Supporting Information for Publication

Synergistic Ramification of Synthesis Criterion and Amine Functionalization of UiO-66-NH_2 MOFs for the Catalytic Degradation of Nerve Agent Simulant: Methyl-paraoxon

Selva Balasubramanian [a,b], Arockia Jayalatha Kulandaisamy [b] and John Bosco Balaguru Rayappan [a,b]*

[a]Centre for Nanotechnology & Advanced Biomaterials (CeNTAB), SASTRA Deemed University, Thanjavur, Tamil Nadu - 613 401, India

[b]School of Electrical & Electronics Engineering (SEEE), SASTRA Deemed University Thanjavur, Tamil Nadu - 613 401, India

---

*Corresponding Author

John Bosco Balaguru Rayappan, Ph.D.

Centre for Nanotechnology & Advanced Biomaterials (CeNTAB) &

School of Electrical & Electronics Engineering

SASTRA Deemed University

Thanjavur – 613 401, Tamil Nadu, India

Phone: +91 4362 350 009; Ext: 2255

Fax: +91 4362 264 120

Email: rjbosco@ece.sastra.edu

Table S1. Synthesis parameters of UiO-66-NH_2 MOFs

S. No.	Sample	$ZrCl_4$ (mmol)	$H_2BDC\text{-}NH_2$ (mmol)	Modulator (Equivalence)	Synthesis Temperature (°C)	Duration (h)
1.	UN1	6 mmol	8.4 mmol	8**	80	24
2.	UN2	6 mmol	8.4 mmol	8***	80	24
3.	UN3	6 mmol	8.4 mmol	8*	80	24
4.	UN4	6 mmol	8.4 mmol	8*	100	24
5.	UN5	6 mmol	8.4 mmol	8*	120	24
6.	UN6	6 mmol	8.4 mmol	4*	80	24
7.	UN7	6 mmol	8.4 mmol	12*	80	24
8.	UN8	6 mmol	6.3 H_2BDC + 2.1 $H_2BDC\text{-}NH_2$#	6*	80	24
9.	UN9	6 mmol	4.2 H_2BDC + 4.2 $H_2BDC\text{-}NH_2$#	6*	80	24
10.	UN10	6 mmol	2.1 H_2BDC + 6.3 $H_2BDC\text{-}NH_2$#	6*	80	24

* HCl, ** Acetic acid, *** Formic acid, # Mixed-ligand approach (H_2BDC + $H_2BDC\text{-}NH_2$)

Section S1: PXRD studies

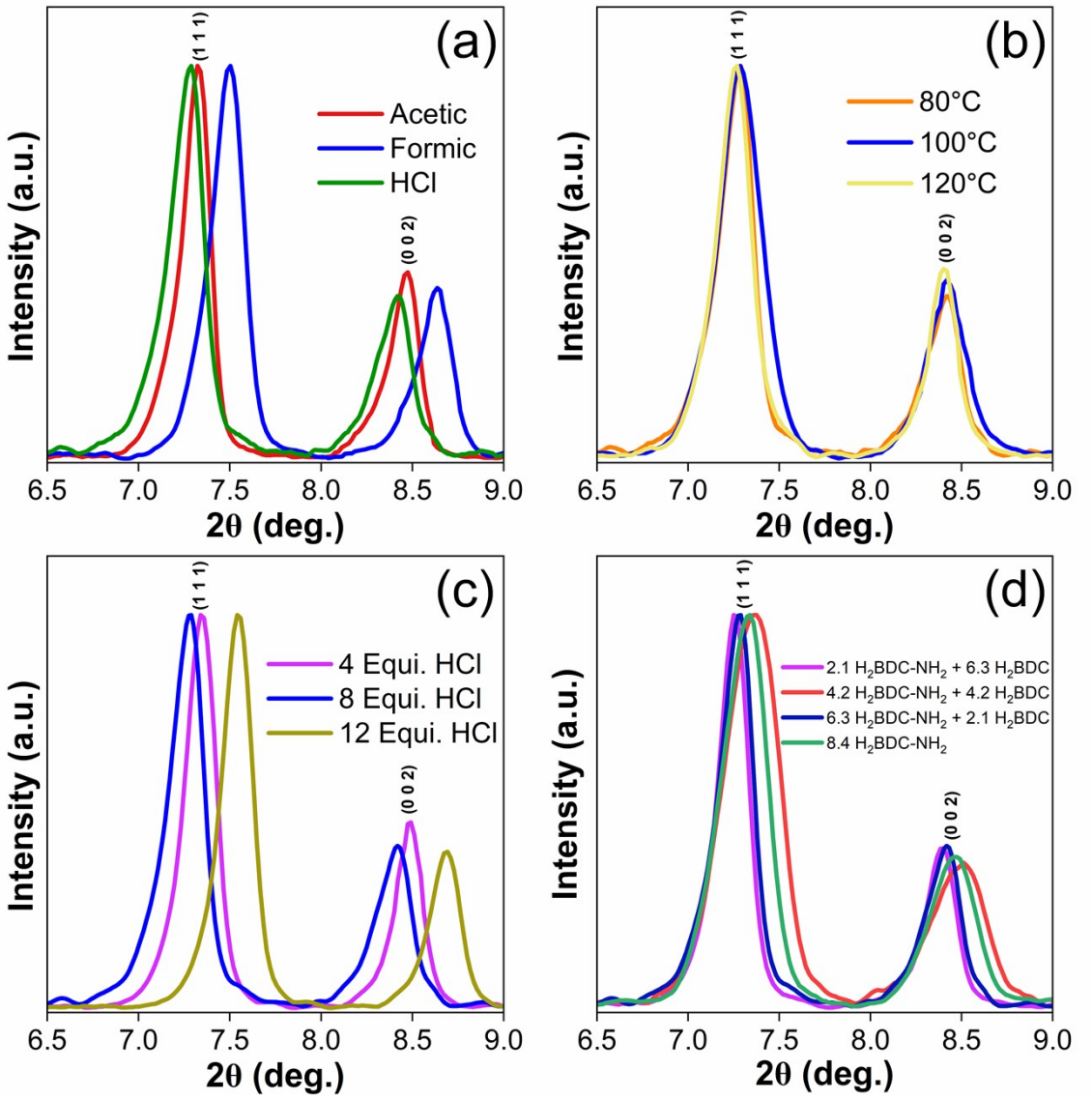

Fig. S1. Changes in the PXRD pattern of UiO-66-NH_2 samples with respect to its synthesis condition: (a) modulators, (b) synthesis temperature, (c) HCl equivalence, and (d) ligand composition.

Table S2. Calculated lattice parameter values from PXRD analysis.

Sample	Crystallite size (nm)	Lattice constant "a" (Å)	Microstrain (ε)	Dislocation density (10^{-4})
UN1	41	20.78	0.70	6.20
UN2	40	20.56	0.71	6.55
UN3	41	20.85	0.70	5.97
UN4	39	20.73	0.73	6.60
UN5	41	20.78	0.71	6.23
UN6	39	20.83	0.74	6.61
UN7	36	20.76	0.81	7.68
UN8	42	20.71	0.68	5.72
UN9	39	20.84	0.75	6.70
UN10	39	20.88	0.75	6.80

Section S2: Morphological studies

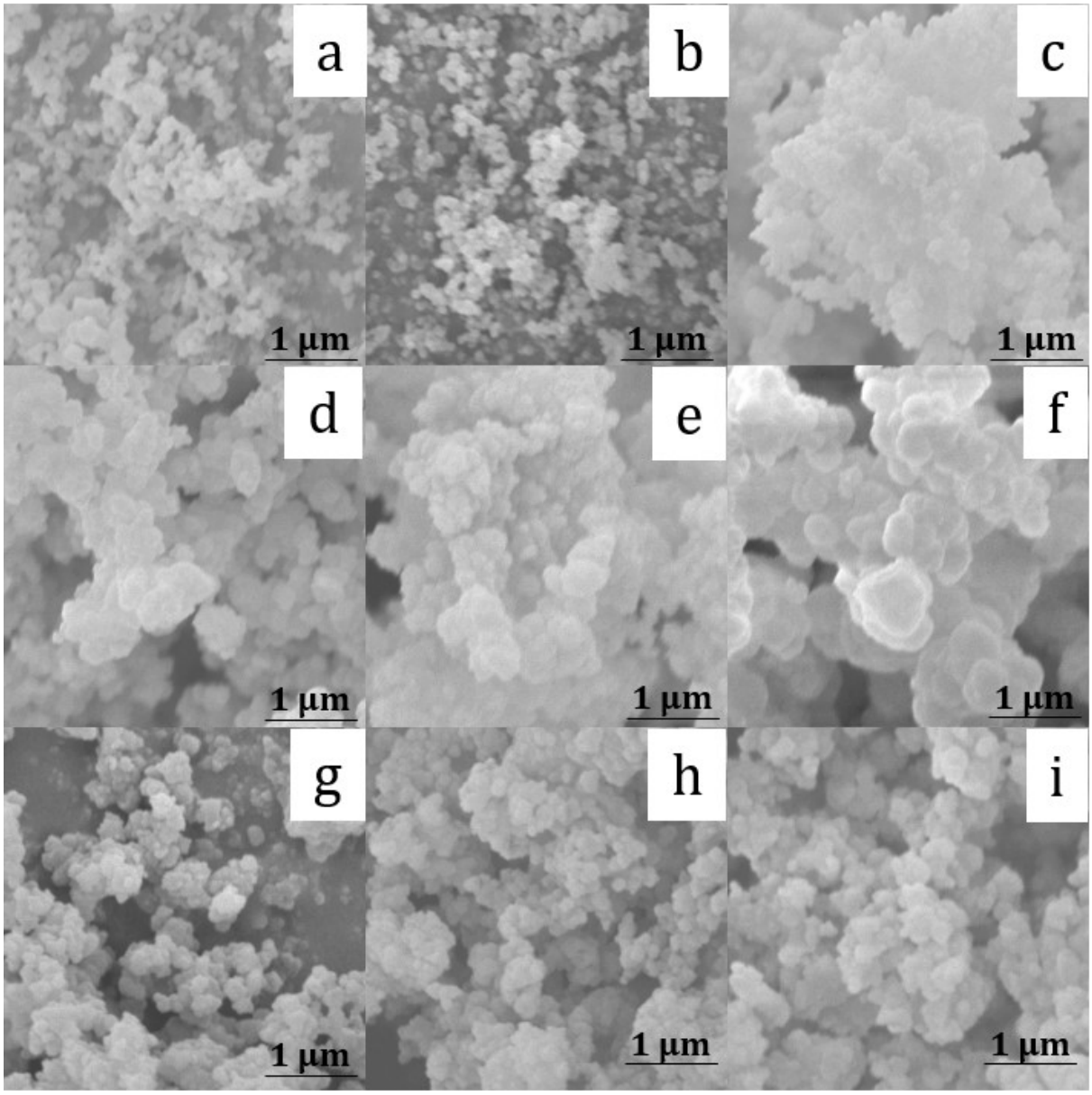

Fig. S2. SEM pictures of UiO-66-NH_2 samples with respect to their synthesis condition: (a) AA modulation, (b) FA modulation, (c) 4 equi. HCl, (d) 12 equi. HCl, (e) 100°C synthesis temperature, (f) 120°C synthesis temperature, (g) 2.1 mmol NH_2-H_2BDC (25% amine), (h) 4.2 mmol NH_2-H_2BDC (50% amine), and (i) 6.3 mmol NH_2-H_2BDC (75% amine).

