

Novel Poly-pyridyl Ruthenium Complexes with Bis- and Tris-tetrazolate Mono-dentate Ligands for Dye Sensitized Solar Cells

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Experimental

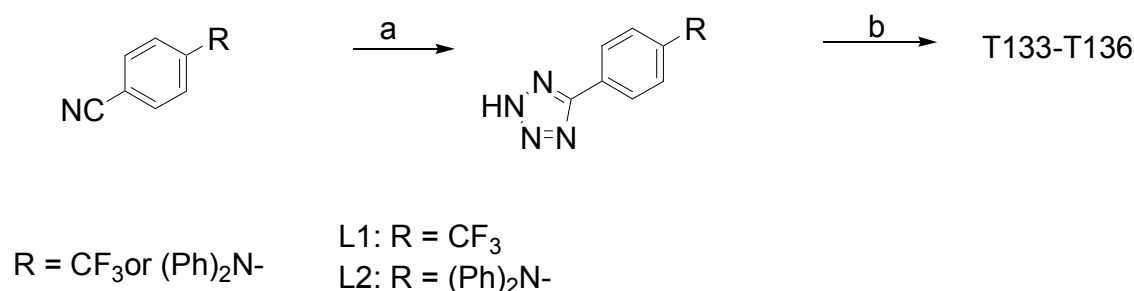
Materials and Instrumentation. All organic chemicals were purchased from Sigma-Aldrich and used as supplied. The N719 dye was purchased from Solaronix (Switzerland). FTO glass "Tec15" was purchased from Pilkington (USA). TiO₂ colloids were purchased from Dyesol (Australia). 4-(Diphenylamino)benzotrile,^[1] (dcbpy)₂RuCl₂^[2] and (4,4',4''-trimethoxycarbonyl-2,2':6',2''-terpyridine)RuCl₃^[3] were prepared according to reported procedures in the literature. The NMR spectra (¹H and ¹³C) were measured on a Bruker AM 300 MHz spectrometer. UV-vis spectra were recorded on a Jasco V-570 UV/vis/NIR. Steady state and lifetime emission spectra were measured on a JobinYvon Horiba Fluorolog-3 spectrofluorometer. The electrochemical setup consisted of a three-electrode cell, with a stained TiO₂ film on FTO with the respective dye as the working electrode, a Pt wire ~ 1 mm diameter as the counter electrode, and Ag/Ag⁺ (10 mM AgNO₃) as the reference electrode. All solution phase electrochemical measurements were done in 0.1 M tetra-butyl ammonium hexafluorophosphate (TBAPF₆) in DMF, and Fc/Fc⁺ standard (0.69 vs NHE in DMF) was used as a reference. Electrochemical impedance spectra of the DSSCs were performed with a CH Instruments 760B (USA). The obtained impedance spectra were fitted with the Z-view software (v2.8b, Scribner Associates Inc.), and the reported fitted parameters are within a 2% error. The spectra were performed at a forward bias voltage (between -0.5 and -0.8 V) in the frequency range 0.1 Hz - 10⁵ Hz with oscillation potential amplitudes of 10 mV at RT under open circuit conditions at different light levels. The photo-anode was connected to the working electrode. The Pt based cathode was connected to the auxiliary electrode and the reference electrode. IPCE spectra were recorded using a Newport 74000 Cornerstone™ monochromator and a solar simulator illuminated by a Xenon arc lamp (Oriel) through an AM1.5 simulation filter (ScienceTech). Photocurrent vs. Voltage characteristics were measured with a Keithley 2400 sourcemeter. The irradiated area of the cell was 0.126 cm².

Computational Methods. Calculations were carried out using *Gaussian 03*.^[4] Geometries were optimized using the 6-31G* basis set with (B3LYP), together with the Los Alamos effective core potential LanL2DZ^[5] in water (C-PCM algorithm).^[6] TD-DFT calculations were performed using the C-PCM with water as the solvent. Fifty singlet excited states were determined from the optimized structures.

