Supporting Information for Publication

Engineering the Defects of UiO-66 MOF for an Improved Catalytic Detoxification of CWA Simulant: Methyl Paraoxon

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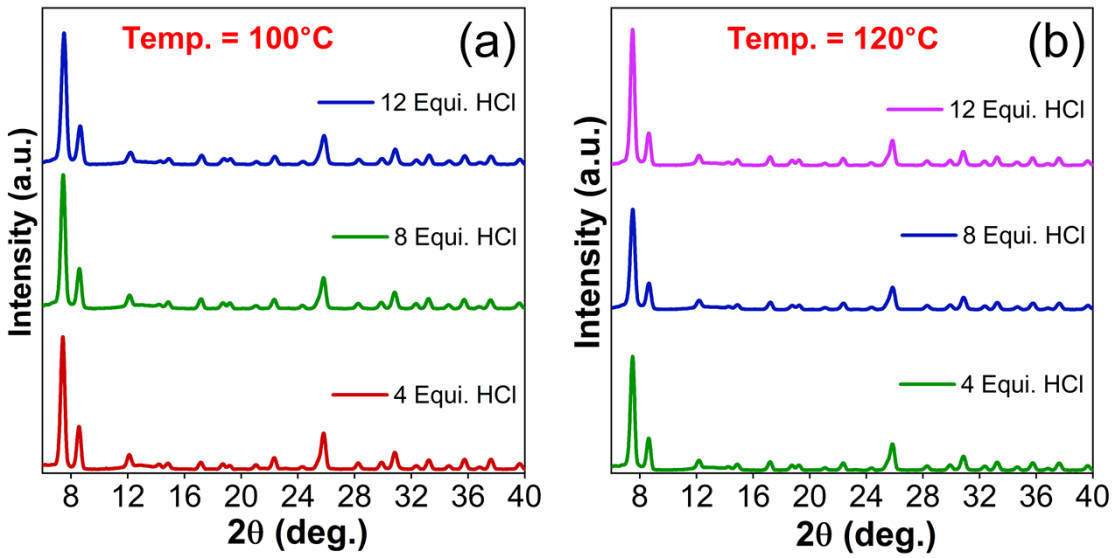
Table S1. Synthesis conditions of UiO-66 MOFs.

S. No.	Sample	$ZrCl_4$ (mmol)	H_2BDC (mmol)	Modulator (Equivalence)	Synthesis Temperature (°C)	Duration (h)
1.	S1	6 mmol	6 mmol	8**	80	24
2.	S2	6 mmol	6 mmol	8***	80	24
3.	S3 – A	6 mmol	6 mmol	4*	80	24
	S3 – B			8*		
	S3 – C			12*		
4.	S4 – A	6 mmol	6 mmol	4*	100	24
	S4 – B			8*		
	S4 – C			12*		
5.	S5 – 0	6 mmol	6 mmol	0*	120	24
	S5 – A			4*		
	S5 – B			8*		
	S5 – C			12*		
6.	S6 – A	6 mmol	6 mmol	0.89 mL#	120	24
	S6 – B			1.39 mL#		

