Supporting Information for:

Assembly of Titanium-Oxo Cations with Copper-Halide Anions to Supersalt-Type Cluster-Based Materials

Wei-Hui Fang, Lei Zhang,* Jian Zhang*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

Corresponding Author

*E-mail: LZhang@fjirsm.ac.cn; zhj@fjirsm.ac.cn

Content

Experimental Section:

Materials and physical measurements. Tetraisopropoxytitanium was purchased from damas-beta, isopropanol, copper(II) chloride dihydrate, cupric bromide, and cuprous iodide were acquired from GENERAL-REAGENT. The TiO_2 was bought from Alfa Aesar. The energy dispersive spectroscopy (EDS) analyses of single crystals were performed on a JEOL JSM6700F field-emission scanning electron microscope equipped with a Oxford INCA system. Elemental analysis was measured on a Vario MICRO Elemental Analyzer instrument. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in air atmosphere with a heating rate of 10 ^{o}C/min from 30 ^{o}C to 800 ^{o}C. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ = 1.54056 Å) under ambient conditions. The UV diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The absorption data are calculated from the Kubelka-Munk function, (F(R) = (1-R)^2/2R),[1] where R representing the reflectance, K the absorption, and S the scattering.

General Methods for X-ray Crystallography. Crystallographic data of complexes **1-4** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic Cu Kα radiation (λ = 1.54178 Å) at room temperature. The variable temperature unit-cell parameters were obtained by indexing the diffraction spots that were obtained with diffraction images. The structure was solved with direct methods using SHELXS-97[2] and refined with the full-matrix least-squares technique based on F^2 using the SHELXL-97.[3] Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. CCDC: 1434297-1434300 for compounds **1-4**.

Synthesis of $[Ti_{12}(\mu_3\text{-}O)_{14}(O\textit{i}Pr)_{18}]\cdot 2[Cu^{I}Cl_2]\cdot 2HO\textit{i}Pr$ (1). Tetraisopropoxytitanium (0.92 ml, 3.0 mmol) and copper(II) chloride dihydrate (0.085 g, 0.5 mmol) are mixed in 5 mL anhydrous isopropanol. The mixture was sealed in a 20 mL vial and transferred to a preheated oven at 100 ^{o}C for 3 days. When cooled to room temperature, grey crystals of complex **1** were obtained (yield: 30 % based on Ti(O*i*Pr)$_4$). The crystals are rinsed with isopropanol and preserved under a sealed and dry environment.

Synthesis of $[Ti_{12}(\mu_3\text{-}O)_{14}(O\textit{i}Pr)_{18}]\cdot[Cu^{II}_2Cl_4(\mu\text{-}Cl)_2]$ (2). Similar to the synthesis of complex **1**, except that the temperature is set to 80 ^{o}C. When cooled to room temperature, red crystals of complex **2** were obtained (yield: 42 % based on Ti(O*i*Pr)$_4$).

Synthesis of $[Ti_{12}(\mu_3\text{-}O)_{14}(O\textit{i}Pr)_{18}]\cdot[Cu^{I}_{4}Br_6]$ (3). Similar to the synthesis of complex **2**, except that copper(II) chloride dihydrate is replaced by cupric bromide. When cooled to room temperature, green crystals of complex **3** were obtained (yield: 50 % based on $Ti(O\textit{i}Pr)_4$).

Synthesis of $[Ti_{12}(\mu_3\text{-}O)_{14}(O\textit{i}Pr)_{18}]\cdot[Cu^{I}_{5}I_7]$ (4). Similar to the synthesis of complex **2**, except that copper(II) chloride dihydrate is replaced by cuprous iodide. When cooled to room temperature, yellow crystals of complex **4** were obtained (yield: 35 % based on $Ti(O\textit{i}Pr)_4$).

Supporting Figures:

