# Supporting Information

Origins of Device Performance in Dicarboxyterpyridine Ru (II) Dye-Sensitized Solar Cells

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### **Synthetic Experiments**

**General procedures**: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

## Synthesis of L1

Compound 2-(tributylstannyl)-4-(trifluoromethyl)pyridine (2.05 g, 4.7 mmol), diethyl 6-bromo-2,2'-bipyridine-4,4'-dicarboxylate (1.3 g, 3.6 mmol), PdCl<sub>2</sub> (24.3 mg, 0.14 mmol), CuI (52 mg, 0.27 mmol), CsF (1.04 g, 6.9 mmol) and PBu<sup>t</sup><sub>3</sub> (0.68 mL, 0.27 mmol) were suspended in dry DMF (80 mL). The mixture was heated to 80 °C for 12 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over MgSO<sub>4</sub>. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate : CH<sub>2</sub>Cl<sub>2</sub> = 1 : 5) to give white solid (433 mg, 27%).



#### Synthesis of PRT-15-Et

Compound L1 (329 mg, 0.74 mmol) and RuCl<sub>3</sub>·3H<sub>2</sub>O (194 mg, 0.74 mmol) were dissolved in ethanol. The mixture was heated to 90 °C for 4 h. After cooling to room temperature, the precipitate was vacuum filtered from the red solution. The product was washed with cold ethanol followed by rinsing with diethyl ether, and air dried to give black powder (413 mg). Next, this powder and TBANCS (1.65 g, 5.52 mmol) were dissolved in dry DMF (30 mL). The mixture was heated to 145°C for 4 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (ethyl acetate :  $CH_2Cl_2 = 1 : 3$ ) to give complex **PRT-15-Et** (271 mg, 38%).



PRT-15-Et

Selected spectral data of **PRT-15-Et**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  9.11 (d,  $J_{\text{HH}}$  = 5.2 Hz, 1H), 9.07 (d,  $J_{\text{HH}}$  = 5.2 Hz, 1H), 8.64 (s, 2H), 8.57 (s, 1H), 8.27 (s, 1H), 8.01 (d,  $J_{\text{HH}}$  = 5.6 Hz, 1H), 7.68 (d,  $J_{\text{HH}}$  = 5.6 Hz, 1H), 4.58 ~ 4.49 (m, 4H), 3.34 (t,  $J_{\text{HH}}$  = 7.2 Hz, 8H), 1.70 ~ 1.64 (m, 8H), 1.57 ~ 1.45 (m, 6H), 1.19 ~ 1.15 (m, 8H), 0.92 (t,  $J_{\text{HH}}$  = 7.6 Hz, 12H).

#### **Synthesis of PRT-15**

Compound **PRT-15-Et** (180 mg, 0.19 mmol) was dissolved in a mixture of acetone (20 mL) and 1 M TBAOH (0.94 mL, 0.93 mmol) in MeOH. The solution was heated to 60 °C for 2 h. After then, the solvent was removed and solid was dissolved in H<sub>2</sub>O (10 mL). The solution was titrated with 1 M HNO<sub>3</sub> to pH 2 to precipitate powdery solid. The product was washed with deionized water and diethyl ether in sequence, giving black solid (155 mg, 90%).



Selected spectral data of **PRT-15**: <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$  9.24 (d,  $J_{\text{HH}} = 5.6$  Hz, 1H), 9.13 (d,  $J_{\text{HH}} = 5.6$  Hz, 1H), 9.02 (s, 1H), 8.92 (s, 2H), 8.84 (s, 1H), 8.20 (d,  $J_{\text{HH}} = 5.6$  Hz, 1H), 8.03 (d,  $J_{\text{HH}} = 5.6$  Hz, 1H), 3.23 (t,  $J_{\text{HH}} = 7.2$  Hz, 8H), 1.69 ~ 1.61 (m, 8H), 1.43 ~ 1.28 (m, 8H), 0.98 (t,  $J_{\text{HH}} = 7.6$  Hz, 12H). Anal. Calcd for C<sub>76</sub>H<sub>96</sub>F<sub>6</sub>N<sub>8</sub>O<sub>8</sub>RuS<sub>4</sub>•2Et<sub>2</sub>O: C, 51.08; N, 9.78; H, 6.00. Found: C, 1.22; N, 9.29; H, 6.30.

## **Dye Loading Measurement**

The dye loading on the  $TiO_2$  film was estimated from UV-vis absorption value of the desorption dye in 0.5 M tetrabutylammonium hydroxide (TBAOH) solution.  $TiO_2$  films with thickness of 8 µm were employed.

## **DFT Calculation**

The geometry optimization of PRT-15 was performed at B3LYP/LANL2DZ (Ru), 6-31G\* (H, C, N, O, S) level in the gas phase. The optimized structure was then used to calculate 60 lowest energy optical excitations with the incorporation of continuous solvent effect using TDDFT method. To mimic the realistic environmental perturbation, a polarizable continuum model (PCM) was applied using dimethylformamide (DMF) as solvent. The frontier orbitals as well as other excitation properties pertinent to the singlet optical transitions were listed in the following table S1. All of the theoretical approaches were carried out using Gaussian 09, Revision A. 02 package.<sup>1</sup>

Table S1. Th	e energies,	transition	probabilities	and charge	transfer cl	haracter of	the
singlet optica	l transition	s for <b>PRT</b>	-15 in DMF.				

