

## Supporting Information

### Axial anchoring designed silicon-porphyrin sensitizers for efficient dye-sensitized solar cells

Jing Liu,<sup>a</sup> Xichuan Yang,<sup>a,\*</sup> and Licheng Sun<sup>a, b,\*</sup>

<sup>a</sup> *State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Linggong Rd. 2, 116024 Dalian, China*

<sup>b</sup> *School of Chemical Science and Engineering, Center of Molecular Devices, Department of Chemistry, KTH Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden*

#### 1. Synthesis of dyes

All reagents and materials were obtained from commercial supplies. Tetrahydrofuran (THF) was purified by using sodium and benzophenone. Methanol (MeOH) was prepared by using CaH<sub>2</sub>.

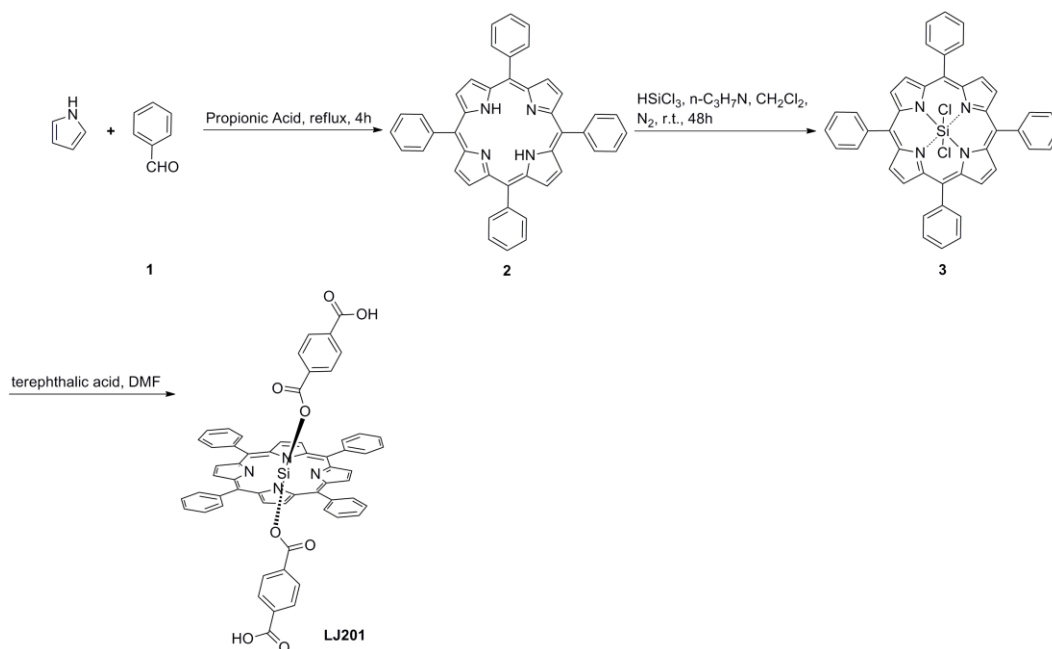
<sup>1</sup>H NMR spectra were carried out by superconducting NMR spectrometer (Varian INOVA 400 NMR). Mass spectroscopy (MS) was used MALDI micro MX (USA) matrix-assisted laser desorption/ionization time of flight mass spectrometry.

#### Synthetic procedure for LJ201

Synthesis of compound **2**: Propionic acid (100 mL) was heated to reflux. Benzaldehyde (**1**, 8.49 g, 0.080 mol) and fresh pyrrole (5.54 mL, 0.080 mol) were added successively. The mixture was stirred for 4 h. After cooling down, the mixture was filtered, and washed by MeOH and hot water. Then purple solid was heated to 45 °C and dried under vacuum for 18 h. Finally, the purple powder was obtained, yielding 10%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 8H), 8.22 (d, J = 7.6 Hz, 8H), 7.81 – 7.71 (m, 12H), – 2.78 (s, 2H). MALDI-TOF (m/z): calcd for C<sub>44</sub>H<sub>30</sub>N<sub>4</sub>, 614.2470; found, [M + H]<sup>+</sup> 615.2888.

