Supporting information

Oxygen Evolution from BF$_3$/MnO$_4^-$

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Materials. CAUTION: *Care should be taken in handling BF_3/MnO_4^- in organic solvents, since the system is very reactive. Although we have not encountered any problems so far, the amount of MnO_4^- used each time should be less than 50 mg.* Potassium permanganate (Aldrich, 97%) was recrystallized from water.[1] $^nBu_4N[MnO_4]$[2] and ^{18}O-labeled $K[MnO_4]$[3] were prepared according to literature methods. Boron trifluoride–acetonitrile solution ($BF_3 \cdot CH_3CN$) (Fluka, 15.2 – 16.8%) was stored at -20 °C and used without further purification. The concentration was determined to be 16% by hydrolysis to H_3BO_3 and HF followed by titration with standard NaOH solution. $H_2^{18}O$ (98 atom % ^{18}O) was purchased from Medical Isotopes and used as received. Acetonitrile (Labscan, HPLC grade) was purified by Pure Solv^{TM} Solvent Purification Systems (Innovative Technology, Inc.).

Instrumentation. Electrospray ionization mass spectra (ESI/MS) were obtained on a PE SCIEX API 365 mass spectrometer. The analyte solution was continuously infused with a syringe pump at a constant flow rate of 5 μL min^{-1} into the pneumatically assisted electrospray probe with nitrogen as the nebulising gas. The declustering potential was typically set at 10-20 V. GC-MS measurements were carried out on a HP 6890 gas chromatograph equipped with a HP-5MS column (30 m × 0.25 mm i.d.) and interfaced to a HP 5975 mass-selective detector.

Kinetic and product analysis. The gas evolved during the experiment was determined as followed. In a typical reaction, a deaerated solution of MnO_4^- (0.139 mmol) in CH_3CN (10 mL) was placed in a two neck round bottom flask (~16 mL) under argon at 293 K. One neck of the flask was connected to a gas burette and the other was sealed with a septum. A solution of deaerated $BF_3 \cdot CH_3CN$ (1.26 mmol, 1 mL) was added through the septum into the MnO_4^- solution with vigorous stirring. The volume of gas evolved was recorded at different time interval. The first-order rate constants, k_{O_2}, were obtained by nonlinear least-squares fits of Y_t versus t according to

the equation $Y_t = Y_\infty + (Y_0 - Y_\infty)\exp(-k_{O_2}t)$, where Y_0 and Y_∞ are the initial and final O_2 produced (mmol), respectively. The gas was also analyzed by GC-MS.

Determination of O_2 isotopic composition by GC-MS.

In a typical reaction, a deaerated solution of 91% ^{18}O-labeled $KMnO_4$ (0.08 mmol) in CH_3CN (6 mL) was placed in a vessel (~8 mL) sealed with a septum under argon at 293 K. A solution of $BF_3 \cdot CH_3CN$ (1.29 mmol, 1 mL) was added into the solution using a gastight syringe. 50 µL gas in the headspace was withdrawn after 20 min and analyzed by GC-MS.

DFT Calculations

DFT calculations were carried out using Gaussian 03 program.[4] The Becke's three-parameter nonlocal exchange functional[5] and the Lee, Yang, and Parr nonlocal correlation functional (B3LYP)[6] were utilized, with standard LANL2DZ basis set and relativistic effective core potential (ECP)[7] for Mn, and the 6-31+G(d) basis set for all non-metal atoms. The geometries of all species were fully optimized and the harmonic vibration frequencies were calculated to obtain the zero-point energies (ZPE) and to verify nature [minimum or a transition state (TS)] of stationary points on the potential energy surfaces.

The calculated singlet-triplet splitting (17.3 kcal/mol) of MnO_4^- at B3LYP/LAN2DZ/6-31+G(d) level is in good agreement with the value (22.8 kcal/mol) obtained at CCSD(T)/LAN2DZ/6-31+G(d) level.

