Supporting Information

New Picolinate-Functionalized Titanium-Oxide Clusters: Syntheses, Structure and Photocatalytic H_2 Evolution

Chang Gao,[a] Dexin Wang,[a] Yanshu Liu,[a] Guanyun Zhang,[a] Caiyun Liu,[a] Amir Said,[a] Huihui Niu,[a] Guo Wang,[b] Chen-Ho Tung,[a] and Yifeng Wang[ac]*

[a]*Key Lab for Colloid and Interface Science of Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China*

[b]*Department of Chemistry, Capital Normal University, Beijing 100048, China*

[c]*State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*

Corresponding author email: yifeng@sdu.edu.cn

S1. The table of crystallographic data

Compound	**1**	**2**
Formula unit	$Ti_{12}O_{52}N_{25}C_{130}H_{151}$	$Ti_{12}O_{57}N_{27}C_{132}H_{135}$
CCDC number	2164406	2164407
Moieties	$[Ti_{12}O_{18}(O_2NC_6H_4)_{16}]\cdot4(NC_4H_{12})\cdot4(CH_3CN)\cdot2(HO^iPr)$	$[Ti_{12}O_{18}(O_2NC_6H_4)_{18}]\cdot3(H_3O)\cdot3(NC_4H_{12})\cdot6(CH_3CN)$
Formula weight (g/mol)	3470.13	3586.03.9
Crystal system	monoclinic	monoclinic
Space group (Nr.)	*$P2_1/c$*	*C2/c*
a (Å)	17.8911(4)	32.8178(7)
b (Å)	14.9531(4)	15.2483(3)
c (Å)	28.9581(6)	32.1138(8)
α (°)	90	90
β (°)	98.617(2)	114.021(3)
γ(°)	90	90
Volume ($Å^3$)	7659.7(6)	14678.5(6)
Z	2	4
$Density_{calc}$ (g/cm^3)	1.505	1.476
Abs. Coeff. μ (mm^{-1})	5.815	6.052
Temperature (K)	173	173
Total reflections	50920	44649
Min-max 2θ (°)	6.174 to 154.34	6.026 to 153.088
Unique reflections	15222	14543
R_1 [I>=2σ]	0.0782	0.1138
wR_2 (all data)	0.2230	0.3215
R_{int}	0.0795	0.0792
Goodness of fit on F^2	1.055	1.102
Parameters	1020	927
Restraints	330	277
Largest diff. peak/hole (e $Å^{-3}$)	1.07/-0.71	1.35/-1.22

