Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Controlled synthesis of Cu,Fe dual-atom catalysts restrained on metal-organic frameworks for efficient O<sub>2</sub> activation

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Supported bimetallic dual-atom catalysts (DACs) have been regarded as a promising class of materials for small molecule activation, despite their challenging syntheses. We have successfully synthesised supported Cu,Fe dual-atom catalysts (DACs) on the  $Zr_6O_4$  secondary building units of UiO-66-NH<sub>2</sub>, enabling efficient activation of O<sub>2</sub>. Our model photocatalytic styrene oxidation reaction achieved remarkably high product selectivity (> 92%) towards benzaldehyde. This superior reactivity is attributed to the well-balanced synergy between the electronic and steric characteristics, enabling efficient O<sub>2</sub> activation by the sterically restrained Cu and Fe sites in proximity for the formation of the bridging peroxy group. This group facilitates the selective oxidation of styrene similar to many peroxide-based oxidants. The confined microporous environment allows for control of the electronic and geometric properties of the DACs, shedding light towards more precise atomistic engineering that approaches the conventional inorganic metal(s)-complex counterparts. Overall, supported bimetallic dual-atom catalysts (DACs) are a promising class of materials for small molecule activation, despite their challenging syntheses.

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#### Introduction

Supported atom-precise metal clusters (with low nuclearity) are increasingly recognised to be the next-generation catalytic materials in the coming era.<sup>1-3</sup> Atom-precise clusters not only are highly atom-economical, but they also offer unique catalytic properties compared with their atomic and bulk counterparts. It is largely related to the widely tuneable electronic and geometric characteristics. Furthermore, the pairing of metals, e.g., in bimetallic dual-atom catalysts (DACs), could alter the electronic states and break the linear scale relationship, which could ultimately be an additional handle to tune the catalytic properties.<sup>4–6</sup> The catalytic properties in this class of supported DACs are often governed by the adsorption configurations of substrates and the corresponding energetics.7-11 However, it has been a grand challenge to decipher the correlations between the structural descriptors and catalytic reactivity, which hinders the 'target-engineering' of a specific structure with regard to a catalytic reaction.

The activation of small molecules, such as O2, water, and methanol, is crucial in many catalytic processes. Interactions between two neighbouring motifs often play a significant role in their activation. Microporous materials, such as zeolites and metal-organic frameworks (MOFs), with spatial restraints, can facilitate the design and engineering of neighbouring active motifs. Our team has recently demonstrated the presence of 'frustrated' active pairs between protonic Brønsted acid sites and metal sites within the confined cavity of zeolites for the initial cleavage of water and methanol, followed by subsequent reactions that produce high selectivity products.<sup>12</sup>

In recent studies, a series of 3d metal-based dual-atom catalysts (DACs) were immobilised on microporous supports, where the bridging O species were identified as pivotal factors in their catalytic reactivities.<sup>13–16</sup> An example worth noting is the Cu2oxo and Cu3-oxo clusters that are supported on zeolites. These clusters have demonstrated remarkable effectiveness in selectively oxidising methane to methanol. The Cu-O-Cu site within the clusters is highly active and specific in activating the normally inert and non-polar C-H bonds in methane.17-19 In addition to M–O–M, M–O<sub>2</sub>–M (in various O<sub>2</sub> binding modes) is also a highly attractive functional group that could facilitate more extensive catalytic possibilities. A popular example is Cytochrome c oxidase (CcO), where the Fe and Cu moieties are held apart by a rigid protein scaffold to a few angstroms distance. This unique arrangement enables the activation of O<sub>2</sub> (by Fe) and subsequent multi-electron reduction (by Cu) to form the well-known 'Cu-O<sub>2</sub>-Fe' co-factor.<sup>20,21</sup> Despite the design of many organometallic complexes with well-defined electronic and steric properties, it remains fundamentally challenging to design well-controlled, atomically dispersed bimetallic dualatom catalysts (DACs) supported on solid materials.

