

Supporting Information

Tuning excited-state intramolecular proton transfer (ESIPT) based luminescence of metal-organic frameworks by metal nodes toward versatile photoluminescent applications

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S1. Experimental section

Chemicals and materials

All chemicals were obtained commercially and used without further purification. The solvents were dried before use to eliminate the effect from the minimal amount of water in organic solvents. 2,5-dihydroxyterephthalic acid (H₂DHT), ice acetic acid, agarose, rhodamine B, and inorganic metal salts and anions were purchased from Sigma-Aldrich (Sigma-Aldrich LLC., USA) and Shanghai Qingxi Technology Co., Ltd. (Shanghai, China). Ultrapure water was used to prepare all aqueous solutions throughout the experiments. For the experiment of test strips, the common medium speed filter papers were cut uniformly into circular paper sheets with 6.0 mm in diameter by using a Deli hole puncher (No. 0102, Zhejiang, China).

Apparatus and measurements

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Ultima-IV unit using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Emission spectra were collected on a Fluoromax-4 spectrophotometer. The excitation wavelength was 365 nm. Solid and solution state emission spectra were recorded using an FL-4600 Fluorescence Spectrometer (Hitachi, Japan) equipped with the solid-state sample holder. Absorption spectra were acquired on a Shimadzu UV-3600 UV/VIS/NIR spectrometer. The Fourier transform infrared (FTIR) spectra were conducted on a FT-IR Prestige-21 spectrometer (Shimadzu Corporation, Japan). Scanning electron microscopy (SEM) was carried out with a FEI Quanta200F scanning electron microscope (FEI Company, USA). Absolute quantum yields (Q_F) and fluorescence lifetime measurements were performed by FLS1000 steady-state and transient fluorescence spectrometer (Edinburgh, UK). All the experiments were performed at ambient temperature. In this study all the emission color images were taken under a 365 nm UV lamp.

Preparation of Mg(DHT)

Mg(DHT) was synthesized according to a previous report with slight modification.¹ Briefly, a mixture of Mg(NO₃)₂·6H₂O (0.5 mmol, 0.128 g), H₂DHT (0.5 mmol, 0.099 g), 15 mL triethylamine, and 8 mL DMF were added in a 23 mL Teflon bomb and the mixture was agitated for 1 h. The Teflon bomb was then put in a steel autoclave and heated at 120 °C for 3 days and finally cooled to room temperature. The obtained solid was isolated by discarding the supernatant and washed three times with DMF. For the activation, the solid was immersed in a MeOH solution

for 3 days. After that, they were filtered and dried at 100 °C, and then all of the samples were heated under vacuum at 50 °C for 2 days to afford Mg(DHT).

Preparation of Al-MIL-53-(OH)₂

Al-MIL-53-(OH)₂ was synthesized according to the literature.² Typically, AlCl₃·6H₂O (8 mmol, 1.932 g) and H₂DHT (8 mmol, 1.584 g) were added to 20 mL DMF, stirring at room temperature for 30 minutes until completely dissolved. The mixture was heated at 125°C for 8 h. After the reaction was completed, the obtained precipitates were centrifuged, and washed with DMF three times to remove unreacted ligands and metal ions. And then, the raw product was dispersed in a 50: 50 (v/v) MeOH and water solution, heated at 100 °C for 12 h under stirring, and centrifuged followed by discarding the supernatant. The obtained solid was dried at 130 °C for 24 h.

Preparation of UiO-66-(OH)₂

UiO-66-(OH)₂ was synthesized according to the previous report with some modifications.³ Initially, ZrCl₄ (1.03 mmol, 1.932 g) and H₂DHT (0.526 mmol, 0.1042 g) were dissolved in 12 mL DMF. After being stirred for 30 min, 4 mL acetic acid and 2 mL EtOH were added to the mixture and blended thoroughly. The mixture was then placed in a steel autoclave (50 mL) and heated at 130 °C for 2 days. Following that, the obtained precipitates were centrifuged and washed with DMF three times. The resultant product was soaked in 50 mL MeOH solution for 3 days (Note that the solution was changed to new one each day). Afterwards, the obtained solid was dried under vacuum at 65 °C for 24 h.

Preparation of Mg(DHT)-immobilized agarose hydrogels

Mg(DHT)-immobilized-agarose hydrogels were fabricated according to our previous report.⁴ Briefly, 0.25 g of agarose dispersed in 10 mL water was completely dissolved by heating. Then, 4 mL of the Mg(DHT) aqueous suspension (0.2 mg mL⁻¹) was injected into the above solution and stirred rapidly. After that, the mixture was cast into wells of a 96-well plate and let to set at room temperature to form the hybrid hydrogels. The hydrogels were taken out and dried in air for further use.