Solar Cell Fabrication. Dye sensitized solar cells were fabricated using standard procedures. The TiO₂ films were made from colloidal solutions using the doctor blading method (2x times) and then heated to 480 °C for 30 mins. This afforded a 12 μm thick TiO₂ film, on top of which a 4 μm TiO₂ scattering layer (300 nm TiO₂ particles) was deposited and

reheated at 480 °C for 30 mins. A TiCl₄ post-treatment was applied to the films following reported procedures in the literature.^[7] These films were then reheated at 480 °C for 30 min. The TiO₂ films were stained by the respective dye solution (0.3 mM) in ethanol for 18 h. The counter electrodes were fabricated by applying a 2-3 μl/cm² of 5 mM H₂PtCl₆ in 2-propanol to the FTO glass, followed by heating in an oven at 400 °C for 20 minutes. Cells assemblies were formed by sealing the counter electrodes to the TiO₂ electrode with a 60 μm Surlyn (Dupont) spacer at ~ 100 °C for 3 mins. The corresponding electrolyte was introduced through two small holes, previously drilled through the counter electrode, which were then sealed with Surlyn.

Preparation of T133 to T136:



Scheme S1: a) NaN₃, NH₄Cl, 120 °C, 24 h in DMF, b) for T133-T134 (dcbpy)₂RuCl₂ and for T135-T136 (4,4',4''-trimethoxycarbonyl-2,2':6',2''-terpyridine)RuCl₃, reflux 24 h in EtOH:*N*-methylmorpholine:water 5:1:1.

CAUTION! *Tetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems during the synthesis, proper protective measures should be used when undertaking work involving these compounds.*

Preparation of 5-(4-(trifluoromethyl)phenyl)-2H-tetrazole, L1: To a solution of 4-(trifluoromethyl)benzonitrile (1.00 g, 5.85 mmol) in DMF (100 mL) was added sodium azide (1.14 g, 17.55 mmol) and ammonium chloride (0.96 g, 17.55 mmol). The reaction mixture was stirred for 24 h at 120 °C. After being cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with ethyl acetate and washed with brine and dried over MgSO₄, filtered and concentrated under vacuum. Purification was accomplished via silica gel column chromatography using hexane:ethyl acetate (2:1) as an eluent to afford 5-(4-(trifluoromethyl)phenyl)-2H-tetrazole as a pure white solid (0.96 g, 77 % yield). ¹H-NMR (300 MHz, CDCl₃): δ 16.19 (*br s*), 8.26 – 8.23 (*d*, *J* = 8.1 Hz, 2H), 7.97 – 7.94 (*d*, *J* = 8.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) 131.54 – 130.26 (*q*, *J* = 31.87 Hz), 128.35, 127.66, 126.36 – 126.21 (*q*, *J* = 3.67 Hz), 125.56, 121.95. APPI MS (*m/z*): calculated for C₈H₅F₃N₄ [M - H⁺]⁻, 213.0; found, 212.7.

Preparation of *N,N*-diphenyl-4-(2H-tetrazol-5-yl)benzenamine, L2: To a solution of 4-(diphenylamino)benzonitrile (1.00 g, 3.70 mmol) in DMF (100 mL) was added sodium azide (0.72 g, 11.11 mmol) and ammonium chloride (0.61 g, 11.11 mmol). The reaction mixture was stirred for 24 h at 120 °C. After being cooled to room temperature, the solvent was evaporated under reduced pressure. The

residue was extracted with water and ethyl acetate (30 ml x 3). The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. Purification was accomplished via silica gel column chromatography using hexane:ethyl acetate (2:1) as an eluent to afford *N,N*-diphenyl-4-(2H-tetrazol-5-yl)benzenamine as a pure solid (0.78 g, 68 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.89 – 7.86 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.16 – 7.09 (m, 8H). ¹³C NMR (75 MHz, CDCl₃) 150.85, 146.61, 129.61, 128.30, 125.64, 125.15, 124.38, 121.38, 115.64. APPI MS (*m/z*): calculated for C₁₉H₁₄N₅ [M - H⁺]⁻, 312.1; found, 311.9.

