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## ARTICLE



## Flexible Metal-Organic Frameworks for Wavelength-Based Luminescence Sensing of Aqueous pH

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Luminescence sensing is commonly based on the change of emission intensity, lifetime, and/or quantum yield of luminescent materials. Wavelength-based luminescence sensing was rarely documented, comparatively. Flexible metalorganic frameworks (MOFs) with rich fluorophores are promising sensory materials due to their unique stimuli-responsive luminescence. However, it is still challenging to construct such materials with high hydrolytic stability, which can be utilized in water systems. Here we present two isoreticular flexible MOFs synthesized by carbazole derived ligands, which show high porosity and excellent stability in aqueous solutions with a wide range of pH values. Interestingly, both MOFs show structural breathing behavior upon the variation of guest molecules inside their pores due to the topologically allowed flexibility. With their frameworks breathing, sensitive fluorescence changes in wavelength of the maximum emission have been observed. Remarkably, the wavelengths of maximum emission are well dependent on the pH values (1 to 8) of aqueous solutions in a linear relationship, suggesting a new means of pH sensing based on emission wavelength instead of intensity. The wavelength-based fluorescence sensing thus offers an alternative way for pH indication free of some drawbacks in intensity-based fluorescence sensing, which should be fundamentally important for the development of new pH sensors in environmental and life science.

## 1. Introduction

Luminescence sensing are essential tools in many fields of science and technology for the sensing and detection of different substances, such as gaseous molecules (O2, CO2, CO, VOCs, etc.), heavy metal ions, explosives, and biological targets (intracellular pH, oligonucleotides, glucose, cancer biomarkers, etc.).<sup>1-4</sup> Most luminescence sensors are based on the changes in the emission intensity of one transition (Scheme 1a). However, such intensity-based luminescence sensing often suffers from interferences from many factors, including drift of optoelectronic system (e.g. lamp for excitation intensity and detector for emission collection), probe concentration, and other substances coexisted in the systems.<sup>5,6</sup> There are generally two ways to overcome these drawbacks. One is the measurement of luminescence lifetime or quantum yield (Scheme 1b), and the other is the ratiometric sensing method which is based on analyte dependent intensity ratio of two

well separated emissions (Scheme 1c). Although analyses based on the two methods are free of above mentioned interferences, associated measurements or syntheses of sensory materials are much more difficult and complicated. New advanced luminescent materials are thus highly desirable for chemical sensing and detection in facile but reliable manners.

Metal-organic frameworks (MOFs) are a class of newly developed porous solid materials, constructed from organic linkers and metal-containing nodes through coordination bonds.<sup>7</sup> These materials have attracted intense attention over the last two decades due to their structural variety and great potential in many fields, such as gas storage, separation and catalysis.<sup>8-10</sup> Many works have also demonstrated that luminescent MOFs are promising materials applicable in molecule sensing and detection.<sup>11-13</sup> Compared with conventional porous materials, such as zeolites and activated carbon, one distinct characteristic of MOFs is their structural flexibility, which, in some cases, is sensitive and responsive toward external stimuli, such as guest accommodation.<sup>14-16</sup> The flexible but crystalline porous structures of MOFs with highly tailorable conjugated organic components thus make them considerably attractive as advanced materials for luminescence sensing, in comparison with rigid porous sensors. One exciting example is  $[Zn_2(bdc)_2(dpNDI)]$  (bdc<sup>2-</sup> = 1,4-benzenedicarboxylate; dpNDI = N,N'-di(4-pyridyl)-1,4,5,8naphthalenediimide) reported by Kitagawa and co-workers.<sup>17</sup> This MOF has a twofold interpenetrated dynamic framework, in which naphthalenediimide fluorophores are incorporated.

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<sup>&</sup>lt;sup>†</sup> Electronic Supplementary Information (ESI) available: Detailed sample activation and gas adsorption of BUT-62 and -63, stability test of BUT-62 and -63, N<sub>2</sub> adsorption of acid or base treated BUT-62 and -63, temperature-dependent PXRD of BUT-62 and -63, fluorescence measurements for pH sensing, fabrication of MOF/CMC plates can be found in ESI. See DOI: 10.1039/x0xx00000x



Scheme 1 Schematic representations of intensity (a), lifetime or quantum yield (b), ratiometric intensity (c), and wavelength (d) based luminescence sensing.

Interestingly, it shows intense luminescent emission when adsorbing a class of aromatic compounds, while its guest-free framework is not luminescent. Particularly, its fluorescent wavelength is dependent on the chemical substituents of the aromatic guests. The observed emission turn-on and changes were proposed to be resulted from the dynamic movement of two sets of interpenetrated networks by dislocation of their leads which mutual positions, to enhanced naphthalenediimide-aromatic guest interactions and the formation of complexes with charge transfer characteristics. This MOF is thus potentially applicable in detecting series of aromatic molecules with small structural difference.

Nevertheless, most flexible MOFs are not stable in aqueous media, restricting their applications in many circumstances (e.g. physiological fluids).<sup>18-20</sup> The prerequisite of simultaneous presence of dynamic long-range ordered framework, high chemical resistance, as well as sensitive luminescence response to external stimuli, thus challenges the construction of porous flexible MOFs for applications in aqueous media as advanced sensory materials. Chemically stable MOFs were usually constructed by the combination of highly charged metal ions with carboxylate-based ligands.<sup>21,22</sup> In the past few years, zirconium-based MOFs (Zr-MOFs) have been demonstrated to be a subclass of MOFs with both high designability and exceptional stability.<sup>23-27</sup> Most of reported Zr-MOFs were constructed by high-valent Zr<sup>4+</sup> species and anionic O-containing organic ligands, including carboxylates, phenolates, and phosphates. Due to the strong hard acid-hard base interaction between Zr<sup>4+</sup> and ligand O atoms, many highly porous Zr-MOFs have been proven stable in organic solvents, water, and even strong acidic and weak basic aqueous solutions.<sup>28-31</sup> On the other hand, the chemical robustness of most Zr-MOFs is often accompanied with their framework rigidness, limiting the occurrence of structural flexibility for specific application.

