## A New Type of Organic sensitizers with Pyridine-*N*-oxide as Anchoring Group for Dye-sensitized Solar Cells

## Lei Wang,<sup>a</sup> Xichuan Yang,<sup>\*a</sup> Shifeng Li,<sup>a</sup> Ming Cheng,<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 Centre on Molecular Devices, Dalian University of Technology(DUT), 2 Linggong Rd, 116024 Dalian, China. E-mail: yangxc@dlut.edu.cn; Fax: +86 411 84986250; Tel: +86 411 84986247

<sup>b</sup> KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Teknikringen 30, 10044 Stockholm, Sweden. E-mail: lichengs@kth.se; Fax: +46 8 791 2333; Tel: +46 8 790 8127

## General experimental details:

MS data were obtained with GC-Tof MS (UK), HP1100 LC/MSD (USA), and LC/Q-TOF MS (UK). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken with VARIAN INOVA 400MHz (USA) using TMS as standard. Absorption spectra were recorded on HP8453 (USA). The UV-Vis absorption spectra of the dye-loaded transparent film (T/SP, SOLARONIX, doctor-blade printed on a clean glass, sensitized 1h in dye bath) and the dye solution (0.02 mM) in DCM were recorded on HP8453 (USA). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) and different pulse voltammetry (DPV) using a three-electrode cell and an electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon disk electrode; the auxiliary electrode was a Pt wire; and Ag/Ag<sup>+</sup> was used as the reference electrode. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte in DCM. The ferrocenium/ferrocene (Fc/Fc<sup>+</sup>) redox couple was used as an internal potential reference. The potentials vs NHE were calibrated by addition of 440 mV to the potentials vs Fc/Fc<sup>+</sup>. The FTIR spectra were collected by the FTIR-GC system (NEXUS, America). The TiO2 films were immersed into the dye solutions (0.2mM in DCM) overnight in the dark, dried and scraped off the glass to form the sample. The molecular orbitals of dyes were calculated using density functional theory (DFT) at B3LYP/6-31 G level with full geometry optimization.

Light source for the photocurrent-voltage (J-V) measurement is an AM 1.5 solar simulator (16S-002, Solar Light Co. Ltd., USA). The incident light intensity was 100 mW/cm<sup>-2</sup> calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.159 cm<sup>-2</sup>. The photocurrent-voltage curves were obtained by the linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan). The Jsc was calibrated by integrating the IPCE value tuned light density of AM 1.5 against wavelength. Electrochemical impedance spectroscopy (EIS) for DSSCs with forward bias under dark was measured with an impedance/gain-phase analyzer (PARSTAT 2273, USA). The spectra were

scanned in a frequency range of  $10^{-2}$ - $10^{6}$  Hz at room temperature. The alternate current (AC) amplitude was set at 10 mV.

The DSCs were fabricated as follows. A double-layer TiO<sub>2</sub> photoelectrode (thickness 14  $\mu$ m, area 6×6 mm) was used as a working electrode. A 10 µm main transparent layer with titania particles (T/SP, SALARONIX) and a 4µm scattering layer with titania particles (DHS-SLP1, Heptachroma, China) were screen-printed on the fluorine-doped tin oxide conducting glass substrate. Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned using an ultrasonic bath by detergent and ethanol each for 30 min. A layer of 10 nm TiO<sub>2</sub> paste (T/SP, SALARONIX) was coated on the FTO glass by screen printing and then dried for 3 min at 130 °C. This procedure was repeated for 5 times to get a 10 µm film, then a 4 µm layer of 300 nm (DHS-SLP1, Heptachroma, China) TiO<sub>2</sub> paste was screen-printed as scattering layer. The double-layer TiO<sub>2</sub> electrodes were gradually heated under an air flow at 520 °C for 60 min. The sintered film was further treated with 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min, then washed with water and ethanol, and annealed at 520 °C for 60 min. After the film was cooled to 80 °C, it was immersed into a  $2 \times 10^4$  M dye solution in DCM and maintained under dark for 5 h. The sensitized TiO<sub>2</sub> electrode was then rinsed with the ethanol and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and sputtered Pt/FTO counter electrode (Heptachroma, China) separated with a hot-melt Surlyn 1702 film (25 µm, Dupont). The electrolyte consisting of 0.3 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), 0.25 M LiI, 0.01 M I<sub>2</sub>, 0.05 M tetrabutyl ammonium iodide (TBAI), 0.1M 4-terbutyl pyridine in acetonitrile : valeronitrile (AN:VN)=85:15 was injected into the cell and sealed with a cover glass.

