

Supporting Information

**A high-valent di- μ -oxo dimanganese complex covalently anchored in
a metal-organic framework as highly efficient and recoverable water
oxidation catalyst**

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Experimental Section

Chemicals and Characterization

All chemicals and reagents were obtained from commercial sources and used without further purification unless otherwise indicated. All solvents were analytical grade and distilled prior to use.

All the powder X-ray diffractions (XRD) measurements were conducted on a Rigaku diffractometer (D/MAX-III A, 3 kW) using Cu K α radiation (40 kV, 30 mA, 0.1543 nm). The nitrogen adsorption/desorption isotherms were measured by using a Micromeritics ASAP 2020M instrument at 77 K. Liquid proton nuclear magnetic resonance ($^1\text{H-NMR}$) data were recorded on a Bruker Avance III 400 spectrometer. Liquid chromatography-high resolution mass spectrometry (LC-HRMS) analyses were performed on an Agilent 1290 Infinity LC interfaced to the Bruker maXis impact. The flow rate of the LC-HRMS analyses was held steadily at 1 mL/min and the methanol : water ratio was kept constant at 40 : 60 for the entire 10 min running time. The manganese contents were quantified by atomic absorption spectroscopy (AAS) on a Hitachi Z-2300 instrument. The Fourier transform infrared spectra (FTIR) were recorded on a Thermo Fisher iS10 spectrometer with potassium bromide pellets. X-band EPR spectra were recorded at 2 K using X-band Bruker EMX-plus spectrometer. The experimental parameters for EPR measurement were as follows: Microwave frequency = 9.39 GHz, microwave power = 200 μW , modulation amplitude = 2 G, modulation frequency = 100 kHz. Simulations were done by Bruker WinEPR Simfonia software Suites.

Preparation of 4'-Ethynyl-2,2':6',2''-terpyridine

4'-Ethynyl-2,2':6',2''-terpyridine was prepared according to the literature procedures.^{S1}

Preparation of MIL-101(Cr)-NH₂ (1-NH₂)

MIL-101(Cr)-NH₂ was synthesized according to the documented method with a few modifications.^{S2-3} In a typical experiment, 300 mg MIL-101(Cr) were added to a mixture of conc. sulfuric acid (21 mL) and conc. nitric acid (15 mL), and stirred at 0 °C for 5 h. The mixture was allowed to warm up to room temperature and then poured into a beaker containing ca. 150 mL ice. The raw product was isolated by centrifugation and then activated by using water (30 mL) and ethanol (30 mL) sequentially, in a microwave oven at 80 °C for 6 h each. The resulting green solid was further dried at 120 °C under vacuum for 12 h to yield MIL-101(Cr)-NO₂. Subsequently, 300 mg MIL-101(Cr)-NO₂ and 9.78 g SnCl₂·2H₂O were suspended in 60 mL ethanol. The mixture was refluxed at 80 °C for 6 h to obtain a greenish-colored solid, which was centrifuged and suspended in 60 mL concentrated hydrochloric acid. After centrifugation and washing with plenty of water until the filtrate pH value was neutral, the resulting material was dried at 120 °C under vacuum for 12 h to give MIL-101(Cr)-NH₂.

Preparation of MIL-101(Cr)-N₃ (1-N₃)

The freshly activated MIL-101(Cr)-NH₂ (100 mg) was added to a glass tube containing 5 mL THF, 0.28 mL tBuONO and 0.3 mL TMSN₃. The mixture was stirred at room temperature overnight. The reaction was quenched by decanting the solvent. Excess reactants were removed by washing the resultant powders three times with THF. The product was dried under vacuum at room temperature overnight.^{S3}

Preparation of MIL-101(Cr)-tpy (1-tpy)

100 mg of MIL-101-N₃ and 5 mg CuI were placed in the deoxygenated 5 mL toluene solution containing 30 mg 4'-Ethynyl-2,2':6',2''-terpyridine (0.12 mmol). The mixture was stirred at 80 °C for 24 h. The resultant precipitate was collected by filtration, followed by washing with toluene and THF to remove unreacted substrates. After drying at 30 °C under vacuum for 12 h, the final product could be obtained.

Preparation of MnTD@MIL-101(Cr)-triazole (2)

The as-formed MIL-101(Cr)-triazole (100 mg) was placed in a 25 mL round bottom flask containing 5 mL water and sonicated for 20 min. Then 23.5 mg $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.12 mmol) was added to the above suspension. The resulting mixture was stirred for 20 h. After the solution was cooled in an ice bath, Oxone (0.09 mmol) dissolved in 5 mL H_2O was added under vigorous stirring. The color of the suspension turned to deep green within a few minutes. After stirring for an extra 1 h in the ice bath, the dark green suspension was then filtered on a 0.45 μm nylon filter membrane under vacuum and washed with excess water to remove excess Mn and washed with diethyl ether finally. Then the product was vacuum dried at room temperature for 12 h to yield $\text{MnTD@MIL-101(Cr)-triazole}$.

