Supporting Information

Water is a Key Factor to Alter the Structure and Electrochemical Properties of Carboxylate-bridged Dimanganese(II) Complexes

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Experimental section

General procedures: All manipulations were performed under anaerobic conditions. All the solvents were distilled under N_2 prior to use; other analytical grade chemicals were used as received. The *m*-terphenyl-based carboxylate ligand,4,4″-difluoro-[1,1′:3′,1″-terphenyl]-2′-carboxylic acid ($HO_2CAr^{4F\text{-}Ph}$), was prepared according to literature procedures.[S1] The sodium salt($NaO_2CAr^{4F\text{-}Ph}$) of this carboxylic acid was prepared by treating a MeOH solution of the free acid with 1 equiv NaOH and removing the volatile fractions under reduced pressure.^{1}H NMR (400MHz, D_2O): δ 7.03–7.07 (m, 4H), 7.22–7.24 (m, 2H), 7.32–7.35 (m, 5H).

$[Mn_2(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(O_2CAr^{4F\text{-}Ph})_2(THF)_2]$ (1). To a rapidly stirred THF solution (20 mL) of $Mn(OTf)_2.2CH_3CN$ (109 mg, 0.250mmol) was added ($NaO_2CAr^{4F\text{-}Ph}$) (166 mg, 0.500mmol) in a single portion inside the glove box. The resulting heterogeneous mixture was stirred overnight. Volatile fractions were removed under reduced pressure, the residual solid was extracted in 10 mL of CH_2Cl_2 and insoluble material was filtered-off. The resulting extract was treated with THF (3mL). Colorless crystals of **1** (40 mg; 11 %) were isolated upon vapor diffusion of pentane into the solution. The structure was determined by X-ray crystallography. FT-IR (KBr, cm^{-1}): 3061(w), 2958(w), 1893(w), 1597(s), 1510(s), 1454(s), 1413(s), 1384(s), 1300(w), 1225(s), 1158(s), 1092(s), 1034(s), 1012(w), 890(w), 859(s), 843(s), 808(s), 793(m), 772(m), 742(w), 712(m), 583(w), 555(s), 532(s), 462(m). Anal. Calcd for $C_{84}H_{60}F_8Mn_2O_{10}$: C, 67.66; H, 4.06; Found: C, 67.44; H, 4.23.

$[Mn_2(OH_2)_2(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(O_2CAr^{4F\text{-}Ph})_2(THF)_2]$(2). To a portion of $Mn(OTf)_2.2CH_3CN$ (109 mg, 0.250 mmol) in 20 mL of THF was added ($NaO_2CAr^{4F\text{-}Ph}$) (166 mg, 0.500mmol) and the resulting heterogeneous mixture was allowed to stir overnight. Volatile fractions were removed

under reduced pressure, the residual solid was extracted in 10 mL of CH_2Cl_2 and insoluble material was filtered-off. The resulting extract was treated with THF (2 mL) and 4 equiv of water (18.0 mg). Colorless block crystals of **2** (50 mg) were isolated upon vapor diffusion of pentane into the solution. The structure was determined by X-ray crystallography. FT-IR (KBr, cm^{-1}): 3612(w) , 3437(br,m), 3061(w), 2958(w), 1893(w), 1597(s), 1510(s), 1454(s), 1413(s), 1384(s), 1300(w), 1225(s), 1158(s), 1092(s), 1034(s), 1012(w), 890(w), 859(s), 843(s), 808(s), 793(m), 772(m), 742(w), 712(m), 583(w), 555(s), 532(s), 462(m). Anal. Calcd for $C_{84}H_{64}F_8Mn_2O_{12}$: C, 66.06; H, 4.22; Found: C, 65.94; H, 4.31.

