

Electronic Supplementary Information for

Solvent-induced luminescence of NH₂-MIL-53(Fe) in H₂O and D₂O: a potential approach for D₂O detection

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Chemicals

FeCl₃·6H₂O, 2-aminoterephthalic acid (NH₂-H₂BDC), p-phthalic acid (H₂BDC) and N,N-Dimethylformamide (DMF) were purchased from Macklin Reagent Co, Ltd. D₂O was purchased from Aladdin Reagent Co, Ltd. Deionized water (18 MΩ·cm⁻¹) was used in all aqueous solutions. All of the above chemicals were used without further purification.

Preparation of NH₂-MIL-53(Fe)

The NH₂-MIL-53(Fe) was prepared according to the reported hydrothermal method.^{1,2} NH₂-H₂BDC (1.45 g) and FeCl₃·6H₂O (2.16 g) were firstly dissolved in DMF (80 mL) by ultrasonic. Next the solution was shifted into a hydrothermal reacted vessel and placed at 155 °C for 72 h. The reaction solution was left undisturbed at room temperature for 24 h. The precipitate was separated by centrifugation and washed by DMF for 3 times. They were dried in the vacuum at 80 °C for 24 h to obtain the reddish-brown powder of NH₂-MIL-53(Fe).

Preparation of MIL-53(Fe)

The MIL-53(Fe) was prepared according to the reported hydrothermal method.^{1,2} H₂BDC (1.33 g) and FeCl₃·6H₂O (2.16 g) were firstly dissolved in DMF (80 mL) by ultrasonic. Next the solution was shifted into a hydrothermal reacted vessel and placed at 155 °C for 72 h. The reaction solution was left undisturbed at room temperature for 24 h. The precipitate was separated by centrifugation and washed by DMF for 3 times. They were dried in the vacuum at 80 °C for 24 h to obtain the dark-brown powder of MIL-53(Fe).

Characterization

The morphology of NH₂-MIL-53(Fe) was characterized by the scanning electron microscope (SEM, Quanta, FEG-250). X-ray diffraction (XRD) data of NH₂-MIL-53(Fe) and MIL-53(Fe) were tested by the Tongda TD-3500 automatic X-ray diffractometer system. Fourier transform infrared (FTIR) transmittance spectra of NH₂-MIL-53(Fe) were characterized by the Nicolet IS10 spectrometer with an attenuated total reflection attachment (PIKE, ATR Max II). The fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrometer under 297 nm excitation. The time-resolved spectra of NH₂-MIL-53(Fe) in H₂O and D₂O were recorded using fluorescence spectrometer (Quanta Master 400, Photon Technology International).

Excitation and emission spectra of NH₂-MIL-53(Fe) and MIL-53(Fe) in solid state

The excitation and emission spectra of NH₂-MIL-53(Fe) and MIL-53(Fe) in solid state are shown in Fig. S1 and S2. The powders of NH₂-MIL-53(Fe) show three emission bands at 434, 446 and 456 nm under 361 nm excitation (Fig. S1a). The emission intensity is lower than the dispersion of NH₂-MIL-53(Fe). Fig. S1 b, c and d are the excitation spectra of NH₂-MIL-53(Fe) at 434, 446 and 456 nm in solid state. The powders of MIL-53(Fe) exhibit a strong emission performance comparing with the dispersion of MIL-53(Fe). Two emission bands are centered at 293 nm and 392 nm, respectively. Fig. S2 b and c are the excitation spectra of MIL-53(Fe) at 293 and 392 nm in solid state.

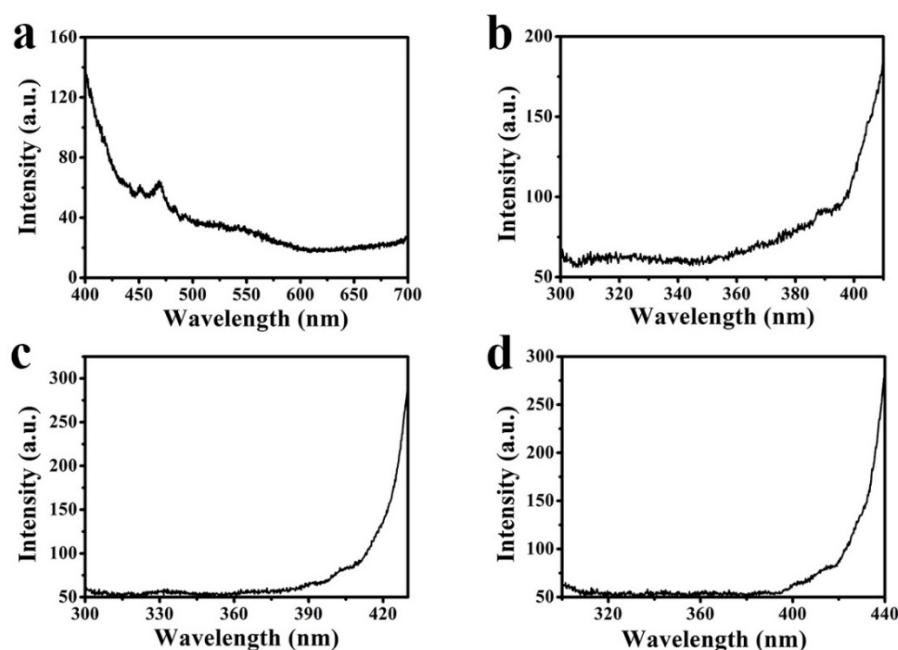


Fig. S1 (a) The emission spectra of NH₂-MIL-53(Fe) in solid state under the 361 nm excitation. (b)