* HCl, ** Acetic acid, *** Formic acid, # water

Section S1: PXRD analysis



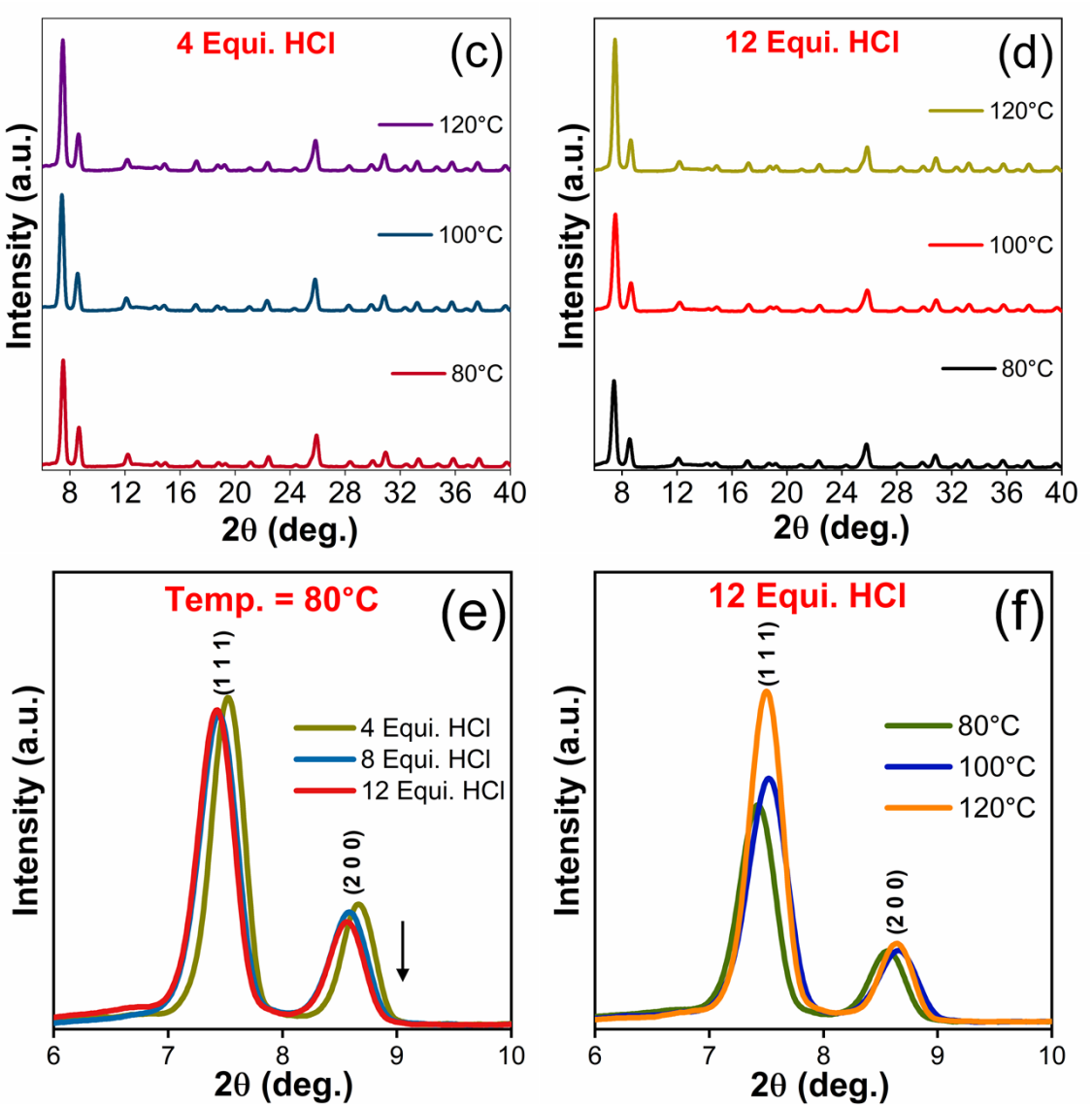


Fig. S1. PXRD pattern of as-synthesized UiO-66 samples resulting from various synthesis conditions: (a) & (b) Influence of HCl at 100 and 120°C synthesis temperature, (c) & (d) Influence of synthesis temperature at constant HCl equivalence of 4 and 12, (e) & (f) Change in intensity of (1 1 1) & (2 0 0) reflection with respect to HCl equivalence, and synthesis temperature.

Table S2. Calculated lattice parameters values of as synthesized UiO-66 samples.

Sample description	**Crystallite Size (nm)**	**Lattice Constant "a"**	**Microstrain (ε)**	**Crystallinity Index (%)**	**Dislocation Density (10^{-4})**
S1	40	20.14	0.68	70.28	6.54
S2	38	20.41	0.75	77.12	6.99
S3 – A	42	20.28	0.66	76.99	5.71
S3 – B	39	20.41	0.72	77.26	6.69
S3 – C	39	20.44	0.73	77.31	6.79
S4 – A	41	20.41	0.68	77.74	5.97
S4 – B	39	20.40	0.72	78.37	6.60
S4 – C	37	20.33	0.78	80.78	7.67
S5 – 0	39	20.30	0.71	78.94	6.60
S5 – A	41	20.35	0.68	77.69	6.62
S5 – B	37	20.33	0.76	78.74	7.34
S5 – C	41	20.35	0.68	81.75	6.19
S6 – A	41	20.21	0.69	77.64	6.16
S6 – B	37	20.21	0.76	79.99	7.34

Section S2: TEM micrographs of UiO-66 MOFs

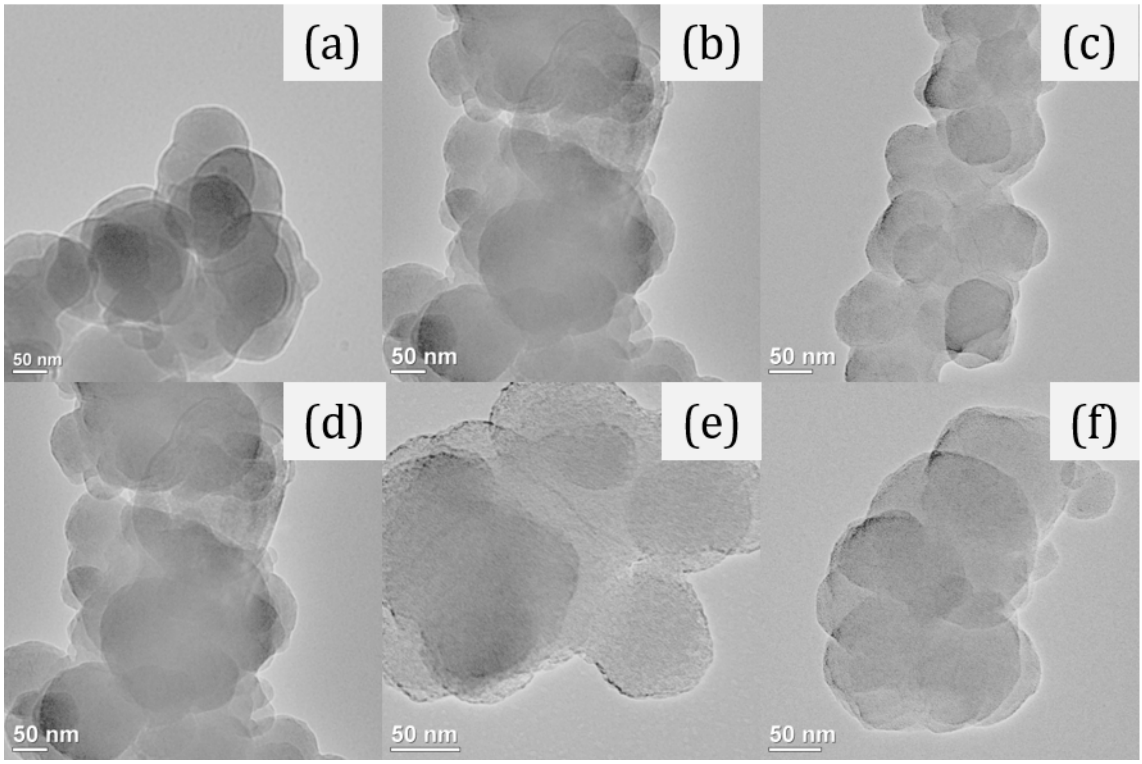
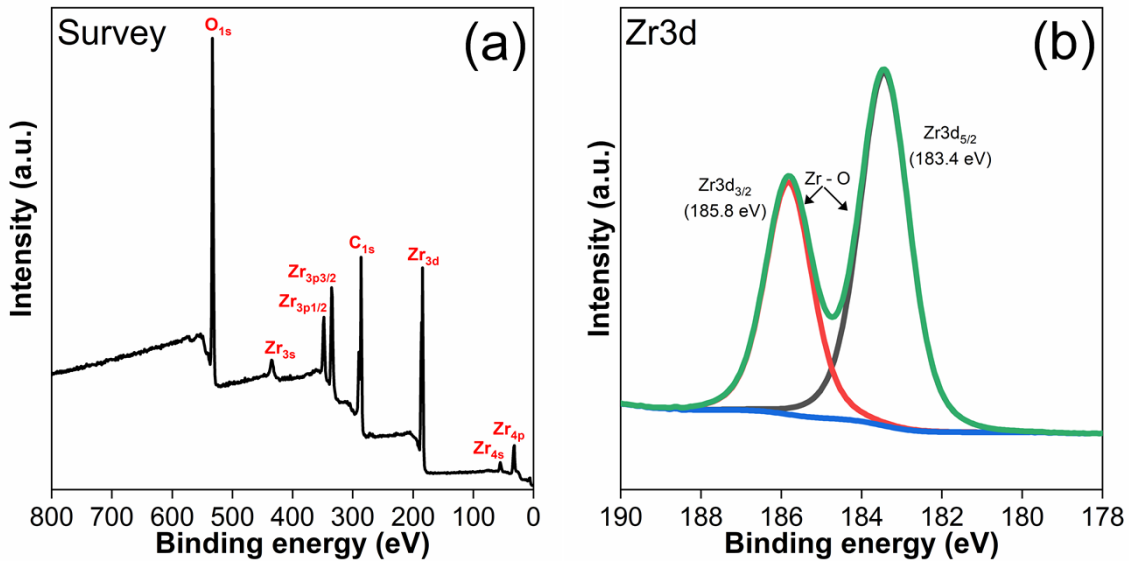