S2. Supplementary figures and discussion

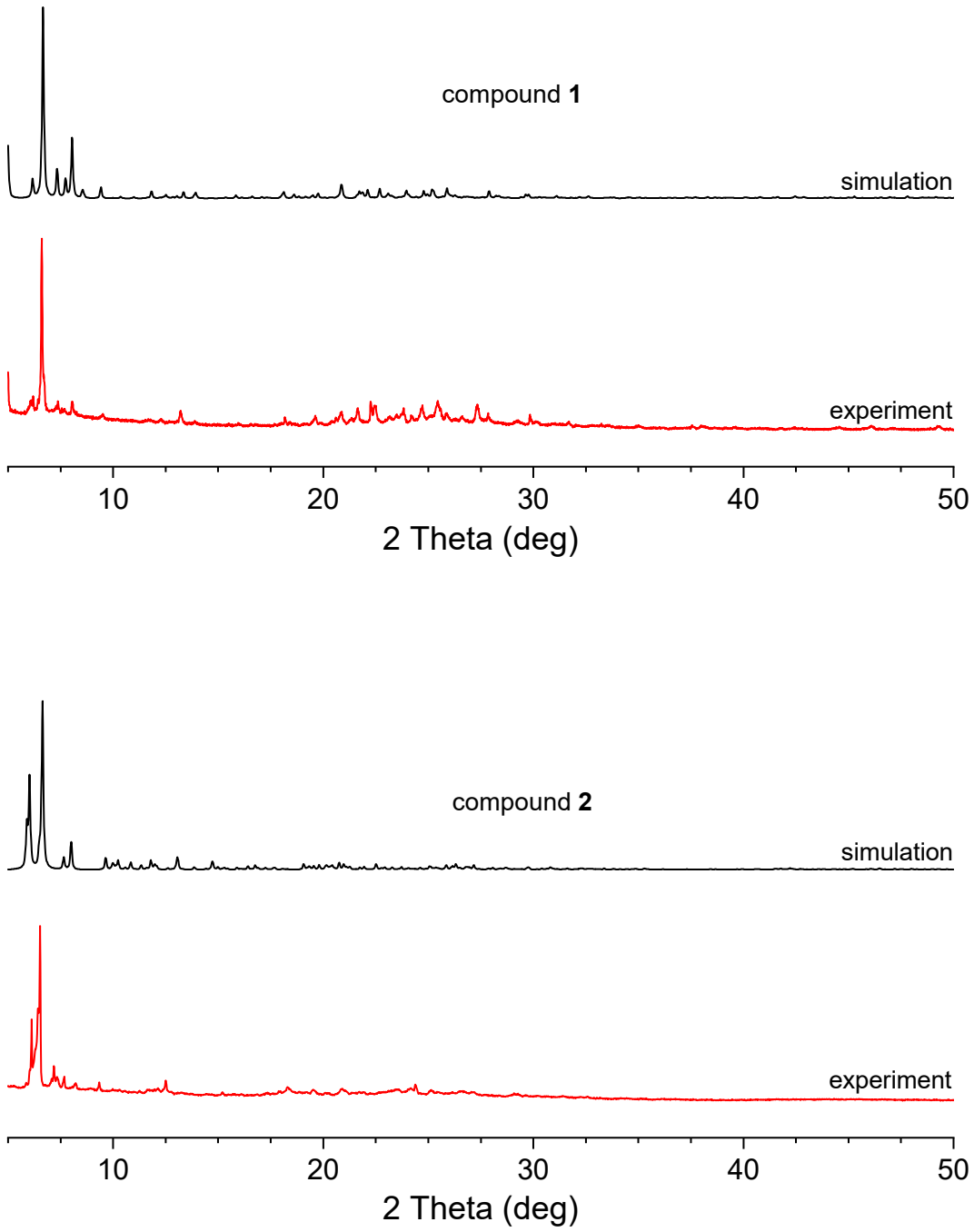

Figure S1. Powder X-ray diffraction pattern of **1** and **2**, recorded on a Rigaku SmartLab 9KW X-ray diffraction instrument.

