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Texaphyrin sensitized near-IR-to-visible photon upconversion

Fan Deng,[a] Wenfang Sun[b] and Felix N. Castellano*[a]

Near-IR (NIR) absorption from a Cd(II) texaphyrin (TXP) has been successfully coupled with rubrene triplet acceptors/annihilators in vacuum degassed dichloromethane to upconvert NIR (670–800 nm) incident photons into yellow fluorescence through sensitized triplet–triplet annihilation. Stern–Volmer analysis of dynamic energy transfer quenching of TXP by rubrene using transient absorption spectroscopy revealed Stern–Volmer and bimolecular quenching constants of 21 000 M^{-1} and 5.7×10^8 M^{-1} s^{-1} respectively, for the triplet–triplet energy transfer process. The upconverted emission intensity with respect to the incident excitation power density at 750 nm was shown to vary between quadratic and linear, illustrating the expected kinetic limits for the light producing photochemistry under continuous wave illumination. Furthermore, with increasing TXP sensitizer concentration, the characteristic quadratic-to-linear crossover point shifted to lower incident photon power density. This is consistent with the notion that stronger photon capture in the sensitizer leads to experimental conditions promoting upconversion under milder excitation conditions. The maximum quantum yield of the TXP-sensitized rubrene upconverted fluorescence was 1.54 ± 0.04% under dilute conditions determined relative to $[Os(phen)_3](PF_6)_2$ under continuous wave excitation conditions. This saturating quantum efficiency was realized when the incident light power dependence reached the quadratic-to-linear crossover point and was constant over the region where the composition displayed linear response to incident light power density. In pulsed laser experiments at higher sensitizer concentrations, the triplet–triplet annihilation quantum yield was determined to saturate at approximately 13%, corresponding to an upconversion yield of ~10%, suggesting that the dichloromethane solvent either lowers the T_2 state of the rubrene acceptor or is somehow attenuating the annihilation reaction between excited rubrene triplets.

Introduction

Photon upconversion based on sensitized triplet–triplet annihilation (TTA) has become recognized as a viable approach towards overcoming the thermodynamic efficiency limits of photovoltaics and photoelectrosynthetic cells through sub-bandgap photon capture and conversion.[1–4] In the sensitized TTA scheme, photon upconversion from low-power continuous-wave excitation sources is facilitated by the use of chromophores that efficiently absorb the incident radiation through an allowed one-photon process, undergo intersystem crossing, and subsequently transfer this energy to the species capable of TTA. Ultimately, two excited triplet acceptors engage in the TTA reaction, producing a singlet excited state characteristic of the acceptor moiety. This process was first introduced by Parker and Hatchard in non-covalent organic compositions whose triplet sensitizers exhibited low intersystem crossing yields, thus limiting potential upconversion efficiencies.[5] Since that time, tremendous advances has been made by utilizing long-lived metal-containing triplet sensitizers with a variety of organic-based triplet acceptors/annihilators in both fluid solution and various host matrices, where the upconverted photons are easily visualized by the naked eye.[6–12] The ultimate goal of this research is to realize real-world device integration imparting sub-bandgap sensitization and numerous examples in this regard have recently emerged.[13–16]

An important facet of research in this area has focused attention on the measurement and improvement of quantum efficiencies in these light conversion processes.[17–22] Recent data has unequivocally demonstrated that through sensitized TTA, upconversion quantum efficiencies do indeed surpass the 11.1% spin statistical upper limit.[12] This restriction would be imposed by the assumption that subsequent to TTA, only the singlet-excited encounter complex produces singlet emitters. The majority of these encounters (56%) would actually produce spin allowed quintets if permitted energetically,