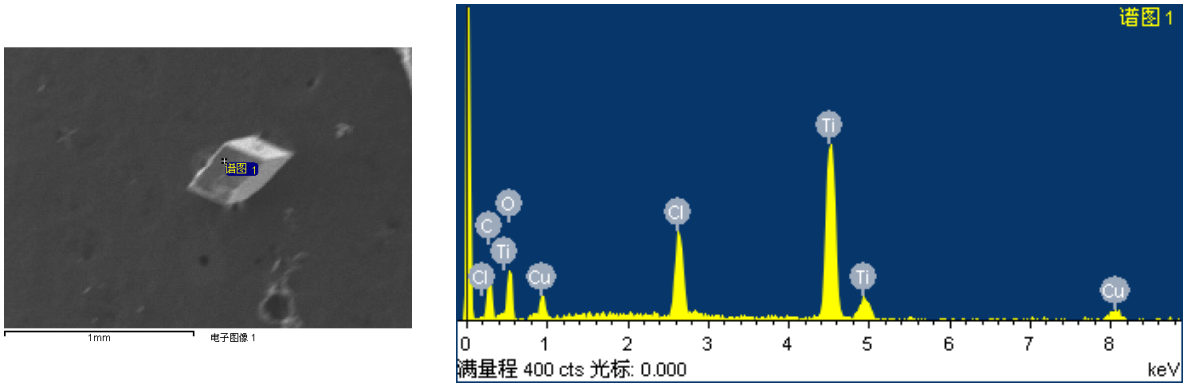

Figure S1 The SEM image and EDS spectrum of compound **1**.

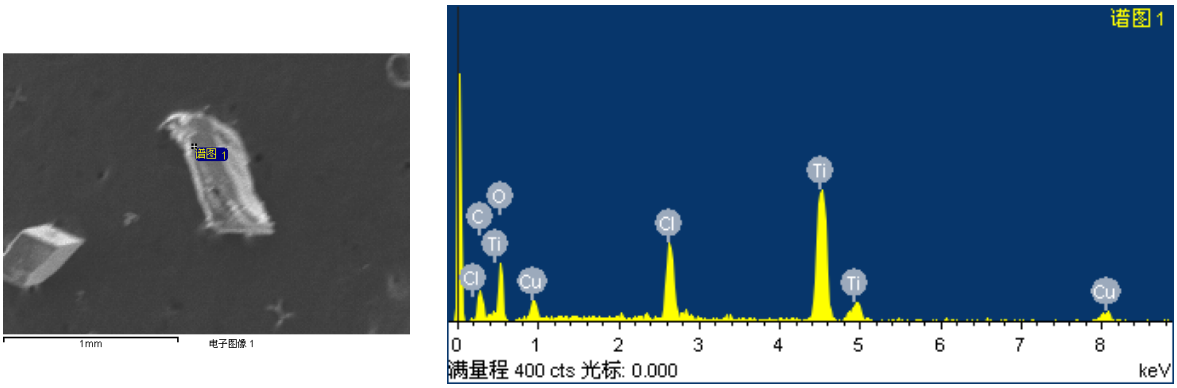

Figure S2 The SEM image and EDS spectrum of compound **2**.

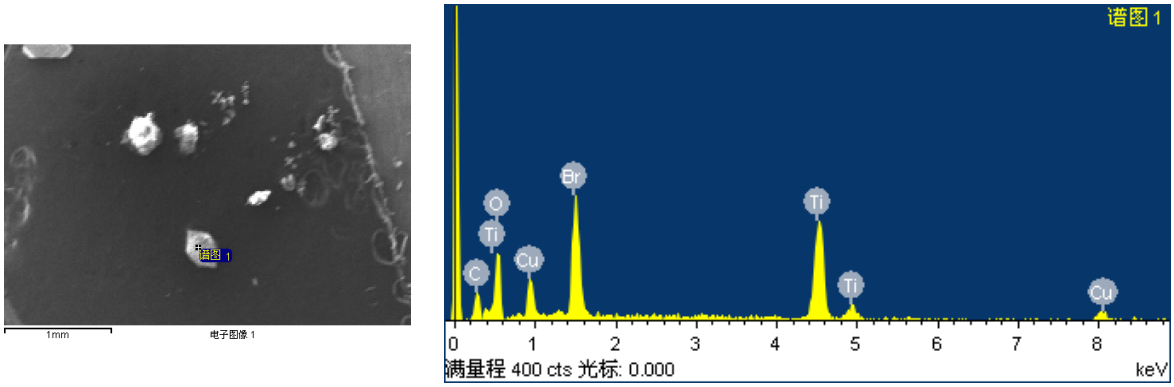

Figure S3 The SEM image and EDS spectrum of compound **3**.

