Supporting Information For

Triphenylamine derived titanium oxo clusters: an approach to effective organic-inorganic hybrid dyes for photoactive electrodes

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EXPERIMENTAL SECTION

FIGURES

Fig. S1. The XRD patterns of freshly isolated crystalline samples **1**−**3**.

Fig. S2. A top view of compounds **1** (a) and **2** (b) in ball-stick plot. The dye molecules are presented as sticks. (H atoms and methyl groups of the isopropanols are omitted for clarity).

Fig. S3. The bridge modes of two Ti3 subunits in the Ti_6 oxo-clusters, (a) **1** and **2**, (b) **3**.

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Fig. S5. ^{1}H NMR spectra of **1** (a), **2** (b) and **3** (c) in $CDCl_3$. Inserted is the enlarged peaks of the tert-H on the iso-propanol groups.

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Fig. S10. (a) Solid-state absorption spectra of **1** and **3**. (b) Absorption spectra of **1**−**3** in a mixed solution of CH_2Cl_2-HO^iPr (3.0×10^{-3} in 4:1 volum ratio).

TABLE

Table S1 Crystal data and structural refinement parameters for **1–3.**

EXPERIMENTAL SECTION

Reagents and general instruments

All analytically pure reagents were purchased commercially and used without further purification. Compound $[Ti_6O_3(MAL)_2(O^iPr)_{14}]$ abbreviated as Ti6-MAL was prepared as that reported previously.[1] Elemental analyses of C, H and N were performed using a VARIDEL III elemental analyzer. The FT-IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. The Raman spectra were recorded on a HORIBA HR-800 spectrometer with 633 nm laser source. Solid-state room-temperature optical diffuse reflectance spectra of the micro crystal samples were obtained with a Shimadzu UV-2600 spectrometer. ^1H NMR spectra were recorded on an AVANCEIII HD-400 spectrometer. Room-temperature X-ray diffraction data were collected on a D/MAX-3C diffractometer using a Cu tube source (Cu-Kα, λ = 1.5406 Å). X-ray photoelectron spectroscopic (XPS) measurements were recorded on an ESCALAB 250Xi spectrometer. The morphologies of the electrodes were recorded with a JSM-5600LV scanning electron microscope (SEM). Cyclic voltammetry (CV) experiments were performed in CH_2Cl_2 with 0.10 mol·L^{-1} tetrabutylamonium perchloride on a CHI600 electrochemistry workstation in a three-electrode system.

Synthesis of compounds

$[Ti_6O_3(L1)_2(O^iPr)_{14}]\cdot HO^iPr$ (1). Analytically pure $Ti(O^iPr)_4$ (0.05 mL, 0.17 mmol), 4-(diphenylamino)benzaldehyde (7.0 mg, 0.026 mmol), and malonic acid (5 mg, 0.05 mmol) were mixed in 0.2 mL of anhydrous isopropanol. The mixture was sealed in a thick glass tube and quickly degassed by argon. The sealed tube was heated at 60 °C for 6 days and then cooled to room temperature to yield reddish yellow crystals (25 % yield based on TPA). The crystals were rinsed with isopropanol, dried in vacuum and were preserved in a desiccator. Anal. Calcd. for $C_{89}H_{136}N_2O_{26}Ti_6$ (MW 1937.23): C, 55.18; H, 7.08; N, 1.45. Found: C, 55.36; H, 6.87; N, 1.38. Selected IR data (KBr,cm^{-1}): 2970(w), 1632(w), 1575(m), 1526(w), 1506(m), 1444(w), 1378(s), 1324(s), 1282(m), 1119(s), 979(s), 845(s), 775(w), 753(w), 693(s), 622(w).

