# Supporting information for

# Accumulative Electron Transfer: Multiple Charge Separation in Artificial Photosynthesis

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### **Electrochemical characterization**

**Cyclic voltammetry in solution.** Table S1 summarizes the cyclic voltammetry results for the imidazole-TA and oxazole-TA ligands shown in Scheme S1.



Scheme S1. Structures of the oligotriarylamine unit OTA (6) and the ligands ImidTA (8), OxaTA (9).

**Table S1.** Half-wave potentials (in V vs. SCE) for oxidation obtained by cyclic voltammetry in  $CH_2Cl_2$  (0.15 M Bu<sub>4</sub>NPF<sub>6</sub>) with ca 2% MeOH.

Compound	E <sub>ox1</sub>	E <sub>ox2</sub>	E <sub>ox3</sub>	E <sub>ox4</sub>
	Amine <sup>0/+</sup>	Amine <sup>+/2+</sup>	Amine <sup>2+/3+</sup>	$\operatorname{Imid}^{0/+}(\operatorname{Oxa}^{0/+})$
6	0.40	0.64	1.14	-
8	0.64	-	-	1.25
9	0.79	-	-	1.47

**Chemical oxidation studies in solution.** Figure S1 presents the chemical oxidation studies that gives the difference spectra of **4** (RuOxaOTA) and **5** (ImidOTA ligand) presented in the main paper.



**Fig S1.** Electronic absorption in solution ( $CH_2Cl_2 + 2\%$  meOH) of the complex **4** (*left*) and ligand **5** (*right*) upon oxidation by gradual addition of NOBF<sub>4</sub>.



Fig S2. Difference spectrum obtained upon chemical oxidation by step-wise addition of  $NOBF_4$  to solutions of the ImidTA ligand 8 in dichloromethane (ca. 2% MeOH). The difference spectrum have been constructed by subtraction of the 8 ground state absorption features.

#### Ground state and excited state properties in solution

**Electronic absorption.** The electronic absorption spectra of compounds 1-4 and 6 in solution are shown in Figure S1. Because of the limited solubility, mostly of compound 4, we found that the best solvent for this series of compounds is a solvent mixture of dichoromethane and methanol (CH<sub>2</sub>Cl<sub>2</sub> with ca. 2% MeOH). Complex 1 displays a Ru(II) metal-to-ligand-charge transfer (MLCT) band at 450-500 nm ( $\varepsilon_{480 nm} \approx 1 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) and ligand-centered (LC) transitions at 280-310 nm, assigned by comparison with similar Ru(II)polypyridine complexes.<sup>1</sup> The oligo-triarylamine 6 has quite strong absorption bands in the visible, with peaks at 410 nm and 290 nm. The electronic absorption of complexes 2-4 fit quite well with the contributions from the Ru(II) moiety and triarylamine, with increased absorption at ca. 400 nm that indicates a non-negligible electronic coupling in the ground state.



**Figure S1.** Room temperature electronic absorption spectra of complexes 1-4 and the free oligo-triarylamine (OTA) **6** in solution ( $CH_2Cl_2$  with ca. 2% MeOH).

**Room temperature emission.** The emission at 298 K upon MLCT excitation (460 nm) of **1-4** in a  $CH_2Cl_2$ :MeOH (ca. 9:1) solution was collected. Results are summarized in table S2. The triaryl-containing complexes **2-4** are significantly less emissive than the Ru reference dye. In particular, compounds **3** and **4** give only very weak emission.

**Emission at 77 K.** From the data presented in table S2 it is clear that at low temperatures (77 K) compounds **2-3** are significantly more emissive and the MLCT emission is blue shifted, as expected. The 77 K emission of **4** could not be determined in these measurements for solubility reasons. Since the  $CH_2Cl_2$ :MeOH solvent mixture does not give a satisfactory glass at 77 K we are very constrained in the choice of solvent for these measurements.