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which is fortunately not the case and these molecules are returned to the bath as excited triplets that reengage in TTA reactions. As a result, the TTA process itself has been shown to have an upper limit exceeding 60% from kinetic analysis of the associated delayed fluorescence intensity decays in one of the champion compositions.[12] Recently, the analogous experiment has been demonstrated through analysis of the triplet acceptor decays in transient absorption spectroscopy.[23] Under continuous wave irradiation, measured quantum efficiencies up to 34% have been recorded to date in solution,[13] and a record of 22% quantum efficiency has been recently achieved in a soft polymer material hosting the donor and acceptor.[24] In addition to quantum efficiency improvements, many investigations have focused on generalizing this phenomenon across energetically relevant triplet sensitizers and acceptors/annihilators resulting in anti-Stokes shifts spanning the visible and near-IR regions of the spectrum. While there are numerous examples of frequency upconversion in the higher energy portions of the visible, there are only a handful of conversions that achieve red- and near-IR-to-visible transformations.[11,18,21,22,25–27] Therefore it is of significant interest to expand the inventory of near-IR absorbing sensitizers that can be successfully applied to this wavelength-shifting technology.

This premise inspired the present contribution, wherein we successfully demonstrate NIR-to-visible upconversion utilizing a Cd(II) texaphyrin (TXP) triplet sensitizer along with rubrene[12,27] as the acceptor/annihilator in deoxygenated CH_2Cl_2 solutions. Dichloromethane was selected as the solvent medium due to solubility limitations of the TXP sensitizer. Following selective near-IR excitation of the sensitizer and intersystem crossing, TXP transfers its triplet energy to rubrene, regenerating the ground state sensitizer. This process repeats resulting in conditions favoring the TTA reaction ultimately producing singlet rubrene fluorescence in the yellow, centered near 560 nm, at a maximum quantum efficiency of 1.5% when pumped at 750 nm under continuous-wave illumination. In pulsed laser experiments at higher sensitizer concentrations, the triplet–triplet annihilation quantum yield was determined to saturate at approximately 13%, corresponding to an upconversion yield of ~10%.

Experimental section

General

Samples of TXP were available from prior investigations.[28,29] Rubrene was purchased from Aldrich and used without further purification. Spectroscopic grade dichloromethane was purchased from Aldrich and used as received.

Photophysical measurements

Static absorption spectra were measured with an 8453 diode array spectrophotometer from Agilent. Steady-state photo-luminescence spectra were recorded using a FL-980 fluorescence spectrometer from Edinburgh Instruments. A Ti:Sapphire oscillator (Chameleon Ultra II, Coherent) was utilized as the excitation light source which provided tuneable photons (670, 750, and 800 nm) at a repetition rate of 80 MHz, considered here as a continuous wave photon source. Incident laser power was varied using a series of neutral density filters. The laser power was measured using either a Molectron Power Max 5200 power meter or an Ophir Nova II/PD300-UV power meter. All luminescence samples were prepared in a specially designed 1 cm² optical cell bearing a sidearm round-bottomed flask and were subjected to a minimum of three freeze–pump–thaw degas cycles prior to all measurements. The TXP-sensitized upconverted fluorescence quantum yield measurements of rubrene in dichloromethane were measured relative to $[Os(phen)_3](PF_6)_2$ in acetonitrile (λ_{ex} = 700 nm) using exactly the same procedures as previously described.[22,24] The photoluminescence quantum yield of $Os(phen)_3^{2+}$ (Φ = 3.0%) was determined using an absolute quantum yield apparatus (Hamamatsu). Nanosecond transient absorption measurements utilized a LP 920 spectrometer from Edinburgh Instruments, equipped with a PMT (R928, Hamamatsu). Excitation of the samples in these experiments was accomplished using a Nd:YAG/OPO laser system from OPOTEK (Vibrant LD 355 II) operating at 1 Hz. Single wavelength absorption transients were kinetically analyzed using Origin 9.0. The LP 920 spectrometer is also equipped with an Andor iStar ICCD detector that permitted the collection of time-resolved emission spectra used in the determination of TTA quantum efficiencies (Φ_{TTA}) from prompt and delayed fluorescence signals as described previously.[12,23] The delayed fluorescence spectrum was integrated for 1 ms from 250 ns after the 750 nm excitation laser pulse, capturing the delayed fluorescence in its entirety while ignoring any prompt fluorescence of rubrene. The prompt fluorescence spectrum, due to the direct excitation of the rubrene at 525 nm, was integrated for 250 ns from 50 ns before the laser pulse. Here, the yield of delayed fluorescence (F_d) from rubrene was measured after selective excitation of the TXP sensitizer ($\lambda_{ex} = \lambda_d$ = 750 nm), which was directly compared to the prompt fluorescence (F_p) from rubrene measured in the identical composite sample, observed by exciting this acceptor directly at 525 nm (λ_p). A mixture of 0.18 mM TXP and 0.34 mM rubrene and the other mixture of 0.22 mM TXP and 0.50 mM rubrene in 1 cm² freeze–pump–thaw degassed dichloromethane were used for detecting prompt and delayed fluorescence. The compositions have large optical density (O.D. ≥ 2.0) at the respective excitation wavelengths of 525 nm and 750 nm, wherein nearly 100% of the excitation photons are absorbed to approximately the same depth in the sample. In both instances the rubrene fluorescence is produced in an identical environment, therefore any trivial fluorescence quenching that occurs will cancel and the TTA yield is readily calculated using eqn (1).

