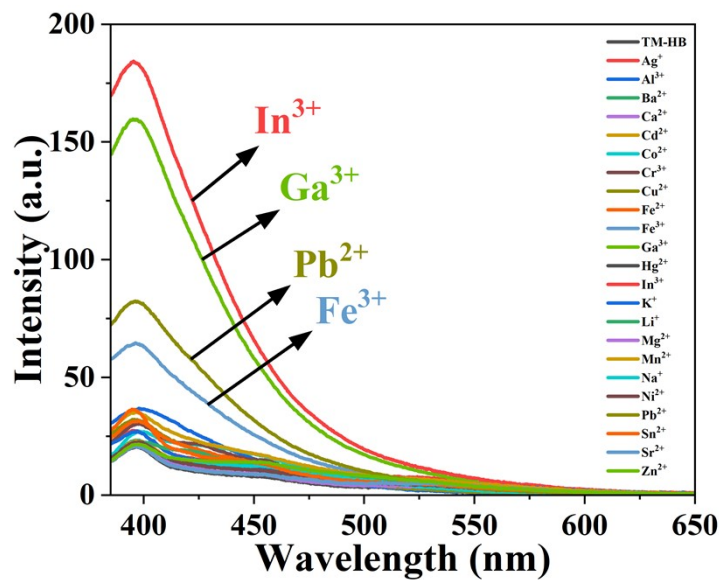


Figure S5. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in THF upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 365 \text{ nm}$)

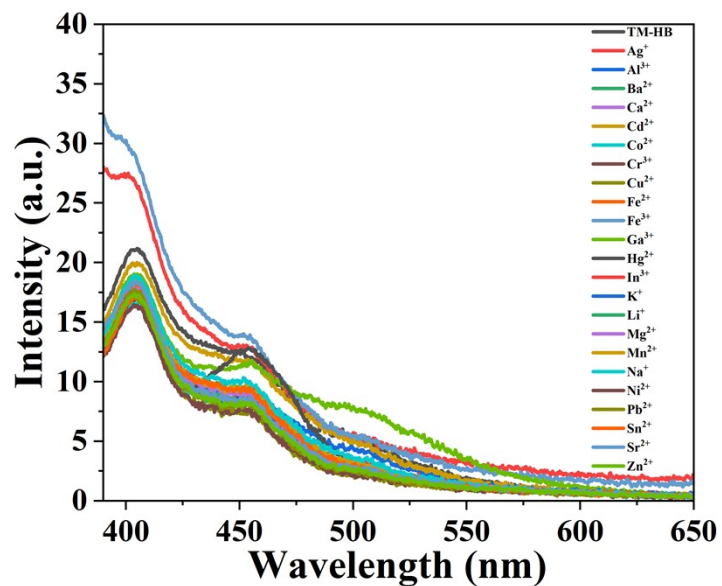


Figure S6. Fluorescence emission spectra of TM-HB (0.05 mg/mL) in water upon the addition of different metal ions (20 mM) ($\lambda_{\text{ex}} = 366 \text{ nm}$)

