#### Supporting information for

#### **RSC** Advances

# Bipodal dyes with bichromic triphenylamine architectures for use in dye-sensitized solar cell applications

by

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**Scheme S1** Synthesis of dyes **OA1**, **OA2**, **OA3** and **OA4**. Reaction conditions i) N-bromosuccinimide (1.10 eq), THF-EtOAc (1:1), overnight; ii) Pd(PPh<sub>3</sub>)<sub>4</sub> (0.10 eq), NaOH (8 eq), THF:water (9:1), reflux 12 hours; iii) cyanoacetic acid (4 eq), piperidine (0.25 eq), CHCl<sub>3</sub>, reflux 8 hours; iv) acetic acid: water (2:1), reflux 12 hours.

Table S1. Physicochemical characterization of aldehyde precursors							
Compound	E <sub>ox</sub> (V vs NHE)	UV-Vis λ <sub>max</sub> nm (ε*10 <sup>-4</sup> M <sup>-1</sup> cm <sup>-1</sup> ) Ε <sub>0-0</sub>					
Formyl	1.515		361	3.08			
ΤΡΑ			(2.6)				
Diformyl	1.585	332	382	3.02			
ΤΡΑ		(0.6)	(1.3)				
2	0.983		374	2.92			
	1.441		(5.2)				
7	0.958		404	2.56			
	1.285		(0.9)				



Figure S1. UV-Vis spectra of aldehyde precursors in DCM.



**Fig S2**. Frontier molecular orbitals as predicted by DFT (B3LYP/6-31G) for **OA1, OA2** and **OA3** with inclusion of the dominant transitions as calculated by TD-DFT.



**Fig S3**. Frontier molecular orbitals as predicted by DFT (B3LYP /6-31G) for **OA4** with inclusion of the dominant transitions as calculated by TD-DFT.

**Table S2.** Absorption wavelengths (nm (eV)) for the free (left panel,  $\lambda_{free}$ ) and anchored dyes (right panel,  $\lambda_{TiO2}$ ), oscillator strengths (f) and the percentage of dominant contributions within the TDDFT configuration expansion (c = cTDDFT\*100 >10) computed at the B3LYP-d3/6-311G(d,p) level of theory.

Dyes	s Free						Anchored						
	Exp.*	$\lambda_{free}$	f	Ad	tive	мо	Contr. %	λ <sub>τίο 2</sub>	f	Act	ive	мо	Contr. %
OA1	471	492(2.52)	1.00	HOMO-1	$\rightarrow$	LUMO	99	539(2.30)	1.09	HOMO-1	$\rightarrow$	LUMO+3	87
	417	369(3.36)	0.66	HOMO	$\rightarrow$	LUMO+2	95						
OA2	422	445(2.78)	1.07	HOMO-1	$\rightarrow$	LUMO+1	70	468(2.65)	0.46	HOMO-2	$\rightarrow$	LUMO+3	79
				номо	$\rightarrow$	LUMO+2	26						
OA3	497	566(2.19)	1.15	HOMO-1	$\rightarrow$	LUMO+1	98	672(1.84)	0.20	HOMO-1	$\rightarrow$	LUMO	86
	394	385(3.22)	0.95	HOMO-2	$\rightarrow$	LUMO+1	83						
OA4	461	494(2.51)	1.21	HOMO	$\rightarrow$	LUMO	99	534(2.32)	1.15	НОМО	$\rightarrow$	LUMO+4	88
	394	415(2.99)	0.21	HOMO	$\rightarrow$	LUMO+1	97						
L1	483	525(2.36)	0.95	HOMO	$\rightarrow$	LUMO	100	616(2.01)	1.01	HOMO	$\rightarrow$	LUMO+3	99
	344	374(3.31)	0.65	HOMO-1	$\rightarrow$	LUMO	93						

Dye	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	η (%)	η (%) for N=7
OA1	0.58	2.89	0.62	1.10	1.01 (+/- 0.20)
OA2	0.59	4.26	0.64	1.70	1.45 (+/- 0.28)
OA3	0.56	2.60	0.64	1.00	0.85 (+/- 0.20)
OA4	0.53	2.85	0.68	1.14	0.60 (+/- 0.55)
L1	0.54	2.78	0.62	1.01	0.60 (+/- 0.41)

**Table S3.** Photovoltaics performance of DSSC devices used in the following J-V (Figure S4), EIS, and IPCE measurements (OA1-OA4 and L1).

