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## AIEgen modulated per-functionalized flower-like IRMOF-3 frameworks with tunable light emission and excellent sensing properties<sup>†</sup>

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A series of functional IRMOF-3 frameworks with solid-state luminescence and tuneable light emission (from 490 to 608 nm) have been synthesized by per-functionalizing AIE-active Schiff-bases with zinc. These precursor AIE-active ligands endowed the functional frameworks with boosted fluorescence emission efficiencies (from 0.16% to 1.03%). IRMOF-3-h revealed a flower-like morphology attributed to the formation of J-aggregates, and could be used as a fluorescent probe for sensitive detection of copper(II) (135 pM) and thiols (subnanomole).

Developing functional luminescent materials with spectral tunability and structural diversity has attracted increasing research attention in the exploitation of chemosensors, light-emitting diodes (LEDs), biomedicine, and so on.<sup>1</sup>

Benefitting from the significant development of metalorganic frameworks (MOFs) in recent decades, endowing MOFs with luminescence characteristics has been considered as a new pathway for the fabrication of solid-state luminescent nanomaterials. In particular, luminescent MOFs (LMOFs) could inherit the unparalleled tunability, structural diversity, and chemical and physical properties of MOFs.<sup>2</sup> Moreover, LMOFs have been considered as a fascinating material class, and applied in a wide range of areas, including bioimaging,<sup>3</sup> chemosensing,<sup>4</sup> intelligent light sensors,<sup>5</sup> and point-of-care testing (POCT).<sup>6</sup> More importantly, the organic–inorganic hybrid nature of MOF materials can provide the LMOFs with

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multiple sources of luminescence, including organic ligands excitation, metal-centered emission, and charge-transfer between the metal ions and organic ligands.<sup>7</sup> Besides, the intrinsic permanent porosity of MOFs can also enable the encapsulation or adsorption of guest luminescent species to obtain guest-induced LMOFs.<sup>8</sup> However, regulating the luminescence properties of LMOF in a controlled and dynamic manner is still a fundamental and challenging research goal.<sup>9</sup>

Reported LMOFs with tuneable fluorescence properties emphasized the ratio adjustment of the metal ions (lanthanide ions) and regulation of charge transfer between the metal ions and organic linkers.<sup>10</sup> Nevertheless, the limited variety of lanthanides severely narrowed their development and applications. Inspired by organic dyes, regulating the fluorescence emission of LMOFs could also be achieved by employing different chromophores or auxochromes as ligands.<sup>11</sup> However, the notorious aggregation-caused quenching (ACQ) effect makes this strategy encounter a bottleneck. The intriguing aggregation induced emission (AIE) effect pioneered by BenZhong Tang<sup>12</sup> has been revealed as a new route of LMOF fabrication. In contrast to the ACQ effect, the AIE luminogens (AIEgens) display less-emission in dilute solution but much higher fluorescence in aggregated states.<sup>13</sup> Previous reports have evidenced that the AIEgen based LMOFs can inherit the AIE properties of AIEgens and numerous merits of MOFs,<sup>14</sup> and show surprisingly boosted fluorescence emission efficiency due to the restricted intramolecular rotations, vibrations, and motions by the MOF framework.<sup>15</sup> However, most of the AIEgen functionalized LMOFs are developed based on tetraphenylethylene and its derivates.<sup>16</sup> Besides, reported AIEgen based LMOFs largely rely on physical doping or conjugation strategies, in which the intermolecular forces between organic AIEgens and ligands would be much weaker than that of the chemical bonding strategy.<sup>17</sup> Therefore, developing new kinds of AIEgen based LMOFs with tuneable emission, intense solid-state luminescence, and large Stokes shifts is still highly demanded.18

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AIE-active Schiff-bases are a newly emerging class of AIEgens and have been proved to be a useful tool for the development of new AIE molecules.<sup>19</sup> More importantly, their independent conjugated moieties would endow them with simultaneous fluorescence emission and bonding ability.<sup>20</sup> Thereby, by adopting a pre-synthesis modification strategy, we herein designed and fabricated a series of Schiff-base based LMOFs with tuneable emission. diverse structure, and detection function. As illustrated in Scheme 1, we firstly designed and synthesised the Schiff-bases featuring conjugated moieties linked by imine bonds via amine aldehyde condensation of salicylaldehyde (SAL) and its derivates with 2-aminoterephthalic acid (ATA), and used them as the precursor of the LMOFs. Thereinto, the ATA portion of the precursor Schiff-bases was designed to react with a zinc ion to form the IRMOF-3 framework, while the imine bond and the benzaldehyde portion would enable the detection of copper ions and fluorescence emission, respectively. By finely varying the substituent groups of SALs and subsequently the Schiff-bases, the fluorescent properties of the resulted LMOFs would be finely tuned, as the fluorescence of Schiff-bases with excited state intramolecular proton transfer (ESIPT) characteristics is strongly dependent on the substituents of SALs.

