Supporting Information (SI)

Improving the capability of UiO-66 for Cr(VI) adsorption from aqueous solutions by introducing the isonicotinate N–Oxide as the functional group

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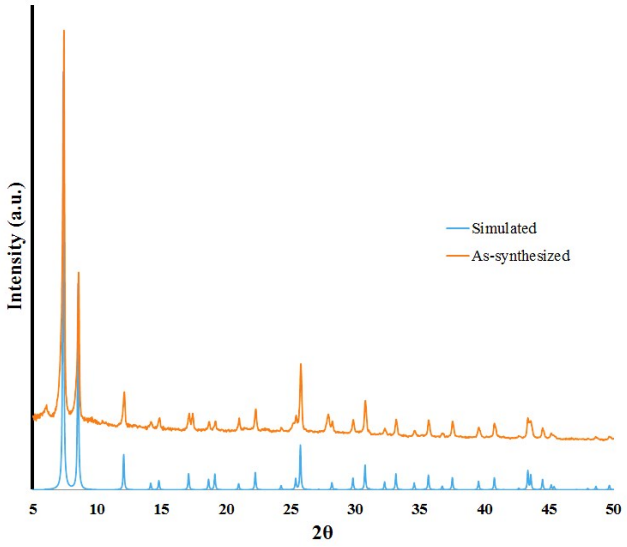
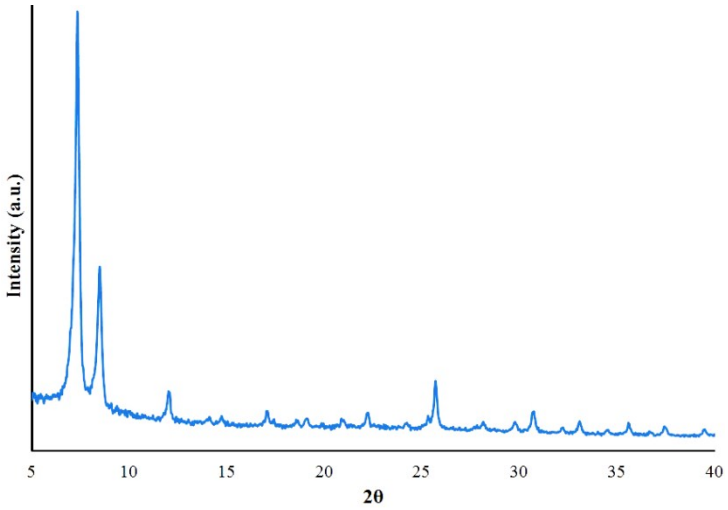
Table S1. Experimental parameters for synthesis of the compounds.

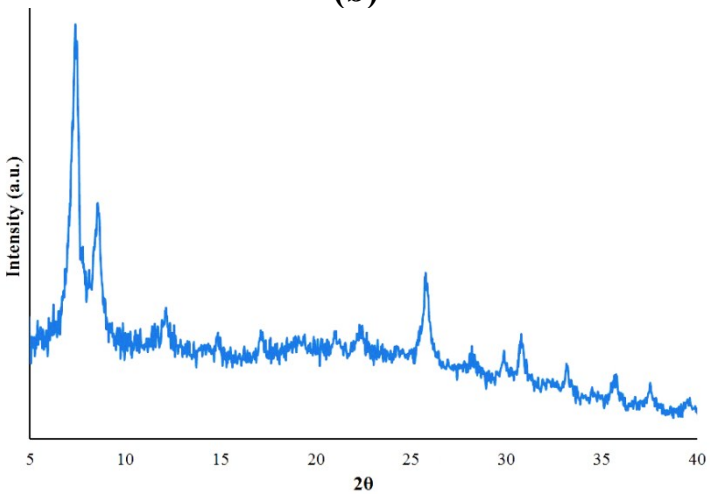
Compound	Ligand mass (X=BDC) (mg)	Ligand mass (Y=INO) (mg)	$ZrCl_4$ mass (mg)	HCl volume (µL)	DMF volume (mL)	Activation temperature (°C)
UiO-66	332 (2 mmol)	0	233 (1 mmol)	34.5	10	120
UiO-66-30%	166 (1 mmol)	139 (1 mmol)	233 (1 mmol)	34.5	10	120
UiO-66-50%	99 (0.6 mmol)	195 (1.4 mmol)	233 (1 mmol)	34.5	10	120
UiO-66-70%	50 (0.3 mmol)	236 (1.7 mmol)	233 (1 mmol)	34.5	10	120
TMU-66	0	278 (2 mmol)	233 (1 mmol)	34.5	10	120



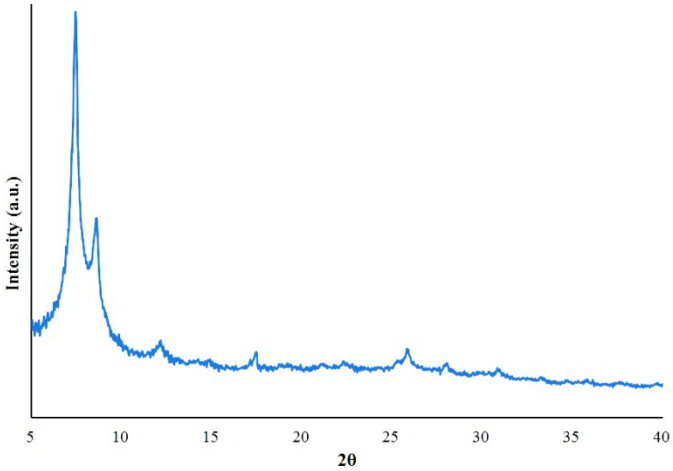
(a)



(b)



(c)



(d)

Figure S1. PXRD patterns of structures: a) as-synthesized and simulated UiO-66, b) UiO-66-30%, c) UiO-66-50%, d) UiO-66-70%.

Table S2. The area under the curve in NMR spectra.