Fig. S2. TEM micrographs of UiO-66 samples with respect to synthesis condition: (a -c) Increase of HCl equivalence (4, 8, 12 Equivalence) modulated samples synthesized at 80°C, and (d – f) Increase of synthesis temperature (80, 100, 120°C) for an 8 Equi. HCl modulated samples.

Section S3: XPS analysis and measurement of atomic elements for the synthesized UiO-66 MOFs



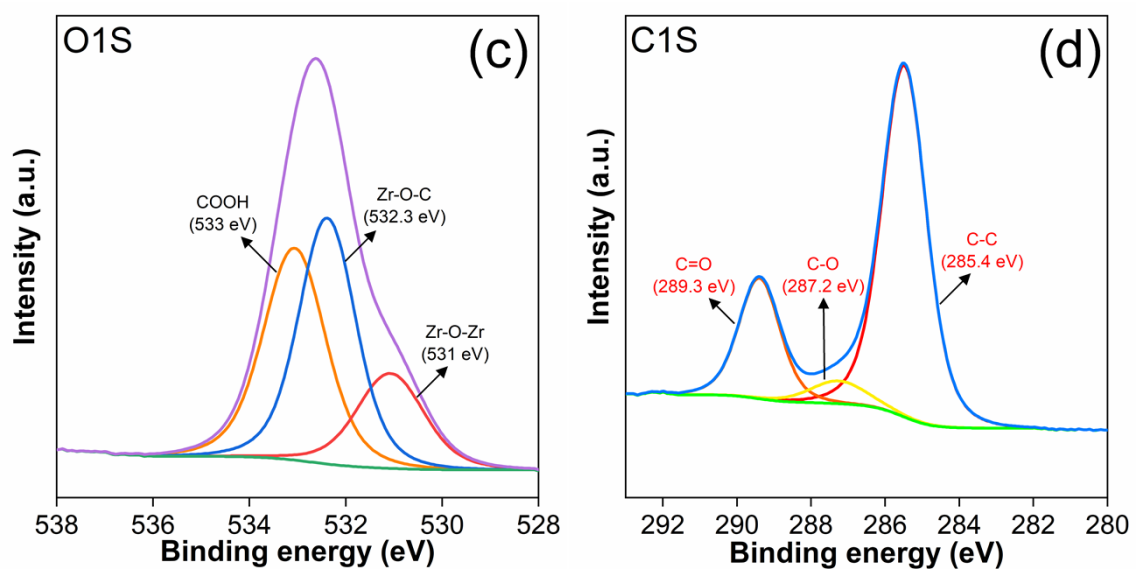
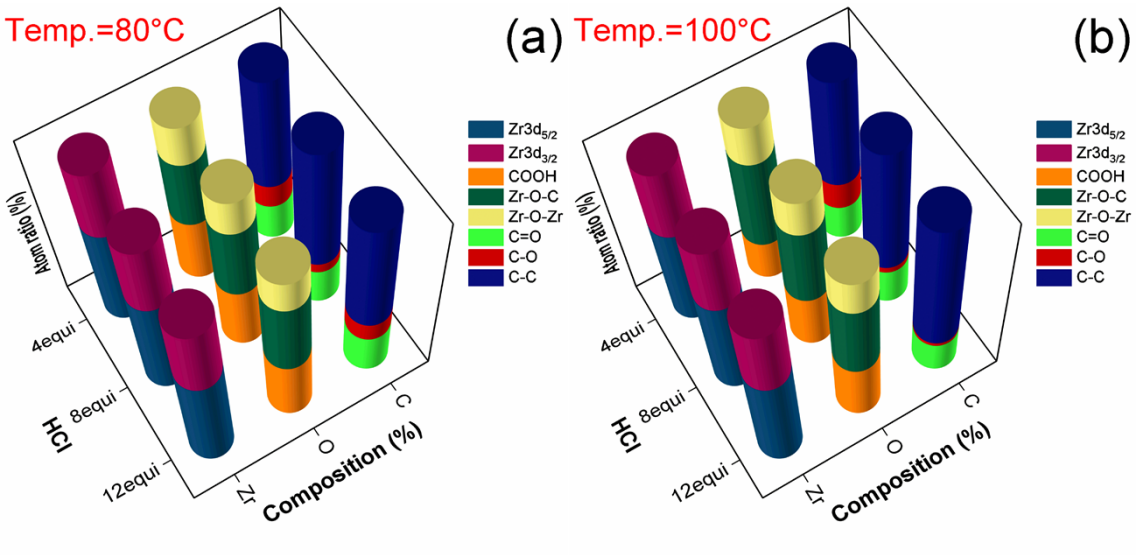


