

Biomimetic Di-Manganese Catalyst Cage-Isolated in a MOF: Robust Catalyst for Water Oxidation with Ce (IV), a non-O-donating oxidant

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1. *Materials and methods:*

All commercially available chemicals and solvents were used as received without further purification unless otherwise stated. All the experiments were done at room temperature and ambient atmosphere unless otherwise stated.

PXRD: All the powder X-ray diffractions were recorded in a Rigaku MiniflexII Desktop X-ray diffractometer.

TGA: All the thermogravimetric analyses were done in a Q 50 TA instrument.

Elemental analysis: Elemental analysis was done at *Intertek Pharmaceutical Services*, 291 Route 22 E Salem Industrial Park, Bldg. #5 Whitehouse, NJ 08888.

FT-IR: All the FT-IR spectra were recorded in a Galaxy 5020 FT-IR spectrometer with 32 scans at 1 cm⁻¹ resolution.

EPR: Bruker EMXplus spectrometer was used to record all the spectra at 7K; microwave source: 9.4 GHz; microwave power: 1 mW; modulation amplitude: 15.66 G.

UV-VIS Study: All UV-VIS studies were carried out in a Shimadzu UV-2101PC spectrophotometer.

GC-MS for Stilbene epoxidation: All GC-MS analyses were carried out in a Shimadzu GC-17A Gas Chromatograph.

GC-MS for identifying evolved gas. Agilent 3000A MicroGC with He as the carrier gas.

Oxygen evolution assays: All oxygen evolution assays were carried out with Clark-type electrode using YSI 5300 A-1 instrument. The data were recorded with National instrument NI SCC-68 using Lab VIEW

Express software. The Clark-type electrode was calibrated using a zero oxygen concentration solution and an air saturated solution. Baseline was set at 100 mV in 6 mL nitric acid solution (pH ~1). For the oxygen assay, definite amount of the substance to be studied was suspended in 6 mL nitric acid solution. Reactions were initiated by adding 250 μ L freshly prepared Ceric Ammonium Nitrate (CAN) solution (550 mM) through a small groove in the Teflon cover of electrode. Reactions with larger amounts of CAN were initiated with larger volumes of CAN solution after the baseline was set. The oxygen evolution assays were done for **MnTDC**MIL-101(Cr), **MnTD**-infiltrated MIL-101(Cr) sample, MIL-101(Cr), molecular **MnTD**, MnO₂, **MnTDC**FDU-12 and for nitric acid solution without catalyst.

Preparation of Nitric Acid Solution:

Nitric Acid Solution was prepared by diluting 10 mL of concentrated nitric acid to 100 mL with distilled water. 10 mL of the diluted solution was then added to 60 mL of distilled water.

2. MIL-101(Cr):

2.1 Synthesis: MIL-101(Cr) was synthesized using a literature procedure.^{S1}

2.2 Characterization: As synthesized MIL-101(Cr) was characterized by using PXRD, FT-IR, and TGA.

2.3 Activation: As synthesized MIL-101(Cr) was washed with 95% EtOH seven times, dried overnight in oven at 150°C. The sample was then placed under vacuum in a Schlenk line with heating at 60°C overnight to activate.

3. Synthesis of (H₂O)(terpy)Mn(O)₂(terpy)(OH₂)](NO₃)₃.xH₂O:

(H₂O)(terpy)Mn(O)₂(terpy)(OH₂)](NO₃)₃.xH₂O was synthesized according to literature procedure.^{S2}

4. *Synthesis, Characterization and Quantification of MnTDCMIL-101(Cr):*

The synthesis, characterization and quantification of **MnTDCMIL-101(Cr)** was done following literature procedure.^{S3}

5. *FDU-12:*

FDU-12 was prepared and characterized following a literature procedure with calcination temperature of 550°C.^{S4}

6. *Further silylation of FDU-12 (Silylated FDU-12):*

As the aperture size of FDU-12 is significantly bigger than the dimensions of **MnTD**, we needed to make the aperture smaller. For this purpose we treated FDU-12 with propyltrimethoxysilane as a silylating agent following literature procedure.^{S5} This, as reported previously, reduces the aperture of FDU-12 to the extent that [Co^{III}(salen)] remains contained.^{S5} As **MnTD** (~14Åx12Åx8Å) is significantly bigger in size compared to [Co^{III}(salen)] (~13.5Åx10.2Åx4Å), we believed that the similar silylation would succeed in containing **MnTD** inside FDU-12.