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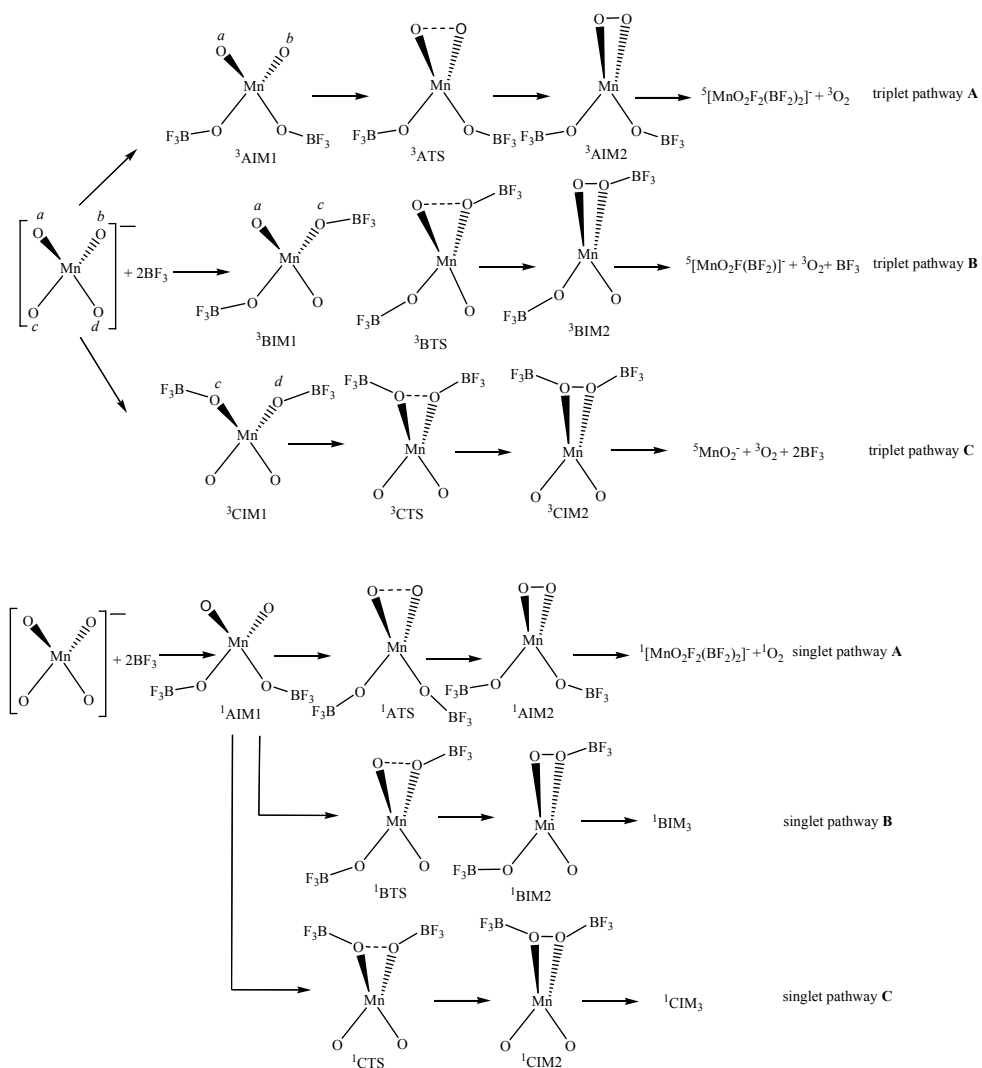
Fig. S1 Possible singlet and triplet decomposition pathways of 1:2 adduct $[MnO_4^- \cdot 2BF_3]$.