Fig. S3. XPS spectra of 8 equi. HCl modulated UiO-66 sample synthesized at 80°C. a) survey, b) Zr 3d, c) O 1S, and d) C 1S.



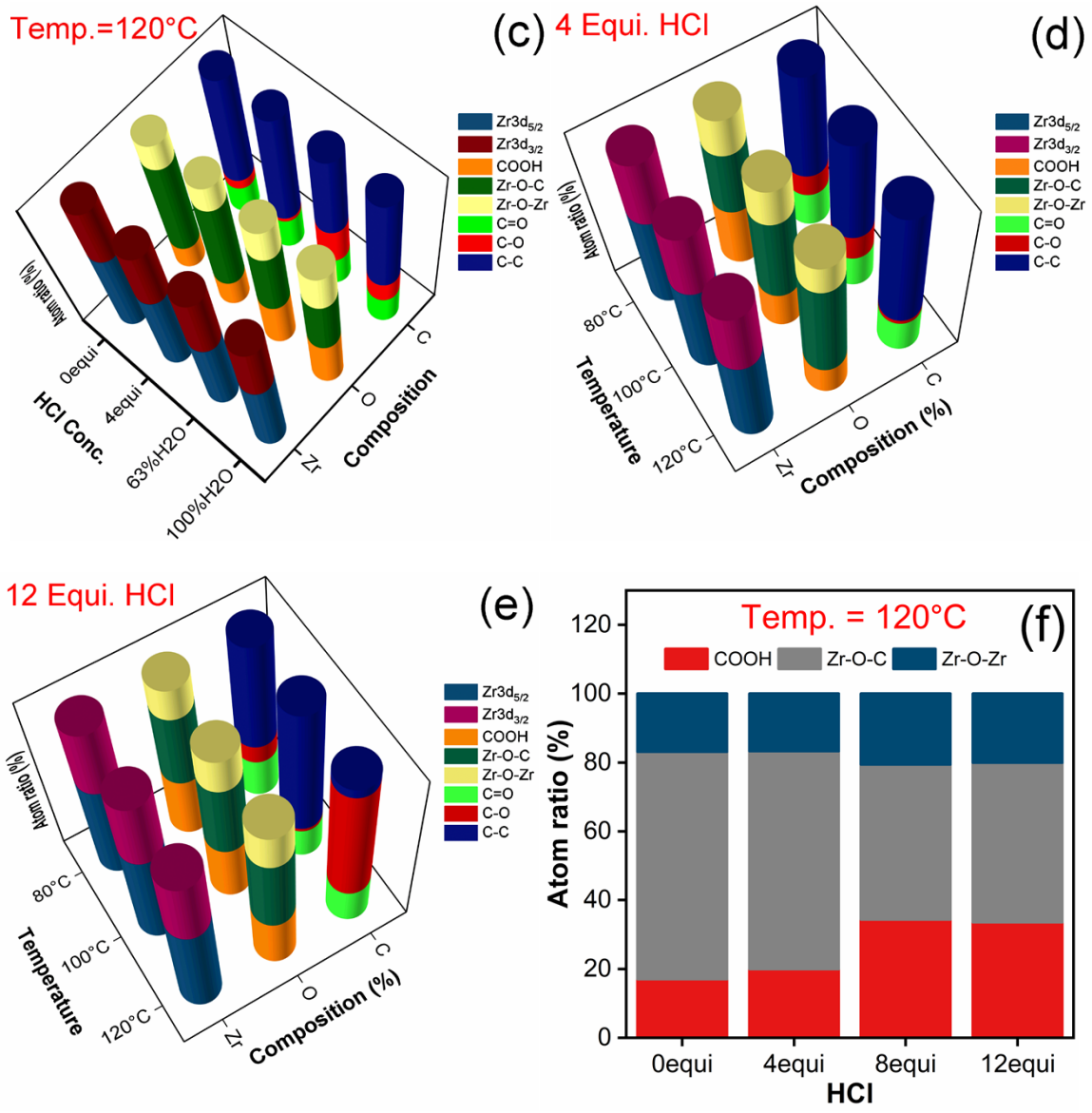


Fig. S4. 3-dimensional representation of elemental composition with respect to the synthesis condition: (a) variation in HCl equivalence @ 80°C, (b) variation in HCl equivalence @ 100°C, (c) comparison of water modulated samples with unmodulated and HCl modulated sample, (d) change of synthesis temperature at constant 4 equi. HCl, (e) change of synthesis temperature at constant 12 equi. HCl, and (f) increase of COOH concentration by increase in HCl concentration @120°C.

