Electronic Supplementary Information

Engineering effective structural defects of metal-organic frameworks to enhance their catalytic performances

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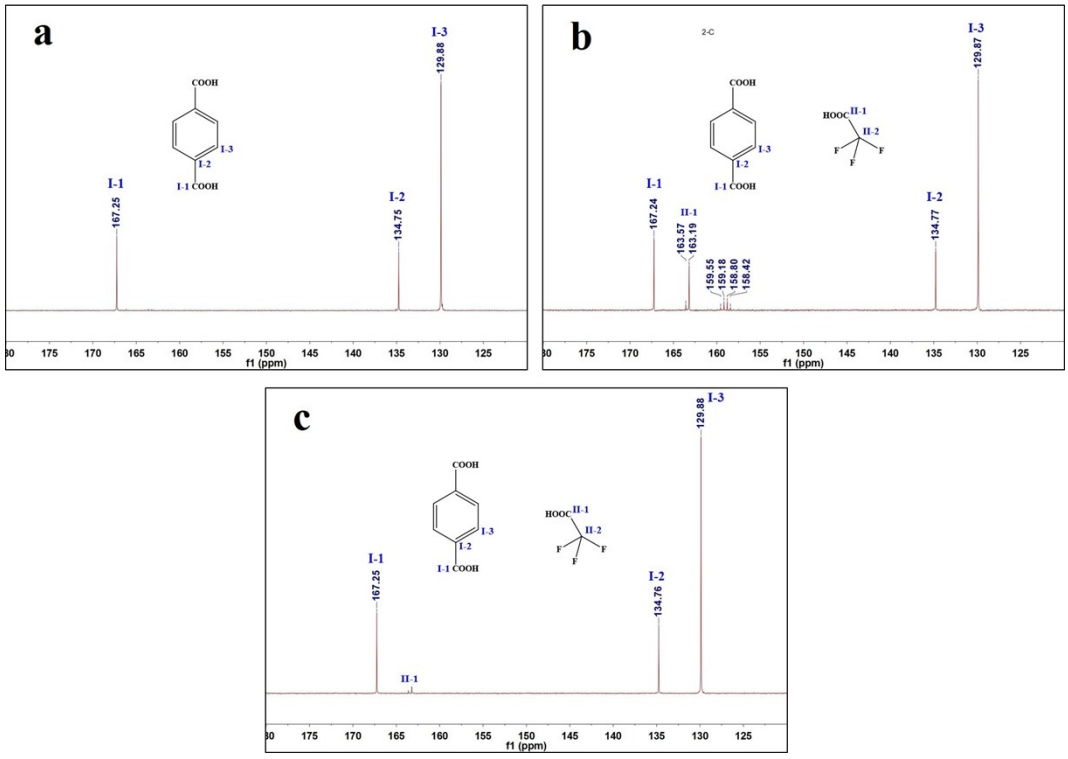

Fig. S1 ^{13}C NMR spectra of acid-digested (a) UiO-66-DF, (b) UiO-66(1d), and (c) UiO-66(1d)-H2 samples. Note: 100 mg of UiO-66 sample was digested by a mixture of 47 wt.% HF (80 μL) and 1 mL of *d*6-DMSO. After centrifugation, the upper clear solution was transferred into a NMR tube and analyzed on a Bruker 600 MHz spectrometer (Ultrashield 600 PLUS).