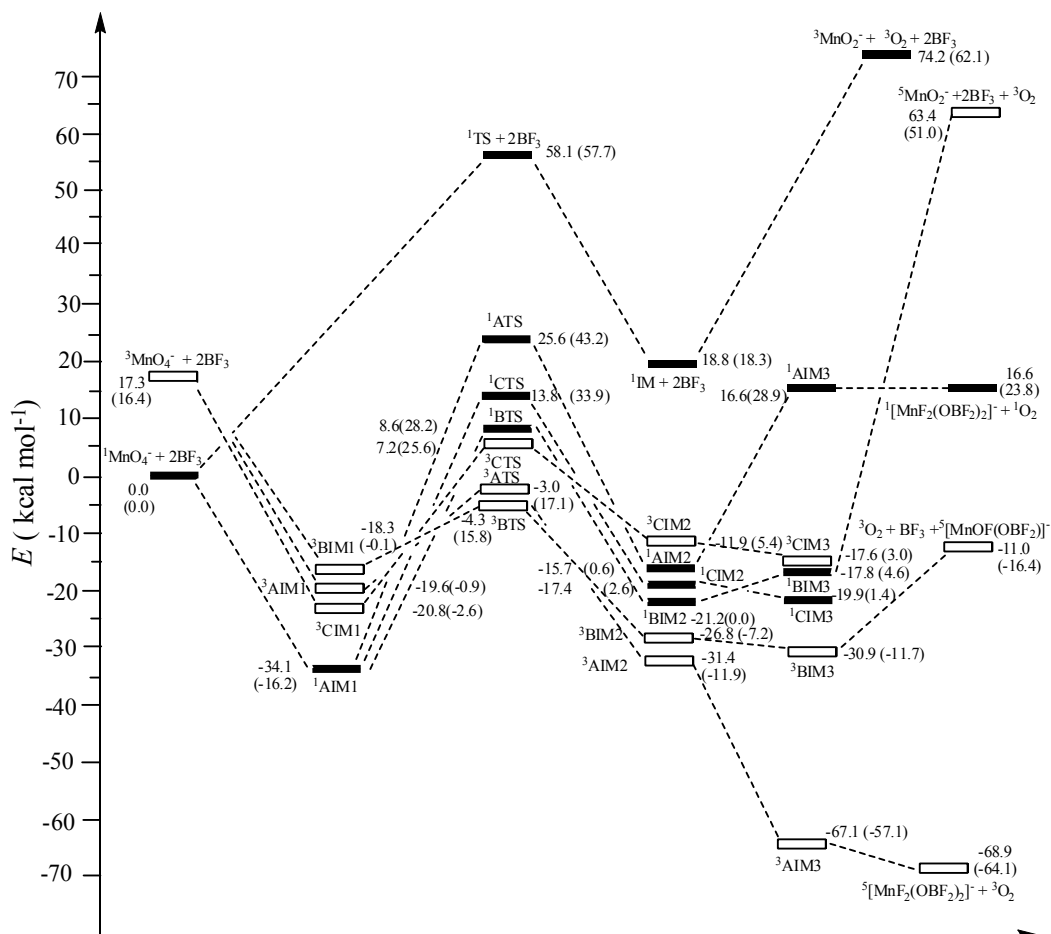**Fig. S2** The potential energy profiles of the singlet and triplet reaction pathways of

1:2 adduct [MnO$_4^-$·2BF$_3$]. The relative energies are the electronic energy with

zero-point energy and thermal corrections at 298 K in normal font while relative 298

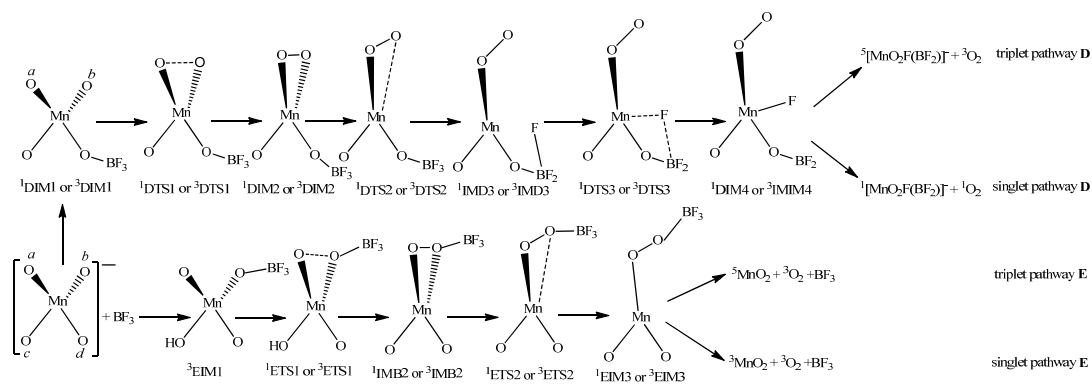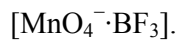K Gibb's free energies are in the parentheses.