Table S3. Elemental composition of Zr, C, O in the synthesized UiO-66 samples.

Sample description	Zr 3d		O 1S			C 1S		
	Zr $3d_{5/2}$	**Zr $3d_{3/2}$**	**COOH**	**Zr-O-C**	**Zr-O-Zr**	**C=O**	**C-O**	**C-C**
S1	60.27	39.73	32.14	43.44	24.42	21.06	19.74	59.20
S2	61.27	38.73	37.11	39.39	23.5	20.28	16.90	62.82
S3 – A	61.18	38.82	39.39	38.95	21.66	22.62	13.84	63.54
S3 – B	61.61	38.39	39.28	41.71	19.01	22.65	5.78	71.57
S3 – C	61.57	38.43	38.86	43.52	17.62	24.87	11.12	64.01
S4 – A	61.24	38.76	24.86	53.67	21.47	21.68	16.2	62.12
S4 – B	61.89	38.11	34.35	46.08	19.57	22.42	3.51	74.07
S4 – C	61.70	38.30	36.67	44.12	19.21	19.63	2.02	78.35
S5 – 0	61.26	38.74	17.08	66.08	16.84	19.58	6.72	73.7
S5 – A	61.68	38.32	19.98	63.38	16.64	22.58	2.61	74.81
S5 – B	61.92	38.08	34.4	45.01	20.60	23.97	7.61	68.42
S5 – C	62.19	37.81	33.58	46.41	20.01	22.94	71.84	5.23
S6 – A	58.03	41.97	34.46	44.02	21.52	21.18	24.90	53.92
S6 – B	61.39	38.61	37.17	38.54	24.29	20.60	14.50	64.90

Section S4: N_2 adsorption-desorption Isotherm

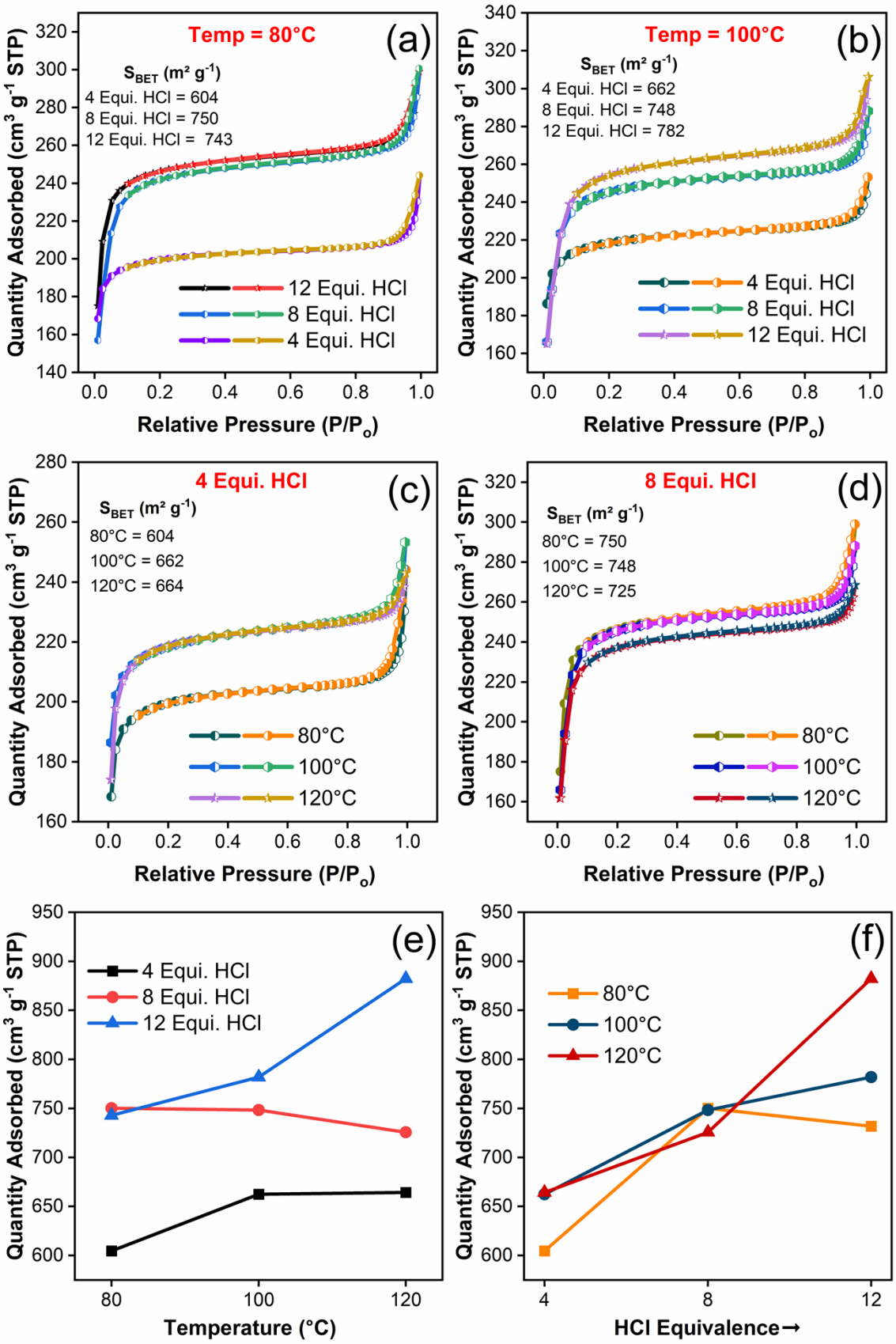


Fig. S5. N_2 adsorption-desorption pattern of UiO-66 samples: various HCl equivalence @ 80°C (a), @100°C (b), 4 equivalence at various synthesis temperature (c), 8 at various synthesis temperature equivalence (d), Changes in BET surface with respect to the HCl equivalence (e) and synthesis temperature (f).