$[Mn(H_2O)_6](O_2CAr^{4F\text{-}Ph})_2$•2THF (3). To a portion (50.0 mg, 33.5 μmol) of $[Mn_2(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(O_2CAr^{4F\text{-}Ph})_2(THF)_2]$ was added a THF solution (3 mL) containing 12.1μL (20 equiv) of H_2O. Dissolution occurred after 15 minutes to yield a very pale yellow solution. Pentane diffusion into the THF solution resulted in the formation of colorless needle crystals and was analyzed by X-ray crystallography. FT-IR (KBr, cm^{-1}): 3458 (w, br), 3061 (w), 2977 (w), 2876 (w), 2331 (w), 1895 (w), 1602 (s), 1540 (m), 1511 (s), 1454 (s), 1411 (s), 1380 (s), 1225 (s), 1160 (s), 1095 (m), 1034 (m), 843 (s), 808 (s), 792 (m), 777 (m), 771 (w), 555 (s), 530 (m), 461 (m). Anal. Calcd for $C_{46}H_{50}F_4Mn_2O_{12}$: C, 56.33; H, 5.14; Found: C, 56.94; H, 5.00.

Cyclic voltammetry studies: were carried out using ZAHNER elektrik IM6 potentiostat. The cell was a standard three-electrode system with a platinum wire as a counter electrode, a platinum working electrode, and an $Ag/AgNO_3$(0.10 M) reference electrode. The measurements were performed under N_2 atmosphere at room temperature in dichloromethane solvent containing 0.1 M Tetrabutylammonium hexafluorophosphate.

Single crystal X-ray Data measurement: Single crystals of each complex were mounted at room temperature on the tips of quartz fibers, coated with Partone-N oil, and cooled under a stream of cold nitrogen. Intensity data were collected on a Bruker CCD area diffractometer running the SMART software package, with Mo Kα radiation (λ= 0.71073 Å). The structure was solved by direct methods and refined on F^2 by using the SHELXTL software package.[S2] Empirical absorption correction was applied with SADABS[S3] part of the SHELXTL program package, and the structure was checked for higher symmetry by the program PLATON.[S4] The structure of **2** contains two coordinated THF molecules which were disordered over two

positions with 0.50 occupancies. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of H_2O molecules were assigned from the electron density map, however, all other hydrogen atoms were assigned at idealized positions and given thermal parameters equivalent to 1.2 times of the thermal parameter of the carbon atom to which they were attached.

Table S1. Bond lengths [Å] and angles [°] of **1**

Bond lengths [Å]		**Bond angles [°]**	
Mn(1)-O(1)	2.194(3)	O(1)-Mn(1)-O(2)	59.30(10)
Mn(1)-O(2)	2.226(3)	O(5)-Mn(1)-O(2)	85.08(11)
Mn(1)-O(3)	2.040(3)	O(3)-Mn(1)-O(1)	110.23(12)
Mn(1)-O(4)	2.061(3)	O(4)-Mn(1)-O(2)	123.57(12)
Mn(1)-O(5)	2.147(3)	O(4)-Mn(1)-O(5)	90.41(12)

Table S2. Bond lengths [Å] and angles [°] of **2**

Bond lengths [Å]		**Bond angles [°]**	
Mn1-O1	2.2151(19)	O2-Mn1-O1	87.18(7)
Mn1-O2	2.0877(16)	O4-Mn1-O2	109.43(7)
Mn1-O3	2.0797(18)	O4-Mn1-O6	91.40(8)
Mn1-O4	2.0776(19)	O2-Mn1-O6	90.91(7)
Mn1-O6	2.1480(17)	O4-Mn1-O1	91.47(8)

Table S3. Bond lengths [Å] and angles [°] of **3**

Bond lengths [Å]		**Bond angles [°]**	
Mn(1)-O(5)	2.2209(12)	O(6)-Mn(1)-O(5)	91.86(5)
Mn(1)-O(6)	2.1579(12)	O(6)-Mn(1)-O(7)	88.11(5)
Mn(1)-O(7)	2.2095(12)	O(7)-Mn(1)-O(5)	94.19(5)
Mn(2)-O(8)	2.1779(12)	O(8)-Mn(2)-O(9)	93.96(5)
Mn(2)-O(9)	2.2398(12)	O(10)-Mn(2)-O(8)	91.32(5)
Mn(2)-O(10)	2.1699(12)	O(10)-Mn(2)-O(9)	92.39(5)