7. *MnTDC FDU-12*

Assembly of MnTD inside the pores of FDU-12: 200 mg (0.860 mmol) of 2,2':6',2''-terypyridine was added to 1.2 mL of water in a 5 mL round bottom flask with a stir bar and was sonicated for 20 minutes. 50 mg of silylated FDU-12 was suspended in the mixture, which was stirred for 24 hrs. Then 212 mg (0.865 mmol) Mn(CH₃COO)₂.4H₂O was added to the suspension and stirred for 4 hrs. Then 1.2 mL K-Oxone (222 mg) solution was added in a dropwise fashion to the suspension. The resulting mixture was stirred for 24 hr. The final brown suspension was then vacuum filtered on 0.45 micron nylon filter membrane and was washed with excess water, until the washing became colorless, to wash out excess [(H₂O)(terpy)Mn(μ-O)₂(terpy)(OH₂)]³⁺, and finally washed with diethyl ether. Then the product was vacuum dried overnight to yield **MnTDCFDU-12**. The IR spectra for each step of synthesizing **MnTDCFDU-12** are plotted below. Elemental analysis showed C: 15.78%, H: 1.69%, N: 2.84%, and Si:

2.46%. As terpyridine in the **MnTD** would be the only source of N in **MnTDC**FDU-12 and FDU-12 would be the source of Si, we used these numbers to calculate the mass %age of **MnTD** in **MnTDC**FDU-12 (13% of the total mass of **MnTD** is contributed by N-atom of terpy; i.e. 2.84% of N-atom corresponds to ~20% mass of the total sample resulting from **MnTD**).