Here, we present a method for the controlled synthesis of atomically precise Cu,Fe dual-atom catalysts (DACs) stabilised by the same  $Zr_6O_4$  secondary building unit of UiO-66-NH2 using a modular assembly approach that exploits fundamental coordination and solid-state chemistry concepts. This approach enables the selective photocatalytic oxidation of styrene to the benzaldehyde product with high selectivity (> 92%). The superior catalytic behaviour is attributed to the formation of a bridging ' $\mu$ - $\eta^1$ : $\eta^1$ - $O_2$ ' species resulting from O2 activation by neighbouring Fe and Cu motifs. Additionally, we employ theoretical calculations to discuss the structure-activity correlations regarding the interactions between the DACs and the MOF framework at atomic resolution.

## **Results and Discussion**

A crystalline UiO-66-NH<sub>2</sub> powder sample as a host solid support has been prepared (as used before<sup>22–24</sup>, see Figures S1–S2 in the Supporting Information (SI) for basic structural and morphological characterisation) with a chemical formula of  $Zr_6O_4(OH)_4(CO_2C_6H_3NH_2CO_2)_{5.8}$  (space group: Fm-3m) with a metal-to-linker ratio of 1:0.97. As shown in Scheme 1, a rational modular approach has been applied to provide an exclusive environment for the formation of Cu,Fe DACs (denoted as 'Cu,Fe-UiO'). This approach takes advantage of the microporous confinement effect and formation of Lewis acid-base adducts. A dibasic 2-methylimidazole linker was applied to connect the step-by-step added Cu<sup>2+</sup> and Fe<sup>3+</sup>. It was then calcined at 180 °C in air to yield the final 'Cu,Fe-UiO' by removing the connecting meIm linker and water ligands. The effectiveness of this modular approach was evaluated by elemental analysis (Table **S1**), and Raman and Fourier-transform infrared (FTIR) spectroscopic results (Figure S3). By the energy dispersive X-ray (EDX) mapping analysis (Figure S4), a homogeneous distribution of Cu and Fe species can be observed. Analogous 'single-atom' Fe1-UiO (Figure S5) and Cu1-UiO (Figure S6) samples (as synthesised before<sup>22,24</sup>) were used for a comparison study.

In-situ synchrotron X-ray powder diffraction (PXRD) at elevated temperatures was employed to serve as a guide to selecting a reasonable calcination temperature (**Figure 1a–1b**, the full patterns are presented in **Figures S7–S8**). This is an important step as a low calcination temperature will not be able to remove water and 2-methylimidazole linker, but a too-high calcination temperature will break the crystallinity of the MOF framework. The crystalline MOF framework was retained upon the post-synthetic metalation approach (see **Figure S9** with the crystallographic parameters summarised in **Tables S2–S3**). As seen in **Figure 1a–1b** the most notable change in the Bragg peak



**Scheme 1.** Schematic illustration of the modular assembly approach that combines the underlying principles of solid-state chemistry and coordination chemistry for the synthesis of Cu,Fe DAC on UiO-66-NH<sub>2</sub> (denoted as '**Cu,Fe-UiO**'). In the preparation of **Cu,Fe-UiO**, a dibasic 2-methylimidazole linker was applied to connect the modularly added Cu<sup>2+</sup> and Fe<sup>3+</sup>. The linker was removed by calcination in air at 180 °C.

intensities (taking (111), the strongest peak, as an illustration, Figure 1c) was observed just above 175 °C, which may indicate the removal of melm and water. Only a few Bragg peaks representative of the microporous void, such as (111) at 3.36°, were altered upon calcination, while the intensities of the majority of the Bragg peaks remained unaltered (see Figure S8). These unaltered peaks were accordingly used as an 'internal standard' for comparison. It is in contrast to the calcination of the analogous  $\mbox{Cu}^{2+}\mbox{-UiO-66-NH}_2$  sample where the most notable change occurs at around 250 °C. In addition, as shown in Figure 1d, the unit cell parameters decrease much more rapidly in the calcination study of Cu<sup>2+</sup>-melm-Fe<sup>3+</sup>-UiO-66-NH<sub>2</sub>. The alternation in the crystallographic parameters up to 200 °C was negligible. At higher temperatures (> 200 °C), the intensity of the Bragg peaks decreased significantly, with the formation of an apparent amorphous phase from structural deformation. The ultraviolet-visible-near Infrared (UV-vis-NIR) spectra before and after calcination also reveal that a notable change in absorption can be observed which can be ascribed to the removal of water and meIm linker species (Figure S10).<sup>25,26</sup>