In this work, we present two flexible Zr-MOFs,  $Zr_6O_4(OH)_8(H_2O)_4(CTTB)_2$  (BUT-62, BUT = Beijing University of

Technology) and Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>(CTNA)<sub>2</sub> (BUT-63), which were synthesized from intentionally chosen low symmetrical ligands (trapezoid) with strong fluorophores, namely, 4,4',4'',4'''-(9H-carbazole-1,3,6,8-tetrayl)-tetrabenzoic acid 6,6',6",6"'-(9H-carbazole-1,3,6,8-(H₄CTTB) and tetrayl)tetrakis(2-naphthoic acid) (H<sub>4</sub>CTNA), as shown in Figure 1. The MOFs show high porosity, high chemical stability, reversible guest-dependent structural flexibility, as well as stimuli responsive fluorescence upon interactions with guest molecules. Remarkably, evident fluorescent emission shifts were observed when the MOFs were treated with aqueous solutions with wide range of pH values. Especially, the wavelengths of maximum emission ( $\lambda_{max}$ ) are well dependent on the pH values of aqueous solutions ranging from 1 to 8 in a linear relationship, rendering a new type of luminescence sensing method by the determination of emission wavelength instead of intensity, lifetime, or quantum yield (Scheme 1d). To the best of our knowledge, the wavelength-based luminescence sensing of pH realized by BUT-62 and -63 is unprecedented in MOF chemistry or other luminescent materials, which should be of high importance for luminescence sensing in some circumstances as an alternative option.

#### 2. Results and discussion

#### 2.1 Synthesis and Crystal Structures of BUT-62 and -63

Solvothermal reactions of  $ZrCl_4$  and the ligands (H<sub>4</sub>CTTB or H<sub>4</sub>CTNA) in N,N-dimethylformamide (DMF) in the presence of an excess of modulator acid (acetic acid or formic acid) yielded crystalline samples of as-synthesized BUT-62 and -63 (hereafter referred as BUT-62W and -63W, W stands for white color of the bulk sample), respectively. It should be pointed out that in the synthesis of Zr-MOFs, additional acid modulator usually plays an important role in controlling the formation of products, as well as the nucleation and growth rate, morphology, and crystallinity of the crystalline products.<sup>23,34</sup>

Without modulators, intergrown micro-sized aggregates of crystals or amorphous phases were usually obtained, as shown in SEM images (SI, Figure 11 and S12). Acetic acid or formic acid was used as the modular reagent to obtain pure crystalline samples of BUT-62 and -63, which were confirmed by powder X-ray diffraction (PXRD) (Figure 2b and c). Tuning the amounts of modulator led to single crystals big enough for the single-crystal X-ray diffraction in each case. In addition, from the FT-IR spectra of BUT-62 and -63, slight blue shifts of carbonyl group characteristic bands compared with corresponding ligands were observed, illustrating the metal coordination of carboxylate groups of ligands (SI, Figure S2 and S3).

Single-crystal structure analysis revealed both BUT-62W and -63W crystallize in the space group Immm and have isoreticular three-dimensional (3D) frameworks consisted of 8connected  $[Zr_6O_4(OH)_8(H_2O)_4]^{8+}$  clusters (hereafter referred as Zr<sub>6</sub>) which are interconnected by 4-connected CTTB<sup>4-</sup> and CTNA<sup>4–</sup> ligands, respectively (Figure 1a, b, g, and h). In the Zr<sub>6</sub> cluster, six Zr atoms arrange in a distorted octahedral geometry, and each facet of the Zr<sub>6</sub> octahedron is capped by a  $\mu_3$ -O<sup>2-</sup> or  $\mu_3$ -OH<sup>-</sup> group, forming a Zr<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub> core. The six Zr atoms are all eight-coordinated, each with eight O atoms

in a tetragonal antidipyramid coordination geometry. For the two Zr atoms at the apical positions, the eight coordinated O atoms are four  $\mu_3$ -OH/O group O atoms and four carboxylate O ones from four different but symmetrically equivalent CTTB<sup>4-</sup> or CTNA<sup>4-</sup> ligands. For the four Zr atoms at the equatorial positions, eight coordinated O atoms come from four  $\mu_3$ -OH/O groups, two terminal OH groups, and two carboxylates from different but symmetrically equivalent CTTB<sup>4-</sup> or CTNA<sup>4-</sup> ligands. Thus, a  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$  core is connected with eight CTTB<sup>4-</sup> or CTNA<sup>4-</sup> ligands through eight carboxylate groups. Each CTTB<sup>4-</sup> or CTNA<sup>4-</sup> ligand links four Zr<sub>6</sub> clusters with each carboxylate group coordinating with two neighboring Zr atoms of one Zr<sub>6</sub> cluster in a bimonodentate fashion. Alternate connection of the CTTB<sup>4-</sup> or CTNA<sup>4-</sup> ligands and the Zr<sub>6</sub> clusters results in the 3D framework of BUT-62 and -63 with intersecting channels (Figure 1c and i). The largest diamondoid channels are along the crystallographic b direction and relatively small ones in the a and c directions. Two diagonals for cross-section of the large diamondoid channels are related to the unit cell a and c axes, respectively, and the lengths are estimated to be ca. 10 and 23 Å for BUT-62W, and 13 and 29 Å for BUT-63W (taking into account the van der Waals radii of the atoms). Diameters of the small channels along the a and c



Fig. 1 Construction, crystal structures, and underlying net topology of BUT-62 and -63. Ligands H<sub>4</sub>CTTB (a) and H<sub>4</sub>CTNA (g) as 4-connected linkers (d) are used to assemble with Zr<sub>6</sub> clusters (b and h) as 8-connected nodes (e) to generate 3D networks of BUT-62 and -63 (c and i) with the scu-a topology (f), respectively (in crystal structures, H atoms are omitted for clarity and color codes are set as Zr, purple; C, O, and N, green; those in Zr<sub>6</sub> cluster are Zr, powderblue; C, grey; and O, red).

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directions are 4~14 and 3~14 Å in BUT-62W and 7~17 and 6~17 Å in BUT-63W, respectively. The total solvent accessible volumes of BUT-62W and -63W are calculated to be 74.6 and 80.0% of their crystal volumes by PLATON, respectively. Clearly, a lot of –OH/O groups on the Zr-based clusters decorate the pore surfaces of the frameworks, which can provide the opportunity of forming host-guest interactions with guest molecules. Topologically, when considering each Zr<sub>6</sub> cluster and each CTTB<sup>4–</sup> or CTNA<sup>4–</sup> ligand as a 8- and 4-connected nodes, respectively, the frameworks of BUT-62 and -63 can be simplified into an augmented 4,8-connected *scu* (*scu-a*) network with the point symbol of  $(4^4.6^2)_2(4^{16}.6^{12})$  (Figure 1d-f).

