

Supporting Information

A breathing MOF: Direct crystallographic observation of the site-selective C(*sp*³)-H functionalization

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Section 1 Experimental Section

1. General methods and materials

All chemical materials were purchased from commercial sources and used without further purification. ^1H NMR was measured on a Varian INOVA-400 spectrometer with chemical shifts reported as ppm (in DMSO- d_6 or CDCl_3 , TMS as internal standard). The elemental analyses (EA) of C, H and N were performed on a Vario EL III elemental analyzer. Inductively coupled plasma (ICP) analyses were performed on a NexION 300D spectrometer. The powder XRD diffractograms were obtained on a Rigaku D/MAX-2400 X-ray diffractometer with Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$). IR spectra were recorded as KBr pellets on a NEXUS instrument. Solid UV-Vis absorption spectra were recorded on a U-4100 spectrometer. Thermogravimetric analyses (TGA) were carried out at a ramp rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in nitrogen flow with a SDTQ600 instrument. Products were purified by flash column chromatography on 200–300 mesh silica gel SiO_2 .

Synthesis of DT–DPDO: The DT–DPDO was synthesized by a diffusion method in a test tube. A mixture of acetonitrile and water (1:1, 7.5 mL) was gently layered on the top of a solution of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (18.5 mg, 0.050 mmol) and 4,4'-bipyridine- $\text{N,N}'$ -dioxide (14.1 mg, 0.075 mmol) in water (7.5 mL). A solution of $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]^{\text{S1}}$ (46.5 mg, 0.014 mmol) in acetonitrile (5 mL) was added carefully as the third layer. Orange block single crystals were separated after five weeks, washed with acetonitrile and water, and dried in air. (Yield: *ca.* 43% based on $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]$). EA and ICP calcd (%) for $\text{C}_{51}\text{H}_{51}\text{N}_{12}\text{O}_{44}\text{W}_{10}\text{Cu}_2$: C 17.49, H 1.47, N 4.80, Cu 3.63, W 52.50; Found: C 17.61, H 1.39, N 4.72, Cu 3.47, W 52.63.

2. X-ray crystallography

Data of DT–DPDO and VN@DT–DPDO were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs.^{S2,S3} Routine Lorentz polarization and Multi-scan absorption correction were applied to intensity data. Their structures were determined and the heavy atoms were found by direct methods using the SHELXTL-97 program package.^{S4} The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Except some partly occupied solvent water molecules, the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at their positions and allowed to ride on the parent atoms. For the DT–DPDO and VN@DT–DPDO several bond distances constraints were used to help the refinement on the DPDO moiety, and thermal parameters on adjacent oxygen atoms of the polyoxometalate anion were restrained to be similar.

Section 2 Characterizations of Catalysts

Substrate Penetration: Before the adsorption of substrate, fresh MOFs were briefly air-dried on a filter paper and used without further processing. Substrate penetration studies were carried out by soaking the MOFs in aliphatic nitrile or acrylonitrile for two days. After the soaked MOFs were rapidly washed with acetonitrile solution several times to remove the substrate molecules adsorbed on the external surfaces of the crystals.

Fig. S1 (a) The IR spectra of valeronitrile (i), DT-**DPDO** (ii), and solids of DT-**DPDO** obtained after the absorption of valeronitrile (iii); (b) The IR spectra of acrylonitrile (i), DT-**DPDO** (ii), and solids of DT-**DPDO** obtained after the absorption of acrylonitrile (iii).

