Supporting Information for

Photochemical Upconversion in Water

Karim A. El Roz^a and Felix N. Castellano*a

^aDepartment of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Corresponding Author

*Email: fncastel@ncsu.edu

Experimental Section

General: [Ru(bpy)₃]Cl₂ was purchased from Sigma Aldrich and used without further purification. Na₄[Ru(BPS)₃] was synthesized and purified as previously reported in the literature.^{1,2} 9-Anthracenecarboxylic acid (AnCO₂H) and 1-Pyrenecarboxylic acid (PyCO₂H) were purchased from Sigma Aldrich. Each carboxylic acid compound was treated with hot sodium hydroxide in water, under vigorous stirring overnight, followed by recrystallization from acetone to yield the sodium salts 9-Anthracenecarboxylate anion (AnCO₂⁻) and 1-Pyrenecarboxyalte anion (PyCO₂⁻) respectively.³ Unlike the conjugate acid form, the aromatic hydrocarbon salts, Na[AnCO₂] and Na[PyCO₂], are watersoluble. Spectroscopic samples were placed in a 1 cm path length Starna cell (quartz) cuvette, bubble-degassed with argon gas for at least 40 min where they remained under positive inert atmosphere during the course of the photospectroscopic experiments. HPLC grade water (H₂O) was purchased from J.T. Baker. Absorption spectra were measured using Cary 50 or Agilent 845 diode array spectrophotometer. Static emission spectra were collected from FL/FL920 spectrofluorometer (Edinburgh Instruments) and corrected for emission detector response.

Stern-Volmer Kinetics: Using steady state dynamic quenching, the Stern-Volmer constant (k_{sv}) and the bimolecular quenching rate (k_q) were extrapolated from photoluminescence lifetime experiments according to the Stern-Volmer relation, $\tau_0/\tau = 1+K_{sv}[Q]$ where τ_0 and τ are the sensitizer lifetimes of the unquenched and quenched emission respectively and $K_{SV} = k_q \tau_0$. The slope (K_{sv}) was linear upon the addition of [Q], molar concentration of quencher/acceptor. The samples were excited using a Nitrogen-pumped dye laser at 442 nm to selectively excite the Ru(II) MLCT band in the absorption spectra. The absorbance of the sensitizers was chosen to be optically-dilute at the excitation wavelength (0.1 - 0.2). All samples were bubbled degassed for 40 min before the start of the experiment.

Transient Optical Spectroscopy: The optical density of the samples at 452 nm excitation wavelength was ~ 0.35. The laser pulse excitation source was from a Vibrant 355 LD-UVM Nd:YAG/OPO system (OPOTEK) (~3 mJ/pulse, 5 ns fwhm). The transient absorption data collected was from an LP920 laser flash photolysis (Edinburgh Instruments) with an iStar ICCD Camera (Andor), and the kinetic traces were acquired using a PMT (R928 Hamamatsu). Exponential decays were fitted accordingly using Origin 9.1.

Upconversion Power Dependence Experiment: The upconverted photoluminescence detected from FL/FLS 920 spectrofluorometer was a result of a continuous laser-beam excitation from an Argon/Krypton ion laser (Innova 70C Coherent) excited at 488 nm or 514.5 nm (~ 1 mm diameter spot). A Nova II/PD300-UV power meter was used to determine the excitation power before reaching the sample. The appropriate filters were positioned in front of the incident laser to filter-out all wavelengths except the excitation wavelength issued from the laser preventing direct absorption of the acceptor. No emission was observed when samples were irradiated at 488 nm in the absence of sensitizer. For the power dependence experiment, neutral density filters were used to

adjust the laser power prior to exciting the sample. To gain an improved upconverted emission profile, a spatial geometry adjustment of sample illumination was used to correct for the inner-filter effect.^{4–6} In the formulations examined here, upconversion was detected when the laser beam was incident along the edge square of the cuvette sample. The concentration of the sensitizer was chosen with an absorbance of ~ 1 at the excitation wavelength, whereas the acceptor concentration was selected so that it can quench the excited state of the sensitizer at least up to 90 % as extrapolated from Stern-Volmer kinetics (k_{sv}). The power dependence data were plotted as a double logarithmic graph showing the integrated upconverted emission as a function of incident power densities.