Compound	MLCT emission 298 K <sup>a)</sup>		MLCT emission 77 K <sup>b)</sup>	
	$\lambda_{max}$ [nm]	$\Phi_{em} (rel.)^{c)}$	$\lambda_{max}$ [nm]	$E_{00} \left[ \mathrm{eV} \right]^{d}$
1	700	1	620	2.25
2	690	0.6	610	2.28
3	710	0.05	605	2.30
4	~ 700 <sup>e)</sup>	$\leq 0.05$	- <sup>f)</sup>	<i>f)</i>

**Table S2.** Results of emission measurements of complexes 1-4 in solution upon 460 nmexcitation at 298 K and at 77 K.

<sup>*a*)</sup> Solvent mixture CH<sub>2</sub>Cl<sub>2</sub>:MeOH 9:1 <sup>*b*)</sup> Glass EtOH:MeOH 1:1.<sup>*c*)</sup> Relative **1**, calculated from the MLCT emission intensity at  $\lambda_{max}$ . <sup>*d*)</sup> For **1** the excited state energy E<sub>00</sub> is determined as the intersection between the electronic absorption (CH<sub>2</sub>Cl<sub>2</sub>:MeOH, 298 K) and 77 K emission. The excited state energy of **2** and **3** are then evaluated from the shift of MLCT emission at 77 K, relative to that of **1**. <sup>*e*)</sup> Room temperature MLCT emission yield is very low, small amounts of ligand impurity dominates the emission spectrum. <sup>*e*)</sup> Very poor solubility in the EtOH:MeOH solvent mixture, could not be determined.

**Excited state behavior in solution.** Transient absorption spectra at selected delay times as obtained upon single-pulse excitation (450 nm,  $\sim$ 120 fs pulse duration) of **1-4** in solution are shown in Figure S3. For **1**, the ground state bleach was observed to increase slightly on the 1 ns time scale, tentatively assigned to a slow relaxation process in the MLCT excited state, possibly related to the protonation state of the dye. However, the dominating process in **1** is the Ru ground state recovery, which occurs on much longer time scales (>> 10 ns).

In compounds 2-4, two time constants were required for a satisfactory fit of the overall dynamics on the < 10 ns time scale. The first process (1-10 ps time constants) corresponds to decay of the Ru ground state bleach/ground state recovery. On a longer time scale (100-800 ps), the features observed in the final spectra (8 ns) grow in. The final spectra correspond quite well to the expected features of a Ru<sup>I</sup>OTA<sup>+</sup> (in 2, Ru<sup>I</sup>TA<sup>+</sup>) state. However, the low yield of this possible charge separated state indicates that also other decay pathways, e.g. T-T energy transfer, are active in quenching the Ru MLCT excited state. The full investigation of possible quenching mechanisms in solution is beyond the scope of our current work and not a central point here since we can show that on TiO<sub>2</sub> film, the injection is mostly pulse limited and thus much faster than the processes identified here (see below).

It can be noted that a prominent feature of the MLCT excited state solution phase transient spectra at early delay times (5ps) of **1-4** is the LC absorption band at  $\lambda \le 400$ .



**Fig S3.** Transient absorption of **1-4** in solution ( $CH_2Cl_2$ :MeOH ca. 9:1) upon single pulse excitation at 460 nm, ~120 fs pulse duration, at selected delay times. The presented data are the binned average of 3-5 spectra. The initial dynamics were followed on shorter timescales.

#### **Dye-sensitized films DSSC performance**

**DSSC performance studies.** As part of the characterization of compunds 1-4, their performance as dye-sensitized solar cells (DSSC) dyes was investigated. The results are presented in table S3. The films were sensitized and the performance studies performed as described below (see Experimental). The open circuit voltage (V<sub>oc</sub>) obtained in these studies was used to obtain an estimate of the TiO<sub>2</sub> conduction band potential. By assuming  $E(I^{-}/I_{3}^{-}) = 0.05 \text{ V}$  vs SCE in propylene carbonate for the 0.05 M I<sub>2</sub>/ 0.5 M LiI electrolyte we obtain  $E(TiO_{2}^{-/0}) \approx 0.5 \text{ V}$  vs SCE as a reasonable estimate for the TiO<sub>2</sub> conduction band under the conditions of our studies.

**Table S3.** Photovoltaic performances of the complexes recorded in a sandwich DSSC under AM 1.5. The active surface area was  $0.5 \text{ cm}^2$  and the electrolyte composition  $0.05 \text{ M } \text{I}_2/0.5 \text{ M}$  LiI in propylene carbonate.