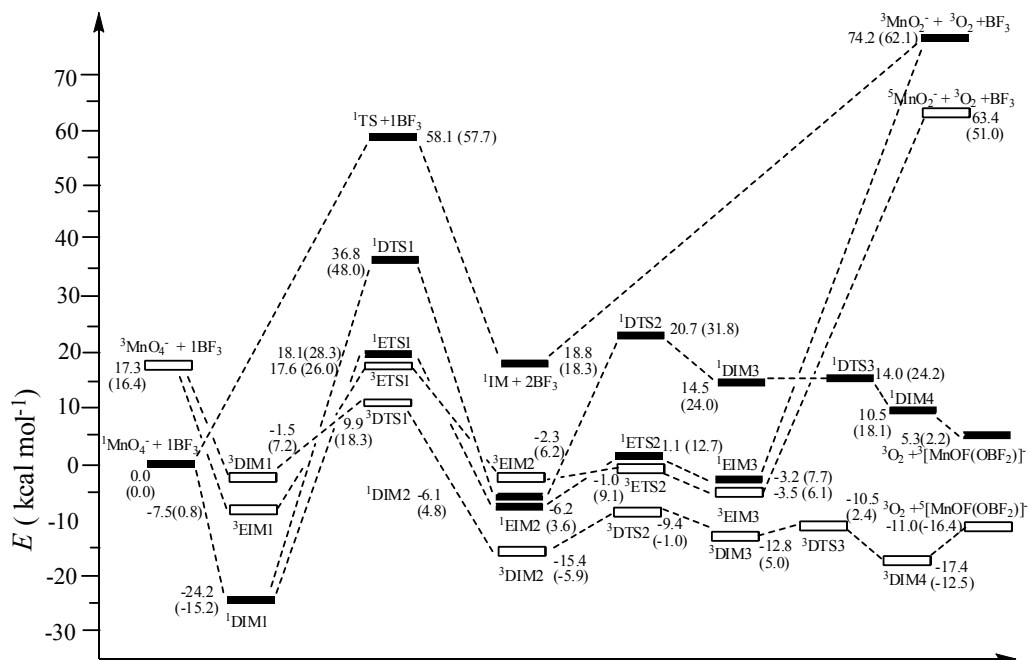**Fig. S3** Possible singlet and triplet decomposition pathways of 1:1 adduct [$MnO_4^-\cdot BF_3$].