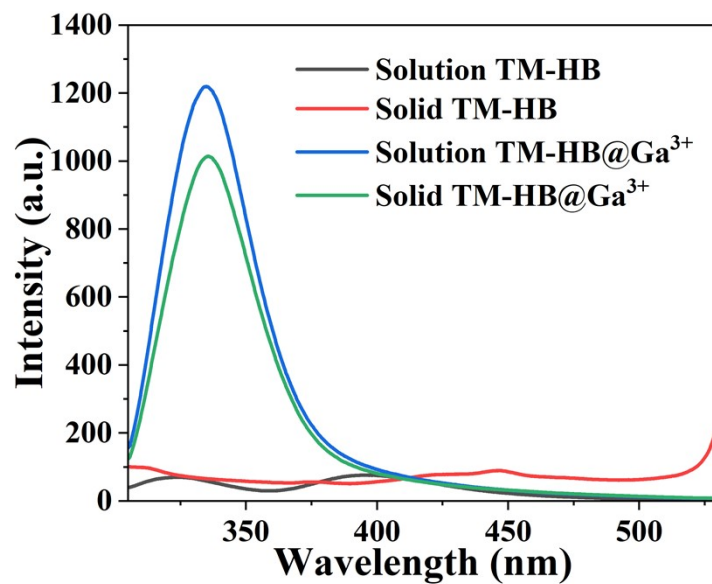


Figure S7. Comparison of fluorescence emission spectrum of TM-HB and TM-HB@Ga³⁺ in solid form and solution form

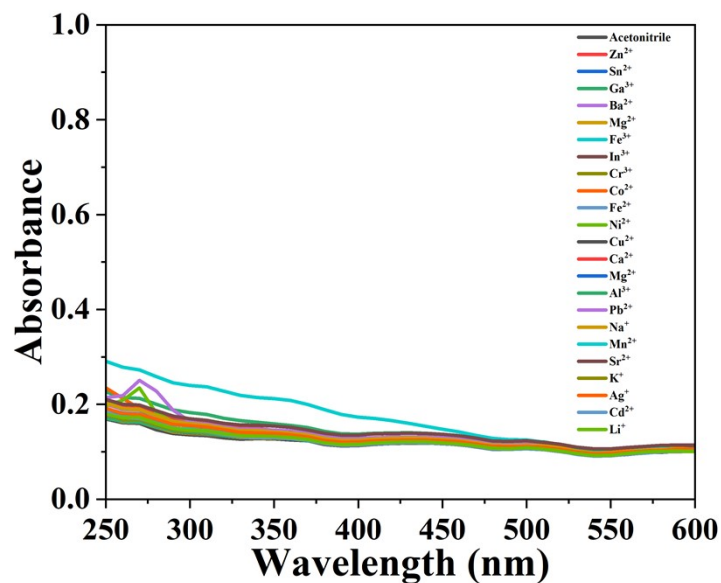


Figure S8. UV-vis absorbance spectra of various metal ions in acetonitrile

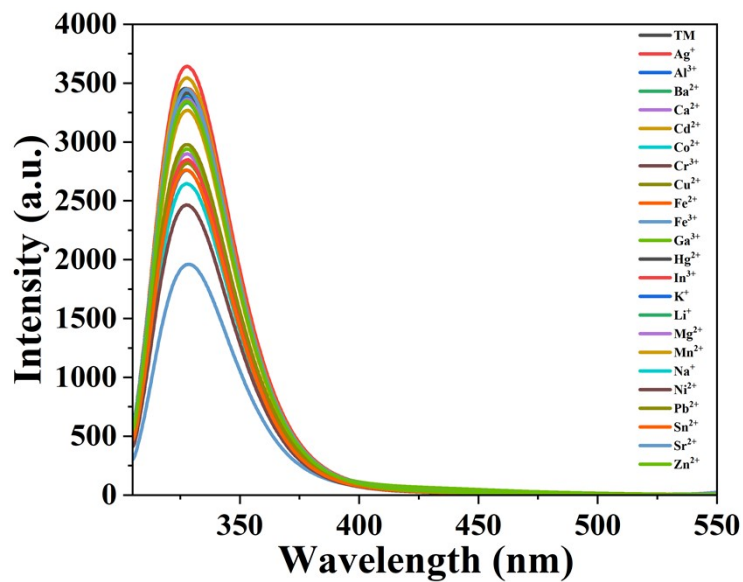


Figure S9. Fluorescence emission spectra of TM (0.05 mg/mL) in acetonitrile in the presence of various metal ions at the excitation wavelength of 285 nm

