

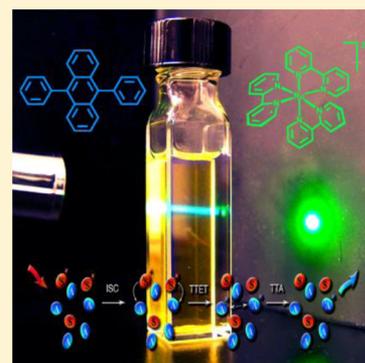
Photochemical Upconversion: A Physical or Inorganic Chemistry Experiment for Undergraduates Using a Conventional Fluorimeter

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S Supporting Information

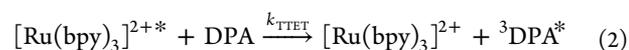
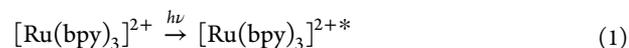
ABSTRACT: Photochemical upconversion is a regenerative process that transforms lower-energy photons into higher-energy light through two sequential bimolecular reactions, triplet sensitization of an appropriate acceptor followed by singlet fluorescence producing triplet–triplet annihilation derived from two energized acceptors. This laboratory directly investigates this phenomenon using the facile photo-induced triplet–triplet energy-transfer reaction between the benchmark inorganic chromophore tris(2,2'-bipyridyl)ruthenium(II), $[\text{Ru}(\text{bpy})_3]^{2+}$, and 9,10-diphenylanthracene (DPA). Selective green excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the presence of DPA results in two observations, the (dynamic) quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ photoluminescence in the red and the production of upconverted DPA singlet fluorescence in the blue. The quadratic nature of the incident light power dependence for the latter process is easily realized by using the percent transmission characteristics of neutral density filters placed in the excitation beam prior to sample illumination. In a single laboratory period, students are able to directly visualize the upconverted fluorescence generated and gain experience in various aspects of fluorescence spectroscopy, triplet energy-transfer processes, quenching, and reaction molecularity.



KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Photochemistry, Fluorescence Spectroscopy, Kinetics, Rate Law, UV-Vis Spectroscopy

The efficiency of a photovoltaic device is largely determined by its ability to capture sunlight and convert these solar photons into electrons in the external circuit. As the majority of operational solar cells are based on semiconductors, the device captures only photon energies above the material's band gap and all lower-energy light is essentially wasted. An emerging concept that may lead to the realization of enhancing thermodynamic efficiency limits of photovoltaics is photon upconversion, wherein low-energy photons are absorbed and reemitted as higher-energy, frequency-upconverted light. Photochemical upconversion, the subject of this laboratory experiment, is an inherently noncoherent process (no laser required) that affords the desired wavelength shifting using two sequential energy-transfer reactions that continuously recycle and result in no net chemical change in the reactants.¹ Given the fact that other two photon-induced processes generally require laser excitation, the current laboratory offers a facile demonstration of such phenomena using widely available apparatus and noncoherent excitation. In the generalized photochemical upconversion process (Figure 1), selective long-wavelength excitation of sensitizer (S) donor chromophores produces the lowest-energy triplet state following intersystem crossing (ISC). Triplet–triplet energy transfer (TTET) then ensues to select molecular acceptor (A) species; this sensitization process cycles many times yielding a substantial population of long-lived acceptor triplets. Two excited triplet acceptors can then undergo a second energy-

transfer reaction that combines the excited-state energy from the two molecules into one, a process known as triplet–triplet annihilation (TTA). The primary evidence supporting TTA typically involves the observation of (delayed) singlet fluorescence observed anti-Stokes (displaced to higher energy) with respect to the excitation light possessing a spectral profile identical to that of the acceptor molecule. Under low continuous photon flux, the intensity of this singlet fluorescence typically displays quadratic (x^2) incident-light power dependence, as TTA requires reaction between two sensitized triplet acceptor molecules. This quadratic incident power dependence provides a clear-cut illustration of the bimolecular (nonlinear) nature of the rate-limiting step, an essential concept in chemical kinetics, performed using a conventional fluorimeter and noncoherent photons at low light flux. The photochemical upconversion process is explored using the commercially available sensitizer tris(2,2'-bipyridyl)ruthenium(II), $[\text{Ru}(\text{bpy})_3]^{2+}$, and 9,10-diphenylanthracene (DPA) acceptors–annihilators with the following sequence of reactions taking place (the asterisks denote molecular excited states):^{2,3}



