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Letter

Spectroscopy of Resonant Intermediate States for Triplet–Triplet Annihilation Upconversion in Crystalline Rubrene: Radical Ions as Sensitizers

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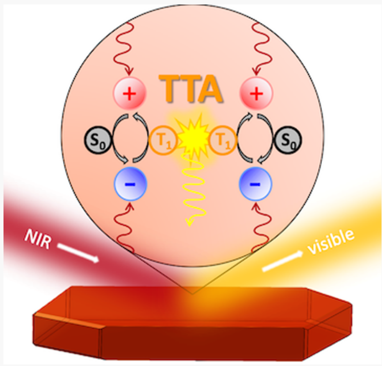
ABSTRACT: Photoluminescence upconversion in crystalline rubrene can proceed without an added sensitizer, but the mechanism for this process has not been well-understood. In particular, the species responsible for photon absorption has not been identified to date. To gain insight into the identity of the intermediate state, we measured the near-infrared (NIR) upconversion photoluminescence (UCPL) excitation spectrum of rubrene crystals and found three distinct spectral features. The UCPL yield has a quartic dependence on the laser intensity, implying a four-photon process. On the basis of electronic spectra of radical cations and anions of rubrene, we propose a mechanism in which photoexcited radical anions and cations undergo recombination, forming an excited neutral triplet while conserving spin. The triplets formed this way ultimately undergo triplet–triplet annihilation, resulting in the observed photoluminescence. This mechanism explains the origin of the NIR absorption as well as the four-photon nature of the UCPL process.



Many organic semiconducting materials have the ability to efficiently transfer energy between singlet and triplet excitons in spin-conserving processes.[1] Maybe the most well-known process taking advantage of this property is singlet fission, where a singlet exciton can share its energy with a neighboring ground-state molecule, creating two triplet excitons.[1,2] This phenomenon could improve the efficiency of organic photovoltaic (OPV) devices by having the potential to create two excitons from only one absorbed photon.[1−3] The reverse process where two triplet excitons fuse to make one singlet exciton can occur as well.[3−5] This process was first observed by Parker and co-workers over 50 years ago.[6] It is referred to as triplet–triplet annihilation (TTA) and has applications in improved OPV efficiency,[7−9] medical imaging,[10] and photocatalysis.[11]

TTA upconversion photoluminescence (UCPL) utilizes a combination of a "sensitizer species", absorbing longer wavelengths and transferring energy to an "emitter" species, which emits radiation at shorter wavelengths. The concept has been successfully demonstrated in solutions[4,5,12−15] as well as solid materials.[16−21] In order for TTA-UCPL to work in a particular system, the sensitizer and emitter combination must fulfill several requirements.[15] The sensitizer must be a sufficiently strong absorber in the region of the spectrum energetically close to the emitter molecule's triplet state. The sensitizer must be able to undergo efficient intersystem crossing into its triplet state once it has absorbed a photon, and many sensitizers therefore incorporate heavy metal atoms to increase spin–orbit coupling.[22,23] Next, energy must transfer from the sensitizer to the triplet state of the emitter, requiring a sufficiently long lifetime of the sensitizer triplet state. The emitter triplet state (as an excited molecule in solution or as a triplet exciton) must then also diffuse in order to interact with another emitter in its triplet state, combine their energy to bring one molecule to the singlet excited state, leaving the other in the ground state. The excited singlet molecule can then fluoresce, emitting light with a higher energy than was originally absorbed by the sensitizer.

Rubrene (5,6,11,12-tetraphenyltetracene, see Scheme 1) has been used widely in UCPL systems in both the solution and solid phase.[12,14,18,24] It is also an important model system for organic semiconductor crystal materials with high carrier mobilities, on the order of 1−20 cm^2 V^{-1} s^{-1}.[25] Orthorhombic rubrene single crystals can be grown using sublimation and physical vapor transport[26] and are usually needle-like with sizes ranging from millimeters to centimeters along the elongated *b*-axis[27] (see also the Supporting Information).