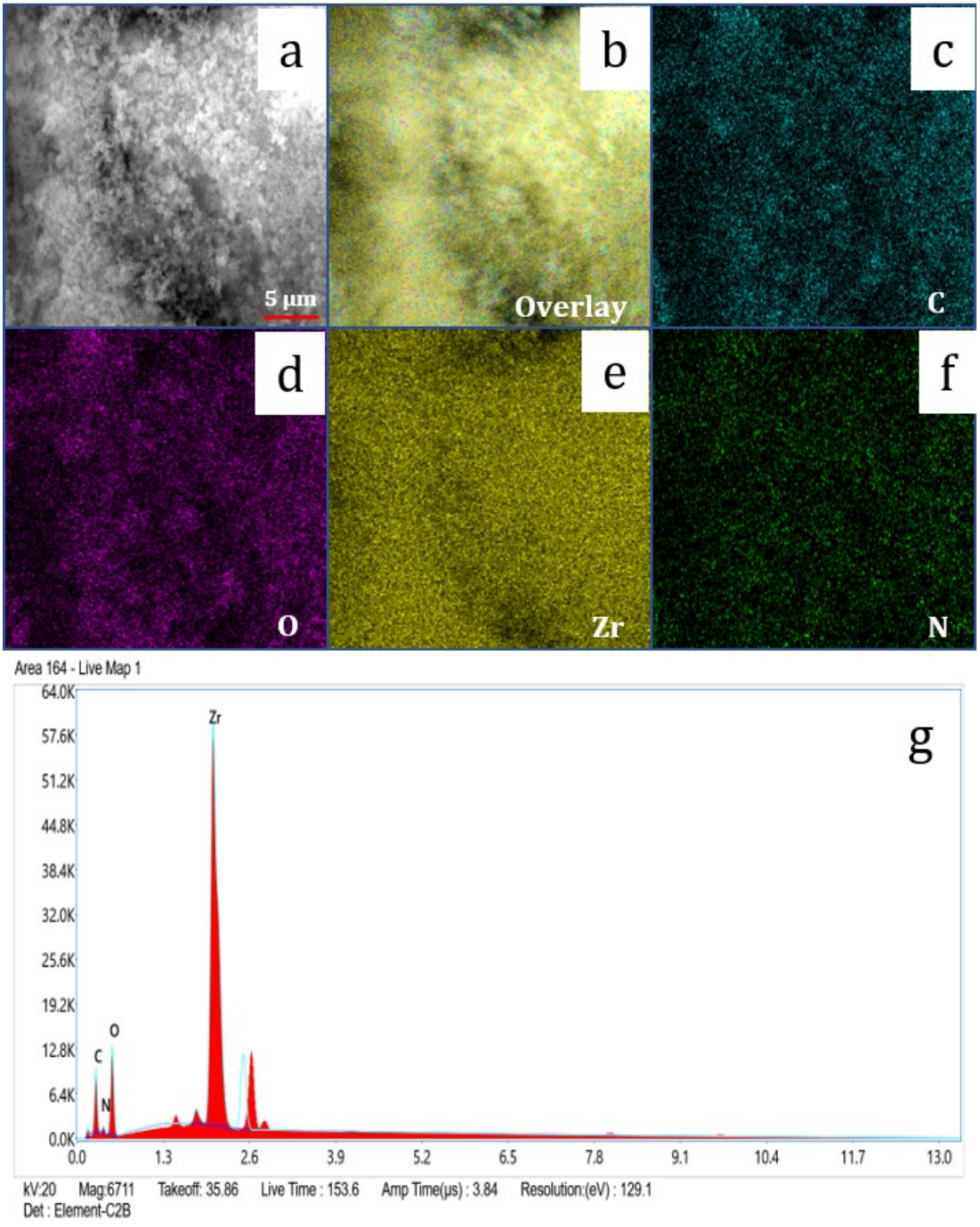

Fig. S3. EDS and elemental mapping of acetic acid modulated UiO-66-NH_2 sample (UN1) synthesized at 80°C.

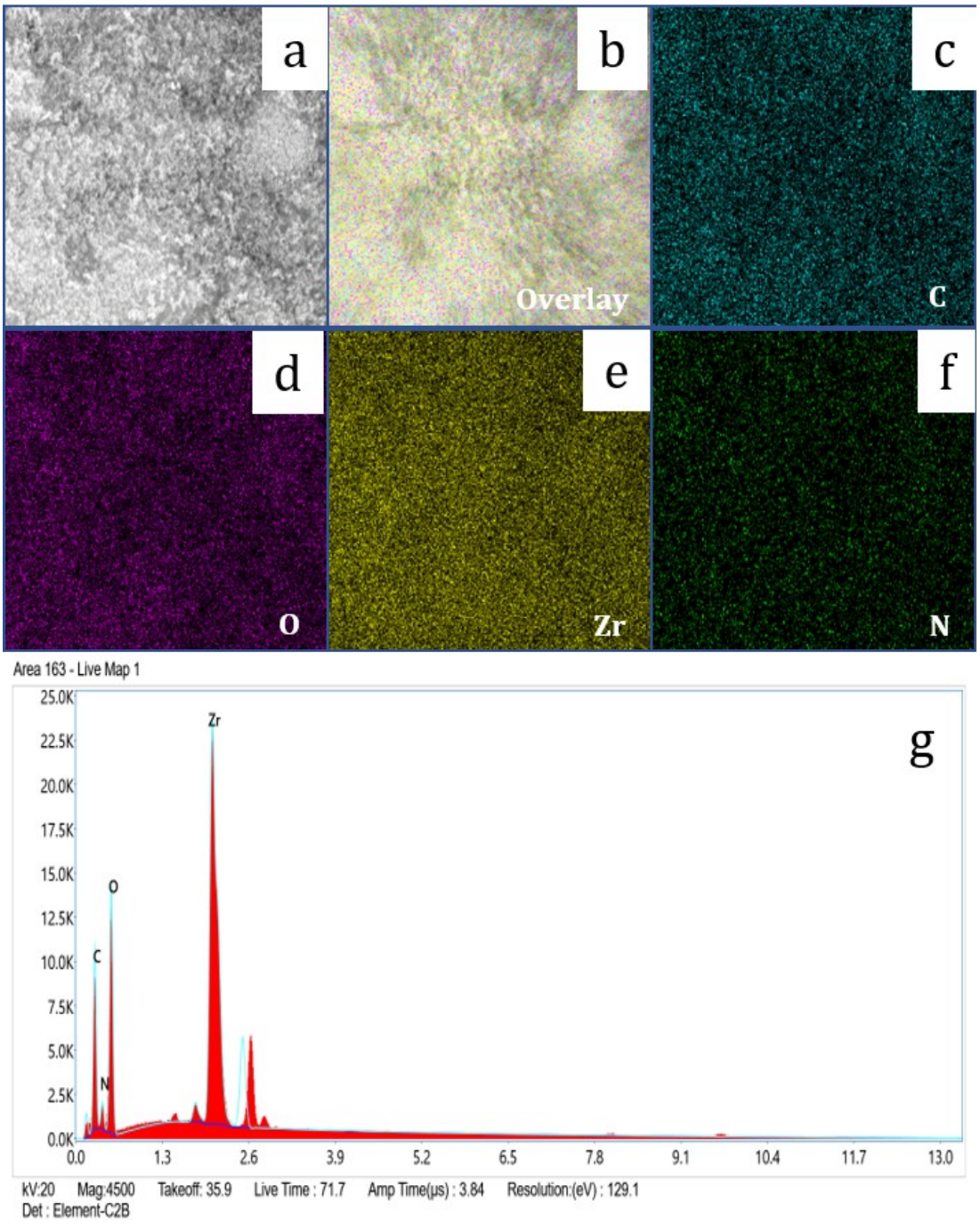

Fig. S4. EDS and elemental mapping of formic acid modulated UiO-66-NH_2 sample (UN2) synthesized at 80°C.

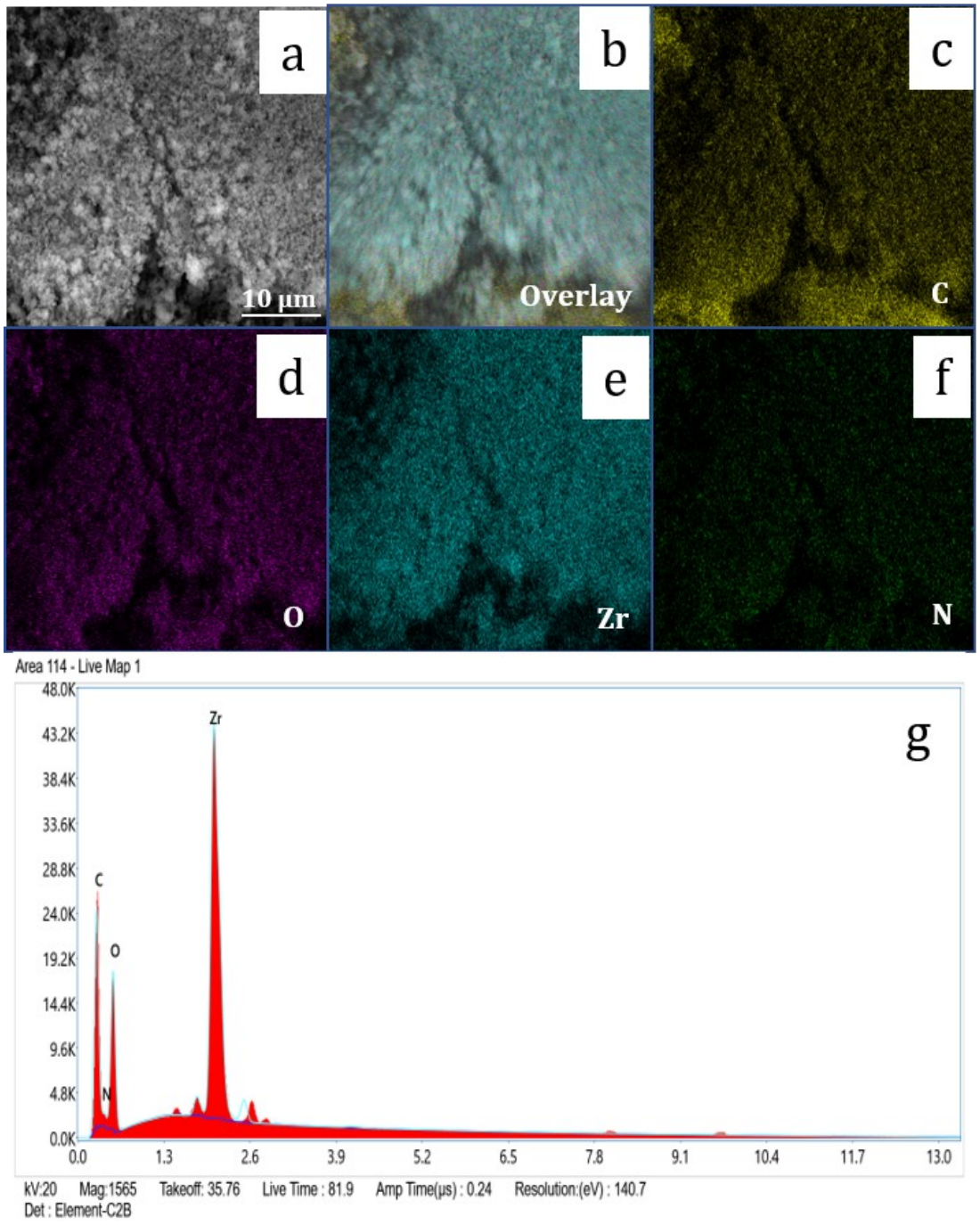

Fig. S5. EDS and elemental mapping of HCl modulated UiO-66-NH_2 sample (UN3) synthesized at 80°C.