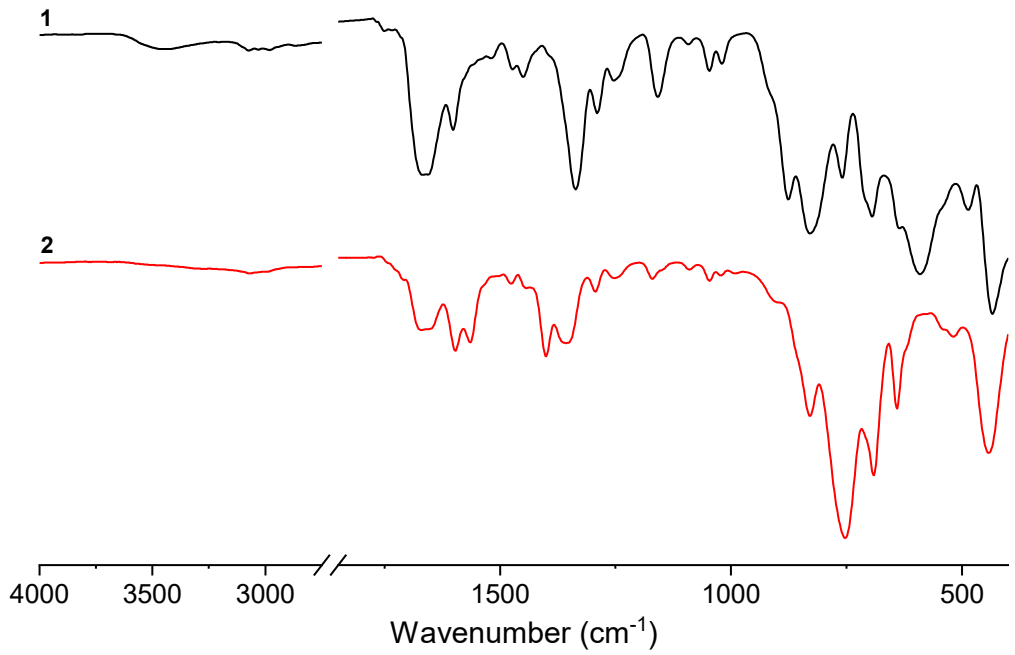

Figure S2. FTIR spectra of **1** and **2**.

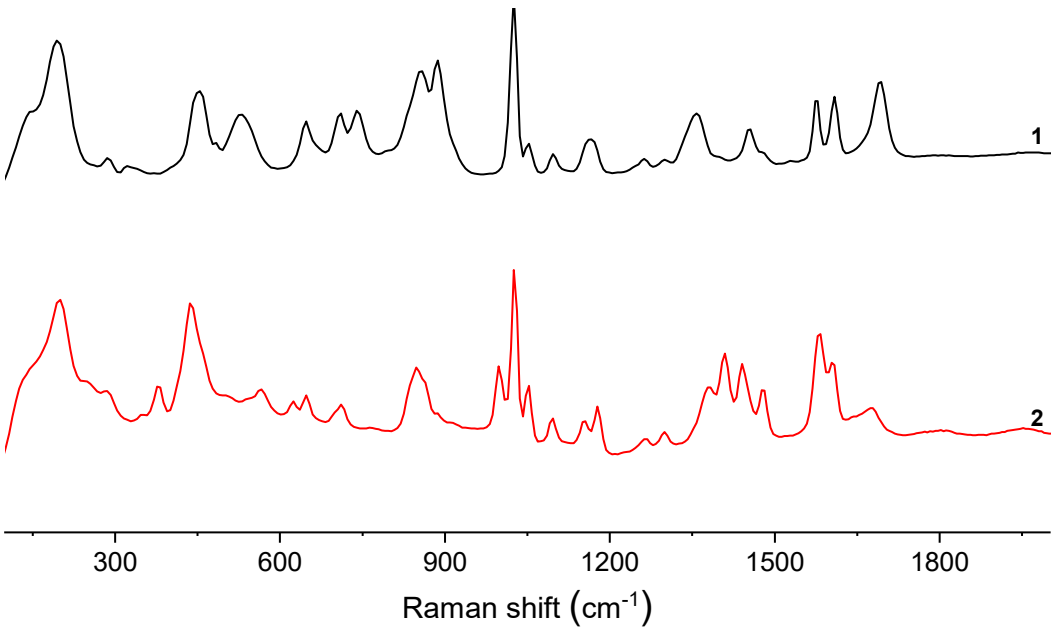

Figure S3. Raman spectra of **1** and **2**.

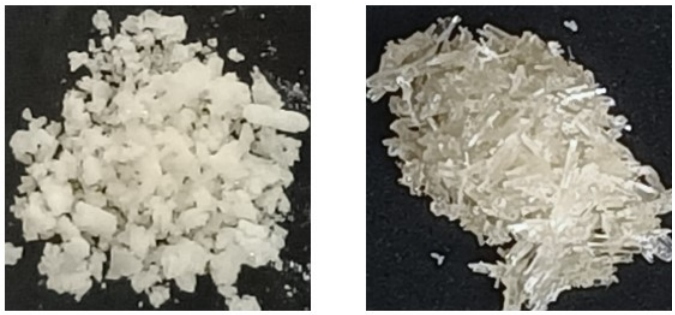

Figure S4. The photos of of **1** and **2**.

