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COMMUNICATION

Ag⁺-sensitized lanthanide luminescence in Ln³⁺ post-functionalized metal-organic framework and Ag⁺ sensing

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The weak fluorescence of Ln³⁺-doped (Ln = Sm, Dy, Nd, Yb, Er) metal-organic framework (MOF) was greatly enhanced by Ag⁺. And Single-phase white-light emitters based on the resulting 4d-4f heterometallic co-doped MOFs could be realized. Furthermore, the Sm³⁺-doped MOF has been used for highly sensitive sensing of Ag⁺.

Metal-organic frameworks (MOFs) are crystalline hybrid materials consisting of metal ions and organic bridging ligands. One of the most interesting behaviours of MOFs is their luminescence properties.¹ Recently, a considerable amount of work on luminescent MOFs, targeting applications such as light-emitting devices,² chemical sensor,³ and biomedicine⁴ is available. Among them, lanthanide MOFs (Ln-MOFs) are regarded as particularly significant due to their intense, long-lived, sharp emission in the visible region. However, because of the higher coordination numbers and more variable nature of the Ln³⁺ coordination sphere, the rational design and preparation of desired Ln-based MOFs still remain a challenge.⁵ Thereby, to exploit their luminescence properties efficiently, alternative strategies have been explored, such as the post-synthetic modification (PSM)⁶ of MOFs whose chemical modification can be performed on the fabricated MOFs rather than on the molecule precursor. Recently, an increasing number of Ln-doped MOFs constructed by PSM have been made. This is the case for bio-MOF-1,⁷ Zn(II)-MOF,⁸ COMOC-4,⁹ MOF-COOH,¹⁰ Al-MIL-53-COOH.¹¹ As Ln-doped materials¹² are widely employed as phosphors for photonic applications such as sensors, solid-state lighting, nonlinear optics, and biomedical analysis, it is obvious that Ln-doped MOFs can pave the way toward novel luminescent materials.

Furthermore, to obtain effective Ln-doped MOFs, besides the binding site and stable architecture of MOFs, powerful luminescence is also needed. The limit of weak fluorescence of lanthanide ions due to low molar absorption coefficients causes considerable exploration of suitable sensitizing chromophores which act as antennas to effectively transfer light energy to the lanthanide ions.¹³ In this regard, two strategies have been developed to enhance the fluorescence of lanthanide ions. One is to use antenna ligands, which can transfer energy to lanthanide ions. This principle has been successfully used to prepare luminescent Ln-MOFs.¹⁴ Another new strategy used for improving Ln³⁺ emission is to employ a transition

metal (d-block) as a sensitizer for Ln³⁺ emission, which can cause more efficient energy transfer from ligands to lanthanide ions.¹⁵

In this work, a new class of Ln-based MOFs (Ln = Sm, Dy, Nd, Yb, Er) was generated by encapsulating the Ln³⁺ cations into MIL-121 crystals. MIL-121¹⁶ (aluminium pyromellitate or Al(OH)(H₂btec)·H₂O, H₄btec = pyromellitic acid) was chosen due to its rigid, permanently porous structure and the presence of non-coordinating carboxylate groups on the H₄btec linker, which are amenable to post-synthetic modification by coordination reaction with metal cations. However, the luminescence of Ln³⁺@MIL-121 (Ln = Sm, Dy, Nd, Yb, Er) was very weak since the ligand H₄btec could not effectively sensitize the luminescence of Ln³⁺. In our previous work,¹⁷ we found that Eu³⁺@MIL-121 showed high sensitivity and selectivity for Ag⁺ ions through greatly enhancing of the Eu-luminescence, because Ag⁺ ions cause more efficient energy transfer from ligands to Eu³⁺. Therefore, we attempt to enhance the fluorescence of Ln³⁺@MIL-121 (Ln = Sm, Dy, Nd, Yb, Er) by a transition metal Ag⁺ so as to obtain a strong emission. As anticipated, strong luminescence of Ag⁺/Ln³⁺@MIL-121 could be successfully attained. Moreover, white light emissions could also be realized by a single component Ag⁺/Sm³⁺@MIL-121 or Ag⁺/Dy³⁺@MIL-121. Furthermore, as a sensing probe for Ag⁺, compared with the previously reported Eu³⁺@MIL-121, the Sm³⁺@MIL-121 shows a higher selectivity and sensitivity for Ag⁺ in aqueous solution.

