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Photochemical Upconversion: Anthracene Dimerization Sensitized to Visible Light by a Ru^{II} Chromophore**

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Upconversion, the generation of photons with higher energy than the incident light, is intrinsically nonlinear and therefore requires high excitation intensities. Recent developments in this area led by our group and others indicate that a plausible route to lowering the optical power requirements for upconversion lies in harnessing triplet–triplet annihilation (TTA) processes.[1–4] In the sensitized TTA mechanism, upconversion becomes linked to sequential, highly allowed one-photon absorption processes, thereby permitting the use of low-power continuous-wave excitation sources. This strategy has been proved quite effective with the metal-to-ligand charge-transfer (MLCT) sensitizer $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) and 9,10-diphenylanthracene, for which the green-to-blue upconversion can be readily visualized by the naked eye in a lighted room by using a laser pointer.[2] Although this advance has obvious relevance in photonic technologies, there are also important ramifications for preparative chemistry. If the TTA process is selected to produce reactive excited singlet species prone to cycloaddition chemistry, then low-energy photons can be used to drive photochemical reactions that traditionally require high-energy ultraviolet light.[5,6] Herein we describe a representative synthetic application in which visible-light-sensitized TTA upconversion efficiently drives bimolecular [4+4] cycloaddition between two anthracene molecules, accomplished through selective excitation of $[Ru(dmb)_3]^{2+}$.

The photodimerization of anthracene (An) is one of the oldest documented photochemical reactions, the nature of which has been investigated extensively by many researchers.[5,6] In 1983 Saltiel and co-workers clearly established that the formation of An dimers by excitation at 366 nm proceeds readily through TTA.[7] The dimerization of An represents a suitable departure point for the search for a prototype addition reaction amenable to sensitized TTA by Ru^{II} MLCT chromophores.

Equations (1)–(3) provide the sequence of chemical steps necessary for photochemical upconversion in the current study. Selective excitation of $[Ru(dmb)_3]^{2+}$ at a variety of visible wavelengths (457.9 nm, 488 nm, 514.5 nm, or 532 nm) initiates bimolecular triplet–triplet quenching by An [Eq. (1)].[1,2,8] Two molecules of excited triplet An ($^3An^*$)

$$[Ru(dmb)_3]^{2+*} + An \rightarrow [Ru(dmb)_3]^{2+} + {}^3An^* \quad (1)$$

can encounter, ultimately resulting in TTA [Eq. (2)].[2,7] The dimer An_2 is then produced from theinteraction between an

$$^3An^* + {}^3An^* \rightarrow {}^1An^* + An \quad (2)$$

excited singlet An ($^1An^*$) and an An molecule in the ground state, thereby completing the photochemical upconversion reaction sequence [Eq. (3)]. The Ru^{II} sensitizer is photo-

$$^1An^* + An \rightarrow An_2 \quad (3)$$

catalytic in nature; its ground state is regenerated following triplet energy transfer [Eq. (1)]. In view of the inherent photochemical and thermal stability of Ru^{II} tris(diimine) complexes, one would expect long-term efficacy and large turnovers in preparative synthetic applications of these chromophores in concert with sensitized photochemical upconversion.

Figure 1 provides representative static UV/Vis absorption data obtained from low-power Ar$^+$ laser photolysis (λ_{ex} = 457.9 nm) of a vacuum-degassed solution containing $[Ru(dmb)_3]^{2+}$ and An in relatively dilute concentrations in CH_3CN. Selective excitation of the Ru^{II} chromophore leads to the net loss of An. This is conveniently monitored by changes in the characteristic An vibronic absorption bands between 325 and 375 nm. After 70 min of photolysis the

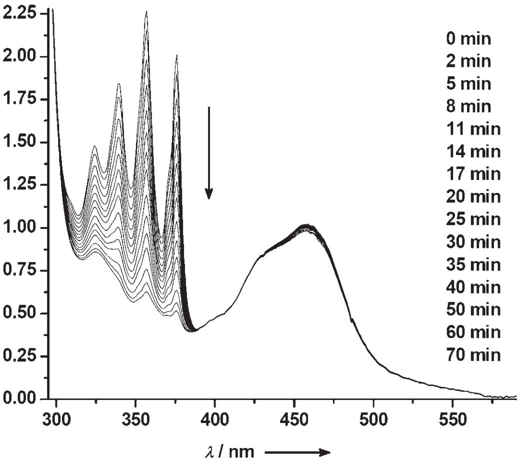

Figure 1. Photolysis of a degassed solution of $[Ru(dmb)_3]^{2+}$ (5.75×10^{-5} M) and anthracene (2.55×10^{-4} M) in acetonitrile by continuous-wave Ar$^+$ laser excitation (λ_{ex} = 457.9 nm; incident power 13.0 mW). Photolysis times are indicated at the side.

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reaction is nearly complete with the low-energy MLCT absorption bands remaining essentially intact.