Table S4. Estimated BET surface area, pore volume and pore size distribution from N_2-isotherm analysis.

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)**	**Micropore s %**	**Mesopore s %**
S3 – A	604	9.19	0.3776	0.2772	0.1004	73.4	26.6
S3 – B	750	6.77	0.4623	0.3281	0.1342	70.9	29.1
S3 – C	743	6.88	0.4650	0.3113	0.1537	66.9	33.1
S4 – A	662	6.50	0.3917	0.2979	0.0938	76.1	23.9
S4 – B	748	5.82	0.4456	0.3123	0.1333	70.1	29.9
S4 – C	782	5.70	0.4735	0.3040	0.1695	64.2	35.8
S5 – 0	635	7.69	0.3856	0.2892	0.0964	75	25
S5 – A	664	5.09	0.3757	0.3011	0.0746	80.2	19.8
S5 – B	725	4.74	0.4153	0.3091	0.1062	74.4	25.6
S5 – C	882	5.08	0.4761	0.3311	0.145	69.5	30.5
S6 – A	611	12.73	0.4881	0.2652	0.2229	54.3	45.7
S6 – B	669	9.84	0.4693	0.2879	0.1814	61.3	38.7

Section S5: Estimation of missing linker defects from TGA plateau

The chemical reaction of ideal defect free UiO-66 can be represented as,

$$Zr_6O_6(BDC)_6 + 57\ O_2\ (g) \rightarrow 6\ ZrO_2 + 48\ CO_2(g) + 12\ H_2O\ (g) \text{.....(1)}$$

Molecular weight of ideal UiO-66 (Zr_6O_6 $(BDC)_6$) = 1626.28 g mol^{-1}

Total number of linker molecules per Zr cluster = 6

Weight of residual ZrO_2 = 739.34 g mol^{-1}

Normalized weight of dehydroxylated UiO-66 (Zr_6O_6 $(BDC)_6$) = 220.20%

The theoretical weight loss corresponds to per linker:

$$W_{th-UiO-66} = \frac{(220.20 - 100)}{6}\% = 20\% \text{.....(2)}$$

The number of experimental linkers per defective Zr_6 – SBU,

$$N_{missed\ linkers} = \frac{(Weight\ loss_{exp} - 100\%)}{20\%} \text{.....(3)}$$

The number of linker deficiencies (x) per Zr_6 cluster can be calculated by following equation and fitted to empirical molecular formula $Zr_6O_{6+x}(BDC)_{6-x}$,

