Supporting information

A new porphyrinic vanadium-based MOF constructed from infinite $V(OH)O_4$ chains: syntheses, characterization and photoabsorption property

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Section S1. Optimal conditions for synthesis of V-MOF-10

No.	Parameter	Result	Comment
1	Molar ratio of VCl_3 : H_2O	The ratio of 2.2:1 supports the formation of V-MOF-10 structure.	High crystallinity quality.
2	Addition of DMF as a solvent	Generation of crystalline X-ray products.	
3	Addition of acetic acid as a modulator	Increase of the crystallinity of V-MOF-10.	High crystallinity quality and reproducibility level more than 80% with introduced acetic acid (150 µL).
4	Temperature	At T ≥ 165 ^{o}C, V-MOF-10 is significantly lost the structural order. At T ≤ 100 ^{o}C, V-MOF-10 structure is not created or found the amorphous X-ray product.	The stable and the best reaction temperature at 150 ^{o}C.
5	Time	2 hours for heating, t hour for reaction, and 4 hours for cooling to room temperature. t < 20 h no formed V-MOF-10. t ≥ 24 h formed V-MOF-10.	The best time for reaction (t) is 24 h.

Section S2. Reaction scheme and microscope image of V-MOF-10

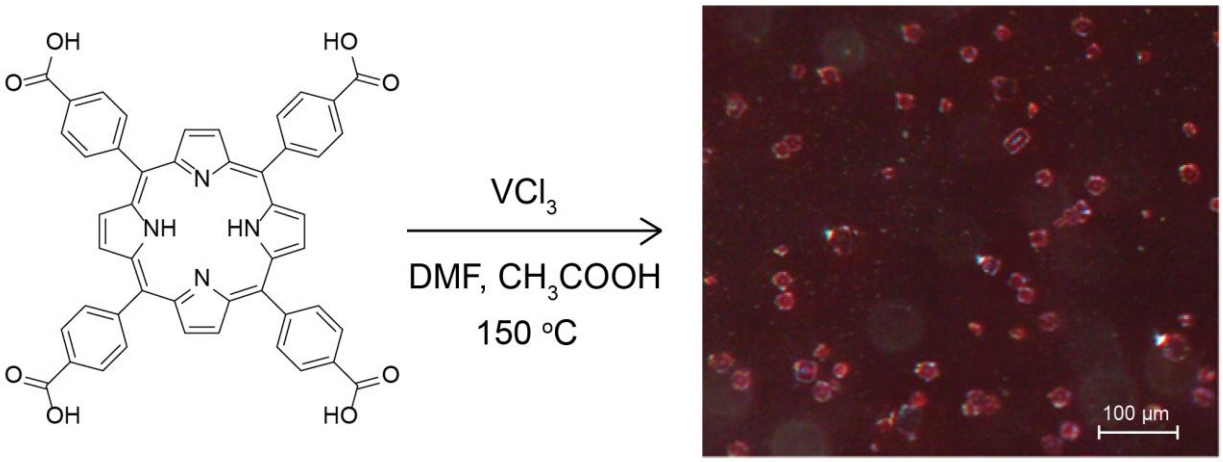


Figure S1. Reaction scheme and microscope image of V-MOF-10 polycrystals.

Section S3. Fourier Transform Infrared Spectroscopy (FT-IR)

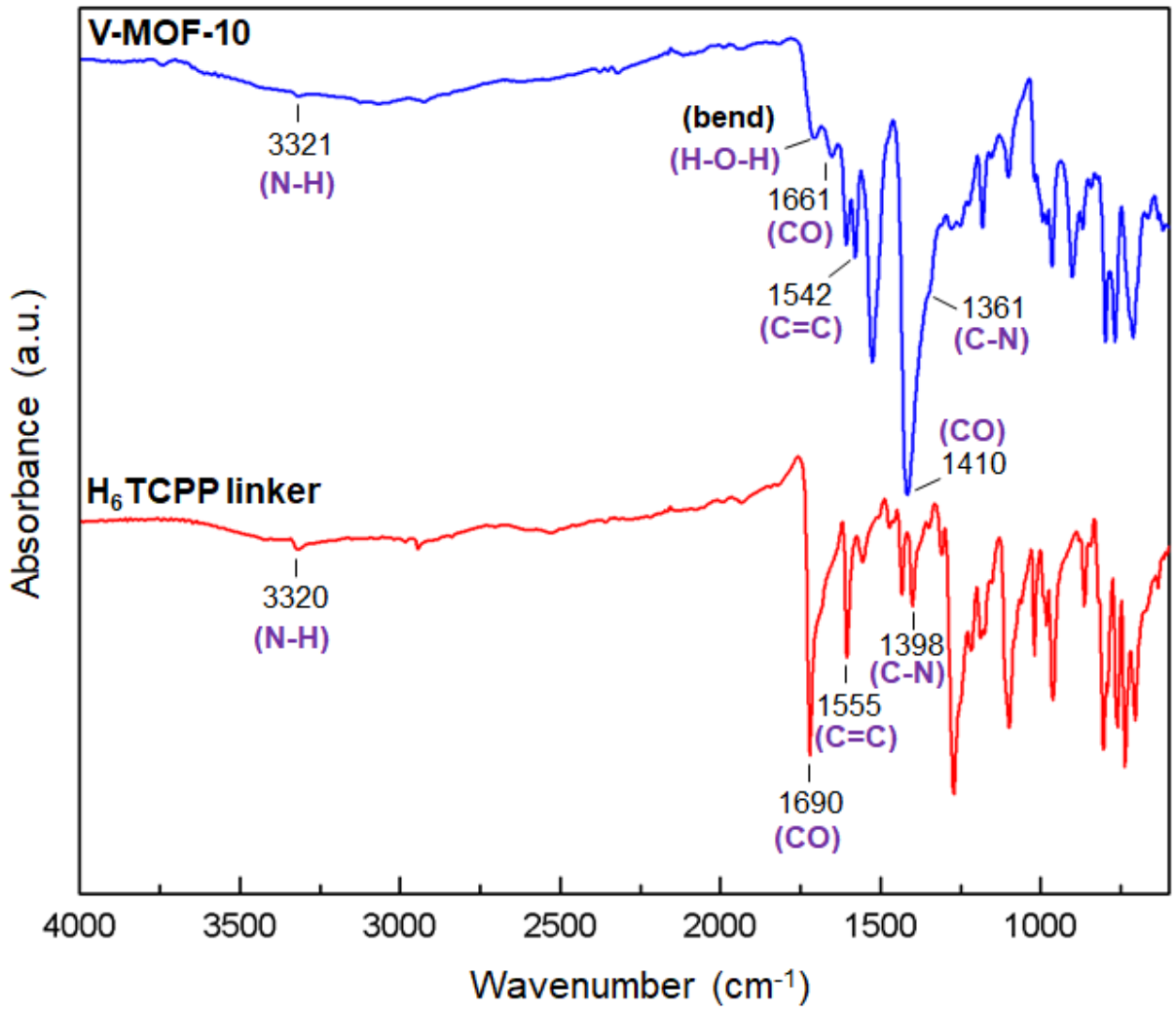


Figure S2. FT-IR spectrum of activated V-MOF-10 (blue) in comparison with porphyrinic linker (red)