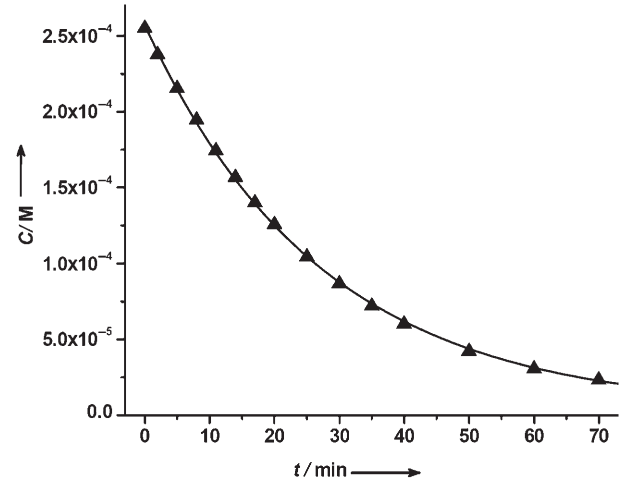

Figure 2. Change in anthracene concentration as a function of photolysis time from the data in Figure 1 (ε(An) at 376 nm = 6450 $\text{M}^{-1}\,\text{cm}^{-1}$). The solid line is the first-order least-squares fit.

Figure 2 shows the changes in An concentration as a function of photolysis time at 457.9 nm calculated from the data in Figure 1 and the extinction coefficient for An measured at 376 nm (6450 $\text{M}^{-1}\text{cm}^{-1}$). The solid line is the first-order least-squares fit to the experimental data points, as the reaction can be considered to take place under pseudo-first-order conditions, in which $[\text{An}] \gg [{}^1\text{An}^*]$. Note that ${}^1\text{An}^*$ forms only as a result of the rate-limiting TTA process [Eq. (2)]. The first-order rate of monomer consumption is consistent with that observed during UV irradiation of An solutions,[9] and we have independently confirmed this finding using acetonitrile as the reaction solvent. We note that Stern–Volmer analysis of the $[\text{Ru(dmb)}_3]^{2+}$ luminescence intensity decays measured as a function of An concentration [Eq. (1)] yields $K_{\text{SV}} = 4490\,\text{M}^{-1}$ with a corresponding bimolecular rate constant of $5.38 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, which approaches the diffusion limit in CH_3CN. These data are valuable because they directly provide the An concentrations necessary for complete quenching of the $[\text{Ru(dmb)}_3]^{2+}$ sensitizers to produce the highest number of ${}^3\text{An}^*$ molecules which in turn annihilate to form the reactive ${}^1\text{An}^*$ species. Therefore the quantum efficiency of sensitized photochemical upconversion should scale with the An concentration up to the point at which the production of ${}^1\text{An}^*$ saturates. It is also known that the quantum yields of direct photochemical An dimerization are sensitive to the monomer concentration.[6,10] Because the photochemically reactive ${}^1\text{An}^*$ state is so short-lived (approximately 4 ns),[6] relatively large concentrations of ground-state An are necessary to observe efficient dimerization. The ionic nature of $[\text{Ru(dmb)}_3]^{2+}$ limited our experiments to CH_3CN solutions, in which the maximum solubility of An is just below 20 mM. According to the Stern–Volmer analysis, 90 % of the $[\text{Ru(dmb)}_3]^{2+}$ molecules are quenched at approximately 2 mM An as measured under optically dilute conditions (optical density (OD) $\approx$ 0.1). Although our photolysis experiments utilize higher sensitizer concentrations (OD $\approx$ 1.0), the Stern–Volmer data imply that working near the An saturation limit will ensure nearly complete quenching of all excited sensitizer molecules. The quantum yields of An dimerization (see the Experimental Section for details) were measured as a function of An concentration at constant sensitizer concentration and incident laser power (Figure 3).

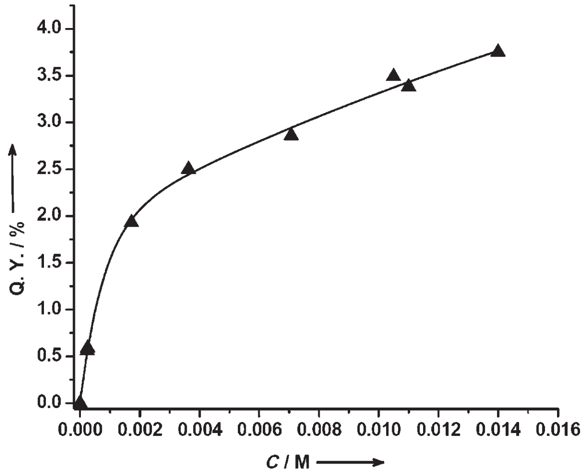

Figure 3. Dependence of the quantum yield (Q.Y.) for anthracene photodimerization on anthracene concentration. Solutions of $[\text{Ru(dmb)}_3]^{2+}$ (5.75×10^{-5} M) and anthracene in acetonitrile were irradiated with an Ar^+ laser ($\lambda_{\text{ex}} = 457.9$ nm, 13.0 mW).