General method for the preparation of the ruthenium complexes T133 and T134: The corresponding ligand L1 or L2 (2 eq.), (dcbpy)₂RuCl₂ (1 eq.) were refluxed overnight under N₂ in 5:1:1 ethanol: water: *N*-methylmorpholine. The solvent was then taken off under vacuum and the obtained dark solid was dissolved in water containing excess tetra-butyl ammonium hydroxide (TBAOH) and applied to a preparative C18-column. The compound was purified by a gradient elution with water/methanol 100%:0% to 80%:20%. Concentrating the solvent that contains the major band under reduced pressure and acidifying to pH 4.2 with 0.1 M HNO₃ resulted in a dark precipitate. The solid was filtered to yield a dark solid, which was dried under vacuum at 60 °C for 24 h. This afforded the two dyes with one TBA⁺ as a counter cation with quantitative yields.

T133.TBA: ¹H NMR (300 MHz, MeOD): δ 10.07 – 10.05 (d, *J* = 5.7 Hz, 2H), 8.94 (s, 2H), 8.82 (s, 2H), 8.16 – 8.13 (d, *J* = 6.1 Hz, 2H), 8.07 – 8.05 (d, *J* = 6.1 Hz, 2H), 7.74 – 7.64 (m, 6H), 7.3 – 7.24 (m, 8H), 7.06 – 6.95 (m, 16H), 3.22 – 3.16 (m, 8H), 1.67 – 1.56 (m, 8H), 1.43 – 1.28 (m, 8H), 1.00 – 0.95 (t, *J* = 7.2 Hz, 12H). APPI MS (*m/z*): calculated for C₇₈H₇₉N₁₅O₈Ru [M - H⁺]⁻, 1454.5; found, 1453.7.

T134.TBA: ¹H NMR (300 MHz, MeOD): δ 9.88 – 9.86 (d, *J* = 5.7 Hz, 2H), 8.91 (d, *J* = 1.2 Hz, 2H), 8.79 (d, *J* = 1.2 Hz, 2H), 8.12 – 8.10 (dd, *J*₁ = 5.7 Hz, *J*₂ = 1.5 Hz, 2H), 8.01 – 7.95 (m, 6H), 7.64 – 7.60 (m, 6H), 3.24 – 3.18 (m, 8H), 1.69 – 1.58 (m, 8H), 1.45 – 1.33 (m, 8H), 1.02 – 0.97 (t, *J* = 7.2 Hz, 12H). APPI MS (*m/z*): calculated for C₅₆H₅₉F₆N₁₃O₈Ru [M - H⁺]⁻, 1256.2; found, 1256.1.

General method for the preparation of the ruthenium complexes T135 and T136: The corresponding ligand L1 or L2 (6 eq., excess), (4,4',4''-trimethoxycarbonyl-2,2':6',2''-terpyridine)RuCl₃ (1 eq.) were refluxed overnight under N₂ in 5:1:1 ethanol: water: *N*-methylmorpholine. The solvent was then taken off under vacuum and the obtained dark solid was dissolved in water containing excess tetra-butyl ammonium hydroxide (TBAOH), refluxed for 2 hr and then applied to a preparative C18-column. The compound was purified by a gradient elution with water/methanol 100%:0% to 80%:20%. Concentrating the solvent that contains the major band under reduced pressure and acidifying to pH 4.2 with 0.1 M HNO₃ resulted in a dark precipitate. The solid was filtered to yield a dark solid, which was dried under vacuum at 60 °C for 24 h. This afforded the two dyes with two TBA⁺ as counter cations with quantitative yields.

T135.2TBA: ¹H NMR (300 MHz, MeOD) δ 10.34 – 10.32 (d, *J* = 5.7 Hz, 2H), 8.90 (s, 4H), 8.45 – 8.42 (d, *J* = 8.1 Hz, 2H), 8.18 – 8.15 (d, *J* = 5.7 Hz, 2H), 7.82 – 7.79 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.73 (d, *J* = 8.1 Hz, 4H), 7.54 – 7.51 (d, *J* = 8.1 Hz, 4H), 3.21 – 3.15 (m, 16H), 1.61 – 1.56 (m, 16H), 1.38 – 1.31 (m, 16H), 1.01 – 0.97 (t, *J* = 7.2 Hz, 24H). APPI MS (*m/z*): calculated for C₇₄H₉₄F₉N₁₇O₆Ru [M - H⁺]⁻, 1588.7; found, 1587.4.