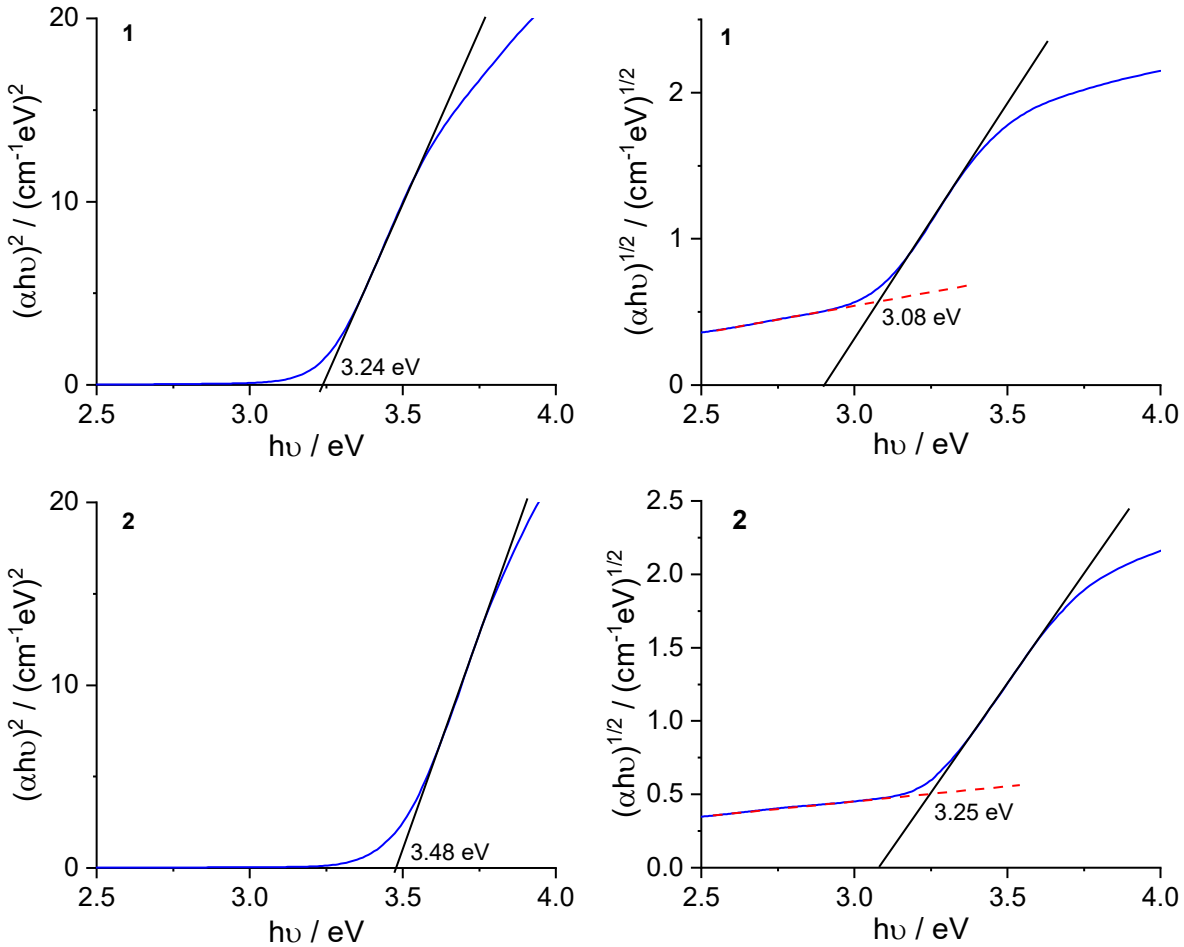

Figure S5. Calculations of direct band gap and indirect band gap values based on UV-vis diffuse reflectance spectra.