Preparation of $\text{MnTD}\subset\text{MIL-101(Cr)}$ ($\text{MnTD}\subset\text{1}$)

$\text{MnTD}\subset\text{MIL-101(Cr)}$ was synthesized according to the literature with a few modifications.^{S4} Typically, 28 mg of terpyridine (0.12 mmol) was added to 2.4 mL water in a 25 mL round bottom flask and sonicated for 20 min, followed by stirring for 15 min. Then 100 mg of freshly activated MIL-101(Cr) was suspended to the resulting mixture and the resulting suspension was stirred for 20 hrs. Then $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.12 mmol) was added to the suspension, followed by immediate addition of Oxone (0.09 mmol, dissolved in 2.4 mL water) over a period of 5 min. The resulting mixture was stirred for 20 hrs. The final dark green suspension was then filtered under vacuum on a 0.45 μm nylon filter membrane. The filter residues were washed with excess water, until the washing became colorless, to wash out excess $[(\text{H}_2\text{O})(\text{terpy})\text{Mn}(\mu\text{-O})_2(\text{terpy})(\text{OH}_2)]^{3+}$ outside and finally washed with diethyl ether. Then the product was vacuum dried overnight to yield $\text{MnTD}\subset\text{MIL-101(Cr)}$.

Preparation of MnTD, MnTD/MIL-101 ($\text{MnTD}/\text{1}$) and MnTD/clay

MnTD was synthesized first, according to a literature procedure.^{S5} Then, 53 mg (0.06 mmol) of MnTD was dissolved in a 5 mL acetate buffer. To the above solution, 100 mg of freshly activated MIL-101(Cr) was suspended and the resulting suspension

was stirred for 24 h in a water bath. The final suspension was filtered under vacuum on a 0.45 μm nylon filter membrane and washed with excess water, until the washing became colorless, and finally washed with diethyl ether. The product was vacuum dried overnight. MnTD/clay was prepared similarly, except that 100 mg clay was used.

Procedures for water oxidation experiments

Catalytic water oxidation experiments were carried out in a Perfectlight Labsolar IIIAG system, which connects to an evacuation system and an online gas chromatograph (TECHCOMP, GC 7900) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column. Typically, the applied catalyst (20 mg) was suspended in a 100 mL acetate buffer (pH 4.5). Then the suspension was stirred and purged with argon for \sim 30 min to remove air. Subsequently, 10mM Oxone (KHSO_5 , 47%) was added to the chamber using a syringe. A quantified gas phase was injected into GC instrument every 30 min with high purity argon gas as the carrying gas. The amounts of evolved O_2 were determined by external standard method.

Determination of the initial rates of O_2 evolution and turnover numbers (TONs)

The first 10 min of the single exponential fitting plot of the time profiles of O_2 evolution was fitted by a linear least-squares function. The obtained slope was determined as the initial rates of O_2 evolution. The TONs were defined as moles of produced O_2 per mole of catalyst, $n_{\text{O}_2}/n_{\text{cat}}$.

Estimation of the yield of click chemistry to install terpyridine ligand

The estimation of the yield of click chemistry is based on two principles: (1) the formula of MIL-101(Cr) could be described as $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ (where n is \sim 25); (2) all BDC^{2-} ligands were functionalized with $-\text{NH}_2$ groups which were full converted to $\text{BDC}-\text{N}_3$. Through the analysis of the contents of C, N, H and Mn, the formula of **2** could be roughly estimated as $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{C}_8\text{H}_4\text{O}_4)_a(\text{C}_8\text{H}_3\text{O}_4\text{N}_3)_b[(\text{C}_8\text{H}_3\text{O}_4)(\text{C}_2\text{HN}_3)(\text{C}_{15}\text{H}_{10}\text{N}_3\text{O}_4)]_c[(\text{C}_8\text{H}_3\text{O}_4)(\text{C}_2\text{HN}_3)(\text{C}_{15}\text{H}_{10}\text{N}_3)\text{Mn}_2\text{O}_2(\text{H}_2\text{O})_2(\text{C}_8\text{H}_3\text{O}_4)(\text{C}_2\text{HN}_3)(\text{C}_{15}\text{H}_{10}\text{N}_3)]_d(\text{Cl})_{0.98}(\text{H}_2\text{O})_{25}$, where $\text{C}_8\text{H}_4\text{O}_4 = \text{BDC}^{2-}$, $\text{C}_8\text{H}_3\text{O}_4\text{N}_3 = \text{BDC}^{2-}-\text{N}_3$, $\text{C}_2\text{HN}_3 = \text{triazole ring}$, $\text{C}_{15}\text{H}_{10}\text{N}_3\text{O}_4 =$

terpyridine, and $a = 0.3$, $b = 0.92$, $c = 1.5$, $d = 0.14$, $a+b+c+2d = 3$. The overall formula is $C_{54.26}H_{83.44}Cl_{0.98}Cr_3FMn_{0.28}N_{13.44}O_{40.56}$, and the theoretical contents of each element should be C, 36.24; H, 4.68; Cl, 1.93; Cr, 8.68; F, 1.06; Mn, 0.86; N, 10.47; O, 36.09, which is consistent with the experimental results: C, 36.23; H, 4.77, N, 10.47 and Mn, 0.85. Therefore, the yield of click reaction should be calculated approximately as: $(c+2d)/3 = 59.3\%$.