$$\Phi_{TTA} = \left(\frac{2F_d E_p \lambda_d}{F_p E_d \lambda_p} \right) / \Phi_q \tag{1}$$

Here E_d and E_p are the respective laser pulse energies, Φ_q is the quenching efficiency at the specified rubrene concentration extrapolated from Stern–Volmer analysis and the factor of 2 in the numerator scales the annihilation yield to unity, as two excited triplets are necessary to produce one fusion product.

Results and discussion

The structures of the TXP sensitizer and rubrene acceptor/ annihilator are presented along with their normalized ground-state absorption and emission spectra measured in dichloromethane, Fig. 1. Note that under these relatively dilute conditions the recorded spectra are pristine and truly representative of the profiles of the constituent chromophores. The TXP sensitizer, whose NIR singlet fluorescence is centered at 825 nm in dichloromethane, exhibits characteristic absorptions at 450 nm (Soret) in the blue along with two Q-band features at lower energy in the red/NIR region (λ_{max} = 700 nm, 750 nm). Rubrene's $^1\pi$–π^* absorption bands all lie below 600 nm ensuring that the TXP Q-band excitation will result in selective excitation of only the triplet sensitizer at long wavelengths. Since it was not possible to observe the static triplet phosphorescence of the TXP in dichloromethane at room temperature, nanosecond laser flash photolysis was utilized to extract the relevant parameters from Stern–Volmer quenching analysis (K_{SV} and k_q) for TXP deactivation by rubrene through triplet–triplet energy transfer.[30] These values are subsequently used to optimize the extent of quenching valuable for maximizing the upconversion photochemistry displayed by the composition. Fig. 2 presents the nanosecond transient absorption difference spectrum of 9 μM TXP measured at several delay times in deaerated dichloromethane upon excitation (1.1 mJ per pulse) at 700 nm. Negative transient signals are observed between 660–800 nm corresponding to ground-state bleaching of this chromophore. Broad positive T_1–T_n excited-state absorptions are observed between 475 and 650 nm. Analysis of the transient features monitored throughout the difference spectrum resulted in identical single exponential decays with a time constant of 37 μs. Since it is well established that TXP manifests ground-state bleaching in the 660–800 nm spectral region, the kinetic decay at 750 nm can be monitored as a function of increasing rubrene concentration.[27] The dynamic Stern–Volmer plot generated from these transient lifetime measurements revealed a Stern–Volmer constant (K_{SV}) of 21 000 M^{-1}, Fig. 3. In absence of quencher, the triplet excited-state lifetime of TXP in vacuum degassed dichloromethane (3 freeze–pump–thaw cycles) was measured to be 37 μs under these experimental conditions, yielding a bimolecular energy transfer quenching rate constant (k_q) of 5.7×10^8 M^{-1} s^{-1}.