Section S4. Nuclear Magnetic Resonance (NMR) Spectroscopy

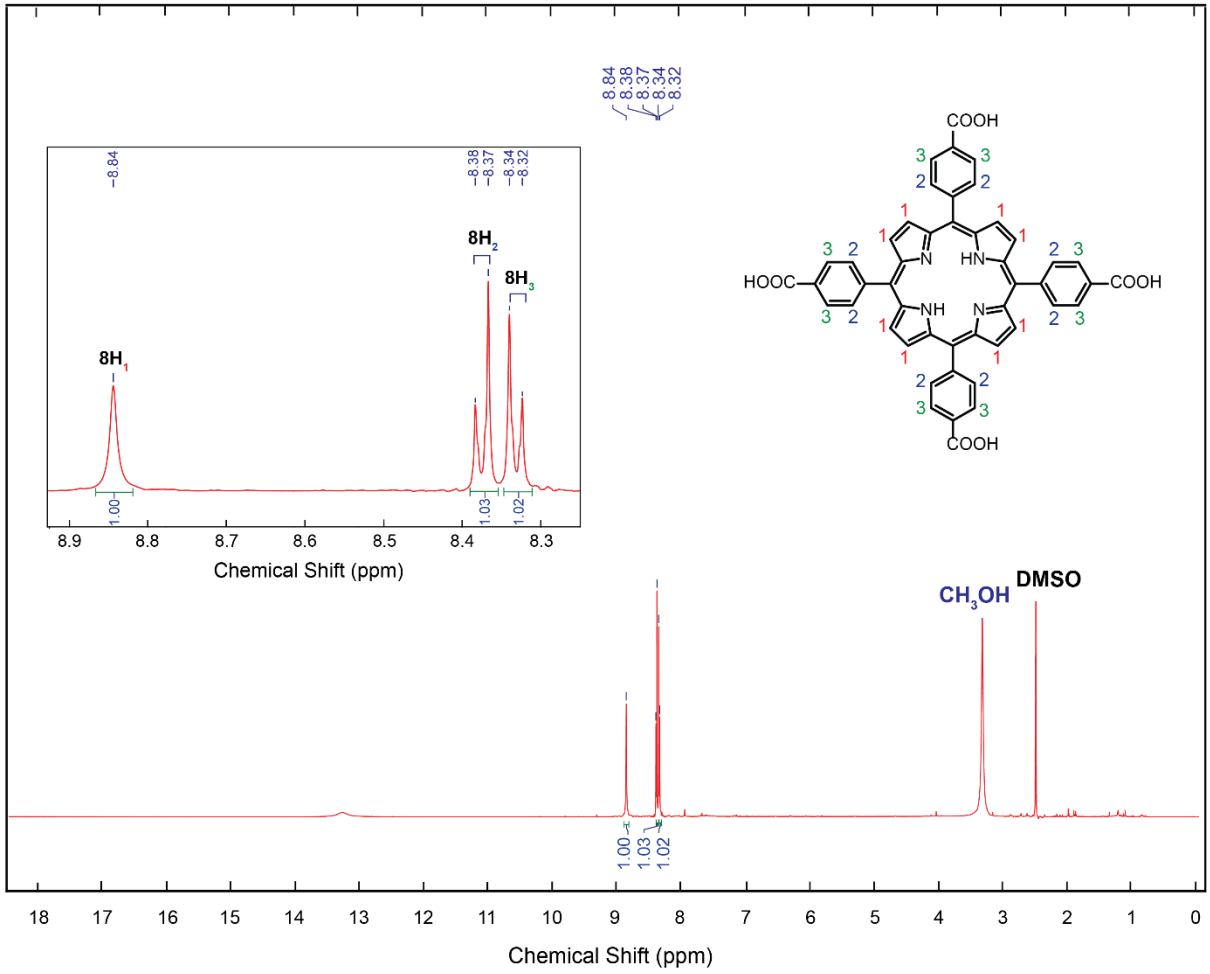


Figure S3. ^{1}H-NMR spectrum of porphyrinic linker (H_6TCPP) in DMSO solvent

Section S5. Powder X-ray Diffraction (PXRD) Analysis

PXRD data collection

PXRD measurements were performed on a Bruker D8 Advance diffractometer in reflectance Bragg-Brentano geometry using Ni filtered Cu Kα focused radiation (1.54059 Å) at 1600 W (40 kV, 40 mA) power, which was equipped with a LynxEye detector. The best counting statistics were obtained by collecting samples using a step scan of 0.02° with 2θ from 3 – 50° and exposure time of 10 s per step. The analysis was conducted at room temperature and atmospheric pressure.

Unit cell determination and structural modeling of V-MOF-10

Unit cell determinations were conducted using *Materials Studio 7.0* software. An initial orthorhombic lattice parameter (a = 31.978 Å, b = 6.5812 Å, c = 16.862 Å) of Al-PMOF material with space group *Cmmm* was chosen for V-MOF-10, in which the Al atoms was substituted by V atoms. Whole pattern profile fitting and extraction of the integrated intensities was performed with data from 2θ = 3 – 50°. A background correction was performed using a 20-parameter Chebyschev polynomial function. Subsequently, the substituted structural model with V atoms was optimized for the generation of an energetic minimization using the universal force field implemented in the *Forcite* module. The unit cell of modeled structure was optimized until the energy convergence reached the value of 0.0001 kcal mol^{-1}.

A full Pawley pattern fitting using synchrotron radiation data from 2θ = 3 – 50° was carried out against the as-synthesized powder pattern of V-MOF-10. The calculated PXRD pattern for modeled structure obtained a good accordance with the experimental PXRD pattern as evidenced by the fitting that converged with reasonable residual values (R_{wp} = 6.91%, R_p = 5.16%) to achieve the unit cell parameters (a = 32.9374(3) Å, b = 6.8549(9) Å, c = 16.6379(9) Å).

To optimize the atom position in the lattice of V-MOF-10, a full range Rietveld refinement has been performed for fitting between the modeled structure and experimental powder pattern with 2θ = 3 – 50°. This resulted a satisfactory agreement with the experimental PXRD pattern at reasonable residual values (R_{wp} = 6.48%, R_p = 4.96%) and the final unit cell parameters (a = 32.9288(4) Å, b = 6.8495(7) Å, c = 16.5912(1) Å). The fractional atomic coordinates and refined cell parameters for V-MOF-10 after the Rietveld fitting could be identify in Table S1 and crystal structure information was indicated in Table S2.

Table S1. Atomic coordinates and refined unit cell parameters of V-MOF-10 after Rietveld refinement

Name	V-MOF-10			
Space Group	*Cmmm* (No. 65)			
***a* (Å)**	32.9288(4)			
***b* (Å)**	6.8495(7)			
***c* (Å)**	16.5912(1)			
Unit Cell Volume (Å^3)	3742.12(1)			
R_{wp}	6.48%			
R_p	4.96%			
Atom Name	*x*	*y*	*z*	Site occupancy
O1	0.78861	0.13200	0.92541	0.00000
C1	0.89160	0.16373	0.77171	0.00000
C2	0.86084	0.15371	0.82929	0.02000
V1	0.25839	0.16874	-0.00009	0.01000
O2	0.27738	-0.04817	-0.00010	0.00000
C3	0.80355	-0.02503	0.89583	0.01000
C4	0.96983	0.03073	0.67878	0.16000
C5	0.98332	0.02975	0.76149	0.00000
C6	0.91761	0.02110	0.56850	0.01000
C7	0.87558	0.01834	0.54324	0.00000
C8	0.92965	0.02411	0.65113	0.00000
C9	0.89742	0.01367	0.71451	0.00000
C10	0.83559	-0.01017	0.83290	0.06000
N1	0.94267	0.02268	0.50214	0.03000
N2	-0.00015	0.03225	0.63125	0.00000
O3	0.20886	0.77254	0.92355	0.09000
O4	0.79576	0.78449	0.07817	0.06000
O5	0.21781	0.12490	0.08498	0.11000
O6	0.20903	0.77346	0.08229	0.03000
O7	0.78562	0.13428	0.08731	0.09000
O8	0.21754	0.12406	0.92099	0.11000
O9	0.79242	0.77882	0.91790	0.00000
O10	0.28419	0.61186	0.92095	0.00000
O11	0.71180	0.29059	0.92228	0.04000
O12	0.29311	0.28596	0.08185	0.01000
O13	0.72056	0.62205	0.08637	0.05000
O14	0.71091	0.29689	0.08137	0.00000
O15	0.28420	0.61176	0.08470	0.25000
O16	0.71799	0.61781	0.92273	0.06000
O17	0.29284	0.28589	0.92315	0.00000
C11	0.10815	0.82534	0.76916	0.00000
C12	0.89579	0.82903	0.23497	0.00000
C13	0.13611	0.15630	0.28349	0.00000
C14	0.10823	0.82657	0.23609	0.00000
C15	0.86898	0.16167	0.28151	0.05000
C16	0.13578	0.15650	0.72285	0.00000
C17	0.87162	0.82546	0.71829	0.00000
C18	0.36572	0.64411	0.72216	0.00000
C19	0.60988	0.34086	0.76964	0.00000

