Supporting Information

Unexpected linker-dependent Brønsted acidity in the (Zr)UiO-66 Metal Organic Framework and application to biomass valorization

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Table S1. Experimental parameters for the synthesis of UiO-66-(NH₂)x(NO₂)_{1-x} MOFs

No.	ZrCl₄ [mg]	H ₂ BDC-NO ₂ [mg]	H ₂ BDC-NH ₂ [mg]	DMF [mL]	-NO₂ mol% in MOF from ¹ H NMR	-NH ₂ mol% in MOF from ¹ H NMR
		[mol%]	[mol%]			
1	810	0(0)	800(100)	90	0	100
2	810	250(26)	600(74)	90	27	73
3	810	450(46)	450(54)	90	51	49
4	810	650(74)	200(26)	90	75	25
5	800	900(100)	0(0)	90	100	0

Table S2. Average linker coordination number around the Zr cluster for the UiO-66-(NH₂)x(NO₂)_{1-x} MOF materials.

No.	MOF	average coordination ^a	Defect concentration ^a
1	UiO-66-NH₂	7.5	37%
2	UiO-66-(NH ₂) _{0.73} (NO ₂) _{0.27}	8	33%
3	UiO-66-(NH ₂) _{0.49} (NO ₂) _{0.51}	8.5	29%
4	UiO-66-(NH ₂) _{0.25} (NO ₂) _{0.75}	9	25%
5	UiO-66-NO ₂	9	25%

^aAverage linker coordination numbers of the Zr_6 clusters in each sample batch, and the corresponding linker deficiencies, were calculated following the method proposed in references [1] and [2], based on the analysis of the TGA curves of the solids, assuming a perfect coordination of 12. Thus, defect concentration is expressed as (12-average coordination)/12.

Table S3. Textural properties of the MOFs.

No.	MOF	BET [m²/g]	Pore volume [cm ³ /g]
1	UiO-66-NH₂	811	0.47
2	UiO-66-(NH ₂) _{0.73} (NO ₂) _{0.27}	487	0.28
3	UiO-66-(NH ₂) _{0.49} (NO ₂) _{0.51}	412	0.25
4	UiO-66-(NH ₂) _{0.25} (NO ₂) _{0.75}	411	0.24
5	UiO-66-NO ₂	422	0.25



Figure S1. ¹H NMR spectra of UiO-66-NH₂ before and after activation at 220 °C for 3 h together with their integration; solvent: DMSO-d₆; 400 MHz, MOFs were digested with HF.



Figure S2. (a) The N₂ sorption isotherm of UiO-66 measured at 77K;



Figure S3. (a) the trend of coordinated number and BET area changes with -NH₂ percentage in MOFs; (b) The pore size distribution of the MOF samples calculated by the DFT method.





Figure S4. The low-angle ($2\theta = 1-10^{\circ}$) region (reo nanoregions) of the PXRD patterns of MOFs; (b) TEM image of UiO-66-NH₂.



Figure S5. The relationship between BET area of MOFs and the yield of HMF.

Potential activity of carboxylic acid groups of the linkers

The fact that clusters are missing in these MOFs, implies that one could also consider a non-coordinating carboxylic group of the ditopic linker as a potential weakly acidic Brønsted site. Note however that BDC-NH₂ (pKa₁ = 3.95) is significantly less acidic than BDC-NO₂ (pKa₁ = 1.69) [3]. Therefore, the catalytic activity of the linkers in fructose dehydration was tested. The ¹H NMR spectra of the reaction solutions after 1 h are shown in Figure S6, together with that of the desired HMF product. Neither H₂BDC-NO₂/NH₂, ZrO₂ or DMF, show any catalytic activity in the fructose dehydration. This suggests that the catalytic activity of UiO-66 is exclusively related to the Zr oxo clusters, or possibly to the interplay between the cluster and -NH₂ sites.



Figure S6. ¹H NMR spectra of crude reaction mixtures after reaction of fructose to produce HMF using different catalysts. Solvent: DMSOd₆, 400 MHz. ¹H NMR peaks of HMF: 9.55 (S, CHO), 7.50 (d, 1H, furan-CH), 6.61 (d, 1H, furan-CH), 4.51 (d, 2H, CH₂O) ppm. In the reaction,

following amounts of catalysts were used: HCI: 8.2 μ L; ZrCl₄: 8 mg; H₂BDC-NH₂: 6.1 mg; H₂BDC-NO₂: 6.5 mg; ZrO₂:8 mg; DMF: 5 mg. The yield of HMF was determined by HPLC measurement.



Figure S7. The effect of activation temperature on the yield of HMF by fructose dehydration over UiO-66-NH₂ in 1 h. MOF was further activated at 60 °C, 100 °C, 120 °C or 150 °C, respectively. Solvent: DMSO-d_{6.} The reaction temperature: 100 °C.



Figure S8. Gas chromatograms of α -pinene oxide isomerization to produce campholenic aldehyde catalyzed by different catalysts.



Figure S9. The comparison of the yield of HMF over different catalysts: UiO-66-NH₂, UiO-66 and UiO-66-NO₂.



Figure S10. ¹H MAS (black), ²H MAS (blue) and T₂-filtered ²H MAS (red) NMR spectra of D₂O exchanged UiO-66-NH₂. Since most of water molecules are D₂O, the signals in the ¹H MAS NMR spectrum are quite narrow and the signal of H₂O is relatively weak. In the ²H MAS NMR spectrum peak maximum is at about 4.9 ppm, because the majority of the signal comes from D₂O molecules. In the T₂-filtered ²H MAS NMR spectrum the quickly relaxing signal of D₂O is suppressed. What remains is a strong signal at 6.9 ppm, which belongs to hydrogen bonded ND₂ (or NHD), and a weak signal at 1.5 ppm, which presumably belongs to framework OD groups.

Table S4. ¹³ C and ¹ H chemical shift prediction (ChemDraw NMR predictor) for H ₂ BDC-NH ₂ and H ₂ BDC-NH ₂	3 ⁺ ,
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			¹³ C ch	emical shift pre	diction			
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	C1	C2	C3	C4	C5	C6	C7	C8
UiO-66-NH ₂	131	120	134	114	151	116	169	166
UiO-66-NH ₃ ⁺	130	130	135	130	139	135	169	169
			¹ H che	emical shift pre	diction		·	
	H(1)	H(2)	H(4)	H(NH2)	H ₂ N	4	+H3N	1
UiO-66-NH ₂	7.9	7.1	7.5	6.3	ноос6	ЗСООН	HOOC6)СООН

8.0



Figure S11. Water sorption isotherm of UiO-66-NH₂ and UiO-66-NO₂ measured at 298 K.



Figure S12. The N₂ sorption isotherm of UiO-66-NH₂ measured at 77K before and after reuse test.



Figure S13. The PXRD patterns of UiO-66-NH₂ at different conditions, after activation at 150oC overnight; dried at 220°C for 3h; and after the 4th run reuse cycle.

Reference

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[2] L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M.H. Nilsen, S. Jakobsen, K.P. Lillerud, C. Lamberti, Chem. Mater. 23 (2011) 1700–1718.

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