Table S4. Data collection and experimental details of **1**

CCDC number	778666
Empirical formula	C84 H60 F8 Mn2 O10
Formula weight	1491.20
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.7747(6) Å α = 67.7730(10)°
	b = 13.2190(7) Å β = 68.4860(10)°
	c = 14.0466(8) Å γ = 76.3580(10)°
Volume	1711.98(16) $Å^3$
Z	1
Density (calculated)	1.446 Mg/m^3
Absorption coefficient	0.454 mm^{-1}
Theta range for data collection	1.93 to 28.29°
Reflections collected	12810
Independent reflections	8377 [R(int) = 0.0270]
Completeness to theta = 28.29°	98.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8377 / 0 / 469
Goodness-of-fit on F^2	1.162
Final R indices [I>2sigma(I)]	R_1 = 0.0633, wR_2 = 0.1007
R indices (all data)	R_1 = 0.1179, wR_2 = 0.1564
Largest diff. peak and hole	0.953 and -1.491 $e.Å^{-3}$

Table S5. Data collection and experimental details of **2**

CCDC number	923655
Empirical formula	C86 H68Cl4 F8 Mn2O12
Formula weight	1697.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.331(3) Å α = 97.29(3) ° b = 14.072(3) Å β = 114.67(3)°. c = 14.127(3) Å γ = 111.21(3))°
Volume	1961.8(7) $Å^3$
Z	1
Density (calculated)	1.436 Mg/m^3
Absorption coefficient	0.540 mm^{-1}
Crystal size	0.30 x 0.20 x 0.20 mm^3
Theta range for data collection	1.64 to 28.27°
Reflections collected	12360
Independent reflections	8706 [R(int) = 0.051]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.952
Final R indices [I>2sigma(I)]	R_1 = 0.0480
R indices (all data)	wR_2 = 0.1225
Largest diff. peak and hole	0.82 and -0.60 $e.Å^{-3}$

Table S6. Data collection and experimental details of **3**

CCDC Number	923654
Empirical formula	C46 H50 F4 Mn O12
Formula weight	925.80
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.3219(2) Å α = 109.2440(10)°
	b = 13.7116(2) Å β = 90.1040(10))°
	c = 15.3645(3) Å γ = 100.7220(10)°
Volume	2207.48(7) $Å^3$
Z	2
Density (calculated)	1.393 Mg/m^3
Absorption coefficient	0.378 mm^{-1}
Crystal size	0.40 x 0.18 x 0.12 mm^3
Theta range for data collection	1.60 to 28.38°
Reflections collected	39434
Independent reflections	10882 [R(int) = 0.0142]
Completeness to theta = 28.38°	98.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10882 / 0 / 601
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R_1 = 0.0443, wR_2 = 0.1256
R indices (all data)	R_1 = 0.0519, wR_2 = 0.1324
Largest diff. peak and hole	1.541 and -0.614 e.$Å^{-3}$