On-site detection of Al³⁺ with a smartphone based on fluorescent hybrid hydrogels

The hybrid hydrogels obtained above were immersed in 2 mL containing Al³⁺ at various concentrations. After incubating 0.5 h, the hydrogels were removed from the solution and dried. Further, the hydrogels treated by Al³⁺ were placed in a matte black background under illumination

of a UV lamp (365 nm) behind the hydrogels. Then, the fluorescence images were captured using a camera of the smartphone positioned at a fixed distance from the hydrogels. Finally, the color information (RGB values) of the captured images was subtracted by a color-processing app ColorPicker in the smartphone. For that, the regions of interest (colored spot) were firstly extracted. The green (G) values were used to represent the signal output for estimating Al^{3+} concentrations.

Preparation of the composites RhB@Al-MIL-53-(OH)₂

10 mg of Al-MIL-53-(OH)₂ were soaked in 2 mL of aqueous or ethanolic solutions of RhB at different concentrations, and the suspensions was sonicated for 2 h in the dark. Then the mixture was centrifuged and washed twice with ultrapure water or ethanol to remove the residual RhB on the surface of the MOF, respectively. The mass fraction of RhB encapsulated into the MOFs was calculated by detecting the luminescence intensity of RhB in the supernatant according to the luminescence intensity-concentration standard curves.

WLED device fabrication

WLED were fabricated by simply coating with a thin CMC (sodium carboxymethyl cellulose) layer containing RhB@Al-MIL-53-(OH)₂ suspensions (0.96 wt% in water, and 0.053 wt% in EtOH for encapsulated RhB) on the surface of a commercial UV LED bead (380 nm). An applied voltage of 3.8 V was used.

S2. Supplementary figures and tables

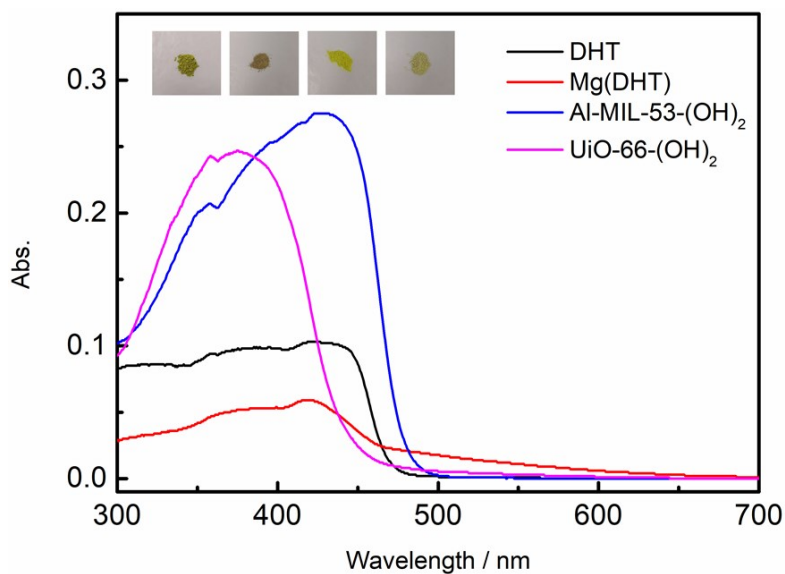


Fig. S1 UV-vis DRS spectra of DHT and the three LMOFs. Inset: the corresponding photograph.

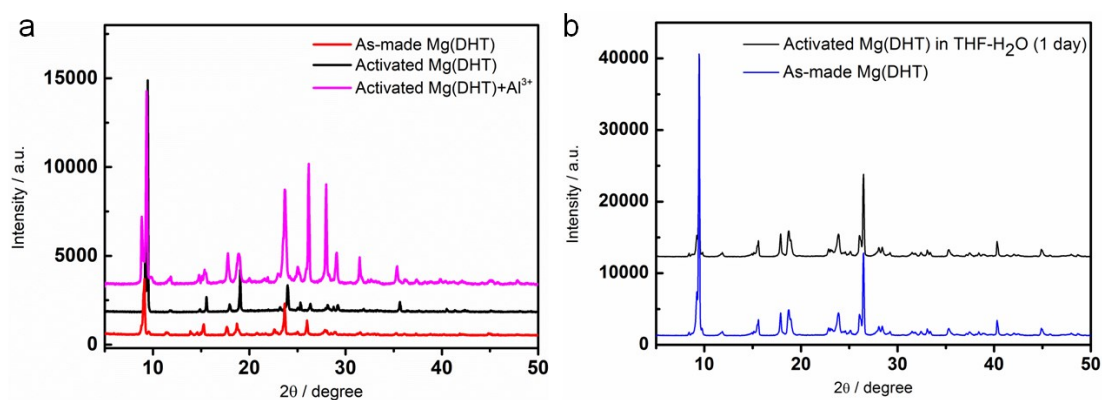


Fig. S2 PXRD patterns of Mg(DHT) in different states: (a) (red line) as-made, (black line) activated, (pink line) activated one in water after addition of Al³⁺, (b) (blue line) as-made, (black line) activated one retracted from the THF-water mixture (5:1,v/v) after 1 day.