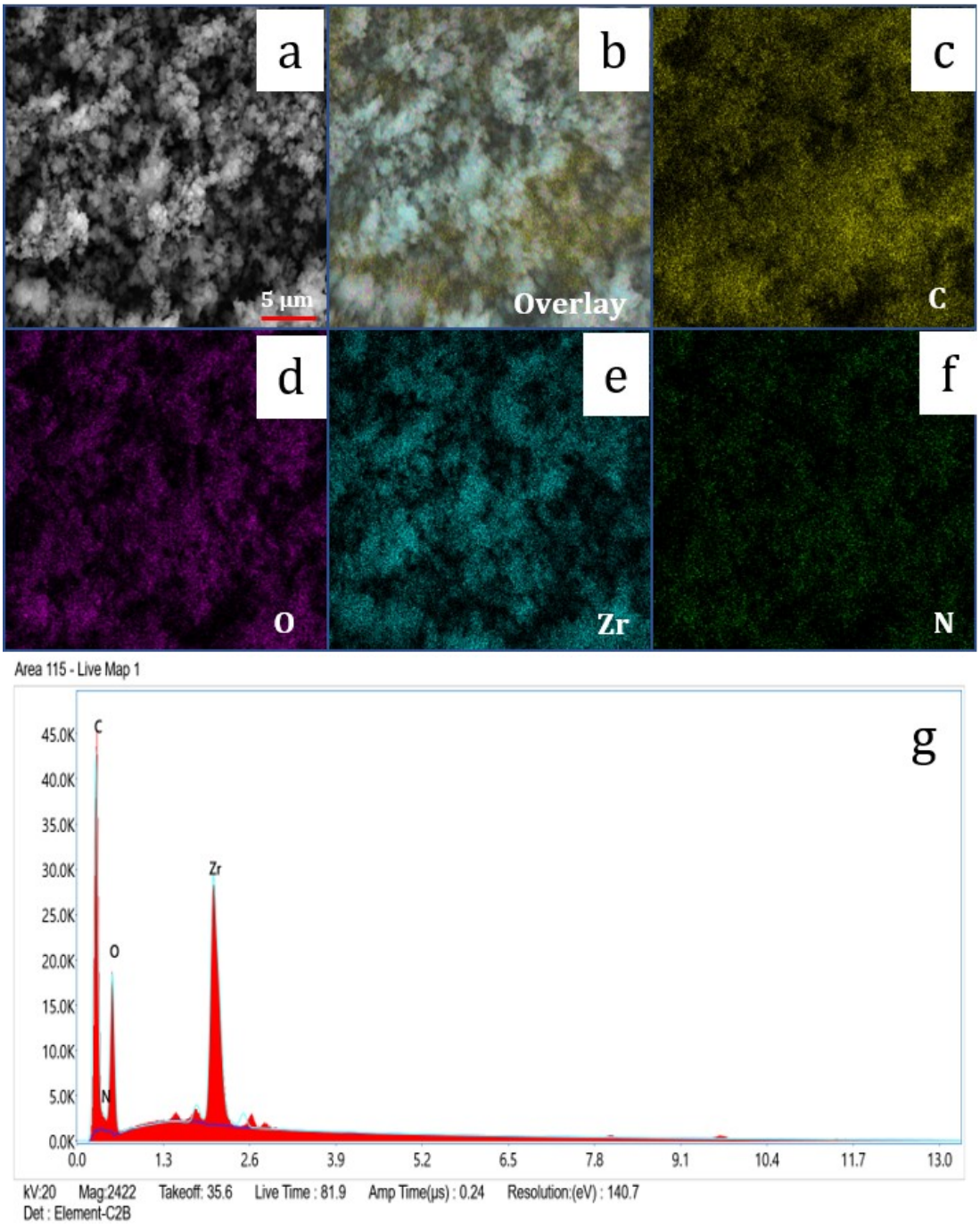

Fig. S6. EDS and elemental mapping of HCl modulated UiO-66-NH_2 sample (UN4) synthesized at 100°C.

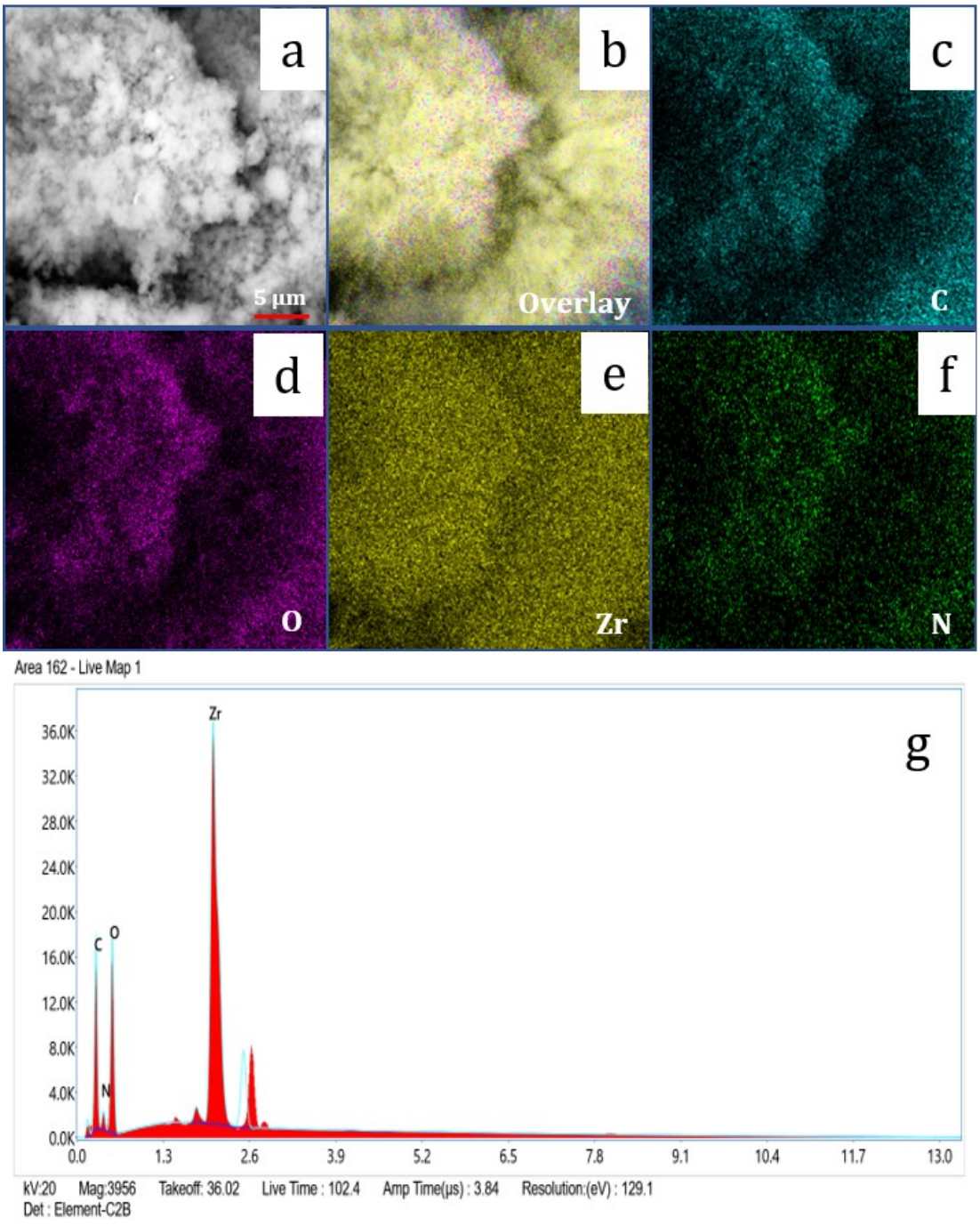

Fig. S7. EDS and elemental mapping of 4 equivalence HCl modulated UiO-66-NH_2 sample (UN6) synthesized at 80°C.

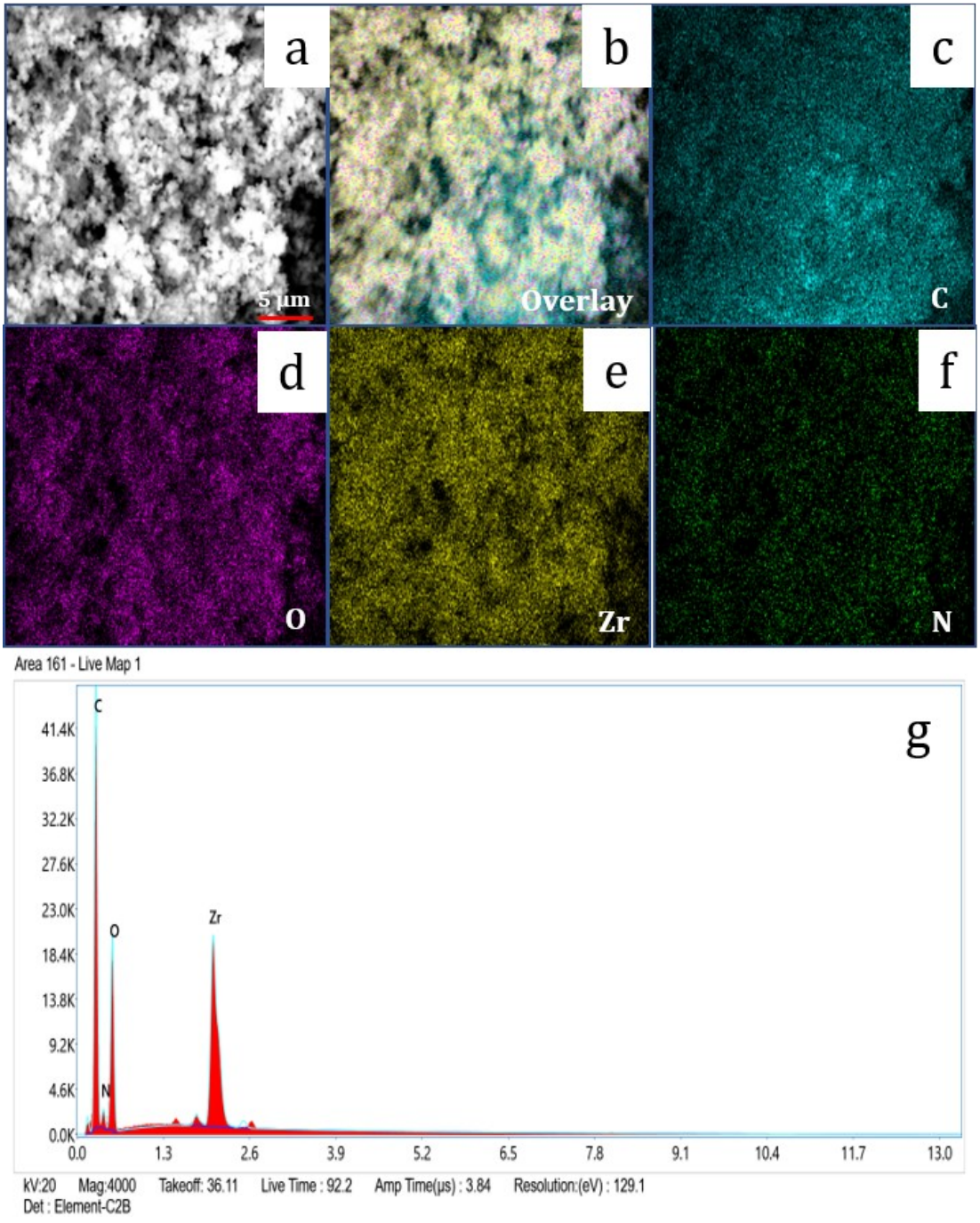

Fig. S8. EDS and elemental mapping of 12 equivalence HCl modulated UiO-66-NH_2 sample (UN7) synthesized at 80°C.

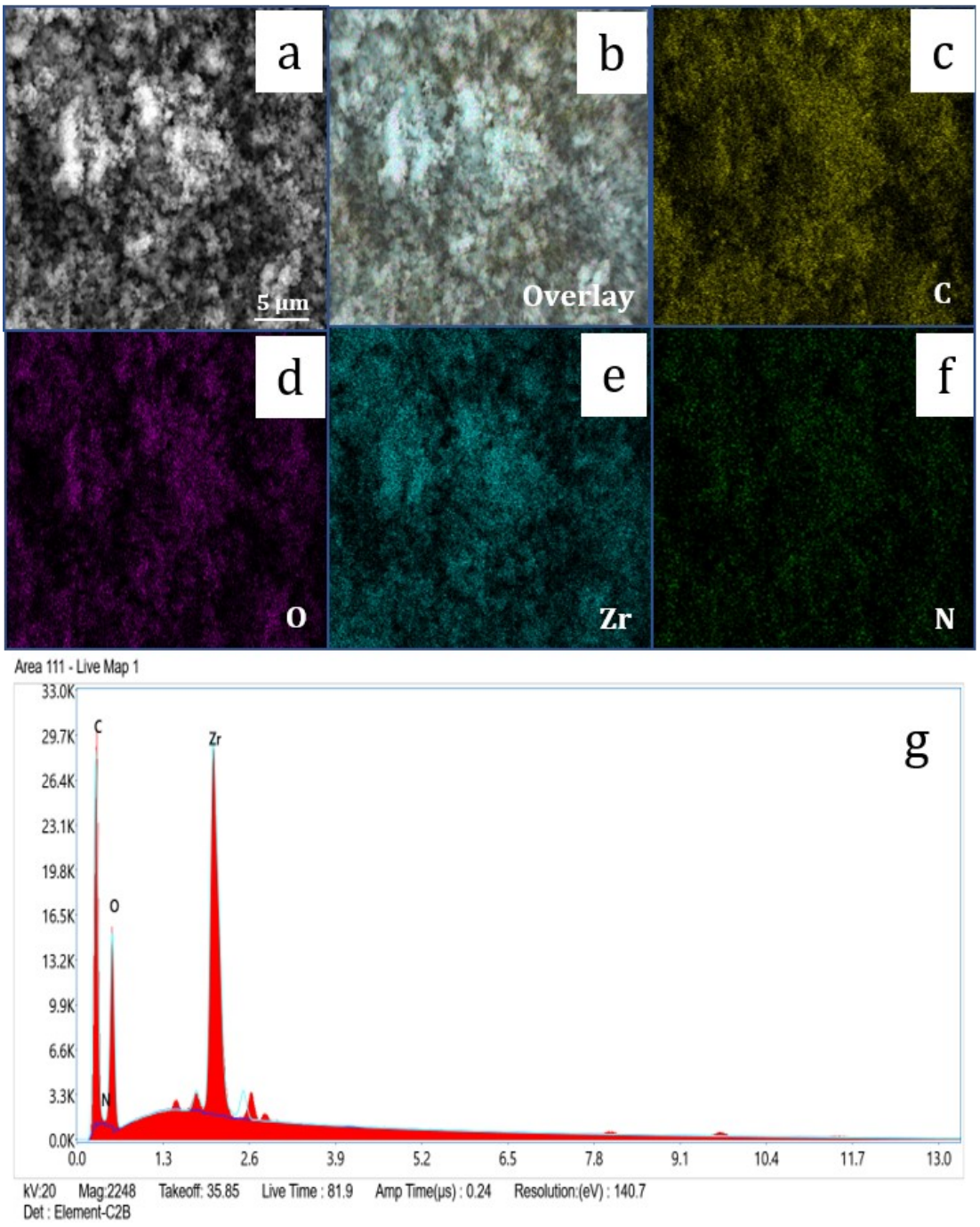

Fig. S9. EDS and elemental mapping of 8 equivalence HCl modulated UiO-66-NH_2 sample (UN8) synthesized at 80°C.