C20	0.39418	0.34141	0.23535	0.04000
C21	0.63817	0.65155	0.28381	0.05000
C22	0.61030	0.34815	0.23559	0.00000
C23	0.36611	0.64548	0.28235	0.00000
C24	0.63752	0.64578	0.72258	0.00000
C25	0.39367	0.33989	0.76922	0.00000
C26	0.13866	0.81038	0.82695	0.00000
C27	0.86524	0.81609	0.17719	0.00000
C28	0.16611	0.14517	0.22436	0.11000
C29	0.13882	0.81175	0.17851	0.00000
C30	0.83889	0.15174	0.22260	0.02000
C31	0.16578	0.14483	0.78198	0.00000
C32	0.84151	0.81225	0.77695	0.00000
C33	0.33581	0.63282	0.78147	0.02000
C34	0.64045	0.32630	0.82734	0.00000
C35	0.36358	0.32566	0.17778	0.01000
C36	0.66822	0.64111	0.22476	0.00000
C37	0.64093	0.33400	0.17807	0.47000
C38	0.33611	0.63346	0.22325	0.00000
C39	0.66745	0.63509	0.78187	0.00000
C40	0.36316	0.32487	0.82700	0.00000
V2	0.75990	0.66503	-0.00137	0.04000
V3	0.24346	0.65585	0.00011	0.01000
V4	0.74609	0.17787	0.00091	0.04000
O18	0.72681	-0.03852	-0.00083	0.02000
O19	0.77937	0.44891	-0.00147	0.00000
O20	0.22443	0.43899	0.00009	0.05000
C41	0.20002	-0.03210	0.89674	0.00000
C42	0.80400	-0.02255	0.10818	0.00000
C43	0.20029	-0.03117	0.10924	0.00000
C44	0.30168	0.45587	0.89648	0.00000
C45	0.70172	0.45990	0.89693	0.89693
C46	0.30187	0.45584	0.10872	0.00000
C47	0.70255	0.46618	0.10943	0.00000
C48	0.03400	0.02972	0.67898	0.00000
C49	0.97015	0.02419	0.32616	0.00000
C50	0.03424	0.02620	0.32662	0.05000
C51	0.46752	0.51859	0.67852	0.03000
C52	0.53583	0.51882	0.67877	0.02000
C53	0.46793	0.52209	0.32637	0.00000
C54	0.53625	0.52417	0.32652	0.08000
C55	0.02042	0.03170	0.76160	0.00000
C56	0.98373	0.04159	0.24387	0.00000
C57	0.02085	0.04311	0.24418	0.02000
C58	0.48094	0.53637	0.76091	0.00000
C59	0.52227	0.53640	0.76108	0.00000
C60	0.48144	0.54202	0.24411	0.00000
C61	0.52278	0.54342	0.24420	0.00000
C62	0.08642	0.01730	0.56926	0.00000
C63	0.91763	0.01940	0.43569	0.03000
C64	0.08650	0.01622	0.43659	0.00000

C65	0.41534	0.50166	0.56858	0.09000
C66	0.58824	0.50337	0.56917	0.01000
C67	0.41552	0.50242	0.43587	0.08000
C68	0.58844	0.50590	0.43646	0.00000
C69	0.12807	-0.01157	0.54429	0.00000
C70	0.87562	0.01417	0.46081	0.00000
C71	0.12813	-0.01202	0.46180	0.00000
C72	0.37379	0.47156	0.54322	0.00000
C73	0.62987	0.47401	0.54422	0.00000
C74	0.37390	0.47195	0.46072	0.00000
C75	0.63001	0.47570	0.46173	0.00000
C76	0.07422	0.02177	0.65172	0.00000
C77	0.92987	0.01993	0.35324	0.01000
C78	0.07444	0.01990	0.35407	0.00000
C79	0.42734	0.50841	0.65111	0.05000
C80	0.57605	0.50920	0.65160	0.03000
C81	0.42773	0.51045	0.35348	0.01000
C82	0.57644	0.51432	0.35395	0.00000
C83	0.10625	0.01032	0.71546	0.00000
C84	0.89802	0.01324	0.28907	0.04000
C85	0.10647	0.01048	0.29037	0.00000
C86	0.39535	0.49832	0.71496	0.01000
C87	0.60802	0.49945	0.71551	0.03000
C88	0.39581	0.50008	0.28948	0.06000
C89	0.60851	0.50574	0.29026	0.01000
C90	0.16779	-0.01657	0.83428	0.00000
C91	0.83639	-0.00953	0.17028	0.00000
C92	0.16807	-0.01563	0.17173	0.05000
C93	0.33390	0.47180	0.83400	0.27000
C94	0.66950	0.47410	0.83439	0.02000
C95	0.33421	0.47210	0.17091	0.09000
C96	0.67022	0.48102	0.17175	0.00000
N3	0.06160	0.03173	0.50286	1.00000
N4	0.44028	0.51751	0.50238	0.00000
N5	0.56348	0.51971	0.50271	0.64000
N6	0.00001	0.01724	0.37393	0.00000
N7	0.50171	0.51150	0.63111	0.00000
N8	0.50207	0.51488	0.37395	0.00000
H1	0.34824	0.44927	0.58319	0.00000
H2	0.34845	0.45021	0.42045	0.00000
H3	0.50207	0.50821	0.43595	0.12000
H4	0.46115	0.54909	0.81300	0.34000
H5	0.54195	0.54927	0.81334	0.20000
H6	0.50170	0.50647	0.56909	0.04000
H7	0.65533	0.45132	0.58440	0.00000
H8	0.65560	0.45470	0.42175	0.12000
H9	0.46171	0.55527	0.19194	0.00000
H10	0.54252	0.55804	0.19210	0.00000
H11	-0.00010	0.03261	0.56917	0.06000
H12	-0.00017	0.01104	0.43596	0.00000
H13	0.84959	0.02004	0.58307	0.00000

H14	0.84968	0.00837	0.42089	0.00000
H15	0.15358	-0.03275	0.58447	0.00000
H16	0.15367	-0.03393	0.42177	0.21000
H17	0.04004	0.03319	0.81419	0.00000
H18	0.04066	0.05720	0.19219	0.03000
H19	0.96365	0.02673	0.81398	0.62000
H20	0.96406	0.05419	0.19158	0.00000
H21	0.36192	0.19930	0.86750	0.46000
H22	0.41625	0.22494	0.76487	0.00000
H23	0.31349	0.74850	0.78710	0.00000
H24	0.36632	0.76847	0.68089	0.00000
H25	0.36237	0.19990	0.13737	0.00000
H26	0.31371	0.74880	0.21765	0.06000
H27	0.36666	0.76998	0.32355	0.00000
H28	0.41684	0.22678	0.23966	0.00000
H29	0.58741	0.22541	0.76528	0.51000
H30	0.63683	0.77003	0.68127	0.00000
H31	0.68967	0.75121	0.78746	0.00000
H32	0.64186	0.20054	0.86772	0.03000
H33	0.63749	0.77523	0.32546	0.00000
H34	0.58770	0.23313	0.23944	0.00000
H35	0.64225	0.20903	0.13725	0.00000
H36	0.69059	0.75674	0.21971	0.00000
H37	0.08567	0.71153	0.24030	0.00000
H38	0.13550	0.28037	0.32492	0.25000
H39	0.14011	0.68616	0.13804	0.51000
H40	0.18844	0.26087	0.21904	0.00000
H41	0.13997	0.68433	0.86717	0.00000
H42	0.08572	0.70975	0.76449	0.04000
H43	0.18808	0.26056	0.78762	0.06000
H44	0.13509	0.28127	0.68179	0.00000
H45	0.86361	0.69043	0.13681	0.00000
H46	0.91794	0.71218	0.23948	0.33000
H47	0.81688	0.26875	0.21705	0.00000
H48	0.87008	0.28678	0.32232	0.00000
H49	0.87551	0.70700	0.67482	0.00000
H50	0.82215	0.68414	0.77933	0.78000
H51	0.91112	0.29146	0.77030	0.00000
H52	0.85635	0.27275	0.87223	0.31000

Table S2. Important crystallographic information for V-MOF-10

Parameters	**V-MOF-10**
Empirical formula	$C_{48}H_{26}N_4O_{10}V_2$
Symmetry	*Orthorhombic*
Space group	*Cmmm*
a (Å)	32.9288(4)
b (Å)	6.8495(7)
c (Å)	16.5912(1)
Unit Cell Volume ($Å^3$)	3742.12(1)
Z	2
Wavelength (CuKα)	1.54059
Temperature (K)	298
Angular range 2θ (º)	3-50