Sample	The area under the curve in NMR spectra		BDC:INO
	7.97 ppm*	8.50 ppm	
UiO-66-30%	0.821	0.1790	7:3
UiO-66-50%	0.2545	0.1354	1:1
UiO-66-70%	0.1932	0.2961	3:7

*Singlet peak located at 7.97 ppm is attributed to BDC linker. The area under the curve of BDC is twice INO.

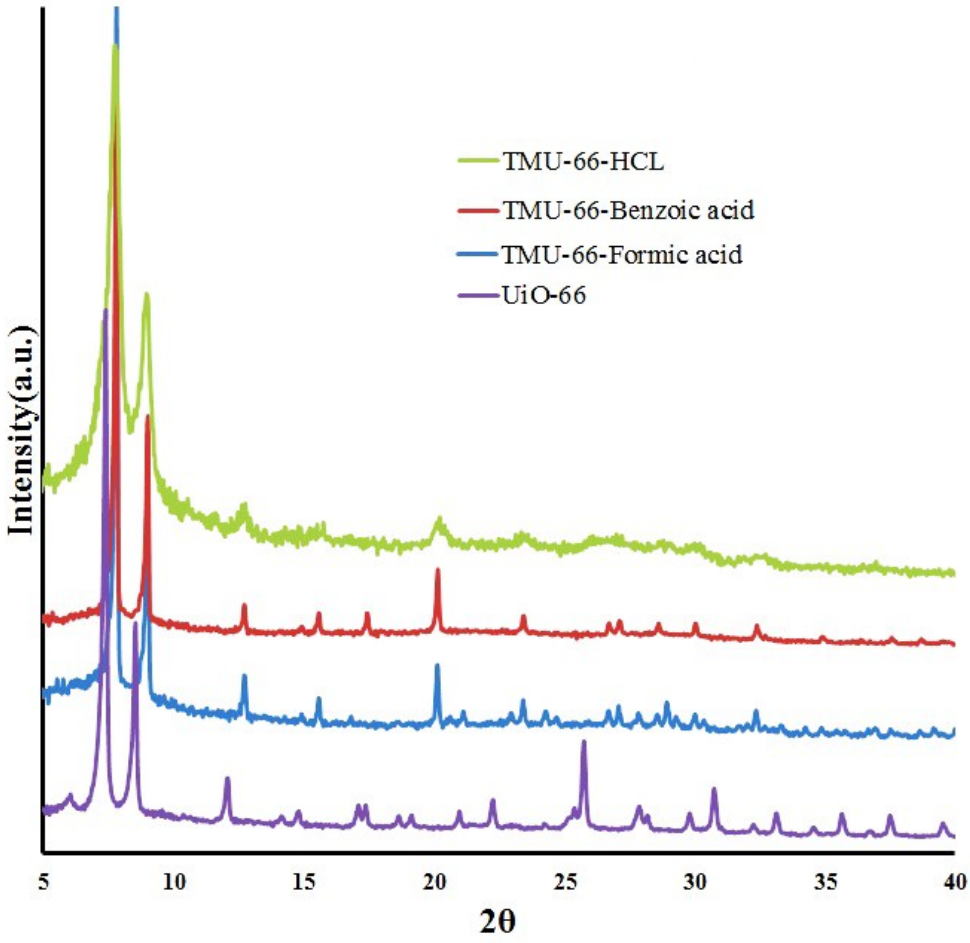


Figure S2. Comparison of the PXRD patterns UiO-66 with TMU-66 was synthesized with modulators and HCl.

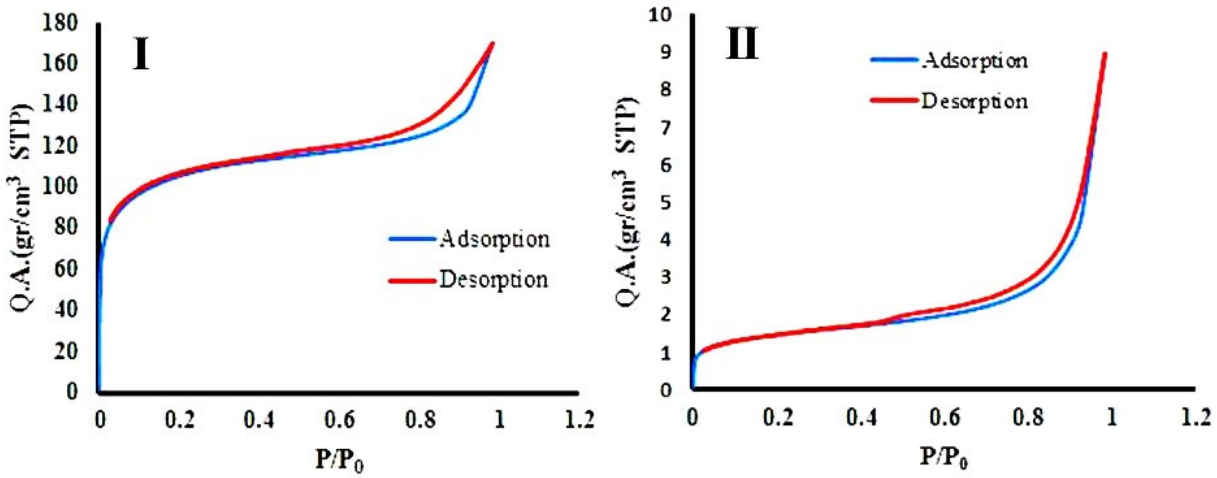


Figure S3. Nitrogen gas adsorption-desorption isotherms: (I) benzoic acid-synthesized TMU-66; and (II) HCl-synthesized TMU-66.

Table. S3. Elemental analysis of TMU-66.