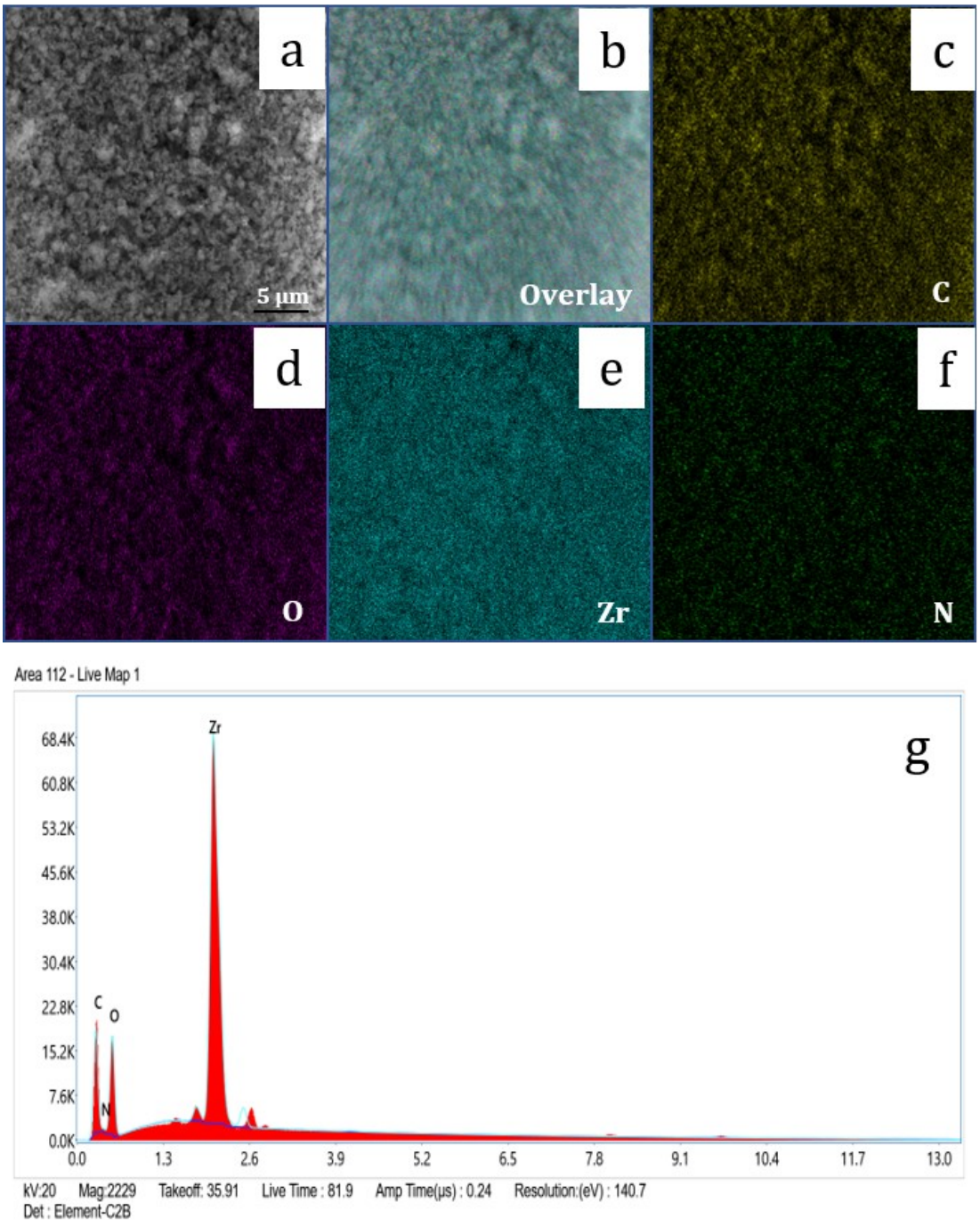

Fig. S10. EDS and elemental mapping of 8 equivalence HCl modulated UiO-66-NH_2 sample (UN9) synthesized at 80°C.

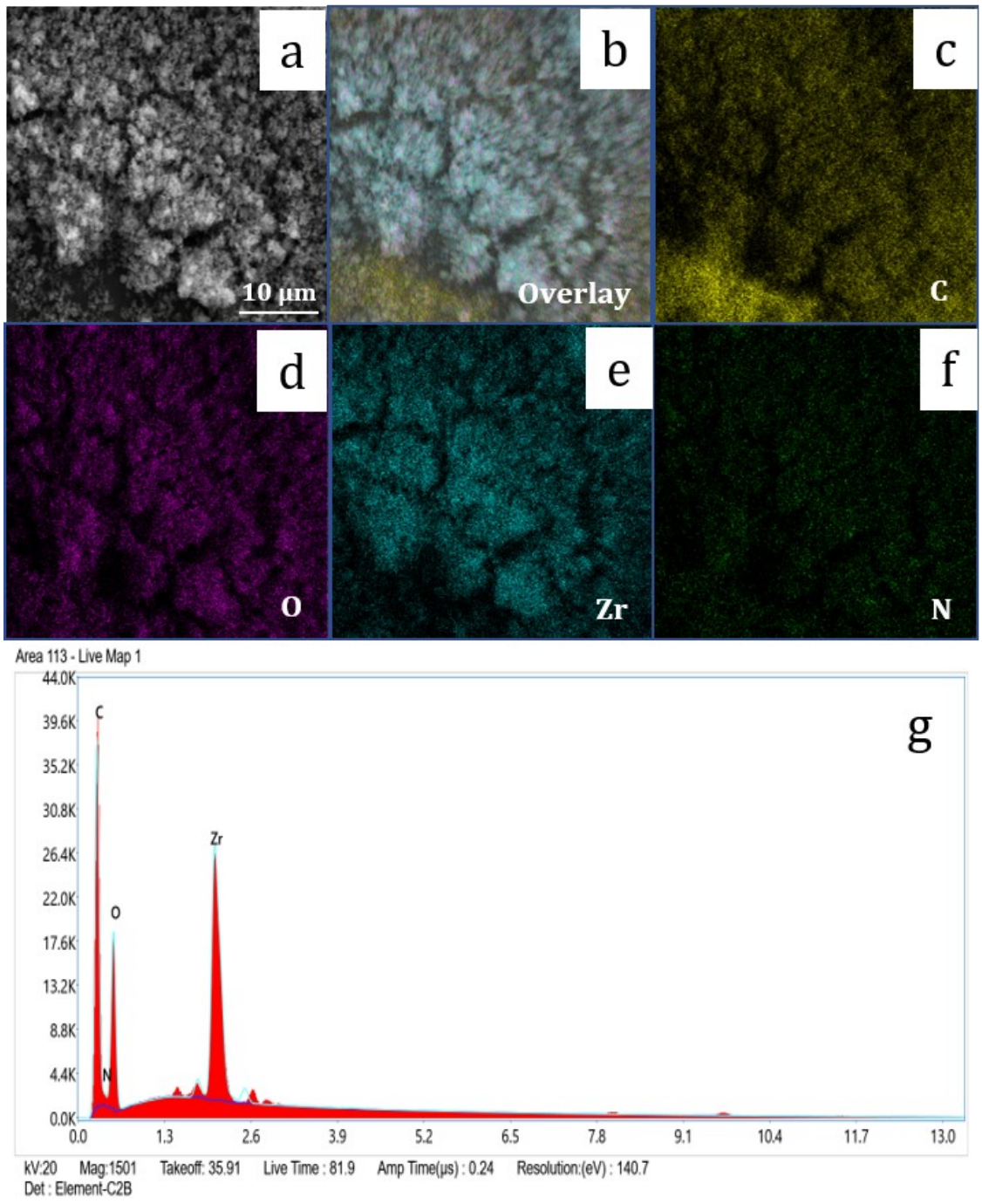

Fig. S11. EDS and elemental mapping of 8 equivalence HCl modulated UiO-66-NH_2 sample (UN10) synthesized at 80°C.

Table S3. Observed atomic percentage values of UiO-66-NH_2 samples from elemental mapping.

Sample Description	Atomic Percentage (%)			
	Carbon	Oxygen	Zirconium	Nitrogen
UN1 - Acetic acid	61.42	27.23	5.91	5.44
UN2 - Formic acid	55.94	32.08	2.66	9.31
UN6 - 4 Equi. HCl	62.10	27.71	2.79	7.39
UN3 - 8 Equi. HCl	70.23	21.73	1.83	6.21
UN7 - 12 Equi. HCl	71.49	21.44	0.95	6.12
UN4 - 100°C	74.87	18.26	0.92	5.96
UN5 -120°C	76.16	17.17	0.67	6.00
UN8 - 2.1 NH_2-H_2BDC	77.29	20.05	1.30	1.36
UN9 - 4.2 NH_2-H_2BDC	71.30	22.57	3.06	3.07
UN10 - 6.3 NH_2-H_2BDC	74.46	19.95	0.95	4.64

Section S3: FTIR analysis

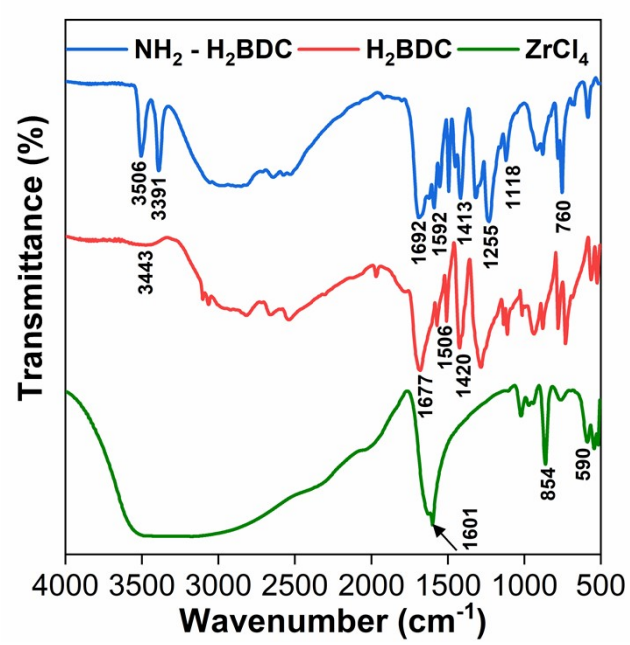

Fig. S12. FTIR spectra of $ZrCl_4$, terephthalic acid, and 2-aminoterephthalic acid.