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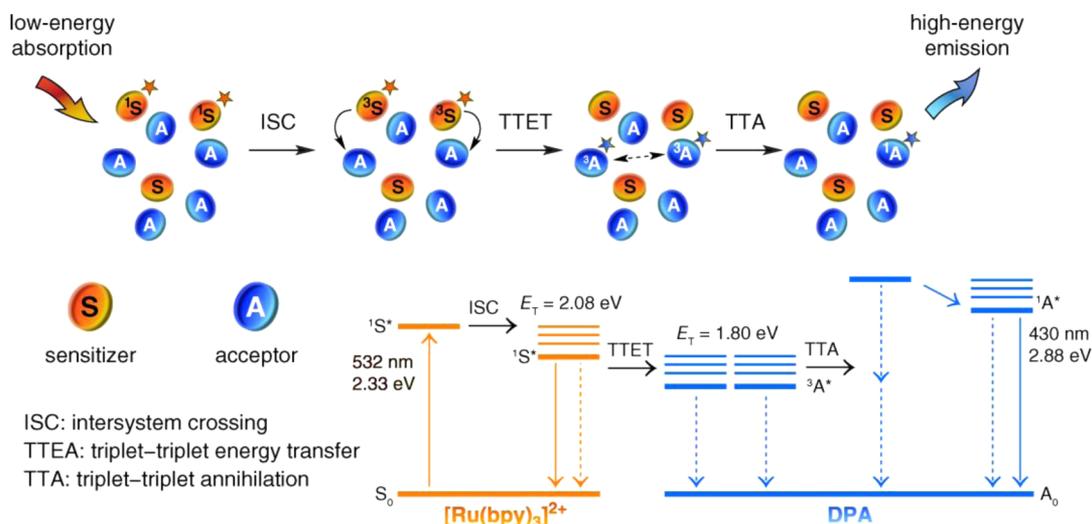
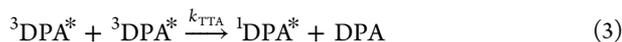


Figure 1. Overview of sensitized triplet-triplet annihilation (TTA) photon upconversion taking place between $[\text{Ru}(\text{bpy})_3]^{2+}$ triplet sensitizers (S) and DPA triplet acceptors-annihilators (A) as well as the associated molecular energetics for the $[\text{Ru}(\text{bpy})_3]^{2+}$ /DPA composition depicted in a Jablonski diagram. Asterisks denote molecular excited states. Note that this phenomenon is general and can incorporate numerous combinations of sensitizers and acceptors as long as the singlet and triplet energies of S are sandwiched between those of A.



In the present experiment, selective excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 500 nm (eq 1) using a conventional fluorimeter sensitizes the triplet energy-transfer of DPA ($^3\text{DPA}^*$, eq 2), which undergoes annihilation (eq 3) yielding the singlet DPA species ($^1\text{DPA}^*$) that ultimately yields fluorescence with a peak at 430 nm, eq 4. On the basis of the experimental conditions, the anti-Stokes shift produced here is simply the difference between the peak of the fluorescence emission and the center excitation wavelength converted to energy units (1240 nm eV), $2.88 \text{ eV} - 2.48 \text{ eV} = 0.40 \text{ eV}$. Note that the solution of the combined chromophores needs to have most of the dissolved O_2 removed as to avoid undesirable competitive triplet reaction pathways in eqs 1–3.