Selective excitation of TXP (19 μM, dichloromethane solvent, λ_{ex} = 750 nm) in the presence of rubrene (0.32 mM) in a freeze–pump–thaw degassed solution generates upconverted rubrene singlet fluorescence in the yellow. Please note that the spectral profile of rubrene under these experimental conditions is attenuated on its high-energy side due to the inner filter effect where some of the generated fluorescence is re-absorbed at these wavelengths. The upconverted fluorescence intensity measured as a function of the incident laser power was evaluated; the double logarithmic plot generated from
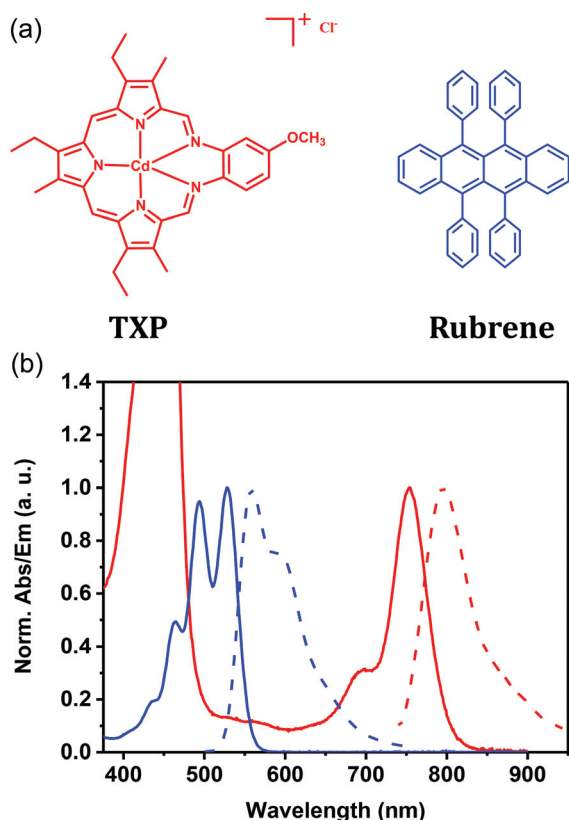

Fig. 1 (a) Molecular structures of TXP and rubrene. (b) Normalized absorption (solid lines) and fluorescence (dashed lines) spectra of TXP (red) and rubrene (blue) in dichloromethane at room temperature.
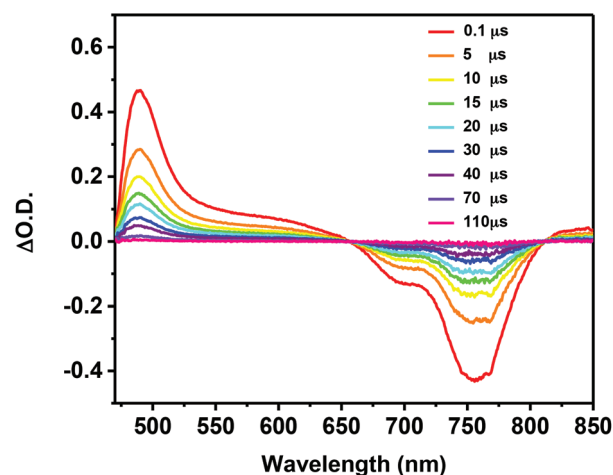