Procedures for recovery of catalysts

After one cycle of water oxidation reaction, the mixture suspension was filtered. The filter cake was washed with plenty of water and then dried at room temperature for 12 h to give dried powder. The resulting filtrate was collected and analyzed by AAS and UV-vis absorption spectroscopy.

References

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- S5. J. Limburg, J. S. Vrettos, L. M. Liablesands, A. L. Rheingold, R. H. Crabtree, G. W. Brudvig, *Science* 1999, **283**, 1524.

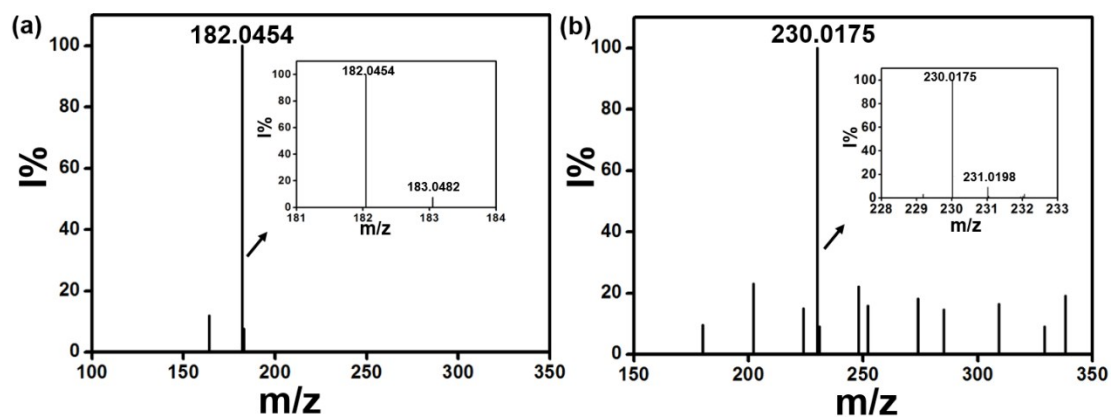


Fig. S1 LC-HRMS spectrogram of the linker molecule of digested **1-NH₂** (a) and **1-N₃** (b). The mass and isotope distribution patterns (insets) of ion peaks at $m/z = 182.0454$ and 230.0175 correspond to $[\text{H}_2\text{BDC-NH}_2 + \text{H}^+]^+$ (calcd. $m/z = 182.04$) and $[\text{H}_2\text{BDC-N}_3 + \text{Na}^+]^+$ (calcd. $m/z = 230.02$), respectively.

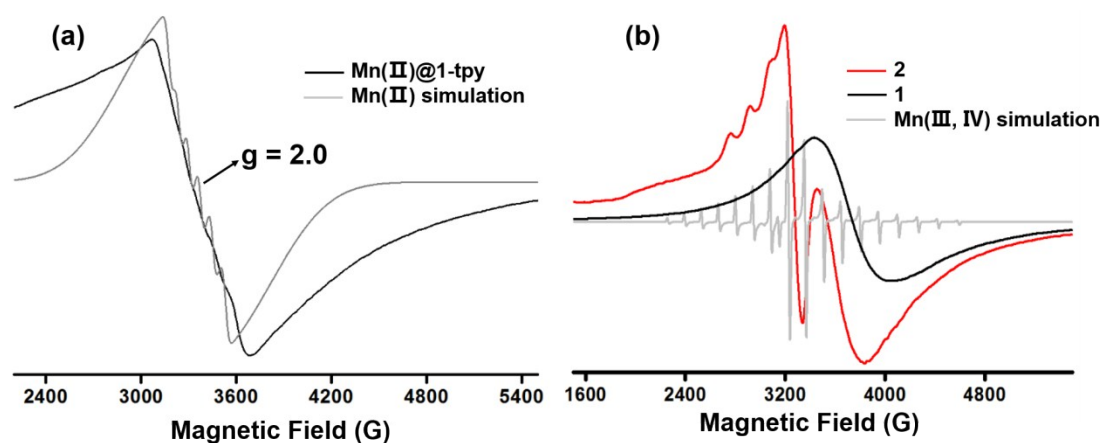


Fig. S2 (a) Experimental (black) and simulated (grey) EPR spectra of Mn(II)@1-tpy recorded at 2 K. The parameters for the simulation are $D = 0.61 \text{ cm}^{-1}$, $E = 0.16 \text{ cm}^{-1}$, $g_x = 2.00$, $g_y = 2.00$, $g_z = 2.00$; (b) Experimental EPR spectra of **1** (black) and **2** (red), and 16-line hyperfine splitting patterns for Mn(III,IV) dinuclear complex. The parameters used for the simulation are $D = 0.61 \text{ cm}^{-1}$, $E = 0.16 \text{ cm}^{-1}$, $g_x = 1.956$, $g_y = 1.956$, $g_z = 1.956$.

