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## COMMUNICATION

## Direct photo-hydroxylation of the Zr-based framework UiO-66

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**We describe the direct post-synthetic hydroxylation of UiO-66 through the photogeneration of hydroxyl radicals. Three approaches have been investigated, and levels of conversion up to 77% have been observed within 48 hrs.**

Metal-organic frameworks (MOFs)<sup>1</sup> are a class of ordered porous materials assembled from metal ions or clusters and organic ligands, with a wide range of applications such as gas storage,<sup>2</sup> separation,<sup>3</sup> sensing,<sup>4</sup> and drug delivery.<sup>5</sup> Due to the enormous choice of potential building blocks, it is relatively straightforward to endow the frameworks with specific functionalities that enhance their utility in these and other applications.<sup>6</sup> Post-synthetic modification (PSM)<sup>7</sup> has also emerged as a powerful strategy to enhance MOF properties, where either the ligand or the metal components<sup>8</sup> can be altered after framework assembly. Many of the early PSM studies focussed on the chemical transformation of diverse functional groups appended to the framework-forming organic ligands, which provides a facile means to tune pore size and functionality, modulate hydrophobicity/philicity<sup>9</sup> and anchor specific catalytic groups within the coordination space defined by the framework.<sup>10</sup> Direct solvothermal synthesis of MOFs bearing additional functional groups can however be challenging since some organic ligands, *e.g.* azides, are not stable under the conditions required for framework assembly.<sup>11</sup> Further, organic groups such as alcohols can show higher binding affinity to metal centres, giving rise to poorly crystalline structures.<sup>12</sup>

More recently, MOFs have also been subjected to post-synthetic linker exchange (PSLE) processes where ligands bound to the metal clusters are readily exchanged by linkers bearing similar metal-binding functionality.<sup>13</sup> PSLE has allowed MOF chemists to control framework interpenetration,<sup>12a</sup> push pore sizes into the mesoporous regime<sup>14</sup> and prepare MOFs that are unattainable by direct combination of the building blocks.<sup>15</sup> While several important discoveries have been reported using these methods, the transformation of unfunctionalised frameworks remains relatively underdeveloped,<sup>16</sup> in particular, the direct functionalisation of aromatic rings within MOFs<sup>17</sup> appears to be a more challenging prospect given incompatibilities between the often harsh chemistry

involved and framework stability and the potential to yield unwanted side products. In this contribution we report three methodologies to directly hydroxylate UiO-66 (to form UiO-66-OH, where the framework-forming aromatic linkers in UiO-66 bear hydroxyl groups) via the clean photo-generation of hydroxyl radicals using i) a commercial TiO<sub>2</sub> photocatalyst and UV-A irradiation, ii) a  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> composite and UV-A irradiation, and iii) H<sub>2</sub>O<sub>2</sub> and UV-C irradiation. Using these methods we are able to prepare highly crystalline phases of UiO-66-OH directly from the UiO-66 parent phase with conversion levels of 40 – 77% more rapidly than other techniques such as PSLE, and overcome some of the difficulties associated with the solvothermal preparation of wholly crystalline UiO-66-OH.

UiO-66 is a Zr-based MOF formed by a cluster of cationic Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>6</sub> nodes and 1,4-benzenedicarboxylate (bdc) linkers.<sup>18</sup> This framework shows high thermal stability and resistance towards many organic solvents and water across a wide pH range.<sup>19</sup> Additionally, high photostability of the UiO-66 family under UV and visible light has also been reported.<sup>20</sup> The parent UiO-66 used in this study was prepared as described by Farha *et al.*<sup>21</sup> Unfortunately, our efforts to synthesise UiO-66-OH directly using the solvothermal methodologies reported in the literature were unsatisfactory, giving rise to largely amorphous material (figure S1 and S2).<sup>12a, 21</sup> It is well known however that bdc can react with hydroxyl radicals, to produce strongly fluorescent 2-hydroxy-1,4-benzenedicarboxylic acid (bdc-OH).<sup>22</sup> Hydroxyl radicals can be generated in several ways, and here we develop strategies to convert UiO-66 into UiO-66-OH without disrupting the framework structure. TiO<sub>2</sub> is one of the most well-established photocatalysts and is able to produce high quantities of hydroxyl radicals under UV irradiation in aqueous media. Figure S3 shows the fluorescence emission spectra of a basic solution of terephthalic acid in the presence of TiO<sub>2</sub> under UV-A lamps (40W). After 1 h of irradiation, an intense emission peak centred at 428 nm is observed, corresponding to the formation of bdc-OH indicating the successful generation of hydroxyl radicals in the media.