Note the performances in this family are not the same as Table 2 in the manuscript, because they were made by a different student during the manuscript edits. They also present the best performing device from a set of 5 devices. While the averages are lower, the trends still hold when compared to Table 2.







Figure S4. Current vs voltage graphs of DSSCs with OA1, OA2, OA3, OA4, and L1, respectively.

Table S4. DSSC parameters based on the circuit model.<sup>a</sup>

DSSC	Units	Description
Parameter		
R <sub>sTCO</sub> , C <sub>TCO</sub>	Ω, F	Charge transfer resistance and the corresponding double-layer capacitance
		at exposed transparent conducting oxide (TCO)/electrolyte interface
R <sub>co</sub> , C <sub>co</sub>	Ω, F	Resistance and capacitance at TCO/TiO <sub>2</sub> contact
R <sub>ctTCO</sub>	Ω	Charge transfer resistance of the charge recombination process at the TCO/ $I_3$
		in electrolyte
R <sub>ctTiO2</sub>	Ω	Charge transfer resistance of the charge recombination process at the
		$TiO_2/I_3^-$ in electrolyte
C <sub>μ</sub>	F	Chemical capacitance of the $\rm TiO_2$ film
Z <sub>d(sol)</sub>	mMho*s^(1/2)	Warburg element showing the Nernst diffusion of $I_3^{\text{-}}$ in electrolyte
R <sub>Pt</sub> , C <sub>Pt</sub>	Ω, F	Charge transfer resistance and double-layer capacitance at the Pt CE
R <sub>ct</sub>	Ω	Charge transfer resistance of the charge recombination process at the
		IIU <sub>2</sub> /I <sub>3</sub> <sup>-</sup> in electrolyte

<sup>a</sup> Sarker S., Ahammad A. J. S., Seo HW, Kim DM. *Int. J. Photoenergy*. 2014, 17.

**Figure S5.** Electrochemical impedance spectra of DSSC cell with L1 (a) Nyquist plot (b) Bode modulus plot (frequency vs Z) (c) Bode phase plot (frequency vs phase) (d) electrochemical circuit model of DSSC (e) DSSC circuit parameter values.



**Figure S6.** Electrochemical impedance spectra of DSSC cell with OA1 (below) (a) Nyquist plot (b) Bode modulus plot (frequency vs Z) (c) Bode phase plot (frequency vs phase) (d) electrochemical circuit model of DSSC (e) DSSC circuit parameter values.



**Figure S7.** Electrochemical impedance spectra of DSSC cell with OA2 (a) Nyquist plot (b) Bode modulus plot (frequency vs Z) (c) Bode phase plot (frequency vs phase) (d) electrochemical circuit model of DSSC (e) DSSC circuit parameter values.



**Figure S8.** Electrochemical impedance spectra of DSSC cell (below) with OA3 (a) Nyquist plot (b) Bode modulus plot (frequency vs Z) (c) Bode phase plot (frequency vs phase) (d) electrochemical circuit model of DSSC (e) DSSC circuit parameter values.



**Figure S9.** Electrochemical impedance spectra of DSSC cell with OA4 (a) Nyquist plot (b) Bode modulus plot (frequency vs Z) (c) Bode phase plot (frequency vs phase) (d) electrochemical circuit model of DSSC (e) DSSC circuit parameter values.





Figure S10 – Normalized IPCE ( $P_{nm}/P_{tot}$ ) data for the best cells listed in Table S3

#### **General Considerations**

All reagents were purchased from Aldrich. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica P60). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Chromotagraphy was performed by dissolving the sample in the eluent system, then eluting down silica. All cross-couplings were sparged with nitrogen. As shown in Figure S1, cyanoacetic acid (4 eq), piperidine (0.25 eq), were used for the final condensation step in dye preparation. A minimal amount of chloroform (~25 mL with heating), was used as a solvent, and reactions were monitored by TLC (chloroform/silica) for the disappearance of the starting aldehyde. Once deemed complete, the reaction was acidified with 1 N HCl (dropwise, up to ~5 mL), and the crude product precipitated out.

