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## COMMUNICATION

# A colloidal water-stable MOF as a broad-range fluorescent pH sensor via post-synthetic modification

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**We report for the first time the pH-dependent fluorescence of UiO-66-NH<sub>2</sub> across the wide range from 1 to 9. By application of a post-synthetic modification (PSM) diazotisation strategy, we synthesized a new material, UiO-66-N=N-ind, which shows increased chemical stability and enhanced sensing up to pH 12.**

Metal-organic frameworks (MOFs) are a class of hybrid materials assembled from organic linkers and metal ions or clusters,<sup>1, 2</sup> that have received enormous attention in the last two decades due to their interesting properties which make them attractive for storage,<sup>3, 4</sup> drug delivery,<sup>5-8</sup> catalysis,<sup>9</sup> and separation,<sup>10</sup> among others. Very recently, MOFs have been explored as sensory materials<sup>11</sup> where their crystallinity and microporous features allow the frameworks to preconcentrate guest species (analytes) according to their size/polarity prior to obtaining an analytical response. Due to the wide variety of metals and linkers available, MOFs can be engineered in order to provide a rapid guest-dependent fluorometric response.<sup>12, 13</sup> Fluorescent MOFs sensitive to the proximity of the guest via energy or electron transfer have also been reported.<sup>14-16</sup> Additionally, the release of a previously adsorbed fluorophore, through disruption of the microporous MOF structure by an appropriate analyte have also been used as sensors.<sup>17-19</sup>

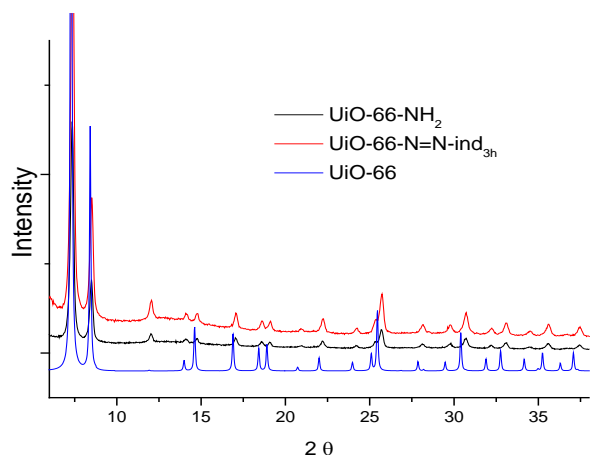
One of the main concerns in the sensing of analytes in aqueous solution is the control of the pH, since small changes in the pH media can be detrimental either for the MOF or the analyte. In addition to the high sensitivities of the fluorescent technique, fluorescent pH probes are highly desirable since they allow the rapid monitoring in a simple manner of small pH changes in biological environments and usually are non-destructive to cells.<sup>20</sup> To our knowledge, only two pH-MOF sensors have been reported: Zhou *et al.*<sup>21</sup> have described the use of a Zr based MOF by using a fluorescent pH-dependent porphyrin ligand in the range from 1 to 11; and Rocha *et al.*<sup>22</sup> reported an Eu based MOF which shows linear pH-dependence across the range from 5 - 7.5. In spite of the low range of sensitivity, the MOF response does not depend on any external calibration, since one of the Eu(III) emission bands is unaffected by the pH change within this range. In this communication we report the pH dependent fluorescence of colloidal

dispersions of UiO-66-NH<sub>2</sub>,<sup>23-25</sup> and demonstrate how framework stability and fluorescent response are readily modulated by post-synthetic modification (PSM) of the pendant amine groups with indole moieties. Further, the degree of post-synthetic modification is easily monitored by fluorescence.