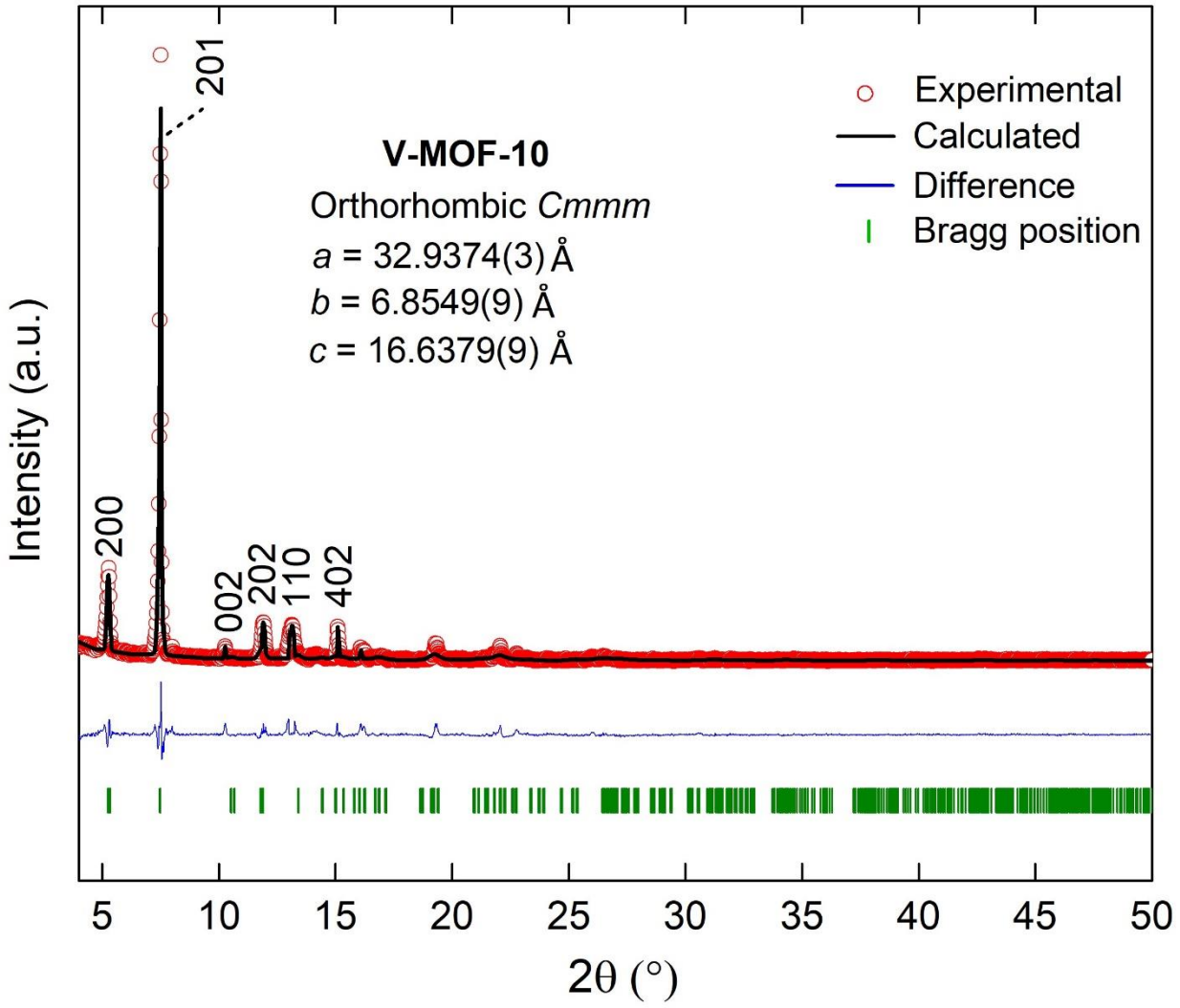


Figure S4. Result of the Pawley fit of as-synthesized V-MOF-10

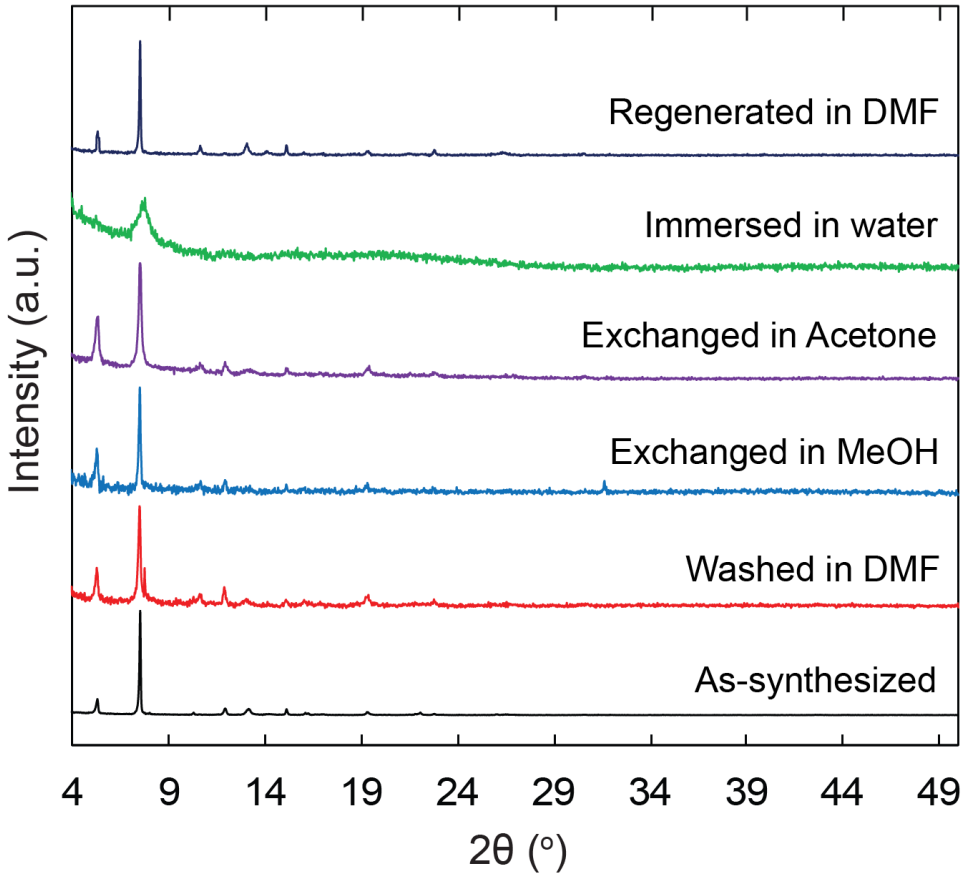


Figure S5. PXRD patterns show the chemical stability of V-MOF-10 in different solvents

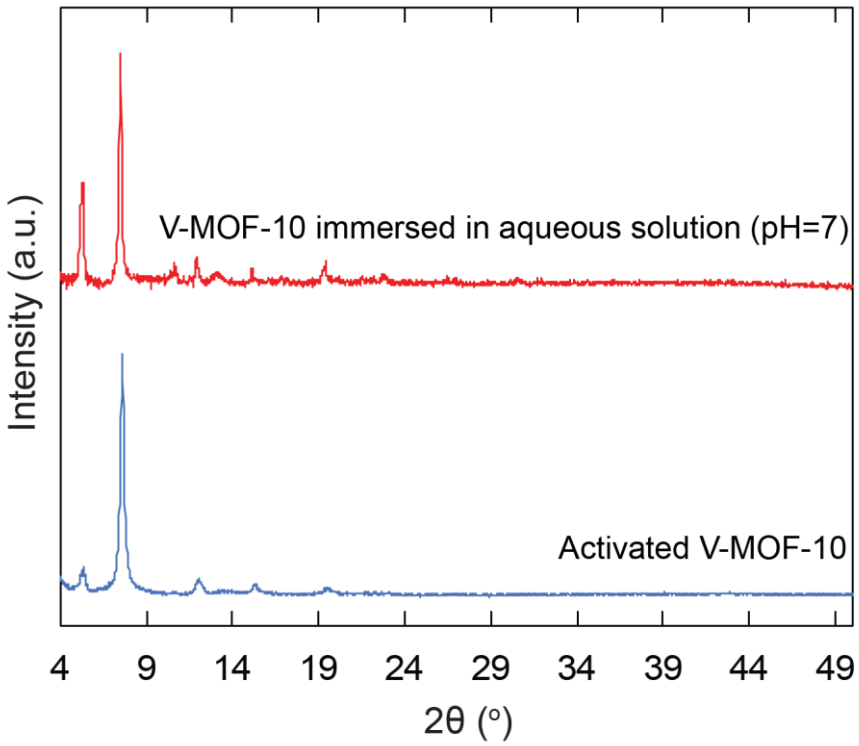


Figure S6. PXRD pattern shows the stability of V-MOF-10 in aqueous solution at pH = 7