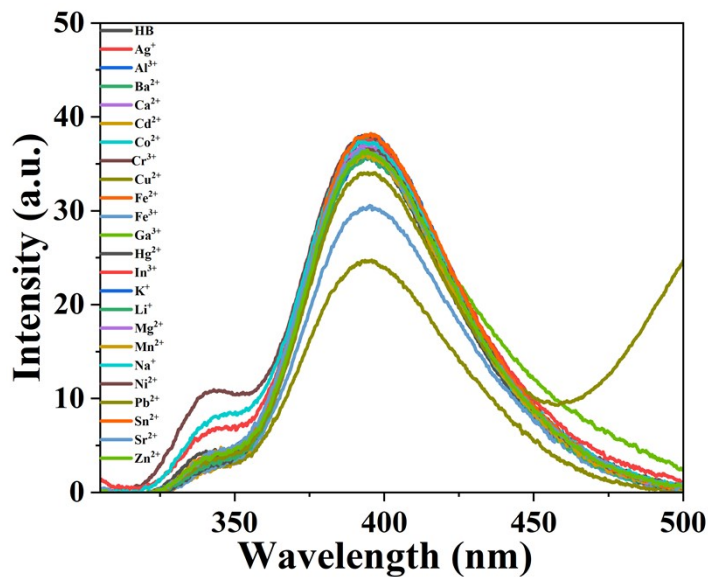


Figure S10. Fluorescence emission spectra of HB (0.05 mg/mL) in acetonitrile in the presence of various metal ions at the excitation wavelength of 285 nm

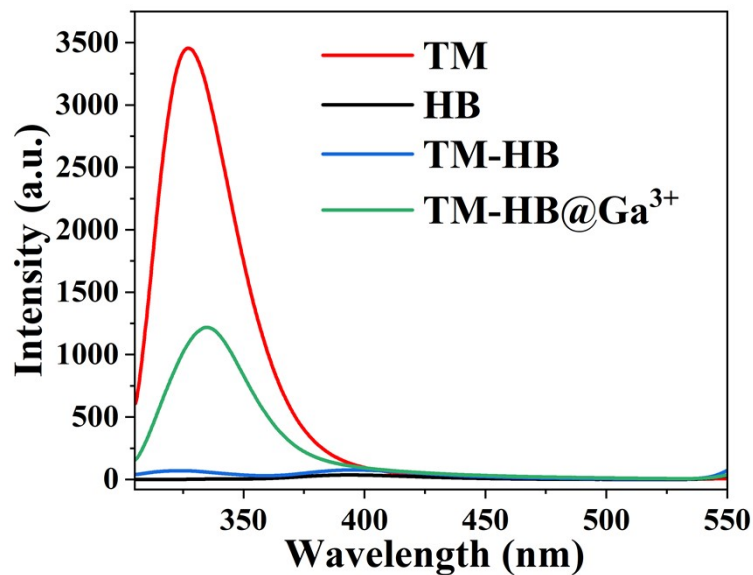


Figure S11. Fluorescence emission spectra of TM, HB, TM-HB and TM-HB@Ga³⁺ (0.05 mg/mL) in acetonitrile at the excitation wavelength of 285 nm

