Supporting Information

A Close-Packed Ti_6 and Ti_{12} Nanocluster Superstructure

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Characterization

All reagents and chemicals were obtained from commercial sources and were of analytical grade. Fourier transform infrared (FT-IR) spectra of the ligand and the cluster were recorded in KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet iS5 spectrophotometer. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the power sample was obtained on a Purkinje IS19-2 spectrometer with $BaSO_4$ as reference. X-ray diffraction (XRD) spectra of the sample was recorded by a Rigaku Ultima IV diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 5-90°.

X-ray Crystallography:

The structure data of **[Ti$_{12}$+Ti$_6$]** were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer with graphite-monochromated Cu K_α radiation (λ = 1.54178 Å) at room temperature. Peak hunting, unit cell finding, lattice selection, data reduction and absorption correction were performed using the program CrysAlis[Pro].[1] The structure was solved by the intrinsic phasing method and refined using Full-matrix least-squares based on F^2 with program SHELXL-97 within OLEX2.[2] All the non-hydrogen atoms were refined anisotropically and H atoms isotropically; all hydrogen atoms were generated geometrically and constrained to ride on their parent atoms. For isopropoxy group, SADI, ISOR, DANG and PART constraints are often applied due to disorder. The bond lengths of C–C were set to ~1.50 ± 0.01 Å, and meanwhile the distances between 1,3-atoms were set to ~2.5 ± 0.01 Å. To maintain reasonable geometry and atomic

displacement parameters, part of the isopropoxy groups is split into two disorder parts. In this structure, some cations were highly disordered and could not be located. OLEX2 solvent masking procedure was used to remove the residual electron density corresponding to disordered components in the crystal lattices; structures were then refined again using the data generated. Crystal data and details of data collection and refinement of **[Ti$_{12}$+Ti$_6$]** are summarized in Table 1. CCDC 2204197 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis

Materials. All the chemicals were of analytical grade, obtained from commercial sources and used as received.

Synthesis of [Ti$_{12}$(μ_3-O)$_{14}$(O^{i}Pr)$_{18}$]·3[Ti$_6$(μ_2-O)$_6$(2-pic)$_6$(O^{i}Pr)$_6$]. Analytically pure Ti(O^{i}Pr)$_4$ (0.075 mL, 0.25 mmol), ethylenediamine (0.02 mL, 0.30 mmol) and 2-picolinic acid (24 mg, 0.19 mmol) were mixed in 1 mL acetonitrile. The mixture was placed in a thick Pyrex tube. The sealed tube was heated under autogenous pressure at 100°C for 24 h in an autoclave. After cooling to room temperature, the colorless block crystals were obtained, namely **[Ti$_{12}$+Ti$_6$]**, rinsed and centrifuged with acetonitrile, and dried.
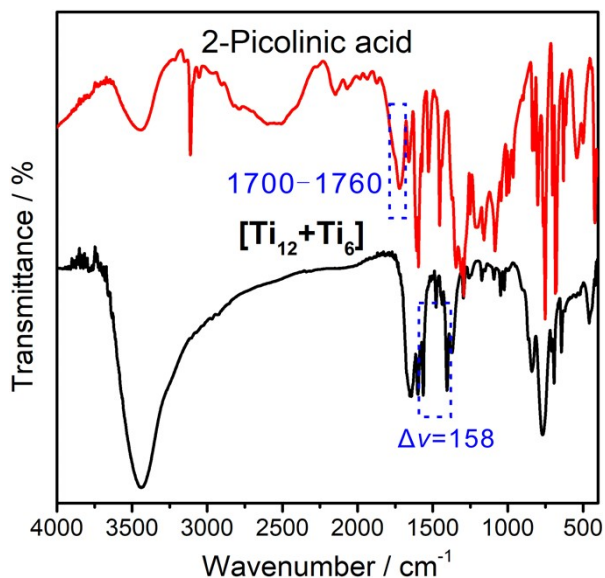
Supporting Figures