It was noted that the CTTB<sup>4-</sup> and CTNA<sup>4-</sup> ligands in BUT-62 and -63 are in a planar trapezoidal coordination configuration with the  $C_{2v}$  symmetry, while all previously reported planar tetratopic carboxylate ligands in Zr-MOFs are rectangular or square usually with the  $D_{2h}$  or  $D_{4h}$  symmetry, respectively, such as TCPP<sup>4-</sup> in PCN-22X (X =  $1^{\sim}5$ ),<sup>26,32,35-37</sup> MMPF-6,<sup>38</sup> MOF-545,<sup>39</sup> MOF-525,<sup>39</sup> and NU-902,<sup>40</sup> Py-XP<sup>4-</sup> in NU-1101,<sup>27</sup> PTBA<sup>4-</sup> in NU-1100,  $^{33}$  and ETTC<sup>4-</sup> in PCN-94<sup>8</sup> and PCN-128,  $^{41}$  etc. (SI, Figure S1 and Table S7). For the  $D_{2h}$  and  $D_{4h}$  symmetric ligands,  $Zr_6$ clusters with higher connectivities seem to be more thermodynamically stable, which often give rise to rigid frameworks, such as 4,12-connected ftw-a network of PCN-94, PCN-228, PCN-229, PCN-230, NU-110X (X = 0~5),<sup>27,33</sup> MOF-525, -535,<sup>39</sup> CPM-99,<sup>42</sup> Zr-BTBA,<sup>24</sup> and Zr-PTBA,<sup>24</sup> and *shp-a* network of PCN-223.<sup>32</sup> The 4,6-connected she-a network of PCN-224, which can be regarded as a partial ligand missing ftw-a type network, is rigid as well. Furthermore, the assembly of  $D_{2h}$  and  $D_{4h}$  symmetric ligands with 8-connected  $Zr_6$  clusters also tends to form csq-a type rigid framework (e.g. NU-1000,<sup>43</sup> MOF-545, MMPF-6, PCN-222, and PCN-128). The rigidity of these MOF frameworks should be related with their intrinsic topologies. As pointed out by Feréy, a topology cannot be flexible when odd cycles of inorganic bricks exist in the network.<sup>44</sup> In all these ftw-a, shp-a, she-a, and csq-a type Zr-MOFs, triangular channels (or ligand-linked circle subunits) can be observed. It should be point out that PCN-128 with a csq-a network and NU-1104 and -1105 with a ftw-a network are slightly flexible, which could be attributed to the rotation freedom of their ligands but not the breathing of whole frameworks.

When the symmetry of the tetratopic ligand is reduced to  $C_{2\nu}$ , rigid frameworks with higher connectivities are excluded, and a *scu-a* network becomes more thermodynamically favored. The *scu-a* type network of BUT-62 and -63 shows only quadrangular channels. Additionally, the 8-connected Zr<sub>6</sub> clusters in BUT-62 and -63 are distorted with a lower symmetry of  $C_{2\nu}$  compared with the 12-connected Zr<sub>6</sub> clusters with  $O_h$  symmetry in UiO-66 or 8-connected Zr<sub>6</sub> clusters with  $D_{4h}$  symmetry in PCN-222. Each Zr<sub>6</sub> cluster contains 1, 2, and 3 symmetrically independent Zr atoms in UiO-66, PCN-222, and BUT-62 (or BUT-63), respectively. These structural characteristics (low symmetries of both ligands and metal clusters) might be responsible to the considerable structural flexibility of BUT-62 and -63, which will be discussed below.

Recently, two examples of rigid Zr-MOFs (NU-902 and NUPF- $1^{43}$ ) with the *scu-a* topology were reported, which are constructed by  $D_{4h}$  symmetric porphyrin ligands and distorted Zr<sub>6</sub> clusters with reduced symmetry.

#### 2.2 Porosity and Stability

Permanent porosity of the BUT-62 and -63 was confirmed by the N<sub>2</sub> sorption measurements at 77 K. After the guest solvent molecules (DMF and water) being removed through the guest exchange with acetone and the subsequent evacuation under vacuum at 100 °C, N<sub>2</sub> adsorption isotherms were recorded at 77 K for the guest-free phases of BUT-62 and -63 (hereafter referred as BUT-62A and -63A, A stands for activated sample). Saturated N<sub>2</sub> uptakes of 652 and 910 cm<sup>3</sup> g<sup>-1</sup> (STP) are achieved, and the BET surface areas of BUT-62A and -63A are estimated to be 2401 and 3060 m<sup> $^{2}$ </sup> g<sup> $^{-1}$ </sup>, respectively (Figure 2a). The pore volumes are calculated to be 1.03 and 1.49  $\text{cm}^3 \text{g}^{-1}$ , respectively, which are lower than the values calculated (1.22 and 1.75  $\text{cm}^3 \text{g}^{-1}$ ) based on single-crystal structure data of BUT-62W and -63W. The lowered pore volumes suggest possible structural alteration after removing guest molecules from the as-synthesized samples, which will be discussed below.

In spite of their high porosity, both BUT-62 and -63 were found to be tolerant in neutral water, weak base, and strong acid aqueous solutions. As shown in Figure 2b and c, PXRD patterns suggest that the two MOFs remain highly crystalline after being immersed in the neutral water, pH = 9 or 2.0 M HCl aqueous solution for 24 h at room temperature, respectively. Note that after BUT-62A and -63A being treated with water or weak base, the PXRD patterns obviously changed, particularly for the latter, in comparison with those of BUT-62W and -63W, respectively, implying structural transformation. This will be discussed in the following sections in detail. Furthermore, after these treated samples being reactivated by following the same procedure as that for as-synthesized samples, N<sub>2</sub> sorption isotherms were found to nearly overlap with those of the pristine samples (Figure 2a), further confirming the high stability of BUT-62 and -63. However, it was found that the two MOFs gradually degraded in the aqueous solutions with pH > 9 (SI, Figure S4 and S5). The chemical stability of BUT-62 and -63 is thus similar to many reported Zr-MOFs, which are stable in acidic condition but unstable in high alkaline solution.<sup>26,28,35</sup> It is commonly believed that the degradation of Zr-MOFs in strong base is the result of the substitution of carboxylate ligands and  $\ensuremath{\mathsf{O}}^{2^-}$  entities by hydroxide groups, which results in more stable Zr-hydroxide with relatively stronger Zr–O<sub>hydroxide</sub> bonds.<sup>37,38</sup>