We subsequently employed FTIR spectroscopy to investigate the location of the Cu,Fe DACs with respect to the UiO-66 framework (**Figure 1e**). The peaks at 577 cm<sup>-1</sup> and 664 cm<sup>-1</sup> are characteristic of the asymmetric and symmetric mode of Zr–(O– C) in UiO-66-NH<sub>2</sub>.<sup>27,28</sup> Noticeable shifts in these peak positions can be observed in **Cu,Fe-UiO**. This suggests a change in the Zr– (O–C) bonding caused by the direct interaction of the Zr<sub>6</sub>O<sub>4</sub> similar observation is also observed in related studies of Cubased DACs on the  $Zr_6O_4$  of UiO-66-NH<sub>2</sub>.<sup>24</sup> As a complementary technique to FTIR, we employed Raman spectroscopy to further study the bonding information in the samples (**Figure 1f**). Characteristic Raman peaks, such as Zr–O stretching at 801 cm<sup>-1</sup>, O–C–O symmetric stretching in-phase peak at 1450 cm<sup>-1</sup> and C=C stretching of aromatic rings, of UiO-66-NH<sub>2</sub> are noted. The peak at 276 cm<sup>-1</sup> can be assigned to Cu–O.<sup>29</sup> Extra peaks observed at 420, 543 and 1122 cm<sup>-1</sup> in **Cu,Fe-UiO** can be attributed to the Fe–O, Fe–O<sub>2</sub> and O–O (in the form of O<sub>2</sub><sup>2-</sup>) stretching modes, respectively.<sup>30</sup> These features agree with previous Raman studies on CcO which contains a highly comparable 'Cu-O<sub>2</sub>-Fe' co-factor.<sup>29–31</sup> The Raman spectra of **Cu<sub>1</sub>-UiO** and **Fe<sub>1</sub>-UiO** are presented in **Figure S11** where the respective Fe–O<sub>2</sub> or Cu–O<sub>2</sub> features were not observed.

X-ray absorption spectroscopy has been accordingly employed to discern the electronic and local geometric structures of **Cu,Fe-UiO**. The Cu and Fe K-edge X-ray absorption near-edge structures are shown in **Figures 2a** and **2b**. The oxidation states of Cu and Fe can be confirmed at +2 and +3, which are highly comparable to the absorption edge of CuO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, respectively. However, as seen in the zoom-in illustration, the Fe K-edge of **Cu,Fe-UiO** locates at a slightly lower energy (closer to the Fe foil standard) than the Fe K-edge of **Fe<sub>1</sub>-UiO**, which indicates that the valence state of Fe in **Cu,Fe-UiO** is less positive than that of **Fe<sub>1</sub>-UiO**. By performing a quantitative linear combination fitting analysis (as summarised in **Table S4** 



secondary building unit with the extra-framework DACs. A and Figure S12), the Fe K-edge of Cu,Fe-UiO possesses 12% Fe

**Figure 1.** (**a**, **b**) Temperature-resolved synchrotron PXRD two-dimensional contour plot of the calcination treatment of the precursor of **Cu,Fe-UiO**. Data collected on BL02B2 SPring-8. Energy optimised at 17.8 keV. (**c**) A temperature-resolved plot of the Bragg peak intensities of the (111) reflection. (**d**) Quantitative analysis of the unit cell parameters by Pawley refinement with the fitting parameters summarised in **Table S3**, and fitting profiles in **Figure S8**. (**e**) FTIR and (**f**) Raman spectra of UiO-66-NH<sub>2</sub> and **Cu,Fe-UiO**.

foil and 88%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> characteristics, which is further verified by our Bader charge analysis (see **Figure S13**). It is in great contrast to that of **Fe<sub>1</sub>-UiO**, which possesses only 1% Fe foil but 99%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> characteristics. Considering the structural similarities between the two samples, the much less positive valence state of Fe in **Cu,Fe-UiO** can be attributed to the combined electronic effect of neighbouring Cu<sup>2+</sup> and bridging peroxy species.