T136.2TBA: ¹H NMR (300 MHz, MeOD) δ 9.95 – 9.93 (d, *J* = 5.7 Hz, 2H), 8.79 – 8.77 (m, 4H), 8.08 – 8.01 (m, 4H), 7.40 – 7.37 (d, *J* = 8.7 Hz, 4H), 7.31 – 7.18 (m, 9H), 7.10 – 6.92 (m, 14H), 6.81 – 6.78 (d, *J*

= 8.7 Hz, 4H), 3.21 – 3.15 (m, 16H), 1.61 – 1.56 (m, 16H), 1.38 – 1.31 (m, 16H), 1.01 – 0.97 (t, $J = 7.2$ Hz, 24H). APPI MS (m/z): calculated for $C_{107}H_{124}N_{20}O_6Ru$ [$M - H^+$] $^-$, 1886.3; found, 1886.4.

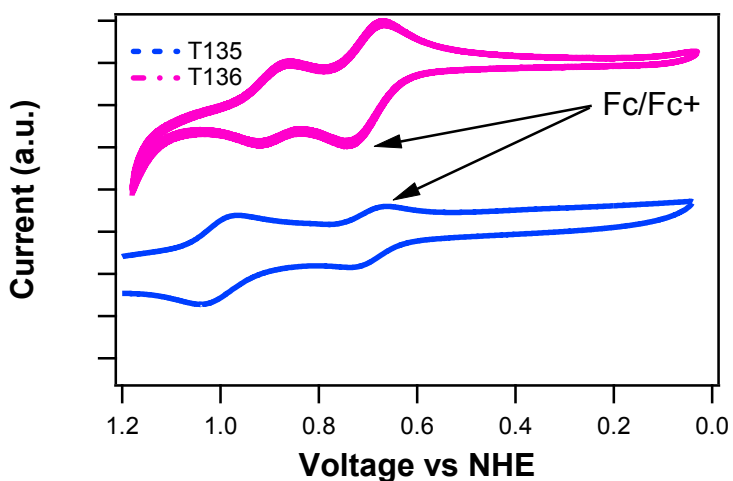


Figure S1: Cyclic voltammograms (0.1 M Bu_4NPF_6 , DMF) scan for T135 and T136.

Table S1: Calculated Spectroscopic Data for T133 to T136

Dye	TDDFT excitation energies, nm	Oscillator Strength ^a	Assignment
T133	694.6	0.0191	HOMO - -> LUMO(79%) HOMO-2 - -> LUMO(18%)
	644.4	0.0122	HOMO-1 - -> LUMO(80%) HOMO - -> LUMO+1(11%) HOMO-2 - -> LUMO+1(5%)
	613.9	0.0123	HOMO-1 - -> LUMO+1(92%)
	481.7	0.1784	HOMO-4 - -> LUMO(40%) HOMO-1 - -> LUMO+2(27%) HOMO-1 - -> LUMO+3(13%) HOMO-3 - -> LUMO+1(8%)
	481.0	0.1044	HOMO-1 - -> LUMO+2(36%) HOMO-4 - -> LUMO(30%) HOMO-1 - -> LUMO+3(12%) HOMO - -> LUMO+2(11%)
T134	624.0	0.0254	HOMO - -> LUMO(97%)
	608.1	0.0138	HOMO - -> LUMO+1(94%)
	533.6	0.0119	HOMO-1 - -> LUMO+1(56%) HOMO-1 - -> LUMO(31%) HOMO-2 - -> LUMO(7%)
	481.8	0.1548	HOMO-2 - -> LUMO(82%) HOMO-1 - -> LUMO+1(9%) HOMO - -> LUMO+2(7%)
	443.6	0.1525	HOMO - -> LUMO+2(91%) HOMO-2 - -> LUMO(5%)