Synthesis of compound **3**: The compound **2** (0.25g, 0.41 mol) was added to CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and then HSiCl<sub>3</sub> (1.4 mL) and n-C<sub>3</sub>H<sub>7</sub>N (13 mL) were added at room temperature under nitrogen. The mixture was stirred for 48 h and then evaporated and further purified with column chromatography on Al<sub>2</sub>O<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the eluant to obtain **3**. The purple solid was obtained, yielding 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.91 (d, J = 5.3 Hz, 8H), 8.10 (d, J = 7.6 Hz, 8H), 7.78 – 7.65 (m, 12H). MALDI-TOF

(*m/z*): calcd for C<sub>44</sub>H<sub>28</sub> Cl<sub>2</sub>N<sub>4</sub>Si, 710.1640; found, [M – 2Cl + OH]<sup>+</sup> 657.2109.



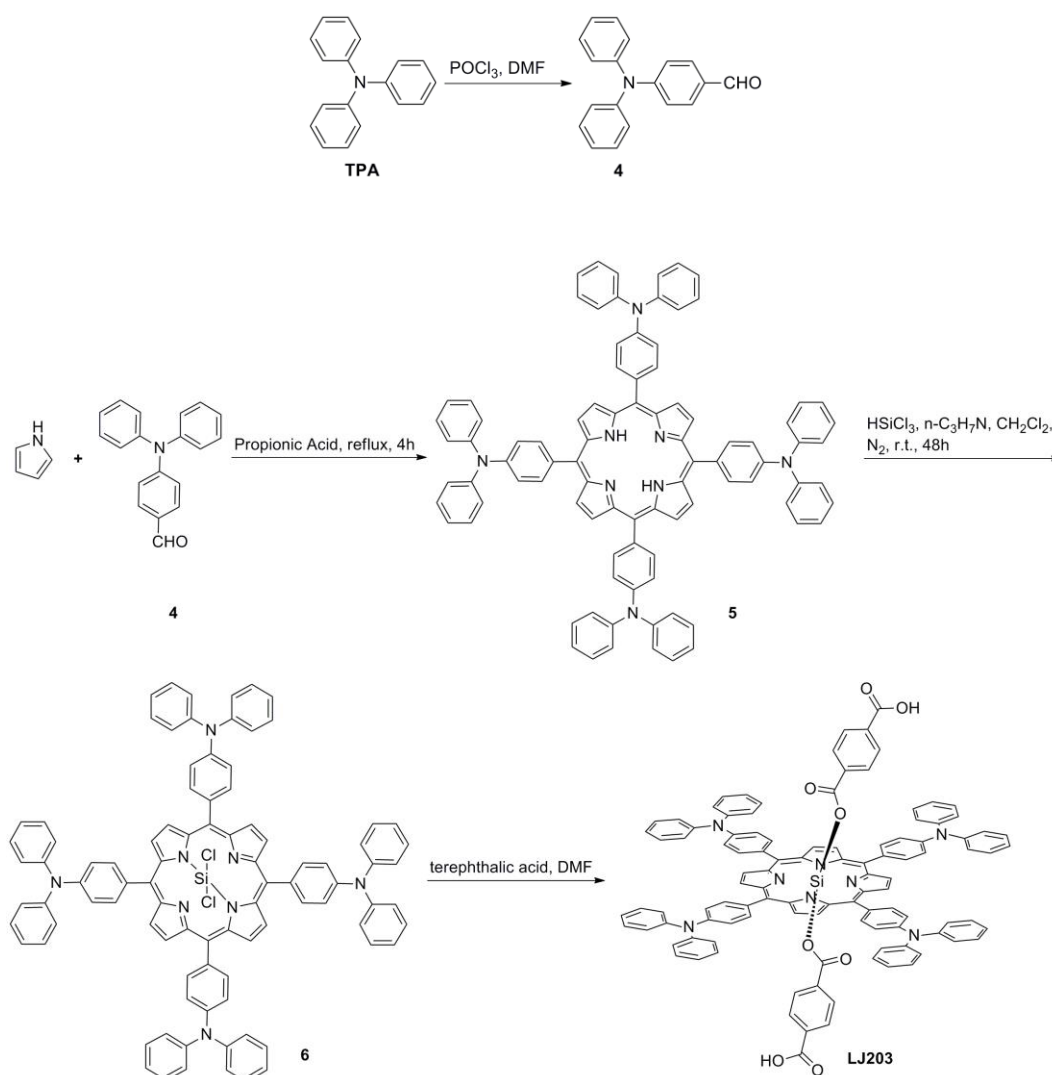
**Scheme S1.** Synthetic procedure for **LJ201**

