Electronic Supplementary Information

A New Cadmium-Doped Titanium−Oxo Cluster with Stable Photocatalytic H_2 Evolution Property

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Experimental Section

Materials and Instrumentation. Commercially available reagents were bought from Sigma-Aldrich and used as received without further purification, except that $Ti(O_iPr)_4$ was bought from Energy Chemical. Fourier transform infrared spectroscopy (FTIR) data was collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer. The composition was studied with an Oxford X-max energy dispersive spectrometer (EDS) equipped on the JSM6700-F FESEM. Inductively Coupled Plasma OES spectrometer is Ultima2 from HORIBA Jobin Yvon. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer.

Synthesis of complex 1: tert-butylacetic acid (1.5g, 15 mmol), $Cd(NO_3)_2.6H_2O$ (0.31g, 1mmol) and CH_3CN (5.5 ml) were mixed at room temperature in a Teflon-lined reaction vessel, then dropwise $Ti(O_iPr)_4$ (0.46 ml, 1.50 mmol) was added. This vessel was heated at 100 ^oC oven for four days and then cooled to room temperature. The complex **1** $H_2\{Ti_4Cd_2(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(OOCC(CH_3)_3)_{12}(O\textit{i}Pr)_2\}$ was obtained. Colorless crystals were collected with a yield of 85% (based on Ti). Anal.Calcd for $C_{66}H_{124}Cd_2O_{30}Ti_4$ (MW 1813.96): C, 43.70; H, 6.89; Ti, 10.56; Cd, 12.39. Found: C, 44.90; H, 5.93. ICP: Ti,10.1 Cd,11.7.

Hydrogen Production Experiment: The sample for photoinduced hydrogen production was located in a closed gas circulation system (Perfect Light Company Labsolar-III (AG). Typically, 50mg of sample was dispersed in 90mL of H_2O with 10mL of methanol as sacrifice agent, and then 33μL 1.0 wt% $HPtCl_4$ was added. The 300W Xe lamp was used as the UV-vis light source. The gas in the system was analyzed by online-GC to determine the amount of hydrogen generated with an interval of two hours.

X-ray Crystallography: The structure data of complex **1** was collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiationon (λ = 0.71073 Å) at room temperature. Absorption corrections were applied using SADABS.[1] Structures were solved by direct method and refined by full-matrix least-squares on F^2 using *SHELXTL*.[2]

CCDC 1448897 contains the supplementary crystallographic data for this paper. This data is provided free of charge by The Cambridge Crystallographic Data Centre.

(1) Sheldrick, G. M. *SADABS, Program for area detector adsorption correction*. Institute for Inorganic Chemistry, University of Göttingen, Göttingen (Germany), **1996**.
(2) Sheldrick, G. M. *SHELXL-97, Program for solution of crystal structures*. University of Göttingen, Göttingen (Germany), **1997**.

Table S1. Crystal data and structure refinements summary for complex **1**.

CCDC No	1448897		
Crystal.determ.formua	C66 H102 Cd2 O30 Ti4	V [Å^3]	2422.4(6)
Mr	1791.78	Z	1
crystal system	Triclinic	T [K]	293
space group	P -1	ρ_c[gcm^{-3}]	1.228
a [Å]	14.1591(19)	μ [mm^{-1}]	0.810
b [Å]	14.3016(19)	reflns coll.	10884
c [Å]	15.0587(19)	unique reflns	8226
α [^{o}]	111.384(2)	GOF	1.072
β [^{o}]	114.428(1)	$R1[I>2\sigma(I)]$[a]	0.0772
γ [^{o}]	98.357(4)	$wR2[I>2\sigma(I)]$[b]	0.2679

