Unique two-dimensional indium telluride templated by a rare wheel-shaped heterobimetallic Mn/In cluster

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General Remarks. All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, N and H) were performed using a PE2400 II elemental analyzer. IR spectra were obtained from a powdered sample pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range of 400–4000cm^{-1}. Energy-dispersive X-ray analysis (EDXA) was taken by using a JEOL JSM-6700F field-emission scanning electron microscope. Room-temperature optical diffuse reflectance spectra of the powdered samples were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance using the Kubelka-Munk function, α/S = (1 - R)^2/2R, where R is the reflection coefficient, α is the absorption coefficient, and S is the scattering coefficient. PXRD patterns were obtained using a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54178 Å). The magnetization of **1** was obtained with a Quantum Design MPMS-XL-5 magnetometer. PXRD patterns were obtained using a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54056 Å). The working electrodes for photocurrent measurements were prepared by following processes. 8 mg of microcrystal sample was dispersed into a mixed solution of ethanol (200 µL) and Nafion (56 µL), followed by ultrasonic treatment for 0.5 h. Then, 210 µL of the above slurry was coated onto the FTO glass (F-doped SnO_2) with an effective area of 1 cm^2 and dried naturally at room temperature. The photocurrent experiment was performed on a CHI650E electrochemistry workstation in a three-electrode system, with the sample coated FTO glass as the working electrode, a Pt slice as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte solution was 0.1 mol·L^{-1} Na_2SO_4 aqueous solution (100 mL). A 450 W high pressure Xe lamp with 420 nm was used as the illumination source. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated at intervals of 100 s.

Crystal Structure Determination

The intensity data of $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$ were collected on a Bruker diffractometer-SMART-APEX II with graphite monochrochromated Mo Kα radiation (λ = 0.71073Å). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure of $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$ was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXL-2018 program package.The refinement with three octahedral metal sites occupied by three Mn^{2+} ions and one tetrahedral metal site occupied by one In^{3+} ion results in a molecular formula of $[Mn_7(ea)_{12}]_n[In_{10}Te_{17}]$. The stoichiometry of $[Mn_7(ea)_{12}]_n[In_{10}Te_{17}]$ creates a charge of -2, which is not obviously rational. The U(iso) values of Mn2-4 are obviously smaller and the U(iso) value of In2 is obviously larger. When three octahedral metal sites are occupied by In6/Mn2, In7/Mn3 and In8/Mn4 atoms with occupation factors of 0.308/0.692, 0.334/0.666 and 0.469/0.531, respectively, and one tetrahedral metal site is occupied by In2/Mn5 atom with occupation factor of 0.893/0.107, the final R and wR factors ($I > 2\sigma(I)$) are decreased from 0.0643/0.2225 to 0.0373/0.0973. So its formula was finally determined as $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$. The Te5, C6 and C8 atoms were disordered over site occupation factors of 0.89/0.11, 0.52/0.48 and 0.34/0.66, respectively. The non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized locations and refined as riding. Technical details of data collections and refinement are summarized in Table S1.

Table S1 Crystallographic data for $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.

formula	$C_{24}H_{72}In_{12}Mn_5N_{12}O_{12}Te_{17}$
Fw	4543.11
crystal system	Monoclinic
space group	*C*2/c
a, Å	25.7155(14)
b, Å	13.4091(7)

c, Å	25.7626(15)
β, deg	101.825(2)
V, Å^3	8695.0(8)
Z	4
T, K	296(2)
Calcd density, Mg.m^{-3}	3.470
abs coeff, mm^{-1}	9.446
$F(000)$	7972
2θ(max), deg	55.76
Total reflns collected	31960
Unique reflns	10221
No. of param	399
$R1[I>2\sigma(I)]$	0.0373
$wR2$(all data)	0.0973
GOF on F^2	1.071