RT refers to room temperature. Routine <sup>1</sup>H, <sup>13</sup>C, spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. In some instances, poor solubility in organic solvents prevented <sup>13</sup>C NMR acquisition. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) from low to high field and referenced to a residual non-deuterated solvent for <sup>1</sup>H and <sup>13</sup>C nuclei). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; q = quartet; m=multiplet; and br = broad. High resolution mass spectroscopy (HRMS) results were obtained from Queens University, Kingston Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series Spectrophotometer from Agilent Technologies and dichloromethane (having the onset peak at 230 nm) was used as a solvent. Infrared spectroscopy data was collected using the Cary 630 series FTIR spectrometer.

#### Device Fabrication: See p. S32

**DFT calculations**. The GAUSSIAN 09 computational package<sup>1</sup> was employed to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang-Parr non-local correlation functional B3LYP-D3 and 6-311G\* basis set was used for all the atoms. The computations of the oxidized states of the dyes were carried out using unrestricted DFT (UDFT)/PCM using the level of theory mentioned above. Time-Dependent Density Functional Theory calculations were also performed using this methodology, and the first 200 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. Implicit solvation effects were incorporated using the polarized continuum model (PCM, e = 35.7) for acetonitrile

Molecules A<sup>2</sup>, B<sup>3</sup>, C<sup>4</sup>, L1<sup>5</sup>, 1<sup>6</sup>, 3<sup>7</sup> and 4<sup>7</sup> have been previously reported and characterized.

### **Experimental**

**Synthesis of 1:** Under an atmosphere of N<sub>2</sub>, diformyITPA (2.83 g, 9.41 mmol) was dissolved in 75 mL of THF:EtOAc (1:1) and *N*-bromosuccinimide (1.84 g, 10.4 mmol) was added in one portion. The flask was covered with Al foil and the mixture was stirred overnight. Volatiles were removed *in vacuo* and the crude was purified via column chromatography over silica using hexanes:EtOAc (3:2) as the eluent, affording the desired product as a yellow-green solid (2.33 g, 65%).<sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$  = 9.91 (a, s, 2 H)



, 7.79 (b, d, 4 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.50 (d, d, 2 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.18(c, d, 4 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.05 (e, d, 2 H,  ${}^{3}J_{HH}$  = 8 Hz). Data matched with previously reported compound.



**Synthesis of 2:** Under an atmosphere of N<sub>2</sub>, molecule **1** (0.282 g, 0.74 mmol) was dissolved in 60 mL of THF:H<sub>2</sub>O (9:1) and molecule **B** (0.42 g, 0.97 mmol) was added into the same flask. The flask was sparged for 15 minutes. The flask was charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) followed by NaOH (8 eq) and refluxed overnight. Volatiles were removed *in vacuo* and an extraction with DCM was performed. The crude was purified via column chromatography over silica using using a gradient elution from DCM to hexanes:EtOAc (3:2) affording the desired product as a yellow solid (0.251 g, 47%).<sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$  = 9.90 (a, s, 2 H), 7.79 (b, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.56 (e, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.40 (f, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.23 (c, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.18 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.09 (h, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.98 (g, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.85 (i, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.81 (j, s, 6 H). Insolubility prevented the ability to acquire a suitable <sup>13</sup>C spectrum.

HRMS (EI): *m*/z 604.23550 ((M+) calculated for C<sub>40</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>: *m*/z 604.23621.

