Supporting information

Title: Impact of partial linker functionalization on the catalytic properties of MTV-UiO-66 for biofuel production

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1. Materials

The chemicals used in this study were commercially provided and used directly in experiments without further purification. Terephthalic acid ($C_6H_4(CO_2H)_2$, 99%), *1,2,4,5*-benzenetetracarboxylic acid ($C_{10}H_6O_8$, 96%), 2,5-Dihydroxyterephthalic acid ($C_8H_7NO_4$, 99%), sodium bicarbonate ($NaHCO_3$, 99%), deuterium oxide (D_2O, 99% atom D), and formic acid (CH_2O_2, 98-100%) were purchased from Sigma Aldrich. Zirconium chloride ($ZnCl_4$, 98%), *1*-butanol ($C_4H_{10}O$, 99%, extra pure), *n*-butyric acid ($C_4H_{18}O_2$, 99%, extra pure), butyl butyrate (98%, Acros Organics), heptane (C_7H_{16}, HPLC grade) and *1*-octanol ($C_8H_{18}O$, 99%, pure), were purchased from Acros Organics. *N*,*N*-dimethylformamide (DMF, Analytical reagent grade), and dichloromethane (DCM, Analytical reagent grade) were purchased from Fisher Scientific.

Table S1: The MOF catalysts synthesis procedure condition details

Sample name	**Molar equivalents (with respect to $ZrCl_4$)**					
	$ZrCl_4$	DMF	Terephthalic Acid	1,2,4,5 Benzenetetra-carboxylic Acid	2,5-Dihydroxytere phthalic acid	Formic Acid
UiO-66	1	350	1	0	0	200
UiO-66(3A:1B)	1	350	0.75	0.25	0	200
UiO-66(1A:1B)	1	350	0.5	0.5	0	200
UiO-66(1A:3B)	1	350	0.25	0.75	0	200
UiO-66$(COOH)_2$	1	350	0	1	0	200
UiO-66(3A:1C)	1	350	0.75	0	0.25	200
UiO-66(1A:1C)	1	350	0.5	0	0.5	200
UiO-66(1A:3C)	1	350	0.25	0	0.75	200

UiO-66(OH)$_2$	1	350	0	0	1	200

2. Powder X-Ray Diffraction (PXRD)

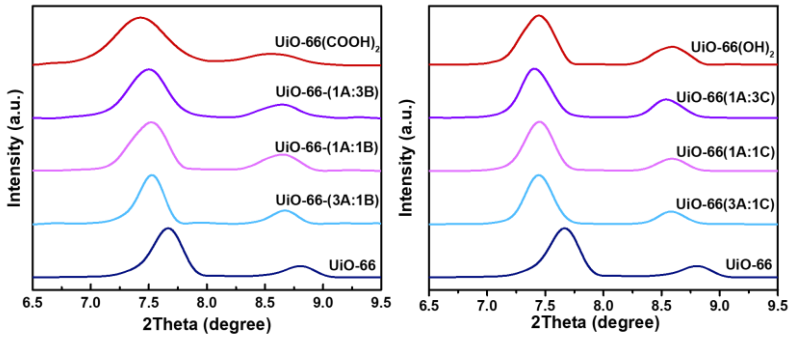

Figure S1: A narrow 2theta range of the PXRD patterns of the MTV-MOFs showing the shift in peaks towards a lower angle with the increase in incorporation of the functionalized linkers

