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A mixed dicarboxylate strut approach to enhancing catalytic activity of a *de novo* urea derivative of metal–organic framework UiO-67†

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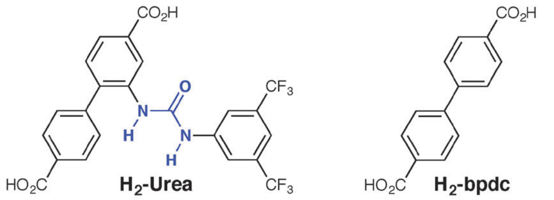
A hydrogen-bond donating MOF catalyst based on the UiO-67 framework, containing both urea-functionalized dicarboxylate and biphenyl-4,4′-dicarboxylate struts, was synthesized by a *de novo* route. The mixed strut framework has larger pore sizes and improved catalytic activity for Henry reactions than the pure strut analogue, which contains only the urea-functionalized dicarboxylate linker.

Metal–organic frameworks (MOFs) constitute one of the most widely studied classes of porous materials.[1] These well-defined crystalline materials are composed of inorganic nodes linked by polytopic organic struts to form three-dimensional arrays of rich topological diversity, which typically exhibit high surface area and porosity.[2] The ability to imbue desired functionalities onto MOFs by tailoring their organic linkers has led to experimental demonstrations of numerous potential applications such as gas storage[3] and separation,[4] chemical sensing,[5] light harvesting,[6] drug delivery,[7] ion exchange[8] and catalysis.[9] Yet, the incorporation of functional struts into a framework of specific topology, particularly for catalysis, often necessitates a subtle balance between sophisticated strut designs and steric considerations, as accessibility of the catalyst site within the framework is essential for a highly active MOF catalyst.

Zirconium-cluster-based MOFs are known for their excellent thermal and chemical stabilities which make them enticing candidates as catalysts.[10] Relevant to this class of frameworks, we have recently disclosed a reproducible method of synthesizing Zr-based UiO-66, **UiO-67** and their derivatives with remarkably high surface area.[11] Specifically, the inclusion of conc. HCl during the solvothermal synthesis of **UiO-67** leads to a systematic absence of four of the ideal twelve bpdc struts (bpdc = biphenyl-4,4′-dicarboxylate) connecting to the $Zr_6O_4(OH)_4$ nodes (Scheme 1). Consequently, the resulting **UiO-67** contains two pore sizes with diameters of 23 and 12 Å (see below). These large cavities within the framework make derivatives of **UiO-67** a favourable choice as catalysts, which thus far have seen limited reports.[12,13]



$$m\ \mathbf{H_2\text{-}Urea} + n\ \mathbf{H_2\text{-}bpdc} \xrightarrow[\text{DMF, 80 °C}]{\text{ZrCl}_4,\ \text{conc. HCl}} Zr_6O_4(OH)_4(\mathbf{Urea})_x(\mathbf{bpdc})_y$$

	m	*n*	*x*	*y*
UiO-67	0	1	0	4
UiO-67-Urea	1	0	4	0
UiO-67-Urea/bpdc	0.5	0.5	1.44	2.56

Scheme 1 Solvothermal synthesis of non-functionalized **UiO-67**, pure strut **UiO-67-Urea** and mixed strut **UiO-67-Urea/bpdc**.

We are particularly interested in incorporating urea derivatives of $\mathbf{H_2}$**-bpdc**, such as $\mathbf{H_2}$**-Urea**, into the **UiO-67** framework as hydrogen-bond donating (HBD) catalysts (Scheme 1). Heterogeneous urea-based MOF catalysts have been shown to be more effective in promoting Friedel–Crafts reactions than their homogeneous urea analogues.[14] Based on this approach, we are investigating the catalysis scope of urea-based frameworks to other reactions commonly promoted by homogeneous HBD catalysts, such as the atom-economic Henry reaction for carbon–carbon bond formation.[15,16] Herein, we describe an investigation of our aforementioned *de novo* solvothermal protocol to access the first example of a catalytically active urea derivative of **UiO-67**. Its efficacy as a HBD catalyst is subsequently illustrated through examples of Henry reactions.

The desired HBD strut, $\mathbf{H_2}$**-Urea**, was synthesized by reacting dimethyl 2-aminobiphenyl-4,4′-dicarboxylate[17] with 3,5-bis(trifluoromethyl)phenyl isocyanate followed by saponification with lithium

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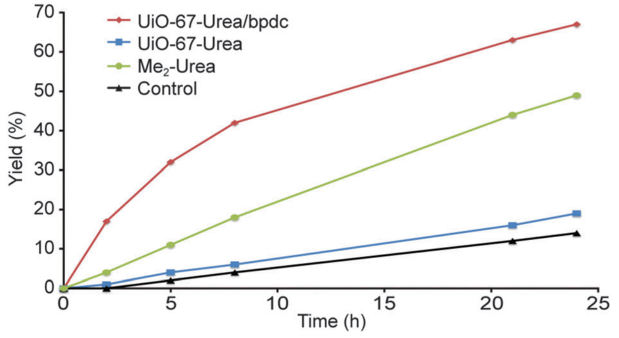
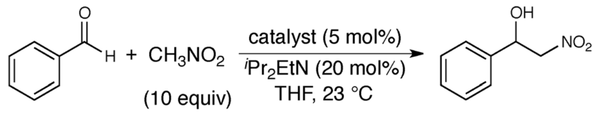


