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**Supporting Information For**

**Dye Molecule Bonded Titanium Alkoxide: A Possible New Type  
of Dyes for Sensitized Solar Cells**

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**1. Experimental**

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**Fig. S5.** (a) The I-V plot of **1**. (b) Band energies of the dye sensitized TiO films.

**Fig. S6.** Absorption spectra of the films, blank mesoporous TiO<sub>2</sub> film, PAR-TiO<sub>2</sub> film and compound **1**-TiO<sub>2</sub> film.

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**3. Table**

**Table S1** Crystal Data and Structural Refinement Parameters for **1**.

## EXPERIMENTAL

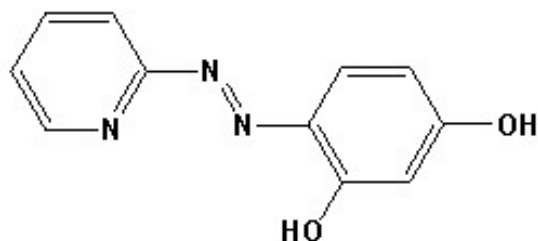
**General remarks.** Dye PAR (PAR = 4-(2-pyridylazo)resorcinol) and all analytically pure reagents were purchased commercially and used without further purification. Dye L0 was synthesized as reported (L0 = 2-cyano-3-(4-(diphenylamino)phenyl) acrylic acid, *Chem. Mater.* 2004, 16, 1806–1812). The FT-IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H and N were performed using a VARIDEL III elemental analyzer. Solid-state room-temperature optical diffuse reflectance spectra of the micro crystal samples and absorption spectra of the films were obtained with a Shimadzu UV-3150 spectrometer. The absorption ( $\alpha/S$ ) data were calculated from the reflectance using the Kubelka-Munk function,  $\alpha/S = (1-R)^2/2R$  (W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966) where  $R$  is the reflectance at a given energy,  $\alpha$  is the absorption, and  $S$  is the scattering coefficient. Room-temperature X-ray diffraction data were collected on a D/MAX-3C diffractometer using a Cu tube source (Cu-K $\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ). The morphologies of the resulting films were observed with a JSM-5600LV scanning electron microscope (SEM). Thermoanalytical measurement was performed using a SDT 2960 microanalyzer and the sample was heated under a nitrogen stream of  $100 \text{ ml min}^{-1}$  with a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$ .

### Synthesis of the clusters.

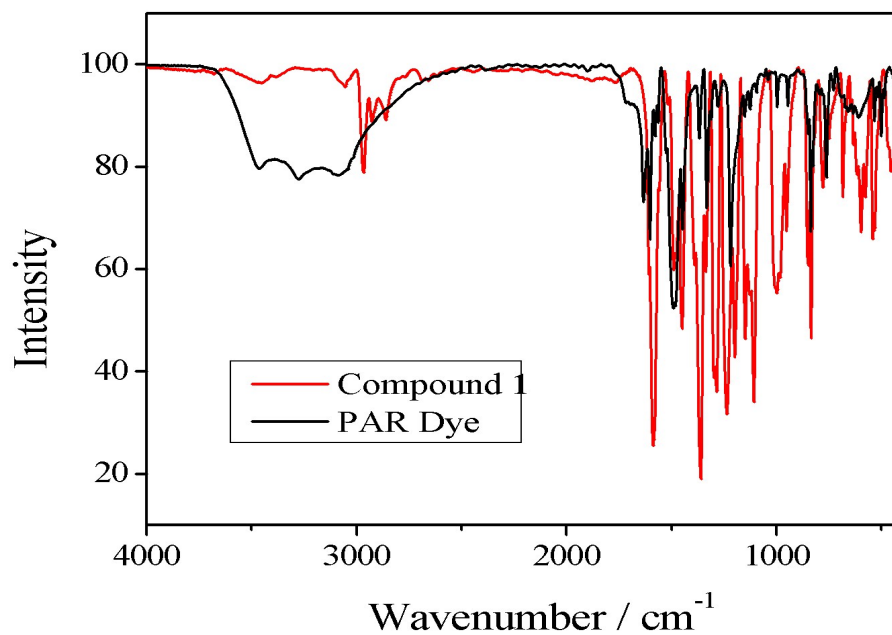
**[Ti<sub>4</sub>(O<sup>i</sup>Pr)<sub>8</sub>(PAR)<sub>4</sub>]·H<sub>2</sub>O (1).** Analytically pure Ti(O<sup>i</sup>Pr)<sub>4</sub> (0.1 mL, 0.26 mmol), and 4-(2-pyridylazo)resorcinol (5.4 mg, 0.0025 mmol) were mixed in 0.3 mL anhydrous isopropanol. The mixture was sealed in a thick Pyrex tube (0.7 cm dia., 18 cm length) and quickly degassed by argon. The sealed tube is heated at  $60 \text{ }^\circ\text{C}$  for 7 days, and then cooled to room temperature to yield sparking golden-black crystals (12.5 % yield based on PAR). The crystals are rinsed with isopropanol, and dried. The compound is preserved under sealed and dry environment. Anal. Calcd for C<sub>68</sub>H<sub>86</sub>N<sub>12</sub>O<sub>17</sub>Ti<sub>4</sub> (MW1535.02): C, 53.21; H, 5.65; N, 10.95. Found: C, 53.89; H, 5.71; N, 11.98. Important IR data (KBr, cm<sup>-1</sup>): 2965(w), 2865(w), 1606(w), 1590(vs), 1489(m), 1451(m), 1360(vs), 1285(s), 1235(vs), 1198(s), 1148(m), 1105(s), 1001(s,b), 833(m), 778(w), 680(w), 596(w,b), 538(w).