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

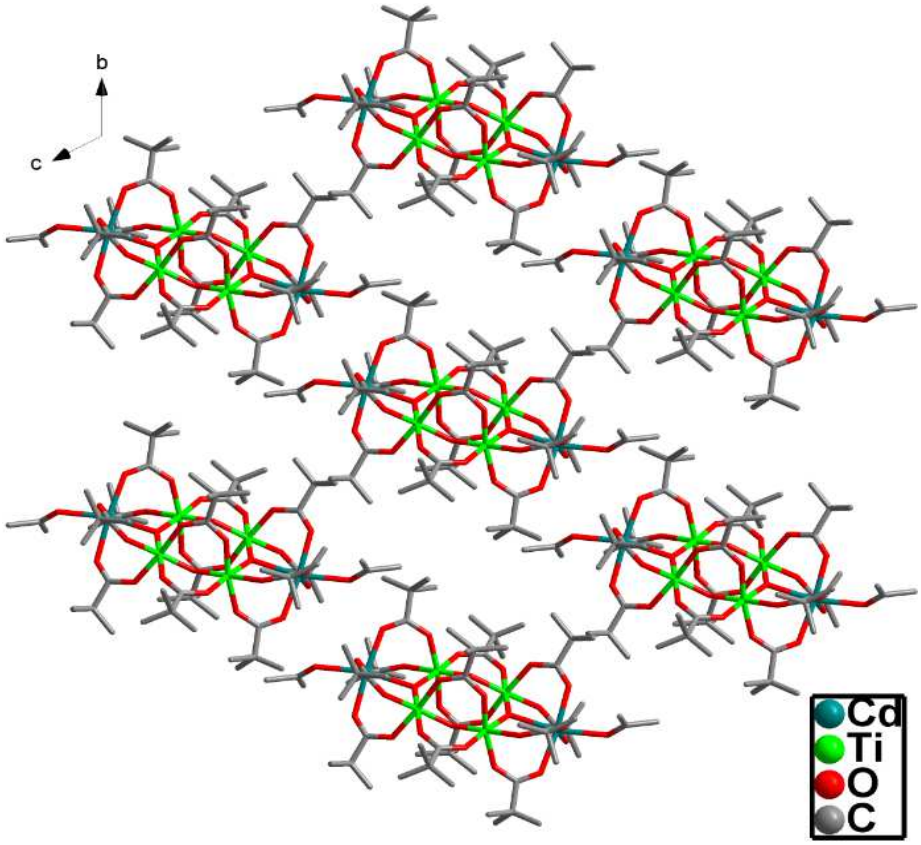

Fig. S1 Packing viewing of complex **1**.

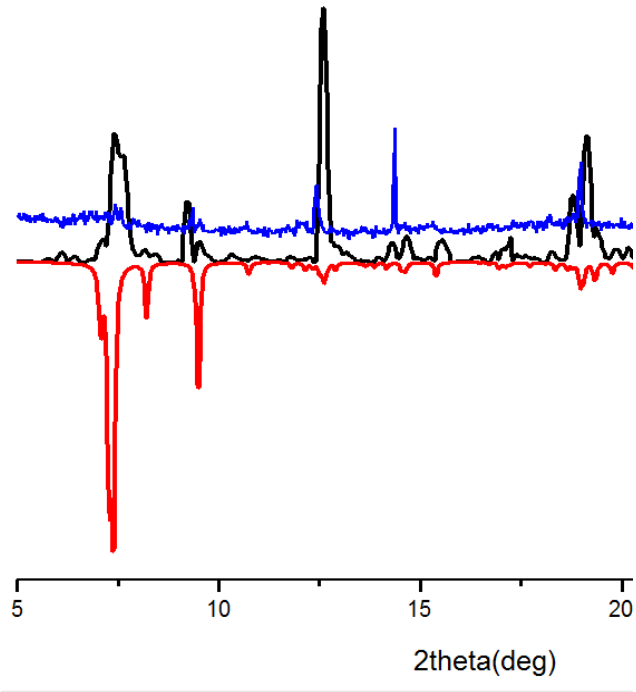

Fig. S2 The PXRD of complex **1:** experimental (black), after photocatalysis (blue) and simulated pattern (red).