Note: Mn(II)@1-tpy and **2** both contain signals for Cr(III), trapped electrons and the Mn unit. It is complicated to simulate all the signals in one spectrum. For this reason, we show the best fits for Mn simulations.

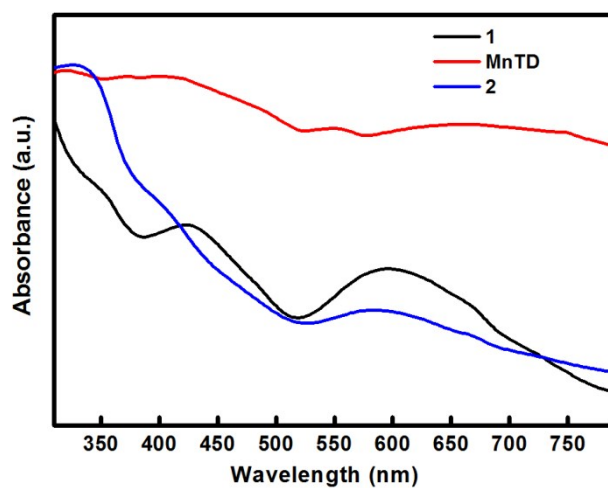


Fig. S3. UV-vis spectra of MnTD (solid state), MIL-101(Cr) (**1**) and **2**. The absorption features around 550 nm and 660 are indicative of the formation of the di- μ -oxo Mn(III/IV) complex. **1** has typical peaks around 420 and 600 nm, and **2** shows decreased intensity at peaks around 600 nm.

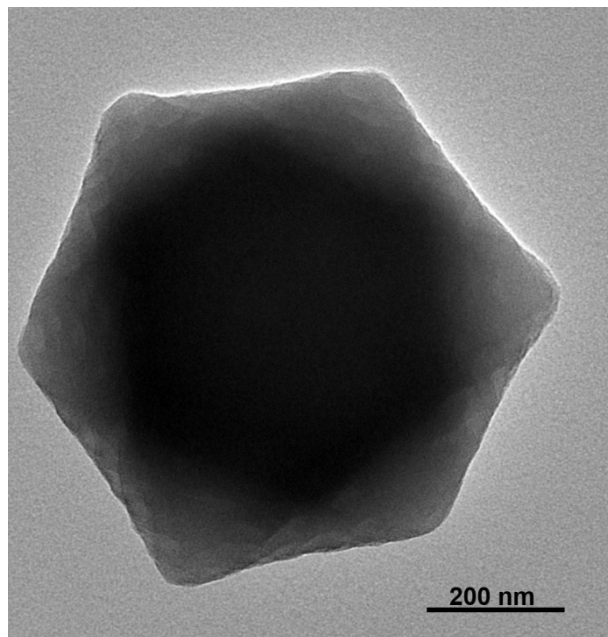


Fig. S4 TEM image of the pristine MIL-101(Cr) (**1**).

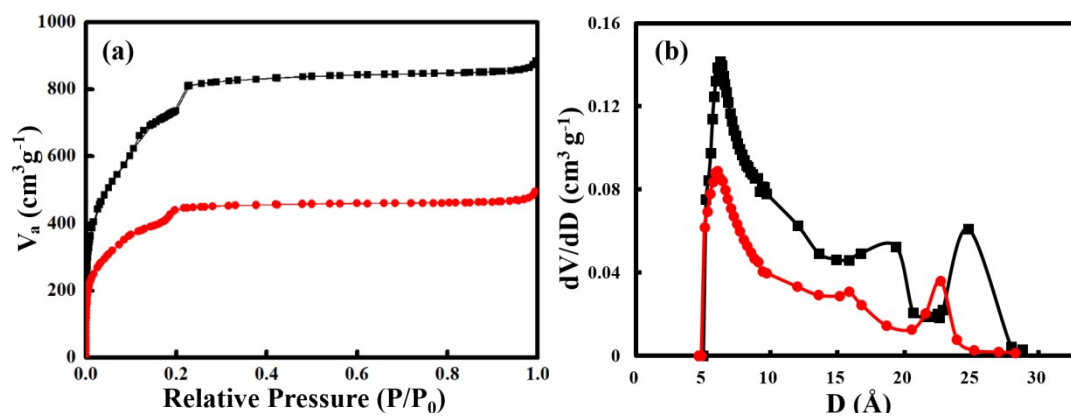


Fig. S5 Nitrogen adsorption/desorption isotherms at 77 K (a) and pore size distribution (b) of MIL-101(Cr) (**1**, black) and MnTD@MIL-101(Cr)-triazole (**2**, red). The apparent BET surface areas are 2861 and 1470 $\text{m}^2 \text{g}^{-1}$ for **1** and **2**, respectively. Pore size distributions of the samples were calculated by using the BJH (Barrett–Joyner–Halenda) method from the desorption branch of the isotherms. Pore sizes of samples decreased from 19.5 Å and 24.8 Å for **1** to 15.8 Å and 22.6 Å for **2**.