$$x = 6 - N_{missed\ linkers} \text{.....(4)}$$

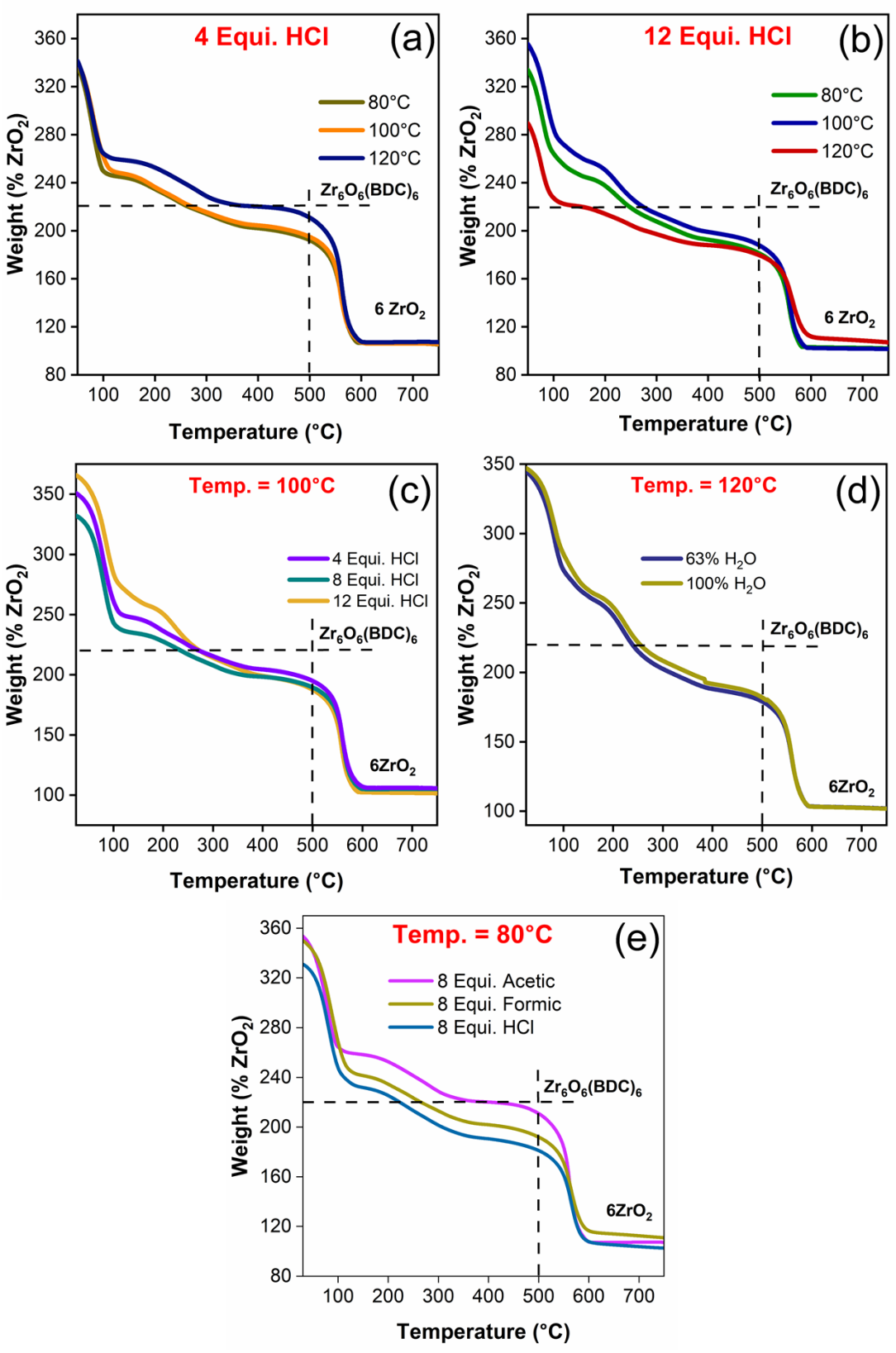


Fig. S6. TGA plateau of UiO-66 synthesized samples under different synthesis condition: (a) 4 Equi. HCl modulated sample at 80, 100 & 120°C, (b) 12 Equi. HCl modulated sample at 80, 100 & 120°C, (c) influence of various HCl equivalence at 100°C, (d) influence of water equivalence at 120°C, and (e) influence of modulators at 80°C.

Table S5. Calculated values of weight loss, missed linkers and corresponding deficiency of as synthesized UiO-66 samples.

Sample description	**Weight loss $_{exp}$ %**	**N $_{missed\ linkers}$**	**Linker deficiencies (x)**	**$Zr_6O_{6+x}(BDC)_{6-x}$**	**Final residue (wt. %)**
S1	212.32	5.616	0.384	$Zr_6O_{6.38}(BDC)_{5.61}$	28.13
S2	193.30	4.665	1.335	$Zr_6O_{7.33}(BDC)_{4.66}$	28.35
S3 – A	192.16	4.608	1.392	$Zr_6O_{7.39}(BDC)_{4.61}$	28.41
S3 – B	181.11	4.0555	1.9445	$Zr_6O_{7.94}(BDC)_{4.06}$	29.98
S3 – C	180.93	4.0465	1.9535	$Zr_6O_{7.95}(BDC)_{4.05}$	28.67
S4 – A	194.92	4.746	1.254	$Zr_6O_{7.25}(BDC)_{4.75}$	28.24
S4 – B	189.45	4.4725	1.5275	$Zr_6O_{7.53}(BDC)_{4.47}$	29.86
S4 – C	187.63	4.3815	1.6185	$Zr_6O_{7.62}(BDC)_{4.38}$	27.14
S5 – 0	219.87	5.9935	0.0065	$Zr_6O_6(BDC)_{5.99}$	26.89
S5 – A	210.94	5.547	0.453	$Zr_6O_{6.45}(BDC)_{5.55}$	27.79
S5 – B	211.21	5.5605	0.4395	$Zr_6O_{6.44}(BDC)_{5.56}$	26.89
S5 – C	184.68	4.234	1.766	$Zr_6O_{7.76}(BDC)_{4.24}$	32.98
S6 – A	179.08	3.954	2.046	$Zr_6O_{8.04}(BDC)_{3.96}$	28.70
S6 – B	182.09	4.1045	1.8955	$Zr_6O_{7.89}(BDC)_{4.11}$	28.61

Section S6: FTIR analysis

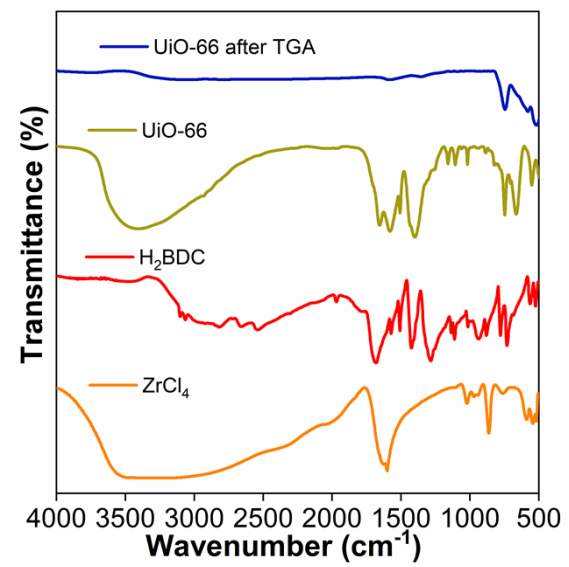
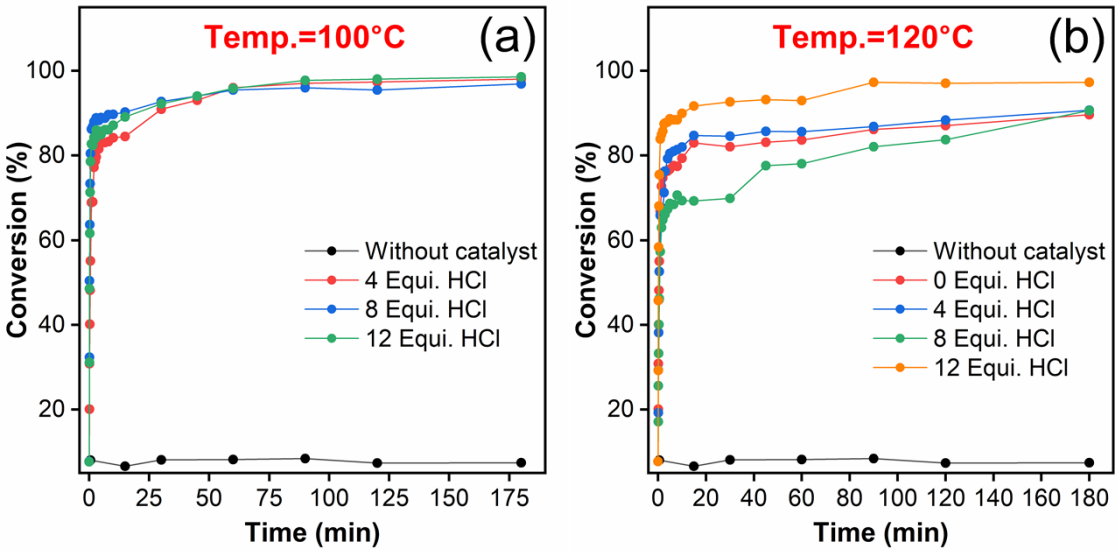