Complex	%C	%H	%N	%Zr
Observed HCl-synthesized TMU-66	27.57	3.04	6.01	27.35
Calculated for $Zr_6O_4(OH)_4(INO)_6(Cl)_4(OH)_2(DMF)_3(H_2O)_4$	27.35	2.99	6.38	27.72
Observed benzoic acid (BzO) -synthesized TMU-66	38.63	3.52	5.33	25.76
Calculated for $Zr_6O_4(OH)_4(INO)_6(BzO)_4(OH)_2(DMF)_2$	38.69	2.95	5.16	25.20

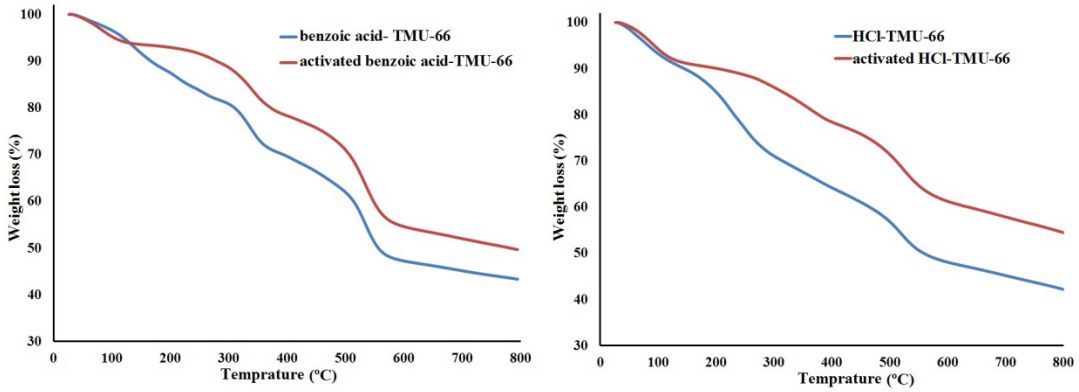


Figure S4. TGA plots of HCl- and benzoic acid-synthesized TMU-66.

Details for crystal structure refinement of TMU-66

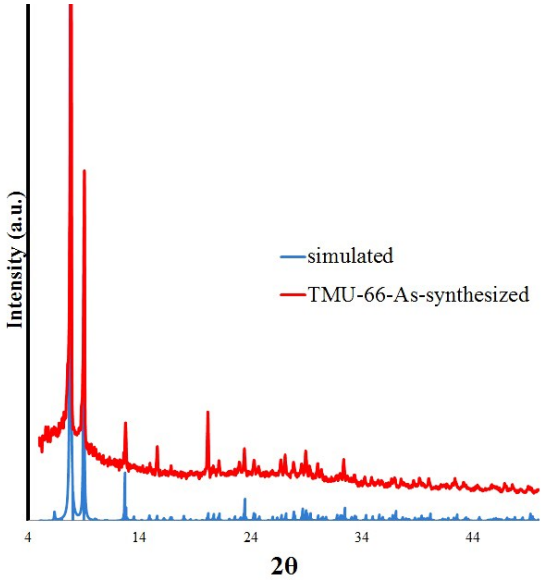


Figure S5. Comparison of the simulated PXRD pattern obtained from synchrotron X-ray with PXRD patterns of TMU-66.

data_TMU-66

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_audit_creation_method 'Materials Studio'

_symmetry_space_group_name_H-M 'PA-3'

_symmetry_Int_Tables_number 205

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loop_

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y,z,x

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O3 O 0.05610 0.94390 0.94390 0.00000 Uiso 1.00

O4 O 0.09600 0.00000 0.17260 0.00000 Uiso 1.00

O5 O 0.36299 -0.00118 0.36088 0.00000 Uiso 1.00

C13 C 0.73570 0.50000 0.31590 0.00000 Uiso 1.00

C15 C 0.85270 0.50000 0.35270 0.00000 Uiso 1.00

C16 C 0.79810 0.50000 0.29810 0.00000 Uiso 1.00

C17 C 0.81590 0.50000 0.23570 0.00000 Uiso 1.00

N19 N 0.70190 0.50000 0.20190 0.00000 Uiso 1.00

C20 C 0.68410 0.50000 0.26430 0.00000 Uiso 1.00

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Zr1 Zr1 3.350 9 S

Zr1 Zr1 3.350 17 S

Zr1 Zr1 3.350 21 S

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Zr1 O5 2.720 18_545 S

Zr1 O3 2.009 21_665 S

Zr1 O5 2.756 2_554 S

O2 C15 1.125 3_645 S

O3 Zr1 2.009 1_566 S

O3 Zr1 2.009 21_566 S

O3 Zr1 2.009 17_566 S

O4 Zr1 2.150 9 S

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O5 Zr1 2.720 24 S

O5 N19 1.776 3_645 S

O5 Zr1 2.756 2 S

C13 C16 1.276 . S

C13 C20 1.436 . S

C15 C16 1.519 . S

C15 O4 1.125 3_655 S

C15 O2 1.125 3_655 S

C16 C17 1.276 . S

C17 C21 1.436 . S

N19 C21 1.276 . S

N19 C20 1.276 . S

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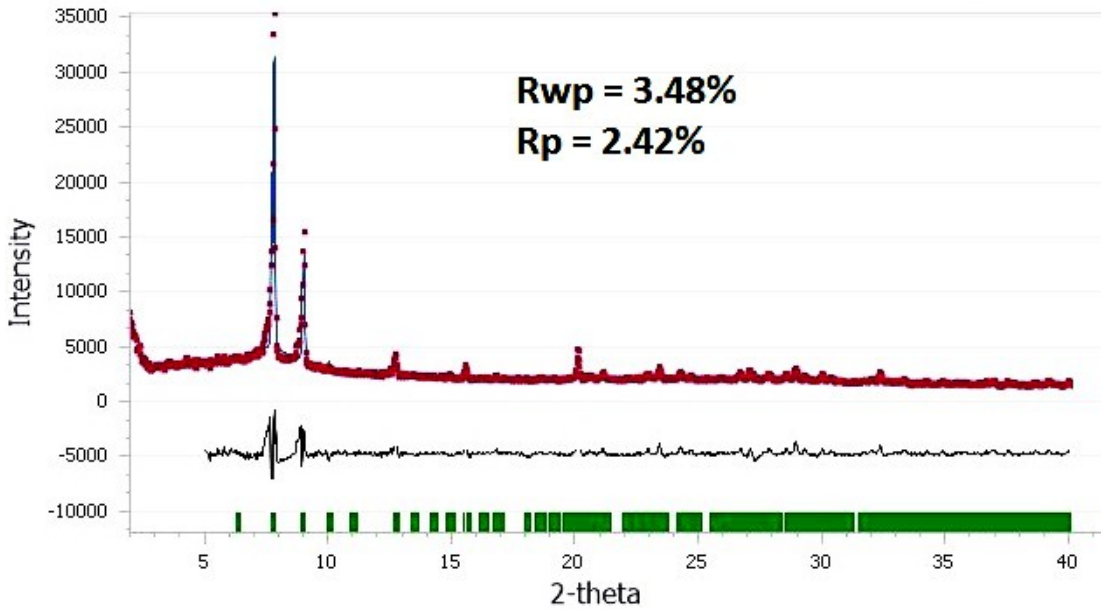