**X-ray crystallographic study.** The measurements were carried out on a Rigaku Mercury CCD diffractometer at low temperature with graphite monochromated MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at 293(2) K. X-ray crystallographic data were collected and processed using CrystalClear (Rigaku 2000). The structure were solved by direct methods using SHELXS-2014 and the refinement was performed against  $F^2$  using SHELXL-2014. All the non-hydrogen atoms are refined anisotropically. The hydrogen atoms are positioned with idealized geometry and refined with fixed isotropic displacement parameters.

**Film preparation and photocurrent measurement.** Substrate film of TiO<sub>2</sub> was prepared by solution coating method. The TiO<sub>2</sub> gel solution was prepared by adding 0.15 mL 37% HCl to a mixture of 1.0 mL Ti(O<sup>i</sup>Pr)<sub>4</sub> and 14.5 mL ethanol. The new prepared gel was spin-coated on a pre-cleaned ITO substrate (100 Ω/□) at 2000 rpm/s for 30 s and then the substrate was annealed at 500 °C for one hour. This procedure yielded uniform thin layered TiO<sub>2</sub> substrate (150 nm in thickness based on SEM) for photocurrent measurements. The dye sensitized films were prepared by solution coating method on the TiO<sub>2</sub>/ITO electrode at 2000 rpm/s for 30 s. All the coating solution concentrations used in a parallel experiment were carefully calculated to be sure that the same molar quantities of Ti, dye or both are contained. A 150-W high pressure xenon lamp, positioned 20 cm far from the surface of the ITO electrode, was employed as a light source. The photocurrent experiments were performed on a CHI650 electrochemistry workstation in a three-electrode system, the sample coated ITO glass as the working electrode, a Pt plate as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The effective irradiation area was about 1.0 cm<sup>2</sup>. An I<sub>2</sub>/I<sub>3</sub><sup>-</sup> solution (0.05 mmol·L<sup>-1</sup> I<sub>2</sub> in saturated KI) in 100 mL CH<sub>3</sub>CN/HO<sup>i</sup>Pr mixed solvent (4:1 in volum) was used as the medium. The applied potential was constantly 0.1 V. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light.