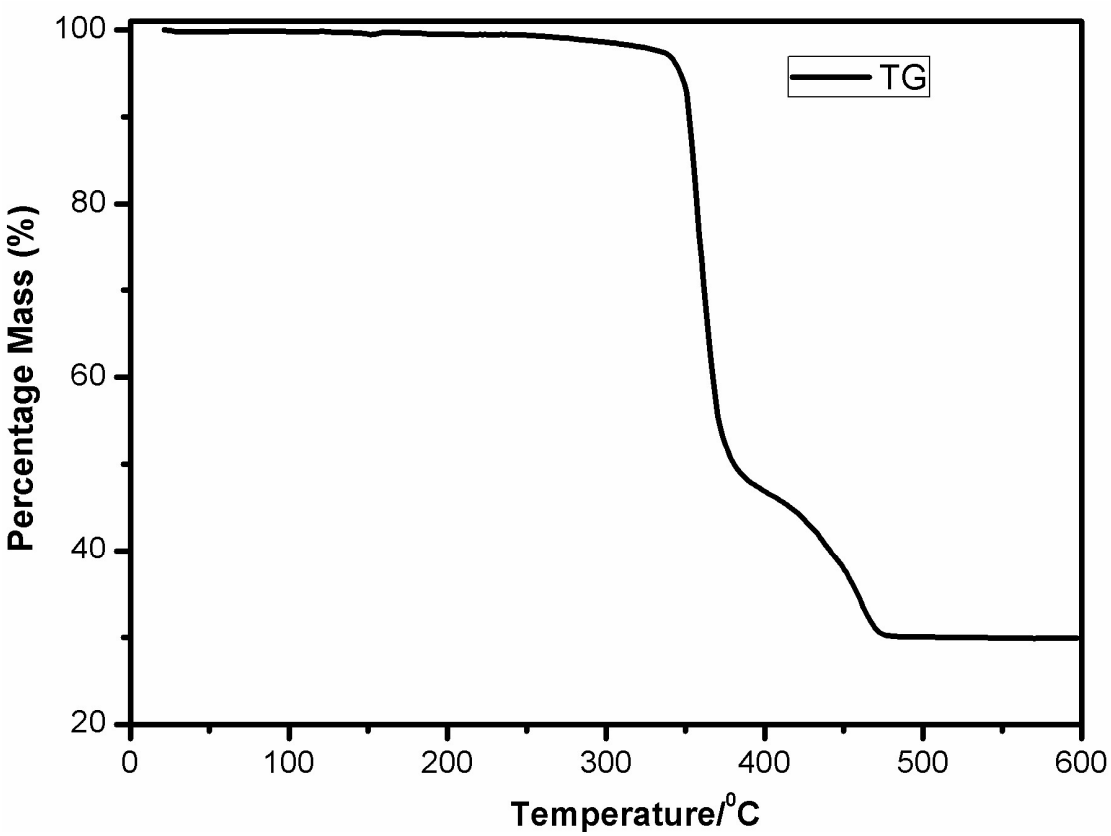

Fig. S3 TGA curve of complex **1**. It lost two O*i*Pr and eight *tert*-butylacetic acid ligands very quickly during 340-380 °C (calculated 51.11%; observed 51.87%), and then gradually lost the remaining organic ligands until about 470 °C.