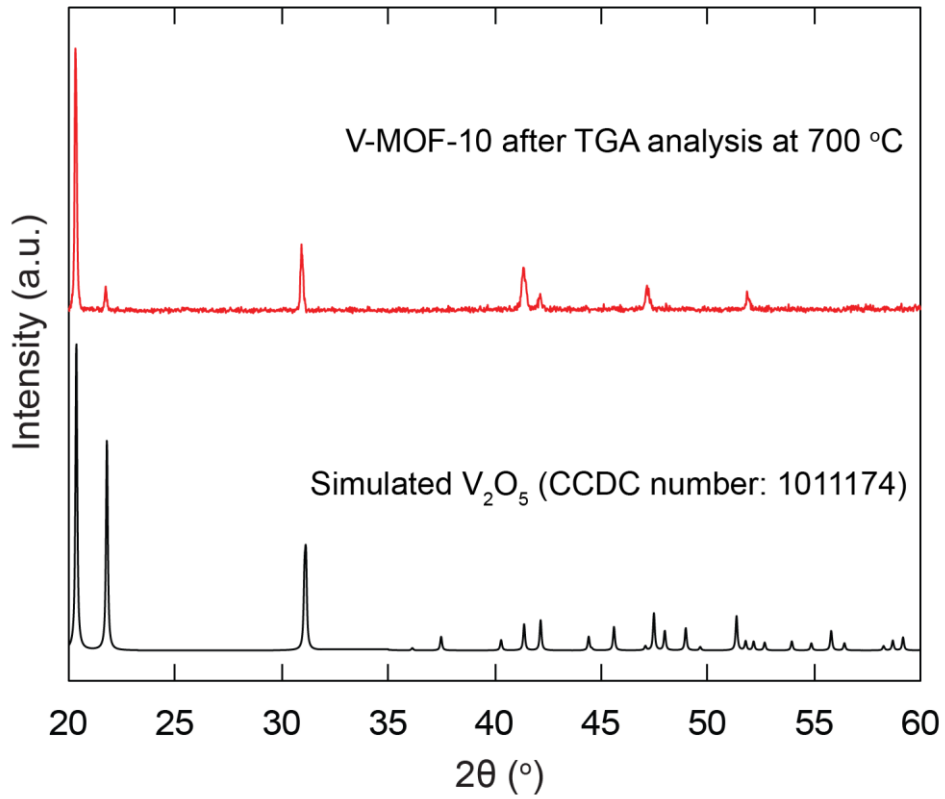


Figure S7. PXRD pattern of V-MOF-10 after annealing at 700 °C (red) in comparison with simulated V_2O_5 (black)

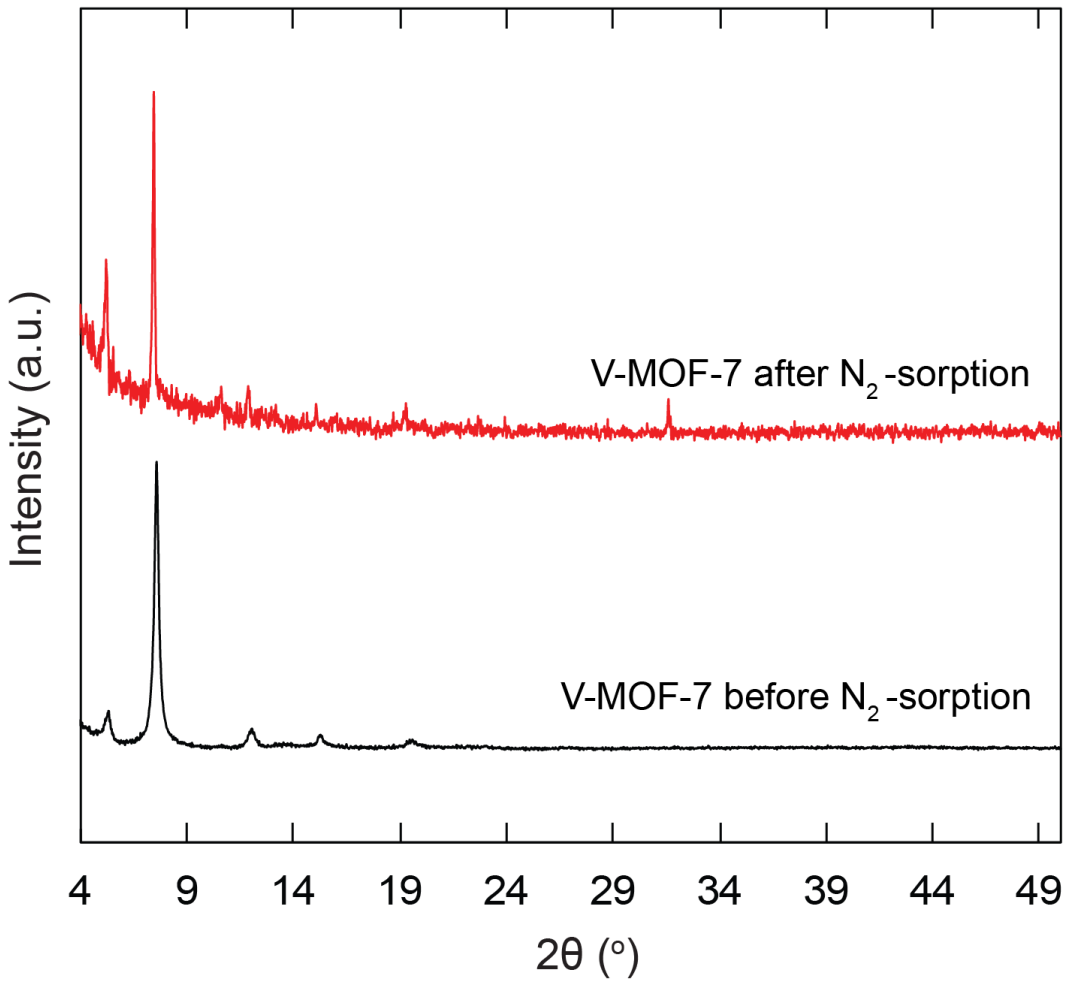


Figure S8. PXRD patterns of V-MOF-10 before and after the N_2 sorption experiments

Section S6. Thermogravimetric Analysis (TGA)

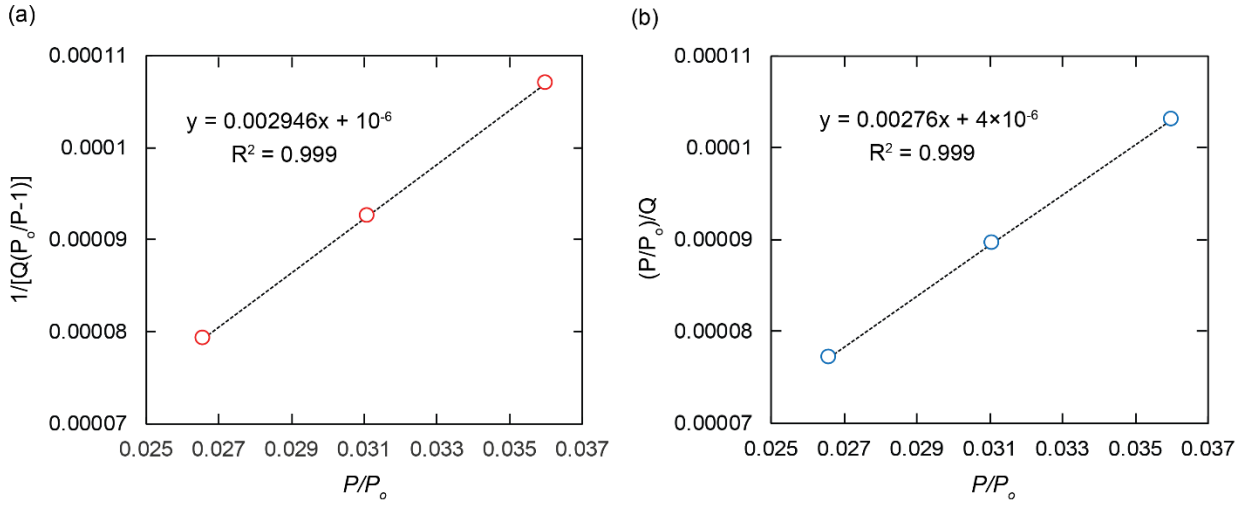
The thermal stability of V-MOF-10 was determined by thermogravimetric analysis (TGA). In this work, an activated V-MOF-10 (15 mg) was heated under airflow (50 mL min^{-1}) from 25 to 700 °C with a gradient of 5 °C min^{-1}. The TGA curve of V-MOF-10 indicated a small weight loss (~ 4.3%) from room temperature to 100 °C, followed by a decrease from 100 to 300 °C before framework decomposition.

Table S3. Calculated and found values of weight loss during heating of V-MOF-10 under airflow

Assignment	**Composition**	**Weight loss (%)**	
		Calculated	**Found**
Residue	V_2O_5	19.7	17.3
Linker and moiety caps	μ-OH and H_6TCPP	78.4	80.9

Section S7. N_2 adsorption measurement and surface area prediction

The porosity analysis of activated V-MOF-10 was measured by N_2 adsorption at 77 K.