Compound	V <sub>OC</sub> (mV)	$J_{SC}(mA)$	η (%)
1	437	8.2	1.98
2	548	8.1	2.06
3	698	9.5	3.96
4	488	1.3	0.34

#### Formation and recombination of the first charge-separated state

**Injection and hole transfer.** Figures S4-S5 show the early dynamics of **1-4** on TiO<sub>2</sub> (propylene carbonate, 1 M LiClO<sub>4</sub>) upon single pulse excitation at 460 nm, ~120 fs pulse duration. In contrast to the solution phase measurements (Fig. S3), the LC excited state absorption band could not be observed. Instead, the instantaneous bleach at 400 nm is due to the presence of electrons in the TiO<sub>2</sub> conduction band, matched by the depletion of excited state absorption at 530-560 nm (monitored at the Ru<sup>III</sup>/ground state isosbestic point). Slower injection components ( $\leq$  7-9 ps) are present, though their contribution to the overall spectral development is minor.

Fig. S6 shows the Ru ground state recovery and, for 2-4, growth of the  $OTA^+$  (in 2,  $TA^+$ ) spectral signatures (hole transfer) that were observed at longer time scales. The four time constants needed to fit the data for 2-4 were assigned with the aid of global fit amplitude plots, as shown in figure S7.



Fig S4. Transient absorption of 1-4 on TiO<sub>2</sub> (propylene carbonate, 1 M LiClO<sub>4</sub>) upon single pulse excitation at 460 nm, ~120 fs pulse duration, at  $t \le 10$  ps (not chirp corrected). Note the absence of the LC absorption band above 400 nm (S/N in this region low because of TiO<sub>2</sub> absorption).



**Fig S5.** Transient absorption of **1-4** on TiO<sub>2</sub> (propylene carbonate, 1 M LiClO<sub>4</sub>) upon single pulse excitation at 460 nm, ~120 fs pulse duration. These wavelengths were chosen as to monitor electrons in the TiO<sub>2</sub> conduction band (at 400 nm) and the Ru excited state absorption (initially at 530-560 nm). The traces presented here are binned to reduce the noise (395-405 nm for the 400 nm trace, at 530-560 nm the width is < 5 nm).



**Fig S6.** Transient absorption of complexes **1-4** on TiO<sub>2</sub> (propylene carbonate, 1 M LiClO<sub>4</sub>) upon single pulse excitation at 460 nm, ~120 fs pulse duration at selected wavelengths,  $t \le 8ns$ . Bold solid lines represent global fit results. The global fits were performed using a set of traces at 5-10 wavelengths spread throughout the spectrum.



**Fig S7.** Amplitudes of global fit coefficients at selected wavelengths. From the fit of transient absorption traces of **1-4** on  $\text{TiO}_2$  (propylene carbonate, 1 M LiClO<sub>4</sub>) upon single pulse excitation at 460 nm, ~120 fs pulse duration.

**Recombination of the first charge-separated state.** The recombination of the first charge separated state upon ns single-pulse excitation was followed and the results are shown in Fig. S8.



**Fig S8.** Transient absorption upon single pulse 10 ns excitation of **1-4** on TiO<sub>2</sub> (1 M LiClO<sub>4</sub>, propylene carbonate). Compound **1** is followed at 480 nm, showing the recovery of the Ru<sup>II</sup> ground state. The lifetime of the first charge separated state  $TiO_2^{(-)}Ru^{II}OTA^+$  is followed at 620 nm or 650 nm for compound **2-4**.

#### Experimental

**General methods.** Electronic absorption spectra in solution were recorded on a Varian Cary 5000 instrument in a 1×1 cm quartz cell or on a UV-2401PC Shimadzu spectrophotometer with a quartz UV-Visible cell (0.5 mm). Spectroscopic grade ( $\geq$ 99.9 %) solvents were used. Compounds were generally dissolved in dichloromethane with a few drops of methanol to increase the solubility. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX 300 MHz or AMX 400 MHz Brucker spectrometer. Chemical shifts for <sup>1</sup>H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl<sub>3</sub>  $\delta$  = 7.26 ppm). Mass spectra were recorded on a EI-MS HP 5989A spectrometer of network geometry equipped with electrospray ionization (ESI) source. Electrospray ionization mass spectrometry (ESI)

analyses were performed on a ThermoFinnigan LCQ Advantage spectrometer. MALDI-TOF analyses were performed on a BRUKER Ultraflex III, micrOTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh) or with SDS neutral alumina (0.05-0.2 mm mesh).