**Synthesis of OA1**: Molecule **2** (0.233 g, 0.38 mmol) was dissolved in a minimal amount of CHCl<sub>3</sub> and cyanoacetic acid. Piperidine was then added. The mixture was refluxed overnight. The organic layer was washed with HCl 1 N and volatiles removed *in vacuo*. The crude was recrystallized in dcm:hexane (1:1) as a crimson red solid (0.091 g, 39%); IR (cm<sup>-1</sup>) 2229, 1720. <sup>1</sup>H NMR (400 MHz, dimethylsulfoxide-d<sub>6</sub>):  $\delta$  8.21 (a, s, 2 H), 8.01 (b, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz),7.66 (e, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz),7.51 (f, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.22 (d, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.19 (c, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.05 (i, d, 4 H), 6.92 (h, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.81 (g, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz) 3.75 (s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, dimethylsulfoxide-d6)  $\delta$  = 198.50, 163.70, 155.93, 152.99, 149.92, 148.05, 143.05, 139.83, 137.88, 132.73, 130.37, 127.61, 127.24, 126.95, 125.99, 122.60, 119.09, 116.63, 115.01, 114.84, 55.25. HRMS (ESI): *m/z* 737.24194 ((M-H]-) calculated for C<sub>46</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>: *m/z* 737.24056.





**Synthesis of 3**: Under an atmosphere of N<sub>2</sub>, molecule A (2.00 g, 5.26 mmol) was dissolved in 60 mL of THF:H<sub>2</sub>O (9:1) and molecule **1** (1.105 g, 5.26 mmol) was added into the same flask. The flask was sparged for 15 minutes and then charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) followed by NaOH (8 eq) and refluxed overnight. Volatiles were removed *in vacuo* and an extraction with DCM was performed. The crude was purified via column chromatography over silica using hexanes:EtOAc (3:2) affording the desired product as a neon yellow, waxy oil.(1.0381 g, 51%). <sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$ = 9.91 (a, s, 2 H), 7.79 (b, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.62 (e, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.31 (d, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.22 (c, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.17 (f+h, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.10 (g, t, 1 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz). HRMS (EI): *m/z* 383.09785 ((M+) calculated for

C<sub>24</sub>H<sub>17</sub>NO<sub>2</sub>S: *m*/z 383.09800. Data matched with previously reported compound.

**Synthesis of 4:** Under an atmosphere of N<sub>2</sub>, Molecule **3** (0.30 g, 0.79 mmol) was dissolved in 75 mL of THF:EtOAc (1:1) and *N*-bromosuccinimide (0.16 g, 0.9 mmol) was added in one portion. The flask was covered with Al foil and the mixture was stirred overnight. Volatiles were removed *in vacuo* and the crude was purified via column chromatography over silica using hexanes:EtOAc (3:1) as the eluent, affording the desired product as a yellow waxy solid.(0.201 g, 57%). <sup>1</sup>H NMR (400



MHz, chloroform-d):  $\delta$  = 9.91 (a, s, 2 H), 7.79 (b, d, 4 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.51 (d, d, 2 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.22 (c, d, 4 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.16 (e, d, 2 H,  ${}^{3}J_{HH}$  = 8 Hz), 7.04 (f+g, s, 2 H). HRMS (EI): *m/z* 461.00920 ((M+) calculated for C<sub>24</sub>H<sub>16</sub>BrNO<sub>2</sub>S: *m/z* 461.00851. Data matched with previously reported compound.



**Synthesis of 5:** Under an atmosphere of N<sub>2</sub>, molecule **4** (.622 g, 1.34 mmol) was dissolved in 60 mL of THF:H<sub>2</sub>O (9:1) and molecule **B** (0.638 g, 1.48 mmol) was added into the same flask. The flask was sparged for 15 minutes. The flask was charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) followed by NaOH (8 eq) and refluxed overnight. Volatiles were removed *in vacuo* and an extraction with DCM was performed. The crude was purified via column chromatography over silica using hexanes:EtOAc (3:1) affording the desired product as a yellow solid.(0.361 g, 39%).<sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$  = 9.90 (a,s, 2 H), 7.79 (b,d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.61 (f+g,d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.43 (d,d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.23 (c, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.16 (h+e,d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.08 (k, d, 4 H), 6.92 (i, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.85 (j,d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.81 (s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.62, 156.21, 151.91, 148.58, 144.58, 144.42, 140.88, 140.67, 132.52, 131.59, 131.49, 127.24, 126.86, 126.40, 126.20, 124.42, 123.08, 122.80,

120.50, 115.1, 114.89, 55.63. HRMS (EI): *m/z* 686.22346 calculated for C<sub>44</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S: *m/z* 686.22393.