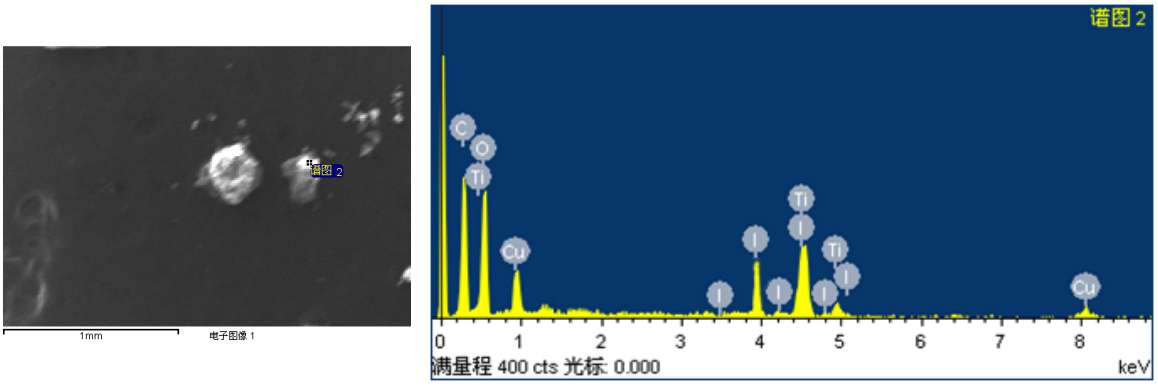

Figure S4 The SEM image and EDS spectrum of compound **4**.

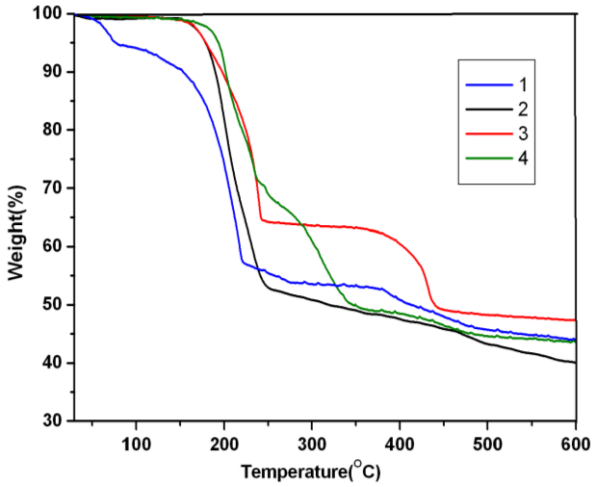

Figure S5 The TGA curves of **1-4**.

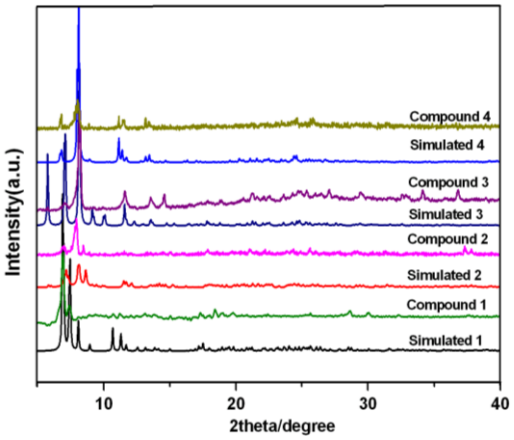

Figure S6 The PXRD of the simulated and experimental patterns for **1-4**.

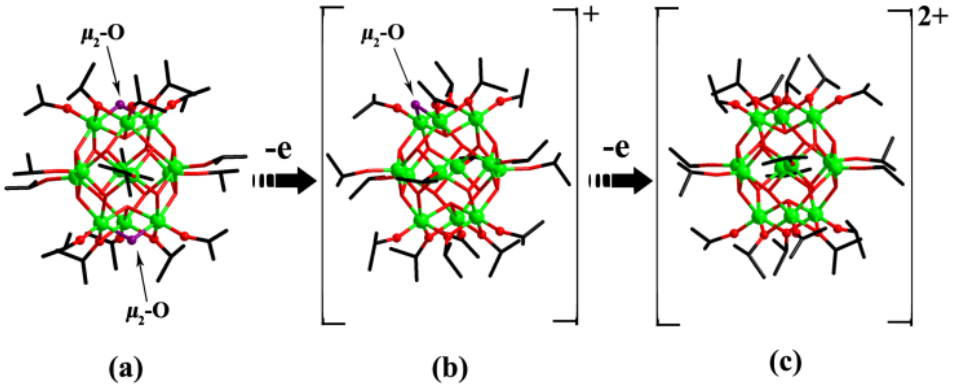

Figure S7 The stepwise substitution of μ_2-O atom by O*i*Pr on the crown of the dodecatitanates, indicating the related charge increase: (a) $[Ti_{12}O_{16}(OiPr)_{16}]$[4]; (b) $[Ti_{12}O_{15}(OiPr)_{17}]^{+}$[5]; (c) $[Ti_{12}\ (\mu_3\text{-}O)_{14}(OiPr)_{18}]^{2+}$ here. Color codes for atoms: Ti-green; μ_2-O purple; *i*Pr O-red; C-black.