In addition, thermal gravimetric analysis (TGA) curves indicate that as-synthesized BUT-62W and -63W are thermally stable up to about 400 and 450 °C, respectively (SI, Figure S6), and temperature-dependent PXRD measurements reveal that they remain highly crystalline and their frameworks are basically persisted up to 270 °C, suggesting good thermal stability of the two MOFs (SI, Figure S7 and S8). Since the two MOFs have isoreticular structures with close Zr–O bond

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strength, the observed different thermal stabilities of them can mainly attribute to the different decomposition temperatures of the corresponding ligands, which are related with their compositions and molecular weights. Similar situation has been observed in the reported literature.<sup>26</sup>



Fig. 2 Porosity and stability of BUT-62 and -63. (a) N2 adsorption isotherms recorded at 77 K and (b, c) PXRD patterns of BUT-62 and -63 samples treated under different conditions, to check their chemical stability. Note that BUT-62A and -63A could adsorb some water from air during recording their PXRD patterns.

#### 2.3 Optical Signal and Fluorescence

Interestingly, obvious color changes were observed when we were preparing the BUT-62A and -63A samples for gas sorption experiments and stability tests (Figure 3a). White crystalline powders of the BUT-62W sample turned to light-yellow after they being activated into BUT-62A. The yellow color of BUT-

62A sample further became deeper after they were soaked in neutral water, to form the water-included phase BUT-62Y (Y stands for yellow color); BUT-63 changes color from white to green yellow and finally to luminous yellow. Furthermore, BUT-62Y and -63Y samples underwent negligible color change when immersed in DMF or acetone. However, when they were immersed into strong acid (2 M HCl aqueous solution), the color changed to white immediately. The color change of the BUT-62 and -63 samples suggests that the electronic band structures of the corresponding frameworks are changed. Zhou and co-workers observed the color change of UiO-66 sample from white to yellow, and then to brown with increasing amount of missing-linker defects.44 The color change mechanism should be different for the two cases, because in BUT-62 and -63 the color change is reversible, while defective UiO-66 cannot change to defect-free UiO-66. The color change for the UiO-66 samples might mainly relate with the coordination change of Zr<sub>6</sub> clusters, while that in BUT-62 and -63 might be resulted from the configurational change of the organic ligands.

Besides directly observed color changes, different phases of BUT-62 and -63 also represent distinct fluorescence emissions, respectively. Carbazole is an attractive fluorophore due to its rigid structure and large conjugated plane,<sup>47</sup> and the MOFs constructed by carbazole-based ligands, such as CTTB<sup>4-</sup> in BUT-62 and CTNA<sup>4-</sup> in BUT-63, are expected to show intense fluorescence. The solid-state fluorescent properties of H<sub>4</sub>CTTB, H<sub>4</sub>CTNA, BUT-62W, -62Y, -63W, and -63Y were studied. As shown in Figure 3a, H<sub>4</sub>CTTB gives a bright-blue emission with the wavelength of emission maximum ( $\lambda_{max}$ ) of 465 nm when excited at 370 nm at room temperature. Under the same excitation, BUT-62W emits pale-blue light with  $\lambda_{max}$  = 425 nm, while BUT-62Y gives a green emission with  $\lambda_{max}$  = 522 nm. Similarly, H<sub>4</sub>CTNA shows a bright-blue emission with  $\lambda_{max}$  = 465 nm when excited at 375 nm. Under the same excitation, BUT-63W emits pale-blue light with  $\lambda_{max}$  = 433 nm, while BUT-63Y gives an orange emission with  $\lambda_{max}$  = 623 nm. For better understanding the fluorescence, we also recorded the fluorescence spectra of the ligands H<sub>4</sub>CTTB and H<sub>4</sub>CTNA after they are dissolved in different solvents (DMF, water, methanol, and toluene). The results are shown in the Figure S35. It can be observed that the emission shifting is dependent on the nature of the solvents, and the energy shifts are evident, revealing a solvatochromic effect of the ligands. Particularly, when the ligands are dissolved in DMF, their emission peaks are at positions (432 nm for H<sub>4</sub>CTTB, and 470 nm for H<sub>4</sub>CTNA) guite close to those for the as-synthesized BUT-62W (432 nm) and BUT-63W (466 nm). From the fluorescence spectra, the ligands and the MOFs share very similar profile of emission. Furthermore, we also carried out DFT calculations for the energies of HOMO and LUMO orbitals of the free ligands, as well as the ligands in the MOFs. The results are given in Figure S29 and Table S9. It was found that the energy gaps are different for the ligands in different statuses, which is consistent with the observations in fluorescence spectrum

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studies. Since Zr(IV) atoms are not fluorescent metal ions, we

speculate that the fluorescence of the MOFs should be based



Fig. 3 Varied color and fluorescence of BUT-62 and -63 samples. Schematic illustration for transitions (a) among H<sub>4</sub>CTTB, BUT-62W, -62A, and -62Y and (b) among H<sub>4</sub>CTNA, BUT-63W, -63A, and -63Y, and photographs for colors/fluorescences of the MOF samples; (c) intensity normalized emissions of BUT-62W, -62A, -62Y, and H<sub>4</sub>CTTB upon the excitation at 370 nm, and (d) those of BUT-63W, -63A, -63Y, and H<sub>4</sub>CTNA upon the excitation at 375 nm.

on the ligands. Notably, the emissions of BUT-62Y and -63Y are significantly red-shifted with respect to those of BUT-62W and -63W by almost 100 and 190 nm wavelengths, respectively. The obvious shift of fluorescent emissions indicates that energy gaps between ground state and excited state of the associated systems are changed.<sup>11,48</sup> Such a large difference in fluorescence emission wavelength in each case should be related with the change of ligand configuration of the MOFs during the structural transformation from BUT-62W to BUT-62Y, or BUT-63W to BUT-63Y.