**Synthesis of OA2**: Molecule **5** (0.434 g, 0.632 mmol) was dissolved in a minimal amount of CHCl<sub>3</sub> and cyanoacetic acid. Piperidine was then added. The mixture was refluxed overnight. The organic layer was washed with HCl 1 N and volatiles removed *in vacuo*. The crude was recrystallized in DCM:hexane (1:1) as a crimson red solid (0.217 g, 50 %). IR (cm<sup>-1</sup>) 2223.819, 1695.602. <sup>1</sup>H NMR (400 MHz, dimethylsulfoxided<sub>6</sub>):  $\delta$  = 8.22 (a,s, 2 H), 8.01 (b, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.70 (e,d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.47 (h+g,m, 3 H), 7.32 (f,d, 1 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.19 (c+d, m, 6 H), 7.03 (k,d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.91 (j,d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.77 (l, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.74 (l,s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.81, 163.67, 155.93, 152.98, 149.75, 148.08, 143.67, 143.28, 140.05, 139.69, 132.72, 131.53, 127.21, 126.82, 126.67, 126.15, 126.10, 125.09, 123.30, 122.79, 119.23, 116.56, 114.99, 100.70, 55.23. HRMS (ESI): *m/z* 819.22961 ((M-H]-) calculated for C<sub>50</sub>H<sub>35</sub>N<sub>4</sub>O<sub>6</sub>S<sup>-</sup>: *m/z* 819.22828





**Synthesis of 6:** Under an atmosphere of N<sub>2</sub>, para-tribromo-triphenylamine (1.5 g, 3.11 mmol) was dissolved in 150 mL of THF:H<sub>2</sub>O (9:1) and molecule **B** (1.475 g, 3.42 mmol) was added into the same flask. The flask was sparged for 15 minutes. The flask was charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) followed by NaOH (8 eq) and refluxed overnight. Volatiles were removed *in vacuo* and an extraction with DCM was performed. The crude was purified via column chromatography over silica using hexanes:EtOAc (7:3) affording the desired product as a white solid.(0.410 g, 19%).<sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$  = 7.44 (d, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.39-7.33 (a+d, m, 6 H), 7.08 (b+c, d, 6 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.97 (h, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.84 (f+g, d, 6 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.80(I, s, 6 H). Insolubility prevented the ability to acquire a suitable <sup>13</sup>C spectrum. HRMS (EI): *m*/z 704.06570 calculated for C<sub>38</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: *m*/z 704.06740.

**Synthesis of 7:** Under an atmosphere of N<sub>2</sub>, **6** (.410 g, 0.58 mmol) was dissolved in 60 mL of THF:H<sub>2</sub>O (9:1) and molecule **c** (0.344 g, 1.22 mmol) was added into the same flask. The flask was sparged for 15 minutes. The flask was charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) followed by NaOH (8 eq) and refluxed overnight. Volatiles were removed *in vacuo* and an extraction with DCM was performed. The crude was purified via column chromatography over silica using hexanes:EtOAc (7:3) affording the desired product as a red solid.( 0.023 g, 5 %).<sup>1</sup>H NMR (400 MHz, chloroform-d):  $\delta$  = 9.87(a, s, 2H), 7.72 (b, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.58 (d, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.51 (c, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.34 (h, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.18 (e+f, m, 6 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.09 (j, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.99 (i, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.85 (k, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.81 (l, s, 6 H). Insolubility prevented the ability to acquire a suitable <sup>13</sup>C spectrum. HRMS (ESI): *m*/z 768.21111 calculated for C<sub>48</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: *m*/z 768.21165.