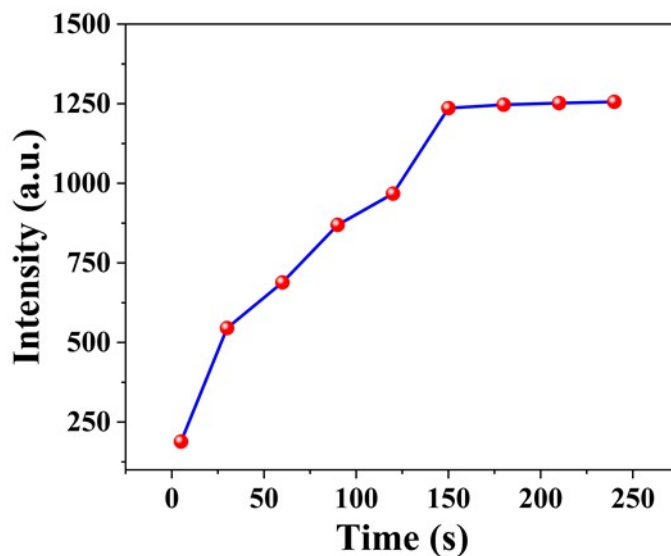


Figure S12. Fluorescence intensity of TM-HB (0.05 mg/mL) in acetonitrile with the addition of Ga³⁺ ion at $\lambda_{em} = 335$ nm and $\lambda_{ex} = 285$ nm

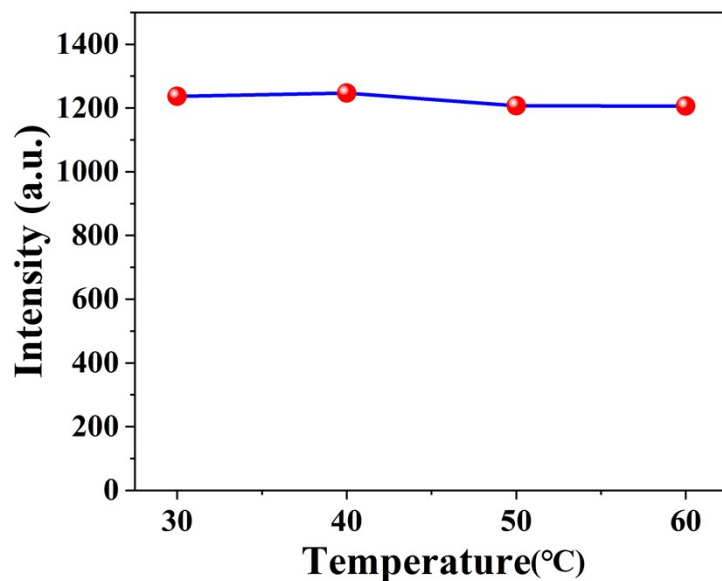


Figure S13. Fluorescence intensity at 335 nm of TM-HB@Ga³⁺ (0.05 mg/mL) at different temperatures in acetonitrile