Air sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich and used as received. Complexes **1** and **4**,<sup>2</sup> *N*,*N*-Bis[4-(di-4-anisylamino)phenyl]-N-(*p*-benzaldehyde)-amine (**5**),<sup>2</sup> N-(*p*-benzaldehyde)-N,N-bis(4-anisyl)amine (**7**)<sup>3</sup>, 1,10-phenanthroline-5,6-dione<sup>4</sup> and 4,4'-diester-2,2'-bipyridine<sup>5</sup> were prepared according to published procedures.

General procedure for the ligands synthesis. In a schlenk tube were placed the aldehyde (0.05 eq.), phenanthroline dione (0.05 eq.), ammonium acetate (1 eq.) and glacial acetic acid. The mixture was heated at 110°C overnight. Toluene was added and the resulting solution was concentrated to ca. few mL. The mixture was extracted with  $CH_2Cl_2$  / NaHCO<sub>3</sub> sat. to reach pH  $\approx$  8 and the organic layer was dried over MgSO<sub>4</sub> and concentrated to dryness. The crude product was purified by column chromatography over alumina (CH<sub>2</sub>Cl<sub>2</sub> : 100).



**Ligand 5.** Following the general procedure, using the aldehyde **6** (250 mg, 0.34 mmol), phenanthroline dione (87 mg, 0.41 mmol), ammonium acetate (520 mg, 6.8 mmol) and glacial acetic acid (12 mL). 6 was obtained as a yellow solid (170 mg, 45%). <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl<sub>3</sub>+1 drop of aqueous NH<sub>3</sub>, 25°C): 3.72 (s, 12H), 6.82-7.10 (m, 26H), 7.51 (m, 2H), 8.4 (m, 2H), 8.97 (d, <sup>1</sup>J = 3.3 Hz, 2H), 9.21 (m, 2H). HR-MS (ES+): m/z: calcd for C<sub>59</sub>H<sub>47</sub>N<sub>7</sub>O<sub>4</sub> 918.3762, found 918.3758 [M]<sup>+</sup>.

**Ligands 8 and 9.** Following the general procedure, using the aldehyde 7 (270 mg, 0.8 mmol), phenanthroline dione (170 mg, 0.8 mmol), ammonium acetate (1.2 g, 16 mmol) and glacial acetic acid (27 mL). Chromatography on alumina yielded ligands **8** and **9**:

**8** as a yellow solid (180 mg, 43%). <sup>1</sup>H NMR δ: (300MHz, CDCl3+1 drop of aqueous NH<sub>3</sub>, 25°C): 3.83 (s, 6H), 6.80 (d, <sup>3</sup>J = 9 Hz, 4H), 6.88 (d, <sup>3</sup>J = 9 Hz, 2H), 7.03 (d, <sup>3</sup>J = 9 Hz, 4H) 7.48 (m, 2H), 7.94 (d, <sup>3</sup>J = 8.7 Hz, 2H), 8.73 (d, <sup>3</sup>J = 7.2 Hz, 2H), 8.96 (d, <sup>3</sup>J = 2.7 Hz, 2H). HR-MS (ES+): m/z: calcd for C33H25N5O2, 523.2008, found 524.2087 [M+H]<sup>+</sup>.

**9** as a yellow solid (30 mg, 7%). <sup>1</sup>H NMR δ: (300MHz, CDCl3, 25°C): 3.83 (s, 6H), 6.89 (d, <sup>3</sup>J = 9 Hz, 4H), 7.00 (d, <sup>3</sup>J = 9 Hz, 2H), 7.15 (d, <sup>3</sup>J = 9 Hz, 4H), 7.74 (m, 2H), 8.10 (d, <sup>3</sup>J = 9 Hz, 2H), 8.62 (dd, <sup>1</sup>J = 6.3 Hz, <sup>3</sup>J = 1.8 Hz, 1H), 8.92 (dd, <sup>1</sup>J = 8.4 Hz, <sup>3</sup>J = 1.8 Hz, 1H), 9.19 (m, 2H). HR-MS (ES+): m/z: calcd for C33H24N4O3 524.1848, found 525.1921 [M+H]<sup>+</sup>.