We first verified the condensation reaction of ATA with SAL, which would afford the original Schiff-base 3a (2-[(2-hydroxy benzylidene)amino]terephthalic acid, Fig. S1, ESI<sup>†</sup>). The results of high-resolution mass spectra (HRMS), and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (Fig. S2–S4, ESI<sup>†</sup>) indicated that, *via* simple and convenient syntheses, the Schiff-base 3a was successfully obtained with a high yield (81%). According to the mechanism of ESIPT, the Schiff-base 3a could feature the AIE effect, which was favourably verified by the fact that the fluorescence of Schiff-base 3a was weak in tetrahydrofuran (THF) solution but enhanced with the increase of the water fraction (Fig. S5, ESI<sup>+</sup>).

With the successful synthesis of the precursor Schiff-base 3a, the AIE-active iso-reticular metal-organic framework-3-a (IRMOF-3-a) was constructed via co-incubating Schiff-base 3a with zinc ions, and compared with IRMOF-3 (Fig. S1, ESI<sup>†</sup>). The FTIR spectra of IRMOF-3 and IRMOF-3-a (Fig. S6, ESI<sup>+</sup>) show that the peaks around 3500 and 3388 cm<sup>-1</sup>, which can be ascribed to the amino stretching vibration of IRMOF-3, disappear for IRMOF-3-a. Besides, like other pre-functionalized MOFs,<sup>21</sup> due to the modification of the organic block and intermolecular hydrogen bonding, the Langmuir surface area and the pore volume of IRMOF-3-a were all decreased with the introduction of SAL (from 1027.38  $m^2~g^{-1}$  and 0.75  $cm^3~g^{-1}$  of IRMOF-3 to 54.10 m<sup>2</sup> g<sup>-1</sup> and 0.28 cm<sup>3</sup> g<sup>-1</sup> of IRMOF-3-a

respectively, Fig. S7, ESI<sup>†</sup>). Nevertheless, type I adsorption observed for both IRMOF-3 and IRMOF-3-a indicated that the microporous nature of IRMOF-3-a was maintained. The different morphology of IRMOF-3-a was also confirmed by field emission scanning electron microscopy (FESEM), and the results revealed that IRMOF-3-a exhibited a uniform flower-like spherical morphology with an average diameter of 2 µm (Fig. S8, ESI<sup>†</sup>) and not the cube morphology of IRMOF-3.<sup>22</sup> Meanwhile, the results of powder X-ray diffraction (PXRD) showed a degraded crystal quality of IRMOF-3-a, which may be attributed to the increased steric hindrance and altered electronic effects after modification (Fig. S9, ESI<sup>†</sup>).<sup>23</sup>

Besides, the results of thermogravimetric analysis (TGA, Fig. S10A, ESI<sup>†</sup>) demonstrated the same thermal stability of IRMOF-3-a and IRMOF-3; a weight loss of about 40% was observed from 450 to 500 °C due to the destruction of the IRMOF-3 framework. Nevertheless, a different weight loss of about 25% from 750 to 800 °C was observed for IRMOF-3-a, which might be ascribed to the decomposition of Schiff-bases. Besides, we also verified the comparable chemical stability of IRMOF-3-a (Fig. S10B and C, ESI<sup>†</sup>). X-ray photoelectron spectroscopy (XPS) revealed that carbon, oxygen and zinc elements were distributed throughout the IRMOF-3-a framework and the C 1s spectrum of IRMOF-3-a could be divided into five components (Fig. S11, ESI<sup>+</sup>). All of the results demonstrated the successful assembly of IRMOF-3-a by adopting the precursor Schiff-base 3a. Significantly, the precursor AIE-active ligands endowed the IRMOF-3-a with a boosted fluorescence emission efficiency (from 0.16% to 1.03%), which might be attributed to the restricted intramolecular rotations, vibrations, and motions by the rigid skeletons and specific topologies of the IRMOF-3 framework.