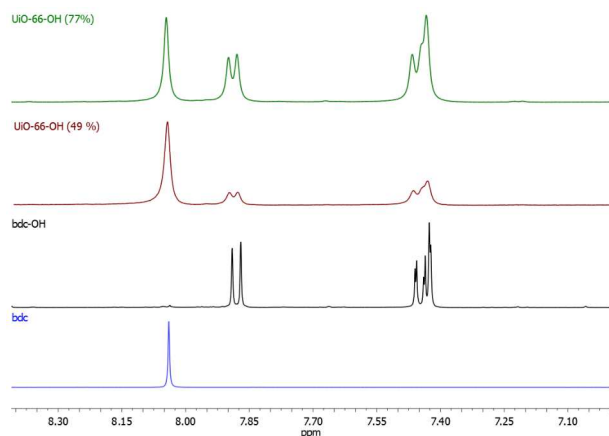
We then subjected UiO-66 to photoirradiation under UV-A light in the presence of TiO<sub>2</sub> (see experimental procedure in ESI) in order to obtain UiO-66-OH. The <sup>1</sup>H-NMR of the material (figure S4) shows a conversion efficiency of 9 %, 41 % and 47 % after 2 h, 24 h and 48 h of irradiation, respectively (table 1). The PXRD pattern of UiO-66-47% (figure S5) reveals full retention of the crystallinity

after 48 h irradiation, consistent with the observed high photostability of UiO-66 irradiated under the same conditions in the absence of the photocatalyst (figure S6). Although irradiation of UiO-66 in the presence of TiO<sub>2</sub> for longer periods of time (5 days) gave rise to higher degrees of bdc hydroxylation, analysis by PXRD indicated almost complete degradation of the framework after this period. Further experiments using a powerful Xe lamp were also performed, with conversion to UiO-66-OH reaching 17 % in just 30 mins.

**Table 1.** Conversions obtained for UiO-66 hydroxylation under UV-A irradiation in the presence of appropriate photocatalysts.

Catalyst	Xe lamps (150 w)	UV-A lamps (365 nm, 40 w)		
	30 min	2 h	24 h	48 h
TiO <sub>2</sub>	17 %	9 %	41 %	47 %
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> @TiO <sub>2</sub>	-	-	49 %	77 %

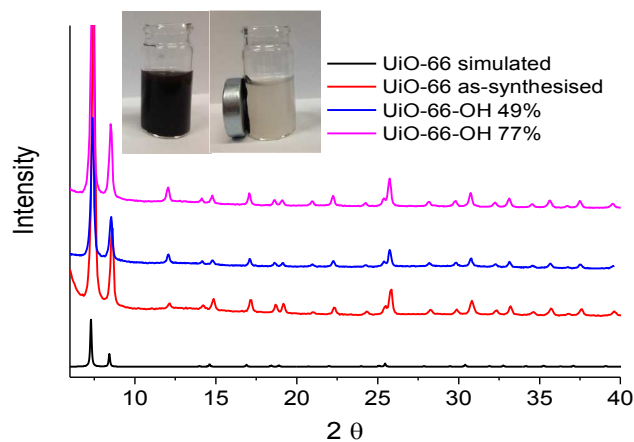
While it is clear that TiO<sub>2</sub> can be used as a photocatalyst for the direct hydroxylation of UiO-66, separation of the photocatalyst from the converted framework is a major issue. After several attempts to isolate UiO-66-OH by density separation<sup>23</sup> with solvents such as bromochloromethane and 1,2-dibromoethane, the PXRD patterns show high quantities of the catalyst still remain (figure S5). In addition, such solvents are highly undesirable due to their high toxicity and should generally be avoided. To circumvent this issue, we carried out the irradiation using magnetic TiO<sub>2</sub> composite nanoparticles, which are easily separated and recovered from the reaction using a magnet. Yu *et al.*<sup>24</sup> have reported the synthesis of superparamagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> (FST) composites, which show higher photocatalytic activity for the degradation of organic dyes than commercial Evonik P25. Fluorescence and electron paramagnetic resonance spectroscopies indicate that this photocatalytic degradation occurs via hydroxyl radicals.