$[Ti_6O_3(L2)_2(O^iPr)_{14}]$ (2). Analytically pure $Ti(O^iPr)_4$ (0.2 mL, 0.66 mmol), 4-(diethylamino)benzaldehyde (17.6 mg, 0.099 mmol), and malonic acid (10.4 mg, 0.10 mmol) were mixed in 0.1 mL of anhydrous dimethylformamide (DMF). The mixture was sealed in a thick glass tube and quickly degassed by argon. The sealed tube was heated at 60 °C for 5 days and then cooled to room temperature to yield reddish yellow crystals (38 % yield based on DEPA). The crystals were rinsed with isopropanol, dried in vacuum and were preserved in a desiccator. Anal. calcd for $C_{70}H_{128}N_2O_{25}Ti_6$ (MW 1685.06): C, 49.90; H, 7.66; N, 1.66. Found: C, 49.89; H, 7.48; N, 1.78. Selected IR data (KBr,cm^{-1}): 2970(w), 1601(m), 1558(m), 1503(m), 1445(w), 1372(s), 1263(w), 1194(m), 1118(s), 983(s), 947(s), 841(m), 772(m), 681(m), 619(w).

[Ti_6O_4(L1')$_2$(BDC)$_2$(O^{i}Pr)$_{10}$] (**3**). Compound **3** was prepared similar to those of **1**, except added *o*-DBC. Analytically pure Ti(O^{i}Pr)$_4$ (0.05 mL, 0.17 mmol), 4-(diphenylamino)benzaldehyde (7.0 mg, 0.026 mmol), malonic acid (5 mg, 0.048 mmol) and *o*-phthalic acid (4.5 mg, 0.027 mmol) were mixed in 0.2 mL of anhydrous isopropanol. The sealed tube was heated at 80 ^oC for 6 days and then cooled to room temperature to yield yellow crystals (30 % yield based on TPA). Anal. calcd for $C_{96}H_{122}N_2O_{30}Ti_6$ (MW 2071.30): C, 55.67; H, 5.94; N, 1.35. Found: C, 55.89; H, 6.10; N, 1.51. Selected IR data (KBr,cm^{-1}): 2970(w), 1702(w), 1549(s), 1485(m), 1422(s), 1322(w), 1263(m), 1193(m), 1110(s), 982(s), 842(w), 753(m), 696(m), 651(w), 615(w).

X-ray crystallographic analysis

The single crystal measurements of **1** was carried out on a Bruker APEX-II CCD diffractometer, and of **2** and **3** were carried out on a Rigaku Saturn CCD diffractometer, respectively, with graphite monochromated MoKα (λ□ = 0.71075 Å) radiation. The structures were solved by direct methods using SHELXS-2014/2016 and the refinements were performed against F^2 using SHELXL-2014/2016. All the non-hydrogen atoms are refined anisotropically. The hydrogen atoms of **1** and **3** are positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal data, collection parameters, and refinement results can be found in Table S1.

Film preparation and photocurrent measurement

The porous TiO_2/ITO electrode was prepared by spin coating then blading method according to the literature[2] using an ITO glass (8 ohm per square). The dye sensitized TiO_2 electrodes for photocurrent measurements were prepared by soaking the TiO_2/ITO electrode in solution of the compounds (5×10^{-4} mol L^{-1}, based on a single dye unit, in a mixture of dichloromethane and isopropanol with volume ratio 4:1) for 20 h and then the electrodes were rinsed with the same solvent and dried in air. The light source was a 150-W high pressure xenon lamp, which was positioned 20 cm from the surface of the photoelectrode. The photoelectrochemical measurements were performed on a CHI660 electrochemistry workstation in a two-electrode cell. The dye sensitized TiO_2 electrodes as the anode electrode and a thermally platinized ITO plate as the cathode electrode. The effective irradiation area was about 0.5 cm^2. An I_2/I_3^- solution (0.05 mol·L^{-1} I_2, 0.1 mol·L^{-1} LiI, 0.6 mol·L^{-1} TBAI in acetonitrile) was used as the electrolyte.