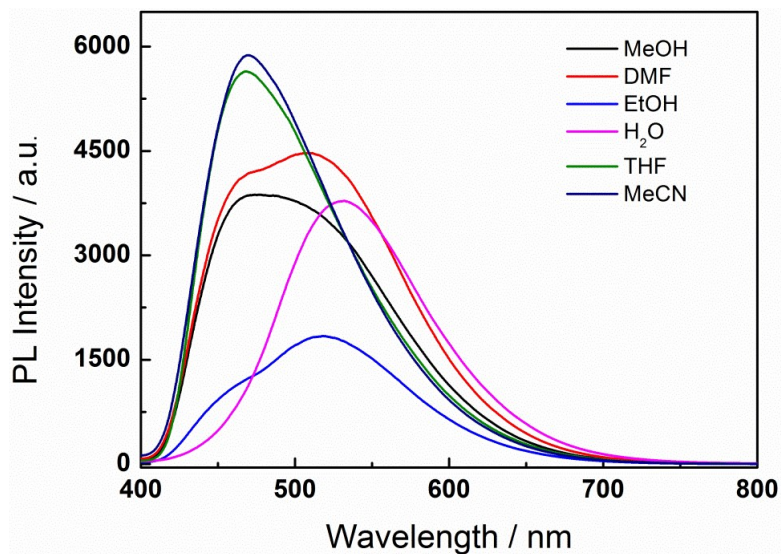


Fig. S3 Emission spectra of DHT in different solvents.

Table S1 Absolute quantum yields (Q_F) of DHT and three LMOFs in the solid state and in solvents.

Compound	$Q_F(\text{Solid})$	$Q_F(\text{H}_2\text{O})$	$Q_F(\text{EtOH})$
DHT	0.139	0.152	0.169
Mg(DHT)	0.127	0.129	0.187
Al-MIL-53-(OH) ₂	0.020	0.074	0.075
UiO-66-(OH) ₂	0.0015	0.0012	0.007

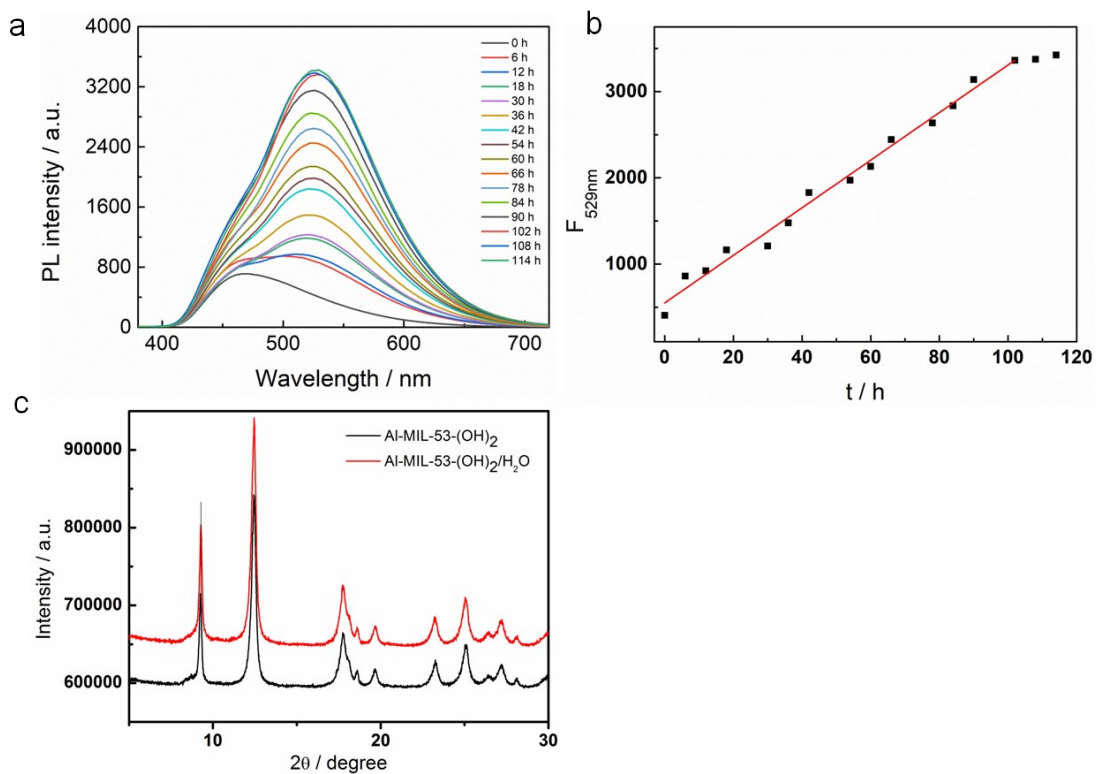


Fig. S4 (a) Temporal profile of emission spectra of Al-MIL-53-(OH)₂ in water. (b) Change in emission intensity at 529 nm in (a) with time. (c) PXRD patterns of Al-MIL-53-(OH)₂ before and after treatment of water 1 day.