Synthesis of compound **LJ201**: The method was according to the literature.<sup>1</sup> A solution of the compound **3** (50 mg, 0.070 mmol) in DMF (5 mL) was heated to 160 °C, and terephthalic acid (1.14 g, 6.84 mmol) was added. The mixture was refluxed for 2 h and cooled down. Then the mixture was evaporated and further purified with column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> : MeOH=30 : 1 as the eluant to obtain the product (**LJ201**) as a purple powder. Yield: 14.3 mg (15%). Anal. calc. for C<sub>60</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub>Si: C, 74.21; H, 3.94; N, 5.77. Found: C, 74.68; H, 4.07; N, 5.51. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.92 (t, J = 3.7 Hz, 8H), 8.15 – 7.99 (m, 8H), 7.73 (d, J = 7.5 Hz, 12H), 7.56 – 7.42 (m, 8H). MALDI-TOF (*m/z*): calcd for C<sub>60</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub>Si, 970.2459; found, [M – 2C<sub>8</sub>H<sub>5</sub>O<sub>4</sub> + C<sub>10</sub>H<sub>6</sub>NO<sub>3</sub>]<sup>+</sup> 828.3290.

### Synthetic procedure for **LJ203**

Synthesis of compound **4**: The synthesis was according to the literature.<sup>2</sup> Phosphorus oxychloride (POCl<sub>3</sub>, 7.60g, 50.49 mmol) was added to DMF (6.20 g, 84.83 mmol) slowly at 0 ~ 15 °C. and then heated to 30 °C. Triphenylamine (TPA, 4.90 g, 19.97 mmol) was added rapidly. The mixture was heated to 45 ~ 50 °C, stirred for 2 h and poured into ice. Sodium hydroxide (NaOH) was used to neutralize the solution to pH = 10 ~ 11, then the suspension was heated to 70 ~ 80 °C and stirred for 0.5 h. The residue was filtered and purified by column chromatography using silica gel with

$\text{CH}_2\text{Cl}_2$  as the eluant to obtain the yellow solid (**4**). Yield: 4.80 g (85%). GC/TOF HRMS-EI ( $m/z$ ): calcd for  $\text{C}_{19}\text{H}_{15}\text{NO}$ , 273.1154; found, 273.1163.



**Scheme S2.** Synthetic procedure for **LJ203**

Synthesis of compound **5**: The synthesis of compound **5** was according to the above synthesis of compound **2**. The purple solid, yielding 13%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 8H), 8.09 (d,  $J = 8.5$  Hz, 8H), 7.49 – 7.44 (m, 16H), 7.42 (d,  $J = 4.2$  Hz, 24H), 7.15 (dt,  $J = 8.5, 4.2$  Hz, 8H), – 2.67 (s, 2H). MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{92}\text{H}_{66}\text{N}_8$ , 1282.5410; found,  $[\text{M} + \text{H}]^+$  1283.1526.

Synthesis of compound **6**: The synthesis of compound **6** was according to the above synthesis of compound **3**. The green solid, yielding 63%, MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{48}\text{H}_{36}\text{Cl}_2\text{N}_4\text{O}_4\text{Si}$ , 1378.4400; found,  $[\text{M} - 2\text{Cl} + \text{OH}]^+$  1325.1753.