Fig. 1 Catalytic activities of the mixed strut **UiO-67-Urea/bpdc**, pure strut **UiO-67-Urea** and **Me_2-Urea** strut. The control experiment was performed with $^iPr_2EtN$ but without catalyst. All of the reactions were performed for 24 h and monitored by ^1H NMR spectroscopy (500 MHz, $CDCl_3$) using mesitylene as an internal standard.

hydroxide monohydrate. Our initial attempt to synthesize a **UiO-67** derivative based on our reported solvothermal protocol,[11] between **H_2-Urea** and $ZrCl_4$ (1 : 1 molar ratio) in DMF using conc. HCl as an additive (Scheme 1) at 80 °C, indeed resulted in **UiO-67-Urea** as a porous material that exhibits sharp peaks in its PXRD pattern (see Fig. S1, ESI†). For the purpose of catalysis, the strongly hydrogen bonded DMF in the pore was exchanged for THF (see Fig. S2, ESI†). Unfortunately, the THF-exchanged **UiO-67-Urea** showed poor catalytic activity in the Henry reaction between benzaldehyde and nitromethane, exhibiting only marginally greater formation of the desired product, 2-nitro-1-phenylethanol, after 24 h than in the background control experiment (Fig. 1).

The protrusion of such a sterically demanding urea functional group from the strut likely precludes access of the substrate to the catalytically active pores and limits the catalysis to occur on the external surface of the **UiO-67-Urea** crystals. We hypothesized that by employing a mixture of **H_2-Urea** and **H_2-bpdc** struts in the solvothermal synthesis, catalytically active urea sites could be incorporated into **UiO-67** framework by *de novo* means with minimal sacrifice of porosity.[18]



The mixed strut **UiO-67-Urea/bpdc** framework was synthesized under the same condition as **UiO-67-Urea**, using a mixture of **H_2-Urea** and **H_2-bpdc** struts (1 : 1 molar ratio). The highly crystalline material shows well-resolved peaks in its PXRD pattern and is clearly isostructural with the parent **UiO-67** framework (Fig. 2). The urea sites in **UiO-67-Urea/bpdc** were activated for catalysis by soaking the material in THF at 50 °C over two days, replacing the supernatant with fresh THF several times a day (for subsequent PXRD, see Fig. S3, ESI†). Afterward, a solution of the THF-exchanged material in D_2SO_4–DMSO-d_6 was analysed by ^1H NMR spectroscopy (500 MHz), which shows the complete exchange of DMF with THF (see Fig. S2, ESI†). The relative composition of the framework was also elucidated from the ^1H NMR spectrum, which indicates 36 mol% of the urea strut was incorporated into the framework relative to the total number of struts. This enabled us to determine the precise catalyst loading required for subsequent catalytic Henry reactions.

The THF-exchanged **UiO-67-Urea/bpdc** framework is an effective catalyst for the Henry reaction between benzaldehyde and nitromethane (10 equiv.) in THF at 23 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy (500 MHz, $CDCl_3$), which shows more than a three-fold increase in the formation of 2-nitro-1-phenylethanol as the desired product by **UiO-67-Urea/bpdc** after 24 h (67% yield) relative to **UiO-67-Urea** catalysed reaction (19%) and control experiment (14%) (Fig. 1). The enhanced catalytic activity of **UiO-67-Urea/bpdc** is consistent with the its high Brunauer–Emmett–Teller (BET) surface area (1550 m^2 g^{-1}) relative to that of **UiO-67-Urea** (390 m^2 g^{-1}) (Fig. 3).[19] Importantly, the pore size distribution indicates that the mixed-strut strategy did not engender a significant decrease in the pore diameters of **UiO-67-Urea/bpdc** (21.5 and 12 Å) in comparison to the parent **UiO-67** (23 and 11.5 Å); notably, both are significantly larger than that of the pure strut **UiO-67-Urea** (12 and 9 Å).[20] Equally notable is the persistence of **UiO-67-Urea/bpdc** crystallinity after use as a catalyst as evidenced by the absence of changes its PXRD pattern (see Fig. S3, ESI†).

For comparison, the diester derivative of the urea strut, **Me_2-Urea**, and 1,3-diphenylurea were examined as homogenous urea catalysts under our reaction conditions. **Me_2-Urea** (see Fig. 1) and 1,3-diphenylurea (see Fig. S5, ESI†) showed similarly lower product formation (49% and 50% yield, respectively). This behavior can be attributed to undesired oligomerization of homogeneous urea catalysts leading to lower catalytic activity,[14] whereas incorporation of urea sites into MOFs, such as **UiO-67-Urea/bpdc**, precludes such process through spatial constraints within the framework.

