

Electronic Supporting Information For
Cluster-to-cluster charge-transfer in a compound with co-crystallized
a dye anchored Ti₆ cluster and a classical Ti₁₂ cluster

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Experimental Section

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Experimental Section

Reagents and general instrument

All analytically pure reagents were purchased commercially and used without further purification. Compound $[\text{Ti}_6\text{O}_4(\text{L}^1)_2(\text{BDC})_2(\text{O}^i\text{Pr})_{10}]$ abbreviated as $\text{Ti}_6\text{-L}^1\text{-BDC}$ 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. ¹H NMR spectra were recorded on an AVANCE III HD-400 spectrometer. Solid-state room-temperature optical diffuse reflectance spectra of the micro crystal samples were obtained with a Shimadzu UV-2600 spectrometer. Room-temperature X-ray diffraction data were collected on a D/MAX-3C diffractometer using a Cu tube source (Cu-K α , $\lambda = 1.5406 \text{ \AA}$).

Synthesis of compound

$[\text{Ti}_6\text{O}_2(\text{L}^1)_2(\text{Cat})_2(\text{O}^i\text{Pr})_{12}] \cdot [\text{Ti}_{12}\text{O}_{16}(\text{O}^i\text{Pr})_{16}] \cdot 2\text{HO}^i\text{Pr}$ (**1**). Analytically pure $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.05 mL, 0.17 mmol), 4-(diphenylamino)benzaldehyde (7.0 mg, 0.026 mmol), malonic acid (5.0 mg, 0.048 mmol) and catechol (3.0 mg, 0.027mmol) were mixed in 0.4 mL of anhydrous isopropanol. The mixture was placed in a thick Pyrex tube and quickly degassed by argon. The sealed tube was heated at 80 °C for 6 days and then cooled to room temperature to yield golden yellow crystals (32 % yield based on TPA). The crystals are rinsed with isopropanol and dried. The compound was preserved under a cool and dry environment. Anal. Calcd. for $\text{C}_{146}\text{H}_{250}\text{N}_2\text{O}_{60}\text{Ti}_{18}$ (MW 3855.13): C, 45.49; H, 6.54; N, 0.73. Found: C, 45.21; H, 6.39; N, 0.58. Selected IR data (KBr, cm^{-1}): 2972(m), 1588(w), 1548(m), 1480(w), 1400(m), 1325(m), 1124(vs), 1008(s), 946(m), 856(w), 736(m), 678(m), 613(w).

X-ray crystallographic analysis

The single crystal measurement of **1** was carried out on a Bruker APEX-II CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71075 \text{ \AA}$) radiation. The structure was solved by direct methods using SHELXS-2016 and the refinement was performed against F^2 using SHELXL-2016.² All the non-hydrogen atoms are refined anisotropically. Relevant crystal data, collection parameters, and refinement results can be found in Table S1.

Theoretical calculations

Density functional theory calculations were carried out using GAUSSIAN 09 program package at the B3LYP level.³ The basis set used for C, N, O and H atoms was 6-31G while effective core potentials with a LanL2DZ basis set was employed for Ti atoms. The crystal structure was used as the initial structures and the O^iPr groups were replaced by OH groups to cut the computational cost with no significant change in the electronic properties.

Electrode preparation and photocurrent measurement

The porous TiO_2/ITO electrode was prepared by spin coating then blading method 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 the solution of compound **1** ($5 \times 10^{-4} \text{ mol L}^{-1}$, based on a single dye unit, in a mixture of dichloromethane and isopropanol with volume ratio 1:1) 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 CHI660E electrochemistry workstation in a two-electrode cell for photocurrent measurements. The **1**

sensitized TiO₂ electrode was used as the anode electrode and a thermally platinized ITO plate as the cathode electrode. The effective irradiation area was about 0.5 cm². An I₂/I₃⁻ solution (0.05 mol·L⁻¹ I₂, 0.1 mol·L⁻¹ LiI, 0.6 mol·L⁻¹ TBAI in acetonitrile) was used as the electrolyte. For photoelectrochemical sensing to saccharides, a three-electrode system was conducted, including a **1** modified TiO₂ working electrode, a Pt plate auxiliary electrode and a saturated calomel reference electrode (SCE). An aqueous solution of Na₂SO₄ (0.1 mmol·L⁻¹) was used as the medium.