Section S3: XPS analysis

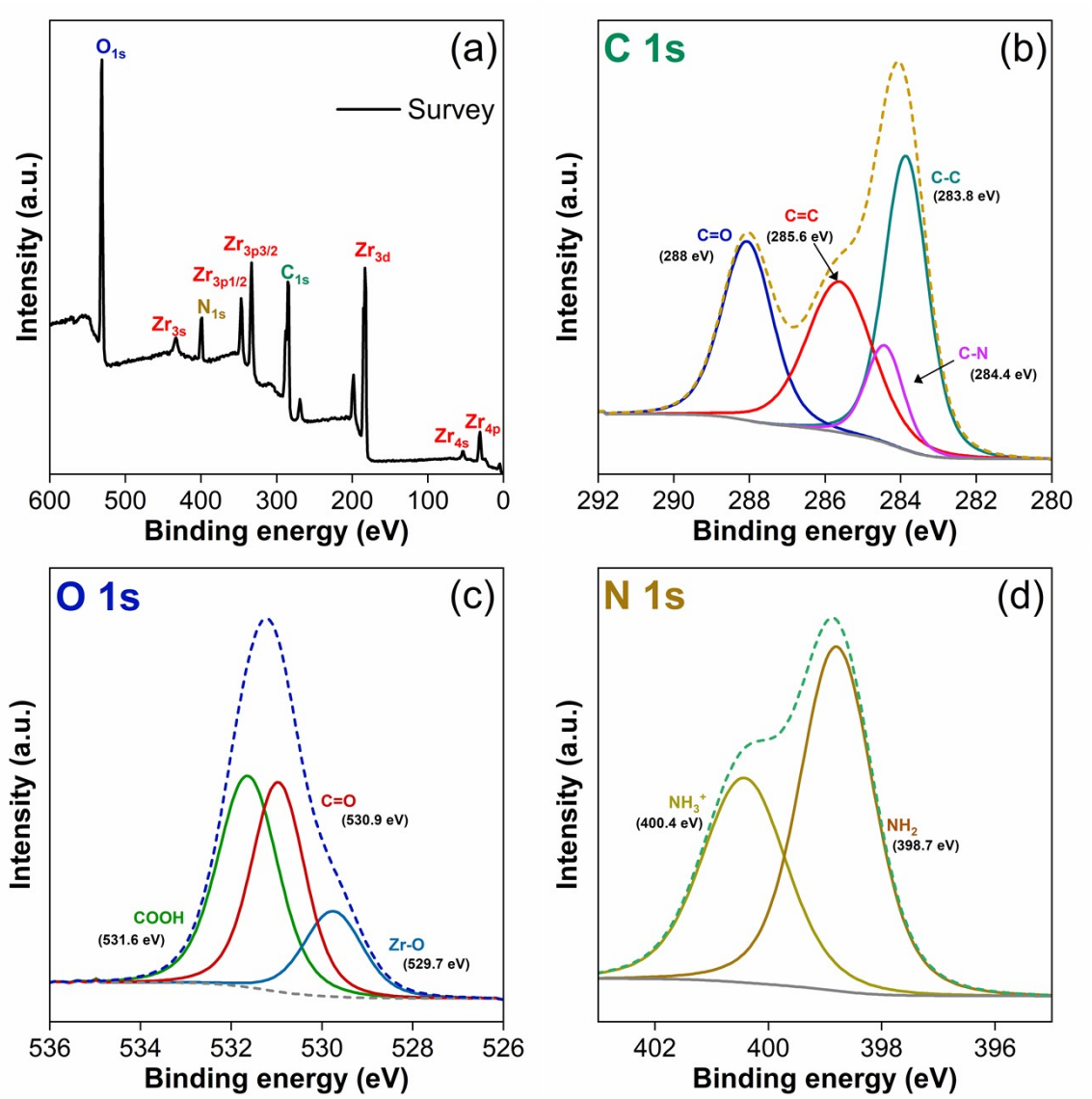

Fig. S13. XPS analysis of acetic acid modulated sample. (a) survey, (b) C, (c) O, and (d) N.

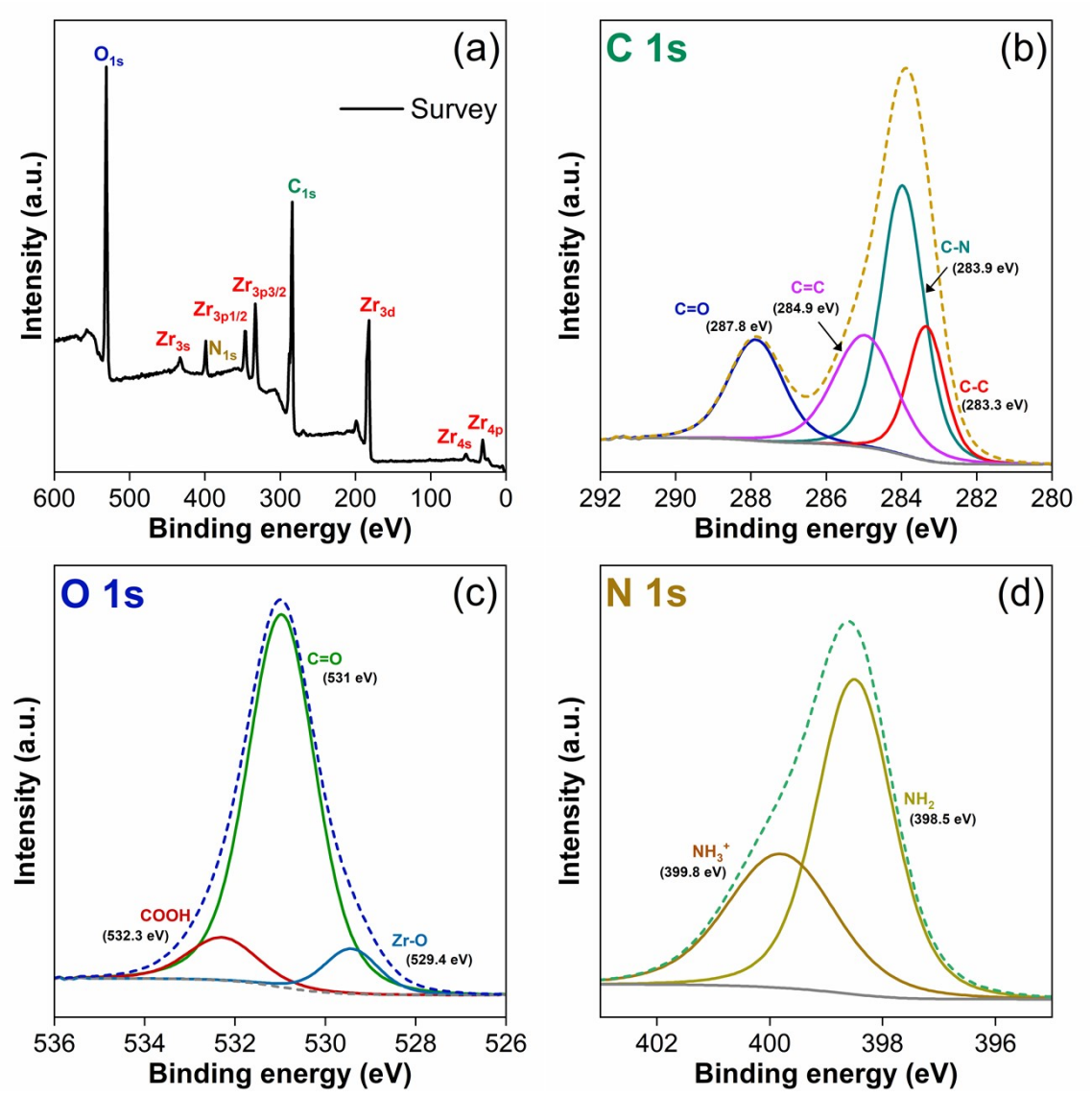

Fig. S14. XPS analysis of formic acid modulated sample. (a) survey, (b) C, (c) O, and (d) N.

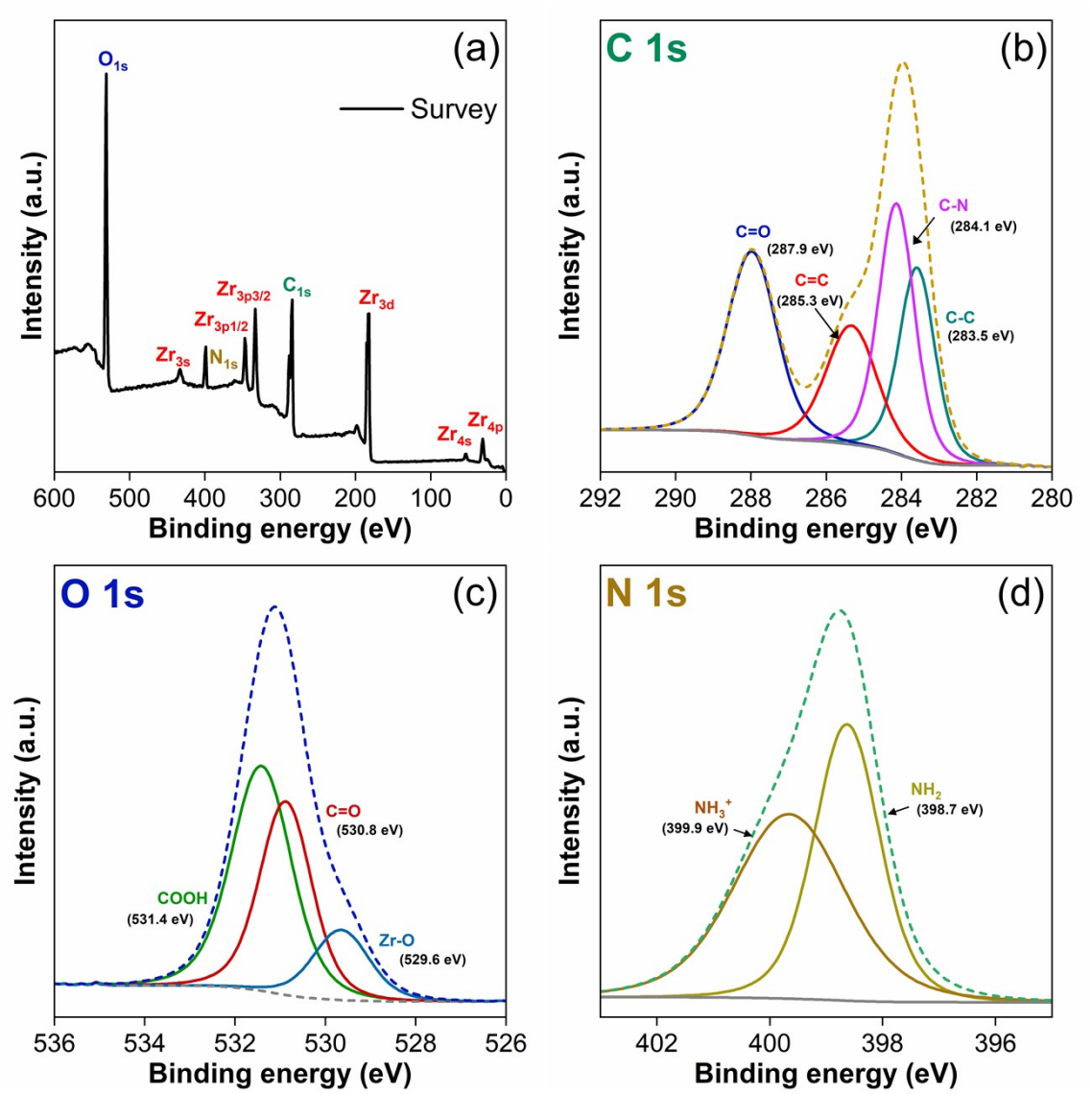

Fig. S15. XPS analysis of HCl modulated sample synthesized at 100°C. (a) survey, (b) C, (c) O, and (d) N.