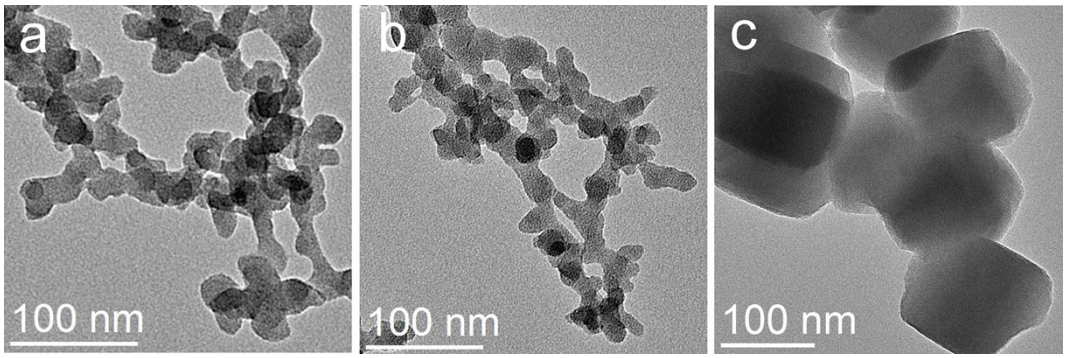

Fig. S2 Low-magnitude transmission electron microscopy (TEM) images of (a) UiO-66(1d), (b) UiO-66(3d), and (c) UiO-66-DF.

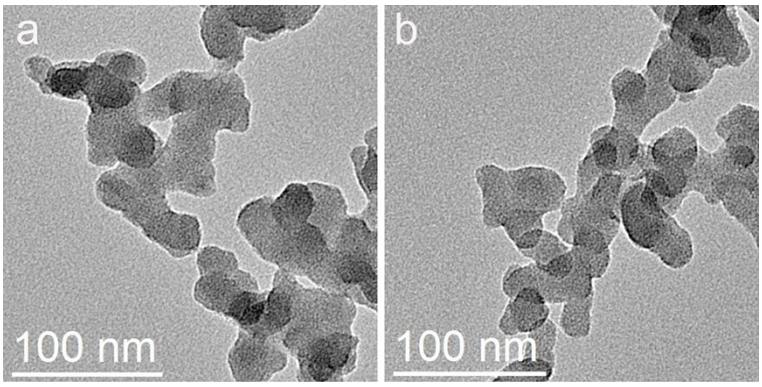

Fig. S3 Low-magnitude TEM images of (a) UiO-66(1d)-H1 and (b) UiO-66(1d)-H2.

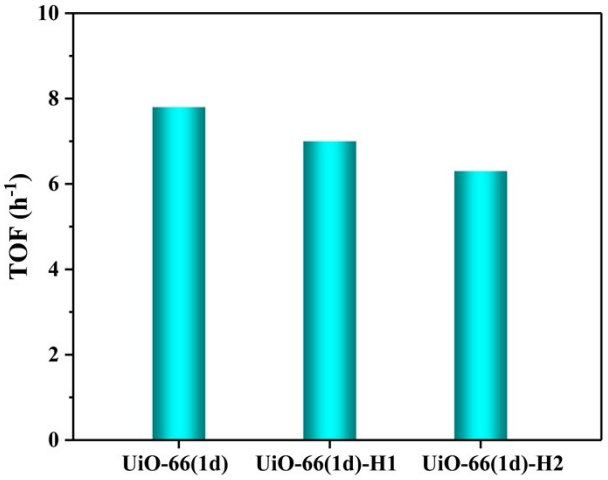

Fig. S4 Turnover frequency (TOF) for UiO-66(1d), UiO-66(1d)-H1, and UiO-66(1d)-H2, where TOF was calculated based on the number of converted cyclohexanone per open metal site per reaction time and the number of open metal site was considered equal to the amount of TFA modulator in defective UiO-66.

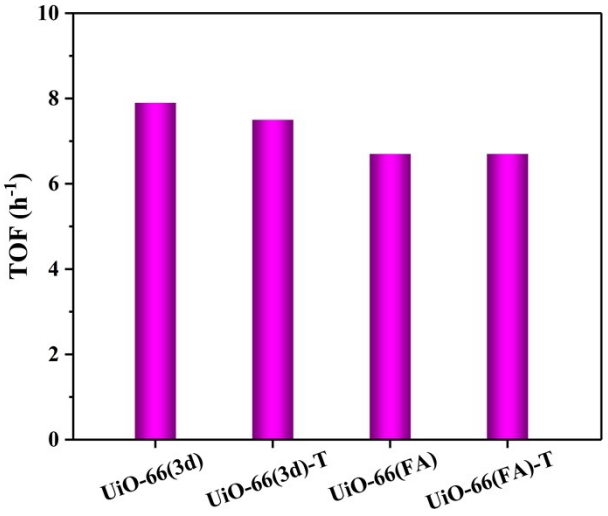

Fig. S5 Turnover frequency (TOF) for UiO-66(3d), UiO-66(3d)-T, UiO-66(FA), and UiO-66(FA)-T, where TOF was calculated based on the number of converted cyclohexanone per open metal site per reaction time and the number of open metal site was considered equal to the total amount of modulator (TFA and FA) in defective UiO-66.