EXPERIMENTAL OVERVIEW

Whereas the primary goal of this laboratory is for students to quantify the upconverted emission intensity with respect to relative incident-light power, the photoluminescence quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by DPA, eq 2, can also be quantitatively evaluated during the laboratory period using the Stern–Volmer relation and related experiments are well established in the chemical education literature.^{4–12} This variation is therefore provided as an optional laboratory exercise and is typically used to establish quencher concentrations necessary for achieving upconversion. Both series of experiments are easily completed within a single three-hour laboratory period with students working independently. Once an appropriate optical sample is prepared and adequately deaerated through inert gas purging, the laboratory instructor can accomplish an easily visualized green-to-blue upconversion demonstration by illuminating this sample with a 532 nm green laser pointer, such as that presented in Figure 2. Then, using a standard fluorimeter, the students record the anti-Stokes emission spectra with the excitation monochromator tuned to 500 nm, whose incident optical power is systematically varied using neutral density filters to verify the quadratic incident-light power dependence

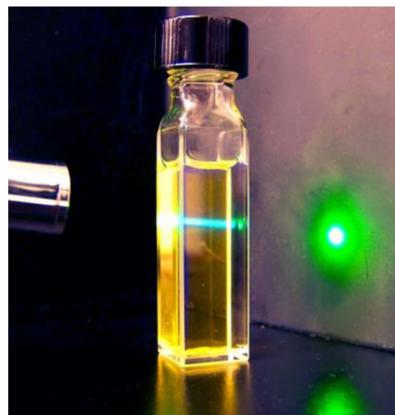


Figure 2. Photochemical upconversion from an argon-saturated dichloromethane solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\sim 1.4 \times 10^{-4} \text{ M}$) and DPA (3 mM). A commercial green laser pointer was used as the excitation source ($\lambda_{\text{ex}} = 532 \text{ nm}$, $< 10 \text{ mW}$ peak power). The blue luminescence is due to the upconversion process.

consistent with the molecularity of eq 3. In this single laboratory period, students gain experience with fluorescence spectroscopy, molecular excited states, luminescence quenching, energy-transfer processes, reaction molecularity, and quantitative analysis.

EXPERIMENT

Materials and Instrumentation

Spectroscopic grade dichloromethane was purchased from Sigma–Aldrich. 9,10-Diphenylanthracene (99%) was purchased from Alfa Aesar. Tris(2,2'-bipyridine)ruthenium dichloride hydrate was purchased from GFS Chemicals and metathesized to the corresponding PF_6 salt in water using excess NH_4PF_6 (Aldrich). Anaerobic glass (fluorescence) optical cells suitable for inert (Ar or N_2) gas purging were obtained from Starna Cells.

A Cary 50 Bio UV–vis spectrophotometer (Varian) was used to measure the absorption spectra of the samples used in these experiments and a standard PTI spectrofluorimeter equipped