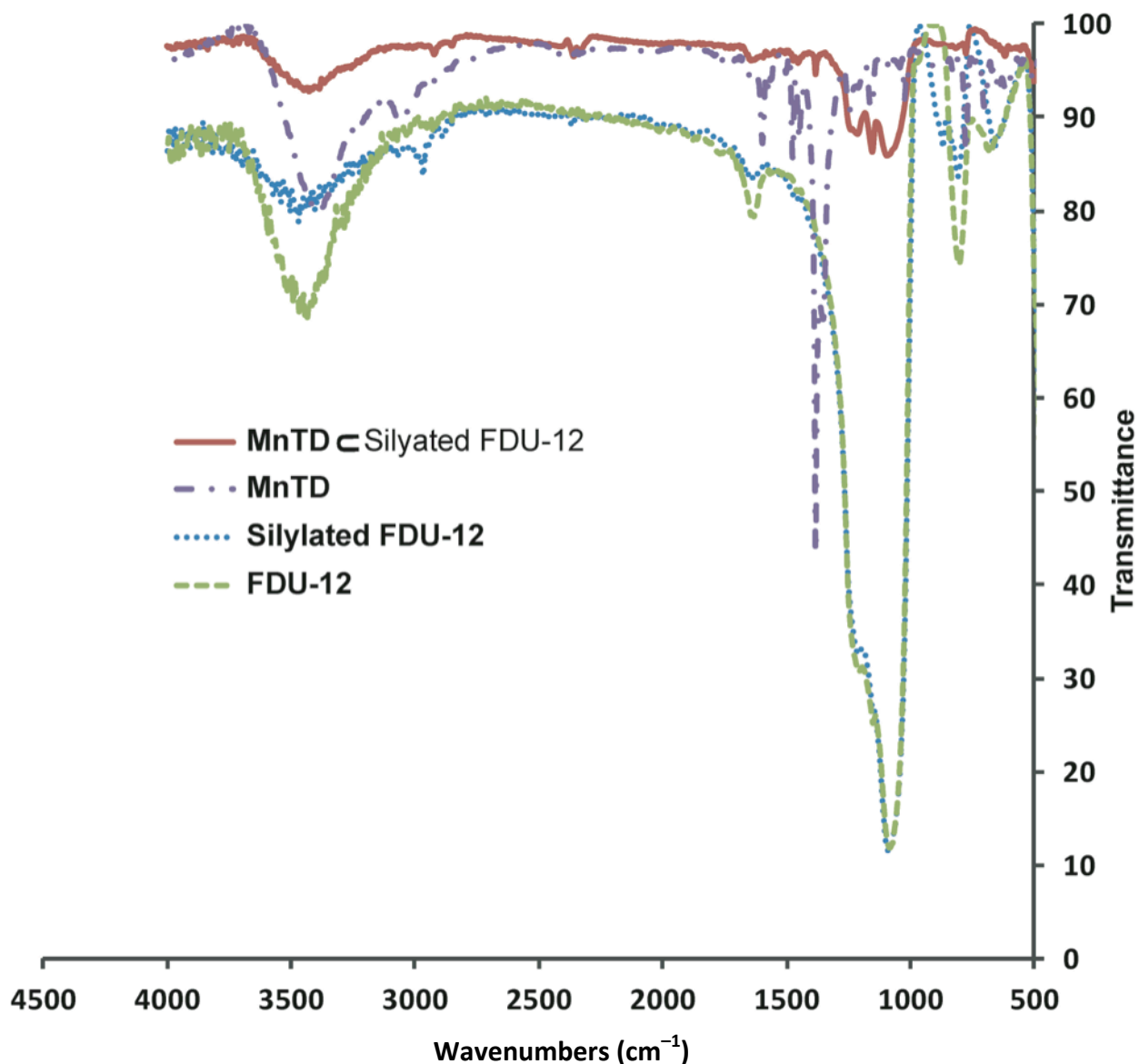


Fig. S1 FT-IR Spectra of FDU-12 as synthesized, Silylated FDU-12, **MnTD**, and **MnTDC** Silylated FDU-12.

8. FT-IR study of MnTDCMIL-101(Cr) after (7 days) Catalysis.

We noticed that the key peak resulting from high-valent $\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}$, at 777 cm^{-1} , persists (Fig. S2). However, a $\text{Mn}^{\text{IV}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}$ species, with terpy as a ligand, gives a peak at 791 cm^{-1} ,^{S6} a $\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}$ species, with phenanthroline as a ligand, gives a peak at 716 cm^{-1} and with bipyridine as a ligand, gives a peak at 688 cm^{-1} .^{S7,S8}