It is well known that certain Lewis acids can catalyse Henry reactions. To determine the role of the Lewis acidic $Zr_6O_4(OH)_4$ nodes within the **UiO-67-Urea/bpdc** framework during catalysis, the Henry reaction between benzaldehyde and nitromethane was performed using the non-functionalized **UiO-67** as the catalyst. Under the same reaction conditions as before, **UiO-67** showed low

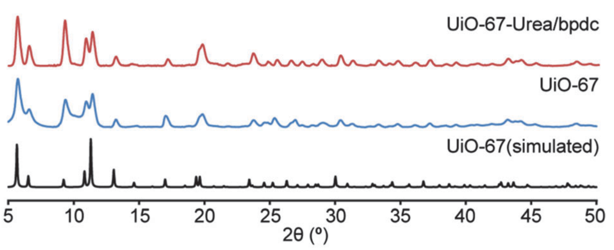


Fig. 2 PXRDs of the mixed strut **UiO-67-Urea/bpdc** and the parent **UiO-67** framework. Intensity from 8–50° is magnified 10× for clarity.

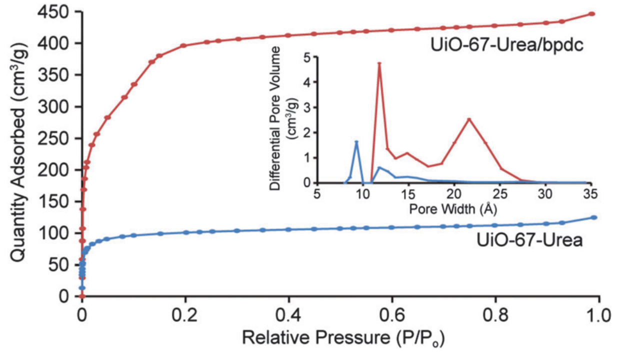


Fig. 3 N_2 isotherms of **UiO-67-Urea/bpdc** and **UiO-67-Urea** at 77 K. Inset shows pore-size distribution as determined *via* DFT (carbon slit pore N_2 77 K kernel).

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product formation (11% yield after 24 h, see Fig. S5, ESI†), which is comparable to the control experiment (14% yield). In addition, when **UiO-67** was used in conjunction with the pure strut **UiO-67-Urea** framework as catalysts (1 : 1 molar ratio), no significant synergistic improvement in catalysis was observed (17% yield, see Fig. S5, ESI†). From these **UiO-67**-based experiments, it is evident that the solvothermal synthesis of **UiO-67-Urea/bpdc** indeed results in individual crystals including both bpdc and urea struts as opposed to a physical mixture of **UiO-67** and **UiO-67-Urea** crystals. Furthermore, the urea sites in the **UiO-67-Urea/bpdc** framework likely play an essential role as HBD catalysts in the Henry reactions.

The efficacy of the mixed **UiO-67-Urea/bpdc** framework as a Henry reaction catalyst was further examined using a more challenging arylaldehyde, the electron-donating *p*-methoxybenzaldehyde. To our delight, **UiO-67-Urea/bpdc** promotes the reaction between *p*-methoxybenzaldehyde and nitromethane to form 1-(4-methoxyphenyl)-2-nitroethanol much more efficiently than **UiO-67-Urea**. While the yield achieved with **UiO-67-Urea/bpdc** is modest (48%), it is five-fold greater than obtained with **UiO-67-Urea** (10%) and *ca.* ten-fold greater (or more) than obtained in a control experiment (<5%). Overall, the catalysis results illustrate the catalytic enhancement obtainable by utilizing a heteroleptic framework, **UiO-67-Urea/bpdc**, over the homoleptic framework, **UiO-67-Urea**.

A functional, sterically demanding urea strut was successfully incorporated into a **UiO-67**-based framework through a mixed-strut *de novo* strategy with bpdc. PXRD analysis confirmed that the resulting **UiO-67-Urea/bpdc** is isostructural to the non-functionalized **UiO-67**. In addition, **UiO-67-Urea/bpdc** framework features large pores, *i.e.* similar to those of a linker-deficient version **UiO-67** framework, significantly greater than expected for defect-free **UiO-67**. The mixed strut **UiO-67-Urea/bpdc** framework is active as a HBD catalyst in promoting Henry reactions and engenders greater product formation than does its pure-strut analogue, **UiO-67-Urea**, which exhibits much smaller pore sizes. The ability to incorporate other functional, organocatalytic struts of sophisticated design through this mixed strut strategy will no doubt broaden the utility of **UiO-67** and its derivatives in catalysis and other applications.

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20 For TGA of **UiO-67-Urea/bpdc** and **UiO-67-Urea**, see Fig. S4, ESI†.

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