Following a previously reported method,¹⁶ the compound MIL-121 was solvothermally synthesized by mixing aluminum nitrate, pyromellitic acid, and H₂O. Figure 1 shows the PXRD pattern of MIL-121, whose diffraction peaks agree well with the literature value. MIL-121 is a three-dimensional (3D) framework containing two uncoordinated carbonyl groups per ligand with one-dimensional pore channels (Figure S1). Infrared spectroscopy (Figure S2) confirms the existence of the free-COOH since the band observed at 1716 cm⁻¹ are assigned to the ν_{C=O} vibrations of non-coordinating-COOH functions. The permanent porosity of MIL-121 was demonstrated by N₂ sorption studies (BET surface area: 173 m² g⁻¹, Figure S3). The reactive nature of the uncoordinated carbonyl group and the permanent porosity of MIL-121 make it suitable as a host for encapsulating metal cations. We therefore loaded Ln³⁺ or Ag⁺/Ln³⁺ into the pores of MIL-121 via PSM, yielding Ln³⁺@MIL-121 and Ag⁺/Ln³⁺@MIL-121, respectively. As shown in Figure S4, after

binding to Sm^{3+} and $\text{Ag}^+/\text{Sm}^{3+}$, the absorption band of MIL-121 shows a significant red-shift by approximately 12 nm and 21 nm, respectively, indicating both Ag^+ and Sm^{3+} cations are linked to the carboxylic acid by the coordination reaction.⁹ And the amount of Ln^{3+} and Ag^+ cations loaded in MIL-121 was determined by ICPMS (Table S1). The incorporation of these cations does not induce a change in the structure and crystalline integrity of MIL-121 (Figure 1).

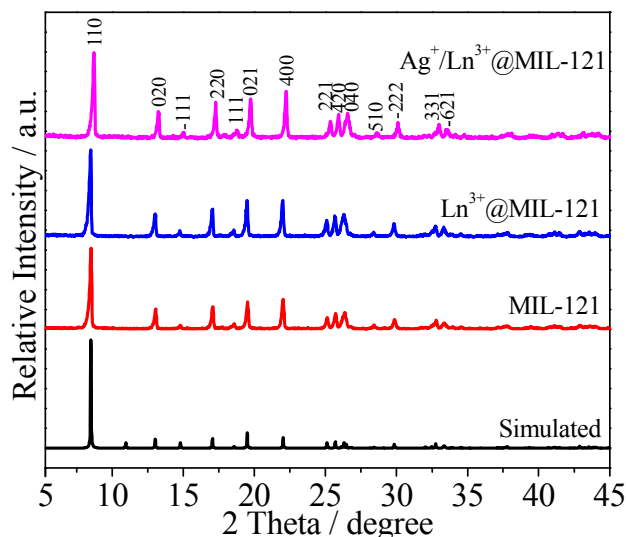


Figure 1 PXRD patterns of MIL-121, Ln^{3+} @MIL-121, and $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121

