Supporting information for:

Photoinduced charge accumulation by metal-ion coupled electron transfer

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Synthesis and product characterization

Compound **3**. 5-Bromo-2,2'-bipyridine (**1**)[1] (1.00 g, 4.25 mmol), 4-(trimethylsilyl)phenylboronic acid (**2**)[2] (1.13 g, 5.10 mmol), and Na_2CO_3 (1.35 g, 12.8 mmol) were suspended in a mixture of toluene (160 ml), ethanol (20 ml) and de-ionized water (8 ml). After de-oxygenating, $Pd(PPh_3)_4$ (246 mg, 0.21 mmol) was added, and the reaction mixture was de-oxygenated again prior to heating to 90 °C for 1.5 days under N_2. Then H_2O (100 ml) was added to the cooled reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and then evaporated. The crude product was purified by chromatography on silica gel column, using as an eluent a 3:1 (v:v) mixture of pentane and diethyl ether containing 1% of triethylamine. The pure product was obtained as a beige solid (1.40 g, 4.21 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (d, *J* = 4.8 Hz, 2 H, bpy), 8.48 (t, *J* = 8.3 Hz, 2 H, bpy), 7.83 (td, *J* = 8.1 Hz, 7.5 Hz, 2.0 Hz, 2 H, bpy), 7.43 (s, 1 H, xy), 7.31 (ddd, *J* = 7.4 Hz, 4.8 Hz, 1.1 Hz, 1 H, bpy), 7.12 (s, 1 H, xy), 2.51 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 0.40 (s, 9 H, $Si(CH_3)_3$).

Compound **4**. Compound **3** (500.0 mg, 1.50 mmol) was dissolved in CH_2Cl_2 (3 ml) under N_2 and cooled to 0 °C. ICl (0.17 ml, 3.00 mmol) in CH_2Cl_2 (10 ml) was added dropwise, and the reaction mixture was stirred at room temperature. Saturated aqueous $Na_2S_2O_3$ (100 ml) was added to quench excess ICl. After phase separation, the aqueous phase was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated. Purification of the crude product by chromatography on silica gel column occurred with a 1:1 (v:v) mixture of pentane and diethyl ether as the eluent. This afforded the pure product as a light yellow solid (0.56 g, 1.45 mmol, 97 %). ^{1}H NMR (400 MHz, acetone-d_6) δ: 8.70 (ddd, *J* = 4.8 Hz, 1.8 Hz, 0.9 Hz, 1 H, bpy), 8.65 (dd, *J* = 2.3 Hz, 0.8 Hz, 1 H, bpy), 8.56 (dd, *J* = 8.2 Hz, 0.8 Hz, 1 H, bpy), 8.53 (dt, *J* = 8.0 Hz, 1.0 Hz, 1 H, bpy), 7.98-7.90 (m, 2 H, bpy), 7.84 (s, 1 H, xy), 7.44 (ddd, *J* = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1 H, bpy), 7.28 (s, 1 H, xy), 2.44 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3).

Ligand **6**. Compound **4** (149 mg, 0.38 mmol), oligotriarylamine **5**[3] (200 mg, 0.32 mmol), NaO^tBu (615 mg, 6.40 mmol), $Pd(dba)_2$ (9.2 mg, 0.02 mol), and $(HP^tBu_3)BF_4$ (4.6 mg, 0,02 mmol) were heated to 110 °C in dry, de-oxygenated toluene (15 ml) under N_2 for 24 hours. Then H_2O (150 ml) was added to the cooled reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and then evaporated. The crude product was purified by chromatography on silica gel column, using CH_2Cl_2 with 1% of triethylamine as the eluent. After re-crystallization from pentane, the pure product was obtained as a brown solid (0.28 g, 0.32 mmol, 99%). ^{1}H NMR (400 MHz, acetone-d_6) δ: 8.71–8.67 (m, 2 H, bpy), 8.54 (td, *J* = 8.2 Hz, 0.9 Hz, 2 H, bpy), 7.97–7.91 (m, 2 H, bpy), 7.42 (ddd, *J* = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1 H, bpy), 7.24 (s, 1 H, xy), 7.12 (s, 1 H, xy), 7.02–6.98 (m, 8 H, AA'BB'), 6.86 (td, *J* = 5.8 Hz, 5.2 Hz, 2.9 Hz, 16 H, AA'BB'), 3.77 (s, 12 H, OCH_3), 2.27 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3).