UiO-66-NH<sub>2</sub> is formed by a cluster of 6 Zr atoms (Zn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>) and the linker 2-aminoterephthalic acid (bdc-NH<sub>2</sub>). The stability of this MOF in both acidic and basic aqueous media allows pH analysis and facile MOF recovery across the range from 1 to 9. The easy and well reported synthesis of UiO-66-NH<sub>2</sub>, in addition to the commercial and cheap availability of the precursors, shows some advantages regarding the low-yield multistep synthesis of for example, porphyrin linkers.<sup>26</sup> We recorded the emission spectrum of UiO-66-NH<sub>2</sub> from pH 1 to pH 12 in order to compare its behavior with the free bdc-NH<sub>2</sub> ligand; note however that the PXRD patterns for the recovered framework from dispersions above pH 9 indicated some disruption of the crystalline structure (figure 1) and MOF recovery was not possible at pH > 10. At  $\lambda_{\text{ex}} = 350$  nm, a ligand-centred emission band at 428 nm with very strong intensity at basic pH is observed. The intensity of this band increases exponentially with pH, where the biggest change in the tendency line is found at pH 10 (figure S8), corresponding to the deprotonation of the amino moiety ( $\text{pK}_{\text{a}} \approx 10$ ). This latter band is absent in UiO-66 itself, and is thus attributed to n- $\pi$  transitions associated with the amine group. However, this behavior is distinct from the free bdc-NH<sub>2</sub> ligand, which displays a hypsochromic-pH dependence (figure S9): at low pH values, an emission band centered at 461 nm is observed which blue shifts as pH is increased, reaching a minimum value of 428 nm at pH 12. UiO-66-NH<sub>2</sub> shows some advantages with respect to bdc-NH<sub>2</sub> ligand solutions for pH sensing since the MOF does not show any solvatochromic effect and is easily recoverable by centrifugation or precipitation. Further, solid-state sensors are highly desirable, as they do not interfere with analytes.

In spite of the high stability in acid conditions of the UiO-66 MOF family, their stability in basic media is less impressive. The difference in the stability with respect to the substituent group on the terephthalic acid linker has already been reported.<sup>25, 27</sup> According to these studies, UiO-66-NO<sub>2</sub> and UiO-66-(CH<sub>3</sub>)<sub>2</sub> show high stabilities in both strong acid and basic media, UiO-66 and UiO-66-Br show

less crystallinity after soaking in NaOH (pH = 14), whilst UiO-66-NH<sub>2</sub> gave rise to a complete MOF decomposition under the same basic conditions. No clear evidence regarding the electronic properties or the steric hindrance of the substituents to explain this behavior have been presented.



**Fig. 1** PXRD patterns for: UiO-66-NH<sub>2</sub> after soaking at pH 9 (black); UiO-66-N=N-ind<sub>3h</sub> after soaking at pH 12 (red) and simulated for UiO-66 (blue).

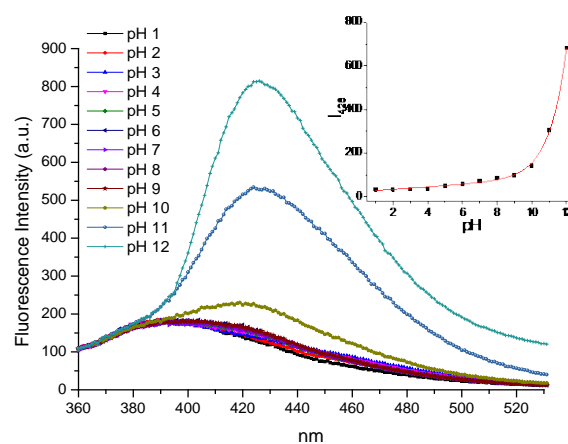
In order to increase the stability of UiO-66-NH<sub>2</sub>, and thus increase the basic range for fluorescent pH sensing, we report a facile strategy for its PSM since such methods have previously been exploited to increase water stability of MOFs.<sup>28</sup> We reasoned that the incorporation of a resonant indole moiety into the framework structure *via* diazotization of the amino groups to obtain UiO-66-N=N-ind could potentially improve the UiO-66-NH<sub>2</sub> stability in basic media.<sup>29, 30</sup> The PSM of the UiO-66-NH<sub>2</sub> was carried out following a diazotization reaction (scheme S1 and ESI<sup>31</sup> using 1-methylindole as a coupling agent to form UiO-66-N=N-ind. The bdc-NH<sub>2</sub> linkers were easily diazotized with NaNO<sub>2</sub> and HCl, and then reacted with the indol compound for 1h to obtain UiO-66-N=N-ind<sub>1h</sub>. We selected this indol derivative in order to avoid the azo-coupling attack of the diazonium ion to the nitrogen of the indole (to form diazoaminobenzene-like structure), since the tertiary amine of this compound does not allow the formation of the mentioned structure.