**Figure 1.** <sup>1</sup>H-NMR spectra of UiO-66-OH obtained after 24 h (red, UiO-66-OH-49%) and 48 h (green, UiO-66-OH-77%) of reaction under UV-A irradiation using FST as photocatalyst. For comparison, bdc-OH (black) and bdc (blue) ligands are also shown. The framework solids were digested in DMSO-HF.

The SiO<sub>2</sub> layer between  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> plays a crucial role in the photocatalytic process by physically separating the magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> core from the TiO<sub>2</sub>, thus avoiding the rapid electron-hole recombination caused by their direct contact. The as-

synthesised FST composite was first evaluated for its ability to photohydroxylate bdc into bdc-OH under UV-A irradiation where very similar conversion was observed for pure TiO<sub>2</sub>. Encouraged by this high activity, we carried out the post-synthetic photohydroxylation of UiO-66. Following UV-A irradiation for 24 h in the presence of FST, the conversion derived from <sup>1</sup>H-NMR was 49 %, while 48 h under UV-A light gave rise to 77 % of UiO-66-OH conversion (figure 1). While the FST composite appears to be more photo-active than TiO<sub>2</sub> alone as previously reported<sup>24</sup>, we note that the degree of conversion is highly dependent on the quality of the as-prepared FST. The FST photocatalyst was successfully separated from UiO-66-OH using a magnet (figure 2) allowing us to easily recover a pure product phase as confirmed by PXRD (figure 2). The preservation of the crystallinity was also confirmed by SEM micrographs (figure S7) which reveal that crystal size and morphology do not change, even after 48 hr of irradiation. Thermogravimetric analysis (figure S8) reveals a small increase in the amount of organic material in the modified frameworks corresponding to the successful introduction of hydroxylate groups into the bdc linkers (table S1). Nitrogen adsorption isotherms (figure S9 and table S2) show a reduction in the BET surface areas with respect to pure UiO-66, which decrease linearly with increasing hydroxylation of the organic linker (figure S10). The BET surface areas calculated following photoirradiation are in the range of those reported previously by Farha *et al.*<sup>21</sup> (1000 m<sup>2</sup>/g for pure UiO-66-OH) and Cohen *et al.*<sup>12a</sup> (1131 m<sup>2</sup>/g for UiO-66-OH-50%).



**Figure 2.** PXRD pattern of as-synthesised UiO-66 (red), UiO-66-OH-49% (blue), UiO-66-OH-77% (pink), and simulated UiO-66 (black). Inset: photograph of UiO-66-OH-49% before (left) and after (right) magnetic separation of the FST photocatalyst. A yellowish hue is clearly visible indicating successful framework hydroxylation.

**Table 2.** Conversion for UiO-66-OH obtained using H<sub>2</sub>O<sub>2</sub> and UV-C.

eq UiO-66	eq H <sub>2</sub> O <sub>2</sub>	Reaction time	UiO-66-OH yield
1	5	2 h	26 %
1	10	6 h	41 %
1	20	6 h	28 %
1	50 <sup>a</sup>	6 h	< 5 %

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> was used as unique solvent for this reaction.