Figure S1. The FT-IR spectra of **[Ti$_{12}$+Ti$_6$]** and 2-picolinic acid. In Fourier transform infrared (FT-IR) spectra, the 1594 cm^{-1} band of the ligand corresponding to ν(C=N) shifted to 1598 cm^{-1} for the **[Ti$_{12}$+Ti$_6$]**. The band corresponding to the stretching vibration of the C=O group of the 2-picolinic acid monomer is situated at 1700–1760 cm^{-1}, and this band disappears in the cluster. The absorption bands of the ν_{as}(COO$^-$) and ν_s(COO$^-$) appear at 1562 cm^{-1} and 1404 cm^{-1}, respectively. The $\Delta\nu$ for the COO$^-$ is 158 cm^{-1}. This suggests the 2-picolinate ligand adopt a bridging coordination mode. The bands below 630 cm^{-1} are attributed to the Ti–O–Ti vibrations.
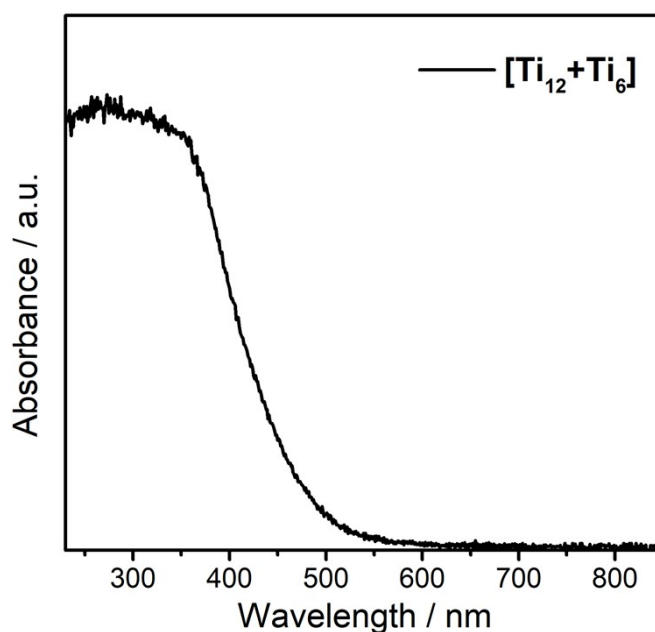

Figure S2. The UV-Vis diffuse reflectance spectrum of **[Ti$_{12}$+Ti$_6$]**. The bandgap of **[Ti$_{12}$+Ti$_6$]** is calculated to be 2.6 eV.
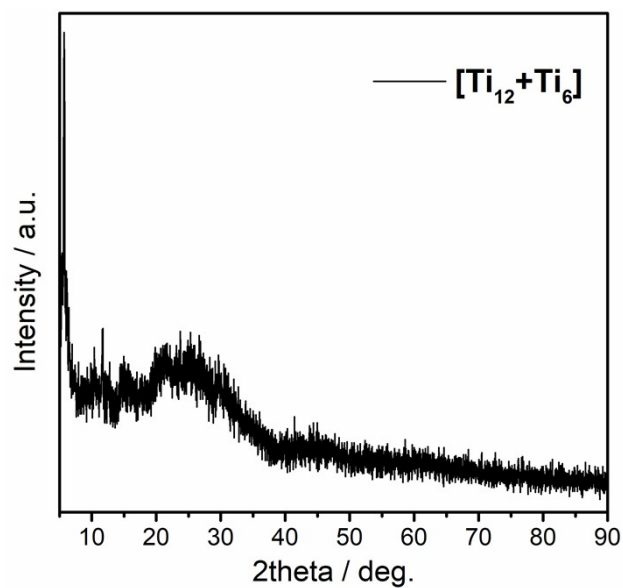
Figure S3. The XRD spectra of **[Ti₁₂+Ti₆]**.
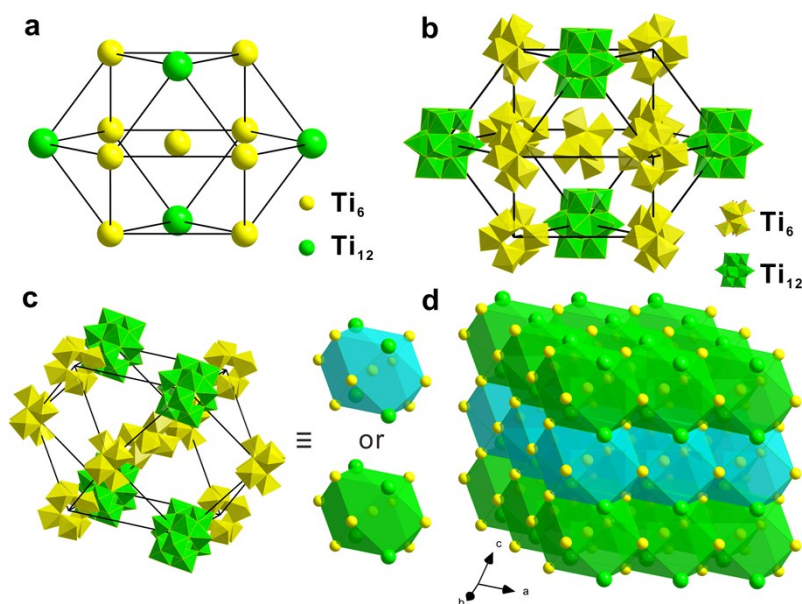
Figure S4. (a-c) The local structure of one **Ti₆** and neighbouring eight **Ti₆** and four **Ti₁₂**. (d) A 3×3×3 cells consisting of 27 cuboctahedra.

References

(1) CrysAlis^Pro Version 1.171.41.64. 2018, Rigaku Oxford Diffraction; Rigaku Corporation, Wrocław, Poland.

(2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl. Cryst.* 2009, **42**, 339.