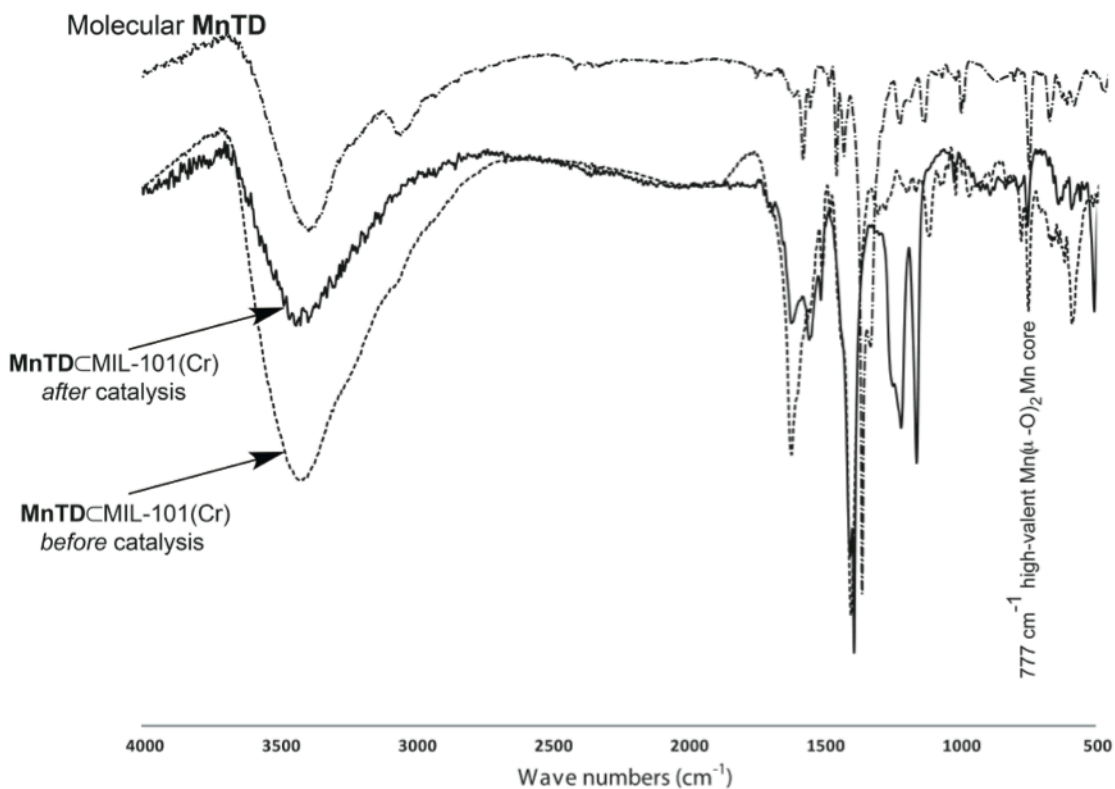


Fig S2. FT-IR of MnTDCMIL-101(Cr) before (dotted line) and after (solid line) (7 days) catalysis with CAN and molecular MnTD (dashed line).