Fig. S4 The potential energy profiles of the singlet and triplet reaction pathways of 1:1 adduct [MnO$_4^-$·BF$_3$]. The relative energies are the electronic energy with zero-point energy and thermal corrections at 298 K in normal font while relative 298 K Gibb's free energies are in the parentheses.
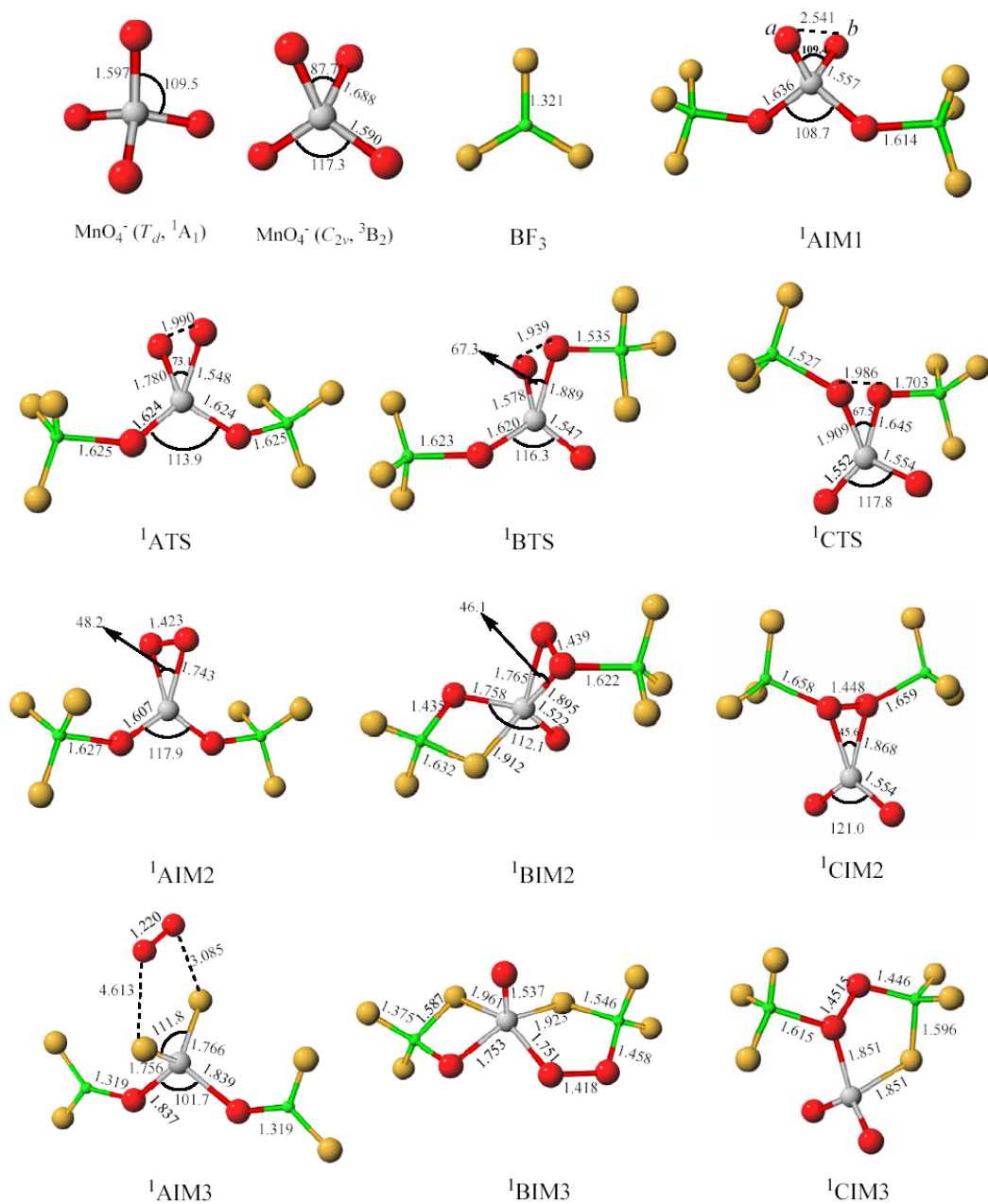
Fig. S5 Optimized structures of the species involved in the triplet and singlet decomposition reactions of 1:2 adduct [$MnO_4^-·2BF_3$]. The bond distances are in angstroms and bond angles in degrees.