Table S2 The selected In-Te, In-O/N, Mn-Te and Mn-O/N bond lengths of

$[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.
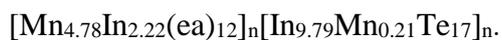
In-Te	2.6953(9)-2.9148(8)	In-O	2.07(3)-2.29(3)
In-N	2.26(3)-2.39(2)	Mn-O	2.09(3)-2.36(2)
Mn-N	2.14(3)-2.36(3)	Mn-Te	2.683(13)-2.855(11)
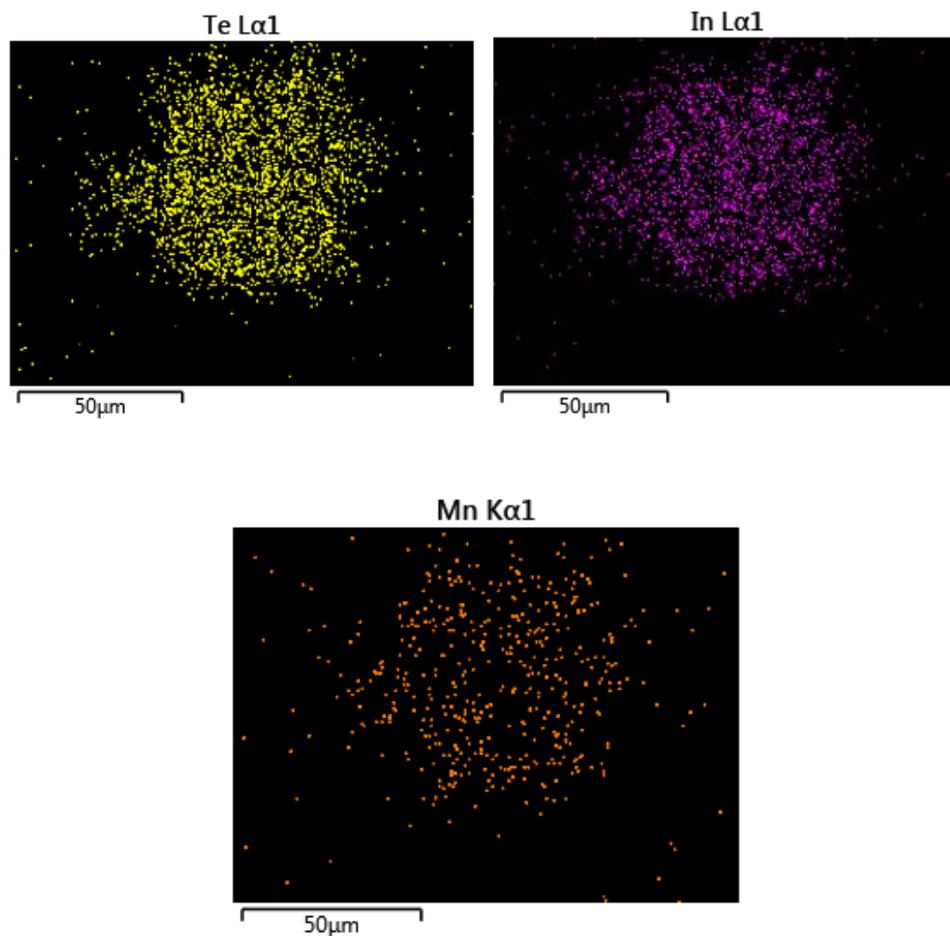
Figure S1 EDXA elemental mappings of Te, In and Mn in