In order to expand the applicability of hydroxyl radicals for direct PSM of MOFs and remove the need for a photocatalyst, we carried out the irradiation of the framework under UV-C in the

presence of controlled amounts of H<sub>2</sub>O<sub>2</sub>. It is well known that H<sub>2</sub>O<sub>2</sub> can directly generate hydroxyl radicals with UV-C irradiation, and the conversion efficiencies of UiO-66 to UiO-66-OH at various reaction times and H<sub>2</sub>O<sub>2</sub> ratios are summarized in table 2. We found a high grade of conversion (41 %) when the framework is irradiated for only 6 h in water containing 10 (framework) equivalents of H<sub>2</sub>O<sub>2</sub>, which is comparable to that achieved after 24 h with TiO<sub>2</sub>/UV-A. PXRD (figure S11) and SEM (figure S12) images reveal retention of the structure and crystallinity as previously observed using TiO<sub>2</sub> or FST as photocatalysts, and the BET surface area (figure S13) is also consistent with the pure UiO-66-OH phases prepared after magnetic separation of the FST photocatalyst (figure S10). Although we did not investigate H<sub>2</sub>O<sub>2</sub>/UV-C for longer irradiation times, increasing the quantity of H<sub>2</sub>O<sub>2</sub> to 20 equivalents led to a reduction in framework hydroxylation over the same time period (table 2), possibly arising from increased self-quenching of the hydroxyl radicals at elevated concentration.<sup>25</sup> Attempts to carry out the reaction using only H<sub>2</sub>O<sub>2</sub> as both radical source and solvent were unsatisfactory due to framework degradation. (Table 2) Although the conversion grades observed with H<sub>2</sub>O<sub>2</sub> and UV-C remain unoptimised, this methodology does provide a viable alternative given the high rate of reaction and the absence of a catalyst thus eliminating the problems of separation associated with TiO<sub>2</sub> or the synthesis required to prepare FST photocatalysts.

In order to fully appraise the direct photohydroxylation of UiO-66, we carried out a series of PSLE reactions with bdc-OH under a range of exchange conditions (times, solvents and ratios) (table S3). The highest degree of exchange was found using water as solvent, where a conversion of 41% was observed following 24 h of reaction at room temperature. By increasing the reaction time to 5 days however, the UiO-66-OH conversion only reached 45 %. By increasing the amount of bdc-OH to 10 molar equivalents (wrt UiO-66) a PSLE level of 53 % was reached after 5 days, agreeing well with previous studies on UiO-66.<sup>12a</sup> It is clear that direct photohydroxylation of UiO-66 is more rapid than PSLE to yield UiO-66-OH with comparable levels of conversion, and when the active FST composite photocatalyst is employed unsurpassed levels of hydroxylation are observed without loss of framework crystallinity. It is also worth noting that the bdc-OH required for direct synthesis or PSLE is significantly more expensive than the unfunctionalised bdc linker employed to form UiO-66 itself. Further, photohydroxylation of UiO-66 appears selective for bdc-OH, since none of the strategies investigated herein showed any evidence of dihydroxy-bdc formation.

In summary, we have demonstrated three methodologies to carry out the direct photohydroxylation of UiO-66. The high degree of conversion to UiO-66-OH without disruption of framework crystallinity reaches up to 77 % when a magnetic titanium composite (FST) photocatalyst is employed and shows a clear enhancement with respect to previously reported PSLE methods. Successful framework hydroxylation will undoubtedly be a balance between the recombination of highly reactive hydroxyl radicals and their diffusion through MOF micropores, and while the latter has been reported for intrazeolite photochemical processes<sup>26</sup> more fundamental studies will be required for coordination-based systems of hybrid composition. Overall however, the use of photochemistry and/or radical reactions to directly post-synthetically modify photostable frameworks that might be difficult to access by solvothermal methodologies, could thus be a powerful alternative to PSM and PLSE to achieve these structures or introduce functional groups such as alcohols.