Figure S6. Rietveld plot of TMU-66; red: experimental pattern; blue: calculated pattern; green: Bragg peaks; and black: the difference between the experimental and calculated data.

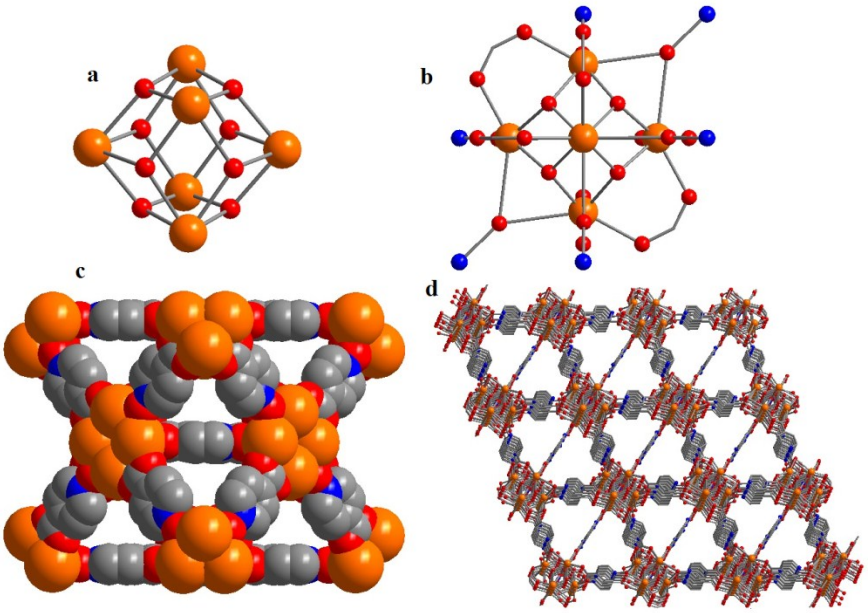

Figure S7. Structural and topological representation of TMU-66: a) $[Zr_6O_4(OH)_4]$ cluster; b) coordination environment around Zr_6 cluster in TMU-66; c) and d) 3-dimensional structures; orange, Zr; red, O; blue, N; and gray, C atoms.

Stability of the compounds

Thermal stability

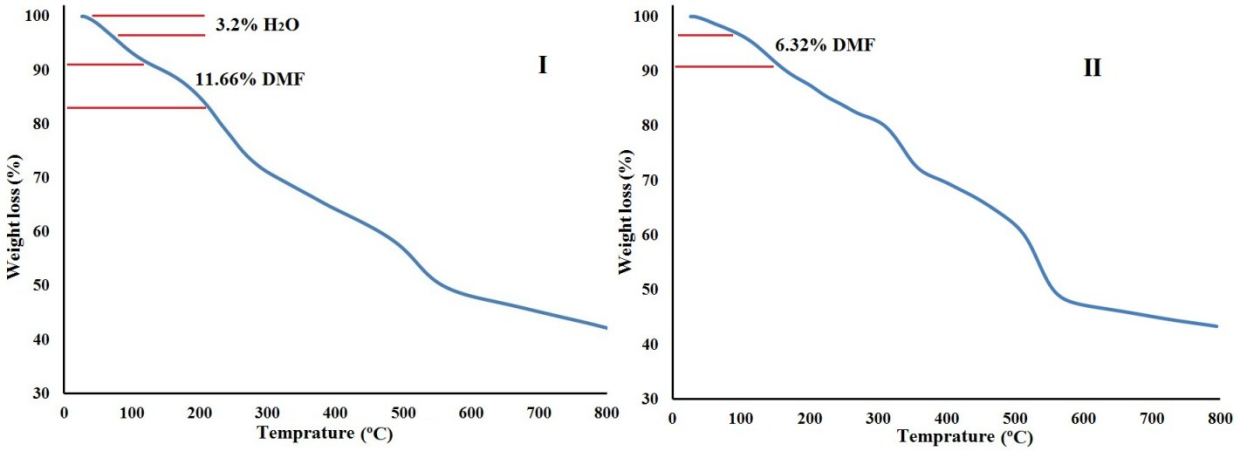

Figure S8. The TGA curves of: I) HCl-synthesized TMU-66 and II) benzoic acid-synthesized TMU-66.

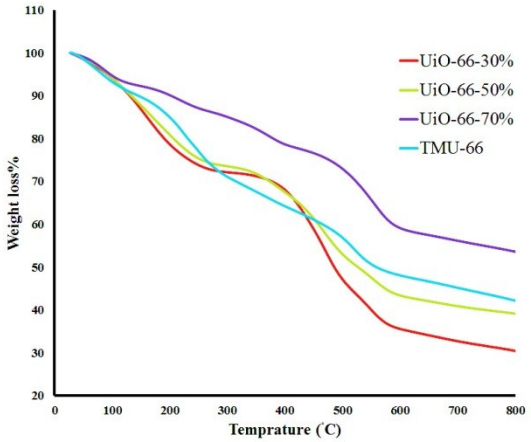

Figure S9. TGA plots of TMU-66 and mixed-ligand compounds.