Photoluminescence studies were performed on each sample of MIL-121 (Figure S5), Ln^{3+} @MIL-121 and $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121. Figure 2 displays the emission spectra of Sm^{3+} @MIL-121 and $\text{Ag}^+/\text{Sm}^{3+}$ @MIL-121. Upon 320 nm excitation (the excitation spectra were shown in Figure S6), Sm^{3+} @MIL-121 shows very similar emission to MIL-121 and almost no luminescence of Sm^{3+} . In the presence of Ag^+ , however, the ligand-centered (LC) emission is significantly suppressed, instead, a series of sharp peaks characteristic of Sm^{3+} luminescence with the strongest peak at 603 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) appear. The fluorescence intensity of Sm^{3+} in $\text{Ag}^+/\text{Sm}^{3+}$ @MIL-121 reaches 30 times stronger than that in Sm^{3+} @MIL-121. Similarly, when excited at 325 nm (the excitation spectra were shown in Figure S7), the emission intensity of Dy^{3+} in the material of Dy^{3+} @MIL-121 is very weak, while that in $\text{Ag}^+/\text{Dy}^{3+}$ @MIL-121 increases greatly and a significant enhanced Dy^{3+} emission by 20 times was observed (Figure 3). Considering the phenomenon that Ag^+ can enhance the luminescence of Ln^{3+} in the visible region, it is also possible to obtain the NIR emission in $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121 ($\text{Ln} = \text{Nd}, \text{Yb}, \text{Er}$) through the enhancement effect of Ag^+ . As expected, the typical NIR luminescence of Nd^{3+} , Yb^{3+} and Er^{3+} in the as-prepared products could be observed (Figure S8). The bands centered at 1067 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, Figure S8a), 985 nm ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$, Figure S8b) and 1538 nm ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$, Figure S8c) are the characteristic emission of Nd^{3+} , Yb^{3+} and Er^{3+} , respectively. It is well-known that the luminescent intensity of the Ln^{3+} relies on the efficiency of the energy transfer from the ligand to Ln^{3+} center.¹⁸ If there is efficient intramolecular energy transfer, Ln^{3+} can be excited more effectively, producing an enhanced fluorescence of lanthanides. It has been reported that the energy transfer process is more effective with the addition of certain transition metal ions.^{15e,19} Herein, the enhancement of luminescent intensity of Ln^{3+} in $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121 results from more efficient energy transfer from ligands to Ln^{3+} ions caused by Ag^+ (Scheme S1). This is consistent with the above PL results shown in Figure 2 and Figure 3. The diminished LC

emission and the emerged intense characteristic luminescence of Ln^{3+} in $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121 ($\text{Ln} = \text{Sm}, \text{Dy}$) indicate that Ag^+ induce an antenna effect to occur, *i.e.*, energy migration takes place upon ligand absorption, followed by intersystem crossing $\text{S1} \rightarrow \text{T1}$ and antenna $\text{T1} \rightarrow \text{f}$ transfer, and then generating f-f emissions of Ln^{3+} ions. To gain more insights into the antenna effect induced by Ag^+ , the fluorescence lifetimes of Ln^{3+} @MIL-121 in the absence and presence of Ag^+ were investigated. As shown in Table S2, the $\text{Ag}^+/\text{Ln}^{3+}$ @MIL-121 have longer emission lifetimes than that of the Ln^{3+} @MIL-121, implying the reduction in the rate constant for non-radiative deactivation and the decrease in energy loss of Ln complexes in the presence of Ag^+ . Moreover, Ag^+ ion can promote intersystem crossing $\text{S1} \rightarrow \text{T1}$ energy transfer due to its heavy-atom effect.^{2a} In addition, the d electrons of Ag^+ in the valence orbital can cause a metal-to-ligand charge transfer, which sensitized the fluorescence of Ln^{3+} . Therefore, all of the three above-mentioned processes contribute to the more effective energy transfer from ligands to Ln^{3+} ions induced by Ag^+ .

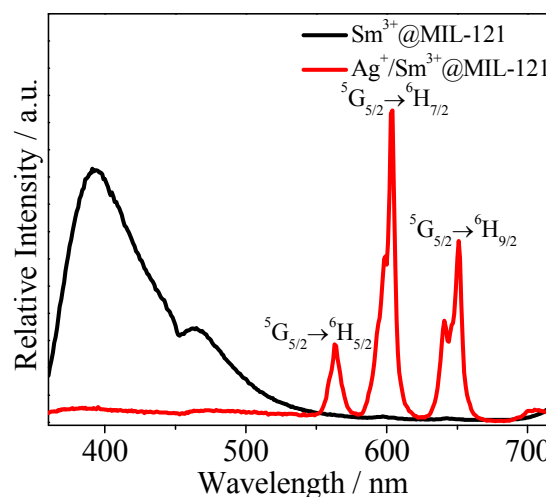


Figure 2 PL spectra ($\lambda_{\text{ex}} = 320$ nm) of Sm^{3+} @MIL-121 (black line) and $\text{Ag}^+/\text{Sm}^{3+}$ @MIL-121 (red line) samples.