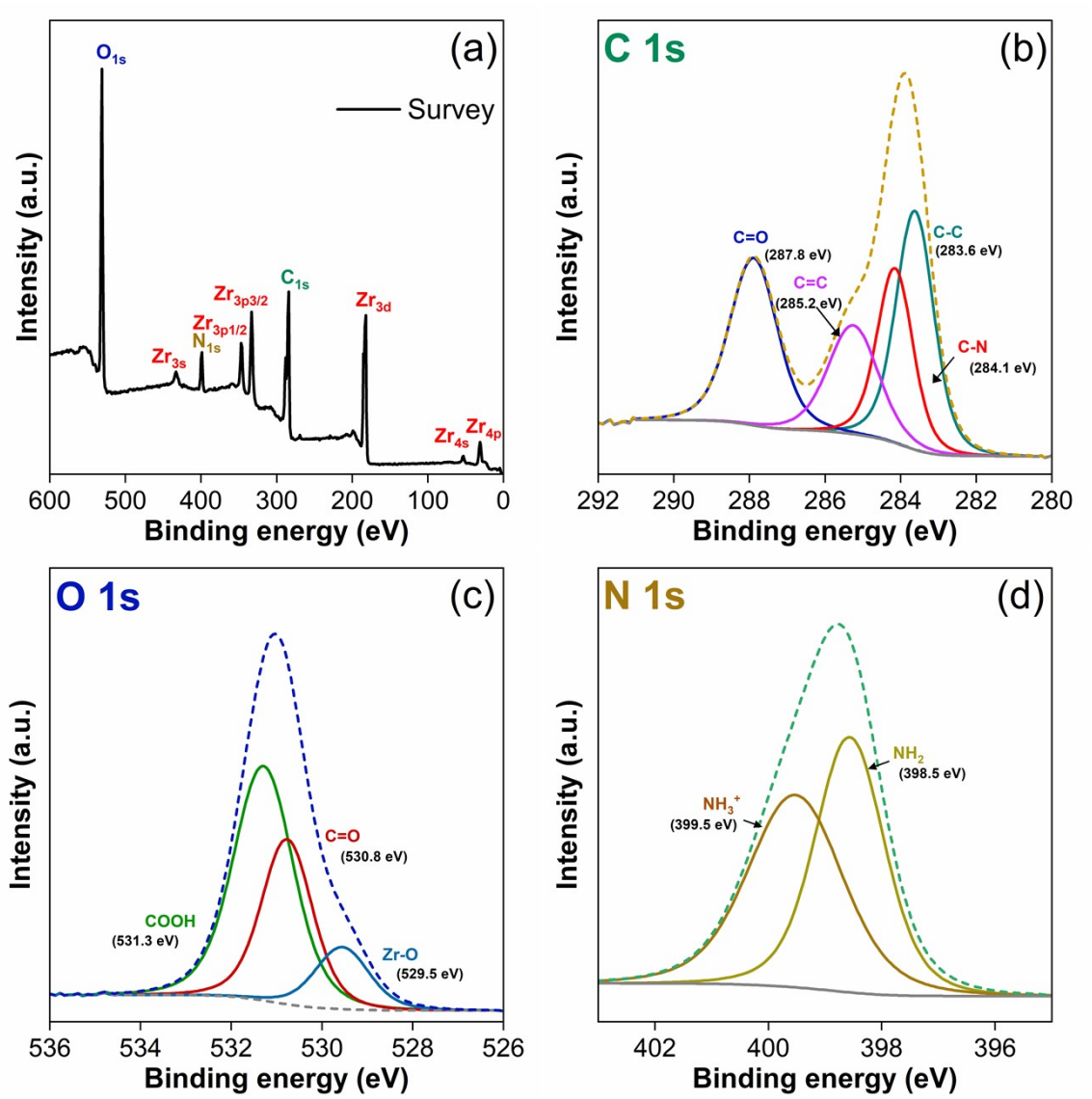

Fig. S16. XPS analysis of HCl modulated sample synthesized at 120°C. (a) survey, (b) C, (c) O, and (d) N.

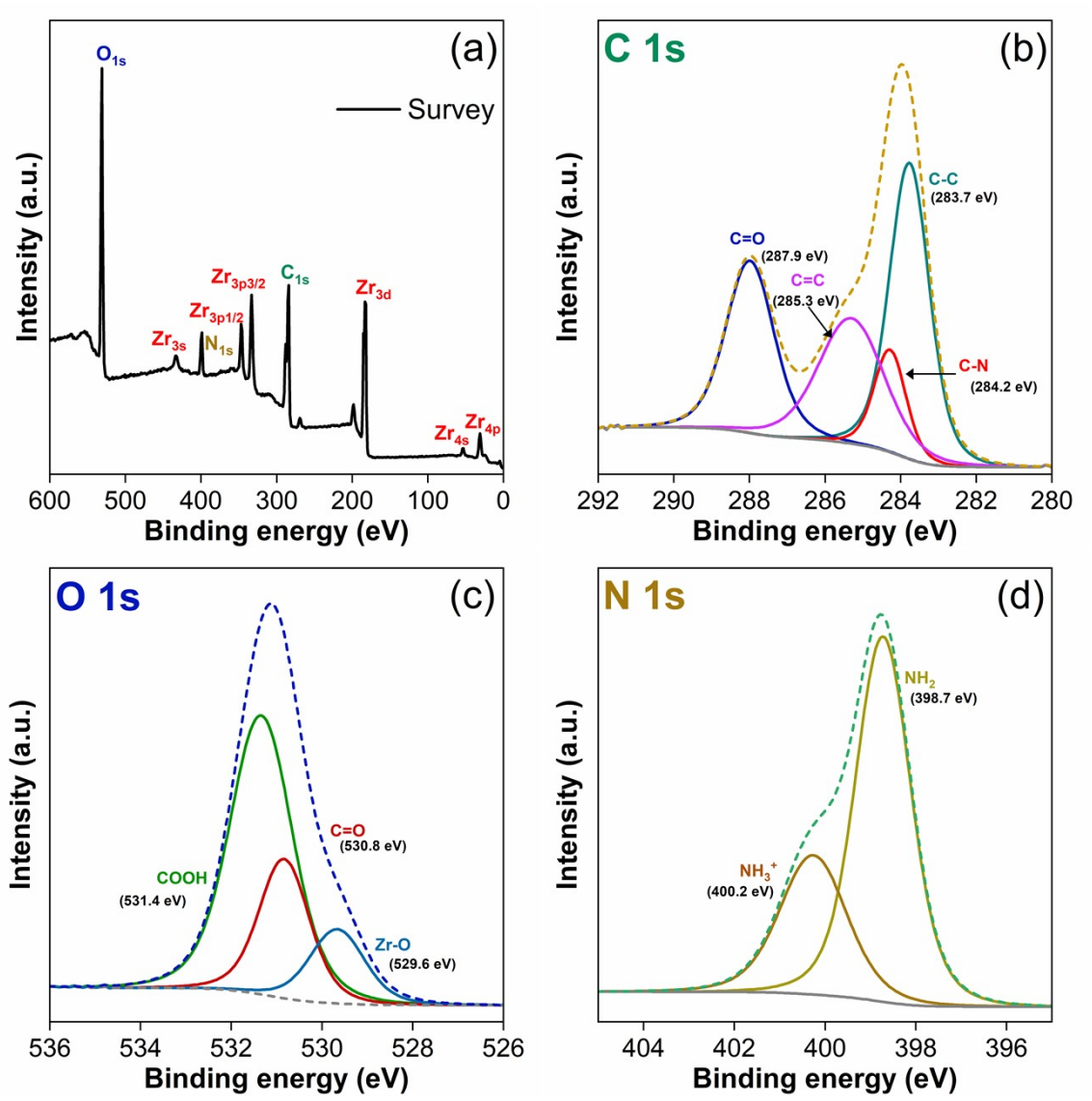

Fig. S17. XPS analysis of 4 equi. HCl modulated sample synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

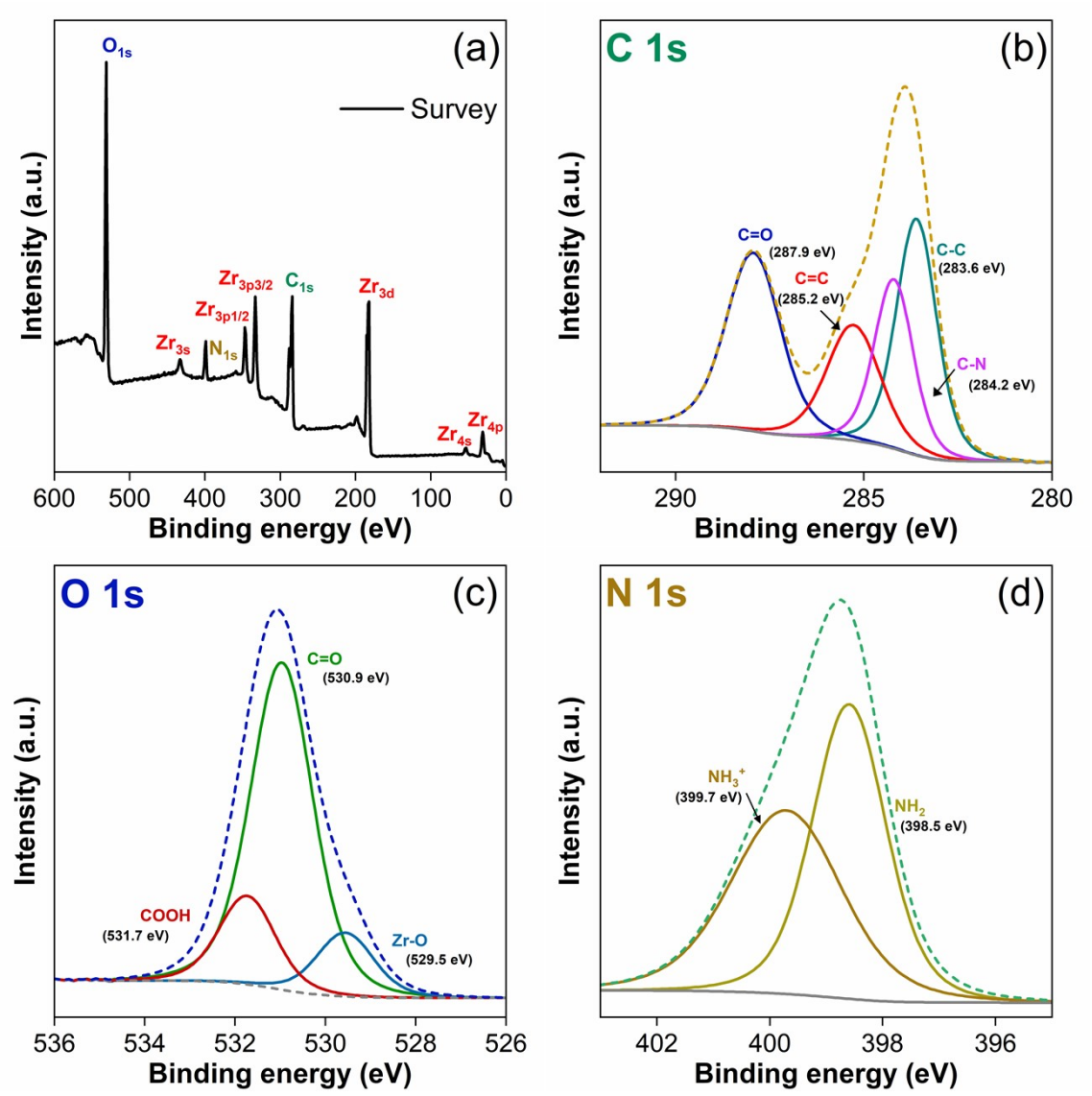

Fig. S18. XPS analysis of 12 equi. HCl modulated sample synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

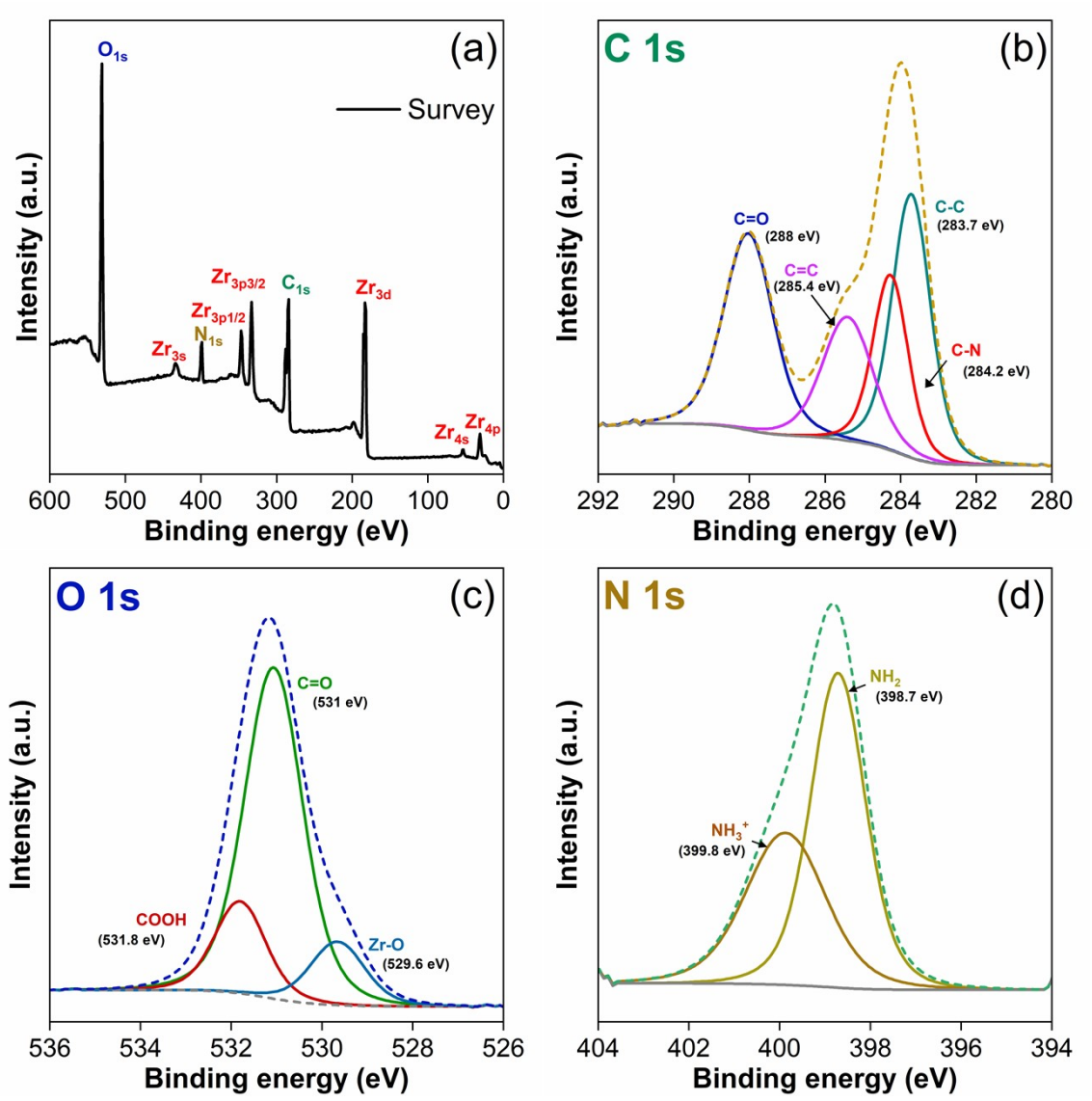

Fig. S19. XPS analysis of 8 equi. HCl modulated sample (8.4 NH_2-H_2BDC) synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