The excitation spectra of NH₂-MIL-53(Fe) in solid state at 434 nm. (c) The excitation spectra of NH₂-MIL-53(Fe) in solid state at 446 nm. (d) The excitation spectra of NH₂-MIL-53(Fe) in solid state at 456 nm.

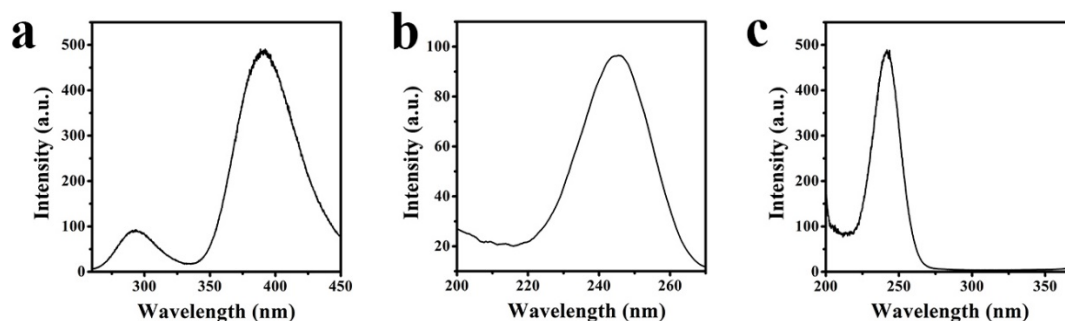


Fig. S2 (a) The emission spectra of MIL-53(Fe) in solid state under the 241 nm excitation. (b) The excitation spectra of MIL-53(Fe) in solid state at 293 nm. (c) The excitation spectra of MIL-53(Fe) in solid state at 392 nm.

Emission spectra of NH₂-MIL-53(Fe) in different solvent

The emission spectra of NH₂-MIL-53(Fe) in H₂O, D₂O, acetone, cyclohexane, ethanol, isopropanol and methanol are shown in Fig. S3.

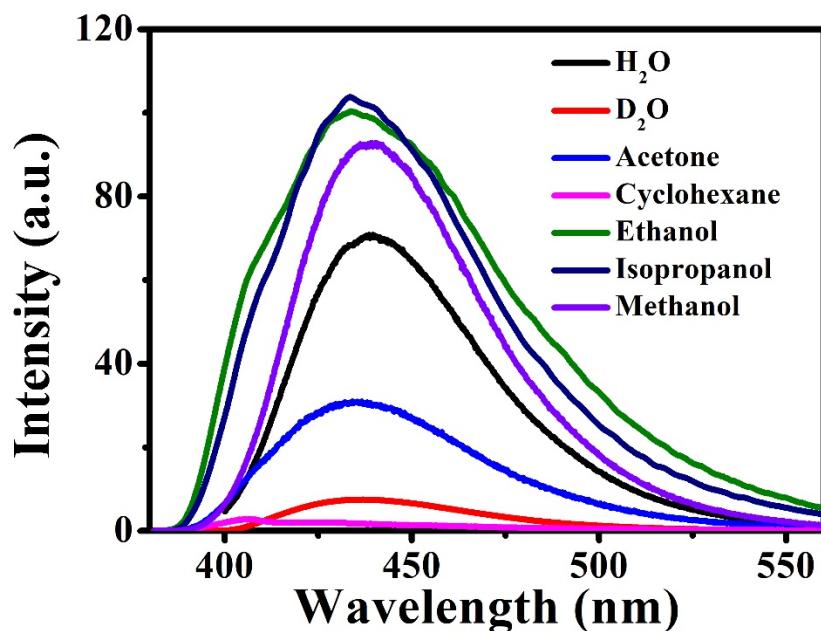


Fig. S3 Emission spectra of NH₂-MIL-53(Fe) in H₂O, D₂O, acetone, cyclohexane, ethanol, isopropanol and methanol under 361 nm excitation.