We further examined the structural properties of **Cu,Fe-UiO** by studying the coordination environments using extended X-ray absorption fine structure (EXAFS) spectroscopy. To better correlate the EXAFS peaks with k-space, wavelet transformation (WT) was employed (**Figure 2c–2d**). The highest intensity belongs to the lobe centred at k ~ 6.5 Å<sup>-1</sup>, R ~ 1.5 Å, which corresponds to the O atoms around the Cu and Fe centres. Lobes with weaker intensity can also be observed at R > 2.0 Å, which can be attributed to the backscattering contribution of

the long-range (second-shell)  $M_A-M_B$  interaction. From the quantitative analysis of the EXAFS results (**Figure 2e, 2f** and **Table S5**), the Cu–O and Fe–O bond lengths are calculated as 1.95(1) and 1.95(1) Å, with the average coordination number (CN) of 3.6(1) and 4.6(1), respectively. The Cu-Fe backscattering contribution is calculated as 3.37(1) Å, with a CN of 1.0(1). The difference in the local environments and coordination environments between **Cu,Fe-UiO** and its single-atom analogous (Cu<sub>1</sub>-UiO and Fe<sub>1</sub>-UiO) is summarised in **Figures S14–S15** and **Table S6**.

The high-resolution synchrotron PXRD patterns of **Cu,Fe-UiO** are shown in **Figure 2g**. The positions of the Bragg peaks are only altered marginally compared to the parent UiO-66-NH<sub>2</sub>, **Cu<sub>1</sub>-UiO**, and **Fe<sub>1</sub>-UiO**, with the space group remained unchanged at *Fm-3m* (see **Figure S16**), suggesting that the extra-framework Cu and Fe species do not significantly alter the



**Figure 2**. XANES measurements of **Cu,Fe-UiO** at the (a) Cu K-edge, and (b) Fe K-edge. Wavelet transforms for the EXAFS signals of (c) Cu K-edge and (d) Fe K-edge. The Fourier-transformed magnitude of the experimental (e) Cu K-edge, (f) Fe K-edge, and the fitting profiles. The quantitative analysis is summarised in **Tables S4–S5**. (g) High-resolution synchrotron PXRD pattern and the corresponding Rietveld refinement profile. Data were collected on beamline BL02B2 at SPring-8 ( $\lambda = 0.700261(10)$  Å; E = 17.8 keV) with the Rietveld refinement profiles using TOPAS v6.0 academic. The atomic parameters are summarised in **Tables S7**. (h) The optimised crystal structure by the Rietveld refinement. (i) Illustration of human Cytochrome *c* oxidase (5Z62) to show the structural similarity.<sup>32</sup>

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crystalline MOF framework. Highly symmetrical Bragg peaks are retained after metalation, suggesting a homogeneous metalation process. The crystallographic parameters are summarised in Table S2. In contrast, the variation in the Bragg peaks' intensities, particularly over the range of higher 20 regime, is apparent, which can be attributed to the significant changes in the scattering factors that arose from the addition of heavier metal atoms. We subsequently employed Rietveld refinement to investigate the atomic parameters, including the fractional coordinates (x, y, z) of the extra-framework species with respect to the parent structure. High-quality of the Rietveld refinement can be confirmed by a small difference between the data and the fitting profile, and a low R<sub>wp</sub> value. The site occupancy factors of the Fe and Cu sites have been fixed based on elemental analysis to ensure the reliability of the Rietveld refinement.

In the refined structure shown in Figure 2h,  $Cu_A$  and  $Fe_B$  are directly anchored on the Zr<sub>6</sub>O<sub>4</sub> secondary building units, with derived bond lengths of 1.914(2) Å for Cu<sub>A</sub>–O and 1.968(1) Å for Fe<sub>B</sub>–O, which were restrained according to the EXAFS findings during the refinement process. The Cu…Fe interatomic distance was found at 3.348(2) Å, which is in close agreement with that derived in the EXAFS analysis (of 3.37(1) Å). A  $\mu$ - $\eta^1$ : $\eta^2$ - $O_2$  bridge is found located between the Cu and Fe sites forming the Cu-(µ- $\eta^1:\eta^2-O_2$ )-Fe, which verifies the spectroscopic findings as discussed above. We have also employed density functional theory (DFT) calculations for the optimisation and verification of the atomic parameters and overall crystal structure (as later discussed). Non-framework oxygen atoms in the form of the terminal –OH<sub>2</sub> are present. Based on the optimised bond angles and distances, we found that both  $Cu_A$  and  $Fe_B$  sites in the refined crystal structures all adopt pseudo tetrahedral geometry, with a slight deviation from perfect tetrahedron.