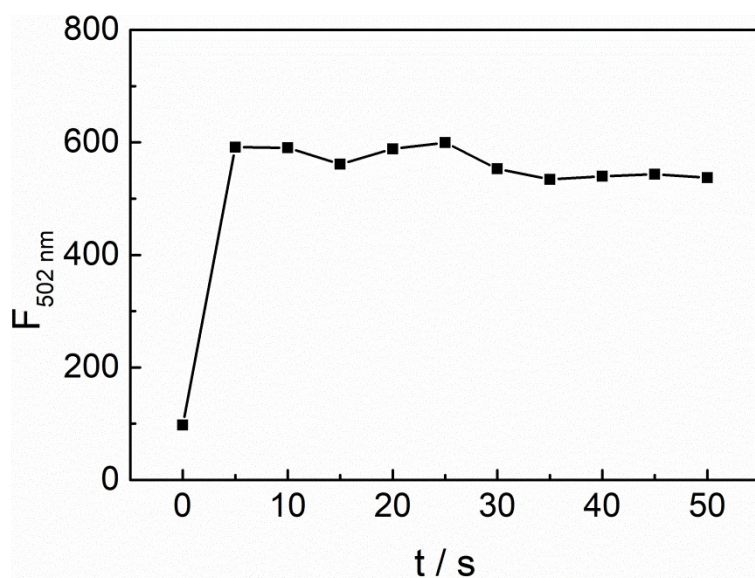


Fig. S5 Time-dependent changes in $F_{502\text{nm}}$ of Mg(DHT) THF suspensions responding to the water content of 0.25%.

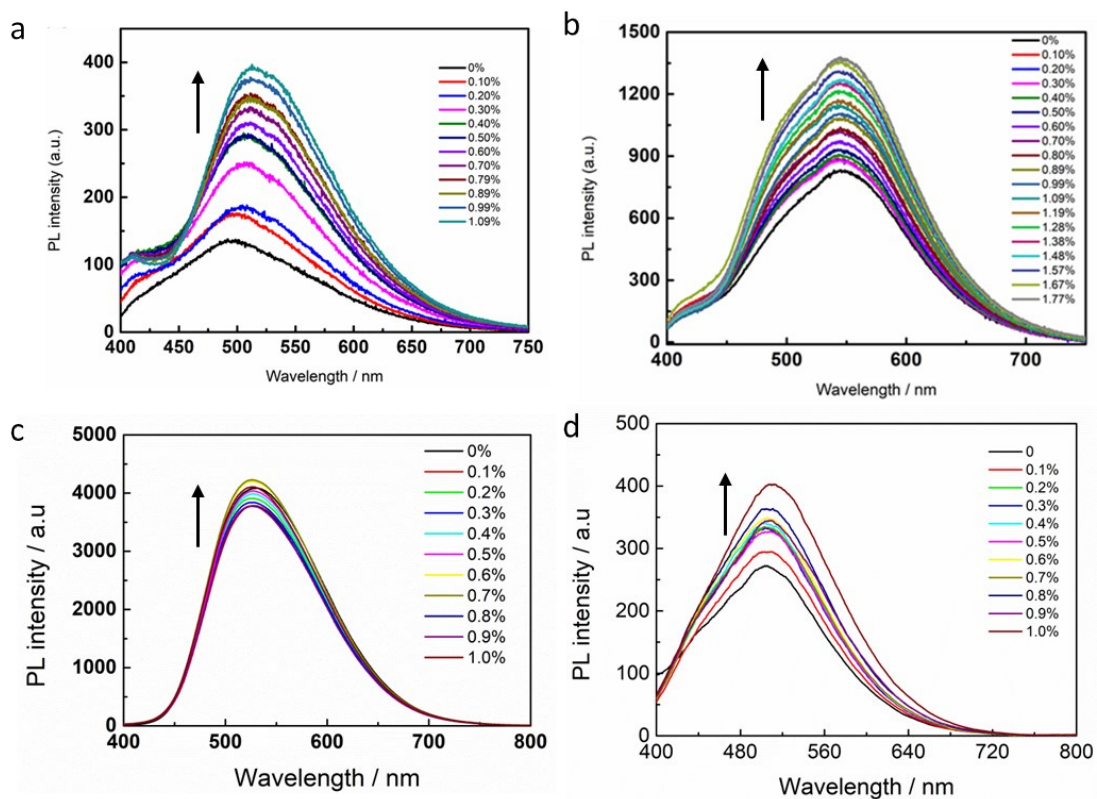


Fig. S6. Emission spectra of Mg(DHT) in (A) ACN, (B) DMF, (C) MeOH, and (D) EtOH responding to different water contents.