$[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.
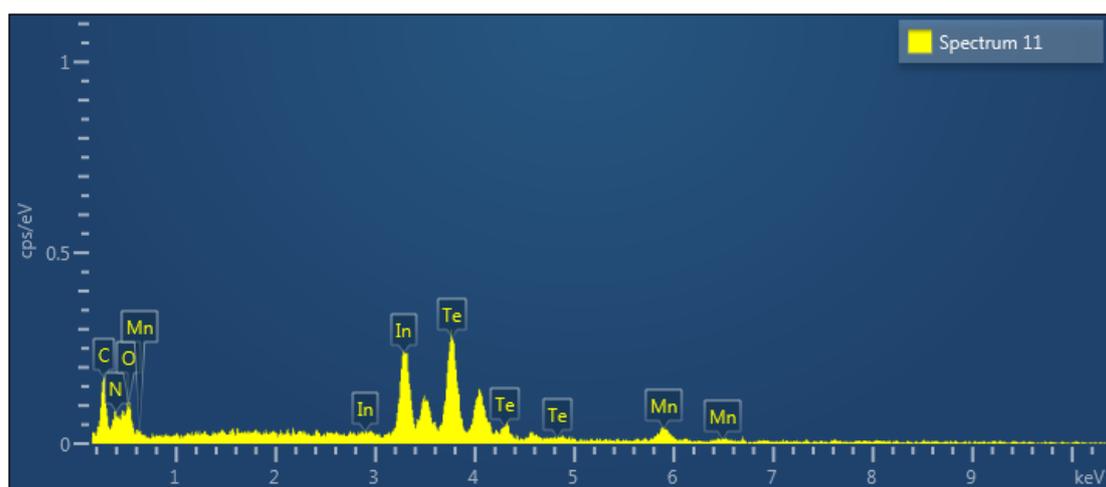
Figure S2 EDXA spectrum of $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.
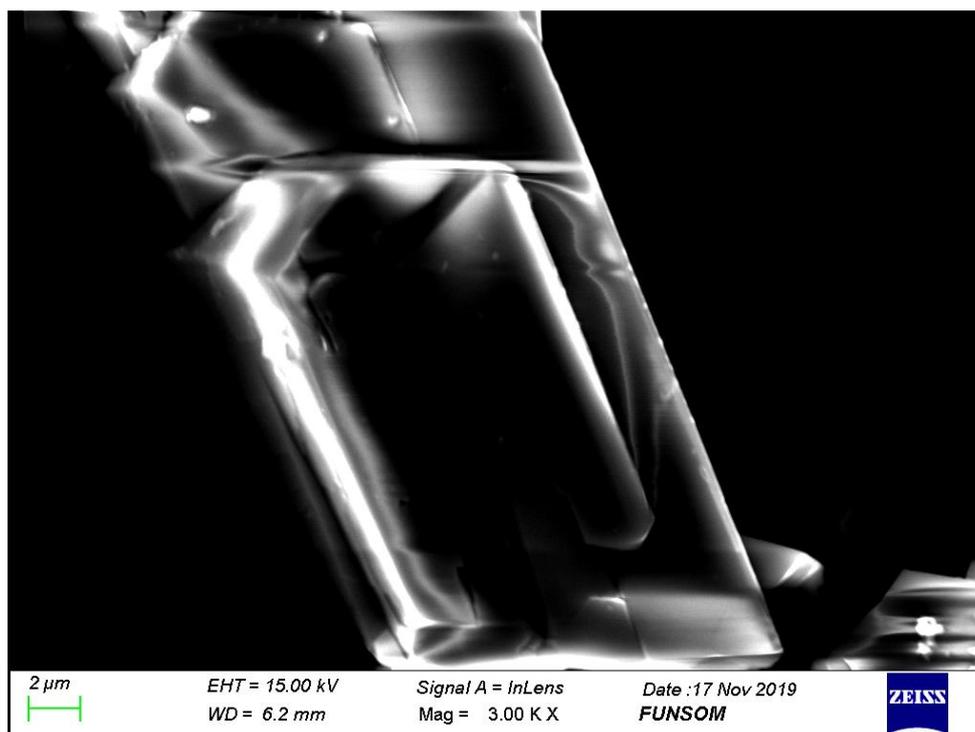
Figure S3 Scanning electron micrograph of $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.
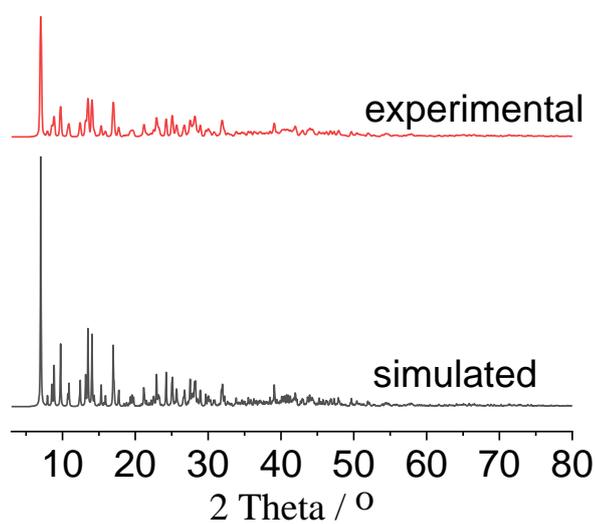
Figure S4 Simulated, and experimental powder XRD patterns of