It should also be pointed out that the guest/structuredependent fluorescence change of BUT-63 is more sensitive than that of BUT-62. As shown in Figure 3c and d, the shift of fluorescence emissions induced bv the structural transformation after water exchange is more pronounced for BUT-63 than that for BUT-62 (190 vs. 97 nm). The different sensitivity of the fluorescence change between the two MOFs should be related with their different ligands. Both CTTB<sup>4-</sup> and CTNA<sup>4-</sup> contain a carbazole core, but four peripheral arms are different, phenyl groups for the former while larger naphthyl groups for the latter. Compared to phenyl rings, the conjugated naphthyl rings are larger in size, and commonly recognized as better fluorescent groups. Here, the replacement of phenyl groups by naphthyl groups not only enlarges the pore size, but also enhances the sensitivity of guest-dependent fluorescent property of the resulting MOF. This result thus suggests that the guest-dependent

luminescence of the breathing Zr-MOFs can be fine-tuned by the modification of the ligands.

#### 2.4 Structural Transformation and Flexibility

Above color and fluorescence changes stimulate us to study the structural transformations between different phases of BUT-62 and -63 in detail. As the two MOFs have similar structures and optical signals, we are mainly focusing on the former here. As mentioned above, PXRD patterns clearly show the structural change of BUT-62 at different states, while remaining good crystallinity in each case (Figure 2b). BUT-62W transformed into BUT-62A after all guest molecules were removed, and then into BUT-62Y when water molecules were re-adsorbed. After treated with strong acid, BUT-62Y then transformed to a phase with PXRD pattern similar to that of BUT-62W. Further studies also confirm the structural transformations are reversible to some extent. These results thus suggest that the framework of BUT-62 is flexible with reversibility.

The structural flexibility of BUT-62 is also approved by the temperature-dependent PXRD measurements starting from BUT-62W sample. From the PXRD patterns, it is obvious that the framework gradually transformed when the sample was heated. It was also found that all PXRD peaks shifted to higher angles after heating, suggesting the shrinkage of the framework upon the guest molecules removal (SI, Figure S7

and S8). The structural shrinkage thus explains the experimentally observed lower pore volume of BUT-62A (or -63A) than that calculated value based on the single-crystal structure of BUT-62W (or -63W) as stated above. Interestingly, the PXRD pattern recovered after the heated sample being immersed in a mixture of DMF and acidic water. These results indicate that the framework of BUT-62 can display a reversible breathing behavior. In addition, water vapor adsorption of BUT-62A was carried out at room temperature. The isotherm shows a steep water uptake at low pressure range ( $P/P_0$  < 0.05) followed by a gradual increase until 0.25  $P/P_0$ , and then another steep uptake between 0.25 and 0.35  $P/P_0$ , followed by again gradual increase at higher pressure range (SI, Figure S17). This stepwise adsorption isotherm also implies the structural change of BUT-62 induced by the water adsorption.47 Similar vapor adsorption isotherms have been observed in several reported flexible MOFs.<sup>49,50</sup> Ar, CO<sub>2</sub>, and methanol vapor adsorption isotherms were also recorded for BUT-62A (SI, Figure S14-16). It was found that almost no hysteresis between adsorption and desorption branches was observed for Ar and CO<sub>2</sub>. The interaction between Ar or CO<sub>2</sub> molecules with the framework is thus not so strong to trigger the flexibility of the MOF. But for methanol, an obvious hysteresis was observed, which should be related with the flexibility of the MOF, as well as the high polarity and hydrogen-bonding potential of the methanol molecules.

Additionally, the flexible property of these two MOFs is also studied by mechanical extrusion. When compression was applied, BUT-62W changed color immediately from white to yellow, indicating the occurrence of a phase transformation. Moreover, after treated with acidic DMF, the yellow sample transformed back to a phase with white color similar to that of as-synthesized BUT-62W, indicating a fully reversible flexibility of the MOF. As shown in Figure S9a and b, the structural flexibility of BUT-62 was also verified by the pressuredependent PXRD measurements. From the PXRD patterns, it is obvious that the framework gradually changed when the sample was compressed. It was found that all PXRD peaks shifted to higher angles after compressing, suggesting the shrinkage of the framework. Furthermore, the PXRD pattern recovered after the compressed sample being immersed in a mixture of DMF and acidic water. These results further indicate that the framework of BUT-62 can display a reversible breathing behavior. We also carried out repeat tests for the structure transformation of the BUT-62 at varied pressures (from 0 to 1 GPa for BUT-62) for 3 cycles (where the samples were recycled by treatment with acidic DMF and dried under vacumm). As shown in Figure 9a, the PXRD patterns of BUT-62 remain nearly unchanged after 3cycles. These results indicated that the structural flexibility of BUT-62 is well reversible and reproducible. Similar phenomena was also observed in BUT-63, according to the results from PXRD measurement (Figure S9b), as discussed above for BUT-62, BUT-63 has similar structural flexibility and reversibility to that of BUT-62 under mechanical extrusion. As shown in Figure S10, the PXRD patterns,  $N_2$ adsorption, and fluorescence studies demonstrate that BUT-62

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In order to further investigate the structural flexibility and associated optical properties, we have attempted to determine the crystal structures of BUT-62W transformed phases. Probably due to large void and/or high flexibility of the BUT-62 framework, after BUT-62W was activated into BUT-62A by the guest removal or after BUT-62A was transformed into BUT-62Y by immersing BUT-62A in water, the resulting crystals all gave weak/bad single-crystal X-ray diffraction patterns, although they look like transparent and well-shaped, and their PXRD peaks are strong. Nevertheless, we found that the BUT-62W could also transform into BUT-62Y through direct guest exchange with pure water as confirmed by PXRD patterns, and obtained BUT-62Y crystals could gave much better single-crystal X-ray diffraction data (SI, Table S2 and S3).

Single-crystal structure determination and analysis shows that the obtained BUT-62Y remains in the same space group of BUT-62W with both the *c* and *b* axes slightly lengthened by 3.58 and 3.80%, respectively, but the *a* axis obviously shortened by 17.90%, thus the unit cell volume decreased by 11.80%. Size changes of the MOF crystals during the phase transition could also observed from their SEM images and optical photographs, although it is quite challenging to precisely record (SI, Figure S13). As a result, the large diamondoid channels along the *b* direction are shrunken, which is reflected by the change of the dihedral angles between the carbazole rings on adjacent channel walls from 114.2(4)° in BUT-62W to 139.0(3)° in BUT-62Y (SI, Figure S27a and b), as well as two diagonals of the channels from 10 and 23 Å to 13 and 29 Å.