Ru-OTA. Ligand **6** (100 mg, 0.11 mmol) and $Ru(bpy)_2Cl_2$ (55 mg, 0.11 mmol) were suspended in a mixture of ethanol (20 ml) and $CHCl_3$ (6 ml) under N_2. After de-oxygenating, the reaction mixture was refluxed for 21 hours, and then the solvents were evaporated. The solid residue was purified by chromatography on silica gel column. The eluent

was a 9:1 (v:v) mixture of acetone and de-ionized H_2O to which 1% saturated aqueous KNO_3 solution was added. Acetone was evaporated from the desired chromatography fractions, and the product was precipitated as a hexafluorophosphate salt by dropwise addition of saturated aqueous KPF_6 solution (0.11 g, 0.07 mmol, 64%). ^{1}H NMR (400 MHz, CD_3CN) δ: 8.59–8.47 (m, 6 H, bpy), 8.06 (dddt, *J* = 8.5 Hz, 7.0 Hz, 3.3 Hz, 1.7 Hz, 5 H, bpy), 7.98 (td, *J* = 8.0 Hz, 1.4 Hz, 1 H, bpy), 7.88–7.84 (m, 1 H, bpy), 7.80–7.76 (m, 1 H, bpy), 7.76–7.72 (m, 3 H, bpy), 7.66 (d, *J* = 1.7 Hz, 1 H, bpy), 7.45–7.37 (m, 4 H, bpy), 7.37–7.31 (m, 1 H, bpy), 7.03 (s, 1 H, xy), 6.98–6.93 (m, 8 H, AA'BB'), 6.93 (s, 1 H, xy), 6.86–6.81 (m, 8 H, AA'BB'), 6.78–6.69 (m, 8 H, AA'BB'), 3.74 (s, 12 H, OCH_3), 1.97 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3). ESI-MS calculated (m/z) for $C_{78}H_{67}N_9O_4Ru^{2+}$: 647.7174; found: 647.7190. Elemental analysis calculated (%) for $C_{78}H_{67}N_9O_4F_{12}P_2Ru_2 \cdot CH_3COCH_3$: C 59.29, H 4.68, N 7.41; found: C 59.24, H 4.85, N 7.63.

Compound **8**. The procedure described below follows a previously published protocol.[4] Commercial 2-bromoanthraquinone (**7**) (3.32 g, 11.6 mmol), 4-(trimethylsilyl)phenylboronic acid (**2**)[2] (3.08 g, 13.9 mmol), and Na_2CO_3 (3.67 g, 34.7 mmol) were suspended in a mixture of toluene (60 ml), ethanol (10 ml), and de-ionized H_2O (12 ml). After de-oxygenating, $Pd(PPh_3)_4$ (1.33 g, 1.16 mmol) was added, and the suspension was de-oxygenated again. Then, the reaction mixture was refluxed under N_2 for 1.5 days. After cooling to room temperature, H_2O (100 ml) was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and then evaporated. Chromatography on silica gel was performed with a 1:1 (v:v) mixture of pentane and CH_2Cl_2 to afford a yellow solid (4.44 g, 11.6 mmol, ~100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32–8.38 (m, 3 H, AQ), 8.30 (d, *J* = 1.8 Hz, 1 H, AQ), 7.82 (m, 2 H, AQ), 7.76–7.79 (dd, *J* = 8.0 Hz, 1.9 Hz, 1 H, AQ), 7.40 (s, 1 H, xy), 7.11 (s, 1 H, xy), 2.49 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 0.38 (s, 9 H, $Si(CH_3)_3$).

Compound **9**. The following procedure follows a previously published protocol.[4] Compound **8** (1.97 g, 5.12 mmol) was dissolved in CH_2Cl_2 (10 ml) under N_2 and cooled to 0 °C. A solution of ICl (0.563 ml, 10.8 mmol) in CH_3CN (40 ml) was added very slowly, and the resulting yellow suspension was stirred at 0 °C for 15 minutes and then at room temperature overnight. After addition of 5% aqueous $Na_2S_2O_3$ solution, the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and then evaporated. This afforded the product as a yellow solid (2.20 g, 5.12 mmol, ~100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31–8.37 (m, 3 H, AQ), 8.25 (d, *J* = 1.8 Hz, 1 H, AQ), 7.80–7.85 (m, 2 H, AQ), 7.79 (s, 1 H, xy), 7.72–7.74 (dd, *J* = 8.0 Hz, 1.8 Hz, 1 H, AQ), 7.14 (s, 1 H, xy), 2.45 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3).