Fig. S7. FTIR spectra of $ZrCl_4$ precursor (orange), H_2BDC (red), 8 Equi. HCl modulated UiO-66 synthesized at 80°C (olive green) and the corresponding UiO-66 after TGA.

Section S7: Conversion of DMNP



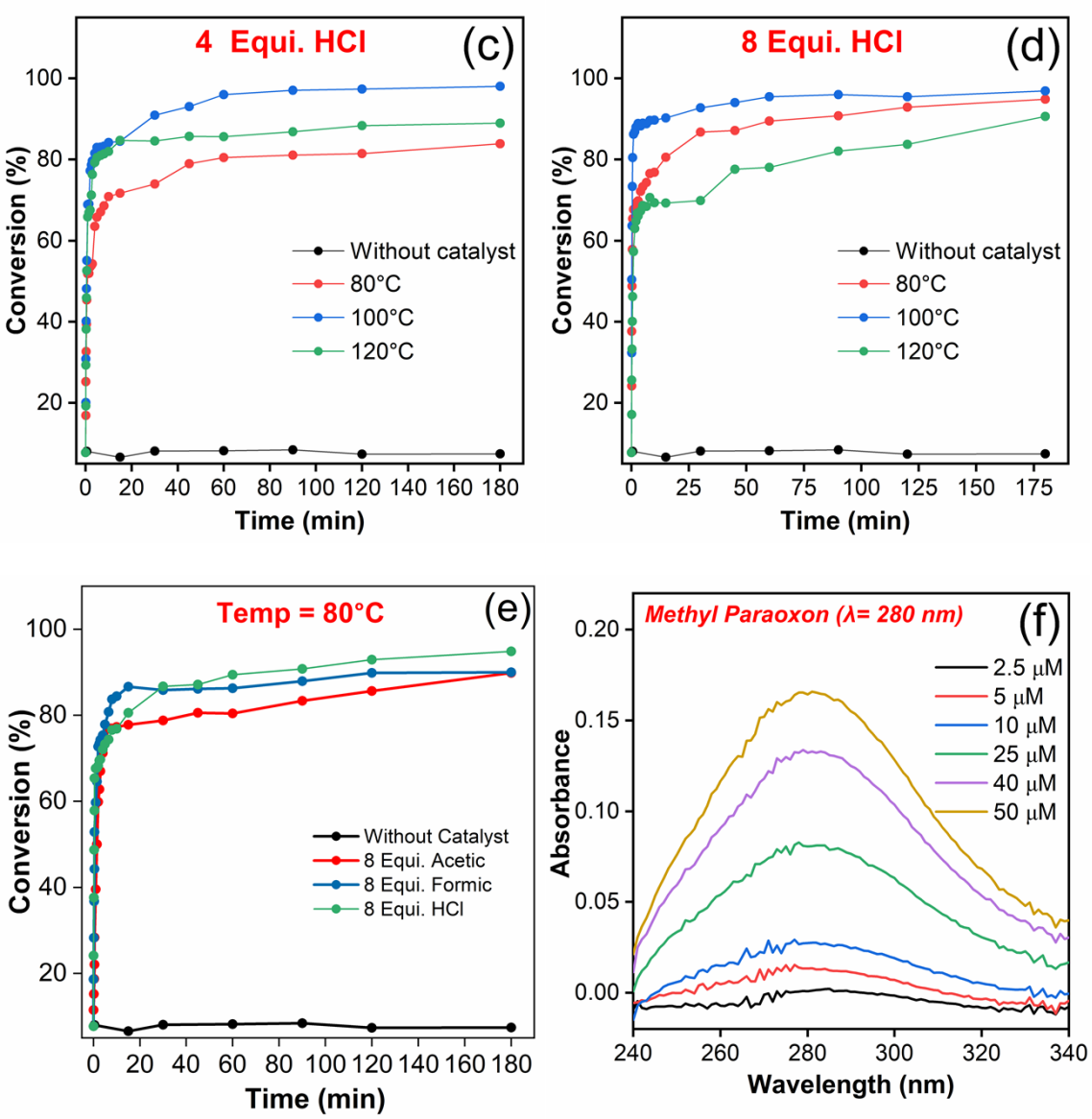


Fig. S8. Conversion profile of DMNP by UiO-66 with respect to its synthesis temperature (a, b) and HCl equivalence (c, d), modulators pKa (e), and calibration curve of DMNP stock for different concentration (f).

Table S6. Zeta potential analysis of modulators assisted UiO-66 samples.

S. No.	Sample Description	Zeta potential (mV)	Conversion Efficiency (%)
1.	S1 (8 Equi. Acetic acid)	31.6	89.8
2.	S2 (8 Equi. Formic acid)	30.2	90.0
3.	S3-B (8 Equi. HCl)	13.4	94.9