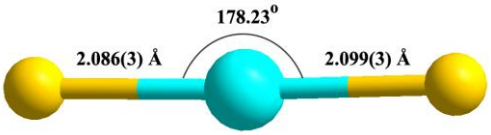

Figure S8 The ball-stick view of the $Cu^{I}Cl_2$ monomer.

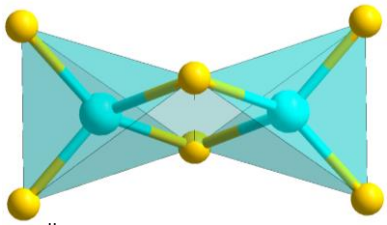

Figure S9 The polyhedral view of the $Cu^{II}{}_2Cl_6$ dimer.

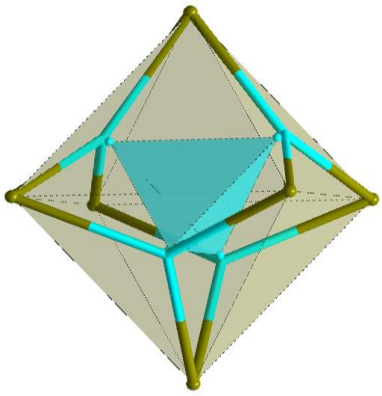

Figure S10 The polyhedral view of the $Cu^{I}_{4}Br_{6}$ tetramer.

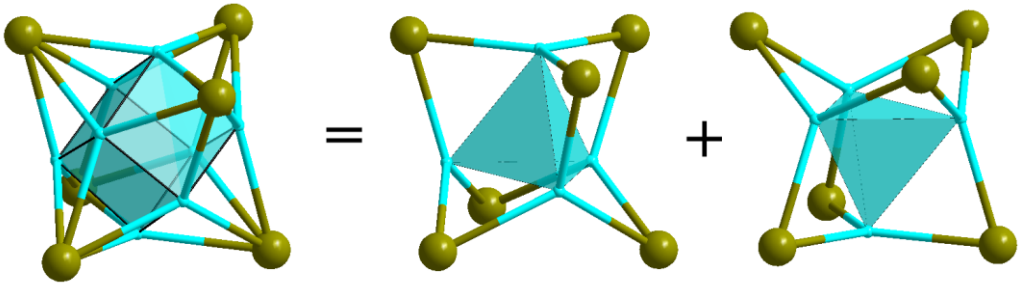

Figure S11 The scheme representation of the disordered $Cu^{I}_{4}Br_{6}$ tetramer.

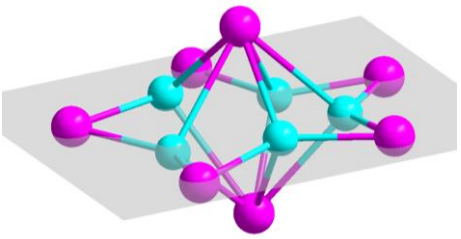

Figure S12 The perspective view of the $Cu^{I}_{5}I_{7}$ pentamer.

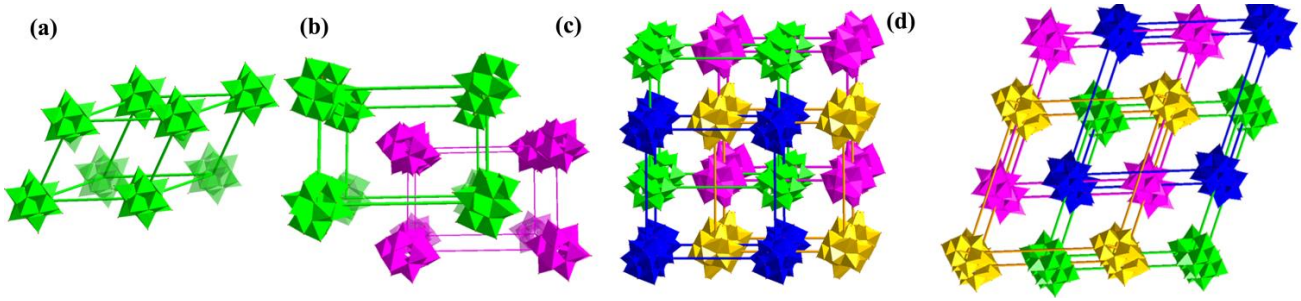

Figure S13 The periodic nature of the cationic Ti_{12} alpha-Po cubic topology: (a) uninodal net in compound **1**, (b) 2(1+1) interpenetrating nets in compound **2**, and (c-d) totally 4(2+2) interpenetrating nets in compounds **3** and **4**. The alpha-Po cubic unit sizes are 14.3 × 15.1 × 15.2 $Å^3$ for **1**, 14.6 × 15.1 × 21.8 $Å^3$ for **2**, 21.5 × 21.7 × 21.6 $Å^3$ for **3**, and 27.9 × 15.2 × 26.1 $Å^3$ for **4**, respectively.