Synthesis of compound **LJ203**: The synthesis of compound **LJ203** was according to the above synthesis of compound **LJ201**. The green solid, yielding 10%, Anal. calc.

for  $C_{112}H_{78}N_4O_8Si$ : C, 82.23; H, 4.81; N, 3.42. Found: C, 82.67; H, 5.03; N, 3.21.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.07 – 8.97 (m, 8H), 8.71 (d,  $J = 14.6$  Hz, 4H), 7.94 (d,  $J = 8.4$  Hz, 8H), 7.63 (d,  $J = 8.5$  Hz, 4H), 7.47 – 7.20 (m, 32H), 7.19 – 7.02 (m, 16H). MALDI-TOF ( $m/z$ ): calcd for  $C_{108}H_{74}N_8O_8Si$ , 1638.5399; found,  $[M - C_8H_5O_4]^+$  1474.6233.

## 2. Experiment.

**Photophysical measurements.** The UV–Vis absorption spectra of the dye solution ( $2 \times 10^{-5}$  M, THF) and the dye-loaded  $TiO_2$  films were measured by UV–Vis spectrophotometer (HP8453, Hewlett-Packard Company, America).

**Electrochemical measurements.** Electrochemical experiments were obtained by an electrochemical workstation (BAS100B, BAS. Company, America). Cyclic voltammetry was carried out by three-electrode system. The  $TiO_2$  photoanode adsorbed the dyes acted as the work electrode,  $Ag/Ag^+$  as reference electrode, and Pt wire as the counter electrode. The supporting electrolyte was 0.05 M tetrabutylammoniumhexafluorophosphate ( $TBAPF_6$ ). The scan rate used was  $100 \text{ mV} \cdot \text{s}^{-1}$ . All the redox potentials were standardized versus a normal hydrogen electrode (NHE).

**Photocurrent–voltage ( $J - V$ ) measurements.** The prepared solar cells were tested by current – voltage measurement and incident photon-to-current conversion efficiency (IPCE). The  $J - V$  measurements were taken by a solar simulator (94023A, Newport Co., America) and a electrochemical test system (PVIV-212V, Newport Co., America). The solar cells were tested with a mask of  $0.126 \text{ cm}^2$ . IPCE measurements were carried out by a spectrophotometer (SM25, JASCO, Japan). The active area of the solar cells was  $0.5 \text{ cm}^2$ .

**Electrochemistry-impedance spectroscopy (EIS).** The EIS measurements were tested with electrochemical workstation (Zennium, Zahner, Germany) with the frequency range from  $10^{-2} - 10^{-5}$  Hz. The solar cells were inspected and compared at the same bias voltage – 0.5 V in the dark at room temperature.