Chemical stability

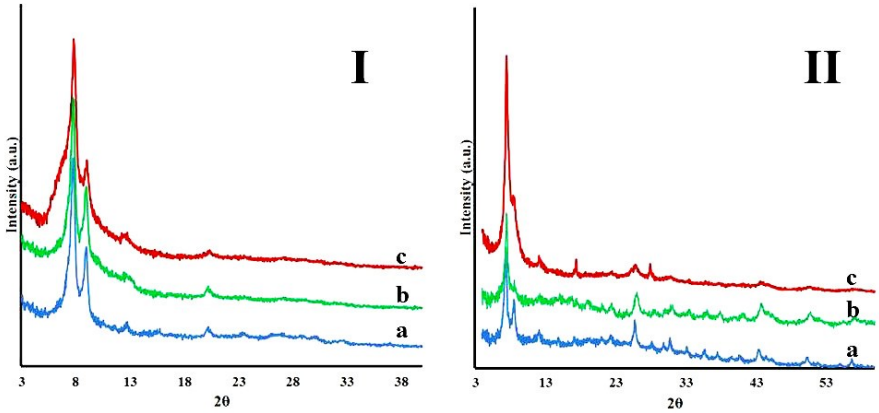

Figure S10. PXRD patterns before and after immersion in H_2O and HCl for 2 h: (I) HCl-synthesized TMU-66; (II) UiO-66-50% (**a**: As-synthesized materials; **b**: in H_2O; and **c**: in HCl).

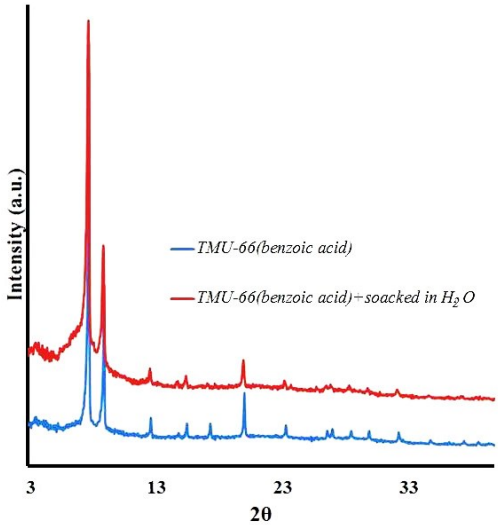

Figure S11. PXRD patterns of benzoic acid-synthesized TMU-66 and the sample immersed in H_2O for 2 h.

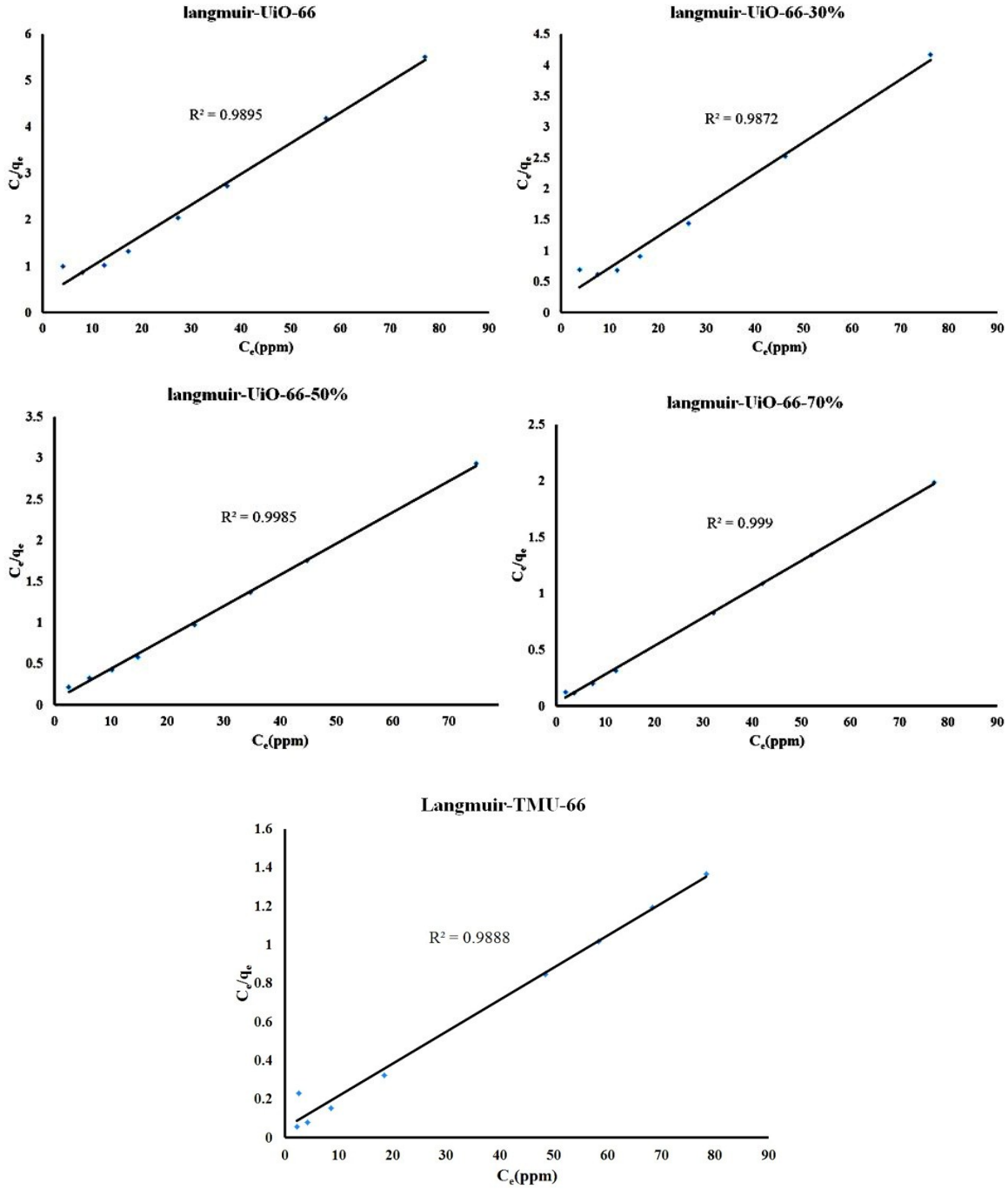

Figure S12. Langmuir linear plots for all of the synthesized compounds (amount of adsorbent: 10 mg, contact time: 2 hours, sample volume: 50 mL, pH: 4.0 and T: 298 K).