3. ^{1}H-NMR results

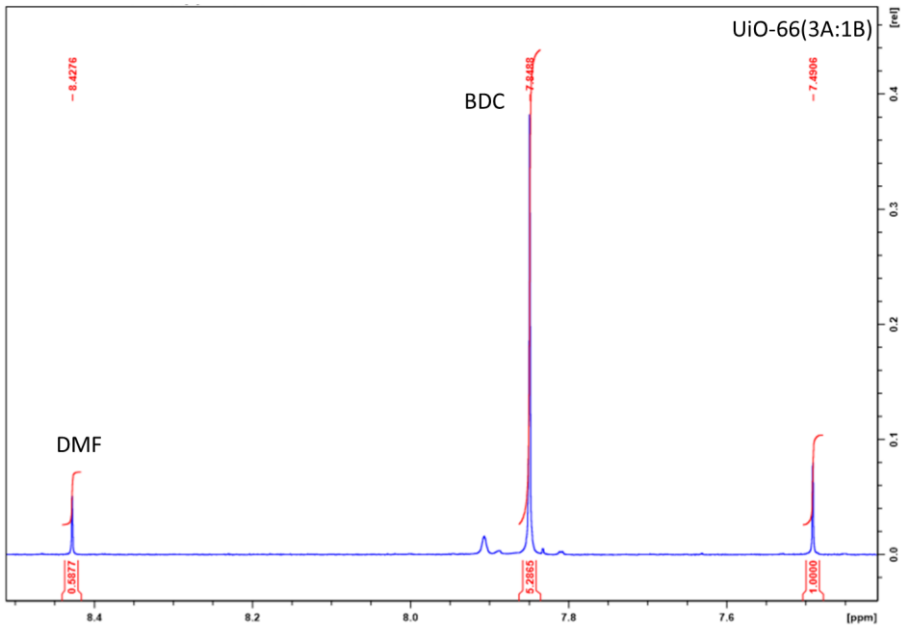

Figure 2: ^{1}H-NMR spectra of UiO-66(3A:1B)

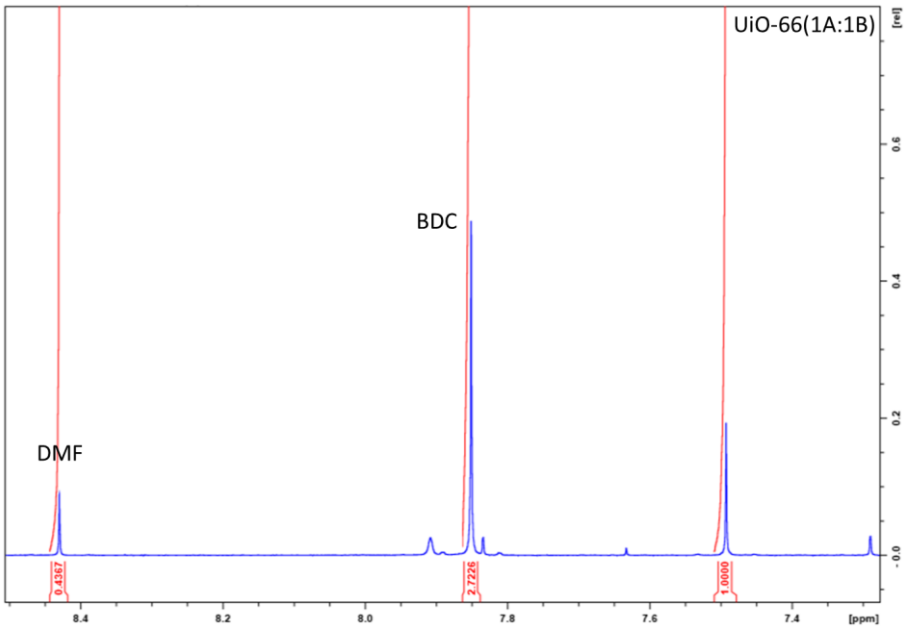

Figure 3: ^{1}H-NMR spectra of UiO-66(1A:1B)