State	$\lambda_{cal} (nm)$	f	Assignments	MLCT
1	730	0.0172	HOMO-1→LUMO(95%)	27.98%
2	669.3	0	HOMO-2→LUMO(94%)	28.61%
3	664.8	0.0551	HOMO→LUMO(87%)	26.69%

			HOMO-1→LUMO+1(9%)	
4	577.4	0.0392	HOMO→LUMO+1(95%)	31.67%
5 5			HOMO-1→LUMO+1(85%)	
	541.5	0.0254	HOMO→LUMO(8%)	32.60%
6	525.4	0	HOMO-2→LUMO+1(96%)	35.34%
_	100.0	0.01.66	HOMO-3→LUMO(92%)	<b>5</b> 0 <b>2</b> 0/
1	480.8	0.0166	HOMO→LUMO+2(7%)	-5.82%
8	467.6	0.0001	HOMO-4→LUMO(99%)	-8.14%
	1.57	0.0505	HOMO→LUMO+2(86%)	<b>2</b> 0.000/
9	467.4	0.0727	HOMO-3→LUMO(6%)	29.99%
10	462.9	0.0187	HOMO-5→LUMO(99%)	-8.40%
11	460	0.0687	HOMO-1→LUMO+2(94%)	35.70%
12	436.2	0	HOMO-2→LUMO+2(96%)	37.41%
13	427.6	0.0169	HOMO→LUMO+3(97%)	32.82%
14	415.8	0.0015	HOMO-3→LUMO+1(97%)	-2.58%
15	410.5	0.0202	HOMO-1→LUMO+3(91%)	33.05%
16	402.8	0.0031	HOMO-4→LUMO+1(98%)	-1.81%
17	401.4	0.0002	HOMO-6→LUMO(88%)	31.67%
18	401.1	0.0004	HOMO-5→LUMO+1(97%)	-2.05%
19	398.9	0	HOMO-2→LUMO+3(94%)	35.07%
20	396.6	0.0061	HOMO-7→LUMO(94%)	23.04%
		0	HOMO-1→LUMO+5(81%)	
21	370.4		HOMO-7→LUMO+5(13%)	-27.73%
			HOMO-3→LUMO+2(42%)	
22	364.9	0.0001	HOMO→LUMO+4(42%)	17.61%
			HOMO-8→LUMO(13%)	
			HOMO-3→LUMO+2(57%)	
23	362.3	0.0132	HOMO→LUMO+4(34%)	13.35%
			HOMO-8→LUMO(7%)	
24	358.2	0.0003	HOMO-1→LUMO+4(94%)	35.66%
			HOMO-8→LUMO(54%)	
25	356.1	0.0099	HOMO-7→LUMO+1(19%)	24.78%
			$HOMO \rightarrow LUMO + 4(19\%)$	
26	353.1	0	HOMO-4→LUMO+2(99%)	0.31%
27	351.5	0.0007	HOMO-5→LUMO+2(100%)	0.05%
28	349.1	0	HOMO-6→LUMO+1(91%)	38.55%

29		0.0007	HOMO-2→LUMO+5(57%)	
	347.1		HOMO-2→LUMO+7(17%)	24 2304
	347.1	0.0007	HOMO-6→LUMO+5(14%)	-24.3370
			HOMO-6→LUMO+7(6%)	
30	339.5	0	HOMO-2→LUMO+4(97%)	37.76%
			$HOMO \rightarrow LUMO + 5(48\%)$	
31	337.3	0.0042	HOMO→LUMO+7(37%)	-27.08%
			HOMO-8→LUMO+7(5%)	
			HOMO-3→LUMO+3(65%)	
32	335.1	0.0099	HOMO-7→LUMO+1(14%)	6.10%
			HOMO-8→LUMO+1(11%)	
			HOMO-7→LUMO+1(38%)	
33	333.0	0.0374	HOMO-3→LUMO+3(34%)	15 7604
55	555.7	0.0374	HOMO-8→LUMO+1(11%)	15.7070
			HOMO-8→LUMO(7%)	
			HOMO-9→LUMO(36%)	
34	331.5	0.0973	HOMO-8→LUMO+1(29%)	12.38%
			HOMO-7→LUMO+1(20%)	
35	324.6	0.0006	HOMO-4→LUMO+3(99%)	-1.34%
36	323.1	0.2381	HOMO-9→LUMO(44%)	0.48%
50			HOMO-8→LUMO+1(42%)	9.40%
37	322.9	0	HOMO-5→LUMO+3(100%)	-1.61%
20	313.8	0	HOMO→LUMO+7(48%)	25 420/
30			HOMO→LUMO+5(38%)	-23.42%
39	308.7	0	HOMO-6→LUMO+2(94%)	41.85%
40	303.2	0.2182	HOMO-7→LUMO+2(87%)	28.74%
			HOMO-2→LUMO+7(57%)	
41	296.5	0.0132	HOMO-2→LUMO+5(19%)	-21.48%
			HOMO-6→LUMO+7(11%)	
42	294.8	0.0009	HOMO-3→LUMO+4(98%)	-0.53%
10	201.1	0.000	HOMO-8→LUMO+2(77%)	22.0.00
43	291.1	0.026	HOMO-9→LUMO+1(9%)	23.96%
	000.0	0	HOMO-1→LUMO+7(87%)	24.50%
44	289.9	0	HOMO-7→LUMO+7(7%)	-24.50%
45	288.7	0.0001	HOMO-6→LUMO+3(93%)	39.86%
46	287.4	0	HOMO-4→LUMO+4(96%)	0.26%
47	286.3	0.0004	HOMO-5→LUMO+4(100%)	0.01%