T135	662.1	0.0368	HOMO --> LUMO(74%) HOMO-1 --> LUMO(19%)
	572.8	0.0546	HOMO-1 --> LUMO(70%) HOMO --> LUMO(12%) HOMO --> LUMO+1(7%) HOMO-1 --> LUMO+1(6%)
	542.6	0.0516	HOMO --> LUMO+1(85%) HOMO --> LUMO(6%)
	442.7	0.1323	HOMO --> LUMO+2(43%) HOMO --> LUMO+3(30%) HOMO-1 --> LUMO+1(19%)
T136	712.3	0.0311	HOMO --> LUMO(75%) HOMO-3 --> LUMO(13%) HOMO-4 --> LUMO(7%)
	630.3	0.0369	HOMO-1 --> LUMO(86%) HOMO-4 --> LUMO(6%)
	586.8	0.0519	HOMO --> LUMO+1(54%) HOMO-4 --> LUMO(28%) HOMO-3 --> LUMO+1(11%)
	555.0	0.0205	HOMO-3 --> LUMO(55%) HOMO-4 --> LUMO(19%) HOMO-4 --> LUMO+1(10%) HOMO --> LUMO+1(6%)
	494.5	0.0272	HOMO --> LUMO+2(79%) HOMO-3 --> LUMO+2(9%) HOMO-4 --> LUMO+1(8%)
	488.9	0.0128	HOMO-3 --> LUMO+1(56%) HOMO-5 --> LUMO+1(24%) HOMO --> LUMO+1(14%)
	466.5	0.0138	HOMO --> LUMO+3(66%) HOMO-3 --> LUMO+3(12%) HOMO-4 --> LUMO+1(12%) HOMO-2 --> LUMO+2(5%)