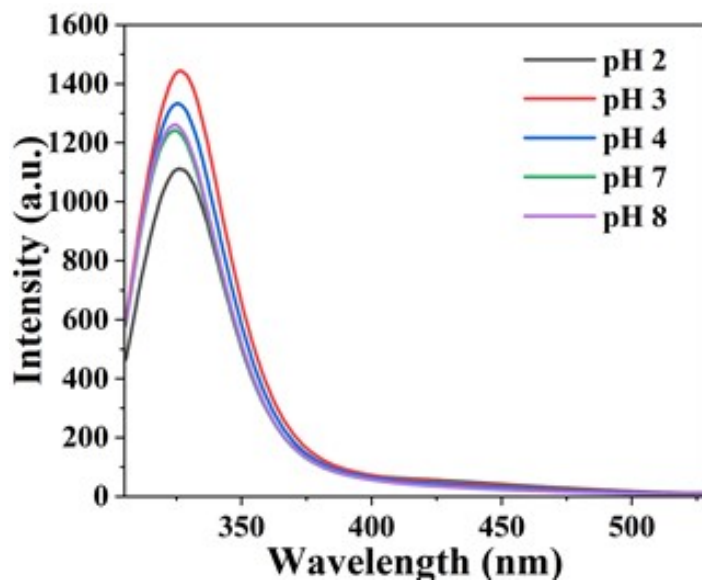


Figure S14. Fluorescence spectra of TM-HB@Ga³⁺ at different pH values

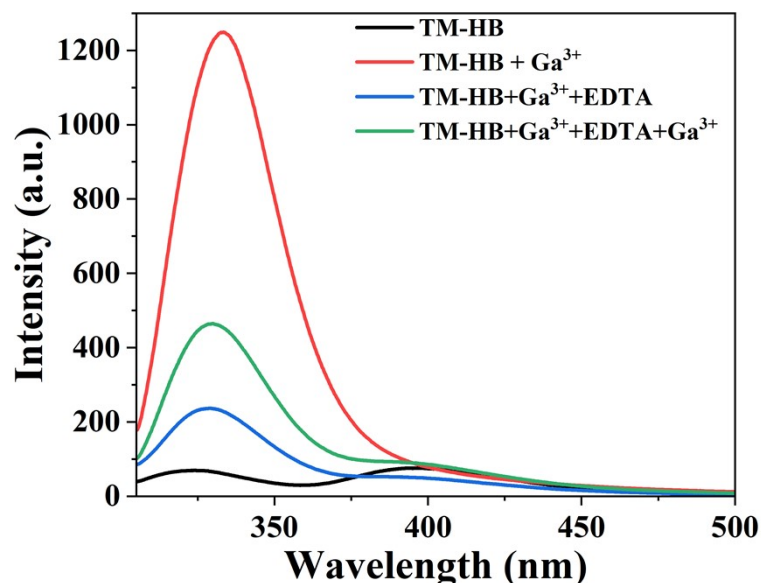


Figure S15. Fluorescence emission spectra of TM-HB, TM-HB@Ga³⁺, TM-HB@Ga³⁺@EDTA and TM-HB@Ga³⁺@EDTA@Ga³⁺ in acetonitrile ($\lambda_{\text{ex}} = 285 \text{ nm}$)

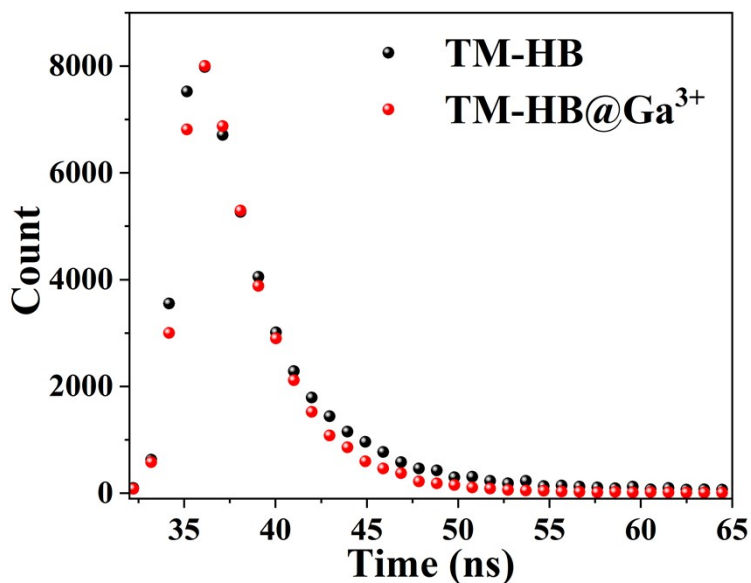


Figure S16. Fluorescence lifetime decay curve of TM-HB and TM-HB@Ga³⁺ in acetonitrile