**Figure 3.** (a) Product distribution from the photocatalytic oxidation of styrene ( $\lambda$  = 365 nm) over **Cu,Fe-UiO**. (b) Time-resolved catalytic reactivity towards benzaldehyde over different catalysts. (c) Evaluation of different reaction conditions. (d) PXRD pattern of **Cu,Fe-UiO** collected after three photocatalytic cycles (Mo X-ray).

Interestingly, the Cu–( $\mu_2$ -O<sub>2</sub>)–Fe moiety is highly analogous to the active site of CcO, as shown in **Figure 2i**.<sup>32</sup>

The photocatalytic styrene oxidation was employed as a model reaction to investigate its catalytic characteristics. The photocatalytic styrene oxidation was performed using a LED lamp with a UV wavelength of 365 nm at the power of 10 W (see experimental details in SI<sup>+</sup>/methods). A typical photocatalytic experiment uses 2.5 mg of catalysts dispersed in 0.5 mL styrene in 1.5 mL of 1,2-dichloromethane in air with UV illumination ( $\!\lambda$ = 365 nm). Interestingly, upon the illumination of Cu,Fe-UiO, the catalytic selectivity towards benzaldehyde reached >92% based on gas chromatography-mass spectrometry (GC-MS) analysis. Other common aromatic products, including benzoic acid, acetophenone, and phenylacetaldehyde, were detected at very low selectivity. In stark contrast, we noted nearly nil products from the catalysis over UiO-66-NH<sub>2</sub>, Cu<sub>1</sub>-UiO, and Fe<sub>1</sub>-**UIO**. The detailed GC-MS spectra are summarised in **Figure S17**. The product selectivity towards benzaldehyde over Cu,Fe-UiO remains extremely high at > 92% for five catalytic cycles (Figure 3a), with the yield decreased marginally possibly due to a small amount of sample being physically washed away from recycling. >92% selectivity towards benzaldehyde using air as the oxidant (instead of using peroxides) is superior to most reported catalysts (as summarised in Table S8, typically in the range of 60% to 80% because of highly competitive the epoxidation pathway). As seen in Figure 3b, the yield of benzaldehyde increased steadily over  $\mbox{Cu,Fe-UiO}$  at a rate of around 10  $\mbox{\mu}\mbox{mol}$ mg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which contrasts with nearly nil product formation over the support UiO-66-NH<sub>2</sub> and its 'single-atom' Cu<sub>1</sub>-UiO and Fe1-UiO analogues. It should be noted that an extremely low yield of catalytic product over UiO-66-NH<sub>2</sub>, Cu<sub>1</sub>-UiO and Fe<sub>1</sub>-UiO (< 0.5  $\mu$ mol mg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), was observed based on our GC-MS analysis. We have also explored the reaction conditions and



**Figure 4. (a)** UV-vis spectra of **Cu,Fe-UiO** and other samples, and **(b)** the corresponding Tauc plots for the extrapolation of the apparent bandgaps. **(c)** Cyclic voltammetric (CV) measurements, and **(d)** the corresponding onset potential (E<sub>0</sub>), half-wave potential (E<sub>1/2</sub>), and current density at 0.85 V<sub>RHE</sub> on different samples in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a scan rate of 100 mV s<sup>-1</sup>.