(c)

Parameters	BET model	Langmuir model
P/P_o range	0.0265 - 0.0359	0.0265 - 0.0359
Correlation Coefficient	0.999	0.999
C	2947	691
Q_m ($cm^3\ g^{-1}$ STP)	339.328	361.795
Molecular cross-sectional area (S / nm^2)	0.1620	0.1620
Surface area ($m^2\ g^{-1}$)	1477.35	1575.16

$$S = \frac{Q_m \times N_A \times A}{V}$$

Where S and Q_m are the BET or Langmuir surface area and quantity adsorbed. N_A is Avogrado's number, A is the molecular-sectional area and V symbolizes the molar volume of adsorbed gas.

Figure S9. Plot of the linear region of the adsorption N_2 isotherm used for the BET equation (a), the Langmuir equation (b), and summary of parameters in the BET and Langmuir analysis (c).

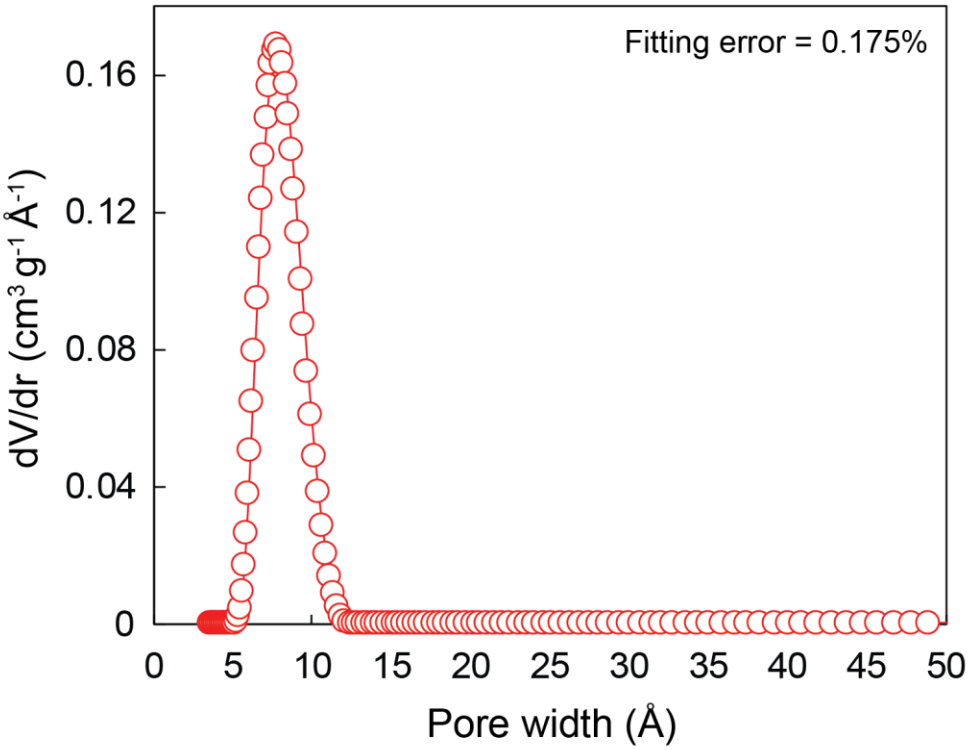


Figure S10. Pore size distribution of activated V-MOF-10. N_2 isotherm was analyzed by quenched solid density functional theory implementing a hybrid kernel at 77 K N_2 adsorption based on a carbon model containing slit/cylinder/sphere pores

Theoretical surface area prediction

The theoretical surface area of V-MOF-10 was determined through the Atom Volumes and Surfaces tool of *Materials Studio 7.0* software. The accessible solvent surface area of V-MOF-10 was calculated to be 505 $Å^2$. This value was converted into the surface area per gram, leading to a theoretical surface area of 1648 $m^2\ g^{-1}$.

Table S4. Summary of surface area calculation for V-MOF-10

V-MOF-10	
Crystal density (g cm^{-3})	0.819
Accessible solvent surface per cell ($Å^2$)	505
Calculated SA ($m^2\ g^{-1}$)	1648
Calculated pore volume ($cm^3\ g^{-1}$)	0.099

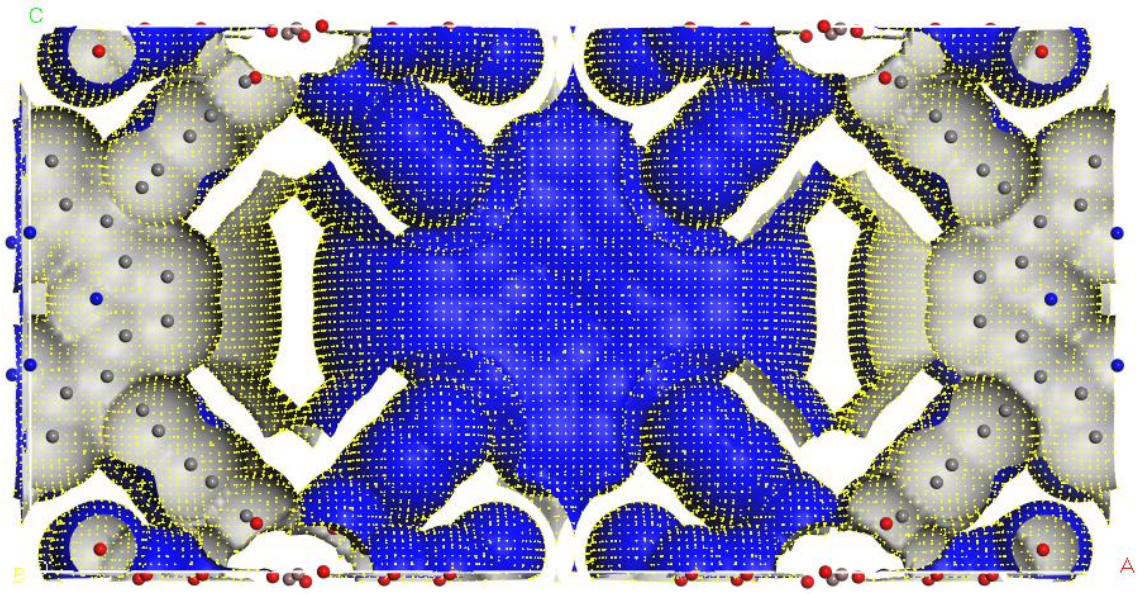


Figure S11. Accessible solvent surface and van der Waals surface of V-MOF-10

Section S8. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Mapping (EDX-mapping) analysis

Scanning electron microscopy (SEM) analysis was conducted on FESEM S-4800 Hitachi by dispersing V-MOF-10 material onto a silicon wafer attached to a flat aluminum sample holder. The material was then measured with accelerating voltage of 10 kV to avoid the damage of the sample structure with the electron beam. Additionally, SEM-EDX-mapping images and analyses were taken with a EDX H-7593 Horiba instrument.