Supporting Tables:

Table S1 Bond valence sum (BVS) analysis[a]

Compound **1**	Compound **2**	Compound **3**	Compound **4**
Ti1 4.186 Ti1-O11 1.148 d=1.764(3) Ti1-O6 0.638 d=1.981(3) Ti1-O14 0.628 d=1.987(3) Ti1-O3 0.597 d=2.006(3) Ti1-O12 0.595 d=2.007(3) Ti1-O7 0.579 d=2.017(3)	Ti1 4.256 Ti1-O11 1.142 d=1.766(6) Ti1-O1 0.645 d=1.977(5) Ti1-O13 0.640 d=1.980(6) Ti1-O12 0.628 d=1.987(6) Ti1-O5 0.615 d=1.995(5) Ti1-O2 0.586 d=2.013(5)	Ti1 4.135 Ti1-O12 1.202 d=1.747(6) Ti1-O2 0.855 d=1.873(7) Ti1-O6 0.774 d=1.910(7) Ti1-O4 0.660 d=1.969(6) Ti1-O1 0.645 d=1.977(7)	Ti1 4.233 Ti1-O18 1.157 d=1.761(6) Ti1-O1 0.663 d=1.967(5) Ti1-O17 0.611 d=1.997(6) Ti1-O7 0.605 d=2.001(6) Ti1-O5 0.600 d=2.004(6) Ti1-O19 0.597 d=2.006(6)
Ti2 4.104 Ti2-O9 1.231 d=1.738(3) Ti2-O4 0.790 d=1.902(3) Ti2-O3 0.747 d=1.923(3) Ti2-O1 0.678 d=1.959(3) Ti2-O2 0.658 d=1.970(3)	Ti2 4.238 Ti2-O15 1.163 d=1.759(6) Ti2-O1 0.669 d=1.964(5) Ti2-O14 0.627 d=1.988(6) Ti2-O3 0.611 d=1.997(5) Ti2-O4 0.594 d=2.008(5) Ti2-O13 0.575 d=2.020(6)	Ti2 4.190 Ti2-O13 1.303 d=1.717(9) Ti2-O14 0.814 d=1.891(7) Ti2-O1 0.771 d=1.911(6) Ti2-O5 0.658 d=1.970(6) Ti2-O2 0.644 d=1.978(7)	Ti2 4.197 Ti2-O20 1.151 d=1.763(6) Ti2-O1 0.667 d=1.965(5) Ti2-O4 0.607 d=2.000(6) Ti2-O19 0.603 d=2.002(6) Ti2-O21 0.592 d=2.009(6) Ti2-O2 0.578 d=2.018(6)
Ti3 4.082 Ti3-O10 1.202 d=1.747(3) Ti3-O2 0.806 d=1.895(3) Ti3-O5 0.743 d=1.925(3) Ti3-O3 0.681 d=1.957(3) Ti3-O7 0.651 d=1.974(3)	Ti3 4.135 Ti3-O10 1.221 d=1.741(6) Ti3-O7 0.797 d=1.899(6) Ti3-O3 0.788 d=1.903(5) Ti3-O2 0.676 d=1.960(5) Ti3-O5 0.652 d=1.973(5)	Ti3 4.203 Ti3-O7 1.170 d=1.757(7) Ti3-O16 0.644 d=1.978(1) Ti3-O3 0.640 d=1.980(6) Ti3-O14 0.587 d=2.012(8) Ti3-O6 0.582 d=2.015(6) Ti3-O8 0.579 d=2.017(6)	Ti3 4.233 Ti3-O23 1.167 d=1.758(6) Ti3-O1 0.660 d=1.969(5) Ti3-O6 0.610 d=1.998(6) Ti3-O21 0.607 d=2.000(6) Ti3-O3 0.600 d=2.004(6) Ti3-O17 0.590 d=2.010(6)
Ti4 4.132 Ti4-O8 1.225 d=1.740(3) Ti4-O7 0.843 d=1.878(3) Ti4-O1 0.743 d=1.925(3) Ti4-O5 0.663 d=1.967(3) Ti4-O4 0.658 d=1.970(3)	Ti4 4.178 Ti4-O16 1.258 d=1.730(6) Ti4-O4 0.801 d=1.897(5) Ti4-O5 0.799 d=1.898(6) Ti4-O6 0.660 d=1.969(5) Ti4-O7 0.660 d=1.969(5)	Ti4 4.160 Ti4-O15 1.117 d=1.774(9) Ti4-O3 0.676 d=1.960(7) Ti4-O10 0.625 d=1.989(6) Ti4-O16 0.610 d=1.998(9) Ti4-O5 0.578 d=2.018(7) Ti4-O2 0.555 d=2.033(6)	Ti4 4.126 Ti4-O16 1.208 d=1.745(6) Ti4-O3 0.803 d=1.896(6) Ti4-O7 0.774 d=1.910(6) Ti4-O2 0.674 d=1.961(6) Ti4-O4 0.667 d=1.965(6)
Ti5 4.262 Ti5-O16 1.170 d=1.757(3) Ti5-O6 0.661 d=1.968(3) Ti5-O1 0.620 d=1.992(3) Ti5-O12 0.618 d=1.993(3) Ti5-O2 0.597 d=2.006(3) Ti5-O15 0.597 d=2.006(3)	Ti5 4.144 Ti5-O8 1.235 d=1.737(7) Ti5-O2 0.817 d=1.890(6) Ti5-O6 0.771 d=1.911(5) Ti5-O4 0.661 d=1.968(5) Ti5-O3 0.660 d=1.969(5)	Ti5 4.210 Ti5-O11 1.215 d=1.743(8) Ti5-O5 0.828 d=1.885(7) Ti5-O4 0.797 d=1.899(7) Ti5-O6 0.706 d=1.944(7) Ti5-O14 0.665 d=1.966(6)	Ti5 4.112 Ti5-O15 1.238 d=1.736(6) Ti5-O5 0.803 d=1.896(6) Ti5-O4 0.749 d=1.922(6) Ti5-O6 0.679 d=1.958(6) Ti5-O3 0.642 d=1.979(6)
Ti6 4.256 Ti6-O13 1.151 d=1.763(3) Ti6-O6 0.674 d=1.961(3) Ti6-O5 0.621 d=1.991(3) Ti6-O15 0.616 d=1.994(3) Ti6-O4 0.602 d=2.003(3) Ti6-O14 0.592 d=2.009(3)	Ti6 4.261 Ti6-O9 1.176 d=1.755(6) Ti6-O1 0.656 d=1.971(5) Ti6-O14 0.625 d=1.989(6) Ti6-O6 0.615 d=1.995(5) Ti6-O7 0.605 d=2.001(5) Ti6-O12 0.584 d=2.014(6)	Ti6 4.282 Ti6-O9 1.221 d=1.741(6) Ti6-O3 0.679 d=1.958(5) Ti6-O1 0.640 d=1.980(7) Ti6-O8 0.607 d=2.000(7) Ti6-O4 0.579 d=2.017(6) Ti6-O10 0.555 d=2.033(8)	Ti6 4.093 Ti6-O22 1.215 d=1.743(6) Ti6-O2 0.788 d=1.903(6) Ti6-O6 0.767 d=1.913(6) Ti6-O7 0.670 d=1.963(6) Ti6-O5 0.652 d=1.973(6)
Cu 1.039 Cu-Cl1 0.528 d=2.086(3) Cu-Cl2 0.510 d=2.099(3)	Ti7 4.194 Ti7-O29 1.269 d=1.727(7)	Ti7 14.209 Ti7-O18 10.643 d=0.940(8)	Ti7 4.165 Ti7-O27 1.255 d=1.731(7)