Fig. 2 Transient absorption difference spectrum of 9 μM TXP in freeze−pump−thaw degassed dichloromethane measured at several delay times. The energy of the excitation beam was 1.1 mJ per pulse at λ_{ex} = 700 nm.
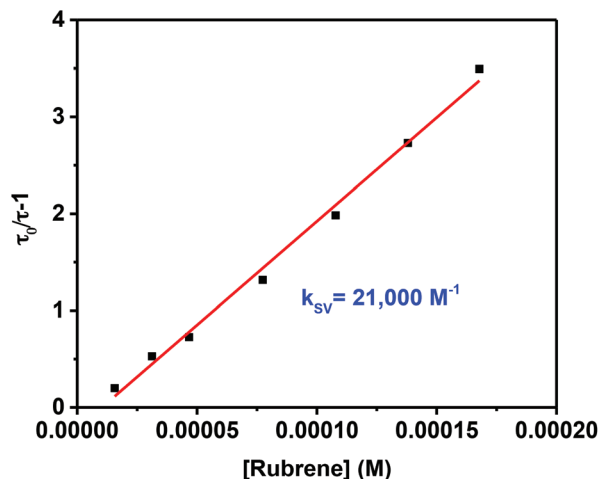
Fig. 3 Stern–Volmer analysis of dynamic triplet–triplet energy transfer quenching between TXP and rubrene in vacuum degassed dichloromethane using transient absorption kinetics.

Fig. 5 Double logarithmic plots of the upconversion emission signals measured as a function of 750 nm incident laser power density in three mixtures of different TXP concentration (14 μM, 28 μM and 42 μM) and rubrene (0.75 mM) in freeze–pump–thaw degassed dichloromethane. The dashed lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. The green dots indicate the quadratic-to-linear crossover thresholds in each upconversion composition.

these experiments are presented in Fig. 4 and 5. As anticipated, at low incident power, the slopes of these plots are 2.0, indicative of quadratic dependence. Upon increasing the NIR photon flux incident on the sample, each plot deviates off its initial slope, a process that perpetuates until the sample ultimately achieves a slope of 1.0 at the highest incident power densities. These are clear illustrations of the anticipated kinetic limits for the photochemical upconversion process as previously shown by the Monguzzi group,[17] the Schmidt group,[18] and this laboratory.[20] Furthermore, with increasing TXP sensitizer concentration, the characteristic quadratic-to-linear crossover point shifted to lower incident photon power density as illustrated in Fig. 5. This result is consistent with the notion that stronger photon capture in the sensitizer leads
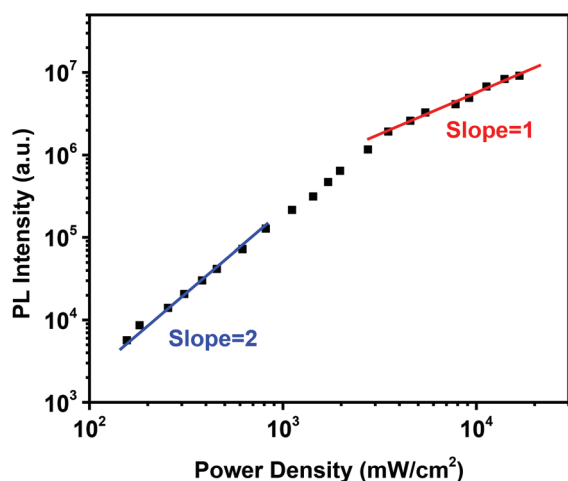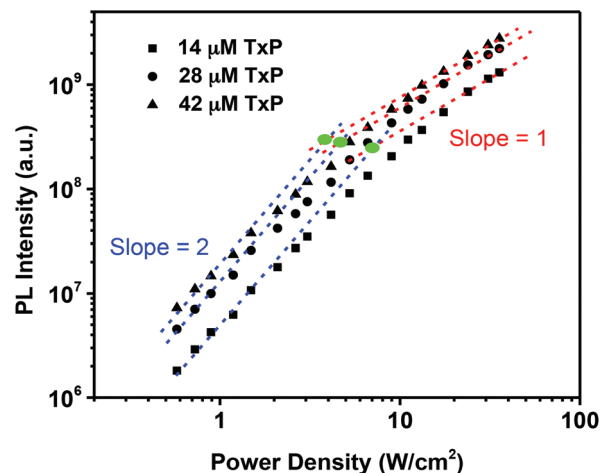
to experimental conditions promoting upconversion under milder excitation conditions.[17] In other words, optically saturated conditions (linear power response) are achieved as lower incident powers when most to all of the photons are absorbed in the composition.