- 1 D.-H. Zou, L.-N. Cui, P.-Y. Liu, S. Yang, Q.-Y. Zhu and J. Dai, *Chem. Commun.*, 2018, **54**, 9933–9936.
- 2 (a) G. M. Sheldrick, *SHELXS-2016, Program for structure solution*; Universität of Göttingen: Germany, 2016. (b) Sheldrick, G. M. *SHELXL-2016, Program for structure refinement*; Universität of Göttingen: Göttingen, Germany, 2016. (c) G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Cryst.*, 2015, **C71**, 3–8.
- 3 (a) *Gaussian 09, Revision A.1*, Gaussian Inc., Wallingford, CT, **2009**. (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270–283.

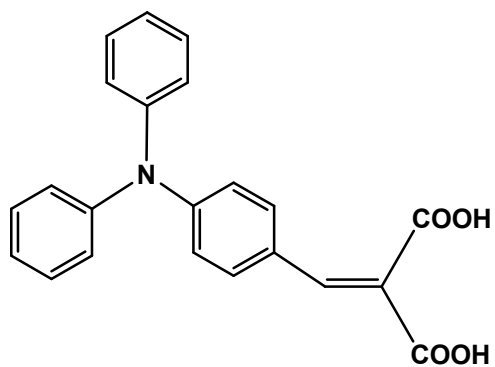


Fig. S1. Structure of the TPA-dye.

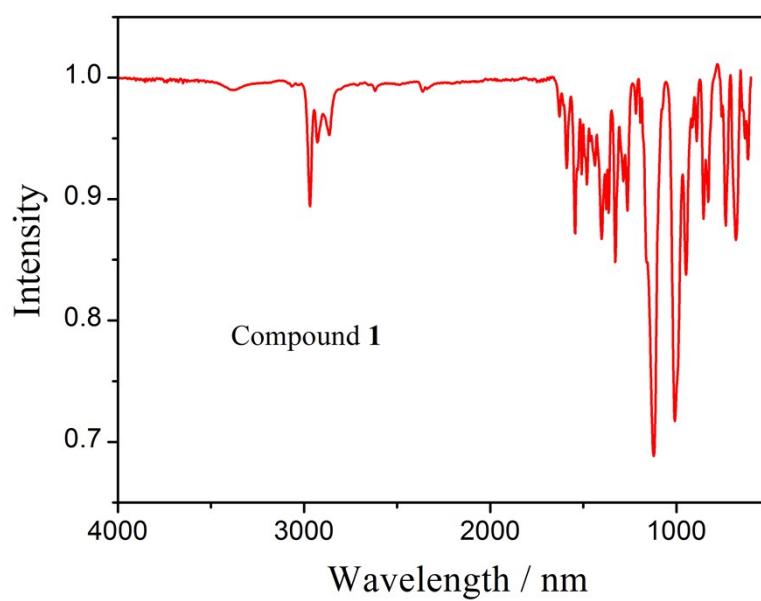


Fig. S2. IR spectra of compound 1.