1. Luo, W.; Ge, G. *J. Clust. Sci.* **2016**, *27*, 635–643.

2. Guo, Y.; Hou, J.-L.; Luo, W.; Li, Z.-Q.; Zou, D.-H.; Zhu, Q.-Y.; Dai, J. *J. Mater. Chem. A* **2017**, *5*, 18270–18275.

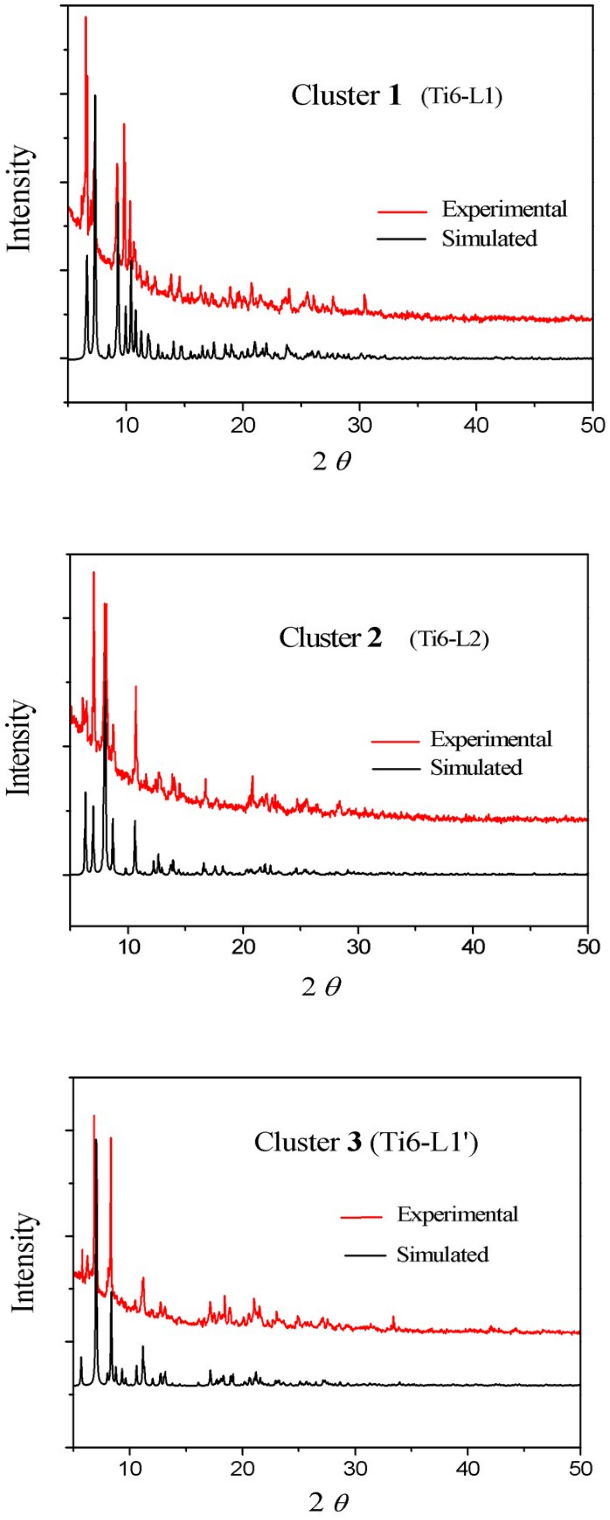

Fig. S1. The XRD patterns of freshly isolated crystalline samples **1**−**3**.