$[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.
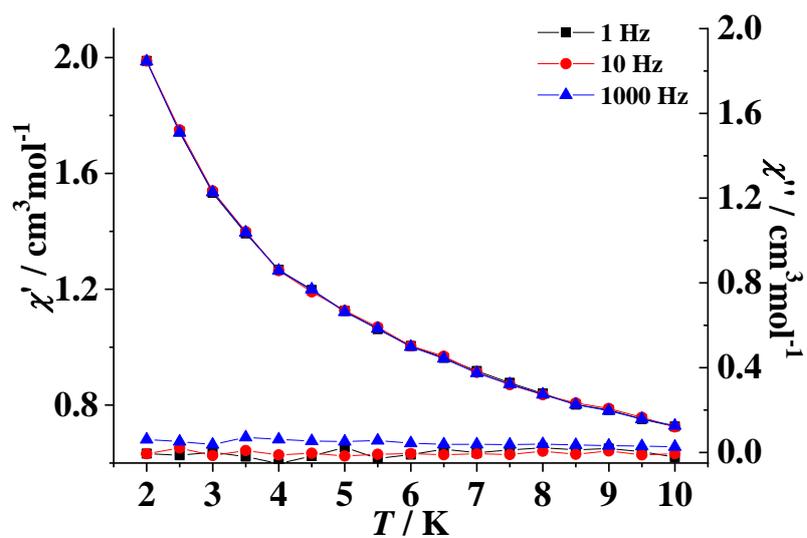
Figure S5 Temperature dependence of the in phase and out-of-phase signals of the ac susceptibility for $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$ under a zero dc field (Hac = 2.5 Oe).
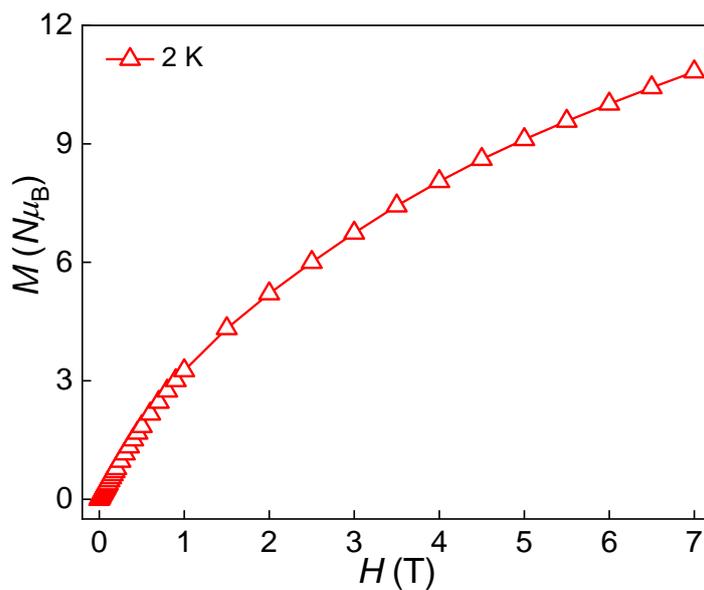
Figure S6 M versus H plot for $[Mn_{4.78}In_{2.22}(ea)_{12}]_n[In_{9.79}Mn_{0.21}Te_{17}]_n$.