Synthesis of the dyes WL101-R - WL103



**Fig.S1** synthetic routes of **WL101-R** - **WL103**: a. Triphenylboric acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; b. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; c. 4-bromopyridine hydrochloride, 2-thiopheneboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; d. NBS, THF, 0°C to r. m., 6h; g. Triphenylboric acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; f. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; g. Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; h. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; g. Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; h. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; g. Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; h. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; g. Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; h. 3-chloroperoxybenzoic acid, DCM, r. m., 8h; g. Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O, reflux, 8h; h. 3-chloroperoxybenzoic acid, DCM, r. m., 8h.

- a. 4-bromopyridine hydrochloride (292 mg, 1.50 mmol), Triphenylboric acid(434 mg, 1.50 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg, 0.07 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10.0 mol) in 50 mL of THF and 5 mL of H<sub>2</sub>O were heated to 70 °C under a nitrogen atmosphere for 8h. After cooling to room temperature, the mixture was extracted with 50mL of CH2Cl2. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 2/1, v/v) to give an orange solid ( 385 mg). Yield: 90.0%. **WL101-R** <sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  8.59 (dd, J = 4.6, 1.5 Hz, 2H), 7.74 7.69 (m, 2H), 7.63 (dd, J = 4.5, 1.7 Hz, 2H), 7.40 7.33 (m, 4H), 7.16 7.08 (m, 8H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 120.88, 122.93, 123.63, 125.00, 127.67, 129.47, 130.93, 147.25, 147.63, 148.95, 150.22. TOF-HRMS EI+ calcd. For C23H18N2 [M+] 322.1470, found 322.1469.
- b. 3-chloroperoxybenzoic acid (190 mg, 1.10 mmol ) in 15ml CH<sub>2</sub>Cl<sub>2</sub> were added in dropwise to **WL101-R** (193 mg, 0.60 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>, then stirred at r. m. overnight. The mixture was dried by rotary evaporation. The residue was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 100/1, v/v) to give an dark orange solid (91 mg, 0.25 mmol). Yield: 45.2%. **WL101** <sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  8.21 8.10 (m, 2H), 7.72 7.64 (m, 4H), 7.35 (tt, J = 4.6, 2.2 Hz, 4H), 7.18 7.05 (m, 8H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 123.113, 124.319, 125.585, 127.526, 129.118, 129.952, 138.944, 139.694, 147.465, 149.489. TOF-HRMS calcd. For C23H18N2O [M+] 338.1419, found 338.1428.
- c. 4-bromopyridine chloride (292 mg, 1.50 mmol), 2-bromothiophene(245 mg, 1.50 mmol) synthesized as procedure a. the mixture was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>OH = 50/1, v/v) to give a white solid 1(190 mg, 1.2 mmol). Yield: 75%. Complex 1 <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.58 (d, J = 4.6 Hz, 2H), 7.74 (dd, J = 3.7, 1.1 Hz, 1H), 7.67 7.59 (m, 3H), 7.21 (dd, J = 5.1, 3.7 Hz, 1H). <sup>13</sup>C NMR

(400 MHz, CDCl<sub>3</sub>) δ: 150.339, 141.324, 141.097, 128.443, 127.223, 125.365, 119.853. TOF-HRMS calcd. For C9H7NS [M+] 161.0299, found 161.0289.