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**Synthesis of OA3**: Molecule **7** (0.027 g, 0.03 mmol) was dissolved in a minimal amount of CHCl<sub>3</sub> and cyanoacetic acid. Piperidine was then added. The mixture was refluxed and monitored via thin layer chromatography. The organic layer was washed with HCl 1 N and volatiles removed *in vacuo*. The crude was recrystallized in DCM:hexane (1:1) as a crimson red solid (0.023 g, 84%). IR(cm<sup>-1</sup>) 2222.788, 1649.201. <sup>1</sup>H NMR (400 MHz, dimethylsulfoxide-d<sub>6</sub>): $\delta$  = 8.44 (a, s, 2), 8.00 (b, m, 2 H), 7.81 (d, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.67 (e, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.54 (c, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.30- 7.23 (g+h, m, 6 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.10 (k, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.93 (j+i, d, 6 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.80(I, s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, dimethylsulfoxide-d<sub>6</sub>)  $\delta$  200.01, 155.86, 147.16, 147.16, 144.51, 144.51, 139.98, 135.90, 135.70, 135.13, 134.93, 130.85, 130.75, 129.30, 127.26, 127.03, 126.80, 125.44, 125.43, 123.95, 123.73, 119.46, 118.80, 115.02, 55.29. HRMS (ESI): *m/z* 901.21652 ((M-H]-) calculated for C<sub>54</sub>H<sub>37</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>:: *m/z* 901.21600

**Synthesis of OA4**: diformyITPA (0.095 g, 0.32 mmol) was dissolved in a minimal amount of CHCl<sub>3</sub> and cyanoacetic acid. Piperidine was then added. The mixture was refluxed and monitored via thin layer chromatography. The organic layer was washed with HCl 1 N and volatiles removed *in vacuo*. The crude was recrystallized in DCM:hexane (1:1) as a dark orange solid (0.056 g, 40.2%). IR (cm<sup>-1</sup>) 2217.502, 1699.994. <sup>1</sup>H NMR (400 MHz, dimethylsulfoxide-d<sub>6</sub>):  $\delta$  = 8.22 (a, s, 2), 8.01 (b, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.48 (e,t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.33 (f, t, 1 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.23 (d, d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.16 (c, d, 4 H, <sup>3</sup>J<sub>HH</sub> = 8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, dimethylsulfoxide-d<sup>6</sup>)  $\delta$  199.40, 163.95, 154.21, 152.60, 150.28, 133.76, 132.19, 129.92, 123.50, 121.89, 116.94, 100.75. HRMS (ESI): *m/z* 432.11488 ((M-H]-) calculated for C<sub>26</sub>H<sub>16</sub>N<sub>3</sub>O<sub>4</sub>-: *m/z* 432.11463.



## <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra



























## **DSSC** Fabrication

Reagents and supplies used for DSSC fabrication were ordered from the suppliers listed below.

Required DSSC materials and suppliers

Item	Item Number	Supplier
FTO Coated Glass	735159	Sigma Aldrich
Titanium (IV) Chloride	208566	Sigma Aldrich
Titania Paste	798495	Sigma Aldrich
Silver Conductive Paste	735825	Sigma Aldrich
Surlyn Thermoplastic Sealant	MS004610	Greatcell Solar (Formerly Dyesol)
Predrilled Platinized Cathodes	MS001651	Greatcell Solar (Formerly Dyesol)

All anodes were fabricated using 2.3 mm thick, 7 ohm/sq (TEC 7) fluorine doped tin oxide (FTO), supplied by Sigma Aldrich. Titania films were prepared with Titanium Dioxide 22 nm, nanocrystalline colloidal paste for transparent film, >95% (Anatase (XRD)) supplied by Sigma Aldrich. Cathodes used were 3.2 mm thick, 15 ohm/sq (TEC 15) pre-platinized and pre-drilled, supplied by Dyesol. Spacers used were 30  $\mu$ m thick Suryn thermoplastic sealant, supplied by Dyesol.

#### Preparation of Fluorine Doped Tin Oxide Substrate

The process by which the FTO is treated, the titania is applied, and the dye is adsorbed, is laid out below for reference, but detailed descriptions are presented in the sections included below.