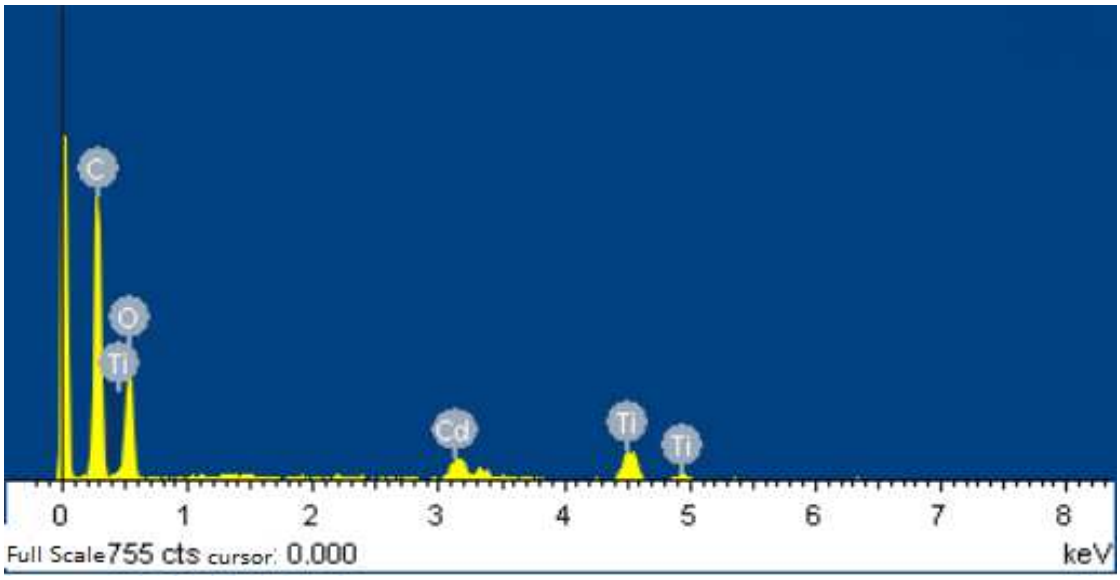

Fig. S4 EDS spectrum of crystal **1**.

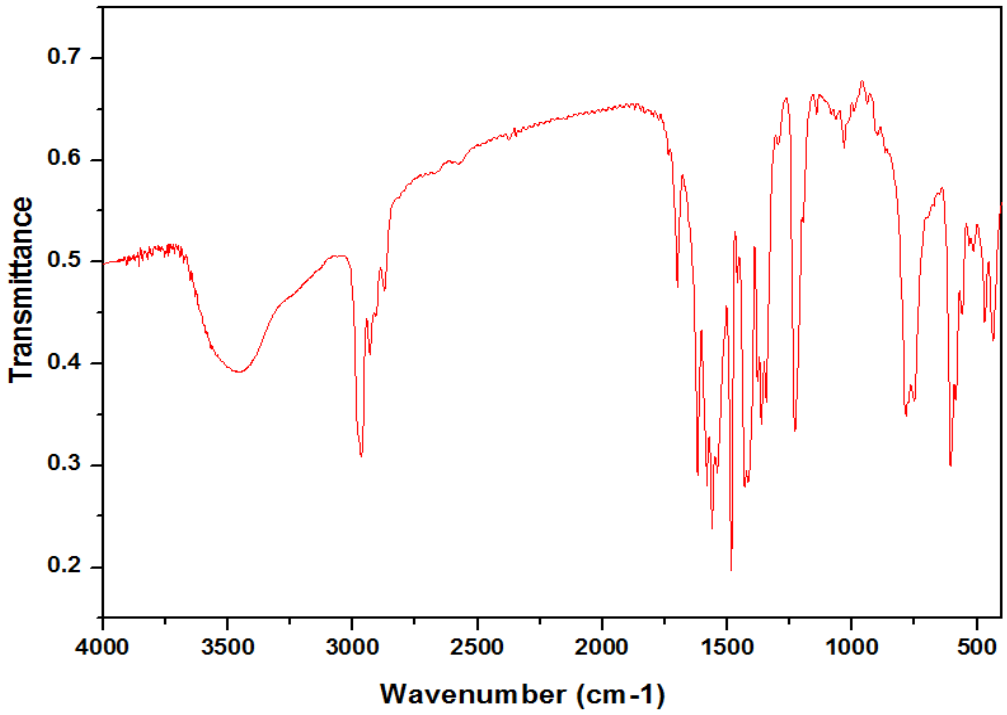

Fig. S5 IR spectrum of complex **1**.