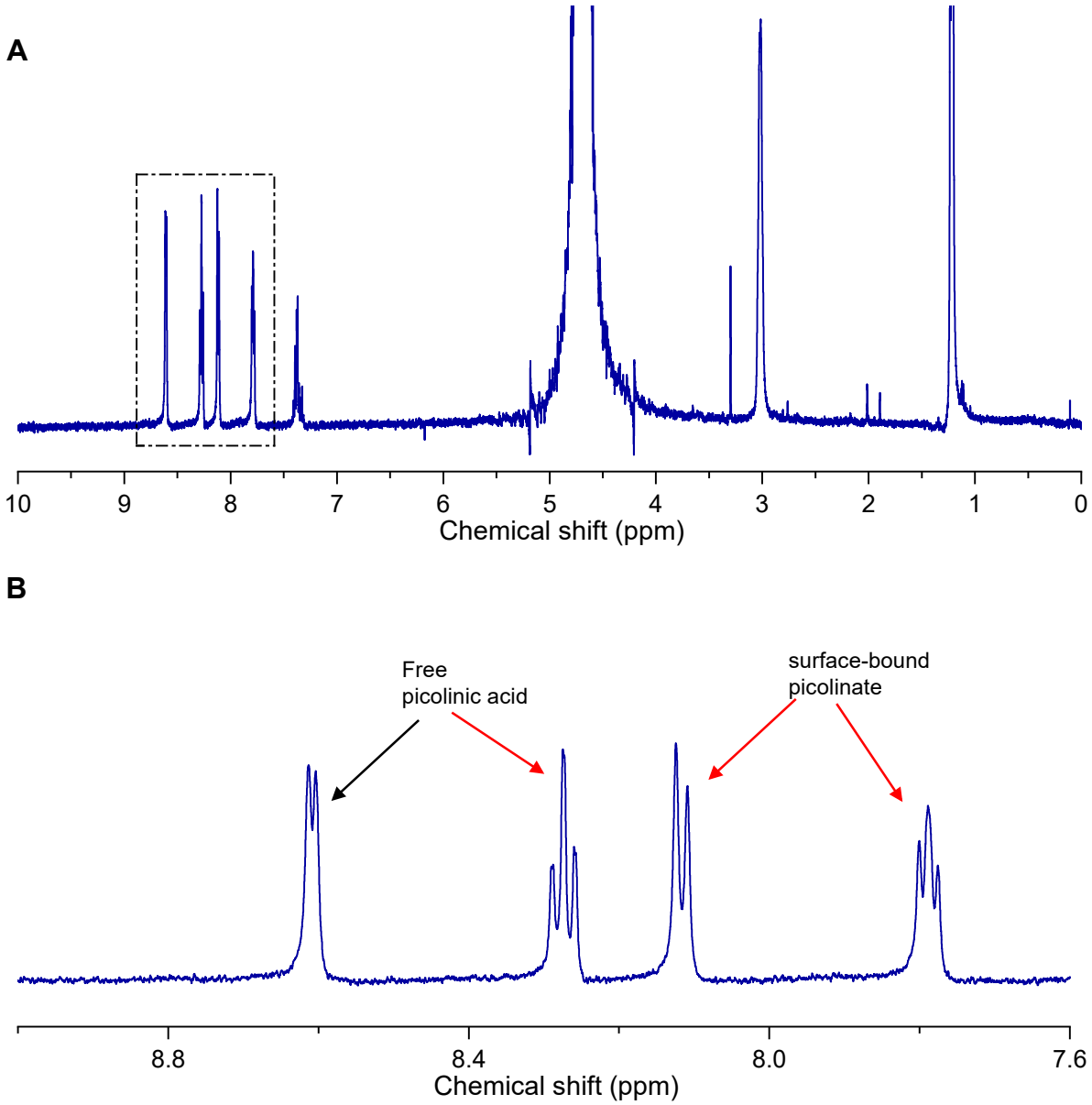

Figure S6. ^{1}H NMR of **1**-Pt solution prepared using D_2O. Panel B is the magnified spectra of panel A. The spectrum implies approximately 50% of PA ligands desorb from the surfaces of **1a** in aqueous solution.