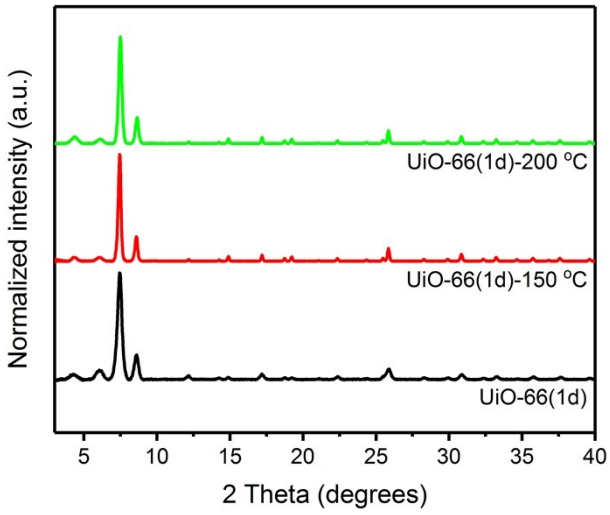

Fig. S6 PXRD patterns of UiO-66(1d), UiO-66(1d)-150°C, and UiO-66(1d)-200°C.

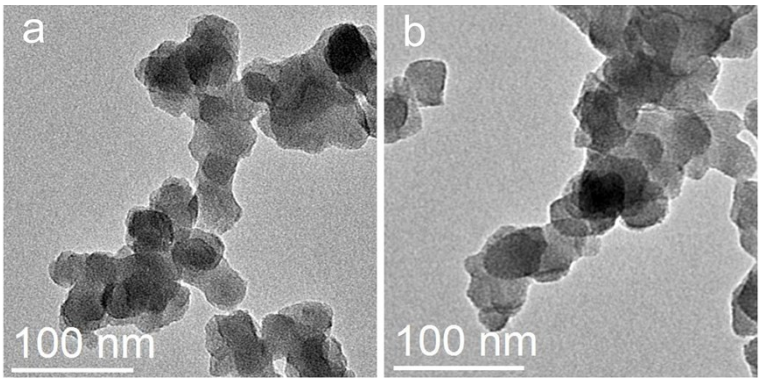

Fig. S7 Low-magnitude TEM images of (a) UiO-66(1d)-150°C and (b) UiO-66(1d)-200°C.

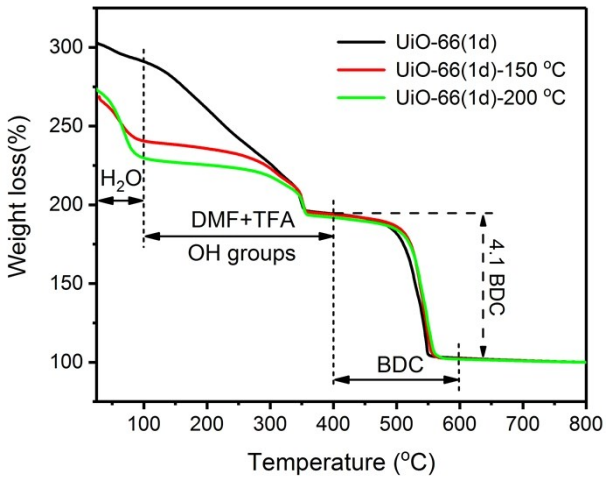

Fig. S8 TGA curves of UiO-66(1d), UiO-66(1d)-150°C, and UiO-66(1d)-200°C.