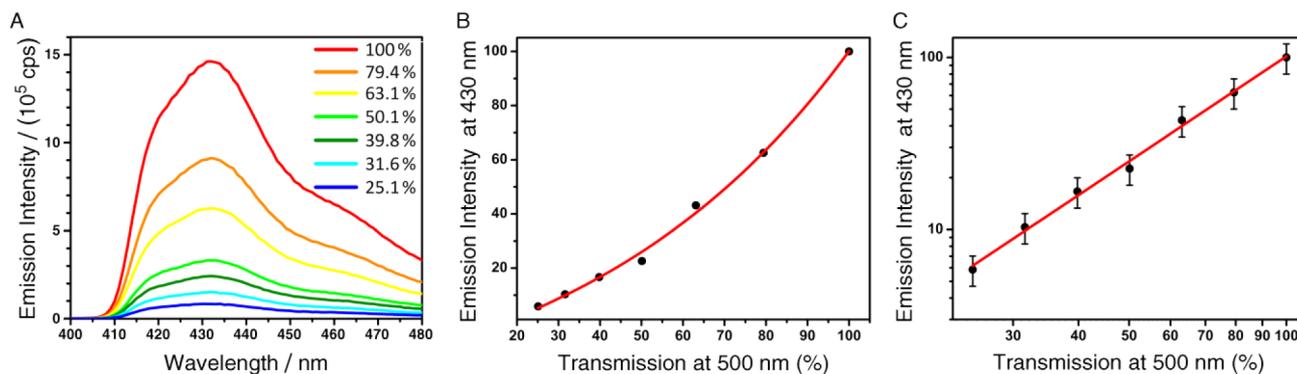


Figure 3. (A) Student acquired (anti-Stokes) emission spectra measured in an argon-saturated dichloromethane solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ (1×10^{-4} M) and DPA (3 mM) recorded as a function neutral density filter percent transmission at the 500 nm excitation wavelength. (B) The photoluminescence intensity at 430 nm, data from panel A scaled to a maximum of 100, plotted against the neutral density filter percent transmission at 500 nm. The function of $y \propto x^2$ is superimposed on this x - y data to illustrate the quadratic incident power dependence. (C) A double logarithm plot of the data from panel B possesses a slope of 2.03 indicating the biphotonic nature of the excitation process. The actual function plotted through the data is $\log y = 2.03 \log x$. Error bars indicate the range of data typically obtained by students.

with a 75 W Xe lamp source was used in the acquisition of all photoluminescence spectra. The emission spectra were not corrected for detection system response. A 455 nm long-pass filter (Newport Optics) was placed in the fluorimeter excitation beam prior to the sample to remove all remnant high-energy photons. A series of neutral density filters (Newport Optics) positioned after the long-pass filter was used to systematically attenuate the incident light power striking the sample.

Quadratic Incident-Light Power Dependence. These experiments can be accomplished using a range of excitation wavelengths and in the procedures developed here students utilized an excitation monochromator setting of 500 nm in the PTI fluorimeter. Students prepared a stock solution of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in CH_2Cl_2 whose absorbance at 500 nm was approximately 0.2, which is pale yellow in color. The peak of the lowest-energy absorbance band in $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ is ~ 450 and 500 nm excitation was selected to effectively separate the excitation from the upconverted emission signal at 430 nm. It is important not to use $\text{Ru}(\text{bpy})_3\text{Cl}_2$ here as this molecule is readily prone to facile ligand substitution photochemistry at room temperature in CH_2Cl_2 .^{13,14} Similarly, a 50 mM stock solution of DPA in CH_2Cl_2 was prepared separately by students. They finally combined 3 mL of the $[\text{Ru}(\text{bpy})_3]^{2+}$ solution with 500 μL of the DPA solution in a fluorescence optical cell equipped with a septum and the sample was slowly purged with argon gas for 20 min. These conditions result in nearly quantitative quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ photoluminescence, necessary for the observation of photochemical upconversion. A quantitative exercise in this regard (Stern–Volmer quenching) is provided as an optional experiment. Once the mixture was degassed, it is possible to directly visualize photon upconversion using a 532 nm green laser pointer passed through the solution. Students also prepared parallel control samples of the separated chromophores diluted to the same concentrations as they are found in the upconversion sample. Students exposed these samples to excitation centered at 500 nm that was first passed through a 455 nm long-pass filter to prevent direct excitation of the DPA and emission collected between 400 and 480 nm, anti-Stokes to the excitation. Once the signal was optimized, the control samples were measured to verify that no upconversion signal was produced unless both compounds are present. Once this was established, students used a series of neutral density filters