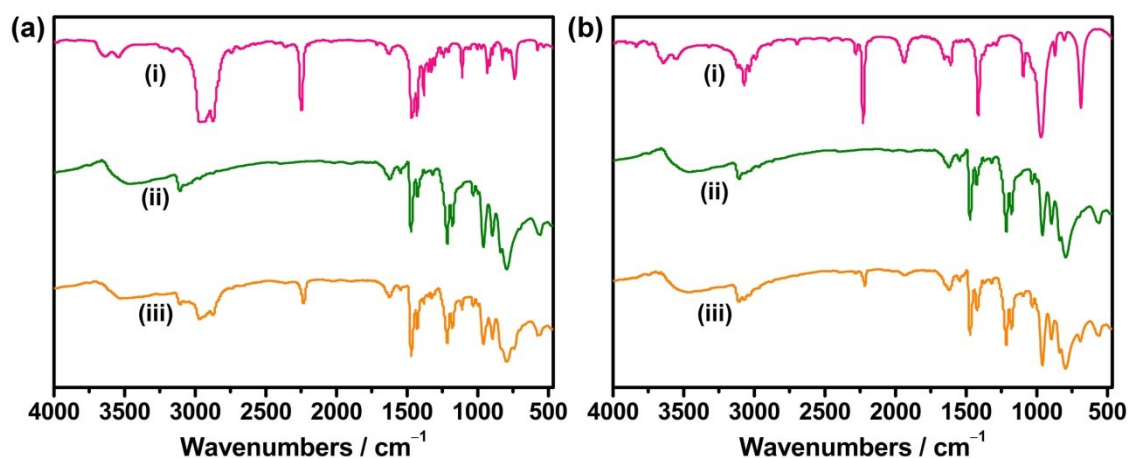


Fig. S2 (a) ¹H NMR in D₂SO₄/DMSO-d₆ of DT-**DPDO** (i), and of DT-**DPDO** impregnated in acrylonitrile (ii); (b) Solid-state IR spectra of DT-**DPDO** (iii), and of DT-**DPDO** impregnated in acrylonitrile (iv). The blue and red triangle represented the signals of acrylonitrile in the ¹H NMR and IR spectra, respectively.

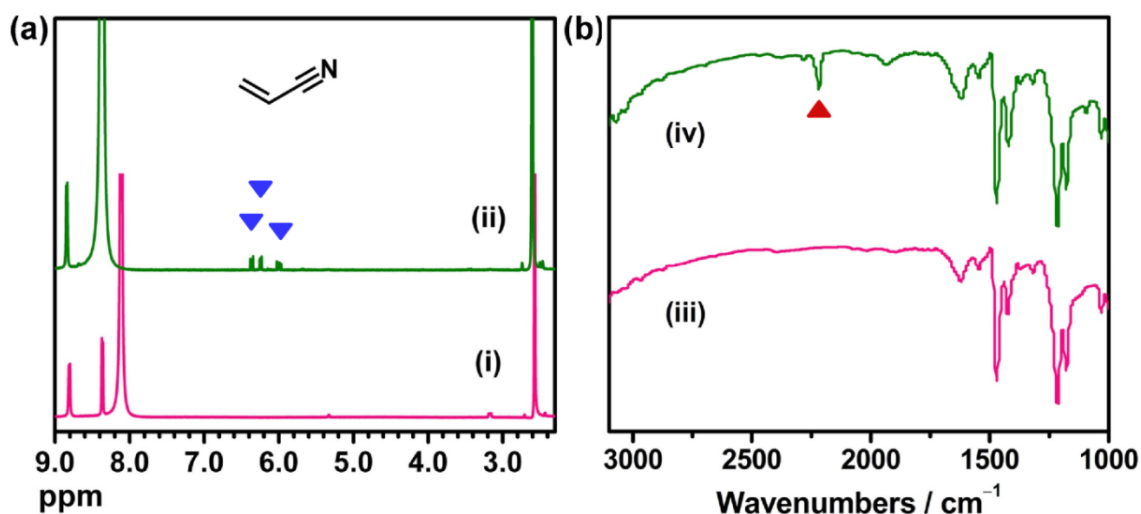


Fig. S3 (a) Solid-state UV–Vis absorption spectra of DT–DPDO and [(n-C₄H₉)₄N]₄[W₁₀O₃₂] (denoted as: TBADT); (b) Family of emission spectra of DT–DPDO (0.1% by weight) in the CH₃CN suspension upon addition of valeronitrile up to 0.50 mM, excitation at 380 nm.

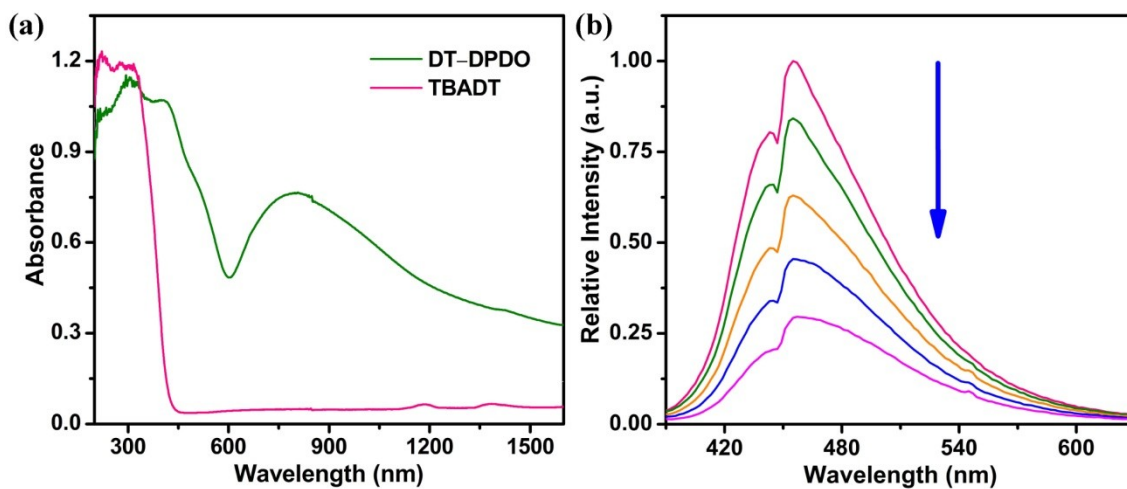
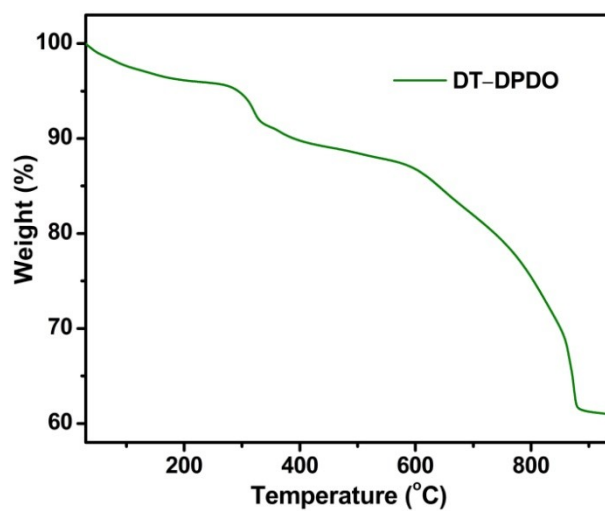