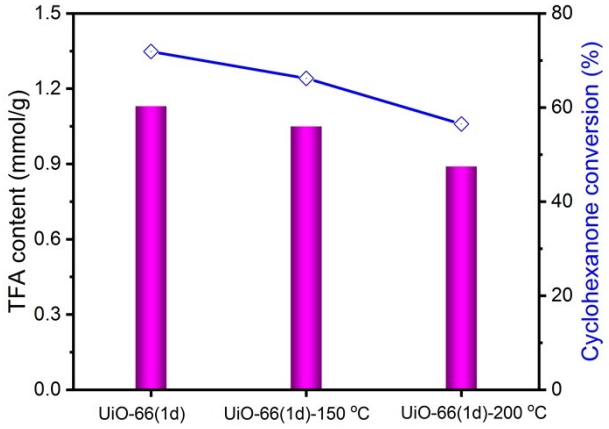

Fig. S9 Catalytic performances of UiO-66(1d), UiO-66(1d)-150°C, and UiO-66(1d)-200°C in cyclohexanone conversion along with their TFA contents after digestion. Reaction conditions: 180 mg of cyclohexanone, 315 mg of dodecane as internal standard, 550 mg of isopropanol, 15 mg of solid catalyst, 10 mL of toluene, 105 °C for 10 h.

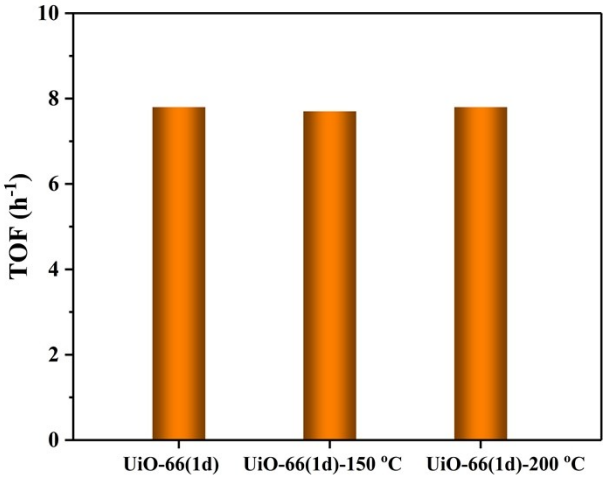

Fig. S10 Turnover frequency (TOF) for parent and heated UiO-66 catalysts, where TOF was calculated based on the number of converted cyclohexanone per open metal site per reaction time and the number of open metal site was considered equal to the amount of TFA modulator in defective UiO-66.

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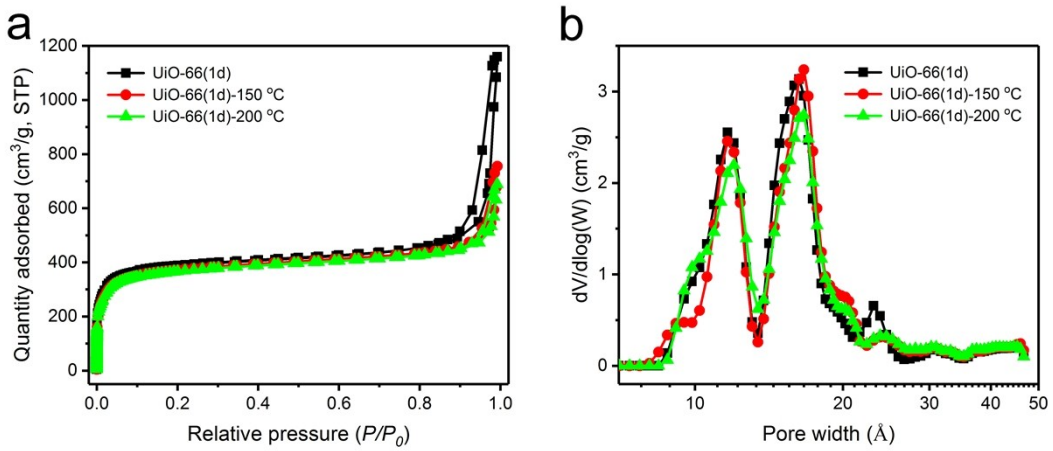