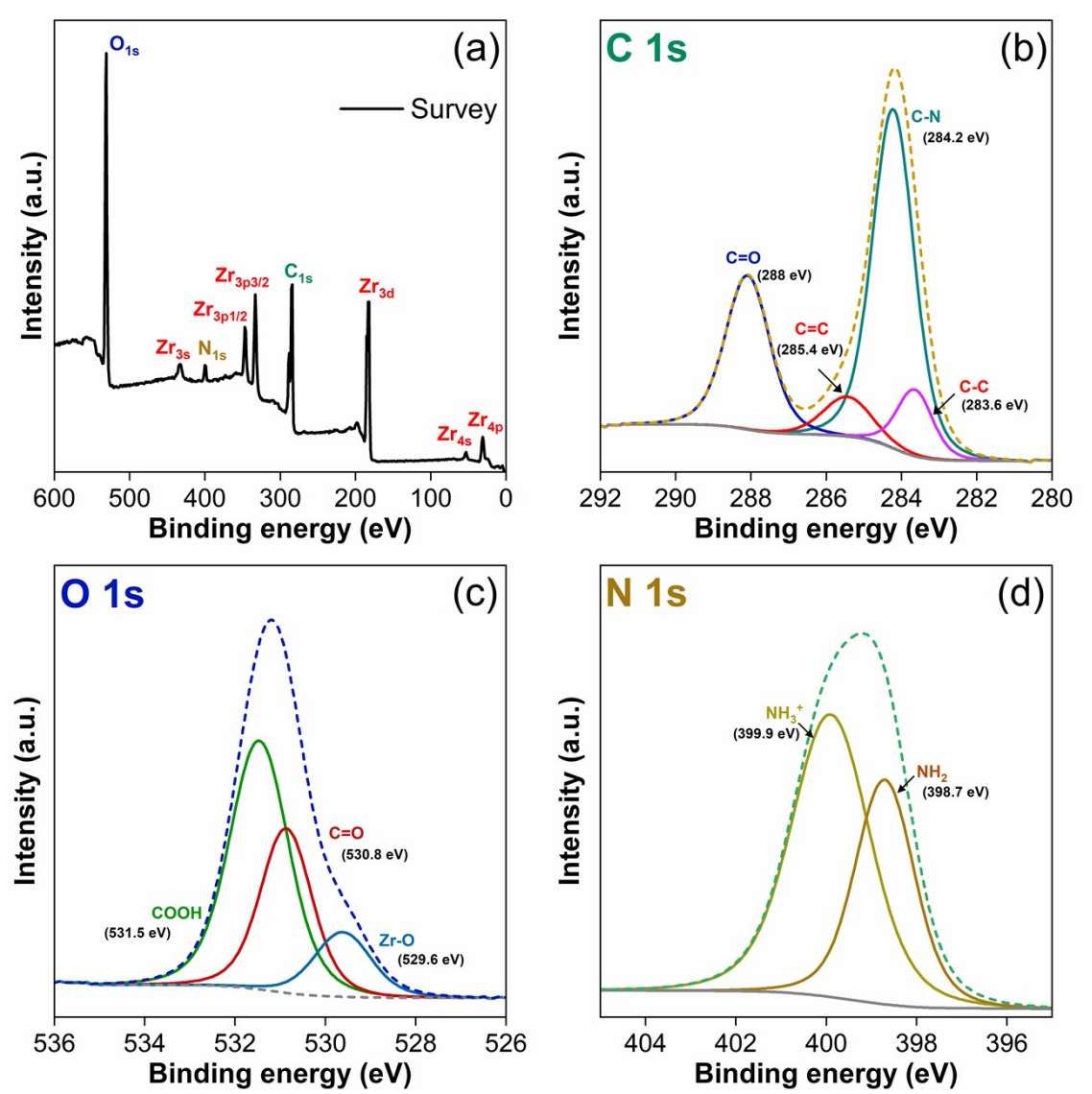

Fig. S20. XPS analysis of 8 equi. HCl modulated sample (2.1 NH_2-H_2BDC) synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

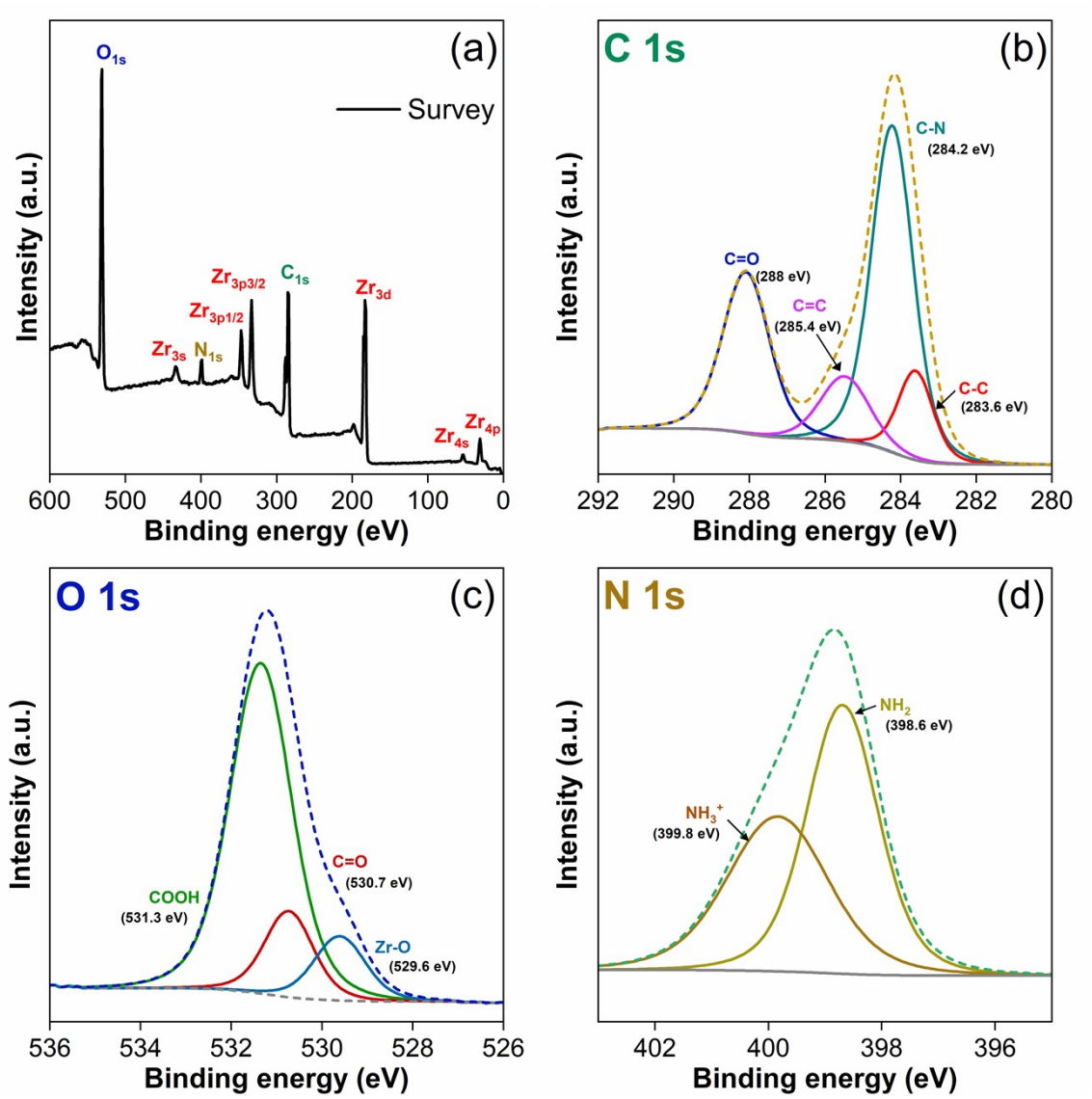

Fig. S21. XPS analysis of 8 equi. HCl modulated sample (4.2 NH_2-H_2BDC) synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

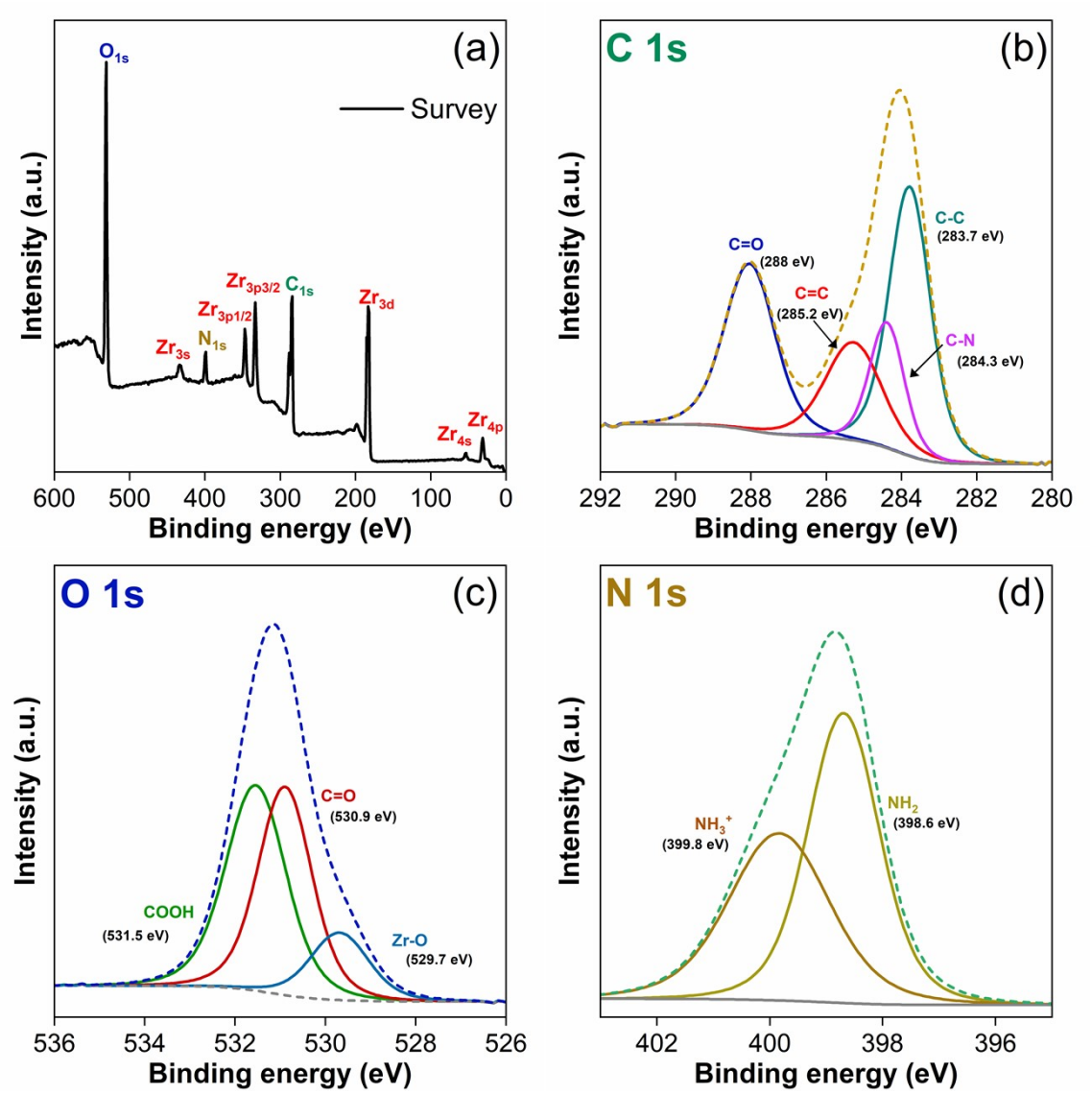

Fig. S22. XPS analysis of 8 equi. HCl modulated sample (6.3 NH_2-H_2BDC) synthesized at 80°C. (a) survey, (b) C, (c) O, and (d) N.