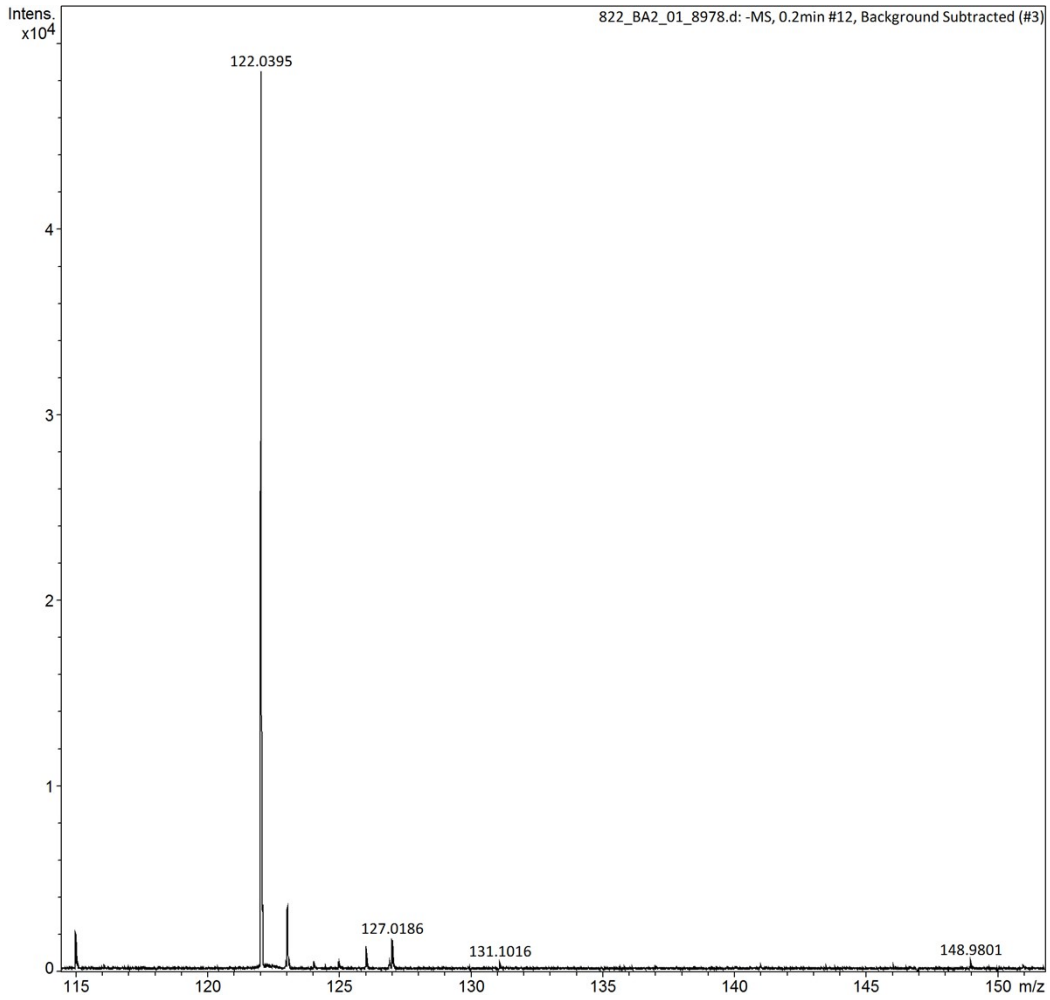

Figure S7. The high-resolution ESI-MS spectrum of the **1**-Pt solution. The spectrum was obtained using an Agilent Q-TOF 6510 instrument in negative mode.