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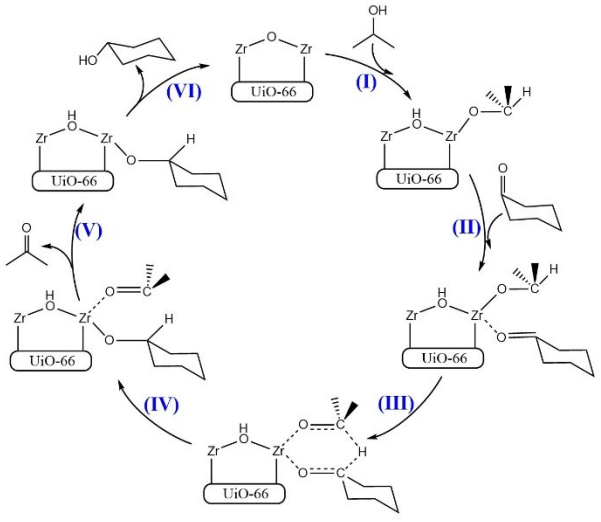
3 **Fig. S11** (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of UiO-66(1d), UiO-
4 66(1d)-150°C, and UiO-66(1d)-200°C.



Scheme S1 Proposed reaction pathway of cyclohexanone conversion over effective open metal sites in defective UiO-66 catalyst. Note: The deprotonized BDC linker and TFA modulator coordinated to Zr metal site was omitted and activation of IPA and cyclohexanone was assumed to proceed on the same open metal site.

Table S1 BET surface areas and pore volumes of various UiO-66 samples derived from the isotherms.

Entry	Samples	BET surface area (m^2/g)[a]	Total pore volume (cm^3/g)[b]
1	UiO-66(1d)	1518	0.71
2	UiO-66(3d)	1694	0.74
3	UiO-66-DF	1025	0.39
4	UiO-66(1d)-H1	981	0.62
5	UiO-66(1d)-H2	953	0.47
6	UiO-66(1d)-150^{o}C	1451	0.67
7	UiO-66(1d)-200^{o}C	1422	0.66

[a] Surface area calculated in the P/P_0 range of 0.005 to 0.05. [b] Total pore volume collected at P/P_0 = 0.8.

Table S2 Controlling nucleation of UiO-66 in various synthetic conditions.

Entry	Solvent	Temperature (oC)	Crystallinity	UiO-66
1	DMF	80	Yes	Yes
2	DMF/H_2O (5:5, V/V)	80	Yes	Yes with impurity
3	DMF/H_2O (5:5, V/V)	60	Yes	Yes with impurity
4	DMF/H_2O (2:8)	80	Yes	Yes with impurity
5	DMF/H_2O (0.5/9.5)	80	No	-

Table S3 Conversion of cyclohexanone in the presence of other catalysts.[a]

Entry	Catalyst	TFA content (mmol/g)[b]	Conversion (%)
1	TFA	-	4.8
2	BDC	-	2.6
3	UiO-66-DF	-	4.0
4	UiO-66(1d)	1.13	71.9
5	UiO-66(1d)-H2	0.35	17.9
6	UiO-66-DF+TFA[c]	-	5.1
7	UiO-66-DF+TFA[d]	-	9.8
8	UiO-66(1d)-H2+TFA[d]	-	18.3
9	UiO-66-DF-T[e]	0.11	13.9
10	UiO-66(1d)-H2-T[e]	0.42	30.6

[a] Reaction conditions: 180 mg of cyclohexanone, 315 mg of dodecane as internal standard, 550 mg of isopropanol, 15 mg of solid catalyst, 10 mL of toluene, 105 ^{o}C for 10 h. [b] Measured by HPLC after digestion of solid catalyst. [c] 1.93 mg of TFA, which was equal to that in UiO-66(1d), was added as co-catalyst. [d] 19.3 mg of TFA was added as co-catalyst. [e] Solid catalyst was treated with TFA thrice via PSE method.