**Synthesis of complex 10.** Ligand **8** (60 mg,  $1.15 \times 10^{-4}$  mol, 1 eq.) and dichloro(*p*-cymene)ruthenium(II) dimer (30 mg,  $5.7 \times 10^{-5}$  mol, 0.5 eq.) were dissolved in dry and degassed ethanol (5 mL). The mixture was refluxed in the dark for 3 h. The solvent was then removed *in vacuo* and the yellow residue was purified by chromatography on sephadex LH20, eluted with CH<sub>3</sub>CN/MeOH/CH<sub>2</sub>Cl<sub>2</sub> (4/4/2 v:v), yielding 76 mg of 8 (78% yield). <sup>1</sup>H NMR

δ: (300MHz, CDCl3, 25°C): 0.74 (d,  ${}^{3}J = 6.9$  Hz, 6H), 1.71 (m, 1H), 1.94 (s, 3H), 3.56 (s, 6H), 5.60 (d,  ${}^{3}J = 6.1$  Hz, 2H), 5.80 (d,  ${}^{3}J = 6.1$  Hz, 2H), 6.65 (d,  ${}^{3}J = 9$  Hz, 2H), 6.71 (d,  ${}^{3}J = 9$  Hz, 4H), 6.92 (d,  ${}^{3}J = 9$  Hz, 4H), 7.74 (m, 4H), 8.84 (d,  ${}^{3}J = 8.4$  Hz, 2H), 9.33 (d,  ${}^{3}J = 5.1$  Hz, 2H). MALDI-TOF: m/z: calcd for C43H39ClN5O2Ru<sup>+</sup>, 794.1837, found 794.1838 [M]<sup>+</sup>.

Synthesis of complex 11. In a schlenk tube were introduced complex 10 (76 mg,  $9.2 \times 10^{-5}$  mol), 4,4'-diester-2,2'-bipyridine (33 mg,  $1.1 \times 10^{-4}$  mol), lithium chloride (12 mg,  $2.8 \times 10^{-4}$  mol) and dimethylformamide (6 mL). The mixture was degassed and heated at 160°C in dark for 2 h. The solvent was removed and the crude was purified by Sephadex® chromatography (CH2Cl2 / MeOH : 8 / 2). 11 was obtained as a purple solid, with 60% yield. <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl3, 25°C): 1.30 (t, <sup>3</sup>J = 7.2 Hz, 3H), 1.5 (t, <sup>3</sup>J = 7.2 Hz, 3H), 3.55 (s, 12H), 4.19 (q, <sup>3</sup>J = 7.2 Hz, 2H), 4.49 (q, <sup>3</sup>J = 7.2 Hz, 2H), 6.8-7.1 (m, 10H), 7.88 (m, 4H), 8.05 (m, 2H), 8.22 (m, 1H), 8.51 (s, 2H), 8.75 (s, 2H), 9.99 (m, 1H), 10.28 (d, <sup>3</sup>J = 6 Hz, 1H), 10.50 (m, 1H). HR-MS (ES+): m/z: calcd for C49H41Cl2N7O6Ru 995.1541, found 995.1565 [M]<sup>+</sup>.

**Synthesis of complex 2.** In a schlenk tube were introduced complex **11** (36 mg,  $3.6 \times 10^{-5}$  mol), potassium cyanide (51 mg,  $7.8 \times 10^{-4}$  mol), aqueous lithine (4 mL, 0.2 M) and THF (10 mL). The mixture was degassed and heated in dark at 90°C overnight. The solvent was removed and the crude was purified by size exclusion chromatography (Sephadex<sup>®</sup> LH20) eluted with pure MeOH to afford **2** in quantitative yield. <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl3, 25°C): 3.72 (s, 6H), 6.80 (d, <sup>3</sup>J = 9 Hz, 4H), 6.88 (d, <sup>3</sup>J = 8.1 Hz, 2H), 7.03 (d, <sup>3</sup>J = 8.1 Hz, 4H), 7.47 (m, 1H), 7.89 (m, 4H), 8.50 (m, 1H), 8.65 (m, 4H), 9.66 (m, 2H), 9.93 (m, 2H). HR-MS (ES+): m/z: calcd for C47H33N9O6Ru 922.1683, found 922.1632 [M]<sup>+</sup>. E.A. : calcd for C: 64.87, H: 8.69, N: 4.51, found C: 64.87, H: 8.25, N: 4.21.