Compound **10**. Compound **9** (200 mg, 0.46 mmol), commercial bis(pinacolato)diborane (174 mg, 0.68 mmol), and KOAc (199 mg, 2.02 mmol) were suspended in dry DMF (10 ml). After de-oxygenating, $PdCl_2(PPh_3)_2$ (8.1 mg, 0.01 mmol) was added, and the reaction mixture was heated to 100 °C under N_2 for 24 hours. Then the DMF was evaporated, and the solid residue was taken up in CH_2Cl_2 (50 ml) and was washed with H_2O repeatedly. After drying over anhydrous Na_2SO_4, the CH_2Cl_2 was evaporated and the crude product was purified by chromatography on silica gel column using a 1:1 (v:v) mixture of pentane and CH_2Cl_2 as the eluent. This procedure afforded the pure product as a yellow crystalline solid (183 g, 0.42 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38–8.30 (m, 3 H, AQ), 8.28 (dd,

J = 1.8 Hz, 0.5 Hz, 1 H, AQ), 7.85–7.78 (m, 2 H, AQ), 7.76 (dd, *J* = 8.0 Hz, 1.8 Hz, 1 H, AQ), 7.72 (s, 1 H, xy), 7.11 (s, 1 H, xy), 2.56 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 1.38 (s, 12 H, CH_3).

Compound **12**. Compound **10** (200 mg, 0.46 mmol), 5,5'-dibromo-2,2'-bipyridine (**11**)[5] (287 mg, 0.91 mmol), and Na_2CO_3 (146 mg, 1.38 mmol) were suspended in THF (10 ml) and H_2O (3 ml). After de-oxygenating, $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) was added. Prior to heating to reflux overnight, the reaction mixture was de-oxygenated again. After cooling to room temperature, the product was filtered and washed with methanol. Chromatography on silica gel column with CH_2Cl_2 containing 1% of triethylamine as the eluent yielded the pure product as a yellow solid (230 mg, 0.42 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (dd, *J* = 3.1 Hz, 2.4 Hz, 1 H, bpy), 8.71 (dd, *J* = 2.2 Hz, 0.9 Hz, 1 H, bpy), 8.47 (dd, *J* = 8.1 Hz, 0.9 Hz, 1 H, bpy), 8.43–8.38 (m, 2 H, bpy), 8.37- 8.34 (m, 3 H, AQ), 7.98 (dd, *J* = 8.5 Hz, 2.4 Hz, 1 H, bpy), 7.85–7.82 (m, 4 H, AQ), 7.27 (s, 1 H, xy), 7.25 (s, 1 H, xy), 2.35 (m, 6 H, CH_3).

Compound **13**. Compound **12** (196 mg, 0.36 mmol), 4-(trimethylsilyl)phenylboronic acid (**2**)[2] (96 mg, 0.43 mmol), and Na_2CO_3 (229 mg, 2.16 mmol) were suspended in toluene (10 ml), ethanol (3 ml), and H_2O (4 ml). After de-oxygenating, $Pd(PPh_3)_4$ (42 mg, 0.04 mmol) was added and the suspension was de-oxygenated again prior to heating to reflux for 2 days. After cooling to room temperature, H_2O (100 ml) was added, and the reaction mixture was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and then evaporated. Chromatography on silica gel column with CH_2Cl_2 containing 1% methanol and subsequent recrystallization from pentane gave the pure product as a light yellow solid (170 mg, 0.26 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (dd, *J* = 14.3 Hz, 2.2 Hz, 2 H, bpy), 8.52 (t, *J* = 8.2 Hz, 2 H, bpy), 8.40 (d, *J* = 8.0 Hz, 1 H, bpy), 8.38–8.33 (m, 3 H, AQ), 7.88 (dd, *J* = 8.1 Hz, 2.2 Hz, 1 H, bpy), 7.85–7.80 (m, 4 H, AQ), 7.41 (s, 1 H, xy), 7.28 (s, 2 H, xy), 7.12 (s, 1 H, xy), 2.50 (s, 3 H, CH_3), 2.37 (m, 6 H, CH_3), 2.33 (s, 3 H, CH_3), 0.38 (s, 9 H, $Si(CH_3)_3$).