	Ti7-O19 0.817 d=1.890(6) Ti7-O23 0.793 d=1.901(6) Ti7-O21 0.685 d=1.955(6) Ti7-O17 0.632 d=1.985(6)	Ti7-O26 1.212 d=1.744(14) Ti7-O17 0.885 d=1.860(10) Ti7-O20 0.817 d=1.890(10) Ti7-O21 0.652 d=1.973(10)	Ti7-O10 0.793 d=1.901(7) Ti7-O14 0.782 d=1.906(6) Ti7-O12 0.691 d=1.952(6) Ti7-O11 0.645 d=1.977(6)
-	Ti8 4.250 Ti8-O28 1.163 d=1.759(7) Ti8-O18 0.678 d=1.959(6) Ti8-O27 0.625 d=1.989(6) Ti8-O26 0.623 d=1.990(6) Ti8-O17 0.607 d=2.000(6) Ti8-O21 0.555 d=2.033(6)	Ti8 3.981 Ti8-O28 1.111 d=1.776(10) Ti8-O22 0.799 d=1.898(8) Ti8-O30 0.761 d=1.916(10) Ti8-O27 0.731 d=1.931(11) Ti8-O19 0.579 d=2.017(9)	Ti8 4.146 Ti8-O32 1.235 d=1.737(7) Ti8-O9 0.808 d=1.894(6) Ti8-O11 0.774 d=1.910(6) Ti8-O8 0.681 d=1.957(6) Ti8-O10 0.649 d=1.975(6)
-	Ti9 4.220 Ti9-O31 1.142 d=1.766(6) Ti9-O18 0.665 d=1.966(5) Ti9-O23 0.616 d=1.994(6) Ti9-O30 0.611 d=1.997(6) Ti9-O22 0.600 d=2.004(6) Ti9-O27 0.586 d=2.013(6)	Ti9 4.123 Ti9-O29 1.248 d=1.733(8) Ti9-O23 0.912 d=1.849(9) Ti9-O17 0.780 d=1.907(8) Ti9-O18 0.621 d=1.991(8) Ti9-O19 0.562 d=2.028(8)	Ti9 4.066 Ti9-O30 1.199 d=1.748(7) Ti9-O12 0.778 d=1.908(6) Ti9-O8 0.776 d=1.909(7) Ti9-O9 0.661 d=1.968(6) Ti9-O14 0.652 d=1.973(6)
-	Ti10 4.175 Ti10-O32 1.286 d=1.722(7) Ti10-O21 0.812 d=1.892(6) Ti10-O20 0.774 d=1.910(6) Ti10-O22 0.661 d=1.968(6) Ti10-O23 0.642 d=1.979(6)	Ti10 4.114 Ti10-O25 1.179 d=1.754(10) Ti10-O24 0.704 d=1.945(11) Ti10-O22 0.645 d=1.977(9) Ti10-O17 0.630 d=1.986(8) Ti10-O21 0.499 d=2.072(10) Ti10-O30 0.457 d=2.105(11	Ti10 4.234 Ti10-O26 1.135 d=1.768(6) Ti10-O13 0.661 d=1.968(5) Ti10-O31 0.627 d=1.988(6) Ti10-O11 0.620 d=1.992(6) Ti10-O25 0.605 d=2.001(7) Ti10-O12 0.586 d=2.013(6)
-	Ti11 4.350 Ti11-O25 1.231 d=1.738(6) Ti11-O18 0.674 d=1.961(5) Ti11-O30 0.620 d=1.992(6) Ti11-O20 0.616 d=1.994(6) Ti11-O26 0.613 d=1.996(7) Ti11-O19 0.595 d=2.007(6)	Ti11 4.163 Ti11-O32 1.215 d=1.743(10) Ti11-O23 0.633 d=1.984(9) Ti11-O22 0.613 d=1.996(9) Ti11-O27 0.587 d=2.012(11) Ti11-O24 0.572 d=2.022(11) Ti11-O20 0.543 d=2.041(11)	Ti11 4.223 Ti11-O29 1.170 d=1.757(7) Ti11-O13 0.660 d=1.969(5) Ti11-O14 0.613 d=1.996(6) Ti11-O9 0.598 d=2.005(6) Ti11-O28 0.595 d=2.007(7) Ti11-O31 0.587 d=2.012(6)
-	Ti12 4.147 Ti12-O24 1.238 d=1.736(6) Ti12-O17 0.812 d=1.892(6) Ti12-O22 0.786 d=1.904(6) Ti12-O19 0.663 d=1.967(6) Ti12-O20 0.647	Ti12 4.372 Ti12-O31 1.279 d=1.724(11) Ti12-O21 0.846 d=1.877(10) Ti12-O19 0.801 d=1.897(9) Ti12-O20 0.799 d=1.898(10) Ti12-O23 0.647 d=1.976(8)	Ti12 4.271 Ti12-O24 1.195 d=1.749(7) Ti12-O13 0.658 d=1.970(6) Ti12-O10 0.608 d=1.999(6) Ti12-O28 0.605 d=2.001(7) Ti12-O25 0.605