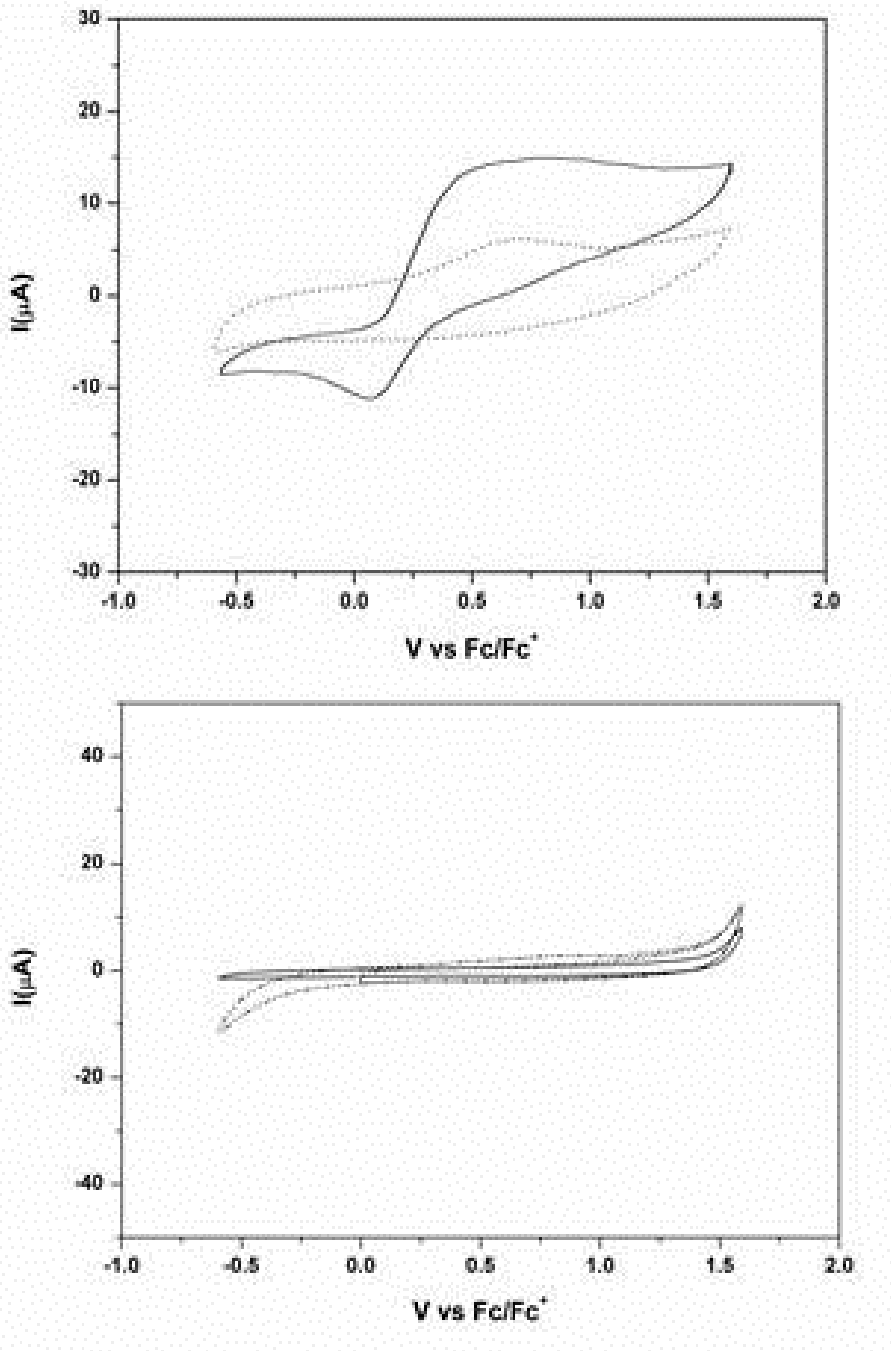

Figure S1. (Top) Cyclic voltammogram of CH_2Cl_2 in DCM (dotted line) and [$Fe_2(\mu\text{-}O_2CAr^{Tol})_4(4\text{-}^tBuC_5H_4N)_2$] in CH_2Cl_2(plain line). Scan rate 100 mV/s. (Bottom)Cyclic voltammogram of $Ar^{4F\text{-}Ph}CO_2H$ (2 mM) in CH_2Cl_2 (dotted line) and Tetrabutylammonium hexafluorophosphate 0.1 M in CH_2Cl_2 (plain line). Scan rate 50 mV/s