9. Cryogenic EPR MnTDCMIL-101(Cr).

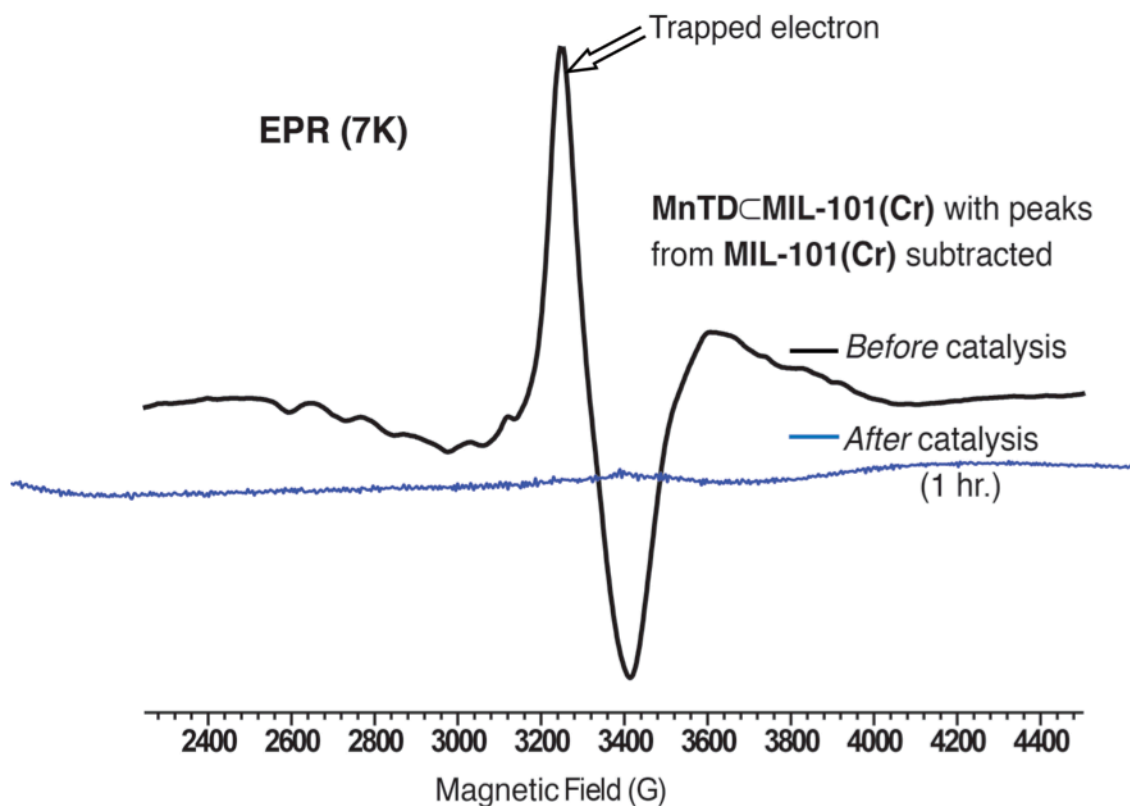


Fig. S3 Cryogenic EPR of **MnTDCMIL-101(Cr)** before and during catalysis; $\text{Mn}_2^{\text{III/IV}}$ is converted to an EPR-silent species in the course of catalysis.

10. Oxygenation of *cis*-stilbene.

To a disposable glass vial containing 2 mL of acetonitrile and 10 μL of water, 1 μmol of catalyst, **MnTD**, was added. The amount of **MnTDCMIL-101(Cr)** needed to supply an equivalent amount was 10 times by weight the molecular **MnTD**, as reported previously.^{S3} 0.1 mmol of *cis*-stilbene was added. After cooling the solution in an ice bath, 260 mg of tetrabutylammonium oxone (TBAO) was added to the solution and stirred for 2 hrs at 20°C. The reaction was quenched by excess addition of aqueous sodium bisulfite. The product mixture was analyzed by GC-MS.

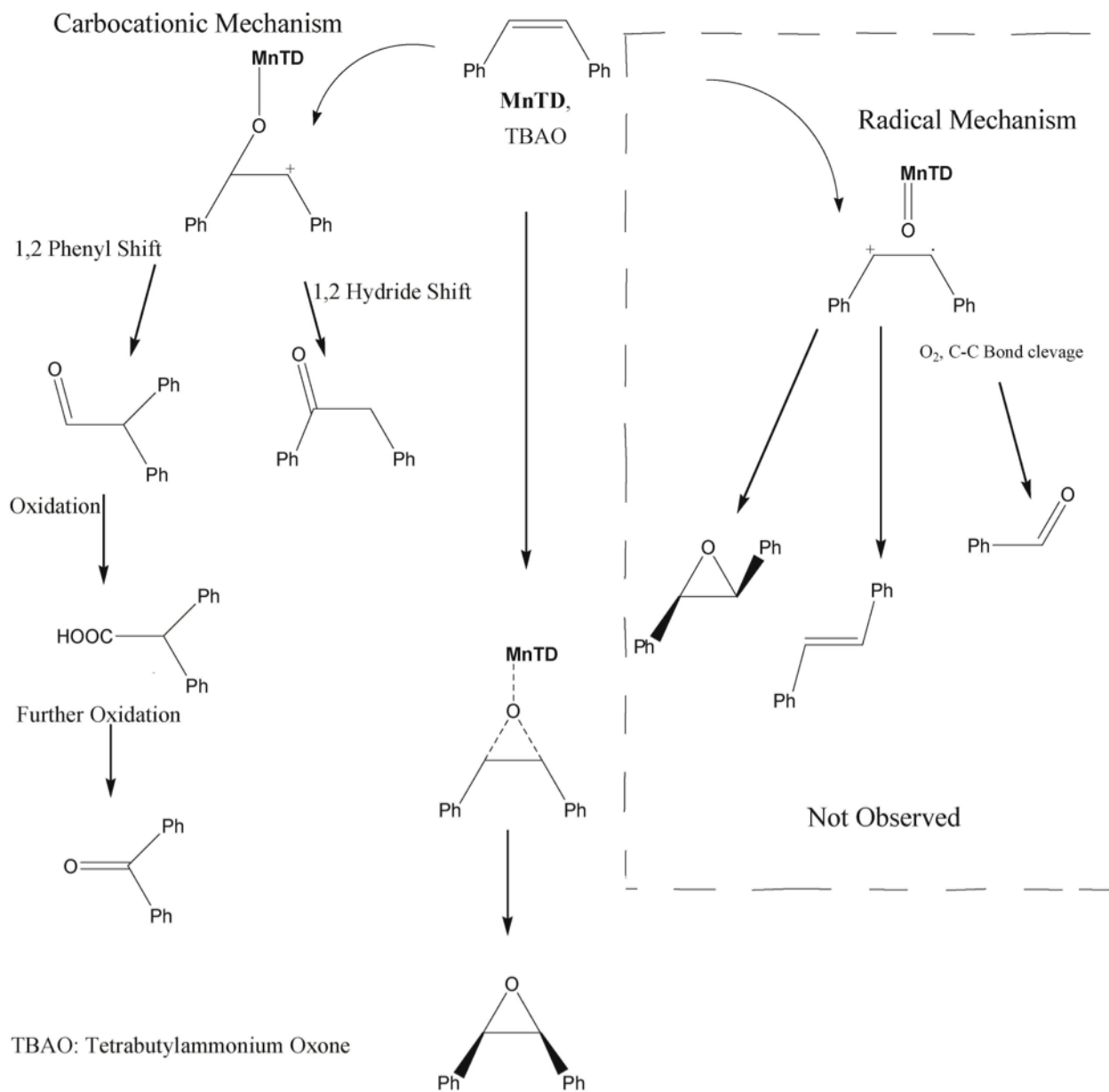
Product distribution of *cis*-stilbene epoxidation is highly sensitive to the oxidation mechanism. With both molecular **MnTD** and **MnTDCMIL-101(Cr)**, we did not see any *trans*-stilbene or *trans*-