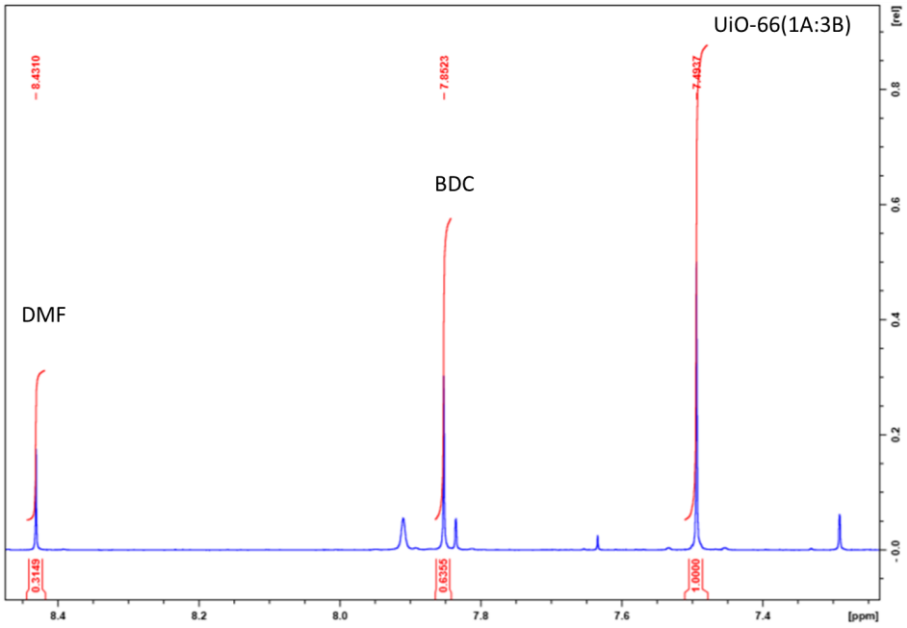

Figure 4: 1H-NMR spectra of UiO-66(1A:3B)

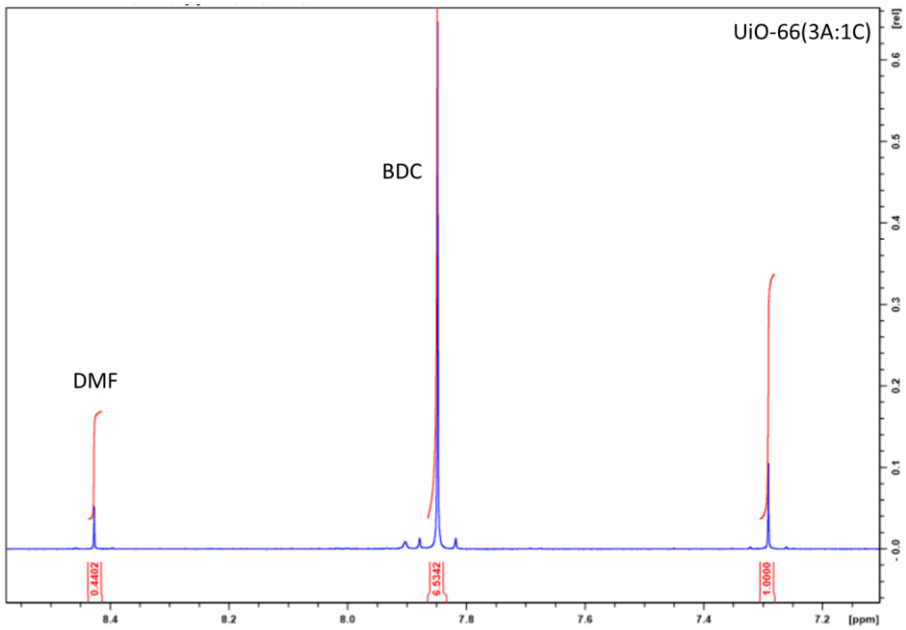

Figure 5: ^{1}H-NMR spectra of UiO-66(3A:1C)