The boosted fluorescence and successful construction of IRMOF-3-a encouraged us to further engineer the luminescence properties of IRMOF-3 by varying the precursor Schiff-bases. We thus designed and synthesised a series of Schiff-bases 3b-3j via a similar condensation reaction, and their structures were also confirmed to be correct via FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS (Fig. S12-S39, ESI<sup>†</sup>). Thereinto, the electronic effect of Schiff-base 3a was modulated by varying the functional groups on the benzene ring of SAL and retained the basic Schiff-base structure with ESIPT properties. We then constructed a series of AIE-active LMOFs via analogously co-reacting the resulting Schiff-bases with zinc ions (Fig. S40-S43, ESI<sup>+</sup>). Similarly, the fluorescence quantum yield (QY) and fluorescence lifetime of IRMOF-3-a were dramatically improved (from 0.16% to 1.03% and 0.672 to 1.101, respectively). And more importantly, the fluorescence emission of the resulting functional IRMOF-3 was finely tuned from blue (490 nm) to red (608 nm) along with the alteration of the precursor Schiff-base (Fig. 1 and Table S1, ESI†).

We then wanted to decipher the possible photophysical mechanism of the resulting AIE-active LMOFs.<sup>24</sup> The molecular geometries in the ground  $(S_0)$  and excited  $(S_1)$  states (Tables S2–S4, ESI<sup>†</sup>) of those precursor Schiff-bases reveal that the Schiff-bases with electron-withdrawing groups at position 4 are more coplanar



**Fig. 1** (A) Tuneable light emission of IRMOF-3-(**a**–**j**). (B) The commission International de L'Eclairage of the fluorescence spectra. (C) Photographs of IRMOF-3-(**a**–**j**) under natural light (bottom) and under 365 nm UV light illumination (top).

(the dihedral angle lose to  $180^{\circ}$ ) than that with electron-donating groups (Tables S5-S14, ESI<sup>†</sup>), and thus benefit the ESIPT. Meanwhile, with the molecule going from the ground state to the excited state, the distance between the N of the imine and H of the hydroxyl is significantly shortened, and the O-H bond length is unchanged (Tables S5-S14, ESI<sup>+</sup>). In addition, HOMO electrons of the ground state are mainly located in the benzene ring with an amino group and with a few in the imine moiety. While in the excited state, the electrons of the LUMO are mainly distributed in the phenol ring and imine moiety (Fig. S44 for Schiff-base 3a and Fig. S45–S53 for Schiff-bases 3b-3j, ESI<sup>+</sup>). The apparent distance between N and H changes and the electron migration from the ground state to the excited state also provides the prerequisite for ESIPT properties of the Schiff-bases. Besides, the attachment of an electron-withdrawing group substituent enables the decrease of the energy gap between the HOMO and LOMO of the keto-form tautomer (Tables S5-S14, ESI<sup>+</sup>). The gap is negatively correlated with its electron-withdrawing ability, which would red-shift the emission wavelength, and vice versa. All these results of the theoretical calculations are consistent with those of the experiments.

Besides, the images of FESEM also revealed different morphologies and structures for those AIE-active LMOFs (Fig. S54, ESI†). Thereinto, the LMOFs with precursor Schiff-bases with electron withdrawing groups including IRMOF-3-b, IRMOF-3-c, IRMOF-3d, IRMOF-3-g, and IRMOF-3-h all demonstrated a flower-like morphology with different sizes. The self-assembly growth process of flower-like AIE-active LMOFs was also investigated via imaging the same sample after 1, 6, 12, and 24 hours of aging time, in which IRMOF-3-h was taken as the proof-of-concept (Fig. 2A-E). The results indicated that every single particle was composed of nanosheets and grew by stacking monomers one by one on a spherical particle core, and finally formed stacked flowers. The unique flower-like morphology of these AIE-active LMOFs may be attributed to the fact that a more stable structure J-aggregate than monomers was formed for Schiff-base based IRMOF-3. Thereinto, due to the intermolecular  $\pi$ - $\pi$  stacking interaction of the benzene



**Fig. 2** The self-assembly growth process: (A) 1 h, (B) 6 h, (C) 12 h, (D) 24 h, (E) low-magnification FESEM image of IRMOF-3-h. (F) Possible mechanism and DFT calculated model of IRMOF-3-h.

rings positioned above or below the C—N double bond (Fig. 2F), there was a special offset face-to-face force between individual molecules of the J-aggregate.<sup>25</sup> The coordination interaction between zinc ions and ligands and the intermolecular  $\pi$ - $\pi$  stacking interaction coexisted in the structure of the LMOFs. The lower the energy of the formed J-aggregate, the easier the morphology stacking, thus making IRMOF-3-**h** a special flower-like morphology (Table S15, ESI†).