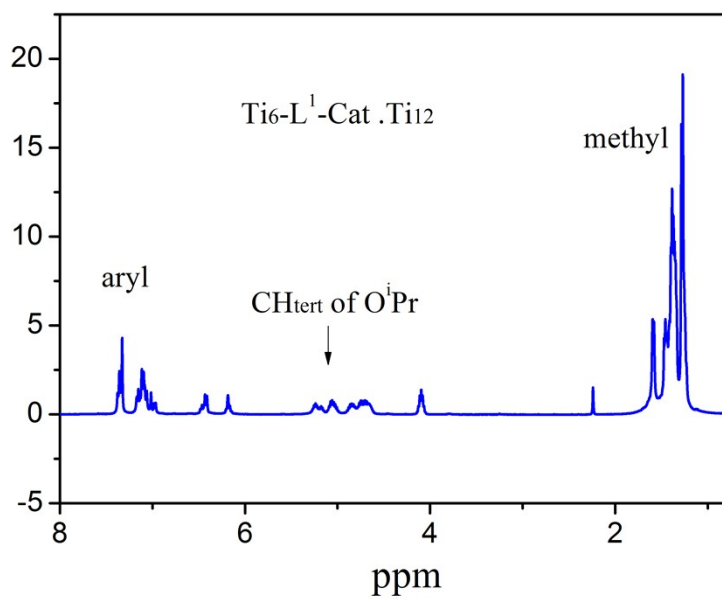


Fig. S3. ^1H NMR spectra of compound 1.

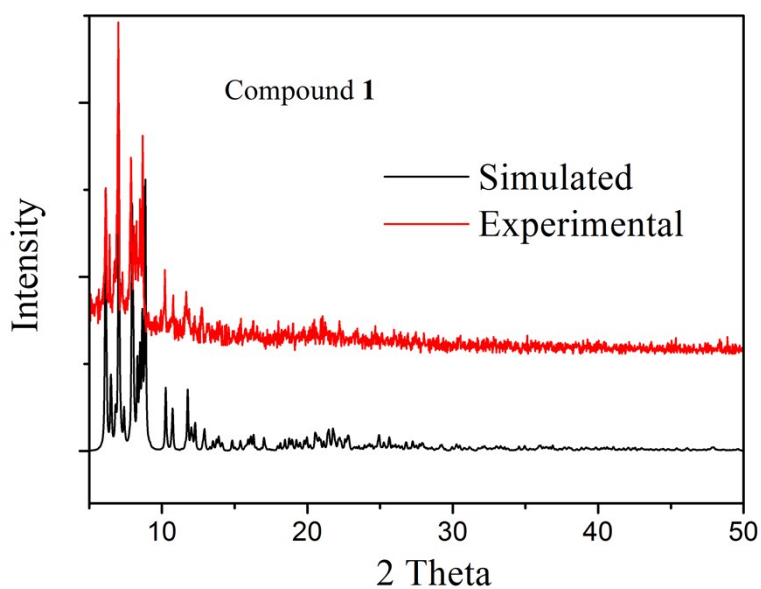


Fig. S4. The XRD patterns of crystalline sample 1.