Synthesis of complex 12. Ligand 5 (85 mg,  $9.3 \times 10^{-5}$  mol) and dichloro(*p*-cymene)ruthenium(II) dimer (28 mg,  $4.6 \times 10^{-5}$  mol) were dissolved in dry and degassed ethanol (5 mL). The mixture was refluxed in the dark for 3 h. Then the solution was concentrated and the crude product purified by size exclusion chromatography (Sephadex<sup>®</sup> LH20) eluted with the mixture CH<sub>3</sub>CN/MeOH (1/1: vol./vol.). 12 was obtained as an orange solid (90%). <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl<sub>3</sub>, 25°C): 1.02 (s, 6H), 1.98 (m, 1H), 2.20 (s, 3H,), 3.76 (s, 12H), 5.96 (m, 2H), ), 6.16 (m, 2H), 6.82-7.10 (m, 26H), 7.9 (m, 2H), 8.0 (m, 2H, H<sub>phen</sub>), 8.70 (m, 1H), 8.83 (m, 1H), 9.73 (m, 2H,). MALDI-TOF: m/z: calcd for C<sub>69</sub>H<sub>61</sub>ClN<sub>7</sub>O<sub>4</sub>Ru<sup>+</sup> 1188.351, found 1188.300 [M]<sup>+</sup>.

Synthesis of complex 13. In a schlenk tube were introduced complex 12 (100 mg,  $8.1 \times 10^{-5}$  mol), 4,4'-diester-2,2'-bipyridine (30 mg,  $1.0 \times 10^{-4}$  mol), lithium chloride (14 mg,  $3.4 \times 10^{-4}$  mol) and dimethylformamide (6 mL). The mixture was degassed and heated at 160°C in dark for 2 h. The solvent was removed and the crude was purified by Sephadex® chromatography (CH2Cl2 / MeOH : 8 / 2). 13 was obtained as a purple solid (60%). <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl3+drop of aqueous NH3, 25°C): 1.36 (t, <sup>3</sup>J = 7.2 Hz, 3H), 1.55 (t, <sup>3</sup>J = 7.2 Hz, 3H), 3.74 (s, 12H), 4.37 (q, <sup>3</sup>J = 7.2 Hz, 2H), 4.51 (q, <sup>3</sup>J = 7.2 Hz, 2H), 6.70-6.98 (m, 26H), 7.32 (m, 2H), 7.42 (m, 2H), 7.64 (m, 2H), 8.11 (m, 2H), 8.63 (s, 2H), 8.80 (s, 2H), 10.35 (m, 2H). HR-MS (ES+): m/z: calcd for C75H63Cl2N9O8Ru 1389.3235, found 1389.3232 [M]<sup>+</sup>.

**Synthesis of complex 3.** In a schlenk tube were introduced complex **13** (36 mg,  $2.6 \times 10^{-5}$  mol), potassium cyanide (51 mg,  $7.8 \times 10^{-4}$  mol), aqueous lithine (4 mL, 0.2 M) and THF (10 mL). The mixture was degassed and heated in dark at 90°C overnight. The solvent was removed and the crude was purified by size exclusion chromatography (Sephadex<sup>®</sup> LH20) eluted with pure MeOH to afford **3** as an orange solid (100%). <sup>1</sup>H NMR  $\delta$ : (300MHz, CDCl3, 25°C): 3.69 (s, 12H), 6.70-6.98 (m, 26H), 7.47 (m, 3H), 7.63 (m, 2H), 7.80 (m, 1H), 8.06 (m, 2H), 8.80 (m, 2H), 8.93 (m, 1H), 9.01 (m, 1H), 9.78 (m, 2H). HR-MS (ES+): m/z: calcd for C73H55N1108Ru 1316.3369, found 1316.3368 [M]<sup>+</sup>. E.A. : calcd for C 46.65, H 3.77, N 7.39, found C 46.48, H 3.76, N 7.17.

**Electrochemistry.** Electrochemical measurements were performed with a potentiostatgalvanostat AutoLab PGSTAT302 controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a Pt disk of 2 mm ø, the auxiliary was a Pt mesh and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.15 N Bu<sub>4</sub>NPF<sub>6</sub> in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s for cyclic voltammetry and the pulse frequency was 15 Hz for square wave voltammetry.