The characterization of all materials is described in the ESI (powder X-ray diffraction pattern, NMR, SEM, FTIR, TGA, BET and ESI-MS: section S5, figures S1-S7; tables S1-S3). The <sup>1</sup>H NMR of UiO-66-NH<sub>2</sub> (figure S10) recorded after complete HF digestion shows the expected signals of the free ligand (bdc-NH<sub>2</sub>). Taking into account the ratio of the newly observed signals at low field in the NMR spectrum of UiO-66-N=N-ind<sub>1h</sub> and the parent phase, we determine that 25% of the amine moieties were successfully functionalized. This is consistent with a reduction in the BET surface area from 1630(10) m<sup>2</sup>/g (UiO-66-NH<sub>2</sub>) to 811(4) m<sup>2</sup>/g. (Figure S1, table S1)

We carried out a pH-dependent fluorescent study on UiO-66-N=N-ind<sub>1h</sub> (see SI for details), and as expected the fluorescence emission of UiO-66-N=N-ind<sub>1h</sub> remains pH-dependent and can also be fitted to a similar exponential (figure S11) as for UiO-66-NH<sub>2</sub>. The UiO-66-N=N-ind<sub>1h</sub> framework shows high stability in acidic conditions, and an increased chemical stability at basic pH as evidenced by PXRD patterns (fig S12) and N<sub>2</sub> adsorption isotherms (fig. S2, table S1) that clearly indicate higher degrees of crystallinity and porosity over UiO-66-NH<sub>2</sub> are retained up to pH 11. This enhancement in the stability at basic pH could be due to the high resonance of the resulting aryl azocompound (extended delocalized

system) (fig S13) which confers enhanced stability to the framework.<sup>29, 30</sup> By comparison, PSM of UiO-66-NH<sub>2</sub> with acetic anhydride<sup>24</sup> at 80% conversion does not offer increased stability in base and the framework is totally disrupted under the same conditions. (Figure S14, S15) The high increase in the fluorescence intensity in UiO-66-N=N-ind<sub>1h</sub> at 428 nm at pH 10 is clearly visible and as before, is attributed to the deprotonation of the remaining free amine groups. Remarkably, the high sensitivity of this material allows its use as an easily recoverable fluorescent pH sensor at μM concentrations (see ESI for details).

We carried out PSM of the UiO-66-NH<sub>2</sub> to UiO-66-N=N-ind for 3 h (UiO-66-N=N-ind<sub>3h</sub>) after addition of 1-methyl indole to UiO-N<sub>2</sub><sup>+</sup>, but avoided longer periods as the yield of product was significantly reduced, likely due to the hard reaction conditions. The PXRD pattern showed the crystalline structure of UiO-66 (figure 1) was maintained and <sup>1</sup>H-NMR revealed the conversion of amines to indols via diazotisation is ~70% (figure S16). The increased conversion over UiO-66-N=N-ind<sub>1h</sub> is confirmed by a further reduction in the BET surface area to 552(4) m<sup>2</sup>/g. (Figure S1, table S1) UiO-66-N=N-ind<sub>3h</sub> follows the same pH dependent fluorescence trend as UiO-66-NH<sub>2</sub> and UiO-66-N=N-ind<sub>1h</sub> (figure 2), since the fluorescence sensitivity to the pH changes arise from the unfunctionalised bdc-NH<sub>2</sub> linkers in the framework. However, despite the reduction in fluorescence intensity of UiO-66-N=N-ind<sub>3h</sub> compared to its precursor, the sensor response remains highly sensitive (μM). We also found a further increase in the chemical stability at basic pH, up to 12 (figure 1), presumably due to the higher grade of conversion over UiO-66-N=N-ind<sub>1h</sub>. After soaking at pH 12 for 2 hrs ICP analysis reveals that < 0.12% of the total Zr(IV) contents of UiO-66-N=N-ind<sub>3h</sub> are present in the supernatant (table S3). Porosity is also maintained (fig S2, table S2), further indicating the superior stability of UiO-66-N=N-ind<sub>3h</sub> under basic conditions.