#### **Cutting Substrate**

The FTO was lightly scored with a glass cutter using a ruler (similar pressure to writing). When broken with pliers only a light amount of pressure was required. If the FTO did not break, rather than applying more pressure, the pliers were repositioned directly over the score line. If FTO still did not break, the FTO was rescored with a small increase in pressure. Pliers were clamped onto glass about 1 cm from the edge as the pliers could damage the FTO surface. When scoring glass, the shorter length of the overall piece was scored first as it was easier to be consistent and generate a clean break over a shorter distance. Lastly, when breaking the glass, the pliers were positioned so that the scored side of the glass would split (scored side facing up), increasing the chances of a clean break.

#### TiCl<sub>4</sub> (pre)Treatment

Deionised water was heated to 70°C in a beaker before TiCl<sub>4</sub> was added by needle and allowed to equilibrate in a fume hood for about 2 hours making a 0.05 M solution (appears pearly white and translucent). The bath was covered with a watch glass while not in use. Electrodes were gently lowered into the bath using tweezers and leaned on the wall so titania films were exposed to the solution. Electrodes were left in the 70 °C solution for 30 min before removing and rinsing clean, first with water, then after repositioning tweezers repeated once more. The overall rinse process was then repeated with EtOH.

#### **Titania Paste Application**

In the same progression as is shown below, Scotch tape was applied to the FTO coated side of the glass (note that only one face of the glass is coated with FTO and the opposite face will not conduct but will fluoresce blue under short wave UV light) to leave an approximately 7 mm x 9 mm square of FTO exposed. 2-3 drops of the titania paste were then placed on the tape directly adjacent to the area to be coated. A glass rod was then used to doctor blade (swipe the titania across the electrode leaving a thin film) the titania onto the electrode. The film was left to cure for ~30 seconds before the tape was then gently removed by pulling on the bottom piece. This ensured that the all pieces of tape were removed together and lowered the chances of damaging the film. The electrode was then allowed to sit in ambient conditions for about 10 min. During this 10 min, the titania film turned from an opaque white consistency to transparent. The anode was then heated to 125 °C for 6 min in a muffle furnace to remove any solvent, depositing a homogenous titania film on the anode (at this point the anodes may be stored until they are to be used).



Titania paste application to FTO glass

#### Cutting Counter Electrode

The counter electrode material came pre-scored, however additional scoring along the line in a similar manner to what was described earlier was needed to ensure a clean break. Once scored, the counter electrode was broken as described earlier.

#### Dye Adsorption

Before the dye was adsorbed, anodes were heated to 350 °C for 10 min, 450 °C for 15 min, and lastly 500 °C for 15 min in a muffle furnace before cooling to room temperature. Another TiCl<sub>4</sub> bath was prepared and the anodes were treated and rinsed as described earlier. The anodes were sintered at 500 °C for 30 min and allowed to cool to room temperature slowly in the muffle furnace. A dilute solution of the dye (0.30mmol/L in EtOH) was prepared in a small beaker and transferred to Teflon dipping chambers or glass beakers as required. Once the anodes cooled (after the previously mentioned TiCl<sub>4</sub> bath and sintering), they were dipped into the dye solution ensuring the TiO<sub>2</sub> area was fully submerged and was not covered by the wall or another anode. The beaker was covered with parafilm and left overnight (16 h).



Adsorption of dye to titania film on anode

When the anodes were removed from the dye solution, the titania film had turned the colour of the dye as seen above. The anodes were then rinsed with EtOH and allowed to dry on the benchtop for about 5 min. It should be noted that saturation of the titania with dye molecules is assumed to take place over the 16 h dipping period. However, to investigate different dye loadings, UV-vis absorption spectroscopy could be carried out and the molar extinction coefficient used to determine relative differences in loading relative to a standard solution. This was done in this study and within the error of the measurement (UV-Vis – absorption mode), dye loadings appeared near parity.

#### **Cutting Spacer**

A border of 30  $\mu$ m Surlyn thermoplastic sealant about 2 mm wide was cut to fit around the active area leaving about 1 mm between the active area and the border (as seen below).