**TiO<sub>2</sub> film preparation.** Conductive glass substrates (F-doped SnO<sub>2</sub>) were purchased from Solems (5Ω/square). For the optical measurements, non-conductive glass was generally used as the substrate. The glass was successively cleaned by sonication in acetone, distilled water and ethanol for 10 minutes before being dried by a flow of air. Nanoparticules of TiO<sub>2</sub> (diameter =20 nm, Solaronix Ti-Nanoxide T) was spread on the glass substrate by doctor blade technique using two layers of Scotch tape. The electrode was sintered at 450°C for 30 minutes and a layer thickness of ≈ 6-8 µm was obtained. Thickness measurements were determined with a Digital instrument Dektak 8 profilometer and the data analysis was done on a Dektak soft v 8.34.

Film sensitization and sample preparation. Sensitizing solutions where prepared in  $CH_2Cl_2$ :MeOH 9:1 solvent mixture by spectroscopic grade solvents. The films were reheated at 350 °C for 15-30 min and kept at 160 °C until put into the dye bath over night. After sensitization, the films were rinsed thoroughly with fresh solvent to desorb excess dye, dried and stored in a desiccator. Films were generally used within 1-2 weeks from sensitization. UV-Vis absorption spectra of the dry films were collected on a Varian Cary 5000 double beam instrument, using a non-sensitized TiO<sub>2</sub> film from the same batch as baseline. Samples were prepared for the time-resolved optical studies by adding a drop of transparent electrolyte

(1 M LiClO<sub>4</sub> in propylene carbonate) to the sensitized film. The film and electrolyte was covered with a thin glass plate. The films were monitored for visible damage throughout the measurements and were not allowed to dry during measurements.

**Spectroelectrochemistry and chemical oxidation studies**. Complex **4** and the free phenatroline-imidazole-OTA ligand (ligand **8**) were oxidized in a stepwise manner by iterative injections of 10  $\mu$ L of a stock solution of NOBF<sub>4</sub> in dichloromethane (4.5×10<sup>-3</sup> mol L<sup>-1</sup>) into the measurement cell. The latter was subjected to a one minute long vigorous stirring, before the absorption spectrum was recorded. For the spectro-electrochemical measurements of **4** on TiO<sub>2</sub> film has been described in detail elsewhere.<sup>2</sup>

**Photovoltaic properties in DSSC.** The film was immersed in a sensitizing solution of the complex dissolved in dichloromethane/methanol (98/2 vol.) overnight in dark. Dye-sensitized solar cells (DSSC) were fabricated by sandwiching a few drops of the electrolyte between the freshly prepared dye coated  $TiO_2$  working electrode and a platinum counter-electrode prepared by magnetron sputtering (100 nm layer of Pt onto FTO glass). The active surface area of the cell was 0.5 cm<sup>2</sup>. The electrolyte composition was [I<sub>2</sub>]=0.05 M and [LiI]=0.5 M in propylene carbonate. The current-voltage characteristics of the cells were measured by a Keythley model 2601 digital source meter controlled by Labview: 2.0 software. The photovoltaic cell was illuminated with an Oriel lamp calibrated to AM 1.5 (air mass) intensity (1000 W m<sup>-2</sup>). The measurements on compound **4** were not repeated due to limited material.

**Emission at 298 K and 77 K.** Emission spectra were recorded on a Horiba Fluorolog (Jobin Yvon) fluorimeter equipped with double monochromators for excitation and emission. The emission upon 460 nm excitation was detected at 900 by a R928P photomoultiplier tube detector in single-photon counting mode with 5 nm resulution on the monochromators. The reported spectra were corrected for varying detector sensitivity at different wavelengths.

For the room temperature (298 K) measurements, samples were prepared in 1\*1 cm<sup>2</sup> optical quartz cells to an optical density of  $\leq 0.1$  at the excitation wavelength. The samples were purged for > 20 min with solvent-saturated Ar(g) prior to and were kept under Ar(g) atmosphere during the measurements. The reported relative emission quantum yields were determined from the maximum intensity of the MLCT emission as obtained by the corrected emission spectrum using the **1** sample as the reference ( $\Phi$ rel.(**1**) = 1), taking into account minor differences in the otical density at 460 nm of each sample.