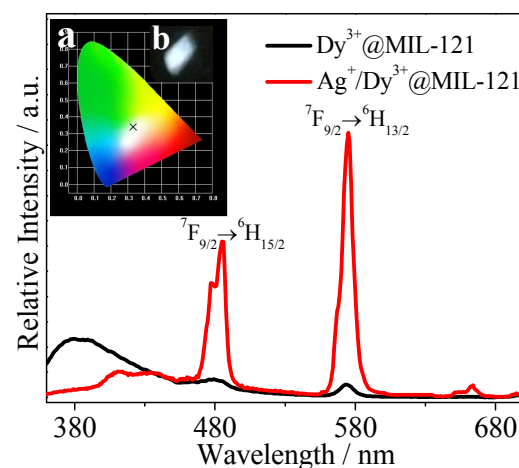


Figure 3 PL spectra ($\lambda_{\text{ex}} = 325$ nm) of Dy^{3+} @MIL-121 (black line) and $\text{Ag}^+/\text{Dy}^{3+}$ @MIL-121 (red line) samples. The inset shows (a) the CIE chromaticity diagram of $\text{Ag}^+/\text{Dy}^{3+}$ @MIL-121 (CIE x: 0.3305; CIE y: 0.3390) and (b) its corresponding white photoluminescence color with UV excitation at 325 nm using a Xe lamp as the excitation source.

It should be mentioned that the white light emission could be realized in both $\text{Ag}^+/\text{Sm}^{3+}@MIL-121$ and $\text{Ag}^+/\text{Dy}^{3+}@MIL-121$. Figure S9 presents the emission spectra of $\text{Ag}^+/\text{Sm}^{3+}$ with excitation wavelength from 320 to 350 nm. When excited at 340 and 350 nm, the PL emission spectra feature in observation of two kinds of luminescence. One is the characteristic Sm^{3+} sharp emissions, and the other is the broad LC emission centered at 450 nm. A striking feature is that the combination of these two kinds of luminescence leads to the overall white light emission. A representative white emission photo, as well as the corresponding CIE coordinates, color-rendering index (CRI) and correlated color temperature (CCT) excited at 340 and 350 nm are illustrated in Figure S9a and Table S3. It was found that, when excited at 340 and 350 nm, the calculated chromaticity coordinates of white light ranged from (0.356, 0.291) to (0.2822, 0.2772), just falling within the white region of the 1931 CIE chromaticity diagram. This verifies that the white-light emitting from $\text{Ag}^+/\text{Sm}^{3+}@MIL-121$ is balanced on synergetic contributions from MC and LC dual emissions, because the excitations at different wavelengths will definitely give rise to different emission intensity relativity of these two kinds of luminescence, thus causing shift of the chromaticity coordinate in the 1931 CIE diagram. As a consequence, the chromaticity coordinates of white light are depending on the excitation wavelength, enabling a potential approach to regulate the white-light property by means of such dual-emissive single-phase compound. Similarly, the white light emission with the CIE coordinate of (0.3305, 0.3390), CRI value of 80.1 and CCT magnitude of 5583 K could also be readily produced in $\text{Ag}^+/\text{Dy}^{3+}@MIL-121$ material (Table S3).