To better understand the structural transformation and the structure-dependent optical property of BUT-62, structures of BUT-62W and BUT-62Y are carefully compared. As shown in Figure S27c and d, the Zr<sub>6</sub> octahedron in BUT-62W is nearly ideal. The distances of two diagonal Zr atoms at equatorial positions and of two at apical positions are 4.99(1) and 4.90(3) Å, respectively. However, in BUT-62Y, the Zr<sub>6</sub> octahedron is obviously distorted. The related distances of diagonal Zr atoms are 4.85(2) and 5.03(3) Å, respectively. Accordingly, the cuboid shaped  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(-COO)_8]$  SBU also changes in shape. The geometrical dimension of the cuboid defined by eight carboxylate C atoms changes from  $6.43(5) \times 4.24(2) \times$ 4.41(3) Å to 6.49(3) × 4.40(2) × 4.24(1) Å (SI, Figure S27e and f). In addition, the Zr-O<sub>carboxylate</sub> bond lengths in BUT-62W and -62Y are in the range of 2.17(3)~2.28(5) and 2.15(9)~2.29(8) Å, respectively, being almost not changed during the structural transformation. Clearly, the change of the related bond angles contributes more to the distortion of the Zr<sub>6</sub> SBU. It was also found that the framework transformation is resulted from not only the change of linkages between the metal atoms and the ligands but also the configurational change of the ligands themselves. In BUT-62W, the dihedral angles between two types of peripheral phenyl rings and the central carbazole are 45.2 and 39.1°, respectively. The geometry of the CTTB<sup>4-</sup> defined by four carboxylate C atoms is a trapezoid with three

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distinct edge lengths of 9.38(5), 12.34(3), and 13.31(3) Å, respectively. In BUT-62Y, however the corresponding dihedral angles and edge lengths change, being 47.4 and 37.6°, and 10.06(3), 11.92(4), and 13.71(4) Å, respectively. These changes can be regarded as that the "arms and legs" of the ligand open slightly from BUT-62W to -62Y, which can be well illustrated by the superposed representation of the ligands as shown in Figure S27. We also measured the single crystal diffraction BUT-62 loaded data with toluene for molecules (Toluene@BUT-62). Structural analysis and comparison reveal that the conformation of ligand also changed when the guests in BUT-62W was exchanged with toluene molecules (SI, Figure S28). As a result, the changes of these structural parameters should be responsible to the observed color and fluorescence changes in BUT-62W and -62Y samples.

In addition, water molecules strongly interacted with the framework in BUT-62Y can be modeled by using the singlecrystal diffraction data (referred as BUT-62Y-H<sub>2</sub>O in SI). It was found that the adsorbed water molecules in the voids of the framework show relatively high electron densities (c.a. 1.3~2.8 e  $Å^{-3}$ ) and reasonable atomic displacement parameters, suggesting that they could strongly interact with the framework surface. The primary water adsorption sites were found to be near the  $\mu_3$ -O<sup>2-</sup> atoms of the Zr<sub>6</sub> clusters in a distance of ca. 2.27~2.42 Å, and the carbazole NH groups with the N…O distance of c.a. 2.75 Å (SI, Figure S26). It should be pointed out that the distances between the adsorbed water O atoms and  $\mu_3$ -O<sup>2-</sup> atoms should be slightly underestimated because of the symmetrical disorder of  $\mu_3$ -O<sup>2-</sup> and  $\mu_3$ -OH<sup>-</sup> entities. The  $\mu_3$ -O<sup>2-</sup> atom is closer to the center of Zr<sub>6</sub> cluster compared to the  $\mu_3$ -OH<sup>-</sup> atom, but the two types of O atoms are not distinguished in the structure. Obviously, strong Hbonding interactions are involved between these adsorbed water molecules and the hydrophilic  $O^{2-}$  or  $OH^{-}$  groups on the framework. Additional adsorbed water molecules might also locate near the  $\mu_3$ -OH<sup>-</sup>, carboxylate O, terminal OH<sup>-</sup>/H<sub>2</sub>O, and primarily adsorbed water. It is proposed that the H-bonding interactions between the adsorbed water molecules in the channels and the hydrophilic sites on the channel walls might lead to the shrinkage of the large diamondoid channels in BUT-62Y compared with those in BUT-62W. Based on this observation, we speculate that the activated phase BUT-62A might have the most expanded channels, because no solvent molecules present in their pores to cause structure shrinkage due to H-bonding or other interactions. However, good single crystallinity could not retain after guest molecules were removed from BUT-62W and BUT-62A showed a PXRD pattern with weak and broad peaks, which limits its structural refinement. Similar structural transformation induced by the water inclusion has also been observed in MIL-53(Al<sup>3+</sup> or Cr<sup>3+</sup>).<sup>51,52</sup> The structural transformation of BUT-62Y to a phase with PXRD pattern similar to that of BUT-62W in strong acid might thus also be related with the involved H-bonding interactions. Due to the protonation of adsorbed water molecules and probably O/N atoms on the channel walls, the H-bonding interactions in the channels are weaken in the acid

treated phase, leading to opened diamondoid channels close to those of BUT-62W. For comparison, distances between Hbonding donor-acceptor atoms in BUT-62W are also evaluated and compared with those in BUT-62Y (SI, Figure S26 and Table S8). It was found that the H-bonding donor-acceptor distances in BUT-62Y are shorter than those in BUT-62W, implying different strengths of associated H-bonding interactions of water and DMF molecules.