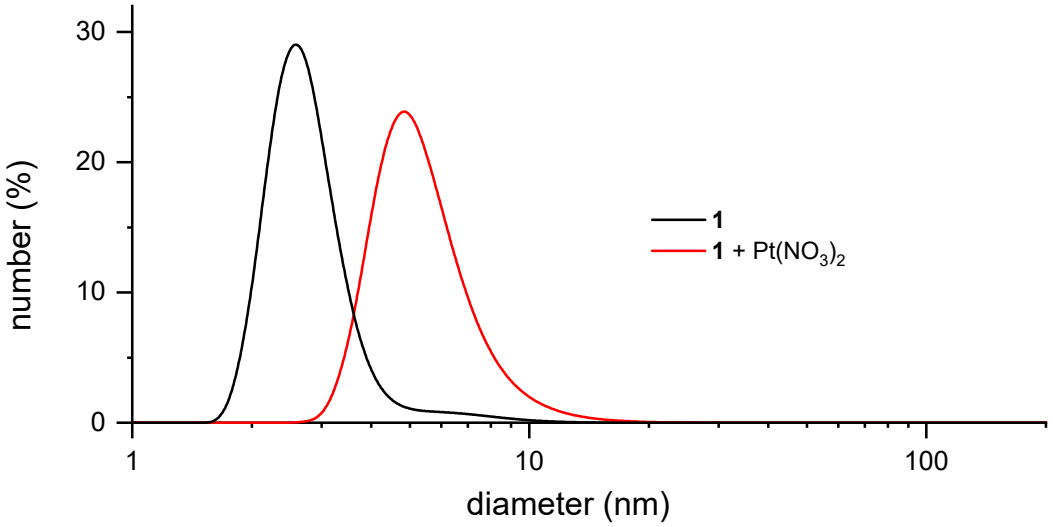

Figure S8. DLS profiles of the various solution samples.

Estimation of apparent quantum efficiency (AQY)

To calculate the AQY value, we assume that all UV photons reaching the solution were absorbed. Hence, the number of photons, *N*, can be calculated using the following equation:

$$N = \frac{\text{photon intensity} \times \text{reaction cross section} \times \text{reaction time}}{hC/\lambda}$$

in which, *h* is the Plank constant, *C* is the velocity of light and λ is the wavelength, respectively. The UV intensity of the 300 W Xenon lamp was 3.6 mW cm^{-2} and the effective irradiated area was ca. 12 cm^2. To simplify the calculations, 380 nm was used as the average wavelength of UV.

$$N = \frac{3.6\times10^{-3}\times12\times3600}{6.626\times10^{-34}\times\frac{3.0\times10^{8}}{380\times10^{-9}}}\div(6.022\times10^{23}) = 4.9\times10^{-4}(mol\ h^{-1})$$

The AQY is then calculated using the following equation. The actual reaction of the catalyst is 50 mg, and the yield of H_2 for **1** and **2** is 9 and 1.16 μmol h^{-1}, respectively.

$$\text{AQY} = \frac{\text{the amount of } H_2 \times 2}{N}\times100\%$$

The AQY of **1** and **2** for H_2 evolution are 3.6% and 0.47%, respectively.

Table S1. H_2 evolution experiment data of some TOCs.