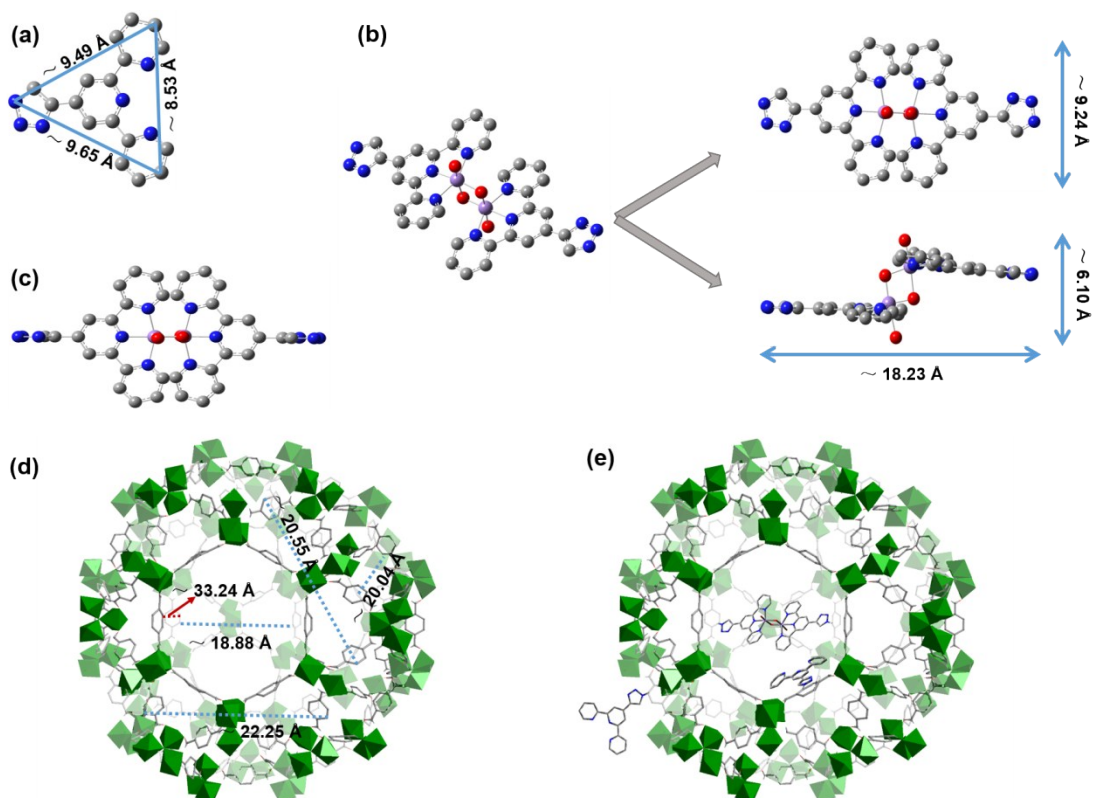


Fig. S6 DFT calculated structures and dimensions of (a) 1,2,3-triazole-linked 2,2'':6',2''-terpyridine (triazole-tpy, tpy = 2,2'':6',2''-terpyridine) and (b,c) $[(\text{OH}_2)(\text{triazole-tpy})\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{tpy-triazole})(\text{OH}_2)]^{3+}$ (**3**). In (b), the triazole-ring is in the same plane with the benzene-ring of the terephthalate ligand and three pyridines; while in (c), triazole ring is perpendicular to the other plane. Counteranions were not included when measuring dimensions; (d) Schematic representation of possible distances (blue dotted line) and a highly unfavored distance (red dotted line) in the larger mesoporous cage of **1** for dimerization; and (e) Schematic representation of **2**.

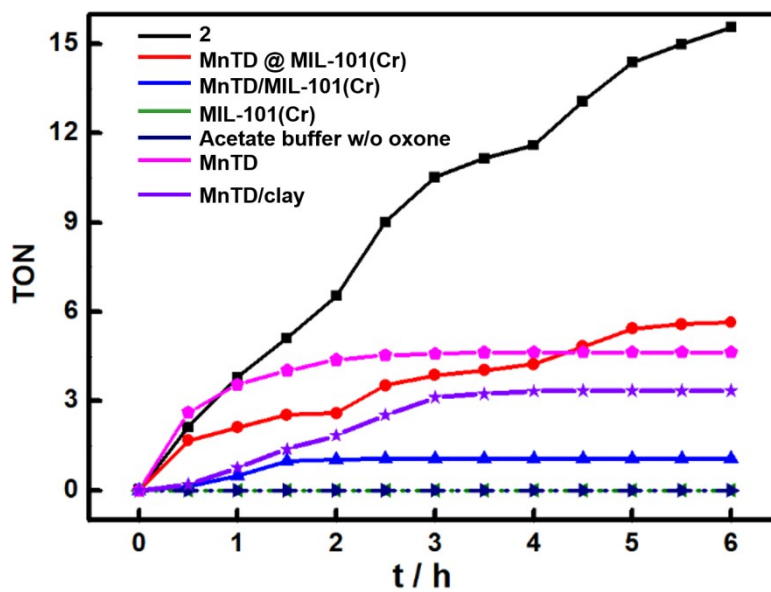


Fig. S7 Oxygen evolution plots for 20 mg catalyst in 100 ml acetate buffer (pH 4.5, 0.2 M) with 10 mM Oxone. A fresh aliquot (2 ml, 500 mM) of aqueous solution of Oxone was added every two hours.