### 3. Device Fabrication.

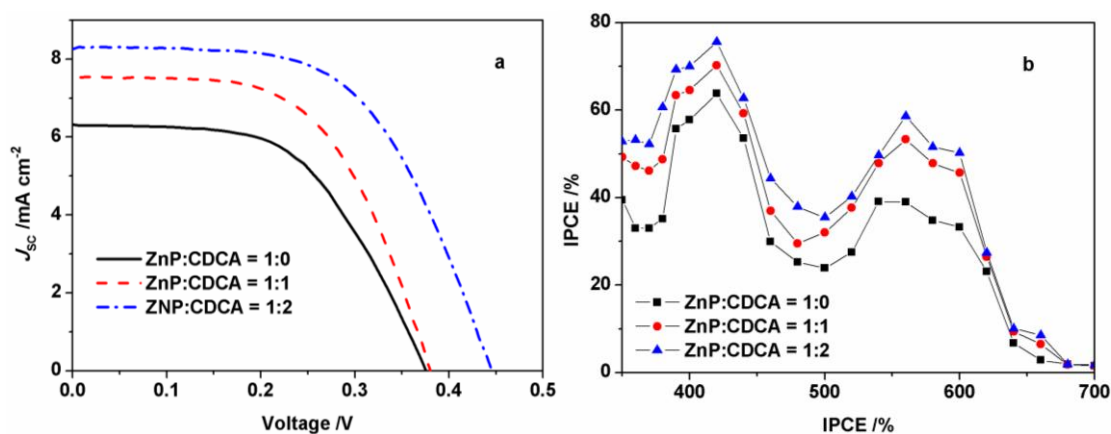
FTO conducting glass was cleaned sequentially with abluent solution, deionized water, acetone and ethanol in an ultrasonic bath. The screen-printing procedure was repeated with  $\text{TiO}_2$  paste (Heptachroma Co. Ltd, China) to get a transparent layers (thickness  $\approx 8 \mu\text{m}$ ). A scattering layer (thickness  $\approx 4 \mu\text{m}$ , Heptachroma Co. Ltd, China) was printed.  $\text{TiO}_2$  electrodes were heated at  $520 \text{ }^\circ\text{C}$  for 30 min and then immersed in the 40 mM  $\text{TiCl}_4$  aqueous solution at  $70 \text{ }^\circ\text{C}$  for 30 min, washed with water and ethanol, and annealed at  $520 \text{ }^\circ\text{C}$  for 30 min again.  $\text{TiO}_2$  electrodes were immersed into a dye solution containing 0.2 mM **LJ201** or **LJ203** in THF for 6 hours and **ZnP** for 1 hour (**ZnP** : CDCA = 1:2, molar ratio).. After adsorption of the dyes, the electrodes were washed by ethanol. The counter electrode is Pt/FTO.



**Fig. S1.** Images of dye solution: **LJ201** (left) and **LJ203** (right).

#### 4. The DSSCs sensitized by ZnP.

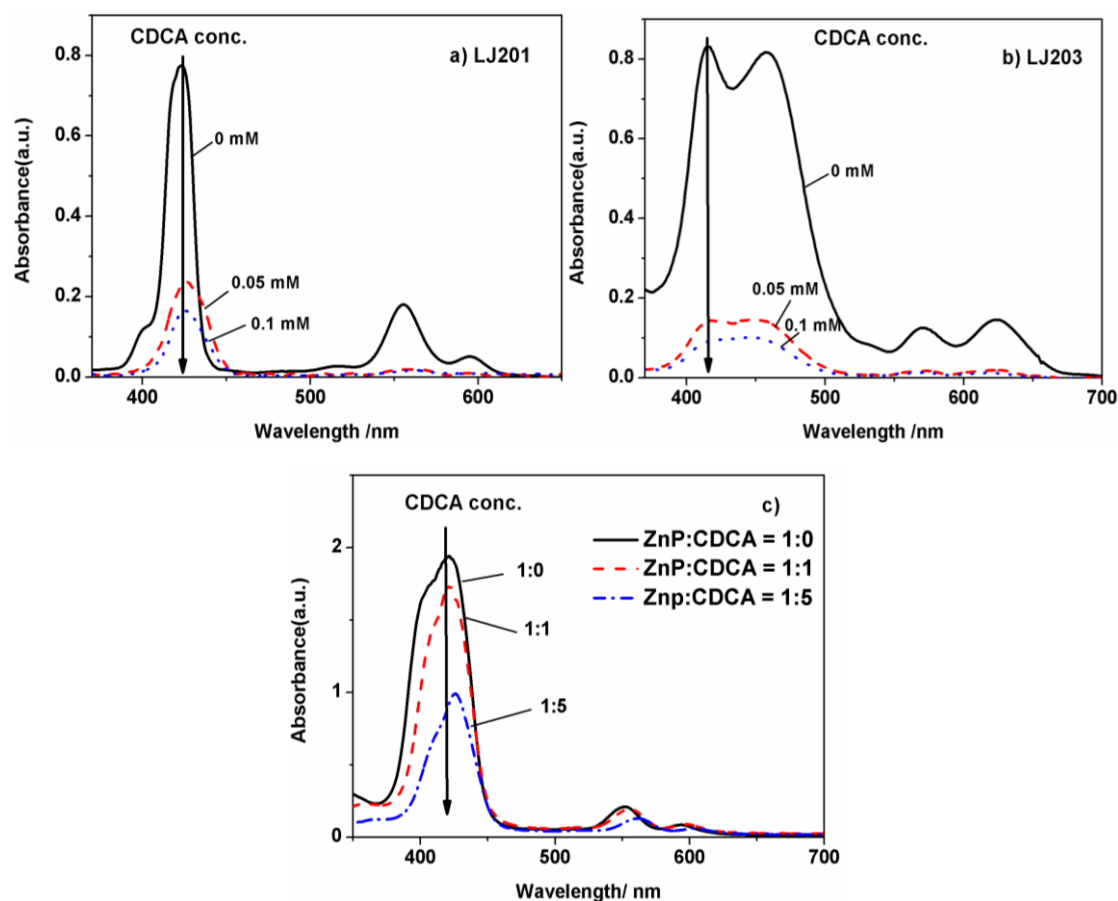
The DSSCs with **ZnP** as sensitizer exhibited a maximal incident photon to current conversion efficiencies (IPCEs) value of 76%, a short-circuit photocurrent ( $J_{sc}$ ) of  $8.27 \text{ mA cm}^{-2}$ , an open-circuit voltage ( $V_{oc}$ ) of 445 mV, a fill factor (FF) of 0.58 and an overall conversion efficiency ( $\eta$ ) of 2.1%, with chenodeoxycholic acid (CDCA, the commonly used coabsorbent) added to the dye solutions, while the ZnP-sensitized solar cell showed  $\eta = 1.3\%$  ( $J_{sc} = 6.29 \text{ mA cm}^{-2}$ ,  $V_{oc} = 375 \text{ mV}$ , FF = 0.55) without CDCA.