Compound **14**. Compound **13** (170 mg, 0.26 mmol) was dissolved in CH_2Cl_2 under N_2 and cooled to 0 °C. A solution of ICl (30 µl, 0.56 mmol) in CH_3CN (3 ml) was added dropwise, and the resulting suspension was stirred at room temperature overnight. Then 5% aqueous $Na_2S_2O_3$ solution (200 ml) was added, and the product was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated. The crude product was filtered over a pluck of silica gel using CH_2Cl_2 with 1% of methanol as the eluent. This procedure afforded the pure product as a yellow solid (120 mg, 0.17 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, *J* = 1.7 Hz, 1 H, bpy), 8.68 (d, *J* = 1.7 Hz, 1 H, bpy), 8.58 (s, 2 H, bpy), 8.41 (dd, *J* = 7.9 Hz, 0.5 Hz, 1 H, bpy), 8.38–8.34 (m, 3 H, AQ), 7.93 (d, *J* = 8.1 Hz, 1 H, bpy), 7.87–7.81 (m, 4 H, AQ), 7.81 (s, 1 H, xy), 7.29–7.27 (m, 2 H, xy), 7.16 (s, 1 H, xy), 2.47 (s, 3 H, CH_3), 2.37 (m, 6 H, CH_3), 2.27 (s, 3 H, CH_3).

Ligand **15**. Compound **14** (70 mg, 0.10 mmol), oligotriarylamine **5**[3] (69 mg, 0.11 mmol), NaO^tBu (192 mg, 2.00 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), and $(HP^tBu_3)BF_4$ (2.9 mg, 0.01 mmol) were suspended in dry de-oxygenated toluene (10 ml). The reaction mixture was refluxed for 27 hours. Then the solvent was evaporated, and the residue was taken up in CH_2Cl_2 (50 ml), washed with H_2O and dried over anhydrous Na_2SO_4. The crude product was purified by chromatography on silica gel column. At first, the eluent was pure CH_2Cl_2, then CH_2Cl_2 with 1% methanol was

employed. Subsequent re-crystallization from hexane gave the pure ligand as a brown solid (0.06 g, 0.05 mmol, 50%). ^{1}H NMR (400 MHz, C_6D_6) δ: 9.01–8.95 (m, 2 H, bpy), 8.95–8.90 (m, 2 H, bpy), 8.50 (d, *J* = 1.8 Hz, 1 H, bpy), 8.36 (d, *J* = 8.0 Hz, 1 H, AQ), 8.33–8.25 (m, 2 H, AQ), 7.53 (dt, *J* = 8.1 Hz, 2.2 Hz, 2 H, AQ), 7.35 (dd, *J* = 7.9 Hz, 1.8 Hz, 2 H, AQ), 7.27 (s, 1 H, bpy), 7.21 (s, 1 H, xy), 7.14–7.08 (m, 16 H, AA'BB'), 6.99 (m, 2 H, xy), 6.96 (s, 1 H, xy), 6.73 (d, *J* = 8.7 Hz, 8 H, AA'BB'), 3.30 (s, 12 H, OCH_3), 2.20 (s, 3 H, CH_3), 2.08 (s, 6 H, CH_3), 1.99 (s, 3 H, CH_3).

AQ-Ru-OTA. Ligand **15** (60 mg, 0.05 mmol) and $Ru(bpy)_2Cl_2$ (24 mg, 0.05 mmol) were suspended in a mixture of $CHCl_3$ (10 ml) and ethanol (3 ml). After de-oxygenating, the reaction mixture was heated to reflux under N_2 for 2 days. Then the solvents were evaporated, and the solid residue was purified by chromatography on silica gel column. At first, the eluent was pure acetone, and then a 100:10:1 (v:v:v) mixture of acetone, H_2O, and saturated aqueous KNO_3 solution was used. Acetone was evaporated from the relevant chromatography fractions, and the desired product was precipitated as a hexafluorophosphate salt by dropwise addition of saturated aqueous KPF_6 solution. After filtration and washing with H_2O and diethyl ether, the product was obtained as a brown solid (64 mg, 0.03 mmol, 68%). ^{1}H NMR (400 MHz, acetone-d_6) δ: 8.97 (dd, *J* = 10.9 Hz, 8.5 Hz, 2 H, bpy), 8.85 (td, *J* = 8.0 Hz, 3.0 Hz, 4 H, bpy), 8.39–8.12 (m, 15 H, AQ, bpy), 8.06 (t, *J* = 1.6 Hz, 2 H, bpy), 8.01–7.95 (m, 2 H, bpy), 7.91 (dd, *J* = 8.0 Hz, 1.9 Hz, 1 H, xy), 7.66 (ddt, *J* = 7.5 Hz, 5.7 Hz, 1.5 Hz, 2 H, bpy), 7.58 (dddd, *J* = 10.1 Hz, 7.4 Hz, 5.7 Hz, 1.2 Hz, 2 H, bpy), 7.24 (m, 2 H, xy), 7.13 (s, 1 H, xy), 6.99 (d, *J* = 8.1 Hz, 8 H, AA'BB'), 6.93–6.68 (m, 16 H, AA'BB'), 3.77 (s, 12 H, OCH_3), 2.29 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3). ESI-MS calculated (m/z) for $C_{100}H_{81}N_9O_6Ru^{2+}$: 802.7675; found: 802.7670. Elemental analysis calculated (%) for $C_{100}H_{81}N_9O_6F_{12}P_2Ru{\cdot}8H_2O$: C 58.88, H 4.79, N 6.18; found: C 58.67, H 4.59, N 6.12.