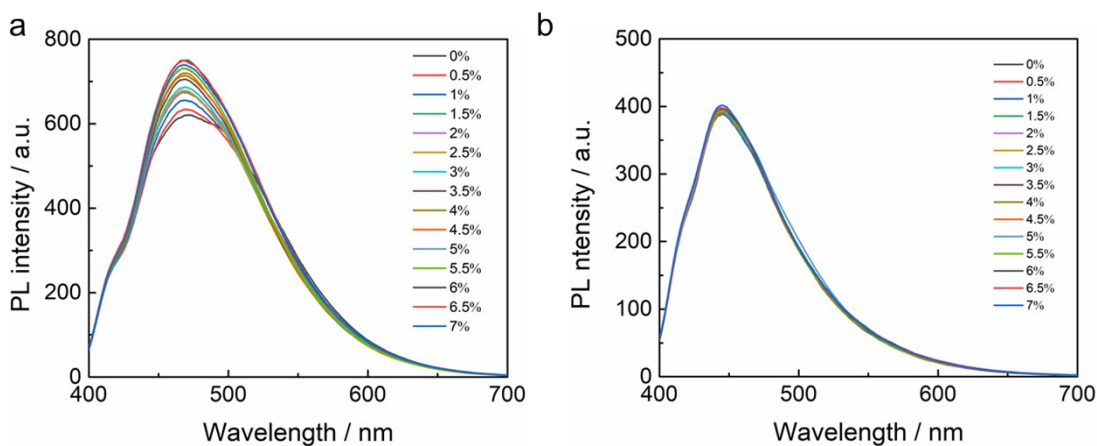


Fig. S7 Emission spectra of (a) Al-MIL-53-(OH)₂ and (b) UiO-66-(OH)₂ in THF responding to different water contents.

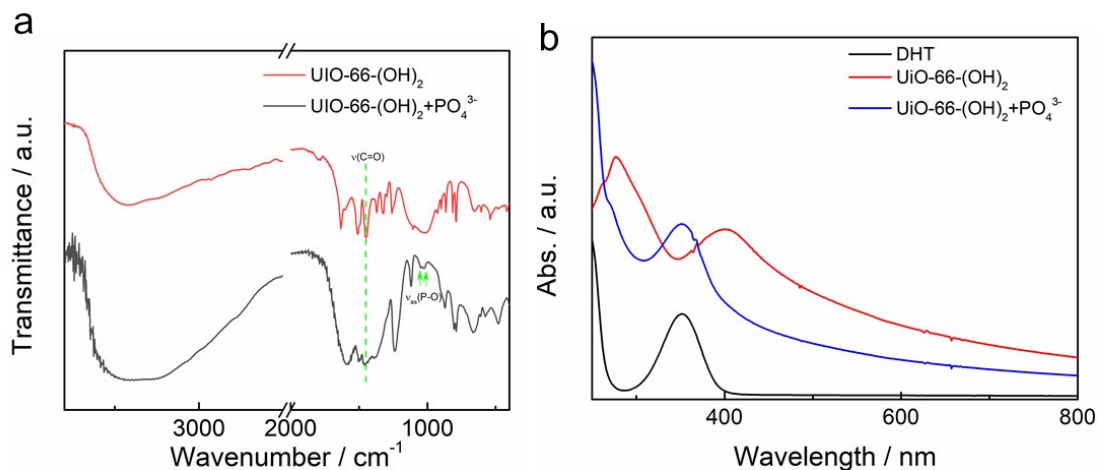


Fig. S8 (a) FTIR spectra of UiO-66-(OH)₂ in the absence and presence of phosphate. (b) UV-vis absorption spectra of DHT, and UiO-66-(OH)₂ in the absence and presence of phosphate.

Table S2 Absolute quantum yields (Q_F) of UiO-66-(OH)₂ upon addition of phosphate with different concentrations.

$C_{\text{phosphate}}/\mu\text{M}$	$Q_F/\%$
0	0.12
50	6.40
100	13.40
200	18.33
300	20.01

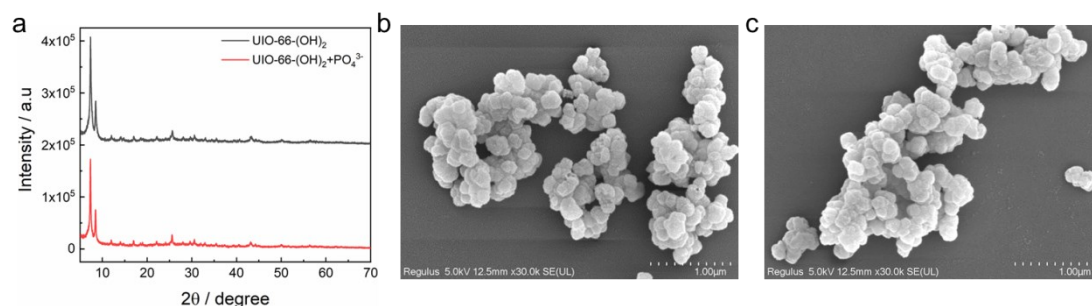


Fig. S9 (a) PXRD patterns of UiO-66-(OH)₂ in the absence of and presence of phosphate (300 μM). SEM images of UiO-66-(OH)₂ in the (b) absence and (c) presence of phosphate.