to variably attenuate the incident power striking the upconversion sample and for each filter or combination of filters selected, the emission spectrum was recorded under identical instrumental conditions as the original sample (Figure 3A). Note that the singlet fluorescence of DPA in these data are distorted as a result of the inner filter effect occurring in right angle detection but does not affect the incident-light power dependence.¹⁵ This inner filter effect results from the ground-state absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ that reabsorbs some of the emitted light from the DPA as their spectra overlap. The total integrated emission profile was plotted against the percent transmittance of the neutral density filter(s) at 500 nm. If this information is not available, the transmission of each filter–filter combination can be easily measured in a UV–vis spectrometer. Similarly, if the integrated emission profile cannot be determined, the peak emission intensity at 430 nm can be plotted versus neutral density filter percent transmission (Figure 3B). The curvature illustrates the quadratic nature of the upconversion process and finally a double logarithm plot applied to the x - y data from Figure 3B possesses a slope of 2.0 (Figure 3C), the expected exponent for the bimolecular rate from eq 3. Please note that this experiment can be further developed using higher light excitation intensities or sensitizer concentrations or vacuum degassing conditions to gain access to the linear incident power regime.^{16,17}

Stern–Volmer Quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ Photoluminescence (Optional)

A typical procedure describing a Stern–Volmer quenching experiment using $[\text{Ru}(\text{bpy})_3]^{2+}$ photoluminescence has been described previously in this *Journal* by Demas.⁴ His approach is easily adapted to the current experiments using the same stock solutions as in the previous section. Each sample should be excited as described above but now with emission detection taking place between 550 and 800 nm to capture the orange metal-to-ligand charge-transfer emission characteristic of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore. The integrated emission profiles or the emission peak intensities of the zero-quencher data (I_0) are each divided by the corresponding quencher containing sample (I) and the ratio $(I_0/I) - 1$ is plotted against the molar DPA concentration, producing a straight line whose slope is the Stern–Volmer constant ($K_{\text{SV}} = k_q\tau_0$) for this energy-transfer quenching reaction, eq 2. The ratio (I_0/I) directly yields the percent quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ energy-transfer at a

particular quencher concentration, that is, $(I_0/I) = 2.0$ implies 50% quenching. Using the excited-state lifetime measured in the absence of quencher ($\tau_0 = 700$ ns), students achieved an average bimolecular quenching constant, $k_q = 2.5 \times 10^9 \pm 0.2$ L mol⁻¹ s⁻¹ from their combined Stern–Volmer plots.

HAZARDS

General laboratory safety procedures, including wearing safety goggles and gloves, must be followed at all times. All optical samples should be prepared and deaerated in a fume hood. 9,10-Diphenylanthracene and dichloromethane should be handled with caution as they are suspected carcinogens and are irritants of skin, eyes, and the respiratory system. Tris(2,2'-bipyridyl)ruthenium(II) may cause skin and eye irritation. If a laser or laser pointer is used as an excitation source either for the experiment or for demonstration purposes, do not bring your eyes to the level of the laser output and do not look directly into any laser beams. The CH₂Cl₂ solutions are easily disposed in halogenated organic waste containers.

CONCLUSIONS

A 3-h laboratory experience was described for upper-division undergraduate students in a physical or inorganic chemistry laboratory to study the emerging concept of photochemical upconversion using readily available reagents and equipment. Using a characteristic photo-induced triplet–triplet energy-transfer reaction between the benchmark inorganic chromophore [Ru(bpy)₃]²⁺ and DPA, students directly visualized the concomitant quenching of the [Ru(bpy)₃]²⁺ photoluminescence alongside the upconverted blue DPA fluorescence generated, enabling a straightforward connection between these coupled processes. Overall, students gained experience in various aspects of fluorescence spectroscopy, triplet energy-transfer processes, quenching, reaction molecularity, and fluorescence data analysis. The optional portion of the laboratory that includes dynamic (lifetime-based) Stern–Volmer analysis has been operated annually since 2001 with typically 6–10 students in each class. The upconversion experiments at the heart of this presentation were first introduced and tested using chemistry major volunteers in their spare time. In the upper-division analytical–physical laboratory course, eight students performed the upconversion experiments, noting that the experiments and associated data analysis were straightforward and easy to understand. The students also appreciated the visual nature of this laboratory and thought that the live demonstration of this effect as shown in Figure 2 was particularly informative.

ASSOCIATED CONTENT

Supporting Information

Student handout and instructor notes. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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