**Fig. S2** (a)  $J - V$  curves of DSSCs sensitized by **ZnP** with different amounts of CDCA measured under the illumination of sunlight AM 1.5 G; (b) IPCE spectra of DSSCs sensitized by **ZnP**.

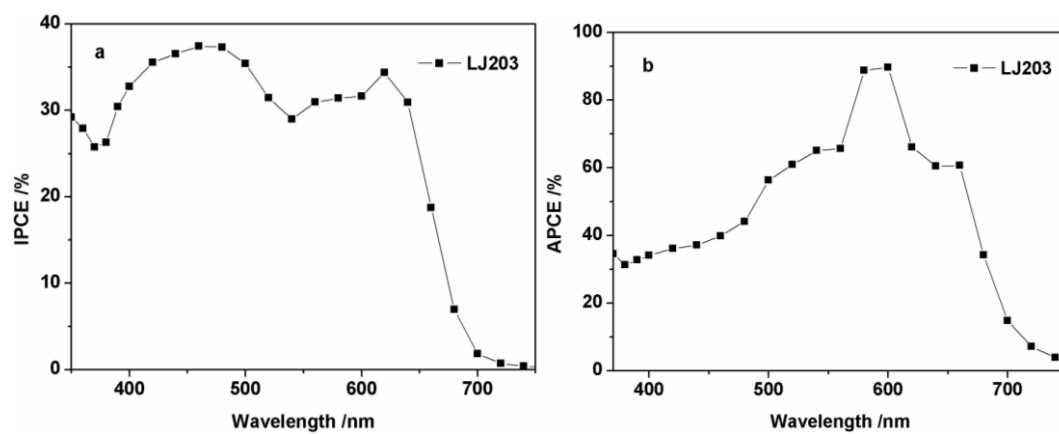
## 5. Dye spectra on TiO<sub>2</sub> films with various CDCA concentrations