Surlyn border cut to fit around the titania film

#### Adhesion of Cathode and Anode

The Surlyn border was carefully placed on the anode and the cathode placed on top with the platinized surface facing the anode. When aligning the two electrodes there were a few important considerations to be mindful of to ensure optimal performance. First, it was important to ensure that the platinized portion of the cathode covered the entire active area as the platinum catalyzes reduction of the electrolyte. Second, the fill hole needed to be as centered as possible on the active area as this reduced the distance the electrolyte needed to diffuse during injection increasing the chances of a complete filling. Lastly, there needed to be sufficient overhang on the cathode and anode so that silver paste (bus bars) could be applied and alligator clips could be attached. Often these priorities will conflict with each other in which case a balance needs to be struck. Once the electrodes are optimally aligned, as demonstrated below, the two electrodes with the cathode side down were pressed firmly onto a hot plate with a cork ring (~185 °C measured by IR thermometer) for about 25 seconds to melt the Surlyn, sealing the electrodes together. The cork ring was rolled back and forth over the DSSC and periodically visually inspected to ensure sealing was occurring uniformly. The presence of bubbles in the Surlyn indicates unsealed portions and that further heat and pressure is required.



Alignment of anode and cathode for adhesion together

#### **Electrolyte Preparation**

Multiple electrolyte mixtures were tested and are described fully in the appendix, however, the baseline mixture chosen was a version of the Z1137 electrolyte which is described fully below. This mixture was chosen because it was used for previous studies<sup>61</sup> with the dye L1 which allowed for comparisons and validation of the fabrication method. The mixture differed in that it used MeCN as a solvent rather than an MeCN:valeronitrile (85:15, v/v) mixture. This change was made to simplify the mixture and decrease viscosity allowing for easier electrolyte injection. The DMII, I<sub>2</sub>, and NaI were added to supply the iodide for the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple. The GuNCS has historically been added because many ruthenium based dyes have incorporated thiocyanate ligands and having additional thiocyanate present in the electrolyte mixture could allow for re-coordination to the metal if they came detached. Presently they are included for consistency sake however. The 4-TBP, as discussed earlier in section 1.7.3, was added to fill trap states in the titania.

Name	Short	Concentration
1,3-dimethylimidazolium iodide	DMII	0.55 M
Iodine	I <sub>2</sub>	60 mM
t-butylpyridine	4-TBP	0.5 M
Sodium iodide	Nal	0.05 M
Guanidinium thiocyanate	GuNCS	0.1 M
Acetonitrile	MeCN	Solvent

#### Z1137 iodide electrolyte composition

#### **Electrolyte Injection**

An O-ring was placed around the fill hole in the cathode and the filling apparatus, which is depicted below was placed onto the O-ring. The stopcock was turned to the vacuum and allowed to evacuate for ~ 2 minutes and 30 seconds (A strong vacuum such as a high vac needed to be used). Next, the stopcock was closed to place the system under a static vacuum. A small quantity of the electrolyte (~0.3 mL) was drawn into a syringe and any air present was pressed out. The needle was then carefully inserted through the septum. 3-4 drops of electrolyte were then injected directly into the fill hole and the needle carefully removed. Looking perpendicular to the fill hole, the DSSC was inspected to make sure the electrolyte had entered the fill hole and then gently shaken to allow the electrolyte to permeate into the edges of the cavity. Next, the DSSC was lowered just above the bench and the vacuum was released allowing the DSSC to fall to the lab bench. As air moved into the apparatus, electrolyte was pushed into the cavity filling it. Any residual electrolyte was wiped off the surface of the DSSC.



Front and side view of DSSC filling apparatus with vacuum hose and septum appropriately placed (designed and fabricated by Dirk Verdoold at York University)

#### Sealing DSSC

The DSSC was left to sit for a few min before sealing, as electrolyte can wick out of the fill hole. Once ready, a small piece of Surlyn was placed over the fill hole and a microscope cover slip was placed over top of the Surlyn. The cover slip was heated with a soldering iron until the Surlyn melted, sealing the DSSC. As described earlier, if any bubbles are present in the Surlyn, the sealing process is incomplete.

#### Silver Paste Application

The silver paste was painted onto the edge of the FTO side of the anode and cathode to increase conductivity to the wires. This was completed with consideration not to connect the cathode and anode with the paste creating a short circuit. Once dried, the DSSC was ready for testing.

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