^a Only bands with oscillator strength $f \geq 0.01$ are listed

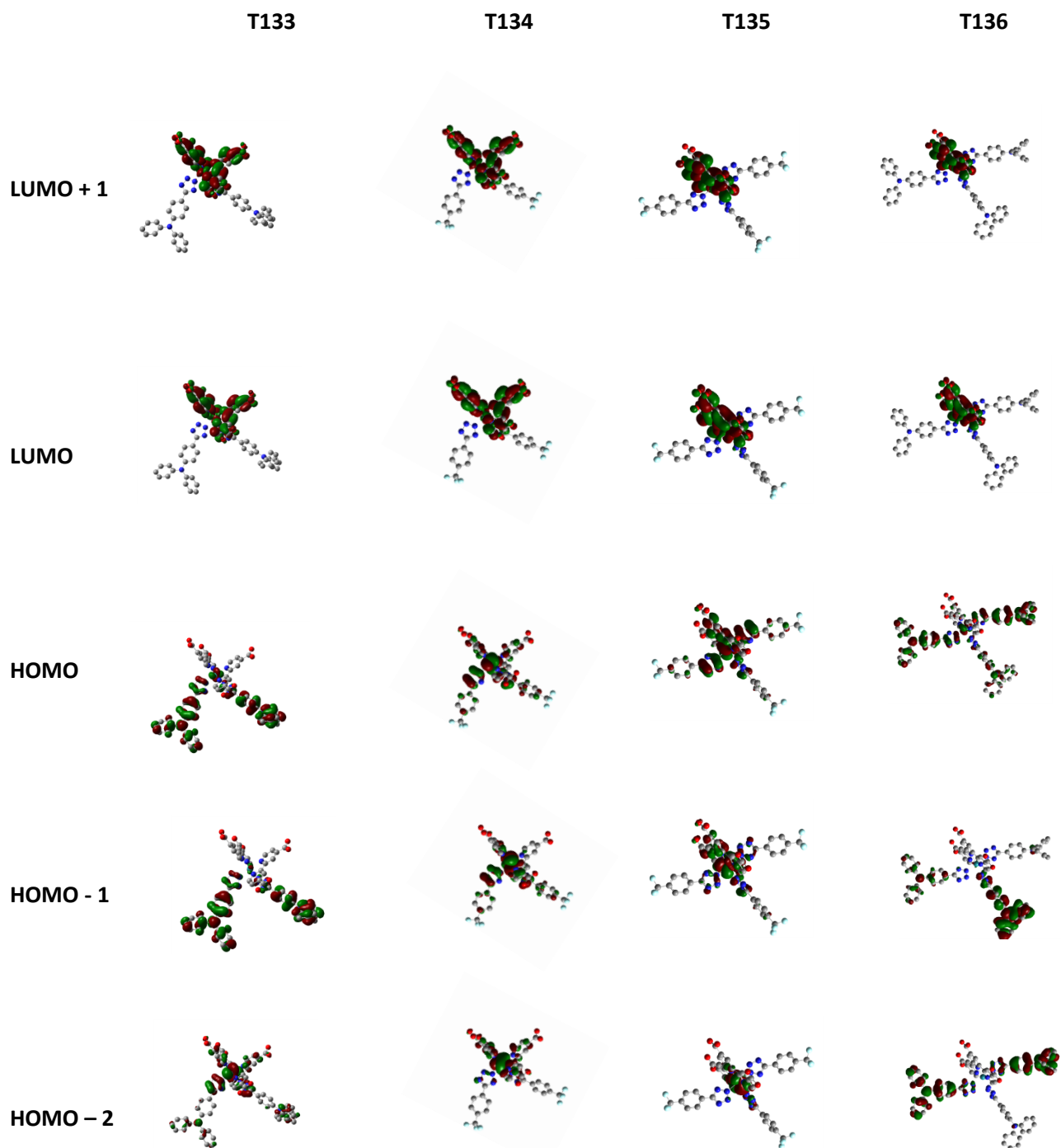


Figure S2: The isodensity plots for the HOMO-2, HOMO-1, HOMO, LUMO and LUMO+1 of T133 to T136.

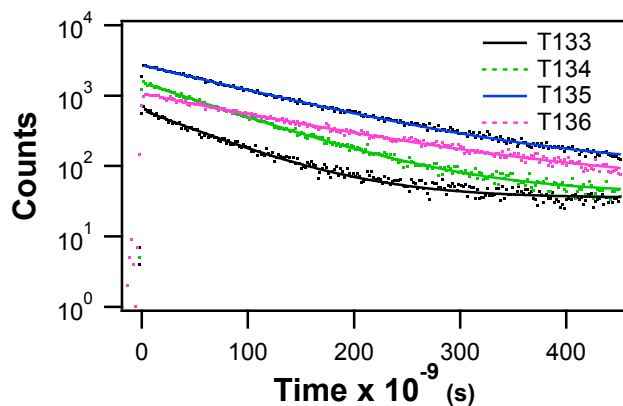


Figure S3: Lifetime emission measurements of T133 to T136 in aerated ethanol with an excitation wavelength $\lambda_{\text{ex}} = 532 \text{ nm}$.

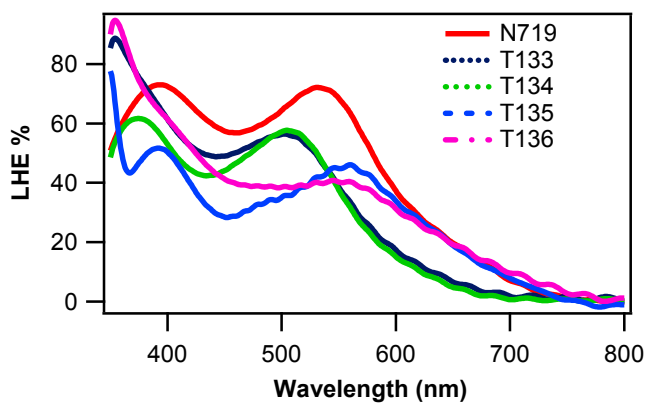


Figure S4: Light harvesting efficiency of T133 to T136 on $6 \mu\text{m}$ TiO_2 film.

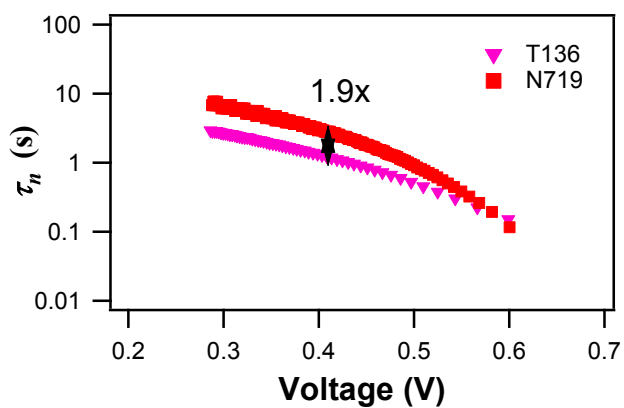


Figure S5: Electron lifetimes obtained from OCVD of N719 (square-red) and T136 (triangle-violet) assembled cells with EL2 as the corresponding electrolyte.

References:

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