The UV – Vis absorption spectra shown below are of **LJ201**, **LJ203** and **ZnP** on thin (2 μ m) meso-porous TiO<sub>2</sub> films deposited on glass substrates. The films were immersed in the dye solutions containing various concentration of the additive CDCA. Following the decrease of concentrations of CDCA, the absorption spectra of **LJ203** has no change, while **ZnP** shows blue shift, which might be owing to H-aggregation on the TiO<sub>2</sub> film.<sup>3</sup> With the concentration of CDCA increase, less and less dye adsorbed on TiO<sub>2</sub> films. When the concentration of CDCA is 1 mM, there is no dye adsorbed on TiO<sub>2</sub> films. This indicated the axial ligands can suppress the dye aggregation on TiO<sub>2</sub> films. In addition, the introduction of triphenylamine units is helpful to restrain the formation of dye aggregation.



**Fig. S3** UV – Vis absorption spectra of **LJ201**(a) and **LJ203** (b) adsorbed onto TiO<sub>2</sub> films with varying amounts (0, 0.05, 0.1 mM) of the CDCA added to the dye solution; (c) UV – Vis absorption spectra of **ZnP** adsorbed onto TiO<sub>2</sub> films with varying amounts (1:0, 1:1, 1:5, ratio of **ZnP** : CDCA) of the CDCA added to the dye solution.