found that air (O<sub>2</sub>) and UV illumination are necessary for this reaction, as nil product was observed when the reaction vessel was degassed with N<sub>2</sub> or using light with longer wavelengths (Figure 3c). From the PXRD pattern collected three catalytic cycles (Figure 3d), the crystalline structure remained at *Fm-3m*. It is intriguing why Cu,Fe-UiO exhibits such high product selectivity, which is possibly related to the synergy between the Cu and Fe sites, as well as the unique Cu-( $\mu$ - $\eta^1$ : $\eta^2$ -O<sub>2</sub>)-Fe bridging structure, that renders peroxide-like property. We first investigated the electronic properties by UV-vis spectroscopy (Figure 4a). The presence of  $Cu^{2+}$  (highlighted in blue) and  $Fe^{3+}$ species (in yellow) can also be seen in Cu,Fe-UiO as seen in their analogous single-atom counterparts. Weak absorption peaks related to the *d*-*d* transitions were observed primarily because of their coordination with framework O atoms (weak field). As shown in the corresponding Tauc plots (Figure 4b), the apparent bandgap of UiO-66-NH<sub>2</sub> was extrapolated at 2.83 eV. An insignificant difference in the apparent bandgaps of other samples has been extrapolated (between 2.74 eV and 2.79 eV), which suggests that the superior catalytic reactivity should be originated from the local structures. It is consistent with our previous study on structurally related **Cu<sub>1</sub>-UiO** and **Cu<sub>2</sub>-UiO** where the remarkably different surface sensitivity and product selectivity (in photocatalytic formic acid reforming reaction) have been attributed to the difference in the adsorption configurations.<sup>24</sup>

Electrochemical measurements were subsequently employed to study if synergy is present, as probed by the UV-vis results above, between the  $Cu^{2+}$  and  $Fe^{3+}$  sites. As seen in the cyclic voltammogram conducted in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> (Figure 4c), much more electropositive curves of Cu,Fe-UiO than those of Cu<sub>1</sub>-UiO and Fe<sub>1</sub>-UiO (which can be reflected by the current



**Figure 5.** (a) The proposed reaction profile, showing the key reaction steps of styrene oxidation to benzaldehyde over **Cu,Fe-UiO**, and (b) the corresponding reaction coordinates. (c) Calculations on the energetics of O<sub>2</sub> activation in **Cu,Fe-UiO** and a hypothetical **Cu,Cu-UiO**. (d) The proposed reaction pathways of styrene oxidation over **Cu,Fe-UiO**, showing the interplay between pathway selection and theoretical product distribution. The same colour scheme as adopted in Figure 2.

density, 'j@0.85 V<sub>RHE</sub>', in Figure 4d) can be seen. This suggests that its much superior ability in the activation of O2 should be originated from the synergistic interactions between the Cu<sup>2+</sup> and Fe<sup>3+</sup> motifs. The onset potentials (E<sub>0</sub>) and half-wave potentials (E<sub>1/2</sub>) for Cu,Fe-UiO are notably different from Cu<sub>1</sub>-UiO and Fe1-UiO, which also infers the presence of Cu-Fe electronic interactions. As shown in Figure 4d, two reduction behaviours were observed in Cu,Fe-UiO with the first one possessing comparable properties with that of  $Cu_1$ -UiO. Another reduction peak was observed with an onset potential of 0.80  $V_{\text{RHE}}$  and a peak potential of 0.85  $V_{\text{RHE}}.$  This could be attributed to the electronic stabilisation by the peroxy bridge between the  $Cu^{2+}$  and  $Fe^{3+}$ , which enhances the peak oxidation potential of Fe<sup>3+</sup> from 0.75 V<sub>RHE</sub> (Fe<sub>1</sub>-UiO) to 0.85 V<sub>RHE</sub> (Cu,Fe-**UiO**).<sup>33</sup> In the absence of  $O_2$ , the oxidation peak disappeared, indicating that the peak is a result of O2 activation but not directly from the catalyst. The presence of the Cu,Fe system promotes the activation of O<sub>2</sub> from the electrolyte, facilitating further styrene oxidation.

