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Supporting Information

A manganese-doped polymeric framework of polyoxotitanate nanoclusters with a narrow band gap

Yang Chen,* Jesse D. Sokolow, ElzbietaTrzop and Philip Coppens*

Chemistry Department, University at Buffalo, SUNY, Buffalo, New York 14260-3000, United States.

E-mail: coppens@buffalo.edu; ychen37@buffalo.edu

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Experimental Section

All of the reagents and solvent were purchased from commercial sources: Titanium(IV) ethoxide (99+%) was purchased from Alfa Aesar; Manganese(II) bromide tetrahydrate, 1,1,1-Tris(hydroxymethyl)ethane (99%), and ethanol (200 proof, anhydrous, ≥ 99.5%) were purchased from ALDRICH.The compounds containing titanium were stored and handled in a glove-box under a nitrogen atmosphere.

Synthesis of $\{Ti_{13}Mn_4O_{16}[CH_3C(CH_2O)_3]_4(OEt)_{12}Br_4\}_\infty$:

To a Teflon-lined Parr bomb with a 23 mL capacity was loaded Titanium(IV) ethoxide (684.3 mg, 3.0 mmol), 1,1,1-Tris(hydroxymethyl)ethane (120.2 mg, 1.0 mmol), Manganese(II) bromide tetrahydrate (143.4 mg, 0.5 mmol), and ethanol (5.0 mL). The resulting mixture was stirred for 5 minutes and sealed. The reactor was heated in an oven to 150 °C for 72 hours and then cooled to 40 °C over 48 hours. After the oven was totally cooled to the room temperature, the yellow block crystals of $\{Ti_{13}Mn_4O_{16}[MeC(CH_2O)_3]_4(OEt)_{12}Br_4\}_\infty$ were taken out from the Parr bomb, and washed with ethanol and dried in the glove-box. Yield: 26.1 mg (8.6% based on Mn). Elemental analysis calcd (%) for $C_{44}H_{96}O_{40}Br_4Mn_4Ti_{13}$: C 21.78, H 3.99; found: C 21.68, H 3.92.

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Table S1. Crystal data and details of data collection and refinement for $\{Ti_{13}Mn_4O_{16}[MeC(CH_2O)_3]_4(OEt)_{12}Br_4\}_\infty$

Compound	$\{Ti_{13}Mn_4O_{16}[MeC(CH_2O)_3]_4(OEt)_{12}Br_4\}_\infty$
Chemical formula	$C_{44}H_{96}O_{40}Br_4Mn_4Ti_{13}$
Formula weight	2426.88
Crystal system	Tetragonal
Space group	$I4_1md$
a / Å	34.8012(10)
b / Å	34.8012(10)
c / Å	14.7872(6)
V / Å^3	17909.1(10)
Z	8
T / K	90(2)
F(000)	9647
μ (Mo Kα, mm^{-1})	3.490
Total reflections	9472
Unique reflections	4957
No. of parameters	485
R [a]	0.0545
ωR[b]	0.1579
GOF [c]	1.043

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] $GOF = \{\Sigma[w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

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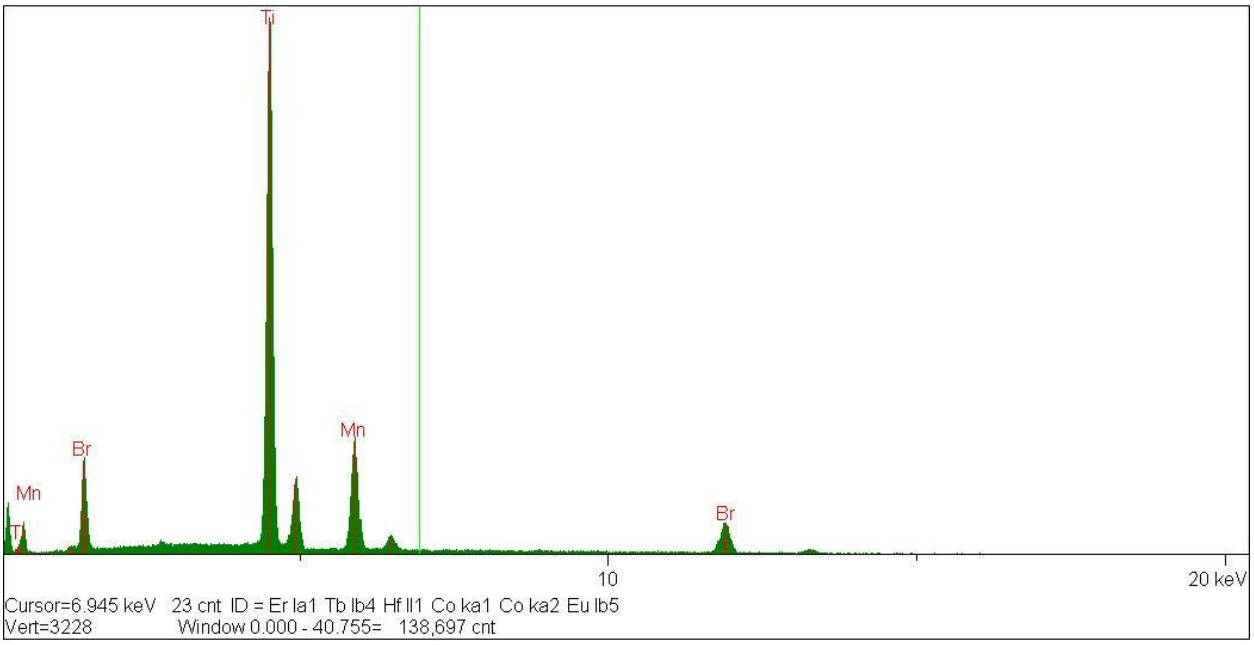

Fig. S1 EDS spectrum of $\{Ti_{13}Mn_4O_{16}[MeC(CH_2O)_3]_4(OEt)_{12}Br_4\}_\infty$.

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
Ti	Ka	1,593.07	16.337	62.943	54.902	wt.%	
Mn	Ka	370.71	8.168	19.470	19.491	wt.%	
Br	Ka	131.11	5.020	17.587	25.607	wt.%	
				100.000	100.000	wt.%	Total

KV	30.0
Takeoff Angle	45.0°
Elapsed Livetime	25.0