## 6. The APCE of DSCs sensitized by LJ203

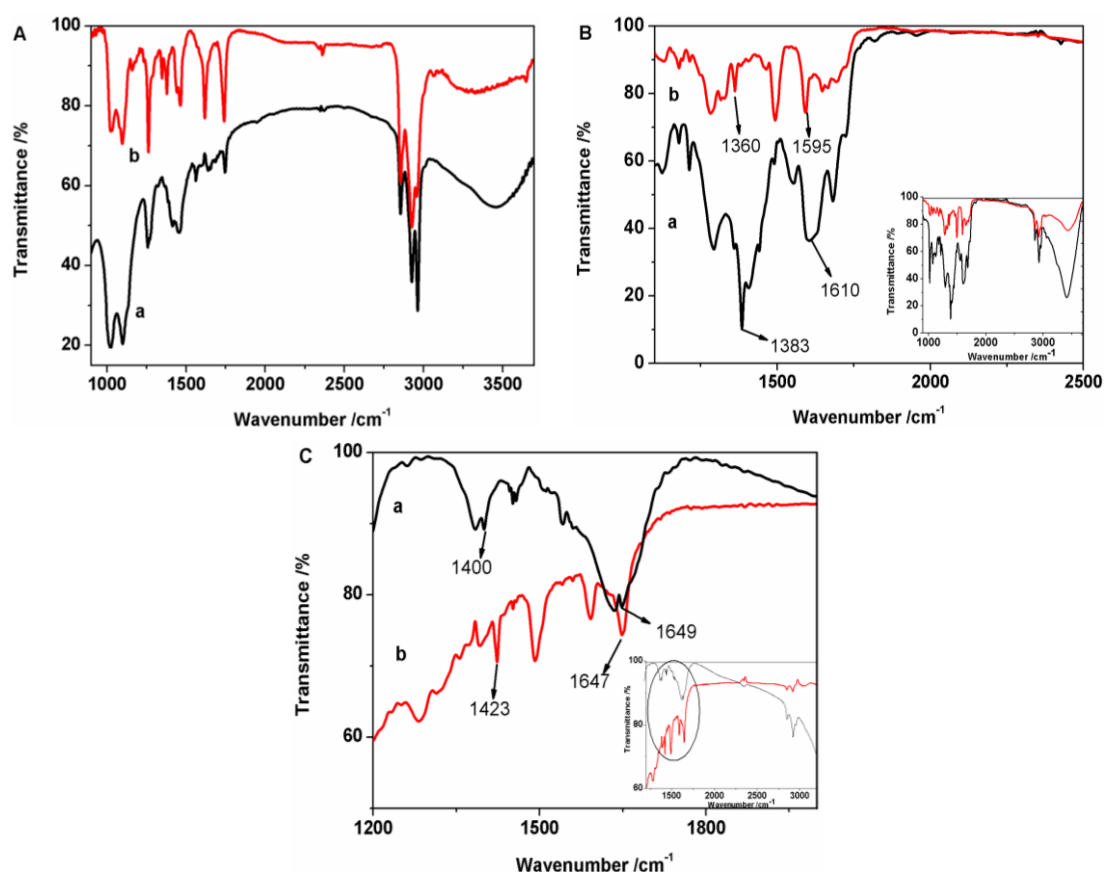


**Fig. S4** (a) The IPCE spectra of DSCs sensitized by **LJ203**, and the TiO<sub>2</sub> films (8 μm) were without scattering layer; (b) the APCE spectra of DSCs sensitized by **LJ203**.



## 7. FTIR of LJ201 and LJ203

The different interfacial binding modes between attached dyes and TiO<sub>2</sub> surface greatly influence the quantum yields of electron injection into the semiconductor.<sup>4</sup> In general, a carboxylate group can adsorb on TiO<sub>2</sub> surface in main three ways, unidentate mode, bidentate bridging mode, and bidentate chelating mode. Among these modes, bidentate mode achieves high quantum yields of electron injection into semiconductor.<sup>5</sup> Deacon and Philips rule can be used to judge the binding mode of **LJ201** and **LJ203** onto TiO<sub>2</sub> surface.<sup>6</sup> That is  $\Delta v_{as-s} = v_{as}(\text{COO}^-) - v_s(\text{COO}^-)$ , the frequency difference between the antisymmetric ( $v_{as}$ ) and symmetric stretching ( $v_s$ ) mode of the COO<sup>-</sup> group. The  $\Delta v_{as-s}$  values are in the order of unidentate > ionic form  $\approx$  bidentate bridging > bidentate chelating. On the basis of this comparison and general conclusions,<sup>7</sup> the unidentate mode for the binding of **LJ201** and bidentate mode for **LJ203** are suggested for the major binding modes between semiconductor surface and anchored dyes.



**Fig. S5.** FTIR spectra of **LJ201** (a) and **LJ203** (b) (A), sodium salt (B) and adsorbed on TiO<sub>2</sub> (C).

**Tab. S1**  $\Delta\nu_{\text{as-s}}$ ,  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  data of all samples.

Sample	$\nu_{\text{as}} (\text{COO}^-) / \text{cm}^{-1}$	$\nu_{\text{s}} (\text{COO}^-) / \text{cm}^{-1}$	$\Delta\nu_{\text{as-s}} / \text{cm}^{-1}$
<b>LJ201</b> sodium salt	1610	1383	227
on $\text{TiO}_2$	1649	1400	249
<b>LJ203</b> sodium salt	1595	1360	235
on $\text{TiO}_2$	1647	1423	224

### Reference

- [1] M. Maree and T. Nyokong, *J. Porphyrins and Phthalocyanines*, 2001, **5**, 555.
- [2] H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2008, **112**, 11023.
- [3] Z. Wang and H. Sugihara, *Langmuir*, 2006, **22**, 9718.
- [4] H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2008, **112**, 11023.
- [5] M. K. Nazeeruddin, R. Humphry-Baker, P. Liska, and M. Gratzel, *J. Phys. Chem. B*, 2003, **107**, 8981.
- [6] G. B. Deacon and R. Phillips, *J. Coord. Chem. Rev.*, 1980, **33**, 227.
- [7] (a) Y. Hao, X. Yang, J. Cong, X. Jiang, A. Hagfeldt and L. Sun, *RSC Adv.*, 2012, **2**, 6011; (b) C. Bauer, G. Boschloo, E. Mukhtar, and A. Hagfeldt, *J. Phys. Chem. B* 2002, **106**, 12693; (c) E. T. Shimomura, M. A. Phillippi, and H. M. Gof, *J. Am. Chem. Soc.* 1981, **103**, 6778.