- d. Complex 1(190 mg, 1.20 mmol) were solved in 30ml THF and cooled to 0 °C, NBS (232 mg, 1.30 mmol) were added slowly. After finished the temperature was rised to r. m. and stirred for about 6h. The reaction was quenched by water and extracted with 50mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 100/1, v/v) to give a pale yellow solid 2 (285 mg, 1.19 mmol). Complex 2 Yield: 98.9%. <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.71 (dd, J = 5.3, 0.6 Hz, 1H), 8.23 (dd, J = 1.8, 0.7 Hz, 1H), 7.97 7.90 (m, 2H), 7.77 (dd, J = 5.1, 1.1 Hz, 1H), 7.27 (dd, J = 5.1, 3.8 Hz, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 150.452, 131.423, 128.549, 127.336, 125.471, 119.982, 119.520. TOF-HRMS calcd. For C9H6NSBr [M+] 238.9404, found 238.9405.
- complex 2 (358 mg, 1.50 mmol) and Triphenylboric acid(434 mg, 1.50 mmol) were synthesized as step a. **Complex 3** <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.58 (d, J = 5.3 Hz, 2H), 7.73 (d, J = 3.9 Hz, 2H), 7.63 (dd, J = 9.0, 7.4 Hz, 4H), 7.46 (d, J = 3.9 Hz, 1H), 7.35 (t, J = 7.9 Hz, 4H), 7.14 7.04 (m, 10H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 150.399, 148.034, 147.389, 146.358, 141.438, 139.042, 129.497, 127.496, 126.722, 126.533, 124.857, 123.508, 123.402, 119.452. TOF-HRMS calcd. for C27H20N2S [M+] 404.1347, found 404.1343.
- f. Complex 3 were oxidized as step b. WL102 <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.15 8.10 (m, 2H), 7.69 7.58 (m, 5H), 7.43 (d, J = 3.9 Hz, 1H), 7.38 7.31 (m, 4H), 7.16 7.03 (m, 8H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 121.57, 123.06, 123.53, 124.85, 126.45, 126.60, 126.96, 129.43, 132.55, 137.08, 139.27, 146.68, 147.21, 148.14. TOF-HRMS calcd. For C27H20N2OS [M+] 420.1296, found 420.1289.
- g. The complex were synthesized as step a. Complex 4 <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.63 (d, J = 5.9 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.47 (dd, J = 7.0, 5.4 Hz, 2H), 7.41 (s, 1H), 7.34 (dd, J = 8.4, 7.4 Hz, 4H), 7.14 7.03 (m, 8H), 2.81 2.76 (m, 2H), 1.77 1.66 (m, 2H), 1.40 1.27 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 150.013, 147.662, 147.382, 144.091, 142.423, 142.006, 129.368, 127.708, 126.495, 125.441, 124.637, 123.417, 123.273, 122.985, 31.620, 30.870, 29.247, 29.194, 22.609, 14.107. TOF-HRMS calcd. For C33H32N2S [M+] 488.2286, found 488.2285.
- h. Complex 4 were oxidized as step b. WL103 <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.18 (d, J = 7.3 Hz, 2H), 7.63 7.58 (m, 2H), 7.50 (d, J = 7.3 Hz, 2H), 7.38 (s, 1H), 7.37 7.31 (m, 4H), 7.16 7.02 (m, 8H), 2.78 (d, J = 3.6 Hz, 2H), 1.76 1.62 (m, 2H), 1.41 1.24 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 147.867, 147.465, 140.202, 139.398, 136.229, 132.840, 129.891, 129.535, 128.102, 127.185, 125.039, 123.599, 122.765, 121.665, 31.734, 31.044, 29.831, 29.255, 28.982, 22.712, 14.288. TOF-HRMS calcd. for C33H32N2OS [M+] 504.2235, found 504.2205.



Fig. S2 CV (left) and DPV (right) curves of dyes.

Dye	Optimized Structure	НОМО	LUMO
WL101-R	33.35	<b>***</b>	
WL101	3 3 3 3 3 1.15		
WL102	8.95	59000 <sup>000</sup>	
WL103		29300 450	

Table S1 The optimized structures and electron distribution in HOMO and LUMO levels of the WL101-R - WL103 dyes