Quantum Yield Measurements: Upconversion quantum yield of acceptor AnCO₂⁻ or PyCO₂⁻ sensitized by Ru(II) sensitizers were calculated relative to $[Ru(bpy)_3](PF_6)_2$ ($\Phi_{std} = 0.018$) in aerated spectrophotometric grade acetonitrile under 514.5 nm excitation.^{7,8} The conditions used to calculate the quantum yield were selected to have optically-dilute samples of sensitizers ($A_{514 \text{ nm}} = 0.1 \sim 0.2$) with acceptor concentration appropriate for at least 90 % quenching rate. The fluorescence quantum yield of the water-soluble AnCO₂⁻ and PyCO₂⁻ resulted from direct excitation at 335 nm were calculated relative to anthracene ($\Phi_{std} = 0.27$) in aerated spectrophotometric grade acetonitrile.⁹

Determination of the triplet decay (k_T) and the triplet-triplet annihilation (k_{TTA}): After populating the triplet-excited state acceptors, the triplet decay (k_T) and the triplet-triplet annihilation (k_{TTA}) rate constants were determined by fitting the kinetic absorption decay data at 420 nm as a function of time according to Eq.S1.

$$\frac{d[{}^{3}M^{*}]}{dt} = -k_{T}[{}^{3}M^{*}] - k_{TTA}[{}^{3}M^{*}]^{2}$$
 Eq.S1

Here, $[{}^{3}M^{*}]$ is the concentration of the triplet excited state acceptor. Fitting the transient absorption decay data of the triplet AnCO₂⁻ or PyCO₂⁻ at 420 nm requires the integration of Eq.S1 to yield Eq.S2.

$$\Delta A = \frac{\Delta A_0 (1 - \beta)}{\exp(k_t) - \beta}$$
Eq.S2

$$\beta = \frac{k_{TTA} [{}^{3} M^{*}]_{0}}{k_{TTA} [{}^{3} M^{*}]_{0} + k_{T}}$$
 Eq.S3

 $[{}^{3}M^{*}]$ can be translated to transient absorption terms where it is directly proportional to ΔA values. The analytical solution to equate for the fraction of acceptors occurring through the bimolecular TTA channel was designated by β (Eq.S3). To simplify the parameters, α was used, where $\alpha = k_{TTA} [{}^{3}M^{*}]_{0}$ and $\beta = \alpha/(k_{T} + \alpha)$. Using the extinction coefficient of the triplet excited state of AnCO₂⁻ ($\epsilon_{T} = 39,000 \text{ M}^{-1}\text{cm}^{-1}$) or PyCO₂⁻ ($\epsilon_{T} = 21,200 \text{ M}^{-1}\text{cm}^{-1}$) (data in Figure S4), a series of kinetic absorption decay data were collected at 420 nm as a function of pulse energy to give k_{T} (s⁻¹), k_{TTA} (M⁻¹ s⁻¹), and the fraction β .



Figure S1. Energy levels showing the triplet/singlet energies for the Ru(II) sensitizers and carboxylate acceptors.



Figure S2. Dynamic photoluminescence quenching of Ru(II) photosensitizers, under optically-dilute conditions in degassed H₂O, monitored at 625 nm. a) $[Ru(bpy)_3]^{2+}$ quenched by AnCO₂⁻ b) $[Ru(BPS)_3]^{4-}$ quenched by AnCO₂⁻ c) $[Ru(bpy)_3]^{2+}$ quenched by PyCO₂⁻ d) $[Ru(BPS)_3]^{4-}$ quenched by PyCO₂⁻.



Figure S3. Stern-Volmer plots of samples prepared in degassed H₂O solvent. a) $[Ru(bpy)_3]^{2+}$ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles). b) $[Ru(BPS)_3]^{4-}$ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles).



Figure S4. Transient absorption difference spectra of $[Ru(BPS)_3]^{4-}$ (A_{452 nm} ~ 0.35) with A) 0.5 mM of AnCO₂⁻ and A') 0.5 mM of PyCO₂⁻ respectively measured as a function of delay time. B) and B') show the kinetic growth (blue line) of the sensitized triplet acceptor of AnCO₂⁻ and PyCO₂⁻ respectively measured at 420 nm and the quenched emission decay (black line) of $[Ru(BPS)_3]^{4-}$ at 630 nm with each acceptor; the red and pink lines represent the single exponential decay fits. Samples were bubble degassed and excited at 452 nm (~ 3 mJ/pulse).



Figure S5. Transient absorption kinetic decay of the triplet excited state of $AnCO_2^-$ (black line) and $PyCO_2^-$ (red line) in degassed H₂O monitored at 420 nm upon 452 nm excitation. The conditions were [Ru(bpy)₃](Cl₂) (3.5 x 10⁻⁵ M) with $AnCO_2^-$ (3.7 mM) and $PyCO_2^-$ (3.9 mM) respectively. The triplet extinction coefficient of $AnCO_2^-$ ($^3\varepsilon = 39,000 \text{ M}^{-1}\text{cm}^{-1}$) and $PyCO_2^-$ ($^3\varepsilon = 21,200 \text{ M}^{-1}\text{cm}^{-1}$) were averaged as a function of pulse energy and calculated using Eq. S4.^{12,13,15,16} [Ru(bpy)₃](Cl₂) in water was used as the donor with an excited state absorption maximum at 370 nm ($^3\varepsilon_{370 \text{ nm}} = 22,000 \text{ M}^{-1}\text{cm}^{-1}$).¹⁷ The inset shows the single exponential fit (magenta line) and the residual (green line) of [Ru(bpy)₃](Cl₂) in water monitored at 370 nm.