			HOMO-7→LUMO+3(39%)		
48	284	0.2041	HOMO-9→LUMO+1(38%)	16.40%	
			HOMO-8→LUMO+2(13%)		
49 283			HOMO-12→LUMO(44%)		
	283.8	0.0001	HOMO-11→LUMO(37%)	-7.50%	
			HOMO-12→LUMO+2(7%)		
			HOMO-11→LUMO(33%)		
			HOMO-12→LUMO(30%)		
50	2827	0.0001	HOMO-11→LUMO+2(10%)	6 35%	
50	202.7	0.0001	HOMO-11 $\rightarrow$ LUMO+1(10%)	-0.33%	
			HOMO-12→LUMO+1(6%)		
			HOMO-12→LUMO+2(6%)		
			HOMO-7→LUMO+3(48%)		
51	278	0.0498	HOMO-9→LUMO+1(37%)	14.69%	
			HOMO-10→LUMO(7%)		
52	272.9	0.0063	HOMO-8→LUMO+3(94%)	27.65%	
	268.2	0.005	HOMO-9→LUMO+2(46%)		
52			HOMO-10→LUMO(26%)	5 5404	
55			HOMO $\rightarrow$ LUMO+6(10%)	5.54%	
			HOMO-1→LUMO+6(7%)		
54	265.8	0.0073	HOMO $\rightarrow$ LUMO+6(82%)	28 54%	
54	203.8		HOMO-10→LUMO(9%)	28.3470	
			HOMO-1→LUMO+6(33%)		
55	263.5	0.0986	HOMO-9→LUMO+2(31%)	14 41%	
55	203.5	0.0980	HOMO-10→LUMO(15%)	14.4170	
			HOMO→LUMO+6(6%)		
56	261.6	0.080	HOMO-1→LUMO+6(53%)	17 58%	
50	201.0	0.089	HOMO-10→LUMO(37%)	17.38%	
57	257.4	0	HOMO-6→LUMO+4(97%)	43.15%	
	256.1		HOMO-7→LUMO+4(76%)		
58		0.0005	HOMO-10→LUMO+1(9%)	25.17%	
			HOMO-9→LUMO+2(6%)		
59	253.7	0	HOMO-2→LUMO+6(97%)	37.88%	
60	240.6	0.0095	HOMO-9→LUMO+3(80%)	2 620/	
60	249.6		HOMO-7→LUMO+4(6%)	2.03%	





**Figure S1**. Frontier orbitals (from HOMO-12 to LUMO+7) pertinent to the singlet optical transitions for the newly synthesized **PRT-15** dye. The isovalue for the contours is set to be 0.02.



**Figure S2**. HOMO and LUMO of **PRT-11** ~ **PRT-15** dyes.<sup>2</sup> The isovalue for the contours is set to be 0.02. See ref. 2 for more detailed description of frontier orbitals



**Figure S3.** The wavelength-dependent absorbance of iodine  $(\alpha_t(\lambda))$  and the transmission of FTO  $(T_{FTO}(\lambda))$  and platinum-coated FTO  $(T_{FTO}(\lambda)T_{Pt}(\lambda))$ .

Tab	le S2	. Groun	d state	and	excited	state	oxidation	potential	of	all	PRT	sensitizers
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	N749	PRT-11	<b>PRT-12</b>	PRT-13	PRT-14	PRT-15
$E_{LUMO}\left(V ight)$	-0.77	-0.85	-0.81	-0.81	-0.80	-0.76
$E^{\circ}_{OX}(V)$	0.89	0.84	0.85	0.85	0.86	0.91

 $E_{OX}^{\circ}$  (*vs.* NHE) was measured in DMF with 0.1 M (*n*-Bu<sub>4</sub>N)PF<sub>6</sub>, while the oxidation potential at the excited state (E<sub>LUMO</sub>) is calculated from the equation  $E_{LUMO} = E_{ox} - E_{0-0}$ , for which  $E_{0-0}$  was determined from the intersection of the absorption and tangent of the emission peak.

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