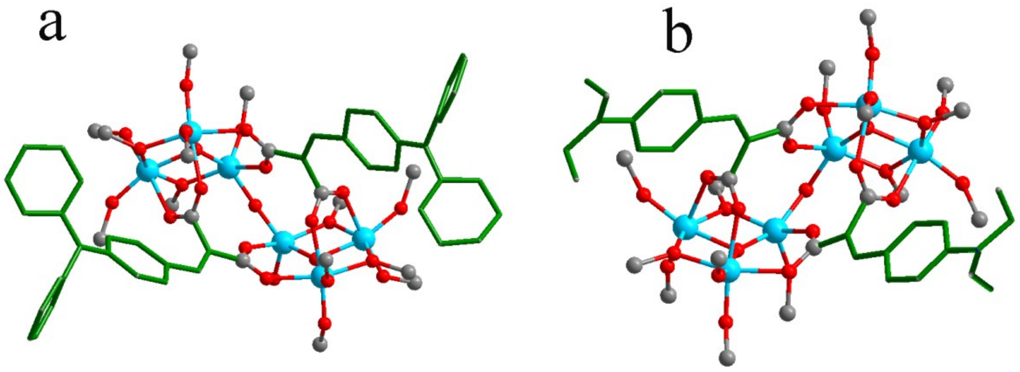

Fig. S2. A top view of compounds **1** (a) and **2** (b) in ball-stick plot. The dye molecules are presented as sticks. (H atoms and methyl groups of the isopropanols are omitted for clarity).

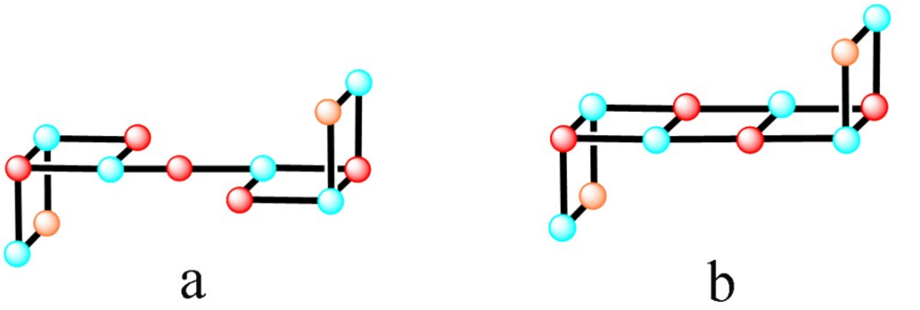

Fig. S3. The bridge modes of two Ti3 subunits in the Ti_6 oxo-clusters, (a) **1** and **2**, (b) **3**.

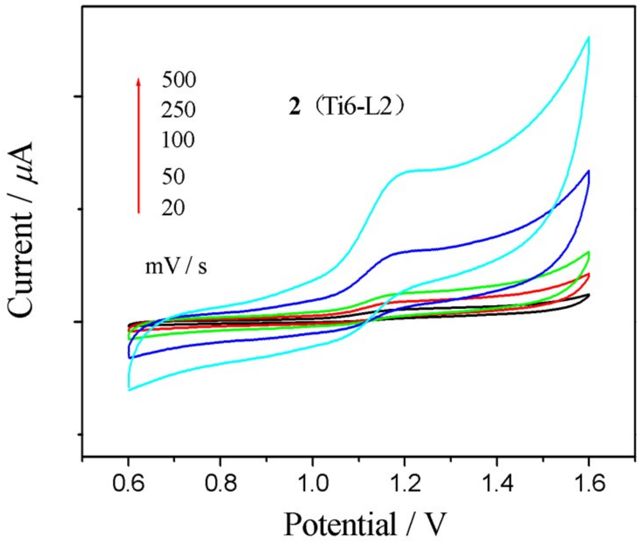

Fig. S4. Cyclic voltammogram of **2** in CH_2Cl_2 ($TBAClO_4$ 0.1 mmol·L^{-1}) at different scan rates.