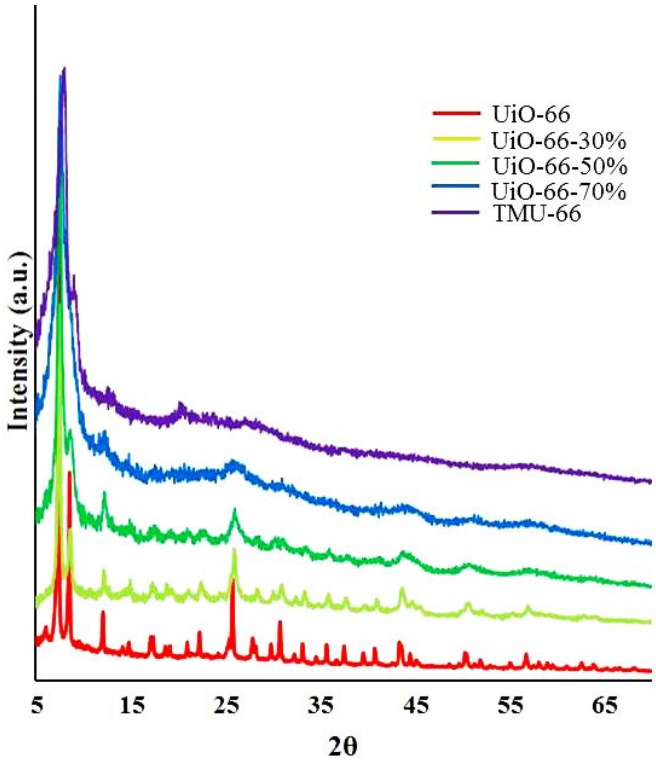

Figure S13. PXRD patterns for TMU-66 and other compounds after Cr(VI) adsorption.

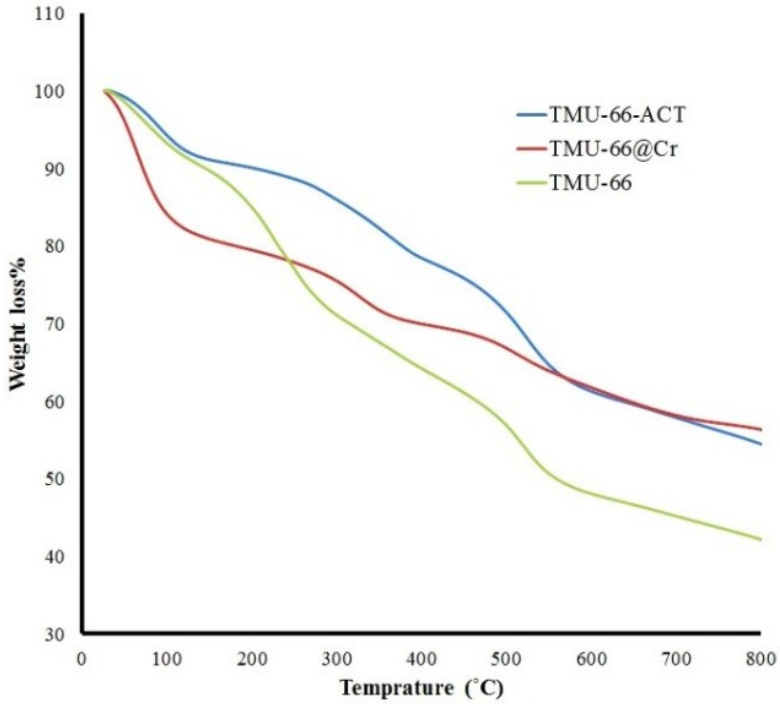

Figure S14. Comparison of TGA profiles before and after Cr(VI) adsorption (ACT means activated).

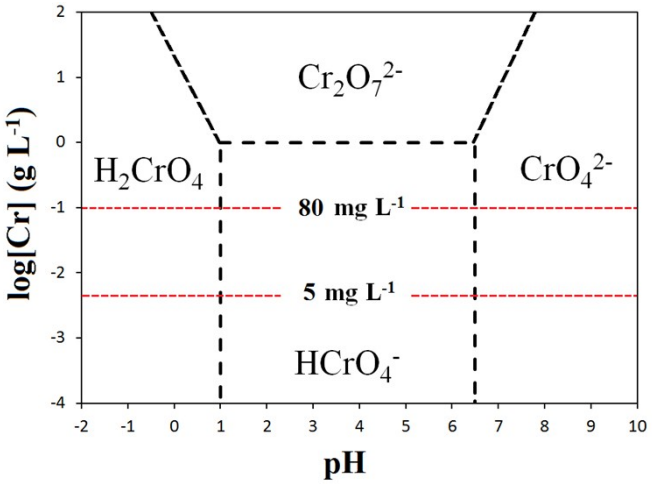

Figure S15. Predominance diagram showing the relative distribution of different Cr(VI) species in water as a function of pH and total Cr(VI) concentration [6].

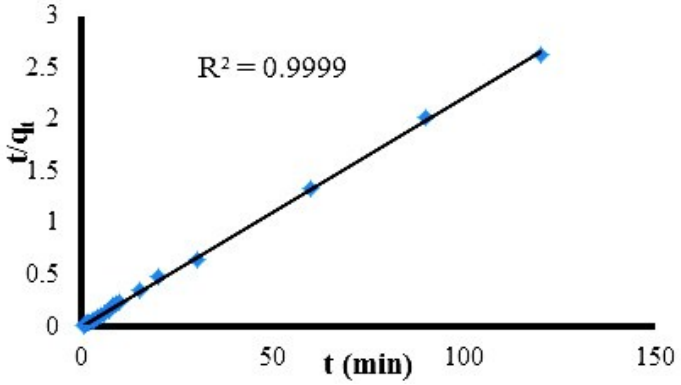

Figure S16. Linear pseudo-second-order kinetic model for adsorption of Cr(VI) on TMU-66 (initial Cr(VI) concentration: 50 mg/L, amount of adsorbent: 10 mg, sample volume: 50 mL, pH: 4.0 and T: 298 K).