stilbene oxide. This kind of product distribution (especially the absence of *trans*-stilbene oxide) is consistent with the ‘rebound’ mechanism and carbocationic intermediate (but not a mechanism involving radicals) that are very characteristic with molecular **MnTD**, as has been discussed previously.^{S9} With bulk MnO₂, we did not observe any epoxidation of *cis*-stilbene. However, with manganese oxides, a radical mechanism is generally invoked, which invariably yields highly stable *trans*-stilbene oxide (See Scheme S1 for a detailed mechanism of *cis*-stilbene epoxidation).^{S10}

Table S1. Epoxidation of *cis*-stilbene to probe the nature of the catalytically active species in **MnTDCMIL-101(Cr)**.

Substrate (mmol)	Catalysts (mg)	Oxidant (mg)	Conversion; Products (% of total product)
<i>cis</i> -stilbene (0.1)	Molecular MnTD (0.8)	[Bu ₄ N] •HSO ₅ (TBAO)	100%; <i>cis</i> -stilbene oxide (26), benzophenone (35), 1,2-dipheylethanone (39)
	MnTDCMIL-101(Cr) (8.0)	(260)	100%; <i>cis</i> -stilbene oxide (23), benzophenone (37), 1,2-dipheylethanone (40)
	MnO ₂ (1.0)		~0%

[†]All catalytic runs were performed at 20°C, for 2 hr. and in 2.5 mL CH₃CN:H₂O (250:1).



Scheme S1. Possible mechanistic pathways for oxidizing *cis*-stilbene with **MnTD** using TBAO as oxidant.

11. Tetrabutylammonium oxone preparation (TBAO): Tetrabutylammonium oxone was prepared following literature procedure.^{S11}

Abbreviations:

MnTD: [(H₂O)(terpy)Mn(μ-O)₂Mn(OH₂)(terpy)]³⁺

CAN: Cerium(IV) Ammonium Nitrate

Terpy: 2,2':6',2''-terpyridine

TBAO: Tetrabutylammonium oxone

References:

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