Instruments and methods

All commercially available chemicals were used without further purification. CH_2Cl_2 and diethyl ether were dried in a solvent purification system from Innovative Technology. Dry toluene and DMF were bought from Sigma-Aldrich (crown cap; over molecular sieve) and used as received. Silica gel (40–63 μm, Silicycle) from Acros was used for column chromatography, and thin-layer chromatography was performed on silica gel plates (60 F254) from Merck. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance III instrument, ^{13}C NMR spectra were measured on a 500 MHz Bruker Avance III instrument. High-resolution mass spectra were measured on a Bruker maXis 4G QTOF ESI spectrometer. Elemental analysis was performed by Ms. Sylvie Mittelheisser in the Department of Chemistry at University of Basel using a Vario Micro Cube instrument from Elementar.

Optical absorption spectra were measured on a Cary 5000 UV-Vis-NIR spectrometer from Varian. Steady-state luminescence spectroscopy was performed using a Fluorolog-322 instrument from Horiba Jobin-Yvon. The same instrument was used for continuous irradiation experiments, using an excitation wavelength of 450 nm and a bandwidth of 14.7 nm. The photon flux obtained under these conditions was found to be $(6.74\pm0.21)\cdot10^{15}$ photons/s using ferrioxalate actinometry.[6] The error reported here corresponds to twice the standard deviation extracted from a linear regression fit of moles of Fe(II) formed versus irradiation time. No significant second-order radiation at 225 nm reached the samples. The continuous irradiation experiments were performed on 3 ml samples of 10^{-5} M solutions. Time-resolved luminescence and transient absorption studies occurred with an LP920-KS spectrometer from Edinburgh Instruments and the frequency-doubled output of a Quantel Brilliant b laser as an excitation source. Cyclic voltammetry was measured with a Versatat3-200 potentiostat using a glassy carbon working electrode and two silver wires as counter- and quasi-reference electrodes, respectively. Chemical oxidation occurred with commercial $Cu(ClO_4)_2$ as reported earlier.[3c, 7]

Reaction free energies for photoinduced electron transfer

The Weller equation (eq.S1) can be used to estimate the reaction free energy (ΔG_{ET}^0) associated with intramolecular electron transfer from the oligotriarylamine unit to photoexcited $Ru(bpy)_3^{2+}$ in **Ru-OTA** and **AQ-Ru-OTA**.[8]

$$\Delta G_{ET}^0 = e\cdot[E^0(OTA^{+/0}) - E^0(bpy^{0/-})] - E_{00} - e^2 / (4\cdot\pi\cdot\varepsilon_0\cdot\varepsilon_s\cdot R_{DA}) \quad \text{(eq. S1a)}$$

$$\Delta G_{ET}^0 = e\cdot[E^0(Ru^{III/II}) - E^0(AQ^{0/-})] - E_{00} - e^2 / (4\cdot\pi\cdot\varepsilon_0\cdot\varepsilon_s\cdot R_{DA}) \quad \text{(eq. S1b)}$$

Using the relevant redox potentials from Table 1 of the main paper and a value of 2.12 eV for the ^{3}MLCT energy of the $Ru(bpy)_3^{2+}$ complex (E_{00}) in **Ru-OTA** and **AQ-Ru-OTA**,[9] one obtains ΔG_{ET}^0 = -0.50 eV for the dyad and ΔG_{ET}^0 = -0.56 eV for the triad. These two estimates are based on a donor-acceptor distance (R_{DA}) of 10.1 Å, corresponding to the geometrical distance between the central N atom of the oligotriarylamine (i. e., the most electron rich N center) and the Ru atom. Thus, in both **Ru-OTA** and **AQ-Ru-OTA**, reductive excited-state quenching by the oligotriarylamine unit is strongly exergonic.