DFT calculations were first employed to optimise the local structures. the crystal structure derived from the chargeflipping algorithm of the high-resolution synchrotron PXRD data as the initial model for DFT computational optimisation. In this initial model, the hydrogen atoms on the Zr<sub>6</sub>O<sub>4</sub> secondary building units (SBUs) were included preliminarily as hydrogen cannot be properly probed by typical hard X-ray techniques. The subsequent DFT calculation was used to (i) optimise the atomic parameters of the extra-framework Cu,Fe DACs, and (ii) evaluate the effect on the SBUs upon metalation. After further confirmation from DFT calculations, the SBUs were fully deprotonated for charge balance due to the added Cu, Fe DACs. We have also conducted additional DFT calculations by keeping all (and part of) the hydrogen atoms on the SBUs. The Cu,Fe DACs were found detached from the SBUs which suggests the importance of SBU-deprotonation for its stabilisation.

We subsequently investigated the energetics of Cu,Fe-UiO which illustrates superior catalytic reactivity in styrene oxidation. We have investigated the strain on the UiO framework by anchoring the Cu–( $\mu_2$ -O<sub>2</sub>)–Fe on the Zr<sub>6</sub>O<sub>4</sub> secondary building units. A cluster model consisting of one Zr<sub>6</sub>O<sub>4</sub> secondary building unit and six benzenedicarboxylate linker species constructed with  $Cu-(\mu_2-O_2)$ -Fe was adopted from the above structure elucidation. As shown in Figure S18a, the structure was optimised by first fixing the linker species perpendicular to each other. We subsequently studied the effect on the structure (in the cluster model) by fully relaxing the framework (see Figure S18b). By fully relaxing the linker rotation, not only the  $\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2$  bridging group becomes  $\mu\text{-}$  $\eta^1\!:\!\eta^2\!-\!O_2$  with  $\eta^2$  on Fe, but we also observed a clear alternation in the inter-linker angles, which deviates from being perpendicular to each other. The transformation from  $\mu$ - $\eta^1$ : $\eta^1$ - $O_2$  to  $\mu$ - $\eta^1$ : $\eta^2$ - $O_2$  agrees with many conventional understandings on the binding of O<sub>2</sub> in related Cu,Fe-containing species.<sup>21,34</sup> However, the rigid UiO framework with linker perpendicular to each other should limit the formation of  $\mu$ - $\eta^{1}$ : $\eta^{2}$ - $O_{2}$  bridging at the ground state. The apparent strain in the ground state

system, as revealed experimentally, may explain why **Cu,Fe-UiO** is particularly catalytically active for O<sub>2</sub> activation.

In general, there are two proposed reaction pathways in the catalytic oxidation of styrene using peroxides or O2 as the oxidant, namely, the epoxidation pathway, and the peroxy pathway.<sup>35–37</sup> The epoxidation pathway typically yields a range of aromatic products, such as acetophenone, benzeneacetaldehyde, benzoic acid, and 1-phenylethane-1,2diol, through rearrangement or further oxidation of styrene epoxide. The catalytic oxidation of styrene using peroxides, such as H<sub>2</sub>O<sub>2</sub> and tert-butyl hydroperoxide as the oxidant can generally yield higher selectivity towards benzaldehyde (often reported >90%), which generally involves the peroxy pathway.<sup>35</sup> High product selectivity towards benzaldehyde can be achieved by the favourable formation of peroxy intermediates via the oxidative cleavage of the C=C bond ('2+2-like' mechanism) while limiting the direct epoxidation pathway.38 Indeed, compared with peroxides, using O<sub>2</sub> (or even more preferably just air) as an oxidant is more desirable from cost consideration. However, the control of product selectivity is more difficult due to the difference in the transient structures, where epoxidation is also a dominant competing route. Attaining high product selectivity towards benzaldehyde using O2 as the oxidant remains challenging as the formation of the epoxidation intermediate cannot be effectively circumvented. From the result of our photocatalytic reaction over Cu,Fe-UiO, we have only detected <10% non-benzaldehyde aromatic products (including benzoic acid, acetophenone, and benzeneacetaldehyde), which indicates the preference for the direct formation of benzaldehyde over the epoxidation pathway.