^{3}IMA1

^{3}IMB1

^{3}IMC1

^{3}ATS

^{3}BTS

^{3}CTS

^{3}AIM2

^{3}BIM2

^{3}CIM2

^{3}AIM3

^{3}BIM3

^{3}CIM3

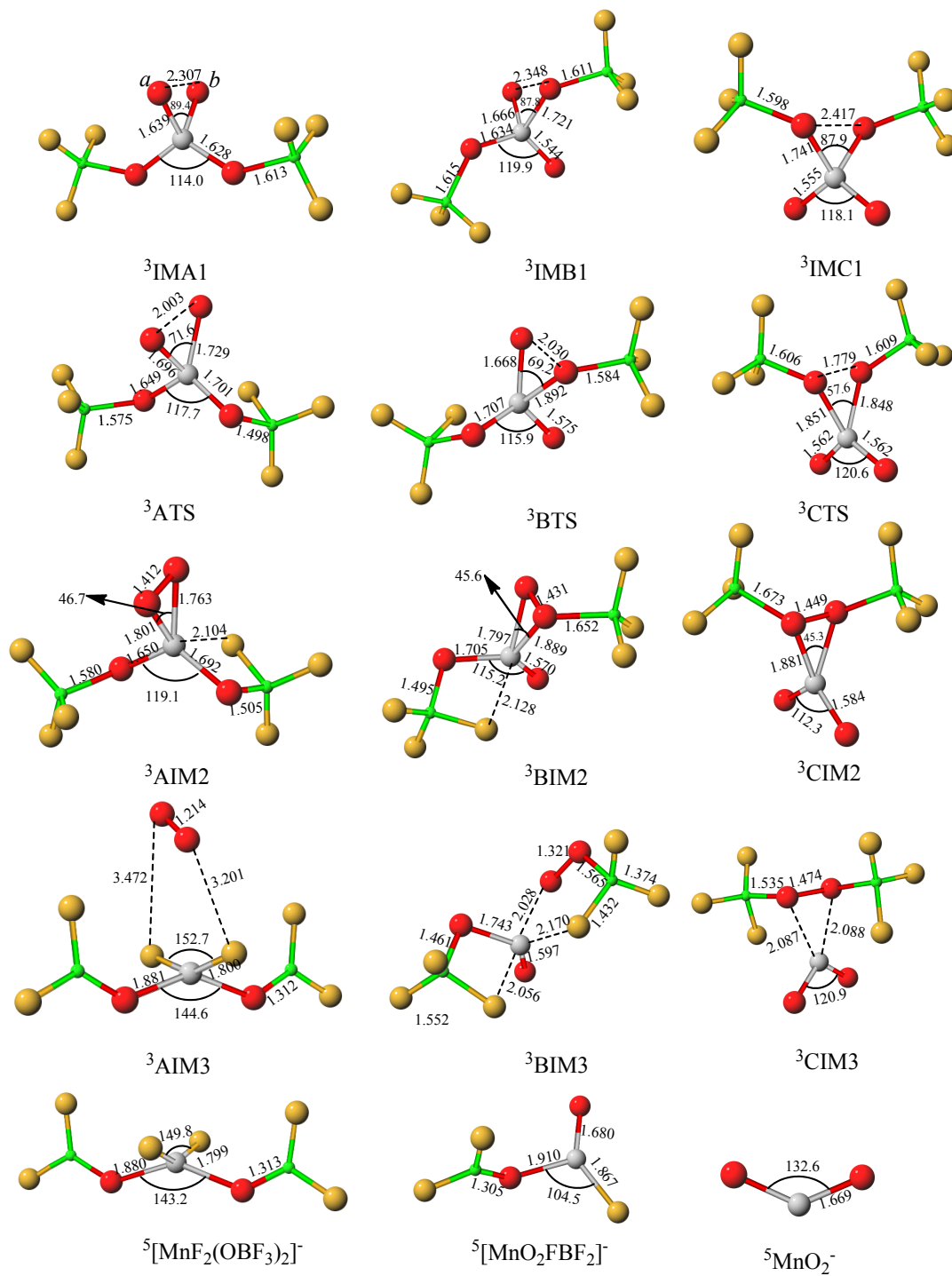^{5}[MnF$_2$(OBF$_3$)$_2$]$^-$
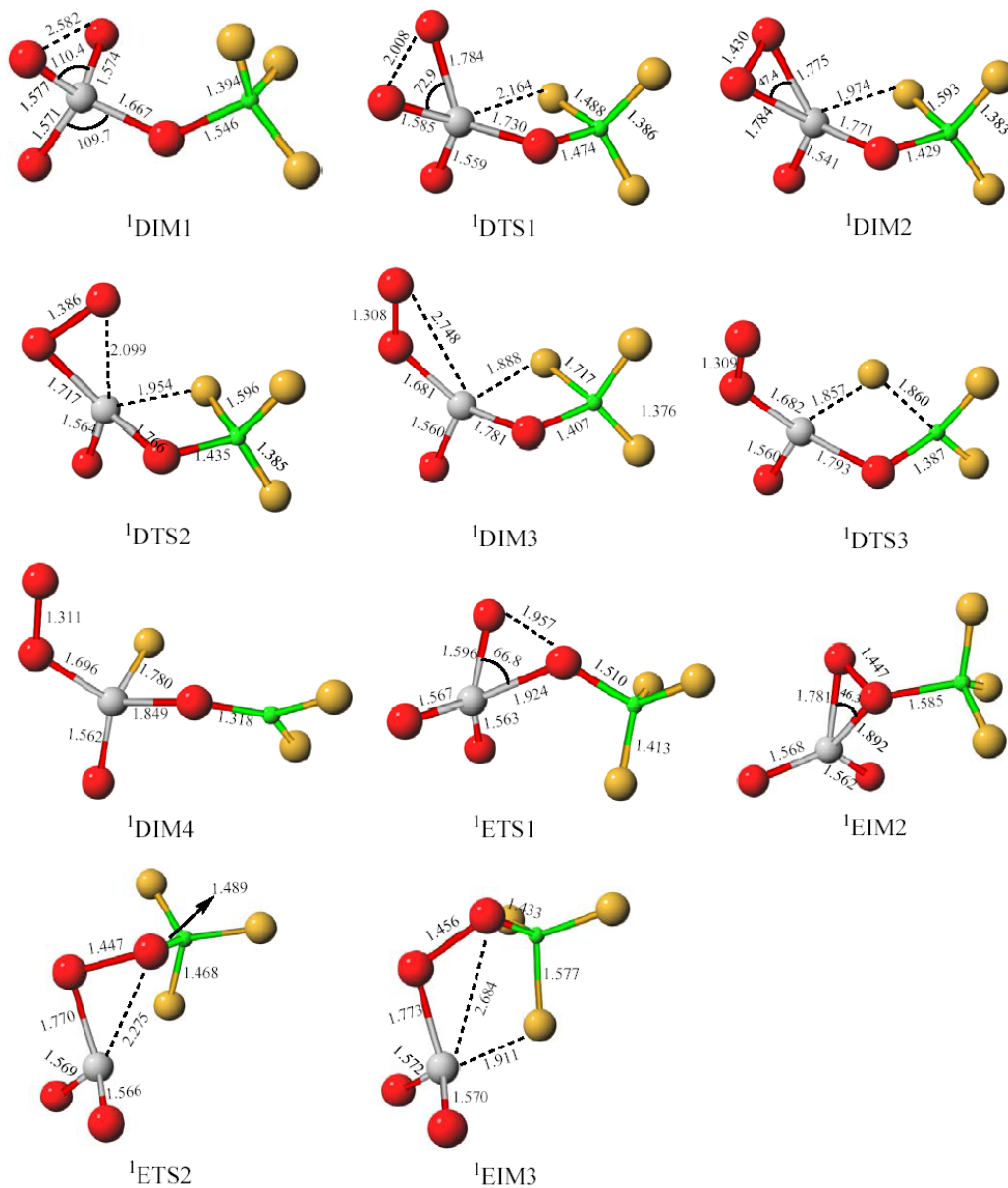
^{5}[MnO$_2$FBF$_2$]$^-$