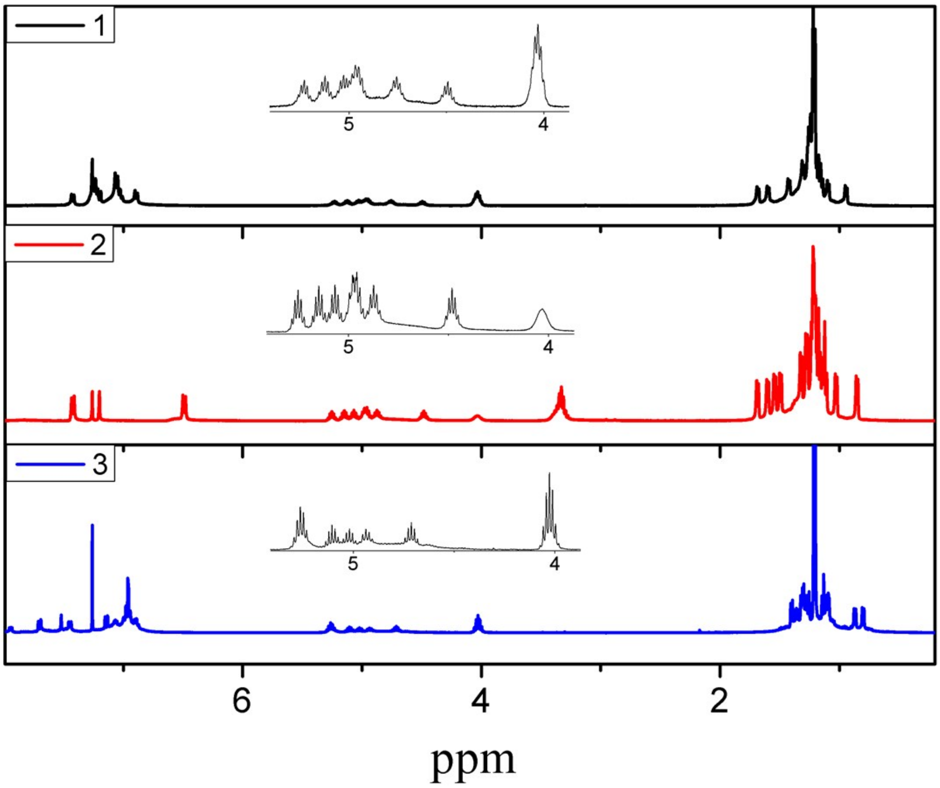

Fig. S5. ^1H NMR spectra of **1** (a), **2** (b) and **3** (c) in $CDCl_3$. Inserted is the enlarged peaks of the tert-H on the iso-propanol groups, where the number is just that of the asymmetric O^{i}Pr groups in the clusters (7 for both **1** and **2**, and 6 for **3**).

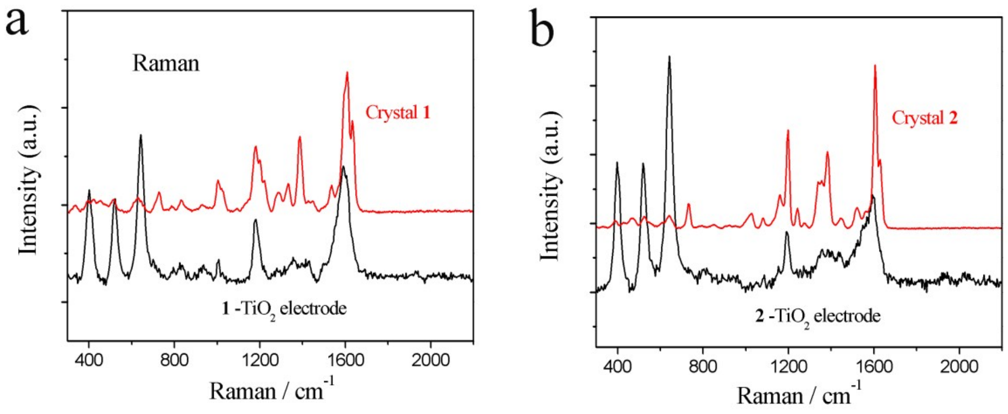

Fig. S6. (a) Raman spectra of crystal **1** and **1** treated TiO_2 electrode. (b) Raman spectra of crystal **2** and **2** treated TiO_2 electrode. The Raman spectra showed a signal superposition of TiO_2 substrate and the clusters except that the peaks of the C-H and Ti-O-C vibrations of TiOR moiety at 1385 and 1015 cm^{-1} are weakened due to the de-alkoxy and condensation of the alkoxyl moieties. The results indicated that the clusters were maintained and only the isopropyl groups were lost when the clusters were condensed on the TiO_2 surface.