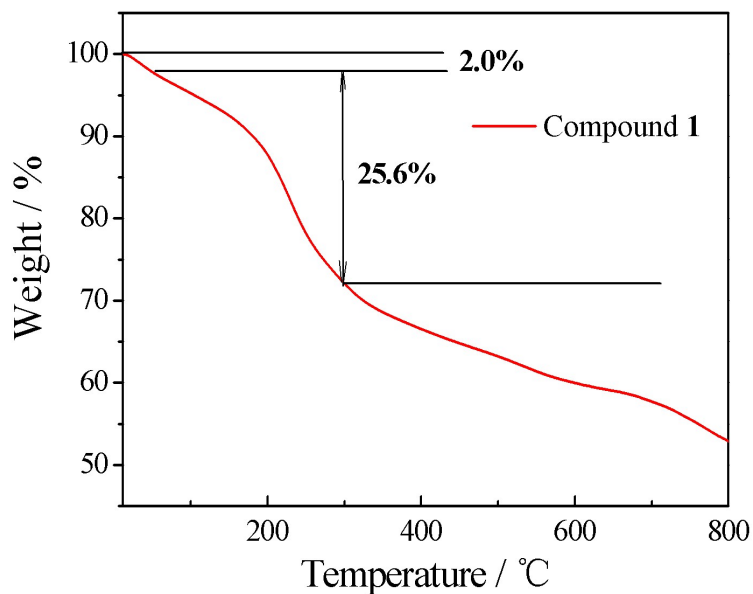


**Fig. S1.** Structure of 4-(2-pyridylazo)resorcinol (PAR).

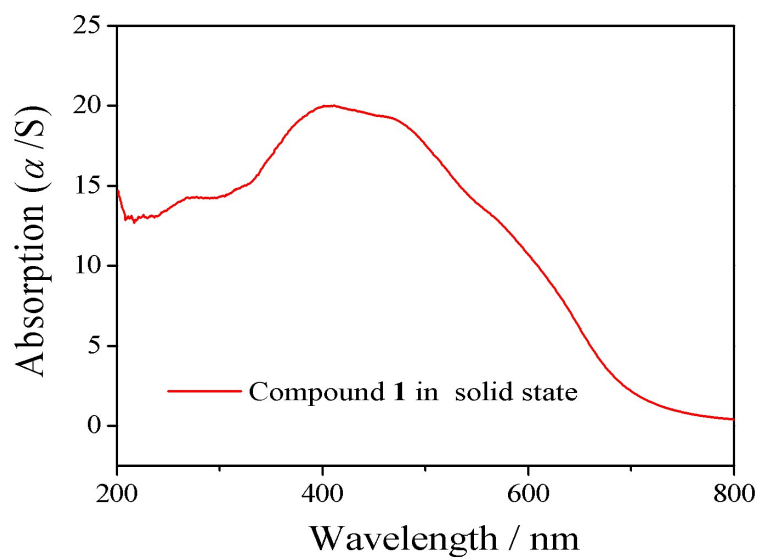


**Fig. S2.** The IR spectra of **1** and dye PAR. The vibration at 1590 cm<sup>-1</sup> indicates the coordinated diazo group of PAR with a red shift. The bands at about 1489 and 833 cm<sup>-1</sup> are assigned to the characteristic bands of the aromatic planes. Isopropoxy groups are detected by the  $\nu_{\text{C-H}}$  (2865–2965 cm<sup>-1</sup> and 1360 cm<sup>-1</sup>), and  $\nu_{\text{Ti-O-C}}$  (about 1001 cm<sup>-1</sup>) vibrations. The bands around 596 cm<sup>-1</sup> are attributed to the Ti–O vibrations.<sup>[\*]</sup>

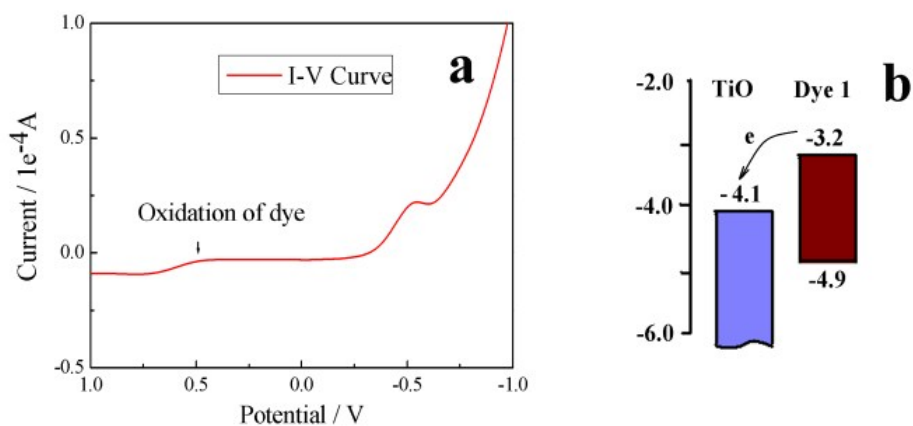
{\*} (a) T. J. Boyle, R. P. Tyner, T. M. Alam, B. L. Scott, J. W. Ziller and B. G. Potter, *J. Am. Chem. Soc.*, 1999, **121**, 12104–12112; (b) P. Piszczek, A. Radtke, T. Muzioł, M. Richert and J. Chojnacki, *Dalton Trans.*, 2012, **41**, 8261–8269; (c) Y.-Y. Wu, W. Luo, Y.-H. Wang, Y.-Y. Pu, X. Zhang, L.-S. You, Q.-Y. Zhu, and J. Dai, *Inorg. Chem.*, 2012, **51**, 8982–8988.