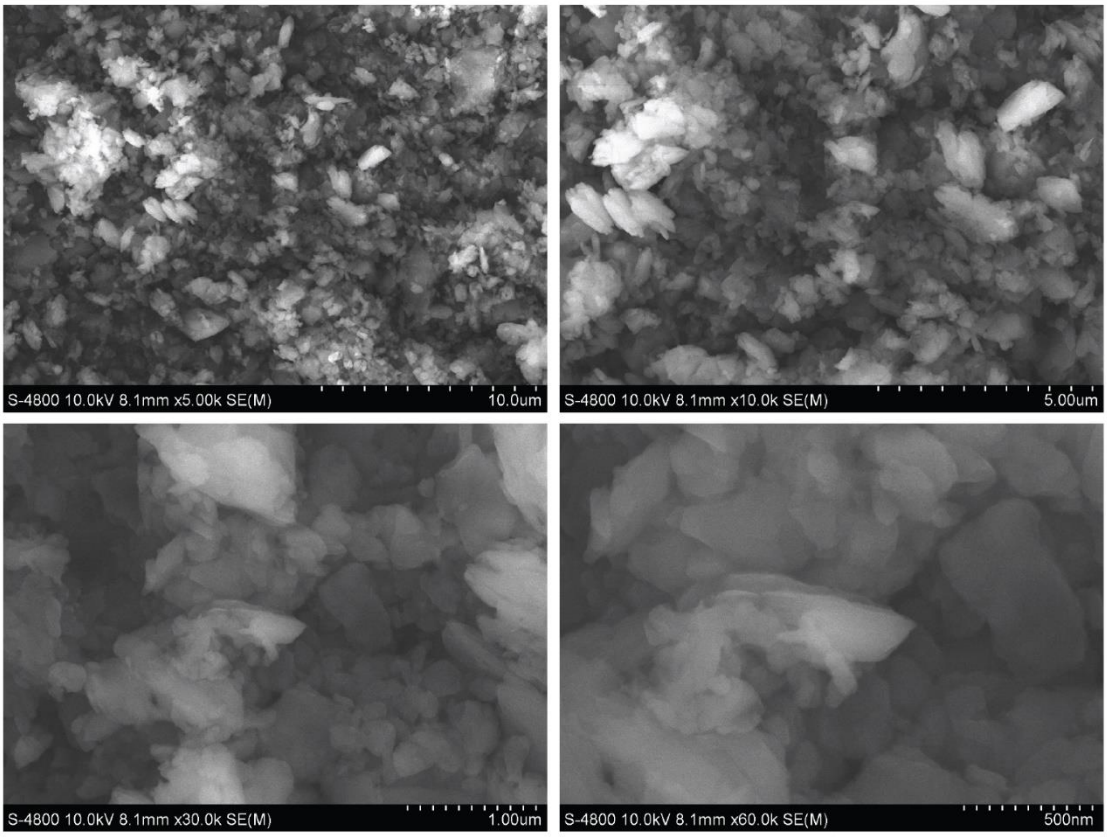


Figure S12. SEM images of V-MOF-10 at different scale bars of 10.0 µm, 5.00 µm, 1.00 µm, and 500 nm, respectively

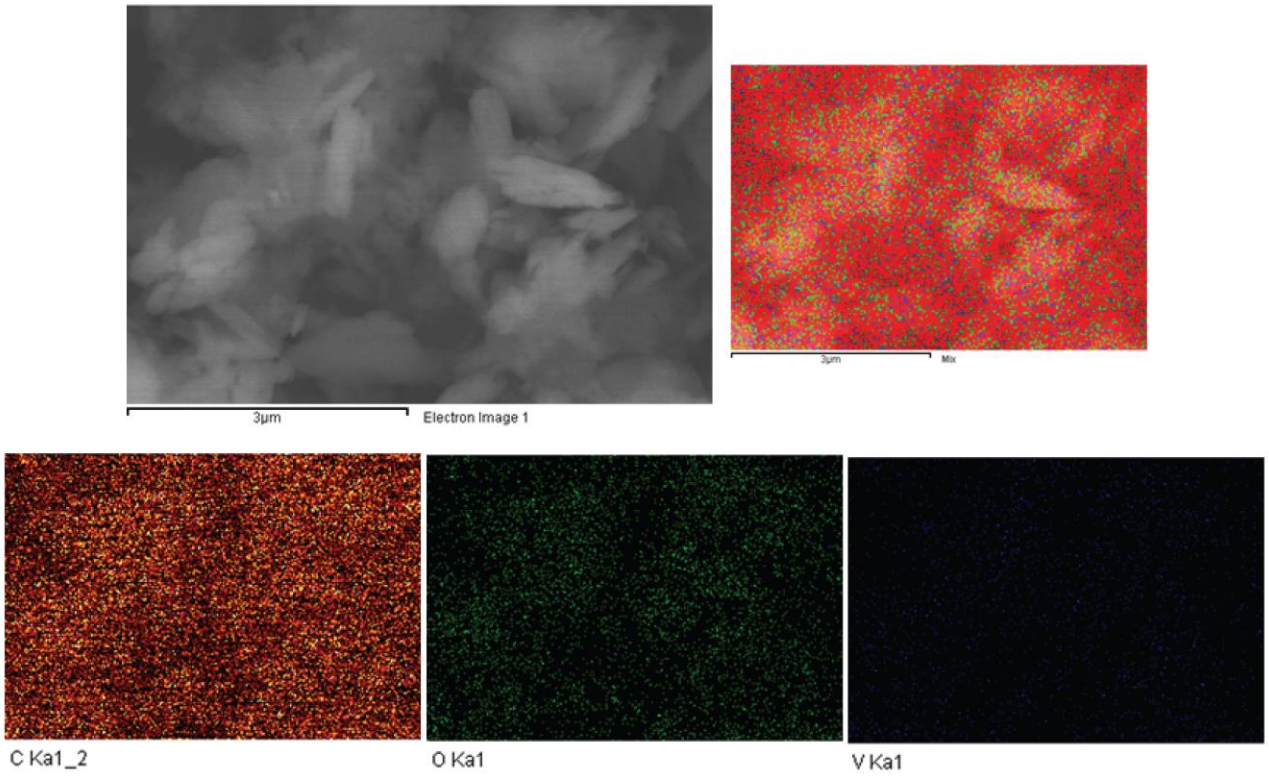


Figure S13. Elemental mapping by SEM-EDX of V-MOF-10

Section S9. Transmission Electron Microscopy (TEM) analysis

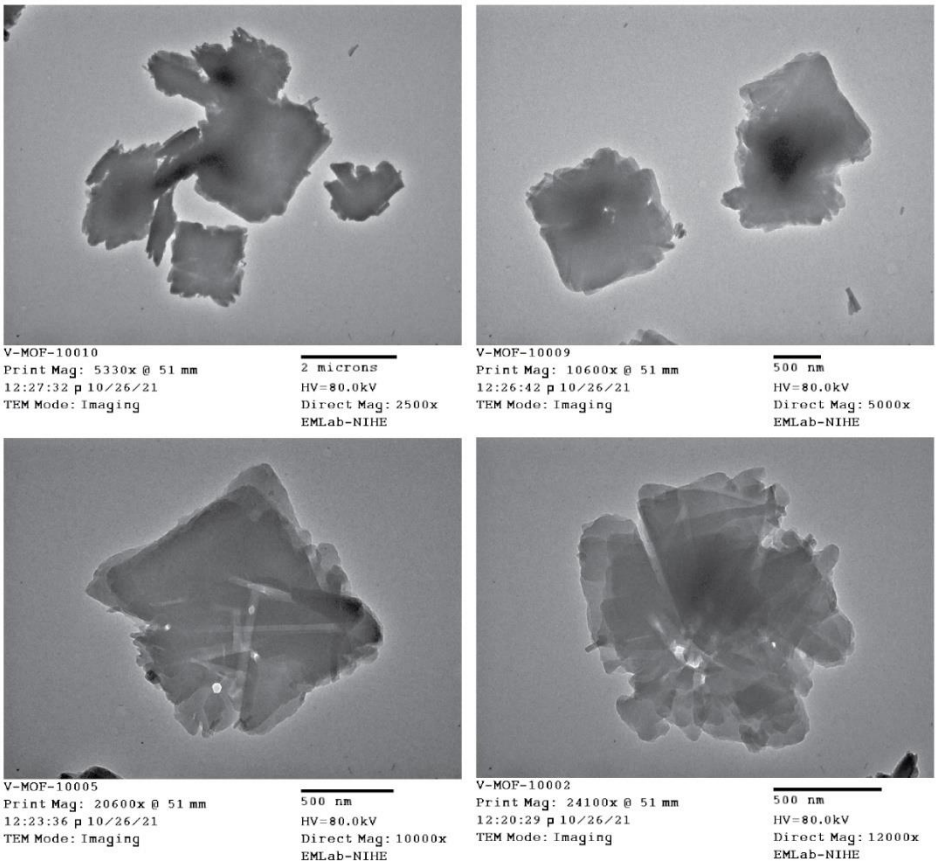


Figure S14. TEM images of V-MOF-10 at different magnifications (×2500, ×5000, ×10000, ×12000, respectively)