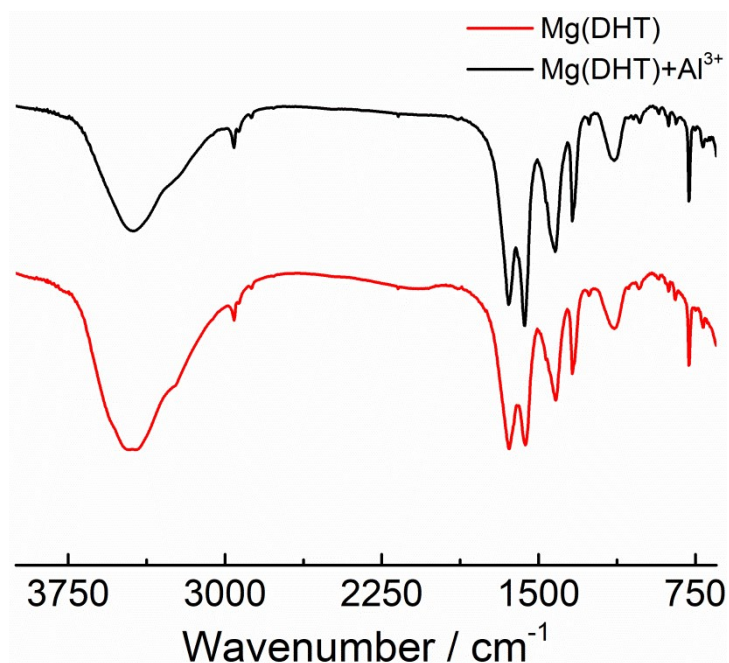


Fig. S10 FTIR spectra of Mg(DHT) in the absence and presence of Al^{3+} . The y axis is presented in transmittance.

As shown in Fig. S10, the stretching band of $-\text{OH}$ group of Mg(DHT) was largely weakened after addition of Al^{3+} , and meanwhile, both the stretching band of $\text{C}=\text{O}$ group and bending vibration of $-\text{OH}$ group showed small shifts in the presence of Al^{3+} (from 1640 to 1642 cm^{-1} , from 1340 to 1338 cm^{-1} , respectively).

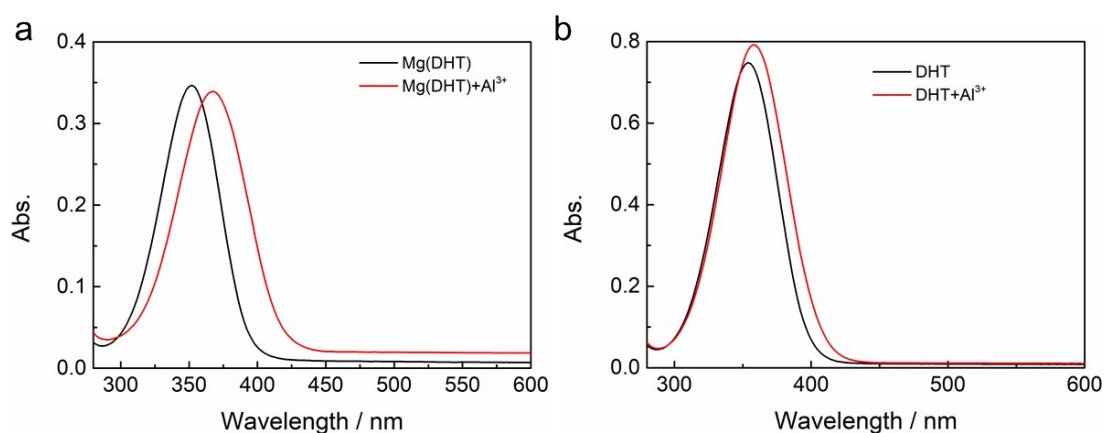


Fig. S11 UV-vis absorption spectra of (a) DHT linker and (b) Mg(DHT) in water in the absence and presence of Al^{3+} , respectively.

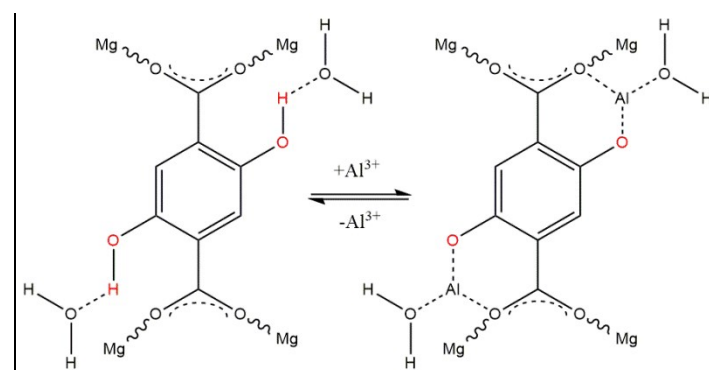


Fig. S12. Proposed chelation enhanced fluorescence sensing mechanism of Mg(DHT) in water for Al^{3+} .