In the **AQ-Ru-OTA** triad there is the additional possibility of oxidative ^{3}MLCT excited-state quenching by the anthraquinone unit. Based on equation 1b and the relevant redox potentials (and E_{00} = 2.12 eV, R_{DA} = 22.5 Å), one estimates ΔG_{ET}^0 = 0.02 eV for this process. Since reductive excited-state quenching is associated with a substantially higher driving-force (-0.56 eV, see above), oxidative quenching by anthraquinone is likely to play a subordinate role for primary depopulation of the ^{3}MLCT excited state. Consequently, anthraquinone acts mainly as an efficient secondary electron acceptor, as noted earlier in similar triads.[10]

Thermal disproportionation experiment

In principle it is conceivable that charge accumulation occurs via thermal disproportionation (eq. S2).

$$OTA^{+} + OTA^{+} \rightarrow OTA^{2+} + OTA \qquad \text{(eq. S2)}$$

In order to test this hypothesis, aerated 10^{-5} M solutions of **Ru-OTA** and **AQ-Ru-OTA** in CH_3CN containing 0.02 M of $Sc(OTf)_3$ were photoirradiated for ca. 1 minute at 450 nm in order to form substantial amounts of **Ru-OTA**$^{+}$ and **AQ-Ru-OTA**$^{+}$ (black traces in Figure S1) and then left standing in the dark for 60 minutes (green traces in Figure S1).

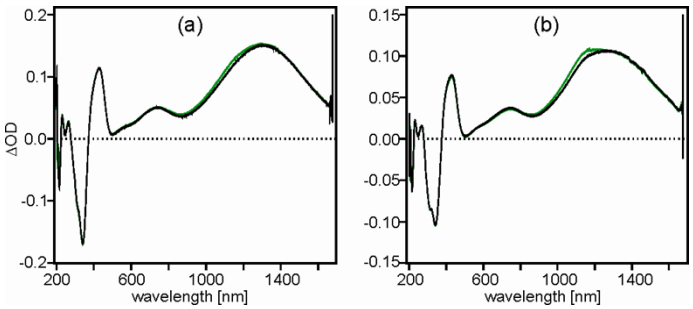

Figure S1. Black traces: UV-Vis difference spectra measured after photoirradiation (λ_{exc} = 450 nm) of 10^{-5} M solutions of (a) **Ru-OTA** and (b) **AQ-Ru-OTA** in aerated CH_3CN in presence of 0.02 M $Sc(OTf_3)$ for ca. 1 minute. The UV-Vis spectra measured immediately after sample preparation (prior to photoirradiation) served as baselines. Green traces: UV-Vis difference spectra measured after letting these same solutions stand in the dark for 60 minutes.

The data in Figure S1 clearly shows that no significant formation of **Ru-OTA**$^{2+}$ and **AQ-Ru-OTA**$^{2+}$ occurs via thermal disproportionation.

Moreover we note that disproportionation is unfavorable based on the redox potentials from Table 1 of the main paper.

Kinetics of photoinduced charge accumulation

Figures S2 and S3 show the complete data sets obtained in the photoirradiation experiments with **Ru-OTA** and **AQ-Ru-OTA** in aerated CH_3CN in presence of Sc^{3+}. Parts of these data sets are shown in Figure 6a/e of the main paper.