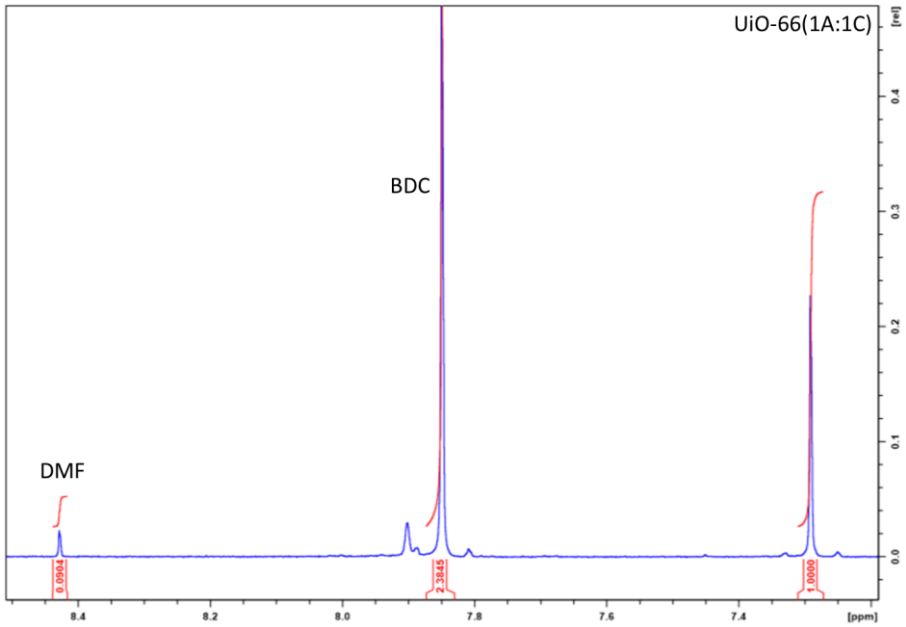

Figure 6: ^{1}H-NMR spectra of UiO-66(1A:1C)

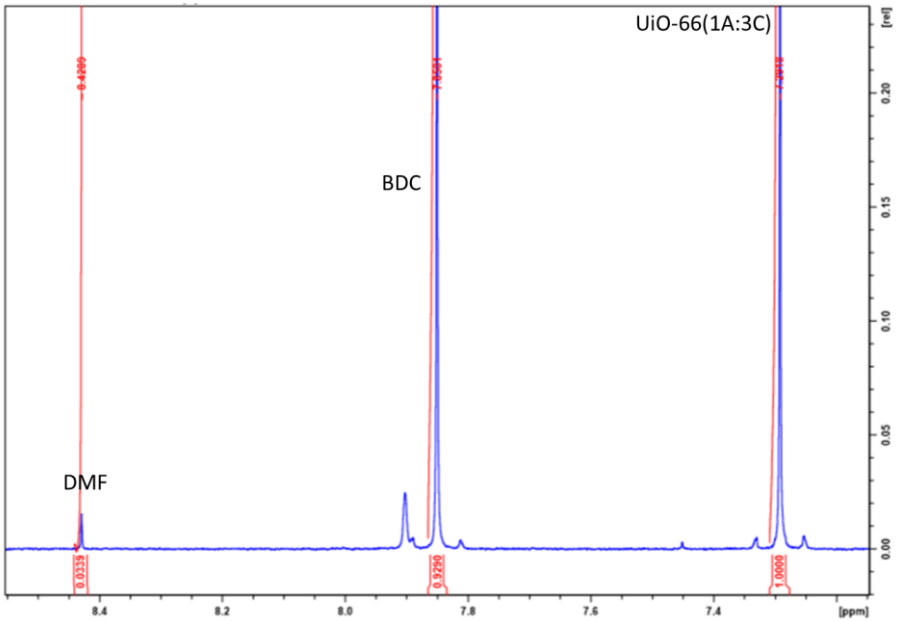

Figure 7: ^{1}H-NMR spectra of UiO-66(1A:3C)