In order to quantify the upconversion efficiency in the present compositions, optically dilute samples were utilized (absorbance at $\lambda_{ex} < 0.1$), where the linear regime can only be reached at large incident optical powers. In these experiments, the TXP concentration was sufficiently low that no self-quenching of its excited state was apparent whereas it has been established that under these conditions the rubrene fluorescence quantum yield is approximately 0.80.[18] The upconversion quantum yields in these solutions were measured as a function of 680 nm incident power density, relative to the $Os(phen)_3^{2+}$ quantum counter ($\Phi = 3.0\%$);[22] the combined results are displayed in Fig. 6. It should be noted that 680 nm was selected as the excitation wavelength as a compromise in order to facilitate light absorption in both $Os(phen)_3^{2+}$ and TXP. The upconversion quantum yields continuously increase until the strong annihilation limit was reached (linear power regime) at which time the quantum efficiencies level out to a constant value of $1.54 \pm 0.04\%$, illustrative of the low sensitizer concentrations utilized. This saturating quantum efficiency was realized when the incident light power dependence reached the quadratic-to-linear crossover point and was constant over the region where the composition displayed linear response to incident light power density. This phenomenon is commonly observed in light-producing upconversion photochemistry and is characteristic of the process operating in the high-efficiency strong annihilation kinetic limit. In order to

Fig. 4 Double logarithmic plot of the upconversion emission signal at 560 nm measured as a function of 750 nm incident laser power density in a mixture of TXP (19 μM) and rubrene (0.32 mM) in a freeze–pump–thaw degassed dichloromethane. The solid lines are linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively.
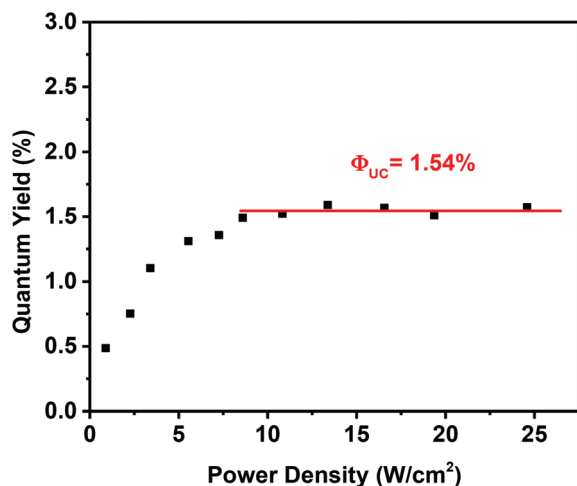
Fig. 6 Upconversion quantum yields with 21 μM TXP and 0.33 mM rubrene in deaerated dichloromethane measured as a function of 680 nm incident light power density.

quantify the maximum possible TTA quantum efficiency for rubrene under the present experimental conditions, two different concentrated samples were utilized, where the absorbance at $\lambda_{ex} \geq 2.0$. The resultant TTA quantum yields calculated from the integrated prompt and delayed (sensitized) rubrene fluorescence spectra using eqn (1) are displayed in Fig. 7. Here, as anticipated, the TTA quantum yield increases with increasing laser pulse energy until a plateau is reached, indicating that the process has saturated, identical to that when linear incident power dependence is achieved in the related cw experiments shown in Fig. 4 and 5. As originally stated by Schmidt and co-workers, the numerator and denominator in eqn (1) both scale linearly once this plateau region is reached, indicating that the efficiency for the process has
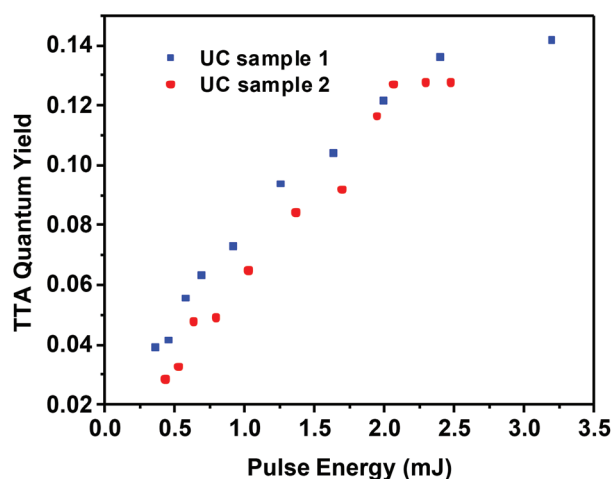
Fig. 7 TTA quantum yields in two mixtures: sample 1 (0.18 mM TXP and 0.34 mM rubrene) and sample 2 (0.22 mM TXP and 0.50 mM rubrene) in freeze–pump–thaw degassed dichloromethane measured as a function of 750 nm incident laser pulse energy.