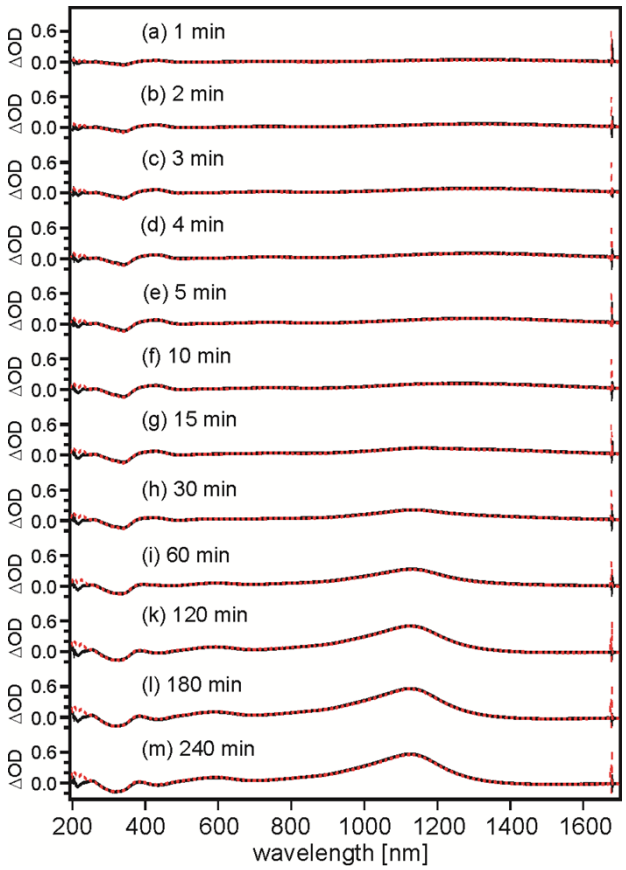

Figure S2. Solid black traces: UV-Vis difference spectra measured after different time intervals following excitation of 10^{-5} M **Ru-OTA** in aerated CH_3CN in presence of 0.02 M $Sc(OTf_3)$. The UV-Vis spectrum measured immediately after sample preparation (prior to photoirradiation) served as a baseline in all cases. The volume of the irradiated sample was 3 ml, the irradiation flux was $(6.74\pm0.21)\cdot10^{15}$ photons per second at 450 nm. Dotted red traces: Linear combinations of the UV-Vis difference spectra obtained for **Ru-OTA**$^+$ (green trace in Figure 3a) and **Ru-OTA**$^{2+}$ (red trace in Figure 3a).

The experimental UV-Vis difference spectra measured after different time intervals can be fitted to a linear combination of the spectra of **Ru-OTA**$^+$ (green trace, Figure 3a) and **Ru-OTA**$^{2+}$ (red trace, Figure 3a):

$$\text{fit function} = x \cdot \text{spectrum of } \mathbf{Ru\text{-}OTA}^+ + y \cdot \text{spectrum of } \mathbf{Ru\text{-}OTA}^{2+} \qquad \text{(eq. S3)}$$

The multiplication factors (x, y) of these linear combinations are plotted graphically in Figure S4a.

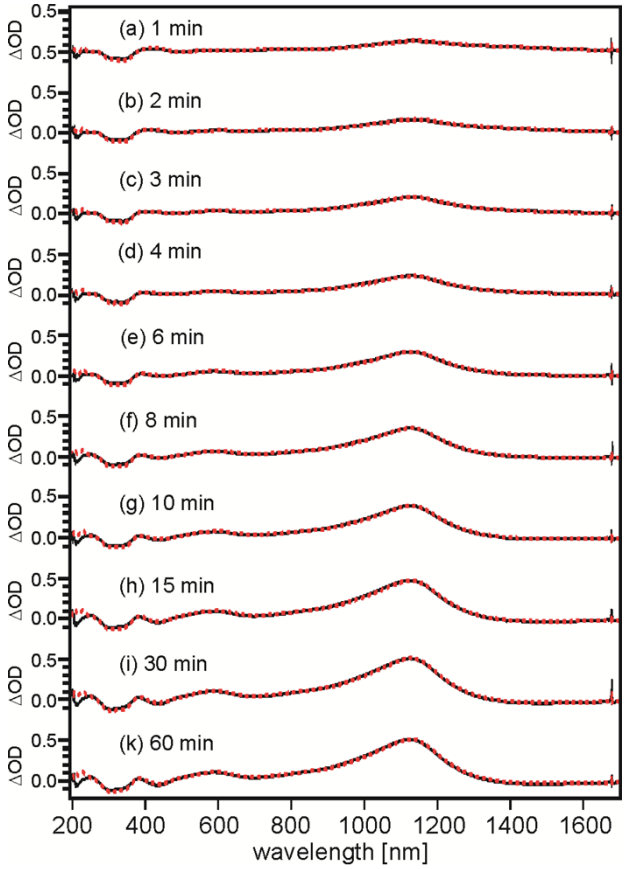

Figure S3. Solid black traces: UV-Vis difference spectra measured after different time intervals following excitation of 10^{-5} M **AQ-Ru-OTA** in aerated CH_3CN in presence of 0.02 M $Sc(OTf_3)$. The UV-Vis spectrum measured immediately after sample preparation (prior to photoirradiation) served as a baseline in all cases. The volume of the irradiated sample was 3 ml, the irradiation flux was $(6.74\pm0.21)\cdot10^{15}$ photons per second at 450 nm. Dotted red traces: Linear combinations of the UV-Vis difference spectra obtained for **AQ-Ru-OTA**$^{+}$ (green trace in Figure 3b) and **AQ-Ru-OTA**$^{2+}$ (red trace in Figure 3b).

The experimental UV-Vis difference spectra measured after different time intervals can be fitted to a linear combination of the spectra of **AQ-Ru-OTA**$^{+}$ (green trace, Figure 3b) and **AQ-Ru-OTA**$^{2+}$ (red trace, Figure 3b):

$$\text{fit function} = x \cdot \text{spectrum of } \mathbf{AQ\text{-}Ru\text{-}OTA}^{+} + y \cdot \text{spectrum of } \mathbf{AQ\text{-}Ru\text{-}OTA}^{2+} \qquad \text{(eq. S4)}$$

The multiplication factors (x, y) of these linear combinations are plotted graphically in Figure S4b.