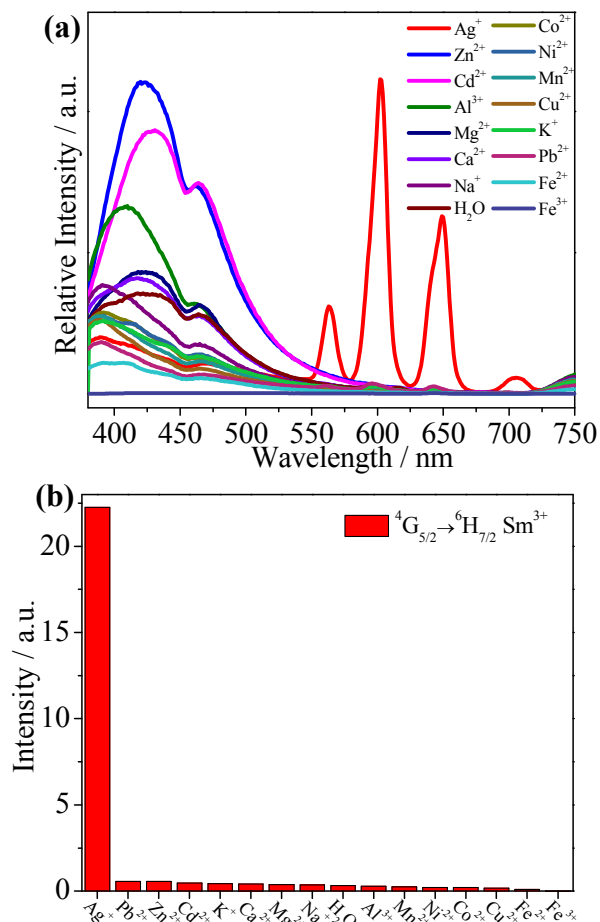


Figure 4 (a) Suspension-state PL spectra and (b) the relative intensities of ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 603 nm for $\text{Sm}^{3+}@MIL-121$ dispersed

in aqueous solutions containing different metal ions (10 mM) when excited at 320 nm.

To examine whether other metal ions had such an enhancement, different kinds of metal ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , and Pb^{2+}) have been introduced into the system of $\text{Sm}^{3+}@MIL-121$, and the $\text{Sm}^{3+}@MIL-121$ is insoluble and stable in aqueous solutions of metal ions, confirmed by the PXRD (Figure S10). The luminescent measurements (Figure 4) illustrate that only Ag^+ can induce a significant fluorescence enhancement of Sm^{3+} and no remarkable fluorescence responses were observed upon the addition of other metal ions. This indicates $\text{Sm}^{3+}@MIL-121$ could be a potential sensor with excellent selectivity for Ag^+ in the aqueous solution.

We further investigated the time-response characteristic of the $\text{Sm}^{3+}@MIL-121$ sensor toward Ag^+ . As demonstrated by Figure 5, Ag^+ -induced fluorescence enhancement reaction is very fast. The intensity of highest peak at 603 nm has been increased to more than 7.0 times in 1 min and a constant value in 30 min.

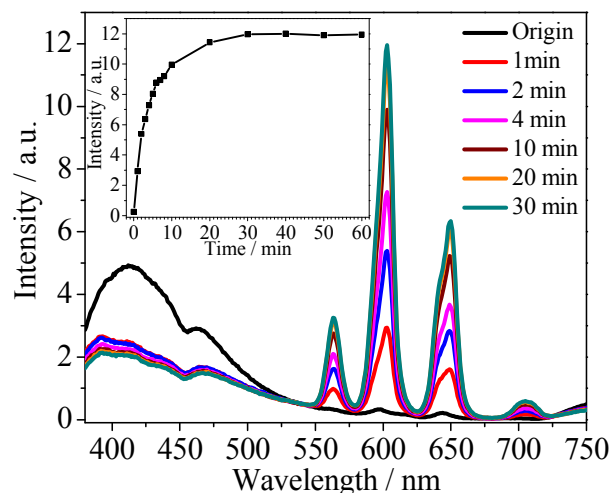


Figure 5 Variation of fluorescence intensity of $\text{Sm}^{3+}@MIL-121$ at 603 nm with immersion time in Ag^+ solution (10 mM), $\lambda_{\text{ex}}=320$ nm; inset: a fluorescence intensity plot depending on the immersion time.