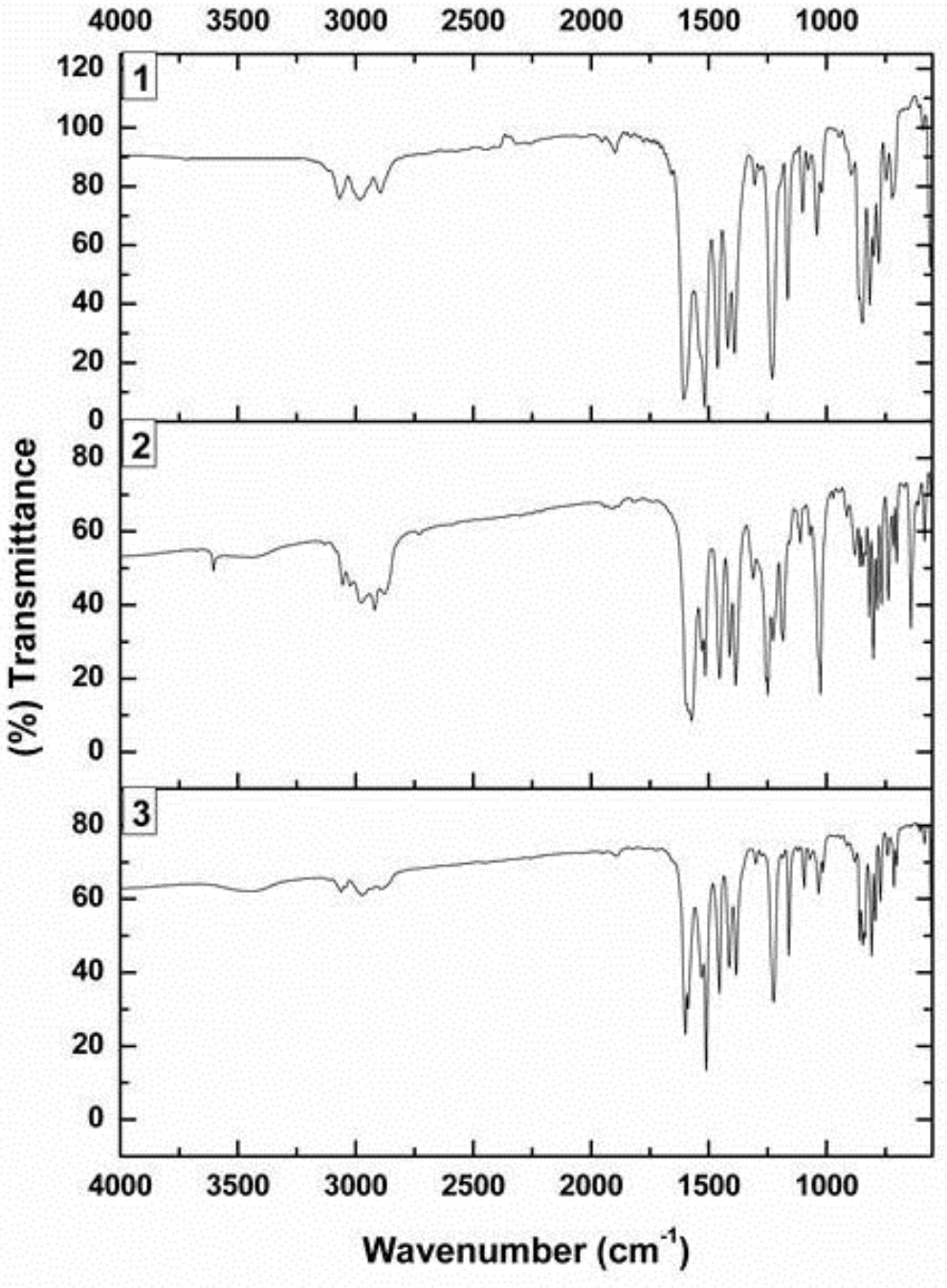

Figure S2. FT-IR spectra of **1, 2** and **3.**

References

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