Section S10. Ultraviolet Visible Spectroscopy (UV-Vis) analysis

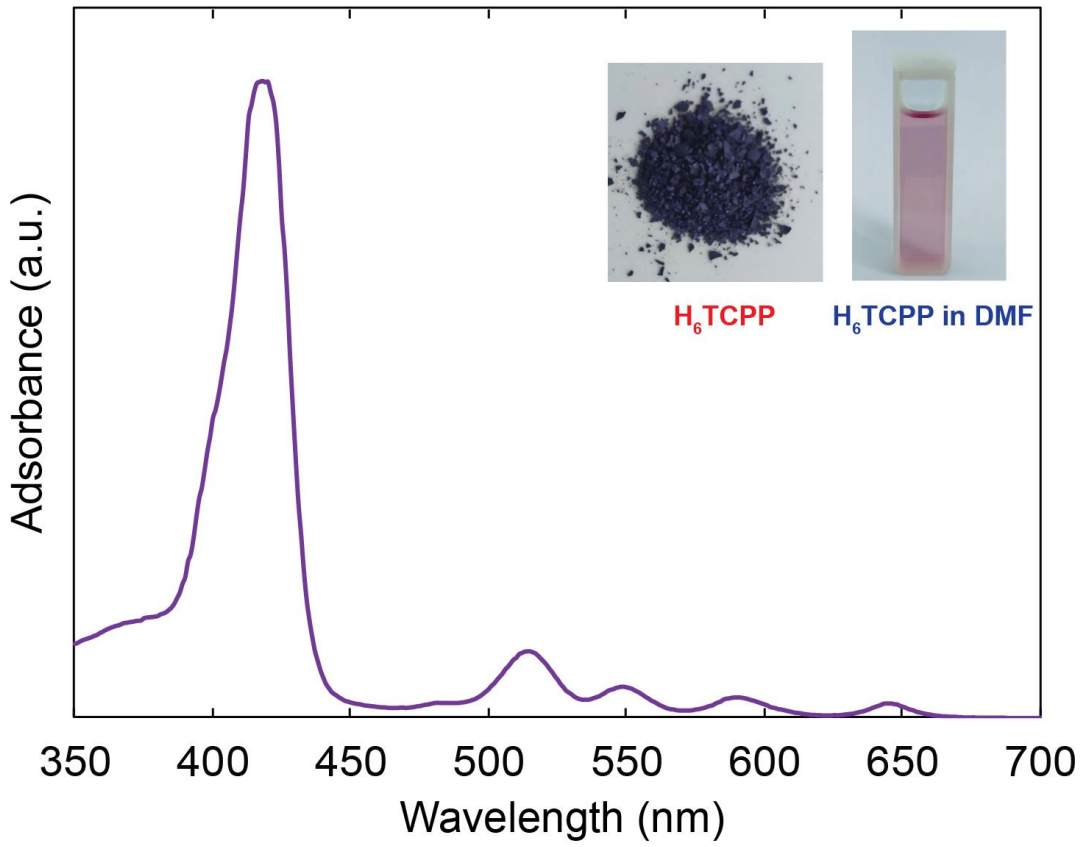


Figure S15. UV-Vis spectrum of pure porphyrinic linker (H_6TCPP) in DMF solvent

Section S11. Photocatalytic investigations for the degradation of MB and MO

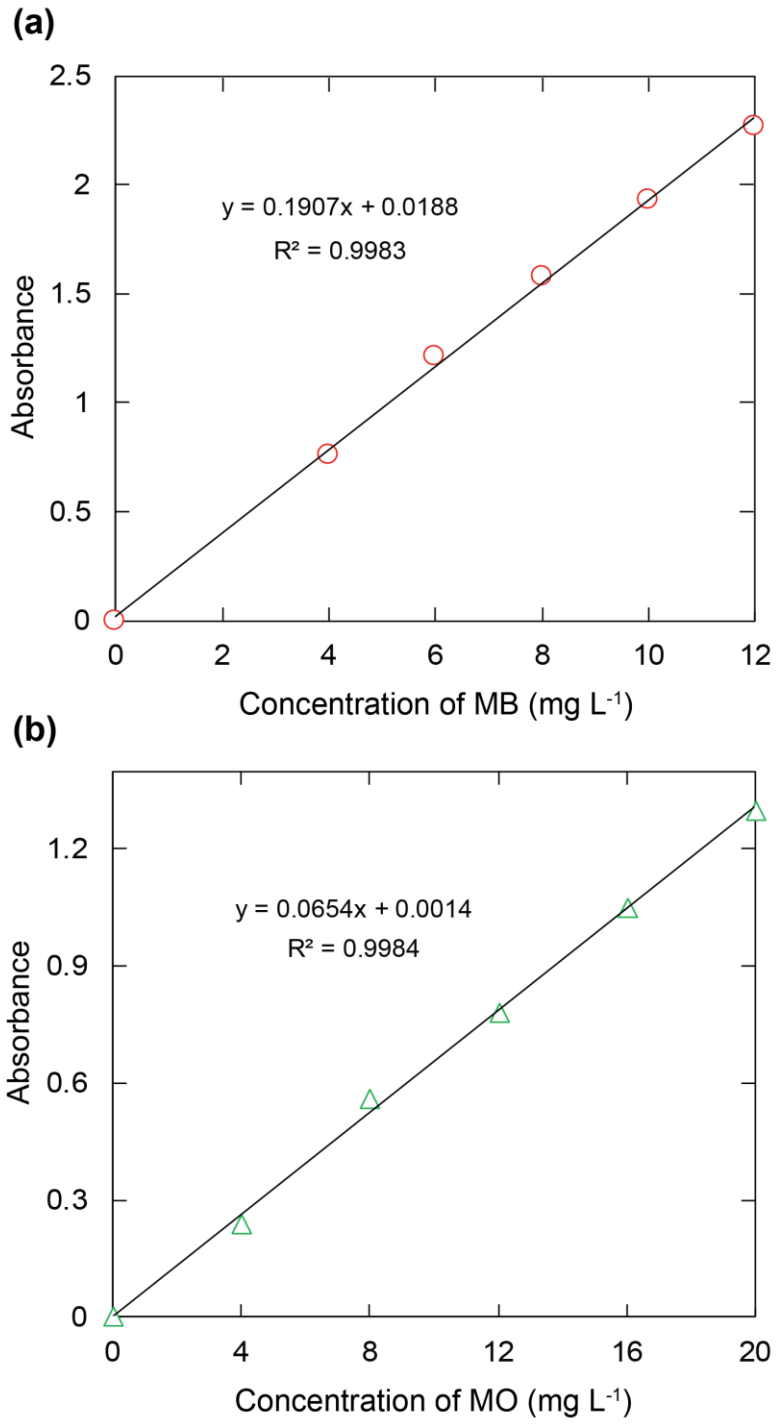


Figure S16. The relationship between the absorbed intensity of MB (a) and MO (b) with different concentrations by linear fitting

Photodegradation kinetics. The pseudo-first-order kinetics are employed to determine the photodegradation rate of MB and MO, which is exhibited by the eqn:

$$\ln\left(\frac{C_t}{C_o}\right) = -k_1 t$$

Where C_t and C_o are each organic dye concentration at t and initial time, k_1 are the rate constant of pseudo-first-order.

Section S12. Stability of V-MOF-10 after photocatalytic recycles

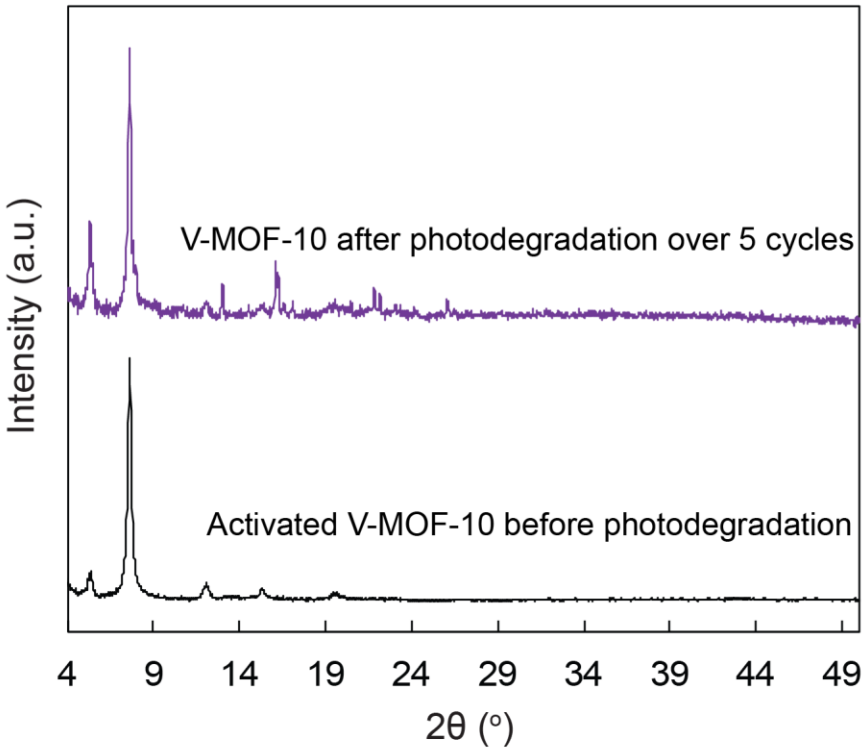


Figure S17. PXRD pattern of V-MOF-10 after photocatalytic reaction over five cycles