4. Suggested Reaction Mechanism

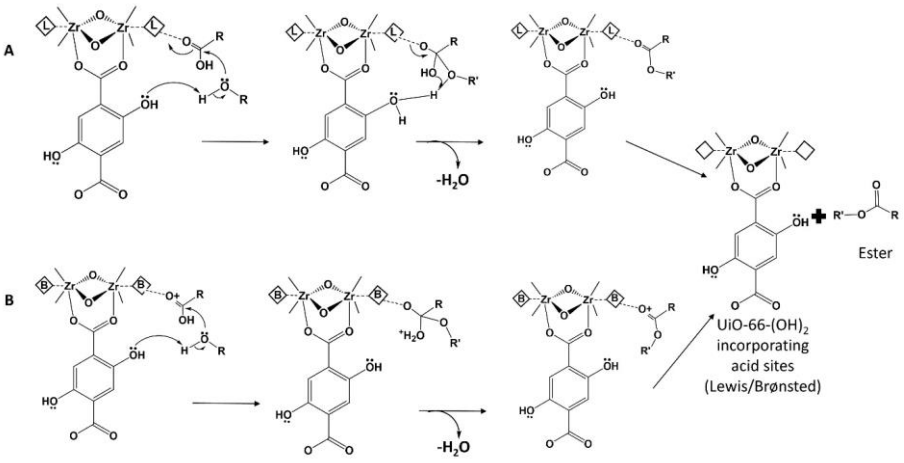

Figure S8: Suggested reaction mechanism for MTV-UiO-66(OH)$_2$ members. On the Zr cluster, L refers to Lewis acid, while B refers to Brønsted acid.

5. MOFs' Recycling & Stability

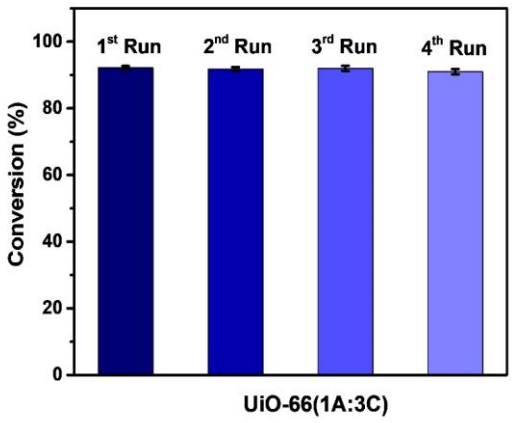

Figure S9: The conversion to butyl butyrate following 24 hours reaction using fresh and recycled UiO-66(1A:3C) as a catalyst over 4 reaction cycles

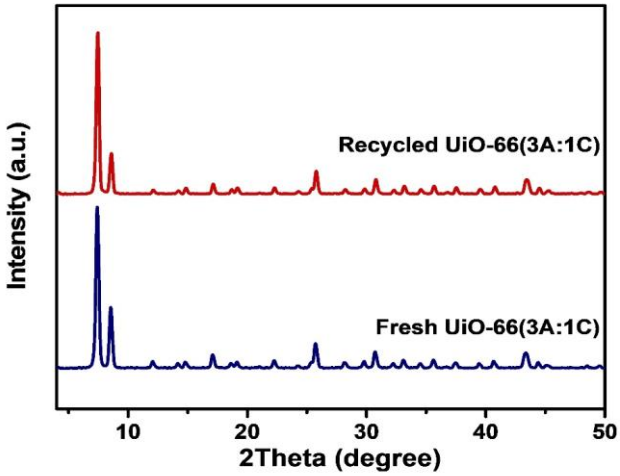

Figure 10: The PXRD patterns of fresh and recycled UiO-66(1A:3C) following 4 reaction cycles