In order to verify whether carbazole NH groups in the CTTB<sup>4–</sup> ligands have an important effect on the flexible behavior of BUT-62, the protons of the NH groups in BUT-62W were substituted with methyl groups by a post-synthetic modification. After substitution, the N atoms are expected less hydrophilic. Experimentally, an as-made sample of BUT-62W was treated with iodomethane in DMF in the presence of K<sub>2</sub>CO<sub>3</sub> at 40 °C for 3 days, producing a phase referred as BUT- $62W-CH_3$ . It was found that the  $CTTB^{4-}$  ligands were completely converted into methyl-substituted derivatives as confirmed by <sup>1</sup>H NMR spectrum of the NaOH aqueous solution digested sample of BUT-62W-CH<sub>3</sub> (SI, Figure S30). BUT-62W-CH<sub>3</sub> retains the same structure as that of BUT-62W, as confirmed by single-crystal diffraction and PXRD patterns (SI, Table S5 and Figure S33). After the BUT-62W-CH<sub>3</sub> sample being activated by removing guest molecules in its pores and subsequently immersed in water for 10 min, it was found that it also changed color from white to yellow, forming the phase referred as BUT-62Y-CH<sub>3</sub>. PXRD measurements reveal that a structural transformation occurred from BUT-62W-CH<sub>3</sub> to BUT-62Y-CH<sub>3</sub> as observed in the phase change from BUT-62W to BUT-62Y (SI, Figure S33). Fluorescence emission of BUT-62Y-CH<sub>3</sub> was also significantly red-shifted compared with that of BUT-62W-CH<sub>3</sub> (SI, Figure S31). These results suggest that the host-guest interactions only between adsorbed water molecules and hydrophilic sites on the  $Zr_6$  clusters ( $\mu_3$ - $O^{2-}$ ,  $\mu_3$ -OH<sup>-</sup>, carboxylate O atoms, and coordinated OH<sup>-</sup> and H<sub>2</sub>O) can also induce the structural breathing behavior of BUT-62-CH<sub>3</sub>, and the hydrophilic NH groups in CTTB<sup>4-</sup> ligand is not determinative for the flexibility of BUT-62. According to the results from PXRD measurement, water vapor adsorption, and solid-state fluorescence study (Figure 2c, 3b, 3d and SI, Figure S8, and S20), as discussed above for BUT-62, BUT-63 has similar structural flexibility to that of BUT-62.

#### 2.5 pH Sensing of Aqueous Solution

Inspired by above confirmed high chemical stability and sensitive guest-dependent fluorescence response with pronounced shift of emissions, the fluorescent properties of BUT-62 and -63 responding to the pH value of aqueous solution were investigated, to explore their potential application in sensing the pH value of water system. As shown in Figure 4a, the fluorescence spectra were recorded after the BUT-62Y samples being suspended in aqueous solutions with pH values from 0 to 9 for 1 min, respectively. It was found that the emission spectra are similar for the samples treated with the pH = 9, 8, 7, and 6 aqueous solutions. As the acidity of the aqueous solution increased from pH = 6 to 0, the emission

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peaks of the fluorescence spectra gradually blue-shifted from  $\lambda_{max}$  = 522 to 426 nm. Considering the complicated conditions in possible real applications, interference experiments (including the temperature and ionic strength) on pH sensing were performed. As shown in Figure S42, the wavelength of  $\lambda_{max}$  only slightly shifts with different temperatures (25, 35, and 45 °C) at pH = 7 for the two MOFs, which suggests that the  $\lambda_{max}$  shifts of the two MOFs are not profound at varied temperatures. The fluorescence emissions of the two MOFs at different pH (2.0, 5.0 and 7.2) in phosphate buffered saline (PBS; ionic strength = 0.05 M) solution are also very similar to those of their suspensions in aqueous solution, indicating strong anti-interference ability of pH sensing functionality with different ionic strength (Figure S43). Moreover, when different acids (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) were used in experiments, the fluorescence changes were substantially the same (Figure S23 and S24), indicating that the acidity of the aqueous solution is the key factor for changing fluorescence emission, but not associated anions or other chemicals. These results suggest that the pH sensing of the two MOFs was not obviously influenced by the temperature, ionic strength or other chemicals. More interestingly, the  $\lambda_{max}$  and the pH values of the aqueous solutions are basically linear-dependent in the pH range of 1~6 for BUT-62 (Figure 4c).

A linear relationship between the  $\lambda_{max}$  and the pH value suggests the feasibility of quantitatively determining pH value of an aqueous media by measuring the  $\lambda_{max}$  of a fluorescent material. It would be an alternative approach for fluorescence

pH sensing which is commonly accomplished by the response of emission intensity.<sup>5,37,53</sup> Especially, in some cases, fluorescence intensity of the sensing material can be influenced by not only pH value but also some other factors (cations, anions, impurities, optical path length, drift of optoelectronic system, etc.) in aqueous systems. A fluorescent sensing material with pH dependent  $\lambda_{max}$  would thus be quite advantageous because the profile of emission peak normally maintains no matter whether its emission intensity is quenched or enhanced. It should be noted that the fluorescence intensity of BUT-62 also changed as the pH value of checked aqueous solution varied (SI, Figure S36), however, a clear relation between its  $\lambda_{max}$  and the acidity of the aqueous solution can still be withdrawn.

For BUT-63, the fluorescence spectra are almost overlapped for the BUT-63Y derived samples after being suspended in the aqueous solutions of pH values at 8 and 9, respectively. However, the  $\lambda_{max}$  gradually blue-shifted from 603 to 422 nm as the pH values decreased from 8 to 0. And, the  $\lambda_{max}$  and pH values of the aqueous solutions are well linearly dependent in the almost full pH range measured (pH = 8 to 1) (Figure 4c). Owing to the wider emission shift in BUT-63 (181 nm) than that of BUT-62 (96 nm), the sensing sensitivity of the former is thus enhanced by over 1.3 times relative to that of the latter, which can be indicated by the slope values (24.63 vs. 18.4) for the linear fittings of the data. In addition, how fast the  $\lambda_{max}$  shifts as the pH varies is also an important factor for such pH sensors. Additional experiments were



Fig. 4 Fluorescent pH sensing of aqueous solution with BUT-62 and -63. Intensity normalized luminescent spectra of BUT-62 (a) and -63 (b) treated in aqueous solutions with different pH values at room temperature; c) the pH dependence of the wavelength of emission maximum ( $\lambda_{max}$ ) and the linear fits for BUT-62 (black) and -63 (red); and photographs of BUT-62Y/CMC plate (d) and BUT-63Y/CMC plate (e) under 365 nm UV irradiation after being dipped in aqueous solutions with different pH values.

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carried out to check this. It was found that the shifting of  $\lambda_{max}$  could completed within 10s after changing the pH values of the suspensions, suggesting a fast kinetics for the pH sensing of the MOFs. To the best of our knowledge, BUT-62 and -63 represent the first MOF example capable of quantitatively sensing/detecting the pH value of aqueous solution by measuring the  $\lambda_{max}$  of the fluorescent emission, but not only the intensity.