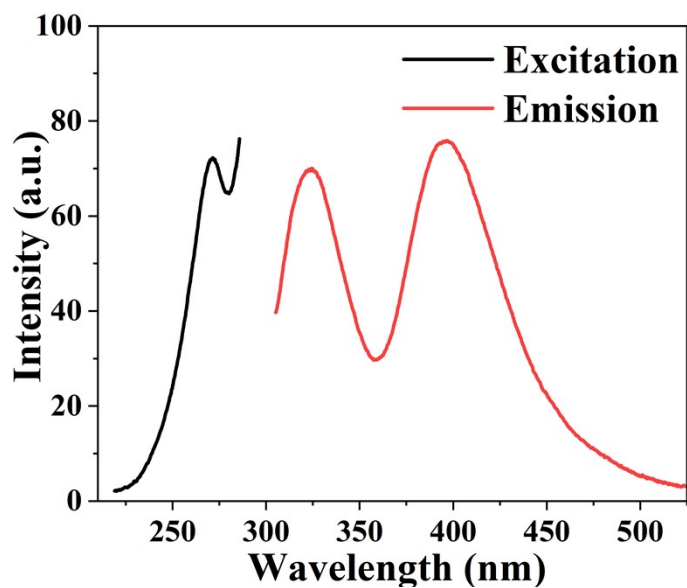


Figure S17. Excitation spectrum (black line) and emission spectrum (red line) of TM-HB in acetonitrile

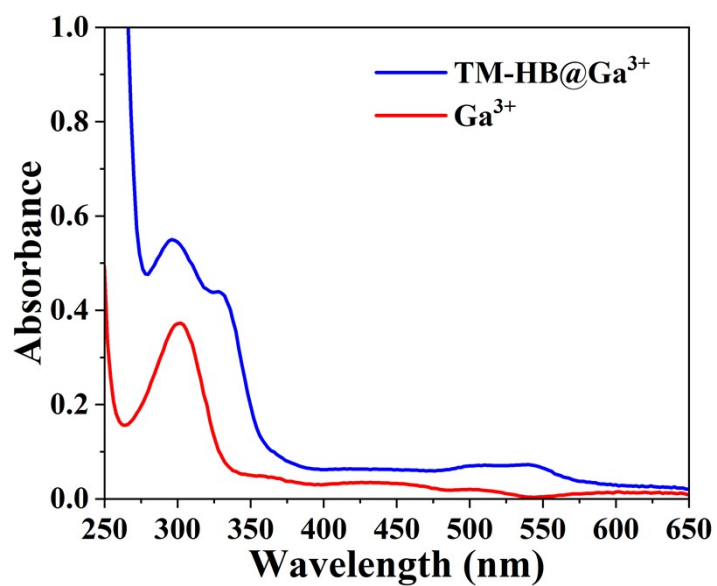


Figure S18. UV-vis absorbance spectra of TM-HB@Ga³⁺ and Ga³⁺ ion

Table S1. Screening of the solvents and different temperature conditions to synthesize TM-HB

Entry	Solvents	Acetic acid	Temperature	Result
1	Mesitylene (1 mL) : 1,4-dioxane (1 mL)	3 M, 0.2 mL	25 °C	Solid
2	Mesitylene (1 mL) : 1,4-dioxane (1 mL)	3 M, 0.2 mL	120 °C	Liquid
3	Mesitylene (0.5 mL) : 1,4-dioxane (0.5 mL)	3 M, 0.2 mL	120 °C	Liquid
4	Mesitylene (1 mL) : 1,4-dioxane (0.5 mL)	3 M, 0.2 mL	120 °C	Liquid
5	Mesitylene (0.9 mL) : 1,4-dioxane (0.1 mL)	3 M, 0.2 mL	120 °C	Liquid
6	Mesitylene (1.7 mL) : 1,4-dioxane (0.3 mL)	3 M, 0.2 mL	120 °C	Liquid
7	Mesitylene (1 mL) : 1,4-dioxane (1 mL)	6 M, 0.1 mL	120 °C	Liquid

General conditions: TM (0.06 mmol, 17.36 mg), HB (0.09 mmol, 13.51 mg), 3 days

Table S2. Contrast of diverse aspects of TM-HB with other reported chemosensors for Ga³⁺ detection

Chemosensors	Linear range (μM)	LOD (μM)	Applications	Reference s
H ₃ L ¹	0-50	0.20	Test strip and logic gate	1
Probe L1	0-75	0.22	Test strips and polystyrene film	2
Probe L3	0-150	0.004	Water Sample	3
PyAP	0-120	0.003	live cell imaging, logic gates and keypad locks	4
DHTC	0-30	0.39	Test strip	5

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