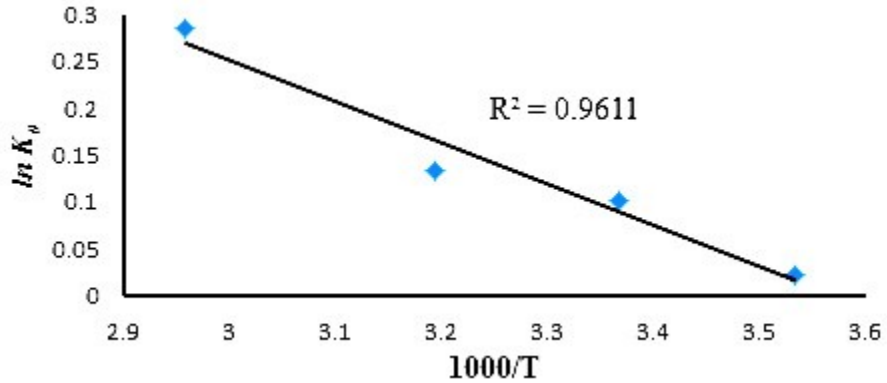

Figure S17. The plot of lnK_0 vs 1/T.

Table. S4. Thermodynamic parameters for Cr(VI) adsorption on TMU-66.

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	R^2
283	-0.027	3.652	0.013	0.9611
297	-0.209			
313	-0.417			
338	-0.742			

Slope = –ΔH/R ✂ ΔH= 3.652 KJ/mol
Intercept = ΔS/R ✂ ΔS= 13.0513 J/mol
ΔG = ΔH–TΔS
ΔS = 13.0513/1000 = 0.013 KJ/mol

Selectivity test for TMU-66

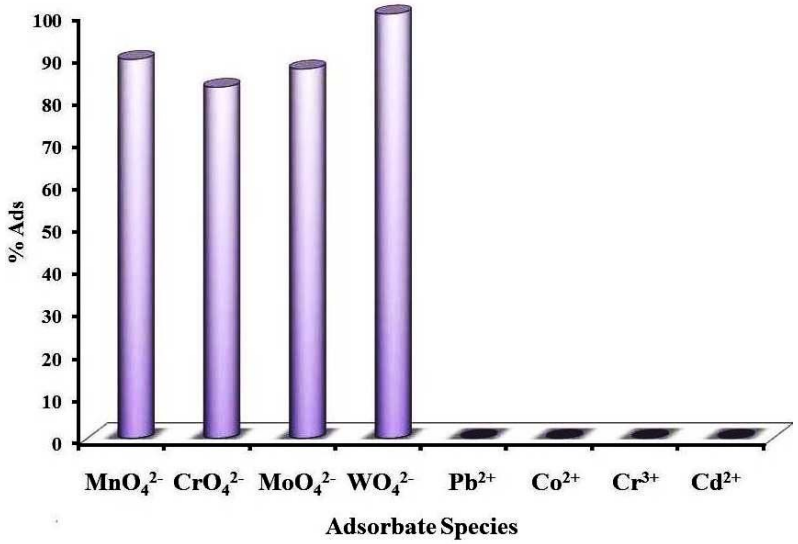

Figure S18. Adsorption of various cationic and anionic adsorbates on TMU-66.

Adsorption mechanism

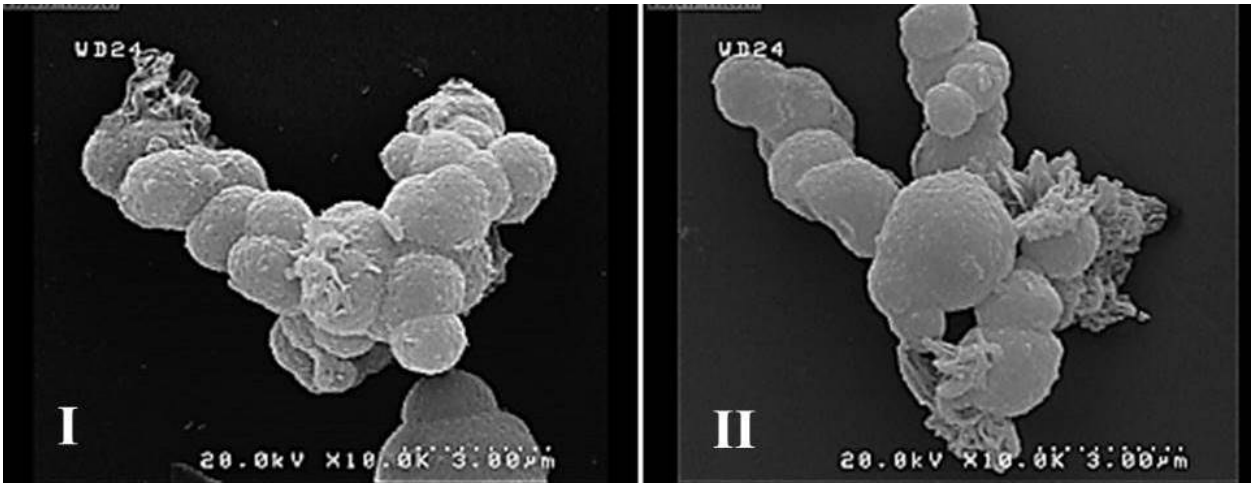

Figure S19. SEM images: (I) as-synthesized TMU-66; (II) Cr(VI)-adsorbed TMU-66.