6. Regression model supplementary data

Table S2: parameters used to build the regression model

MOF	Defects Number	Surface Area	Catalyst Loading	% T	%A	% C	Conversion	Reference
UiO-66	1.39	1052	5	1	0	0	83.4	[1]
UiO-66(COOH)2	1.32	284	5	0	0	1	90.2	[1]
UiO-66(NH)2	1.72	801	5	0	1	0	74.7	[1]
UiO-66	1.39	1052	2	1	0	0	75.4	[1]
UiO-66(COOH)2	1.32	284	2	0	0	1	81.5	[1]
UiO-66(NH)2	1.72	801	2	0	1	0	67.7	[1]
UiO-66	1.39	1052	1	1	0	0	69.9	[1]
UiO-66(COOH)2	1.32	284	1	0	0	1	75.4	[1]
UiO-66(NH)2	1.72	801	1	0	1	0	60.15	[1]
TB	1.36	1049	2	1	0	0	57.2	[2]
T1AA	1.5	1490	2	1	0	0	70.4	[2]
T2AA	1.53	1593	2	1	0	0	78.1	[2]
T1FA	1.72	1695	2	1	0	0	83.6	[2]
T2FA	1.86	1813	2	1	0	0	89.1	[2]
CB	0.88	51	2	0	0	1	63.3	[2]
C1AA	1.38	268	2	0	0	1	77.4	[2]
C2AA	1.44	376	2	0	0	1	81.5	[2]
C1FA	1.9	517	2	0	0	1	88.2	[2]
C2FA	1.93	522	2	0	0	1	91.5	[2]
AB	1.5	1016	2	0	1	0	64.2	[2]
A1AA	1.67	1294	2	0	1	0	69.6	[2]
A2AA	1.73	1434	2	0	1	0	77.2	[2]
A1FA	1.87	1570	2	0	1	0	80.3	[2]
A2FA	2.02	1723	2	0	1	0	84.7	[2]
T2FA (1%)	1.87	1812	1	1	0	0	75	This study
C2FA(1%)	1.93	522	1	0	0	1	76.4	This study
UiO-66(OH)2	1.51	602	1	0	0	0	80.4	This study
UiO-66(3A:1B)	1.83	773	1	0.84	0	0.16	70.3	This study
UiO-66(1A:1B)	2.14	657	1	0.73	0	0.27	85.3	This study
UiO-66(1A:3B)	1.98	609	1	0.39	0	0.61	88.8	This study
UiO-66(3A:1C)	1.33	1290	1	0.87	0	0	72.5	This study
UiO-66(1A:1C)	1.73	947	1	0.74	0	0	86.5	This study
UiO-66(1A:3C)	1.9	761	1	0.48	0	0	82.2	This study

Table S3: Normalazied parameters used to build the regression model

MOF	Defects Number	Surface Area	Catalyst Loading	% T	%A	% C	Conversion	Reference
UiO-66	0.40	0.57	1.00	1.00	0.00	0.00	83.4	[1]
UiO-66(COOH)$_2$	0.35	0.13	1.00	0.00	0.00	1.00	90.2	[1]
UiO-66(NH)$_2$	0.67	0.43	1.00	0.00	1.00	0.00	74.7	[1]
UiO-66	0.40	0.57	0.25	1.00	0.00	0.00	75.4	[1]
UiO-66(COOH)$_2$	0.35	0.13	0.25	0.00	0.00	1.00	81.5	[1]
UiO-66(NH)$_2$	0.67	0.43	0.25	0.00	1.00	0.00	67.7	[1]
UiO-66	0.40	0.57	0.00	1.00	0.00	0.00	69.9	[1]
UiO-66(COOH)$_2$	0.35	0.13	0.00	0.00	0.00	1.00	75.4	[1]
UiO-66(NH)$_2$	0.67	0.43	0.00	0.00	1.00	0.00	60.15	[1]
TB	0.38	0.57	0.25	1.00	0.00	0.00	57.2	[2]
T1AA	0.49	0.82	0.25	1.00	0.00	0.00	70.4	[2]
T2AA	0.52	0.88	0.25	1.00	0.00	0.00	78.1	[2]
T1FA	0.67	0.93	0.25	1.00	0.00	0.00	83.6	[2]
T2FA	0.78	1.00	0.25	1.00	0.00	0.00	89.1	[2]
CB	0.00	0.00	0.25	0.00	0.00	1.00	63.3	[2]
C1AA	0.40	0.12	0.25	0.00	0.00	1.00	77.4	[2]
C2AA	0.44	0.18	0.25	0.00	0.00	1.00	81.5	[2]
C1FA	0.81	0.26	0.25	0.00	0.00	1.00	88.2	[2]
C2FA	0.83	0.27	0.25	0.00	0.00	1.00	91.5	[2]
AB	0.49	0.55	0.25	0.00	1.00	0.00	64.2	[2]
A1AA	0.63	0.71	0.25	0.00	1.00	0.00	69.6	[2]
A2AA	0.67	0.78	0.25	0.00	1.00	0.00	77.2	[2]
A1FA	0.79	0.86	0.25	0.00	1.00	0.00	80.3	[2]
A2FA	0.90	0.95	0.25	0.00	1.00	0.00	84.7	[2]
T2FA (1%)	0.79	1.00	0.00	1.00	0.00	0.00	75	This study
C2FA(1%)	0.83	0.27	0.00	0.00	0.00	1.00	76.4	This study
UiO-66(OH)$_2$	0.50	0.31	0.00	0.00	0.00	0.00	80.4	This study
UiO-66(3A:1B)	0.75	0.41	0.00	0.84	0.00	0.16	70.3	This study
UiO-66(1A:1B)	1.00	0.34	0.00	0.73	0.00	0.27	85.3	This study
UiO-66(1A:3B)	0.87	0.32	0.00	0.39	0.00	0.61	88.8	This study
UiO-66(3A:1C)	0.36	0.70	0.00	0.87	0.00	0.00	72.5	This study
UiO-66(1A:1C)	0.67	0.51	0.00	0.74	0.00	0.00	86.5	This study
UiO-66(1A:3C)	0.81	0.40	0.00	0.48	0.00	0.00	82.2	This study