Fig. S4 TG curve of DT–DPDO at a ramp rate of 5 °C·min⁻¹ in the flowing nitrogen atmosphere.



Section 3 Catalysis Details

1. Typical Procedure for the Selective C–H Alkylation of Isovaleronitrile:

To a quartz glass tube equipped with a magnetic stirring bar was added isovaleronitrile (2.5 mmol), acrylonitrile (0.5 mmol), photocatalyst (1 mol %), TBA (4 mol %) and acetonitrile (1 mL). The reaction mixture was then degassed by three freeze-pump-thaw cycles. The reaction mixture was irradiated by a Xe lamp (500 W) at room temperature for 48 h. After the reaction, the resulting suspension was centrifuged, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/diethyl ether = 1/1).

Fig. S5 Powder XRD pattern of DT–DPDO showing the calculated pattern based on the single-crystal solution and after three runs of the selective C–H alkylation [(i)-Simulated, (ii)-Experimental, (iii)-Recovery catalyst after three times runs].

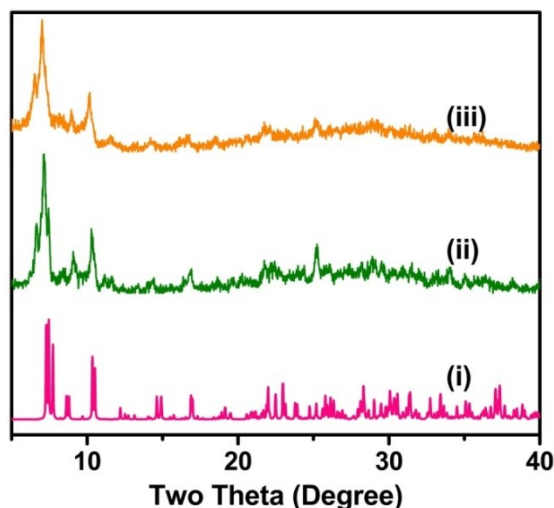


Table S1 Study on the recyclability of DT–DPDO as well as control experiments for isovaleronitrile and acrylonitrile reactions.

Entry	Catalysts	State	Yield (%)
1	DT–DPDO (Round 1)	Heterogeneous	86
2	DT–DPDO (Round 2)	Heterogeneous	86
3	DT–DPDO (Round 3)	Heterogeneous	85
4	DT–DPDO (No light)	Heterogeneous	0
5	No catalyst	Homogeneous	0
6	(TBA) ₄ [W ₁₀ O ₃₂]	Homogeneous	86

2. ¹H NMR Spectra for the Catalytic Product:

(Entry 1, Table 2) ¹H NMR (500 MHz, CDCl₃) δ 1.13 (s, 6H), 1.79-1.85 (m, 2H), 2.30 (s, 2H), 2.34-2.38 (m, 2H).

(Entry 2, Table 2) ¹H NMR (500 MHz, CDCl₃) δ 0.94-1.05 (m, 1H), 1.53 (dd, 1H), 1.77 (dd, 1H), 2.39 (dd, 4H).

(Entry 3, Table 2) ¹H NMR (500 MHz, CDCl₃) δ 0.95 (s, 6H), 1.65-1.68 (m, 4H), 2.29-2.34 (m, 4H).

Section 4 References

- S1. Fournier, M.; Klemperer, W. G.; Silavwe, N. *Inorg. Synth.* **1990**, 27, 81–83.
- S2. SMART, *Data collection software (version 5.629)*; Bruker AXS Inc., Madison, WI, **2003**.
- S3. SAINT, *Data reduction software (version 6.45)*; Bruker AXS Inc., Madison, WI, **2003**.
- S4. Sheldrick, G. M. *SHELX-97, Program for crystal structure solution*; University of Göttingen: Göttingen, Germany, **1997**.