reached its maximum.[18] Under the present experimental conditions, the TTA efficiency (Φ_{TTA}) only approaches 13% in this composition in dichloromethane, which is significantly lower in comparison to the 40% previously measured for sensitized rubrene annihilation in toluene using a similar experiment.[18] The corresponding upconversion yield (Φ_{UC}) can be readily calculated from knowing the quenching efficiency (Φ_q), the TTA efficiency, and the approximate rubrene fluorescence quantum yield at high concentrations (Φ_f)[18]: [$\Phi_{UC} = \Phi_q\Phi_{TTA}\Phi_f = (0.9)(0.13)(0.8) = 0.094$]. Previous results from our own laboratory has already suggested that nonpolar aromatic solvents such as toluene and benzene appear to support sensitized TTA processes superiorly with respect to more polar solvent systems. We therefore conclude that dichloromethane solvent either lowers the T_2 state of the rubrene acceptor, shunting the possible intersystem crossing channel of T_2 to S_1, or is somehow attenuating the annihilation reaction between excited rubrene triplets within the encounter cage. Unfortunately, the TXP sensitizer is completely insoluble in benzene and toluene, preventing the best possible quantitative comparison. We do note that sensitized TTA chemistry with anthracene exhibits much larger quantum efficiencies in toluene with respect to acetonitrile.[23]

Conclusions

The present investigation demonstrated that sensitized NIR-to-visible photon upconversion *via* sensitized triplet–triplet annihilation can be achieved utilizing TXP as sensitizer and rubrene as acceptors/annihilators in dichloromethane solution. Stern–Volmer analysis of the triplet transient absorption TXP decays by rubrene produced a K_{SV} of 21 000 M^{-1}, with a corresponding triplet–triplet energy transfer quenching constant of 5.7×10^8 M^{-1} s^{-1}. The upconverted emission intensity with respect to the incident excitation power varies between quadratic and linear, illustrating the expected kinetic limits for the light producing upconversion photochemistry under continuous wave illumination. The characteristic quadratic-to-linear crossover point shifted to lower incident photon power density with increasing TXP concentration, consistent with the notion that stronger photon capture in the sensitizer leads to experimental conditions promoting upconversion under more benign incident photon flux. The upconversion quantum yields continuously increase with increasing excitation power until the strong annihilation limit was reached at which time the quantum efficiencies level out to a constant value of 1.54 ± 0.04%. In pulsed laser experiments, the triplet–triplet annihilation quantum yield was determined to saturate at approximately 13%, with a corresponding $\Phi_{UC} = 0.094$, suggesting that the dichloromethane solvent either lowers the T_2 state of the rubrene acceptor or is somehow attenuating the annihilation reaction between excited rubrene triplets. The results suggest that the dichloromethane solvent is serving to impede the TTA reaction in the case of rubrene triplets. Although important

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from a fundamental standpoint and is illustrative of a high precision quantitative study, the present composition unfortunately does not appear to represent a viable combination for future device integration.

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