For 77 K measurements a cold finger setup was used. Several solvents and solvent mixtures were tried in order to have the whole series of compounds into solution. We found that a mixture of ethanol and methanol (1:1) was the best option, although the solubility of **4** was

very poor in this solution mixture. The samples were immersed in liquid nitrogen (77 K) to make a transparent glass. Ar(g) was purged through the sample chamber to avoid ice on the outside of the sample cell.

Ultrafast transient absorption. The Ti:sapphire laser system and experimental setup for ultrafast transient absorption pump-probe measurements used here has been described elsewhere.<sup>6</sup> Pump light of 480 nm and ~120 fs pulse duration was obtained by three-wave mixing of the optical paramagnetic amplifier (TOPAS) output at 1440 nm and 720 nm. Filters were used to remove stray light and obtain a clean pump. The white light probe was generated from a fraction of the 800 nm Ti:sapphire output passed through an optical delay line (10 ns total delay) and focused onto a moving CaF<sub>2</sub> plate. The polarization of the pump was set at magic angle (54.7°) relative to that of the probe using a polarizer and a  $\lambda/2$  plate. Samples were prepared as described above and mounted on a vertically moving holder. The pump energy at the sample cell was reduced by filters to  $\leq 0.5 \mu$ J/pulse (diameter  $\leq 400 \mu$ m) to avoid sample degradation and nonlinear effects. The reported spectra are averages of 500-10000 individual measurements. The chirp is < 5 ps which is the earliest delay time at which spectra are shown. Time constants were obtained by global fitting, performed on the transient absorption traces on 5-10 wavelengths.

Single-pulse nanosecond transient absorption. Transient absorption measurements on the nanosecond to millisecond time scale were performed with a frequency tripled Q-switched Nd:YAG laser pumping an MOPO (Spectra-Physics Quanta-Ray system) to obtain 480 nm pump light of  $\sim 10$  ns pulse duration at 10 Hz. The pump laser was coupled to a transient absorption detection system (Edinburgh Instruments), equipped with a monochromator, a pulsed Xe arc lamp for short timescale measurements and a Tungsten/Halogen lamp for probing at timescales  $>100 \ \mu$ s. A 400 nm cut off filter was used in the probe light in front of the sample to avoid direct excitation of the  $TiO_2$ . the sample was prepared as described above and mounted at approximately 45° vs the incoming pump. Transient absorption traces were collected at right angle to the incoming laser beam by a Tektronix 500MHz digital oscilloscope coupled to a R928-type photomultiplier tube. A CCD camera (Andor DH720) was used to record transient absorption spectra. The output was processed with Edinburgh Instruments L900 software. The maximum pump energy at the sample was *ca* 10 mJ/pulse. Single-pulse measurements were typically performed with  $\leq 2$  mJ/pulse pump energy at 1 Hz. For the single-pulse intensity dependence studies the pump was attenuated by use of neutral density filters. The number of photons per dye molecule was estimated from the obtained  $\Delta O.D.$  at 495 nm and 600 nm at different intensities and from the extinction coefficients of the mono- and dication of 4 on  $TiO_2$  obtained by spectroelectrochemistry on  $TiO_2$  film as described above, assuming 100% yield of formation for the first charge separated state.

**Double-pulse nanosecond transient absorption.** An digital delay (Stanford Research Systems) triggered by the LP920 Controller (Edinburgh Instruments) was used to trigger two Nd:YAG lasers with independent optical paramagnetic oscillators. One of them is described in detail above (Spectra-Physics Quanta-Ray Nd:YAG laser and MOPO). In addition, a Brilliant B frequency tripled laser (Quantel) pumping an OPO (Opotek) to obtain pump light of ~ 10 ns pulse duration was used. The delay between the two lasers was controlled by the Stanford delay. For the measurements described herein, the effective delay between the two 480 nm pump pulses was set to 1  $\mu$ s. The maximum intensities of the two pump beams were  $\leq 9$  mJ/pulse (pulse 1) and  $\leq 10$  mJ/pulse (pulse 2) in front of the sample chamber, but they are attenuated further before the sample ( $\leq 1$  mJ/pulse). Transient absorption traces and spectra were recorded as described above and processed with the Edinburgh Instruments L900 software. By blocking one of the pump pulses it was possible to directly alternate between single-pulse and double-pulse excitation.



**Figure S9.** Experimental setup for the double-pulse nanosecond transient absorption measurements.

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