TOC	light source	solution medium	Pt (wt%) to Ti	rate (μmol h^{-1} g^{-1})	ref
$Ti_{52}O_{72}(OH)_2(pa)_{34}(O^iPr)_{28}$	300-W Xe lamp	H_2O, MeOH	~1.64	398	Fang, W.-H., et. al. *J. Am. Chem. Soc.* **2016**, *138*, 7480
$Ti_6O_6(pa)_6(O^iPr)_6$	300-W Xe lamp	H_2O, MeOH	~0.66	268	Fang, W. H., et. al. *Dalton Trans.* **2017**, *46*, 803
$Ti_{14}O_{19}(phn)_8(Ac)_{12}(O^iPr)_2$	300-W Xe lamp	H_2O, MeOH	0	236	Hong, Z.-F., et. al. *Cryst. Growth Des.* **2018**, *18*, 4864
$[Ti_6O_6(pp)_2(PhO)_6(phn)_6]Cl_2$	300-W Xe lamp	H_2O, TEOA	~0.66	~217	Narayanam, N., et. al. *Chem. Commun.* **2017**, *53*, 8078
$Ti_6O_4(BDC)_2(pa)_2(O^iPr)_{10}$	300-W Xe lamp	H_2O, MeOH	~1.64	206	Fang, W.-H., et. al. *J. Am. Chem. Soc.* **2016**, *138*, 7480
1	**300-W Xe lamp**	**H_2O, MeOH**	**0.5**	**180**	***this study***
$Ti_6O_4(Cec)_4(O^iPr)_{12}$	300-W Xe lamp	H_2O, MeOH	~0.33	109	Gao, M.-Y., et. al. *Dalton Trans.* **2017**, *46*, 10630
$[Ti_{28}O_{48}(PhO)_{14}(phn)_{14}]Cl_2$	300-W Xe lamp	H_2O, TEOA	~0.66	~100	Narayanam, N., et. al. *Chem. Commun.* **2017**, *53*, 8078
$Ti_6O_2(pp)_4(PhO)_6(O^iPr)_6$	300-W Xe lamp	H_2O, TEOA	~0.66	~77	Narayanam, N., et. al. *Chem. Commun.* **2017**, *53*, 8078
$H_2[Ti_{18}O_{25}(Cec)_{20}(O^iPr)_4]$	300-W Xe lamp	H_2O, MeOH	~0.33	74	Gao, M.-Y., et. al. *Dalton Trans.* **2017**, *46*, 10630
$H_2[Ti_4Cd_2O_4(Pa)_{12}(O^iPr)_2]$	300-W Xe lamp	H_2O, MeOH	~0.66	63	Liu, J., et. al. *Dalton Trans.* **2016**, *45*, 4501
$[Ti_6O_6(pp)_2(PhO)_6(bpy)_6]Cl_2$	300-W Xe lamp	H_2O, TEOA	~0.66	~60	Narayanam, N., et. al. *Chem. Commun.* **2017**, *53*, 8078
$[Ti_4O(PPA)_3(O^iPr)_8]_2[Ti_6O_4(PPA)_2(O^iPr)_{10}](ANA)_2$	300-W Xe lamp	H_2O, MeOH	~0.33	42.8	Gao, M.-Y., et. al. *Cryst. Growth Des.* **2017**, *17*, 3592
2	**300-W Xe lamp**	**H_2O, MeOH**	**0.5**	**23.1**	***this study***
$[Ti_4O(PPA)_3(O^iPr)_8]_2(PIP)$	300-W Xe lamp	H_2O, MeOH	~0.33	~8	Gao, M.-Y., et. al. *Cryst. Growth Des.* **2017**, *17*, 3592
$[Ti_4O(PPA)_3(O^iPr)_8]_2(APZ)$	300-W Xe lamp	H_2O, MeOH	~0.33	~7	Gao, M.-Y., et. al. *Cryst. Growth Des.* **2017**, *17*, 3592
$[Ti_4O(PPA)_3(O^iPr)_8]_2(ADN)$	300-W Xe lamp	H_2O, MeOH	~0.33	~4	Gao, M.-Y., et. al. *Cryst. Growth Des.* **2017**, *17*, 3592
$H_2[Ti_{18}O_{20}(pp)_2(pa)_{16}(O^iPr)_{14}]$	300-W Xe lamp	H_2O, MeOH	~0.66	~3	Fang, W. H., et. al. *Dalton Trans.* **2017**, *46*, 803

O^iPr = isopropoxide; BDC = 1,2-benzenedicarboxylate; Hpa = propionic acid; HPa = pivalic acid; pp = phenyl phosphonate; PhOH = phenol; phn = 1,10-phenanthroline; bpy = 2,20-bipyridyl; PIP = piperazine; AND = adenine; APZ = aminopyrazine; ANA = 2-aminoisonicotinic acid; HCec = cyclohex-3-ene-1-carboxylate; Ac = acetate; LF = 3-fluorosalicylic acid; TEOA = triethanol amine.