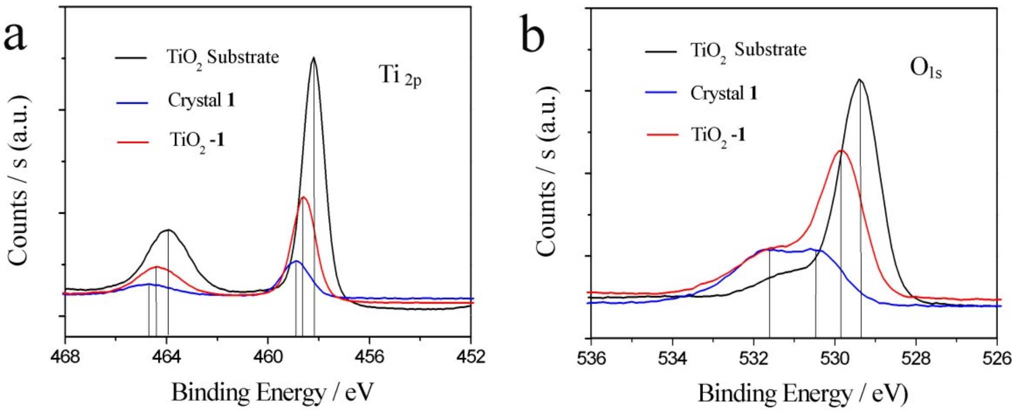

Fig. S7. XPS spectra of crystal **1**, **1** treated TiO_2 electrode and blank TiO_2 electrodes, (a) Ti2p peaks and (b) O1s peaks. Compared with Ti2p peaks of TiO_2 substrate (458.20 eV), those of **1-**TiO_2 electrode and crystal **1** are shift to high binding energy (458.60 and 458.90 eV) due to the ligand coordination. The main O1s peak of TiO_2 substrate is 529.8 eV and the weak shoulder peak at 531.7 eV is assigned to the surface hydroxide group. For crystal **1**, two peaks appear at 531.6 an 530.4 eV assigned to carboxyl O and cluster O atoms. For the **1** treated TiO_2 electrode, the carboxyl peak evidences that the dye molecules are firmly anchored to the electrode, and the peak at 530.4 eV should be the oxygen of the condensed cluster core that fused with the TiO_2 substrate.

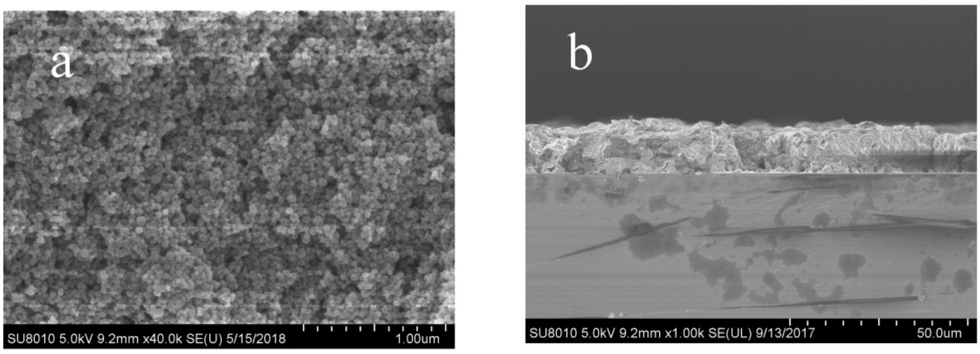

Fig. S8. SEM morphology of the TiO_2 electrode and the cross section.