Powder X-ray patterns and emission spectra of NH₂-MIL-53(Fe) after immersed in H₂O and D₂O

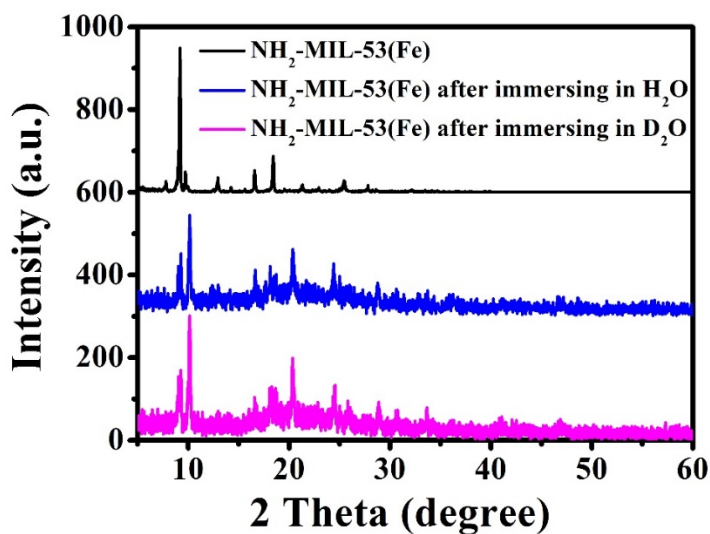


Fig. S4 Powder X-ray patterns of NH₂-MIL-53(Fe) after immersed in H₂O and D₂O

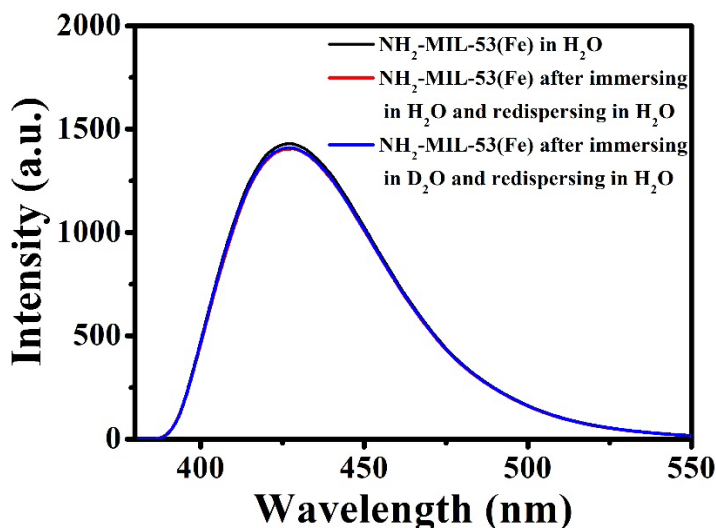


Fig. S5 Emission spectra of NH₂-MIL-53(Fe) dispersing in H₂O, NH₂-MIL-53(Fe) after immersing in H₂O and redispersing in H₂O and NH₂-MIL-53(Fe) immersing in D₂O and redispersing in H₂O under 361 nm excitation.

Selectivity of NH₂-MIL-53(Fe) for D₂O detection

The selectivity of NH₂-MIL-53(Fe) for D₂O detection was evaluated. The emission intensity at 427 nm of NH₂-MIL-53(Fe) dispersion (50% H₂O and 50% D₂O) is used as a blank value. The NH₂-MIL-53(Fe) was dispersed in the mixture. The mixture contains common ions (Na⁺, K⁺, Ca²⁺, Mg²⁺ and Zn²⁺) or miscible species (methanol, ethanol and acetone). The ion concentration is 1 mM. The volume ratio of miscible species is 50%.

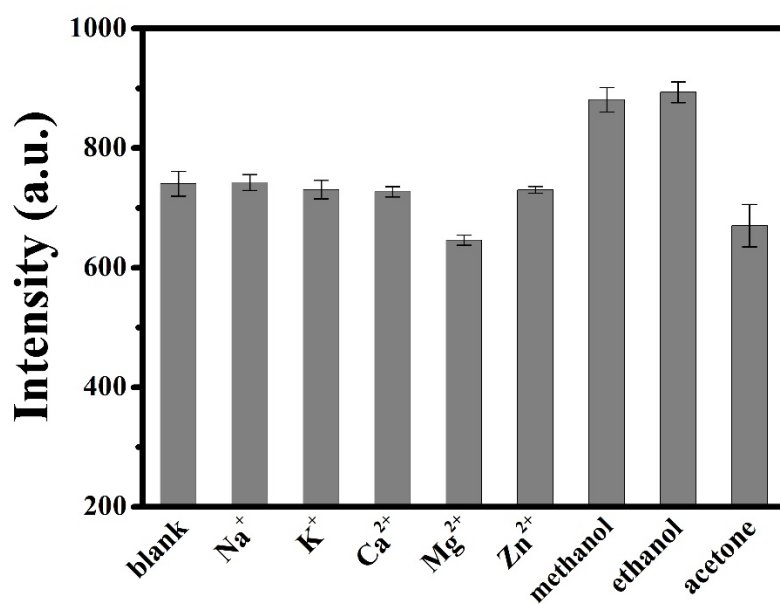


Fig. S6 Emission intensity at 427 nm of NH₂-MIL-53(Fe) dispersion in the presence of other common species (Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺, methanol, ethanol and acetone). The dispersion contains 50% D₂O. The ion concentration is 1 mM.