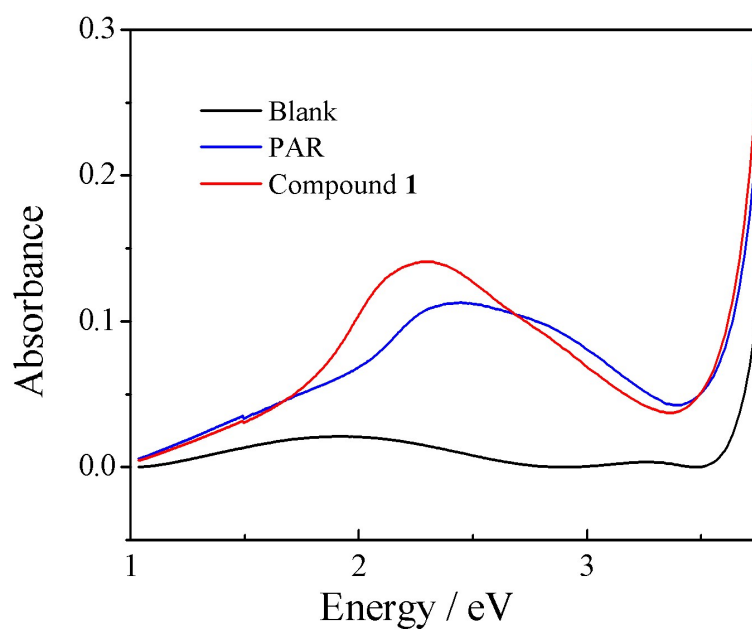
**Fig. S3** Thermal gravimetric analysis shows that compound **1** lost one water molecule below 100 °C (2.0%, calculated 1.2%) and followed by decomposition of the iso-propoxide in the range of 50 to 300 °C to evolution of di-isopropoether (25.6%, calculated 26.8%). The mass loss over 300 °C might be assigned to the incomplete decomposition of the aromatic dye molecule.



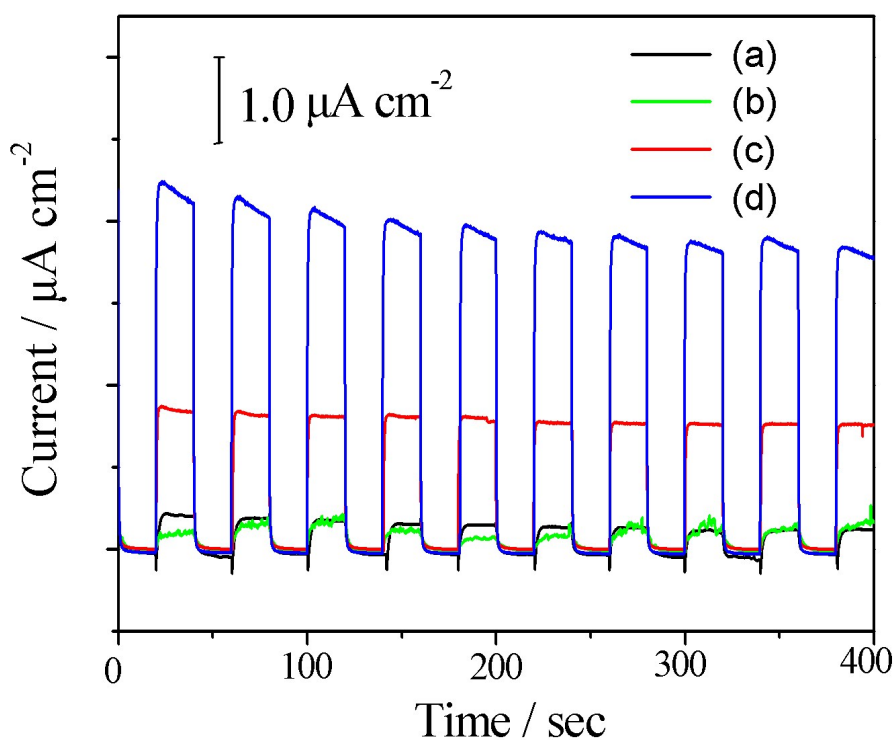
**Fig. S4.** Solid-state UV-vis-NIR absorption spectrum of **1** in nm scale.



**Fig. S5.** (a) The I-V plot of **1**. (The electrode prepared by coating a water solution of **1** on TiO<sub>2</sub>/ITO substrate, three-electrode system, Na<sub>2</sub>SO<sub>4</sub> solution in 100 mL MeCN- HO<sup>i</sup>Pr by 4:1 volume, vs. SCE) (b) Band energies (eV) of the dye sensitized TiO film.



**Fig. S6.** Absorption spectra of the films, blank mesoporous TiO<sub>2</sub> film, PAR-TiO<sub>2</sub> film and compound **1**-TiO<sub>2</sub> film, which shows the increased CT band (2.3 eV, 540 nm) of the film prepared from **1**.