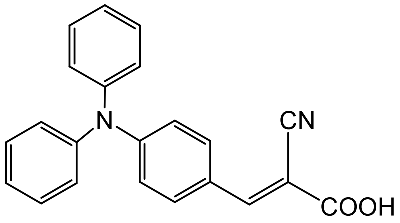

Fig. S9. Molecular structure of dye L0, 2-cyano-3-(4-(diphenylamino)phenyl) acrylic acid.

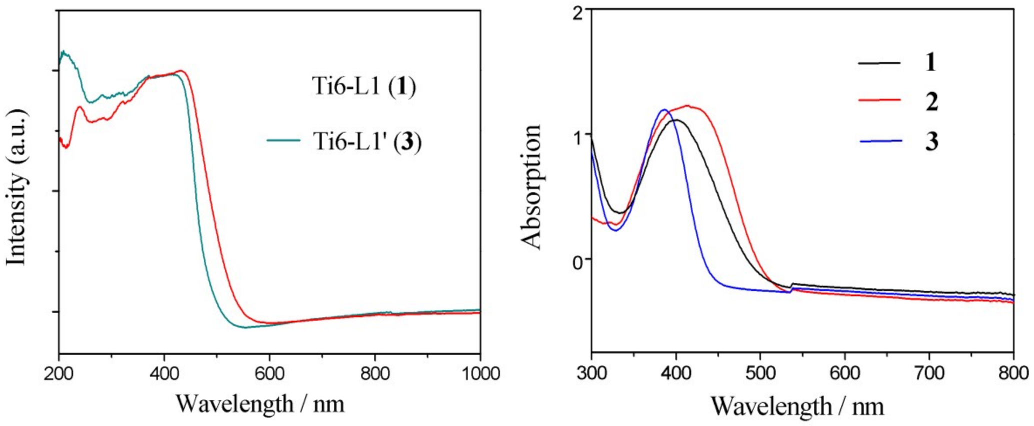

Fig. S10. (a) Solid-state absorption spectra of **1** and **3**. (b) Absorption spectra of **1**–**3** in a mixed solution of CH_2Cl_2-HO^{i}Pr (3.0 × 10^{-3} in 4:1 volum ratio).

Table S1 Crystal data and structural refinement parameters for **1-3**

	1	**2**	**3**
formula	$C_{89}H_{136}N_2O_{26}Ti_6$	$C_{70}H_{128}N_2O_{25}Ti_6$	$C_{96}H_{122}N_2O_{30}Ti_6$
fw	1935.23	1685.06	2071.30
cryst size (mm^3)	0.35 × 0.20 × 0.15	0.50 × 0.40 × 0.30	0.30 × 0.20 × 0.15
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$I2/a$	$P2_1/c$
a (Å)	26.6207(9)	26.227(5)	15.5612(11)
b (Å)	20.7575(8)	25.660(5)	15.6396(11)
c (Å)	17.7843(7)	29.043(14)	21.2233(15)
α (deg)	90	90	90
β (deg)	90.4930(10)	105.67(3)	95.892(4)
γ (deg)	90	90	90
V (Å^3)	9826.9(6)	18819(11)	5137.8(6)
Z	4	8	2
ρ_{calcd} (g cm^{-3})	1.236	1.098	1.271
F(000)	4088	6128	1960
μ (mm^{-1})	0.535	0.545	0.517
T (K)	120(2)	120(2)	120(2)
reflns collected	50968	54439	64886
unique reflns	18542	16332	11723
observed reflns	11772	9281	7027
no. params	1089	907	632
GOF on F^2	1.057	1.180	1.035
$R_1[I>2\sigma(I)]$	0.0875	0.1005	0.0732
wR_2	0.1892	0.1861	0.1663