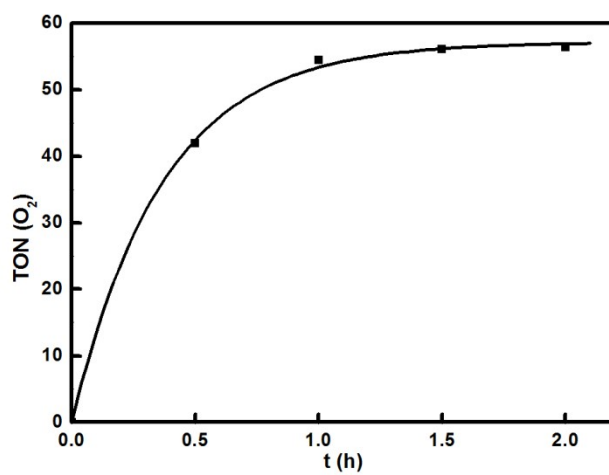


Fig. S8 O₂ evolution in the reaction of **2** (20 mg) and Oxone (80 mM) in 100 ml acetate buffer (pH 4.5, 0.2 M).

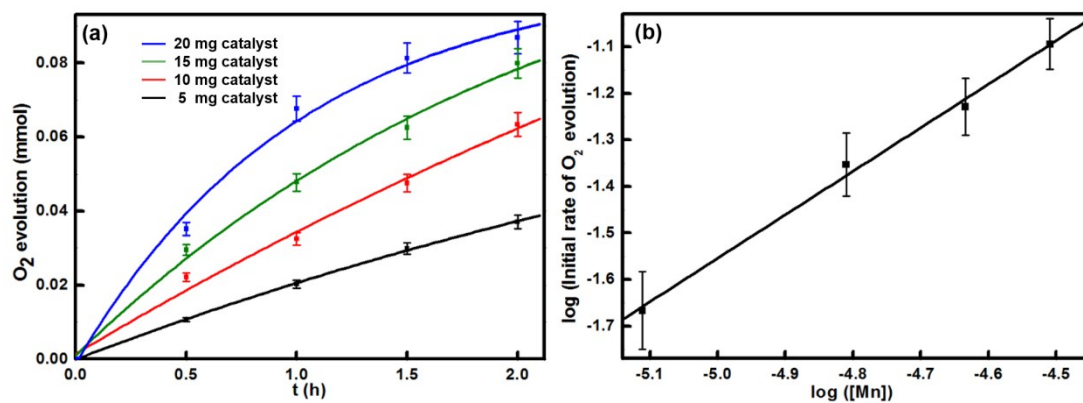


Fig. S9 Time course for O₂ evolution in the reaction of **2** (5-20 mg, Mn content: 0.85 wt%) and Oxone (30 mM); (b) Logarithmic plot showing the dependence of the rate of O₂ evolution on [Mn] with a slope of 0.956.

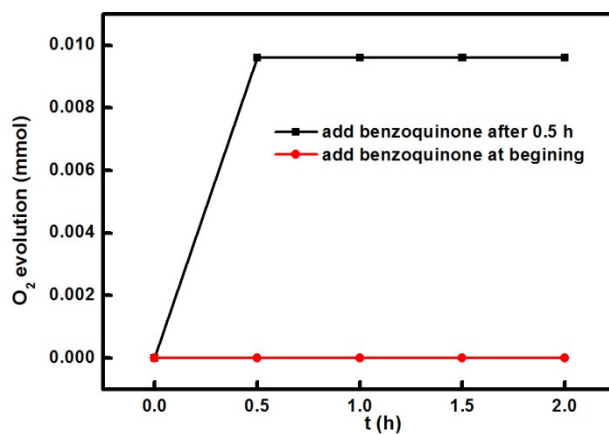


Fig. S10 O₂ evolution in the reaction of **2** (20 mg) and Oxone (10 mM) in the presence of *p*-benzoquinone (100 mM) in 100 ml acetate buffer (pH 4.5, 0.2 M).

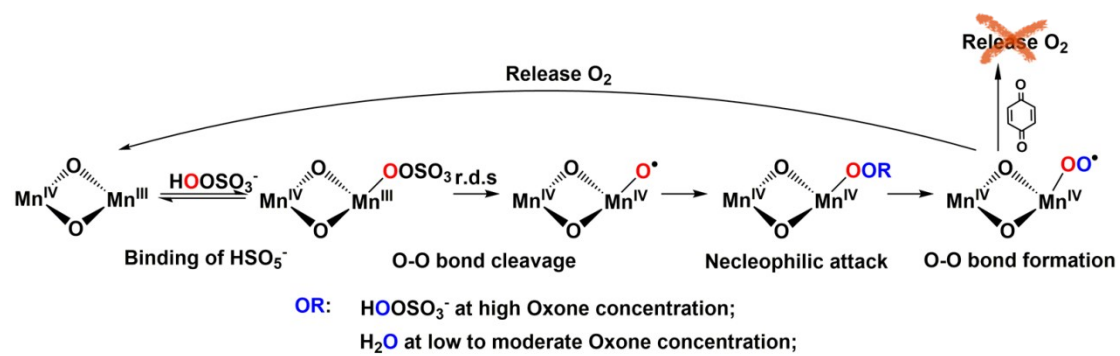


Fig. S11 Proposed mechanism for O₂ evolution from reaction of **2** and Oxone (KHSO₅).