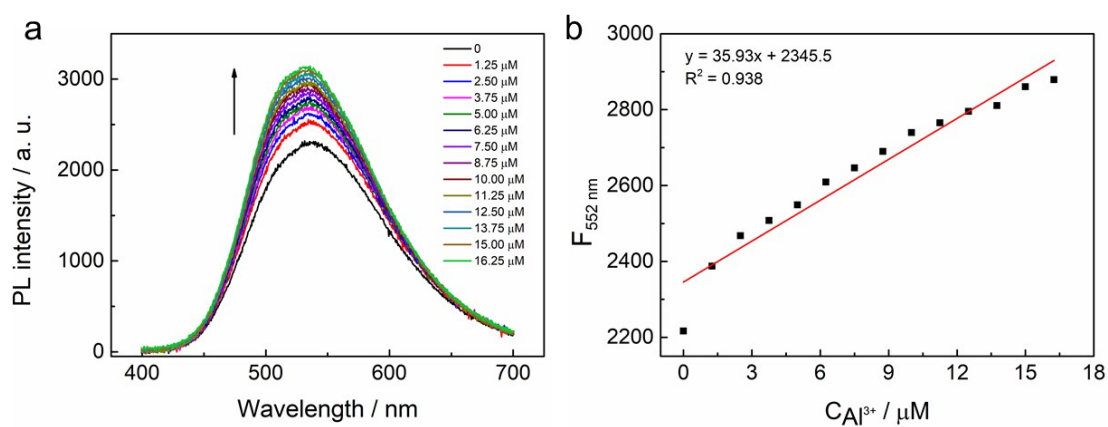


Fig. S13 (a) Emission spectra of DHT linker in water upon addition of different concentrations of Al^{3+} . (b) Fitting curve between the emission intensity at 552 nm and the concentration of Al^{3+} .

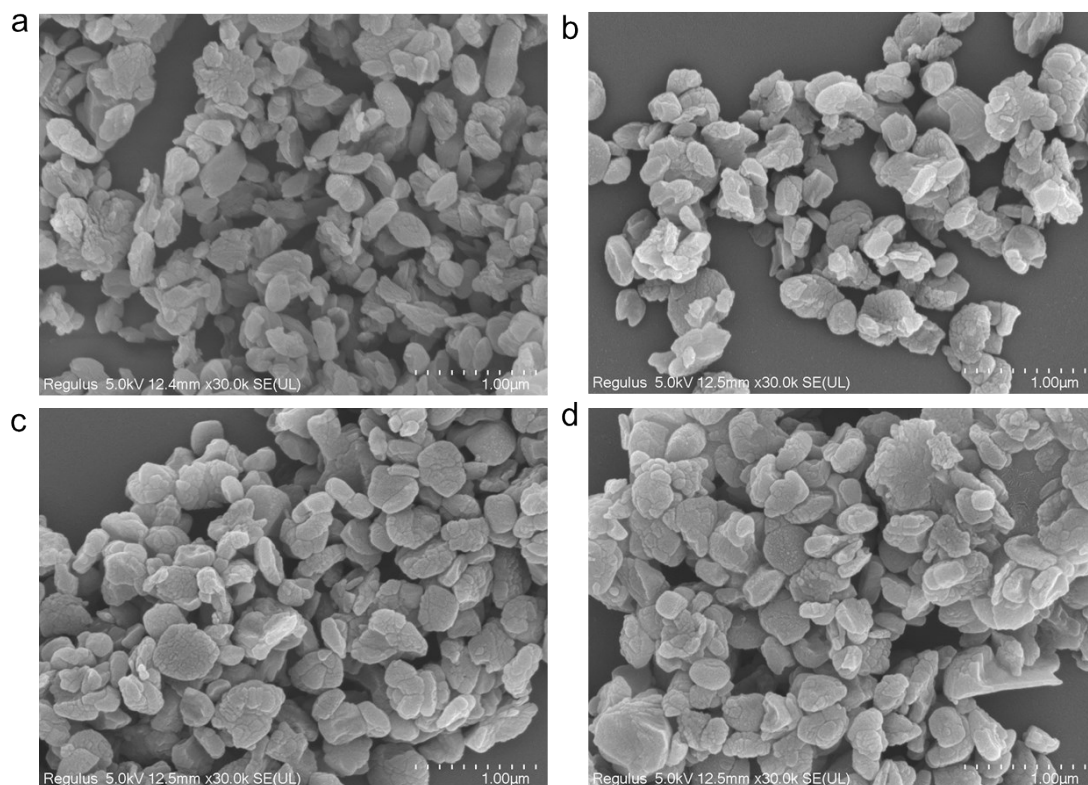


Fig. S14 SEM images of (a,c) Al-MIL-53-(OH)₂ and (b,d) RhB@Al-MIL-53-(OH)₂ in water and EtOH, respectively.