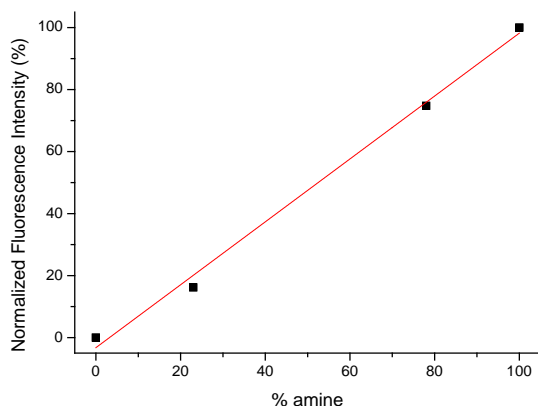


**Fig. 2** Normalized fluorescence emission of UiO-66-N=N-ind<sub>3h</sub> vs. pH ( $\lambda_{ex} = 350$  nm). Inset: Exponential correlation between the fluorescence response of UiO-66-N=N-ind<sub>3h</sub> ( $\lambda_{ex} = 350$  nm,  $\lambda_{em} = 428$  nm) and pH.

In addition to <sup>1</sup>H NMR, we evaluated the degree of PSM by following the fluorescence of the unfunctionalised bdc-NH<sub>2</sub> ligands remaining after the diazotisation reaction at a fixed pH. (figure 3 and S17) After functionalization for 1 h the fluorescence intensity at 428 nm is decreased by 25%; similarly, after 3 hours of reaction, we obtained a loss of fluorescence intensity of 75%. These values are in excellent agreement with the conversion efficiencies

determined by  $^1\text{H}$  NMR and indicate that fluorescence can be used as a probe of levels of PSM under appropriate conditions.

Finally, we have judiciously employed polystyrene (PS) cuvettes as an internal system reference for the colloidal pH sensor. The PS cuvettes emit at 380 nm after excitation at 300 nm, which is invariant with changes in pH. In this way, the ratiometric response of UiO-66-N=ind<sub>3h</sub> to the pH change can be obtained from figure S18. Using the colloidal MOF-based fluorescent pH sensor, we successfully determined the pH of standard buffer solutions by using the ratiometric response provided by the cuvettes as an internal reference (figure S19 and equation S1). We measured 3 solutions at pH 2, 6 and 10. The solutions at pH 6 and 10 were measured within a satisfactory error using the described equation S1, whereas that at pH 2 was 0.08 pH units from that determined with a pH meter (pH = 2.13), arising from the slightly lower sensitivity at very acidic pH.



**Fig. 3** Normalized correlation between the degree of functionalization in the diazotisation reaction determined from  $^1\text{H}$ -NMR vs. the fluorescence of bdc-NH<sub>2</sub> remaining in the framework at pH 10 ( $\lambda_{\text{ex}} = 350$  nm,  $\lambda_{\text{em}} = 428$  nm).

In summary, we have reported for the first time the pH dependent fluorescent response of UiO-66-NH<sub>2</sub> across the range from 1 to 9. Through PSM of this MOF with indole groups we were able to increase framework stability under basic conditions, extend the accessible sensing range to pH 12 and modulate the size of the fluorescent response. These pH sensors could be widely used due to i) easy and widely reported preparation of UiO-66-NH<sub>2</sub>, ii) facile PSM of this framework, iii) rapid and highly sensitive pH response, and iv) reliable and almost complete recovery of the material.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis of MOFs, detailed description of the experimental fluorescence measurements, XRD,  $^1\text{H}$ -NMR, SEM and fluorescence spectra. See DOI: 10.1039/c000000x/

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