For better understanding the response of fluorescence of $\text{Sm}^{3+}@MIL-121$ to Ag^+ , concentration-dependent luminescence measurements were also carried out. The $\text{Sm}^{3+}@MIL-121$ solid samples were immersed in different concentrations of Ag^+ for 30 min, and then their luminescence spectra were recorded in Figure S11. The fluorescence intensity of $\text{Sm}^{3+}@MIL-121$ was proportional to Ag^+ concentrations in the range of 0 – 500 μM . And based on these, we estimated the detection limit of $\text{Sm}^{3+}@MIL-121$ to be 0.09 μM . This detection limit met a 50 $\mu\text{g L}^{-1}$ (about 0.46 μM) standard of U.S. Environmental Protection Agency (EPA) for a maximum allowable level of Ag^+ in drinking water.²⁰

In summary, a facile strategy, PSM was utilized to fabricate luminescent lanthanide functionalized MOFs by encapsulating Ln^{3+} cations into the pores of MIL-121 whose uncoordinated carboxyl groups could act as postsynthetic modification sites. And the Ag^+ ion was found to be able to greatly enhance the visible and NIR fluorescence of the Ln^{3+} -doped MOF ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Nd}, \text{Yb}, \text{Er}$). Thus, 4d-4f heterometallic Ag-Ln co-doped MOFs ($\text{Ag}^+/\text{Ln}^{3+}@MIL-121$) was also assembled by PSM. The framework, MIL-121, can serve as both a scaffold and an antenna for hosting and sensitizing the luminescence of the Ln^{3+} cations in the presence of Ag^+ , since Ag^+ can induce efficient energy transfer from ligands to Ln^{3+} . Moreover, the resulting bimetallic MOFs $\text{Ag}^+/\text{Sm}^{3+}@MIL-121$ or $\text{Ag}^+/\text{Dy}^{3+}@MIL-121$ is capable of directly generating white light via

a dual-emitting (the metal-centered (MC) f-f emission characteristic of Ln^{3+} ion and ligand-centered (LC) emission) pathway by a single-phase phosphor. It is rarely reported about the single-phase white-light emitters based on 4d-4f heterometallic co-doped MOF. As a sensing material for Ag^+ , the Sm^{3+} @MIL-121 has features including simple preparation procedure, robust rigid structure, excellent selectivity for Ag^+ , fast detection time (< 1 min), and highly sensitivity with a detection limit of $0.09 \mu\text{M}$. The investigations of this series of Ln-Ag heterometallic co-doped MOFs may provide a new approach to obtain Ln^{3+} -based MOFs with strong visible and NIR emission, and also greatly expand their application range as functional luminescent materials (for example, emitters and sensors).

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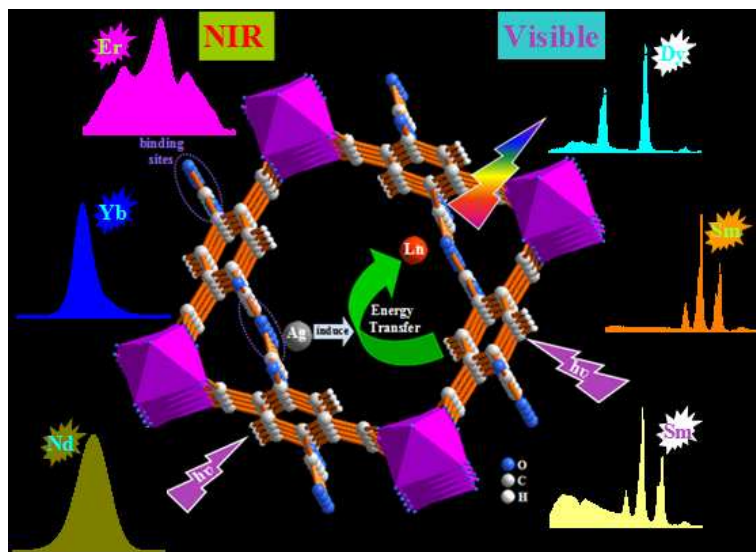
Notes and references

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A new class of lanthanide luminescent MOFs was constructed by encapsulating Ln³⁺ into the pores of MIL-121 (Ln³⁺@MIL-121). And Ag⁺ was found to be able to greatly enhance the weak fluorescence of Ln³⁺@MIL-121 since it could induce more efficient intramolecular energy transfer from ligand to Ln³⁺, thus leading to the visible and NIR luminescence in Ag-Ln co-doped MOFs.