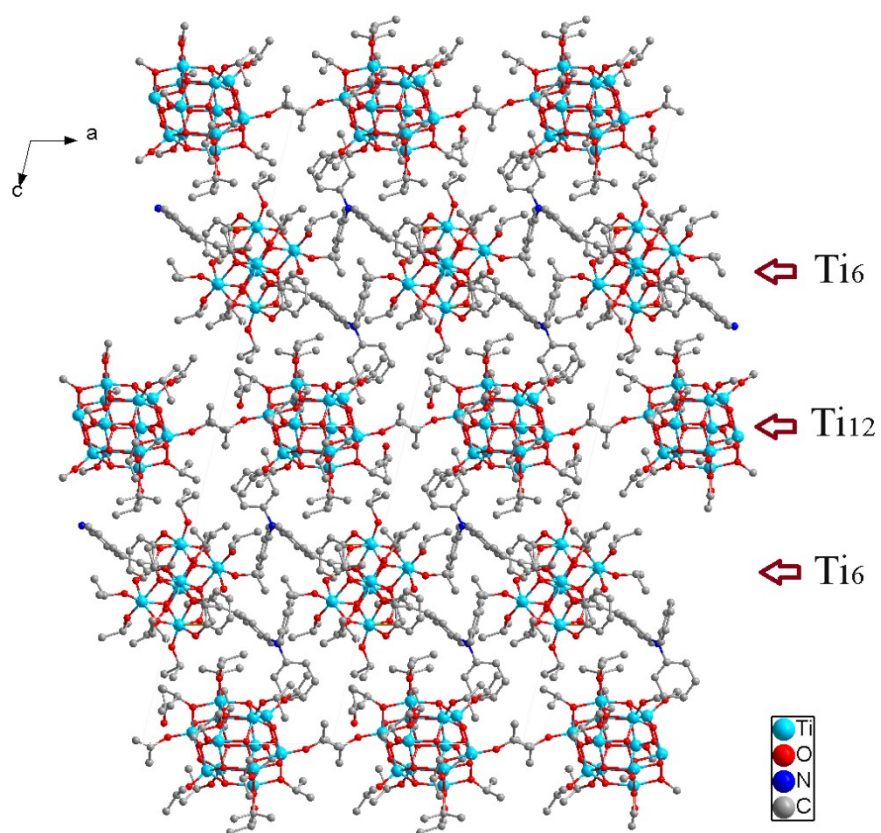


Fig. S5. Molecular packing of 1.

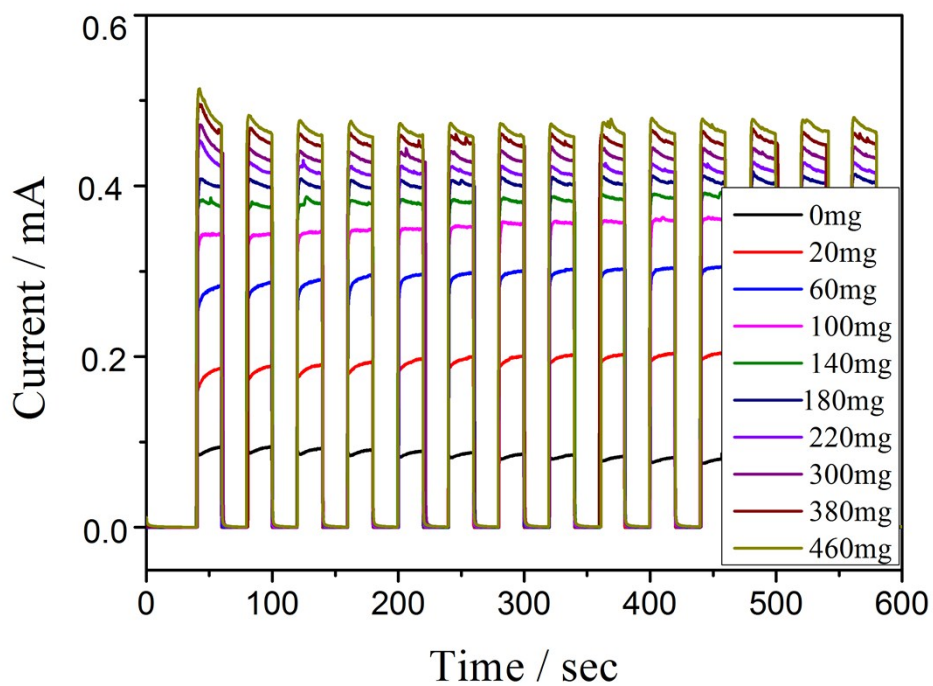


Fig. S6. Photocurrents of **1** treated electrode with different amount of fructose (three electrode system with a Pt auxiliary electrode and an SEC reference electrode in a water solution of $0.1 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$).

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

	1
formula	C ₁₄₆ H ₂₅₀ N ₂ O ₆₀ Ti ₁₈
fw	3855.13
cryst size (mm ³)	0.10 × 0.20 × 0.30
cryst syst	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.1466(18)
<i>b</i> (Å)	15.6568(19)
<i>c</i> (Å)	23.301(3)
α (deg)	99.803(3)
β (deg)	99.129(4)
γ (deg)	108.462(3)
<i>V</i> (Å ³)	4697.5(10)
<i>Z</i>	1
ρ_{calcd} (g cm ⁻³)	1.363
<i>F</i> (000)	2016
μ (mm ⁻¹)	0.794
<i>T</i> (K)	120(2)
reflns collected	59771
unique reflns	17091
observed reflns	10634
no. params	1084
GOF on <i>F</i> ²	1.028
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0571
<i>wR</i> ₂	0.1658