Table S4. Calculated chemical composition of elements in UiO-66-NH_2 MOFs from XPS analysis.

Sample	Zr 3d		O 1S			C 1S				N 1S	
	$Zr3d_{5/2}$	$Zr3d_{3/2}$	COOH	C=O	Zr-O	C=O	C=C	C-N	C-C	NH_3^+	NH_2
	Modulator										
UN1	60.80	39.20	43.96	38.69	17.35	25.66	28.10	10.26	35.98	40.48	59.52
UN2	59.56	40.44	9.7	82.29	8.01	19.09	24.02	39.63	17.26	37.60	62.40
UN3	60.86	39.14	17.12	70.31	12.57	30.19	19.32	19.13	31.36	41.20	58.80
	Synthesis Temperature										
UN3	60.86	39.14	17.12	70.31	12.57	30.19	19.32	19.13	31.36	41.20	58.80
UN4	60.88	39.12	49.04	36.64	14.32	29.36	19.48	29.01	22.15	53.12	46.88
UN5	60.72	39.28	54.31	32.69	13	27.76	19.00	21.81	31.43	50.67	49.33
	HCl Concentration										
UN6	60.82	39.18	61.12	24.61	14.27	26.27	25.96	10.39	37.38	31.59	68.41
UN3	60.86	39.14	17.12	70.31	12.57	30.19	19.32	19.13	31.36	41.20	58.80
UN7	60.61	39.39	17.15	70.28	12.57	30.41	19.32	20.58	29.69	48.32	51.68
	Ligand Ratio										
UN8	61.01	38.99	54.62	31.69	13.69	27.00	7.64	55.92	9.44	62.46	37.54
UN9	60.96	39.04	73.09	15.06	11.85	27.54	11.58	49.53	11.35	44.79	55.21
UN10	60.87	39.13	44.98	40.78	14.24	28.68	18.78	14.80	37.74	44.80	55.20
UN3	60.86	39.14	17.12	70.31	12.57	30.19	19.32	19.13	31.36	41.20	58.80

Table S5. Atomic % ratio of Zr, C, O and N elements from XPS analysis

Sample Description	Atomic Percentage (%)				Stochiometric values		
	Carbon	Oxygen	Zirconium	Nitrogen	C/Zr	O/Zr	N/Zr
UN1 - Acetic acid	51.55	32.84	6.47	9.14	7.96	5.07	1.41
UN2 - Formic acid	60.70	29.45	4.39	5.46	13.82	6.76	1.24
UN6 - 4 Equi. HCl	52.32	33.96	5.89	7.83	8.88	5.76	1.32
UN3 - 8 Equi. HCl	50.93	36.26	5.76	7.05	8.84	6.29	1.22
UN7 - 12 Equi. HCl	50.44	36.10	5.99	7.47	8.42	6.02	1.24
UN4 - 100°C	51.55	35.03	5.61	7.81	9.18	6.24	1.39
UN5 -120°C	52.92	34.51	5.37	7.20	9.85	6.42	1.34
UN8 - 2.1 NH_2-H_2BDC	52.68	37.53	6.17	3.62	8.53	6.08	0.58
UN9 - 4.2 NH_2-H_2BDC	52.13	37.12	6.02	4.74	8.65	6.16	0.78
UN10 - 6.3 NH_2-H_2BDC	50.93	36.31	5.75	7.01	8.85	6.31	1.21

Section S5: Thermogravimetric analysis

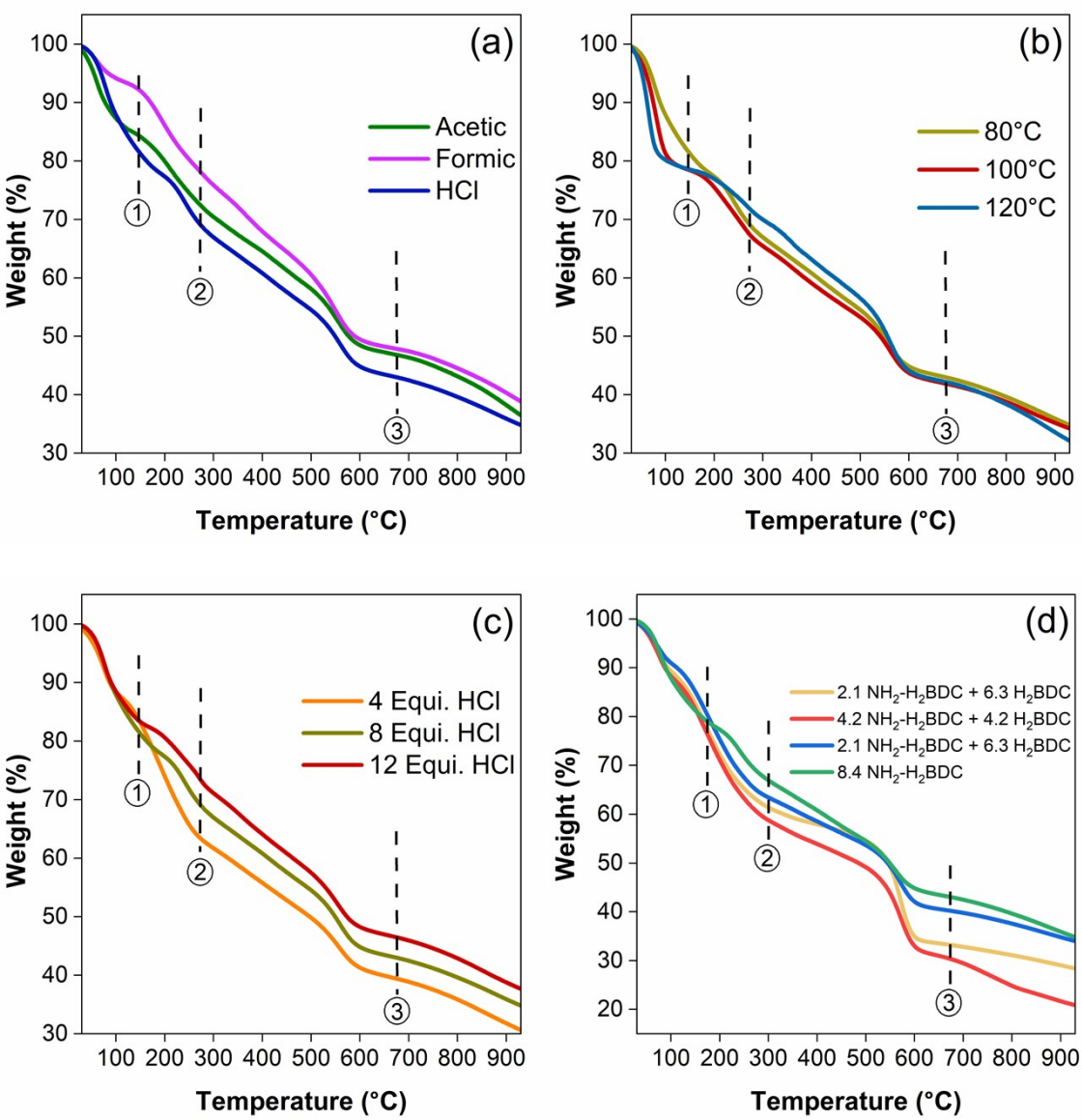

Fig. S23. TGA curve of UiO-66-NH_2 samples to its synthesis condition: (a) various modulators, (b) synthesis temperature, (c) HCl equivalence, and (d) ligand composition.

Table S6. Calculated weight loss and missed linker values from TGA curve.

Sample description		**Weight loss $_{exp}$ %**	**N $_{missed\ linkers}$**	**Final residue (wt. %)**
Modulator 8 Equi.	Acetic	195.95	1.63	36.04
	Formic	197.73	1.55	38.42
	HCl	194.17	1.71	34.50
T-80°C	4 Equi. HCl	203.88	1.27	30.33
	8 Equi. HCl	194.17	1.71	34.50
	12 Equi. HCl	190.27	1.89	37.37
8 Equi. HCl	80°C	194.17	1.71	34.50
	100°C	193.04	1.77	33.97
	120°C	221.40	0.48	31.71

Section S6: N_2 adsorption-desorption analysis

Table S7. Estimated BET surface area, pore volume and pore size of as-synthesized UiO-66-NH_2 samples.

Sample description		**BET surface area (m^2/g)**	**Pore size (nm)**	**V_{total} pore volume (cm^3/g)**	**Micropore volume (cm^3/g)**	**Mesopore volume (cm^3/g)**	**Micropores %**	**Mesopores %**
Modulator 8 Equi.	Acetic	553	10.6	0.425264	0.224791	0.200473	53	47
	Formic	568	8.5	0.394475	0.234044	0.160431	59	41
	HCl	562	8.8	0.386850	0.240214	0.146636	62	38
T-80°C	4 Equi. HCl	578	8.2	0.374873	0.254962	0.119911	68	32
	8 Equi. HCl	562	8.8	0.386850	0.240214	0.146636	62	38
	12 Equi. HCl	742	5.4	0.437024	0.321167	0.115857	74	26
8 Equi. HCl	80°C	562	8.8	0.386850	0.240214	0.146636	62	38
	100°C	562	6.4	0.342057	0.246694	0.095363	72	28
	120°C	499	5.5	0.288414	0.223562	0.064852	78	22
Linker Composition	2.1* + 6.3#	675	6.5	0.417081	0.291388	0.125693	70	30
	4.2* + 4.2#	623	7.3	0.401946	0.261394	0.140552	65	35
	6.3* + 2.1#	574	7.7	0.376547	0.245985	0.130562	65	35
	8.4#	562	8.8	0.386850	0.240214	0.146636	62	38

* NH_2-H_2BDC # H_2BDC

Section S7: p-nitrophenoxide calibration studies

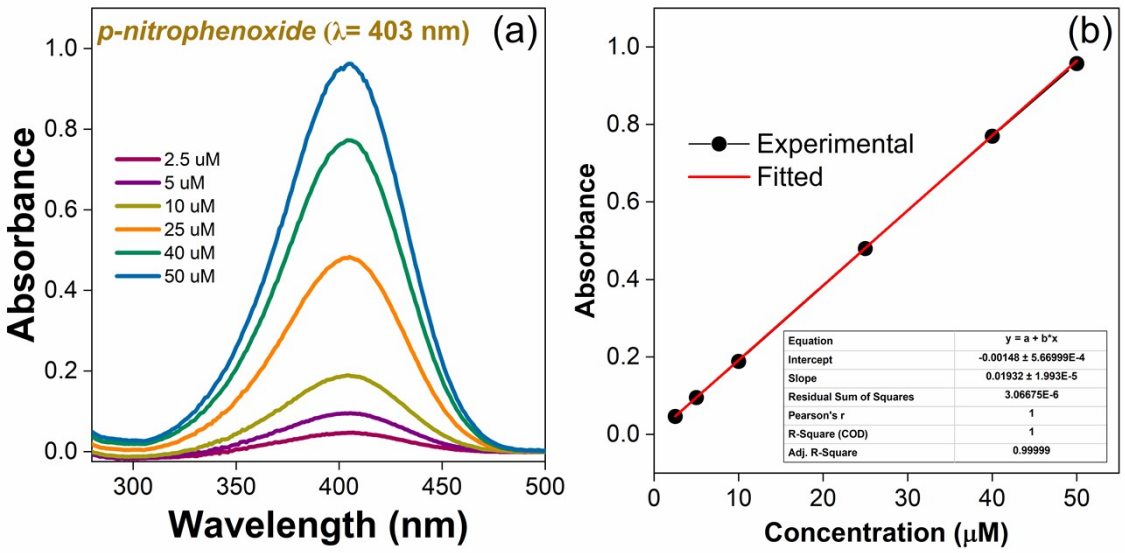

Fig. S24. Calibration curve of p-nitrophenoxide for the concentration between 2.5 and 50 μM.