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## Notes and references

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- 1 S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334.
- 2(a) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939; (b) J. Ren, H. W. Langmi, B. C. North, M. Mathe and D. Bessarabov, *Int. J. Hydrogen Energy*, 2014, **39**, 890.
- 3 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- 4(a) J. Aguilera-Sigalat and D. Bradshaw, *Chem. Commun.*, 2014, **50**, 4711; (b) K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsá, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119.
- 5(a) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, *Nat Mater*, 2010, **9**, 172; (b) C. He, K. Lu, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 5181.
- 6 W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle Iii, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561.
- 7 Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2009, **131**, 16675.
- 8 C. K. Brozek and M. Dinca, *Chem. Soc. Rev.*, 2014, **43**, 5456.
- 9 J. G. Nguyen and S. M. Cohen, *J. Am. Chem. Soc.*, 2010, **132**, 4560.
- 10 K. K. Tanabe and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2009, **48**, 7424.
- 11 M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel and D. Farrusseng, *J. Am. Chem. Soc.*, 2010, **132**, 4518.
- 12(a) M. Kim, J. F. Cahill, Y. Su, K. A. Prather and S. M. Cohen, *Chemical Science*, 2012, **3**, 126; (b) F. M. Al-Sogair, B. P. Operschall, A. Sigel, H. Sigel, J. Schnabl and R. K. O. Sigel, *Chem. Rev.*, 2011, **111**, 4964.
- 13 O. Karagiari, W. Bury, J. E. Mondloch, J. T. Hupp and O. K. Farha, *Angew. Chem. Int. Ed.*, 2014, **53**, 4530.
- 14 T. Li, M. T. Kozłowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 11688.
- 15 W. Bury, D. Fairen-Jimenez, M. B. Lalonde, R. Q. Snurr, O. K. Farha and J. T. Hupp, *Chem. Mater.*, 2013, **25**, 739.
- 16 M. Meilikov, K. Yusenko and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 9644.
- 17(a) M. G. Goesten, J. Juan-Alcañiz, E. V. Ramos-Fernandez, K. B. Sai Sankar Gupta, E. Stavitski, H. van Bekkum, J. Gascon and F. Kapteijn, *J. Catal.*, 2011, **281**, 177; (b) S. Bernt, V. Guillermin, C. Serre and N. Stock, *Chem. Commun.*, 2011, **47**, 2838.
- 18 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.
- 19 M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632.
- 20(a) C. Wang, Z. Xie, K. E. deKrafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445; (b) S. Chavan, J. G. Vitillo, M. J. Uddin, F. Bonino, C. Lamberti, E. Groppo, K.-P. Lillerud and S. Bordiga, *Chem. Mater.*, 2010, **22**, 4602; (c) J. Long, S. Wang, Z. Ding, S. Wang, Y. Zhou, L. Huang and X. Wang, *Chem. Commun.*, 2012, **48**, 11656.
- 21 M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449.

- 22 L. Villeneuve, L. Alberti, J. P. Steghens, J. M. Lancelin and J. L. Mestas, *Ultrason. Sonochem.*, 2009, **16**, 339.
- 23(a) O. K. Farha, K. L. Mulfort, A. M. Thorsness and J. T. Hupp, *J. Am. Chem. Soc.*, 2008, **130**, 8598; (b) T. D. Keene, D. J. Price and C. J. Kepert, *Dalton Transactions*, 2011, **40**, 7122.
- 24 X. Yu, S. Liu and J. Yu, *Applied Catalysis B: Environmental*, 2011, **104**, 12.
- 25(a) G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513; (b) D. M. Hambly and M. L. Gross, *J. Am. Soc. Mass. Spectrom.*, 2005, **16**, 2057.
- 26 X. Liu, G. Zhang and J. K. Thomas, *The Journal of Physical Chemistry B*, 1997, **101**, 2182.