Reusability is an important feature for an effective sensing material. To check if the samples of BUT-62 and -63 could be reused to test multiple pH values, we carried out repeated tests for the fluorescence of the MOFs in varied pH aqueous solutions (pH from 6 to 1 for BUT-62, and pH from 8 to 1 for BUT-63) for 3 cycles, where the samples were recycled by centrifugation and washing with deionized water after each measurement. As shown in Figure S40, the fluorescence spectra of the two MOFs are reproducible after regeneration with a simple treatment.

For better understanding the sensing mechanism of the MOFs for pH values, we performed the control experiment on BUT-62-CH<sub>3</sub>. The fluorescence spectra of BUT-62-CH<sub>3</sub> suspended in aqueous solutions with different pH values were recorded. As shown in Figure S32, the  $\lambda_{max}$  of BUT-62-CH<sub>3</sub> shifted on varying the pH values, similar to that observed in BUT-62, but the emission shifting for  $BUT-62-CH_3$  (515 nm at pH = 7 to 438 nm at pH =1) is slightly weakened in comparison with that for BUT-62 (522 nm at pH = 7 to 426 nm at pH = 1). This result thus confirms that the presence N-H group in the MOFs is not a determinative factor for their fluorescence response, but has slight influence on the florescence of MOFs. We have also checked the fluorescence spectra of pure organic ligands H<sub>4</sub>CTTB and H<sub>4</sub>CTNA in water with different pH values. As shown in Figure S41, for both of the two ligands,  $\lambda_{max}$ slightly shifts with varying pH values. For H<sub>4</sub>CTTB, the  $\lambda_{max}$ changes from 459 to 432 nm when the pH values change from 0 to 9. For H<sub>4</sub>CTNA, it changes from 495 to 466 nm when the pH values change from 0 to 9. Clearly, the  $\lambda_{\text{max}}$  shifts of the two ligands are not profound in comparison with those of their corresponding MOFs, BUT-62 (from 426 to 522 nm) and -63 (from 432 to 603 nm) in the pH ranges from 0 to 9. Particularly, it was noted that for the ligands,  $\lambda_{\text{max}}$  are redshifted as decreasing of pH values, in contrast, those for BUT-62 and -63 are blue-shifted as decreasing pH values. Furthermore, considering that the ligands H<sub>4</sub>CTTB and H<sub>4</sub>CTNA are deprotonated and coordinated with metal atoms in the MOFs, checking the fluorescence of their esterified partners should be more informative. Fluorescence spectra of the methyl-esterified H<sub>4</sub>CTTB (referred as M<sub>4</sub>CTTB) and H<sub>4</sub>CTNA (referred as M<sub>4</sub>CTNA) dissolved in water with different pH values were then recorded. As shown in Figure S41, the fluorescence emissions of  $\mathsf{M}_4\mathsf{CTTB}$  and  $\mathsf{M}_4\mathsf{CTNA}$  are nearly independent on the pH values. Above results suggest that the pH sensing mechanism of the MOFs should not be simply resulted from the pH responding behavior of ligands themselves. The pH sensing effect of the two MOFs might be attributed to their structural flexibility, which leads to the

configuration changes of ligands. We further measured the PXRD patterns of the two MOFs after they are treated in aqueous solutions with different pH values. The results are shown in the Figure S38 and S39. The PXRD patterns are different, showing that the structures of the MOFs transformed with respect to different pH values. This is similar to the observations from PXRD patterns of the MOFs loaded with different guest molecules. Large  $\lambda_{max}$  shifts in fluorescence for the MOFs are thus probably due to the sensitive response of the ground (LUMO) and excited states (HOMO) of the ligands to stimuli, such as their conformation changes as well as different host-guest interactions. Under the stimuli, the energy gaps between HOMO and LUMO of the systems changed, resulting in the fluorescence wavelength shifts.

To further verify the sensitive pH dependent fluorescence variation of BUT-62 and -63, and make the pH detection easy and feasible, fluorescent test plates with a thin layer of MOF/CMC (CMC = carboxymethyl cellulose, commonly used in making thin layer chromatography plates) mixture on glass slide substrate were fabricated. The prepared plates were dipped in the aqueous solutions with the pH value ranging from 9 to 0 for a few seconds, and then dried in air for few minutes. Under the irradiation of UV light, the fluorescent images of the plates were recorded by digital photograph. As shown in Figure 4d, the fluorescence of the plates for BUT-62 changed from yellow green to green, and finally blue as the acidity of the aqueous solutions increased from pH = 9 to 0. The fluorescence change for the BUT-63 plates is more marked, from yellow at pH = 9 and 8, green at pH = 4, to blue at pH = 0 (Figure 4e). These results are in accordance with those observed in fluorescence spectra for the BUT-62 and -63 suspensions in acidic aqueous solutions, and also demonstrate a rapid and sensitive fluorescent response of them to the pH values of aqueous solutions.

## Conclusions

In summary, we have synthesized two highly porous and chemically stable Zr-MOFs by using newly-designed trapezoid organic linkers with a carbazole core as main fluorophore. The two MOFs exhibit structural breathing behavior responsive to adsorbed guest molecules in their pores, due to the changed interactions between the frameworks and the guest molecules. Accompanied with slight configurational changes of the ligands during the framework breathing as demonstrated by single-crystal structure analysis, these MOFs represent sensitive fluorescence changes in the wavelengths of emission peaks. Based on the guest-dependent structural flexibility and associated fluorescence change, as well as the chemically robust nature of the frameworks, the two MOFs have been tested in aqueous media for pH sensing in the pH values ranging from 0 to 9. The observed linear relationship between the fluorescence  $\lambda_{max}$  and the pH value of aqueous solution suggests the capability of these MOFs in quantitatively sensing the pH value in a unique manner, which is only based on the

emission wavelengths other than intensities. They are thus expected to be potentially useful in the wavelength-based fluorescence pH sensing for environmental and biological systems.

## **Conflicts of interest**

There are no conflicts to declare.

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## TOC

# Flexible Metal-Organic Frameworks for Wavelength-Based Luminescence Sensing of Aqueous pH

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Two new metal-organic frameworks (MOFs) constructed from trapezoidal carbazole-core based ligands show high porosity, good chemical stability, reversible guest-dependent structural flexibility, as well as sensitive stimuli responsive fluorescence. It is demonstrated that these MOFs are highly potential in the wide-range quantitative pH sensing by facilely determining the wavelengths of maximum emission.