$$\frac{{}^{3}\varepsilon_{Acceptor}}{{}^{3}\varepsilon_{Donor}} = \frac{\Delta A_{Acceptor}}{\Delta A_{Donor}}$$
(Eq. S4)



Figure S6. a) Transient absorption decay at 420 nm of 3.4 x 10^{-5} M $[Ru(bpy)_3]^{2+}$ and 3.78 mM AnCO₂⁻ in degassed water measured as a function of pulse energy. ($\lambda_{exc} = 452$ nm). b) shows the representative kinetic fit (4.9 mJ/ pulse data) to Eq. S2 (red line), and the residual fit is represented by the green line.

| Pulse Energy (mJ) | ΔA ₀ | k _T (10 ⁴ s ⁻¹) | k _{TTA} (10 ⁹ M ⁻¹ s ⁻¹) | α (10 ⁴ s ⁻¹) | β |
|----------------------|-----------------|---|---|--------------------------------------|-------|
| 4.9 | 0.316 | 1.89 | 6.79 | 5.49 | 0.744 |
| 5.9 | 0.362 | 1.88 | 6.07 | 5.61 | 0.749 |
| 7.9 | 0.415 | 1.84 | 5.55 | 5.91 | 0.763 |
| 8.5 | 0.422 | 1.89 | 5.38 | 5.81 | 0.754 |

Table S1. Parameters Obtained from the Fits of the Transient Absorption Decay Data at 420 nm for the sample containing $[Ru(bpy)_3]^{2+}$ (3.4 x 10⁻⁵ M) and AnCO₂⁻ (3.78 mM) in H₂O.



Figure S7. Comparison of the emission intensity for $AnCO_2^-$ (black line) and $PyCO_2^-$ (red line) in water, matched at optically-dilute conditions under 335 nm excitation. Anthracene in acetonitrile with ($\Phi_f = 0.27$) was used as reference for quantum yield calculations.

| | AnCO ₂ | PyCO ₂ |
|----------|-------------------|-------------------|
| Trial 1 | 0.08395 | 0.53214 |
| Trial 2 | 0.06169 | 0.49899 |
| Trial 3 | 0.06021 | 0.5011 |
| Average | 0.0686 | 0.5107 |
| St. Dev. | 0.0132 | 0.0185 |

Table S2. Quantum Yield Values



Figure S8. a) Time resolved emission intensity monitored at 630 nm in water for $[Ru(BPS)_3]^{4-}$ in with no additives (black line), with 3 mM of $AnCO_2^{-}$ (blue line), and with 3 mM of $AnCO_2^{-} + 0.3$ M of NaOTf (red line). b) shows the upconverted emission intensity unaffected by the presence of salt in solution.

References:

- 1 S. Zanarini, L. Della Ciana, M. Marcaccio, E. Marzocchi, F. Paolucci and L. Prodi, *J. Phys. Chem. B*, 2008, **112**, 10188–10193.
- L. Della Ciana, S. Zanarini, R. Perciaccante, E. Marzocchi and G. Valenti, *J. Phys. Chem. C*, 2010, **114**, 3653–3658.
- 3 M. Ruthkosky, F. N. Castellano and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 6406–6412.
- C. Mongin, J. H. Golden and F. N. Castellano, ACS Appl. Mater. Interfaces, 2016, 8, 24038–24048.
- 5 C. A. Parker and W. J. Barnes, *Analyst*, 1957, **82**, 606.
- 6 P. L. Lutz, H.-P.; Luisi, Helv. Chim. Acta, 1983, 66, 1929–1935.
- 7 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850.
- 8 C. E. McCusker and F. N. Castellano, *Inorg. Chem.*, 2015, 54, 6035–6042.
- 9 M. Montalti, A. Credi, L. Prodi and M. Gandolfi, *Handbook of photochemistry*, *3rd edn. CRC Press, Boca Raton*, 2006.
- 10 F. Deng and F. N. Castellano, J. Phys. Chem., 2013, 117, 4412–4419.
- 11 T. W. Schmidt, J. Phys. Chem. Lett., 2010, 1795–1799.
- 12 T. N. Singh-Rachford and F. N. Castellano, *Inorg. Chem.*, 2009, 48, 2541–2548.
- 13 T. Singh-Rachford, A. Nayak, M. L. Muro-Small, G. Goeb, M. J. Therien and F. N. Castellano, *J. Am. Chem. Soc.*, 2010, **132**, 14203–14211.
- 14 Y. Y. Cheng, T. Khoury, M. J. Crossley and T. W. Schmidt, 2010, 66–71.
- 15 I. Carmichael and G. L. Hug, J. Phys. Chem. Ref. Data, 1986, 15, 1–250.
- 16 R. Bensasson and E. J. Land, Trans. Faraday Soc., 1971, 67, 1904–1915.
- 17 R. S. Khnayzer, V. S. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang and F. N. Castellano, *Energy Environ. Sci.*, 2014, 7, 1477–1488.