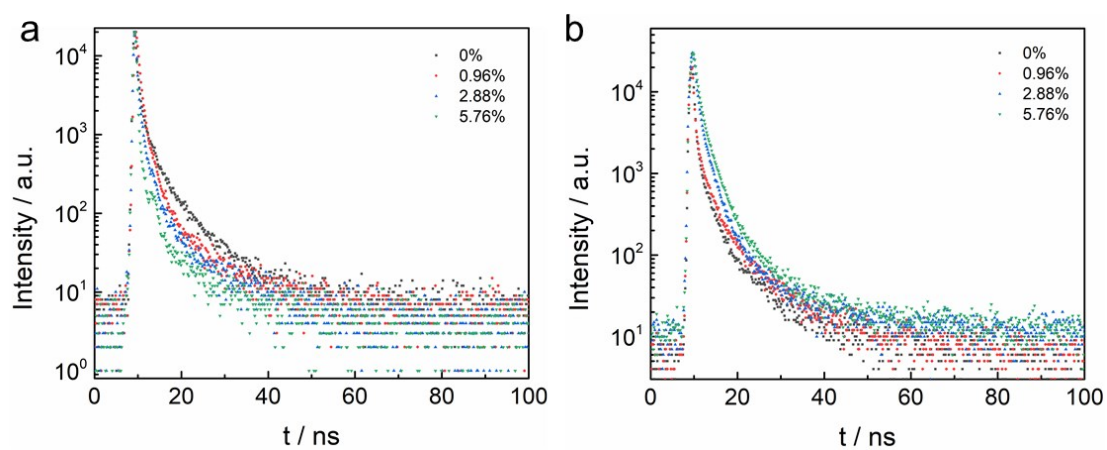


Fig. S15 Decay curves of (a) Al-MIL-53-(OH)₂ and (b) RhB within the composites with different amounts of encapsulated RhB in water.

Table S3 Fluorescence lifetime (ns) of (a) Al-MIL-53-(OH)₂ and (b) RhB within the composites with different amounts of encapsulated RhB in water.

wt% (RhB)	Al-MIL-53-(OH) ₂	RhB
0	2.52	2.06
0.96	1.89	2.24
2.88	1.55	2.65
5.76	1.24	2.91

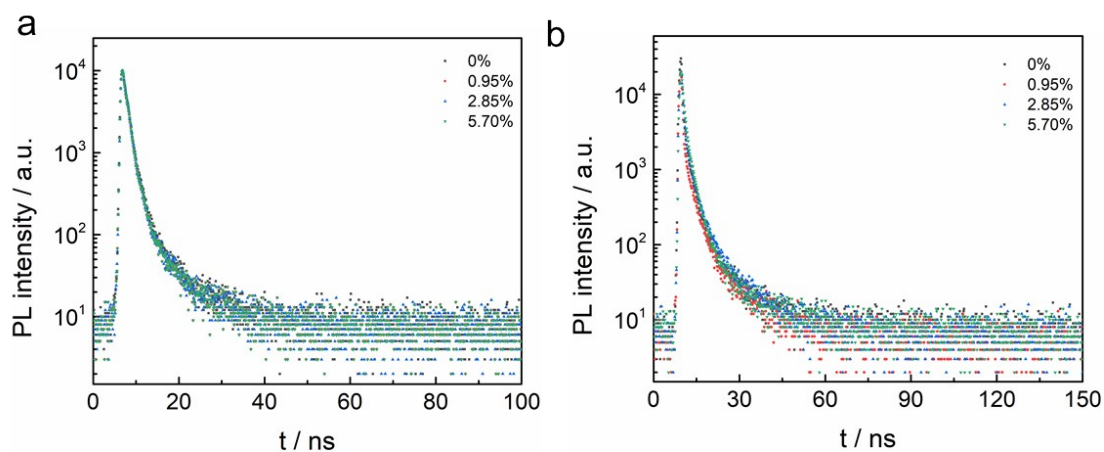


Fig. S15 Decay curves of (a) Al-MIL-53-(OH)₂ and (b) RhB within the composites with different amounts of encapsulated RhB in EtOH.

Table S4 Fluorescence lifetime (ns) of (a) Al-MIL-53-(OH)₂ and (b) RhB within the composites with different amounts of encapsulated RhB in EtOH.

wt% (RhB)	Al-MIL-53-(OH) ₂	RhB
0	2.04	2.17
0.95	1.97	2.12
2.85	2.02	2.39
5.70	1.90	2.30

S3. Supporting references

1. K. Jayaramulu, P. Kanoo, S. J. George and T. K. Maji, *Chem. Commun.*, 2010, **46**, 7906-7908.
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