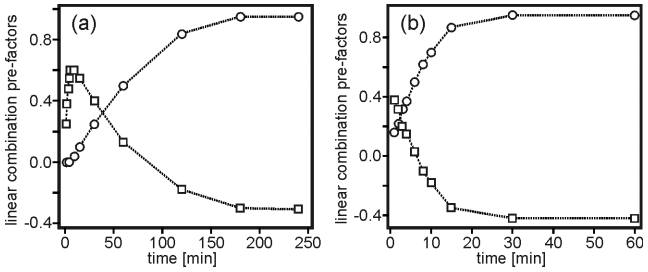

Figure S4. Multiplication factors *x* and *y* extracted from the data set in Figures S2/S3 using equations S3/S4. The dotted lines are guides for the eye, not fits.

For the multiplication factor *x*, negative values are obtained after sufficiently long irradiation times. This is because some OTA^+ is already formed during sample preparation, and this turned out to be impossible to avoid.

The data from Figure S4 were converted to the data shown in Figure 7 of the main paper as follows: The total concentration of dyads or triads is 10^{-5} M. At the end of the photoirradiation experiments, both samples have been essentially completely oxidized to **Ru-OTA**$^{2+}$ or **AQ-Ru-OTA**$^{2+}$. Using this logic, the multiplication factors *x* and *y* can be converted to concentrations of **Ru-OTA**$^+$ / **AQ-Ru-OTA**$^+$ and **Ru-OTA**$^{2+}$ / **AQ-Ru-OTA**$^{2+}$.

In both Figure S2 and Figure S3 experimental and fitted difference spectra deviate from each other at ~250 nm. One reviewer pointed out that this might be related to superoxide or peroxide species, but this is speculative.

References

(1) Fang, Y. Q.; Hanan, G. S., *Synlett* **2003**, 852.

(2) (a) Hensel, V.; Lutzow, K.; Jacob, J.; Gessler, K.; Saenger, W.; Schlüter, A. D., *Angew. Chem. Int. Ed.* **1997,** *36*, 2654. (b) Hensel, V.; Schlüter, A. D., *Liebigs Ann.* **1997**, 303.

(3) (a) Bonn, A. G.; Neuburger, M.; Wenger, O. S., *Inorg. Chem.* **2014,** *73*, 11075. (b) Bonn, A. G.; Wenger, O. S., *J. Org. Chem.* **2015,** *80*, 4097. (c) Karlsson, S.; Boixel, J.; Pellegrin, Y.; Blart, E.; Becker, H. C.; Odobel, F.; Hammarström, L., *J. Am. Chem. Soc.* **2010,** *132*, 17977.

(4) (a) Hankache, J.; Hanss, D.; Wenger, O. S., *J. Phys. Chem. A* **2012,** *116*, 3347. (b) Hankache, J.; Wenger, O. S., *Chem. Commun.* **2011,** *47*, 10145.

(5) Liu, S. J.; Zhao, Q.; Chen, R. F.; Deng, Y.; Fan, Q. L.; Li, F. Y.; Wang, L. H.; Huang, C. H.; Huang, W., *Chem.-Eur. J.* **2006,** *12*, 4351.

(6) (a) Hatchard, C. G.; Parker, C. A., *Proc. R. Soc. Math. Phys. Eng. Sci* **1956,** *235*, 518. (b) Pozdnyakov, I. P.; Kel, O. V.; Plyusnin, V. F.; Grivin, V. P.; Bazhin, N. M., *J. Phys. Chem. A* **2008,** *112*, 8316. (c) Vitz, E. W., *J. Chem. Educ.* **1981,** *58*, 655.

(7) Sreenath, K.; Thomas, T. G.; Gopidas, K. R., *Org. Lett.* **2011,** *13*, 1134.

(8) Weller, A., *Z. Phys. Chem.* **1982,** *133*, 93.

(9) (a) Lever, A. B. P., *Inorg. Chem.* **1990,** *29*, 1271. (b) Roundhill, D. M., *Photochemistry and Photophysics of Metal Complexes*. Plenum Press: New York, 1994.

(10) Hankache, J.; Niemi, M.; Lemmetyinen, H.; Wenger, O. S., *J. Phys. Chem. A* **2012,** *116*, 8159.