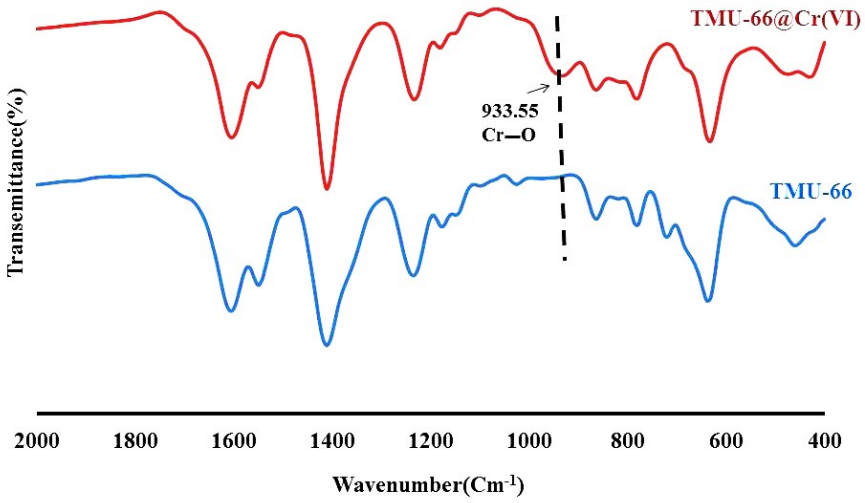

Figure S20. FT-IR spectra for TMU-66 before and after the Cr(VI) adsorption.

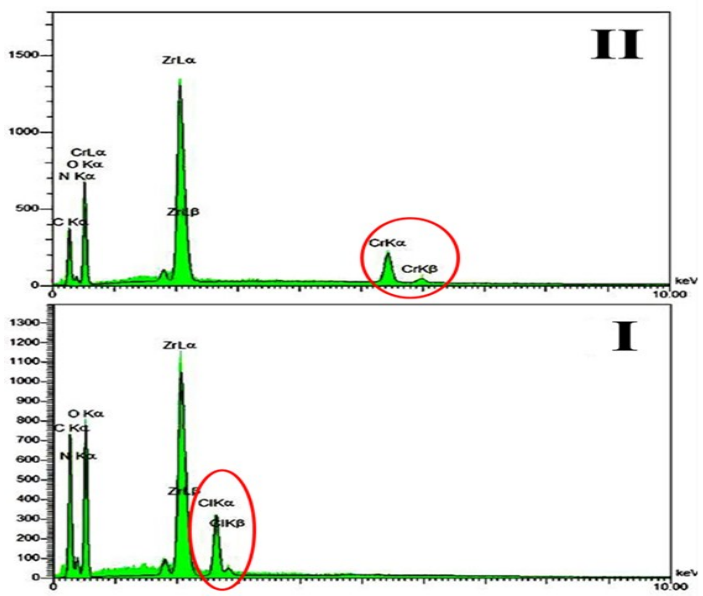

Figure S21. EDS images of TMU-66 for: (I) as-synthesized TMU-66; (II) Cr(VI)-adsorbed TMU-66.

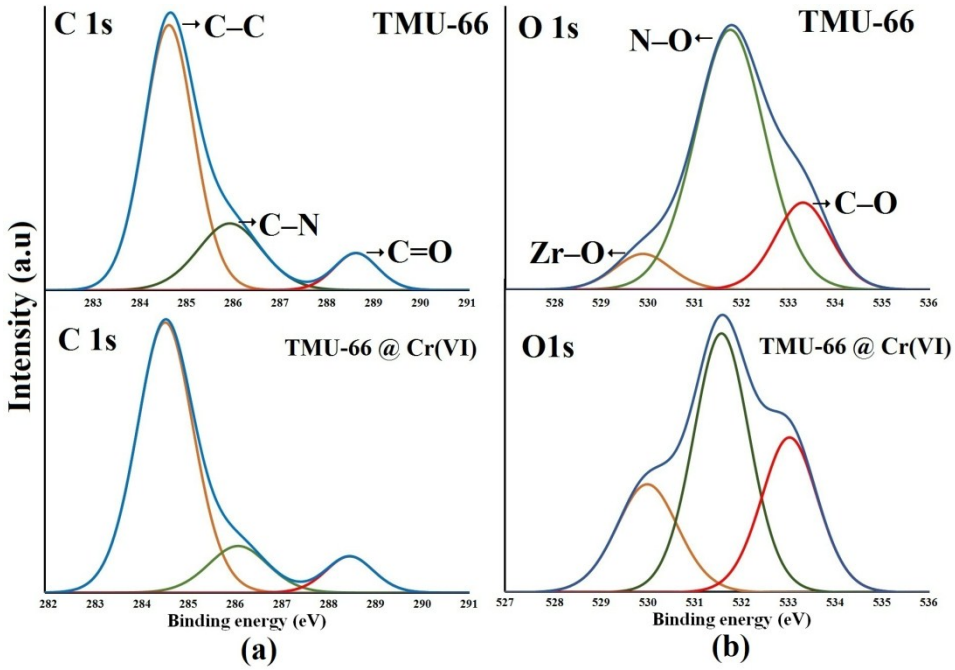

Figure S22. High-resolution XPS spectra of: a) C 1s and b) O 1s.

Table S5. Adsorption Capacities and Time of Equilibrium for Cr(VI) on Various MOFs.

MOF adsorbent		Maximum capacity (mg/g)	Kinetic studies: Equilibrium time at RT	BET surface area (m^2/g)	Ref.
Zr-MOFs	MOF-867	53	> 12 h	1862	1
	NU-1000	75	< 3 min	2072	2
	JLU-MOF50	92	< 10 min	1101	3
	TMU-66	60	< 3 min	79	This study
	UiO-66	15	NM	1350	This study
	UiO-66-NH_2	32	> 5 min	710	4
	PCN-134	57	> 10 min	1946	5
Other MOFs	1.ClO4	63	6 h	NM	6
	SLUG-21	60	48 h	NM	7
	TMU-30	145	< 10 min	NM	8
	1·SO4	166	72 h	NM	9

NM: not measured.

References

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