Table S4: The parameters suggested for the model along with their corresponding regression coefficients and p-values

Independent Variables	Coefficients	P-value
Cst	39.95	1.82×10^{-8}
% A	6.87	1.10×10^{-2}
% B	21.94	3.90×10^{-6}

%C	25.25	1.18×10^{-4}
DN	25.07	1.57×10^{-5}
SA	16.19	1.12×10^{-2}
CL	15.38	2.75×10^{-4}

Table S5: The regression model statistics summary

Model Evaluation Parameter	Value
Multiple R	0.850
R^2	0.723
Adjusted R^2	0.659
Standard Error	5.191
Observations	33
Significance F	3.286×10^{-6}

Table S6: Model-predicted vs. experimentally obtained conversion to butyl butyrate and the average error between the two for the set of experiments done

Observation	MOF	$Conv_{mod}$	$Conv_{exp}$	*Residuals*
1	UiO-66	81.6	83.4	1.84
2	UiO-66$(COOH)_2$	88.2	90.2	2.03
3	UiO-66$(NH)_2$	78.9	74.7	-4.24
4	UiO-66	70.0	75.4	5.39
5	UiO-66$(COOH)_2$	76.6	81.5	4.87
6	UiO-66$(NH)_2$	67.4	67.7	0.30
7	UiO-66	66.2	69.9	3.73
8	UiO-66$(COOH)_2$	72.8	75.4	2.62
9	UiO-66$(NH)_2$	63.6	60.15	-3.41
10	TB	69.4	57	-12.19
11	T1AA	76.2	70.4	-5.83
12	T2AA	77.8	78.1	0.33
13	T1FA	82.5	83.6	1.11
14	T2FA	86.4	89.1	2.74
15	CB	65.7	63.3	-2.43
16	C1AA	77.7	77.4	-0.28
17	C2AA	79.9	81.5	1.64
18	C1FA	90.3	88.2	-2.11
19	C2FA	91.0	91.5	0.55
20	AB	65.0	64.2	-0.80
21	A1AA	70.9	69.6	-1.34
22	A2AA	73.4	77.2	3.78

23	A1FA	77.4	80.3	2.85
24	A2FA	81.8	84.7	2.86
25	T2FA (1%)	82.7	75	-7.70
26	C2FA (1%)	87.1	76.4	-10.71
27	UiO-66$(OH)_2$	82.8	80.4	-2.40
28	UiO-66(3A:1B)	74.8	70.3	-4.47
29	UiO-66(1A:1B)	81.53	85.3	3.77
30	UiO-66(1A:3B)	83.03	88.8	5.77
31	UiO-66(3A:1C)	69.55	72.5	2.95
32	UiO-66(1A:1C)	76.75	86.5	9.75
33	UiO-66(1A:3C)	83.20	82.2	-1.00

Conflict of interest

The authors declare no conflict of interest

References

[1] A. Jrad, B.J. Abu Tarboush, M. Hmadeh, M. Ahmad, APCATA Applied Catalysis A, General 570 (2019) 31.
[2] A. Jrad, M. Hmadeh, B.J. Abu Tarboush, G. Awada, M. Ahmad, Chemical Engineering Journal 382 (2020) 122793.