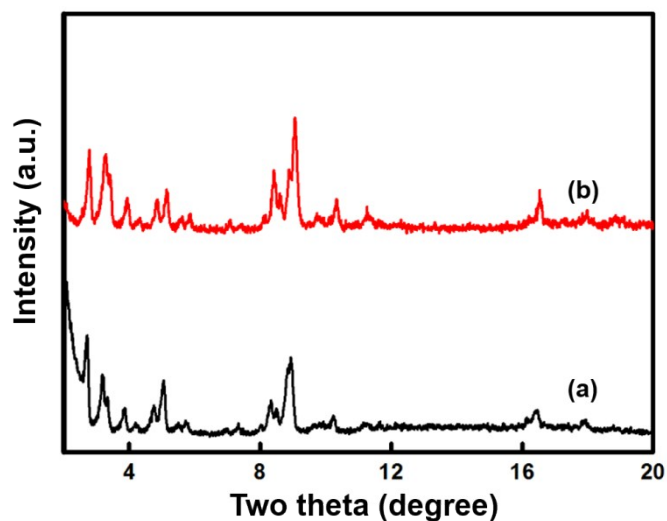


Fig. S12 PXR D patterns of MnTD@MIL-101(Cr)-triazole (**2**) before (a) and after (b) water oxidation reaction.

Note: Here sample of **2** after water oxidation for XRD measurements was prepared under milder conditions to avoid the breaking of functional units. Thus, sample of **2** before water oxidation was also prepared under identical condition for the direct comparison, which might cause the difference of the relative intensities of diffraction peaks for **2** in this figure, as compared with those in Fig. 2b.

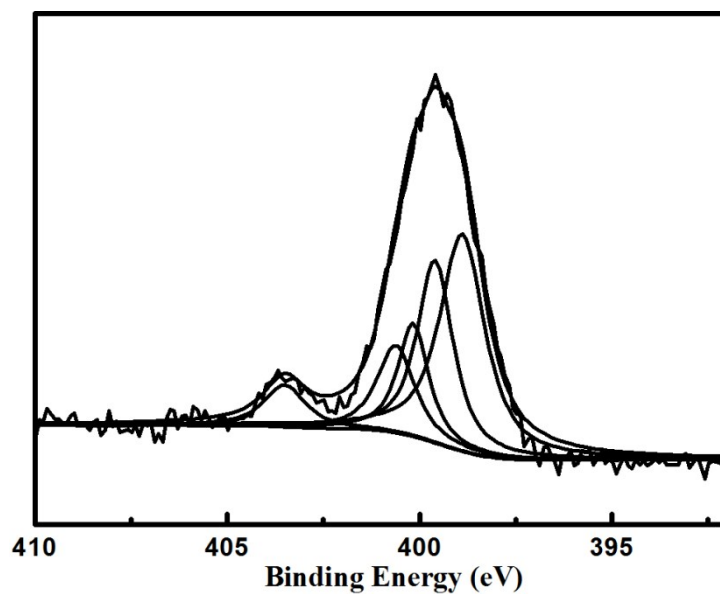


Fig. S13 N 1s XPS of **2** after water oxidation reaction.

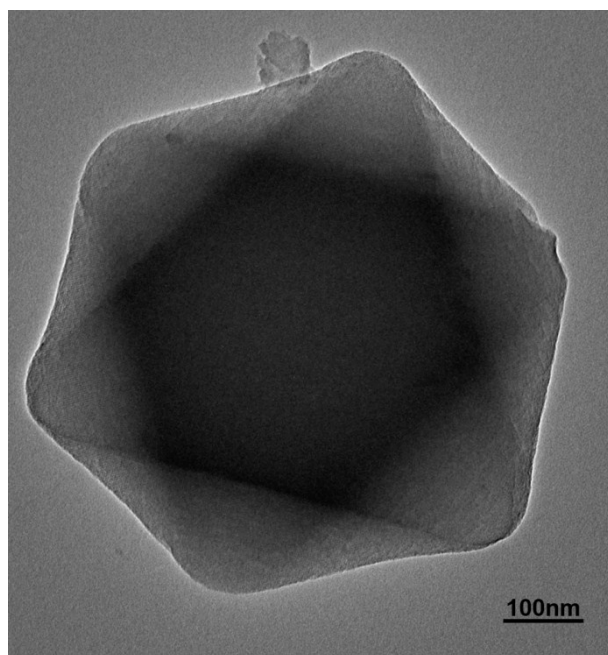


Fig. S14 TEM image of **2** after water oxidation reaction.