The reaction steps of styrene oxidation over Cu,Fe-UiO are summarised in Figure 5b, with a styrene molecule first placed close to the peroxy group at the initial stage of the calculation (supported by our probe-assisted FTIR measurements in Figure **S9**). Upon UV illumination, the peroxy group undergoes homolytic cleavage to form two O radicals, which then attack the electron deficit C=C bond of styrene to form the intermediate species. This step shows a high resemblance to those of many peroxide oxidants, such as  $H_2O_2$  and tert-butyl hydroperoxide.<sup>35</sup> The intermediate species will accordingly rearrange to yield the final benzaldehyde and formaldehyde products. With regard to the low production of styrene oxide (or other styrene oxide-derived products), the calculations have shown that the total energy of the epoxidation pathway (black line) is 1.8 eV higher than that of the peroxy pathway (red line). As presented in the proposed catalytic cycle (see Figure S20), the oxidation states of the Cu and Fe sites should reduce from +2 and +3 to +1 and +2 in the rearrangement step (Step (4) in Figure S20), respectively.

To complete the catalytic cycle, a final O<sub>2</sub> activation step (Step (5) in **Figure S20**) was included in the calculation at the end, with the reaction coordinates presented in **Figure 5c**. The O<sub>2</sub> molecule is reduced by then-vacant neighbouring Cu<sup>I</sup> and Fe<sup>II</sup> motifs to re-create the initial Cu–( $\mu$ - $\eta^1$ : $\eta^2$ -O<sub>2</sub>)–Fe structure. The facile activation of O<sub>2</sub> to render peroxy property is particularly noteworthy which can be attributed to the well-balanced electronic and steric properties within the MOF support with

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the Cu and Fe sites located at *ca*. 3.35 Å apart. A hypothetical analogous Cu,Cu-UiO has been modelled for a comparative study. The change in the total energy in the  $O_2$  activation process in Cu,Fe-UiO was calculated as -3.17 eV, which is noticeably more negative than that in Cu,Cu-UiO (cf. change of energy of -2.54 eV). In addition, the binding energy of  $O_2$ between Cu and Fe is also much stronger than that between two Cu sites (cf. E<sub>binding</sub> (O<sub>2</sub>) of -3.64 eV versus -2.05 eV). Much more favourable energetics in the activation of  $\mathsf{O}_2$  has been noted in Cu,Fe-UiO when compared with the hypothetical Cu,Cu-UiO. As shown in the Bader charge analysis in Figure S13, the Bader charges of Cu and Fe decrease by 0.23 e and 0.25 e, respectively, suggesting the simultaneous oxidation of Cu<sup>I</sup> and  $Fe^{II}$  to  $Cu^{II}$  and  $Fe^{III}$  during the  $O_2$  activation process. Interestingly, this is highly analogous to the catalytic cycle of the structurally related CcO that involves an  $O_2$  activation step, where the Cu and Fe sites undergo a similar redox cycle. In brief, the interplay between pathway selection and theoretical product distribution of styrene oxidation over Cu,Fe-UiO has been presented in Figure 5d to offer a more comprehensive understanding of the structure-reactivity correlation.

# Conclusion

In conclusion, we have demonstrated the precise engineering of supported bimetallic Cu,Fe dual-atom sites on the Zr<sub>6</sub>O<sub>4</sub> SBUs of UiO-66-NH2. A multi-modal characterisation approach was employed to determine the atomic and crystallographic parameters, ensuring data reliability. Our study revealed that Cu,Fe-UiO enables efficient activation of O2 in a model photocatalytic styrene oxidation reaction, leading to the direct formation of benzaldehyde while avoiding the competing epoxidation reaction pathway. The ultra-high product selectivity towards benzaldehyde can be attributed to two factors: (i) the unique bridging O<sub>2</sub> group, and (ii) the wellbalanced synergy between the Cu<sup>II</sup> and Fe<sup>III</sup> sites in close proximity (approximately 3.35 Å). By manipulating the electronic and geometric characteristics in Cu,Fe-UiO, we have achieved sophisticated control over catalytic reactivity and product selectivity. We believe that the preparation and application of this class of dual-atom catalysts (DACs) warrant further research and urgent attention.

#### **Author Contributions**

All authors have given approval to the final version of the manuscript.

# **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (22172136), the Hong Kong

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Research Grants Council (15305722, 15301521 and 15300819), PolyU fund (P0042930, P0039335, P0042646). We also thank Prof. Zhengtao Xu (A\*Star) for the valuable discussion on this project.

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