The dimerization quantum yields sharply increase from 0 to 2.5 % between 0 and 3 mM and then slowly rise, ultimately reaching 3.75 % at 14 mM in CH_3CN, the highest concentration used in this experiment. At low An concentration, the steep slope in Figure 3 likely results from more-efficient production of ${}^3\text{An}^*$, as suggested by the Stern–Volmer analysis. At higher An concentrations, the dimerization quantum yield continues to increase linearly with concentration, which is consistent with a dimerization process under strict kinetic control by ground-state An molecules. This finding strongly suggests that the An molecule that reacts in Equation (3) is not the geminate An ground-state molecule produced from annihilation in Equation (2). A limitation of the annihilation approach is that it relies on long-lived excited triplet states to produce excited singlet molecules. This reliance inherently limits the quantum yield of excited singlet-state molecules that result from TTA encounters to a maximum value of 1/9 (11.1 %).[7] If the quantum yield for the relevant singlet-state reaction is below unity, the efficiency of the analogous TTA-controlled process will be reduced accordingly, as is likely the case in the present work. Higher concentrations of ground-state An molecules facilitate the quenching of ${}^3\text{An}^*$, which diminishes its lifetime and concentration and leads to fewer annihilation events.[7,11] On the basis of these facts, it can be anticipated that increasing the An concentration much beyond that employed in the current work will likely lead to diminished dimerization yields in photochemical upconversion. However, even when these limitations are considered, millimolar concentrations of An are indeed suitable for synthetic chemistry utilizing upconversion phenomena, as described below.

The ^1H and ^{13}C NMR spectra of An and the product that precipitates from the MLCT-sensitized TTA reaction mixture containing approximately 14 mM An are provided in the Supporting Information. Both sets of spectra decisively indicate the formation of pure [4+4] An dimers. In the ^1H NMR spectrum, the characteristic chemical shift of the bridgehead protons are observed as a singlet at $\delta =$ 4.56 ppm.[4] The phenyl protons also display characteristic chemical shifts in comparison with those in the parent An structure. The bridgehead carbons show a resonance at $\delta =$ 53.66 ppm in the ^{13}C NMR spectrum, which confirms the conversion to the [4+4] dimerized structure.

If the photolysis is carried out in aerated CH_3CN, no precipitation occurs after 130 minutes of irradiation, and the low-energy An absorption bands disappear as a function of photolysis time. These observations suggest the efficient formation of endoperoxide and complete suppression of dimer production.[5] Photodimer formation is clearly observed in the deaerated solution in CH_3CN, as the nonpolar dimer readily crystallizes during the course of the photolysis. A digital photograph taken after 40 minutes of visible light irradiation (Figure 4) illustrates the extent of reaction and the ease with which sensitized photochemical upconversion takes place.

Figure 4. Photograph of the optical cell containing crystallized anthracene photodimer produced by Ar^+ laser photolysis of a solution containing $[Ru(dmb)_3]^{2+}$ (5.25×10^{-5} M) and anthracene (ca. 1.4×10^{-2} M) in acetonitrile.

The current work establishes the feasibility of applying sensitized TTA in preparative chemistry by using anthracene dimerization as a prototypical reaction. This concept could be extended to other intermolecular cycloaddition reactions, including mixed dimers, to yield new insight into how TTA-driven reactions influence product distributions. In materials science applications, TTA may provide a means of carrying out desired chemical reactions in media that do not permit transmission of ultraviolet light.

Experimental Section

Anthracene gold label (Aldrich) and spectroscopic-grade acetonitrile (Fisher Chemicals) were used as received. $[Ru(dmb)_3](PF_6)_2$ was prepared according to the published procedure.[12] Static absorption spectra were measured on a HP 8453 diode-array spectrometer. The excitation was accomplished with an argon-ion laser (Coherent Innova 300) whose multiline output was split into the selected wavelength component ($\lambda = 457.9$ nm) by a diffraction grating in concert with several optics. The laser power was measured with a Molectron Power Max 5200 power meter. ^1H and ^{13}C NMR were measured on a Bruker 300 spectrometer. All samples in 10-mm pathlength anaerobic quartz cells (home-made) were deoxygenated by five freeze, pump, thaw cycles under pressures of less than 10^{-3} mm Hg. Emission lifetimes were measured with an apparatus described previously,[13] by using a nitrogen-pumped broadband dye laser (PTI GL-3300 N_2 laser, coumarin 460) as the excitation source.

Quantum yields of anthracene photodimerization were measured by Ar^+ laser irradiation (457.9 nm, 13 mW incident power) of deaerated solutions in acetonitrile containing $[Ru(dmb)_3]^{2+}$ (OD at 458 nm maintained at 1.0) and varying An concentrations. The dimerization quantum yield was calculated from the quantum yield for the disappearance of the An monomer at low conversions (< 10%) by using the equation: $\Phi_{\text{dimerization}} = 0.5\,\Phi_{\text{An loss}}$.[9] The quantum yield of An disappearance was determined by evaluating changes in An concentration (mol min^{-1}) relative to the number of absorbed photons (mol photons min^{-1}) in the constant sample volume. All An concentrations were determined spectrophotometrically at 376 nm, and absorbed photons were determined from the difference between the power of the incident and transmitted light (both measured using the Molectron power meter). When large concentrations of An were utilized, the samples were diluted after photolysis for appropriate concentration determination in the linear range of the diode-array spectrometer.

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