^{5}MnO$_2^-$

Fig. S5 (Continued)

Fig. S6 Optimized structures of the species involved in the triplet and singlet decomposition reactions of 1:1 adduct [MnO$_4^-$·BF$_3$]. The bond distances are in angstroms and bond angles in degrees.
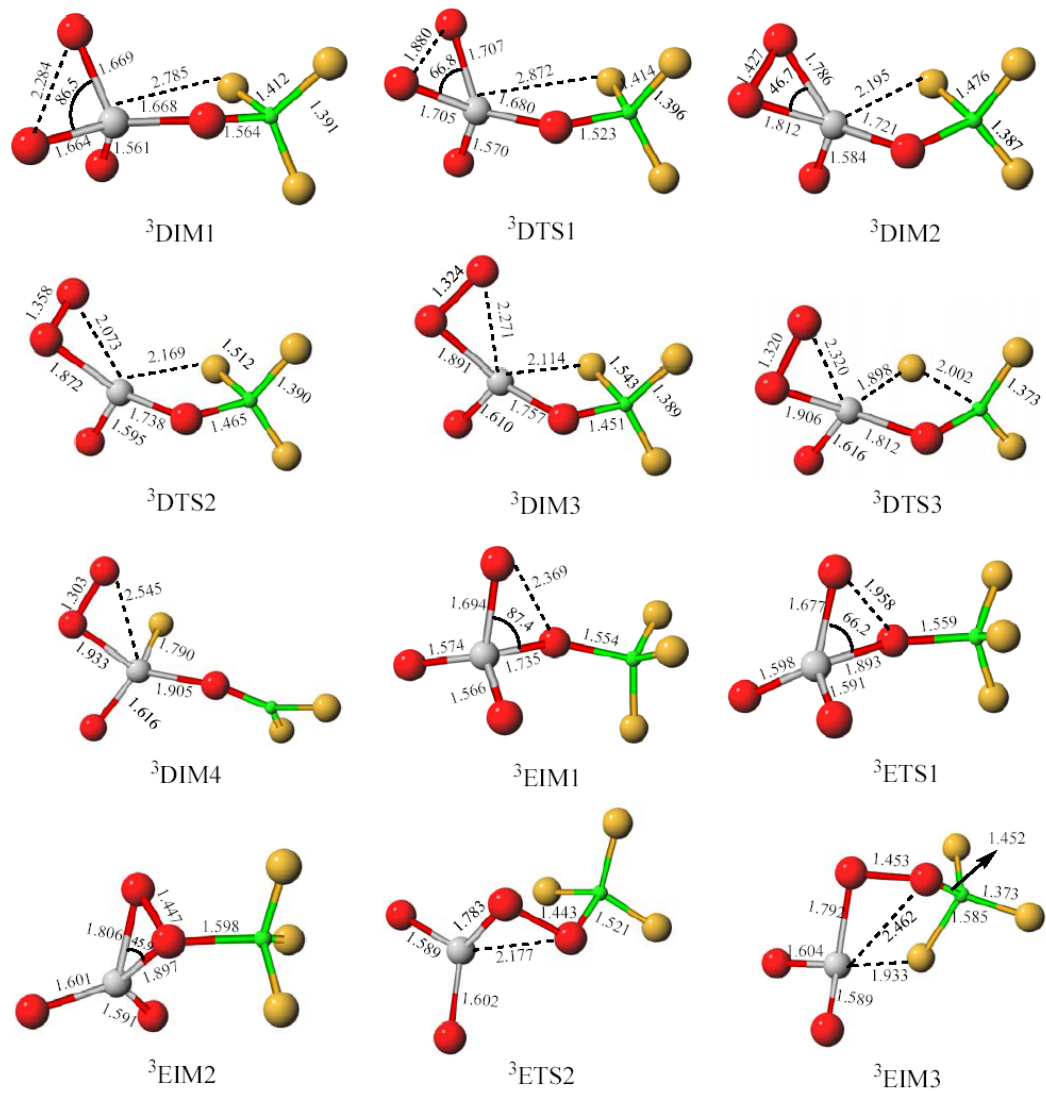
^{3}DIM1

^{3}DTS1

^{3}DIM2

^{3}DTS2

^{3}DIM3

^{3}DTS3

^{3}DIM4

^{3}EIM1

^{3}ETS1

^{3}EIM2

^{3}ETS2

^{3}EIM3

Fig. S6 (Continued)