**Fig. S7.** Photocurrent densities of the blank mesoporous  $\text{TiO}_2/\text{ITO}$  electrode (line a, black) and the  $\text{TiO}_2/\text{ITO}$  electrodes dipped with PAR dye (line b, green), compound **1** (line c, red) and L0 dye (line d, blue), respectively. (three-electrode system,  $\text{I}_2/\text{KI}$  solution in 100 mL MeCN- $\text{HO}^i\text{Pr}$  by 4:1 volume).

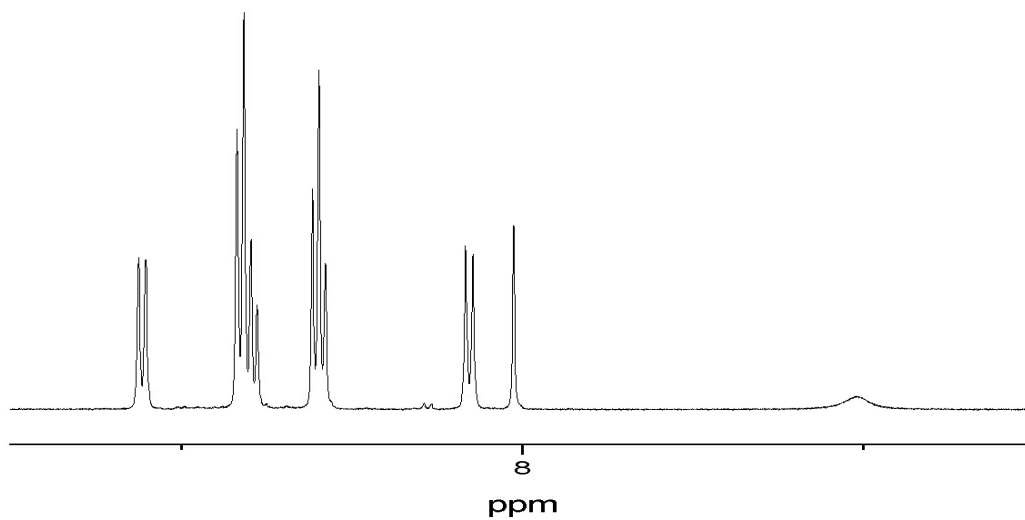
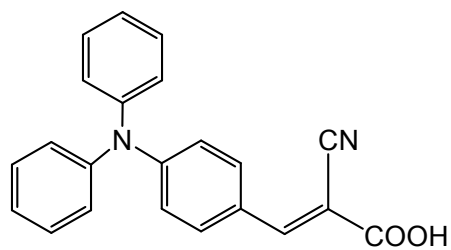
The mesoporous  $\text{TiO}_2/\text{ITO}$  was prepared by rolling a layer of slurry of  $\text{TiO}_2$  nano particles (25 nm) on a pre-coated thin  $\text{TiO}_2$  substrate film that is described in experimental section. Then the substrate was annealed at 500 °C for another one hour. The dye sensitized electrodes were prepared by solution dipping method. <sup>{\*\*}</sup>

<sup>{\*\*}</sup> D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschio, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* 2007, **72**, 9550–9556.

P.S.

Dye L0 [2-cyano-3-(4-(diphenylamino)phenyl) acrylic acid] is a basic arylamine reference dye, which is easily synthesized and has been used in real DSSC studies (*Chem. Soc. Rev.*, 2013, **42**, 3453-3488, *Chem. Mater.* 2004, 16, 1806–1812).

L0 =





**Table S1** Crystal Data and Structural Refinement Parameters for **1**

	<b>1</b>
formula	C <sub>68</sub> H <sub>86</sub> N <sub>12</sub> O <sub>17</sub> Ti <sub>4</sub>
fw	1535.02
cryst size (mm <sup>3</sup> )	0.70 × 0.40 × 0.30
cryst syst	tetragonal
space group	<i>P</i> -42 <sub>1</sub> <i>c</i> (114)
<i>a</i> (Å)	17.367(3)
<i>b</i> (Å)	17.367(3)
<i>c</i> (Å)	13.730(3)
$\alpha$ (deg)	90.00
$\beta$ (deg)	90.00
$\gamma$ (deg)	90.00
<i>V</i> (Å <sup>3</sup> )	4141.2(14)
<i>Z</i>	2
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.208
<i>F</i> (000)	1548
$\mu$ (mm <sup>-1</sup> )	0.437
<i>T</i> (K)	293(2)
reflns collected	12612
unique reflns	3549
observed reflns	2951
no. params	211
GOF on <i>F</i> <sup>2</sup>	1.141
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0807
<i>wR</i> <sub>2</sub>	0.1887