	d=1.976(6)		d=2.001(7) Ti12-O8 0.600 d=2.004(7)
-	Cu1 2.095 Cu1-Cl2 0.410 d=2.180(4) Cu1-Cl3 0.408 d=2.182(4) Cu1-Cl1 0.296 d=2.301(4) Cu1-Cl1 0.284 d=2.316(4)	Cu1 1.001 Cu1-Br2 0.354 d=2.374(4) Cu1-Br1 0.328 d=2.403(4) Cu1-Br3 0.320 d=2.412(4)	Cu1 1.072 Cu1-I5 0.474 d=2.384(4) Cu1-I1 0.433 d=2.418(4) Cu1-I6 0.085 d=3.018(6) Cu1-I7 0.079 d=3.046(6)
-	Cu2 2.057 Cu2-Cl5 0.408 d=2.182(4) Cu2-Cl6 0.390 d=2.198(4) Cu2-Cl4 0.296 d=2.301(4) Cu2-Cl4 0.278 d=2.324(4)	Cu2 1.002 Cu2-Br2 0.340 d=2.389(4) Cu2-Br3 0.339 d=2.390(4) Cu2-Br1 0.323 d=2.408(4)	Cu2 1.010 Cu2-I2 0.442 d=2.410(4) Cu2-I1 0.370 d=2.476(4) Cu2-I6 0.059 d=3.155(5) Cu2-I7 0.139 d=2.839(5)
-	-	Cu3 0.404 Cu3-Br5' 0.0656 d=2.998(4) Cu3-Br4 0.215 d=2.559(18) Cu3-Br6' 0.114 d=2.802(3)	Cu3 1.077 Cu3-I2 0.469 d=2.388(4) Cu3-I3 0.393 d=2.454(4) Cu3-I6 0.146 d=2.819(5) Cu3-I7 0.069 d=3.097(5)
-	-	Cu4 1.401 Cu4-Br6' 0.336 d=2.393(4) Cu4-Br4 0.947 d=2.01(2) Cu4-Br5 0.151 d=2.69(3)	Cu4 0.950 Cu4-I3 0.383 d=2.463(3) Cu4-I4 0.365 d=2.481(4) Cu4-I6 0.060 d=3.148(5) Cu4-I7 0.142 d=2.831(5)
-	-	-	Cu5 1.037 Cu5-I5 0.435 d=2.416(4) Cu5-I4 0.398 d=2.449(3) Cu5-I6 0.137 d=2.844(5) Cu5-I7 0.067 d=3.109(5)