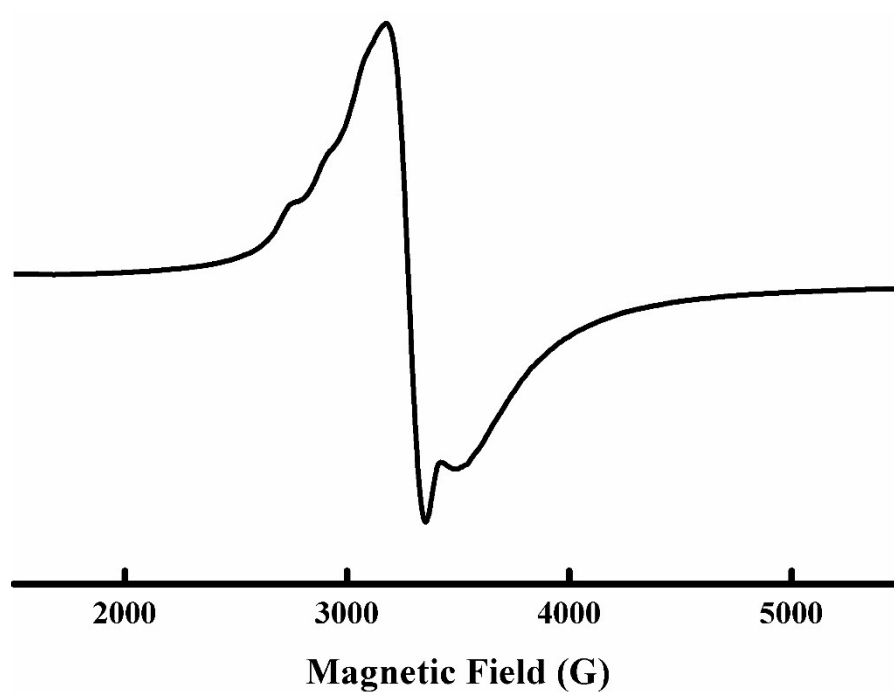


Fig. S15 EPR spectrum of **2** after water oxidation reaction, recorded at 2 K.

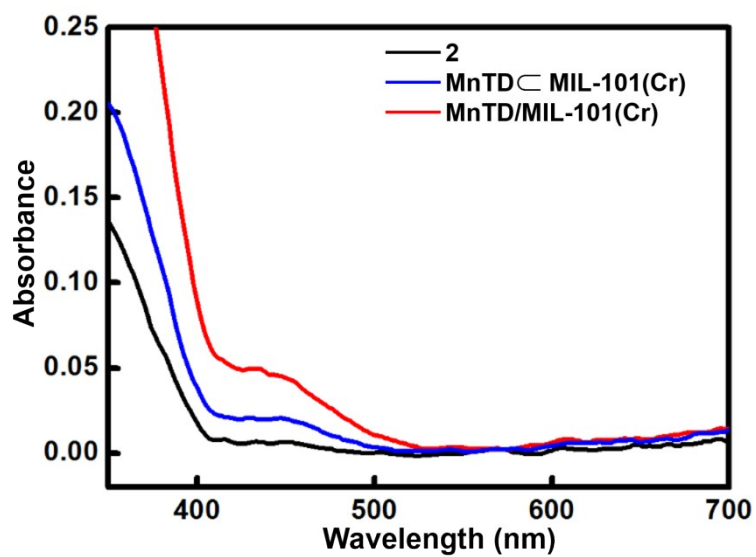


Fig. S16 UV-vis spectra of the filtrate from the reaction of MnTD/1, MnTD \subset 1 and 2 with Oxone in 100 ml acetate buffer (pH 4.5, 0.2 M). The absorption shoulder around 450 nm is the characteristic of typical Mn(IV/IV) dimer.

Table S1. Elemental analysis and AAS results of materials^a

Catalyst	C (wt%) ^{a,b}	N (wt%) ^{a,b}	H (wt%) ^{a,b}	Mn (wt%) ^{a,c}	N/Mn Ratio ^d
MIL-101(Cr)	35.21	-	3.13	-	
MnTD@MIL-101(Cr)-triazole	36.23	10.47	4.77	0.85	49.86
MnTD⊂MIL-101(Cr)	32.80	1.24	6.41	1.60	3.04
MnTD/MIL-101(Cr)	36.23	0.95	8.36	1.20	3.11

^a Average of three runs. ^b Measured by elemental analysis. ^c Measured by AAS. ^d N/Mn ratio is based on the moles of elements per gram of sample.

MnTD⊂**1** and MnTD/**1** and **2** were prepared by using identical amounts of Mn²⁺ (0.12 mmol) and tridentate ligand (0.12 mmol). The varied Mn loading is due to the different synthetic approach. The N/Mn ratio for MnTD⊂**1** and MnTD/**1** is consistent with theoretical values for MnTD (Mn:N 1:3). The large excess of N for **2** supported the IR and XPS results for 1-N₃ and 1-tpy that only a small portion of azide group participated in the formation of triazole product.