In view of the enhanced fluorescence intensities of the obtained LMOFs, we considered the potential application of the resulting LMOFs in Cu<sup>2+</sup> detection, since a copper ion is an essential element for plants and animals, and abnormal copper concentrations are associated with the death of bacteria and algae, dysfunction of the brain and gastrointestinal tract, and so on. Therefore, the detection of copper ions is of great significance in environmental protection and human health. As a proof-of-concept, we employed IRMOF-3-h as the fluorescent probe in the developed sensor, and the specificity and selectivity of the fluorescence sensor were verified satisfactorily by challenging the detection with similar ions and interferents (Fig. 3A). And under the optimized conditions (Fig. 3B), the sensor also exhibited an excellent performance with a low limit of detection (LOD) of 135 pM, which was much lower than the allowed concentration of Cu<sup>2+</sup> (32 mM) in drinking water permitted by the World Health Organization (WHO) and most



**Fig. 3** (A) Selectivity of the IRMOF-3-h based sensor for  $Cu^{2+}$  detection. The concentrations of the targets were 100 nM. (B) Fluorescence emission spectra of the IRMOF-3-h based sensor exposed to various concentrations of  $Cu^{2+}$ . Fluorescence emission spectra of the IRMOF-3-h based sensor exposed to various concentrations of  $Cu^{2+}$ . Fluorescence emission spectra of the IRMOF-3-h based sensor exposed to various concentrations of  $Cu^{2+}$ . 0, 1, 2, 4, 6, 8, 10, 15, 20, 30, 50, 100 nM from top to bottom.

of the reported references (Table S16, ESI<sup>†</sup>). Besides, when we generalized the fluorescent sensor to real water samples (from the Yudai river in Hunan), the detection method showed high accuracy (in comparison with the results of ICP-MS) and satisfactory recoveries ranging from 98.5% to 102.2% (Table S17, ESI<sup>†</sup>). These results exemplified that the functionalized LMOF fluorescent probes can be applied for environmental water samples.

Since biothiols can coordinate with copper ions and thus the IRMOF-3-**h** would be recovered,<sup>26</sup> we then used the IRMOF-3-**h**/Cu complex as a biothiol fluorescent probe. And as expected, the quenched fluorescence intensity of the IRMOF-3-**h**/Cu<sup>2+</sup> complex could be selectively recovered by adding biothiols (Fig. S55B–D, ESI†). Meanwhile, it was found that the flower-like structure of IRMOF-3-**h** was destroyed by Cu<sup>2+</sup> (Fig. S56A and B, ESI†), but could be well restored after being bonded with biothiols (Fig. S56C and D, ESI†), and organic molecules were obviously attached to the surface (Fig. S56E, ESI†).

Then, the possible fluorescence quenching mechanism of IRMOF-3-h by  $Cu^{2+}$  was investigated. The fluorescence decay time of IRMOF-3-h was found to be 3.77 ns and slightly decreased to 2.96 ns with the addition of  $Cu^{2+}$  (Fig. S57, ESI†). And the UV-Vis absorption spectra of IRMOF-3-h before and after the addition of  $Cu^{2+}$  (Fig. S58, ESI†) showed that the absorption peak at 330 nm (black line), which might be assigned to  $n-\pi^*$  transition of the C=N bond, migrated to 390 nm (red line) with the addition of  $Cu^{2+}$ . These results indicate that the fluorescence quenching of IRMOF-3-h by  $Cu^{2+}$  is a static mechanism. Besides, the separation of the photoexcited electron-hole pair in IRMOF-3-h would facilitate the electron transfer from IRMOF-3-h to the paramagnetic  $Cu^{2+}$  with an unfilled shell,<sup>27</sup> thus resulting in the fluorescence quenching of IRMOF-3-h *via* electron or energy transfer.

In summary, we developed a pre-synthesised modification strategy of functional IRMOF-3 fabrication by AIE-active Schiff-bases with zinc. We demonstrated that the fluorescence properties including emission of the functional IRMOF-3 could be finely engineered with the precursor Schiff-bases. Besides, a special flower-like morphology was observed for the functional IRMOF-3 constructed based on precursor Schiff-bases with electron withdrawing groups, and the formation mechanism of the flower-like morphology was reasoned as the formation of J-aggregates. More importantly, by employing AIE-active Schiff-bases as the ligands, the fluorescence emission of functional IRMOF-3 was surprisingly boosted, thus guaranteeing the improved sensing performance of the functional IRMOF-3 based fluorescent probe.

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### Conflicts of interest

There are no conflicts to declare.

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