[a] $V\mathrm{i} = \Sigma S_{ij} = \Sigma \exp[(r_1 - r_{ij})/B]$, where r_0 is the length of a single bond (here r1=1.815 for Ti^{iv}-O and Cu^{i}-Cl, 2.00 for Cu^{ii}-Cl,1.99 for Cu^{i}-Br, 2.108 for Cu^{i}-I), r_1 is the bond length between atoms *i* and *j*; B is a constant, the "universal parameter" ~0.37 Å; S_{ij} is the valence of a bond between atoms *i* and *j*; V_i is the sum of all bond valences of the bonds formed by a given atom *i*.

Table S2 Crystal data and structure refinements for compounds **1-4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{60}H_{142}Cl_4Cu_2O_{34}Ti_{12}$	$C_{54}H_{126}Cl_6Cu_2O_{32}Ti_{12}$	$C_{54}H_{126}Br_6Cu_4O_{32}Ti_{12}$	$C_{54}H_{126}Cu_5I_7O_{32}Ti_{12}$
Mr	2251.42	2201.79	2595.97	3068.35
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P2(1)/c	P2(1)/c
a (Å)	14.2993(6)	14.632(3)	21.5530(4)	27.9309(6)
b (Å)	15.1330(7)	15.107(3)	21.6943(3)	15.1805(2)
c (Å)	15.1938(9)	21.839(4)	21.4667(3)	26.0787(5)
α/°	117.300(5)	91.04(3)	-	-
β/°	95.635(4)	91.22(3)	90.935(2)	109.756(2)
γ/°	111.286(4)	93.17(3)	-	-
V (Å^3)	2579.4(2)	4818.0(16)	10036.0(3)	10406.7(3)
Z	1	2	4	4
ρ(g cm^{-3})	1.449	1.518	1.718	1.958

μ(mm^{-1})	9.402	1.598	11.883	25.281
F(000)	1164	2260	5184	5944
GOF on F^2	1.020	1.060	1.244	1.024
Collected reflns	14567	31750	38638	40415
Unique reflns (R_{int})	7913	16096	17436	18816
Obsd reflns[$I>2(I)$]	6025	8165	11054	12872
R_1[a]/wR_2[b][$I>2(I)$]	0.0497/0.1360	0.0791/0.1899	0.1197/0.3191	0.0793/0.2208
R_1[a]/wR_2[b](all data)	0.0682/0.1561	0.1509/0.2465	0.1547/0.3517	0.1134/0.2577

[a]$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b]$wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

References

[1] W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience, New York, **1966**.

[2] G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution (University of Göttingen, Göttingen, Germany, 1997).*

[3] G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement (University of Göttingen, Göttingen, Germany, 1997).* .

[4] V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park, *J. Am. Chem. Soc.* **1993**, *115*, 8469-8470.

[5] Y. Lv, J. Willkomm, A. Steiner, L. Gan, E. Reisner, D. S. Wright, *Chem. Sci.* **2012**, *3*, 2470-2473.