Interestingly, UCPL has been demonstrated in rubrene crystals and powder samples without any added sensitizing material.[24,28] Rubrene crystals are able to convert sufficiently intense near-infrared (NIR) light to visible light matching the fluorescence spectrum of solid rubrene.[24,28] One obvious

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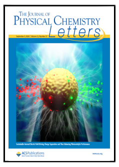
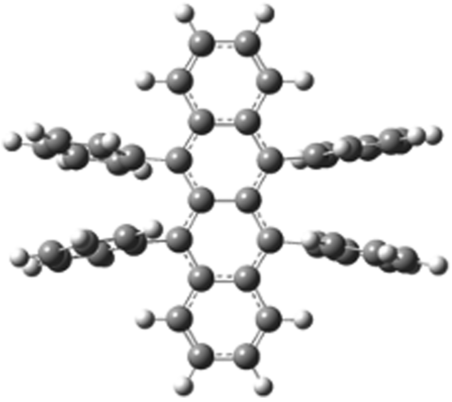


Scheme 1. Rubrene (5,6,11,12-tetraphenyltetracene) Molecular Structure



explanation of this phenomenon would be that rubrene is undergoing two-photon absorption (TPA, resonant or nonresonant), emitting from its singlet excited state, in which case the upconversion yield would vary with the square of the incident light intensity. However, using both cw and fs-pulsed radiation at ca. 800 nm, Bardeen and co-workers[28] discovered a quartic dependence on the laser intensity at the lowest laser intensities, implying a four-photon process rather than the quadratic signature of TPA. This result led Bardeen and co-workers to propose the existence of a resonant intermediate state in the rubrene crystal which absorbs NIR light. This intermediate state then transfers the energy to rubrene triplet excitons, which can then undergo TTA. The authors were not able to identify the species responsible for the resonant NIR absorption, but they suggest that impurities in the crystal or defect sites are responsible. In this Letter, we report the identity of the absorbing species and propose a new mechanism which is consistent with known properties of rubrene, explaining the four-photon process involved.

We used upconversion photoluminescence excitation (UCPLE) spectroscopy to measure the wavelength-dependent absorption characteristics of the species giving rise to the intermediate absorption in the NIR, using rubrene powders (Sigma-Aldrich, sublimed grade 99.99%) as well as single crystals grown using physical vapor transport[26,29] (see the Supporting Information, sections S1.1−S1.4 for full details). For collecting UCPLE spectra, we scanned the frequency of an optical parametric oscillator pumped by a Nd:YAG laser (pulse duration 5−7 ns, see the Supporting Information, section S1.4 for details), and measured the intensity of the upconverted photoluminescence as a function of laser frequency (Figure 1). We observed three distinct features in the NIR with enhanced upconverted photoluminescence, at ca. 11100, 12200, and 13000 cm^{-1}, respectively. Rubrene does not absorb resonantly in this region (at least not in its neutral form, see below), and there is disagreement in the literature over the nonresonant TPA spectrum of rubrene.[30,31] To rule out TPA as a source of UCPL, we measured the UCPL intensity as a function of laser intensity with the laser frequency resonant with the observed peaks. If TPA were the origin of UCPL, the UCPL intensity would scale quadratically with the intensity. However, we found a quartic dependence on intensity, in agreement with Bardeen and co-workers (Figures 2 and S7).[28]

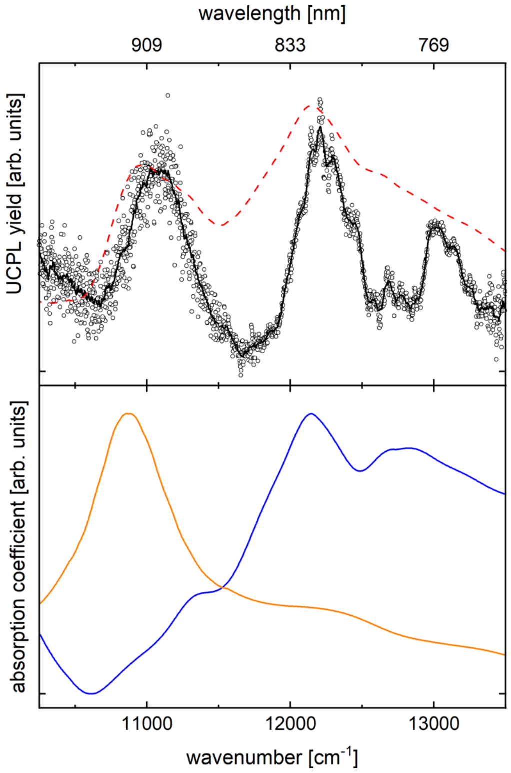


Figure 1. Bottom panel: solution absorption spectra of the rubrene radical cation (orange line) and radical anion (blue line). Data in the lower panel were adapted from Tagawa and co-workers.[32] Top panel: UCPLE spectrum of crystalline rubrene, corrected for a four-photon process by dividing the raw UCPL intensity by the fluence to the fourth power. The open circles are individual data points, and the black trace is a 20-point-smoothed curve to guide the eye. The dashed red line is the product of the absorption spectra of the radical ions shown in the lower panel.

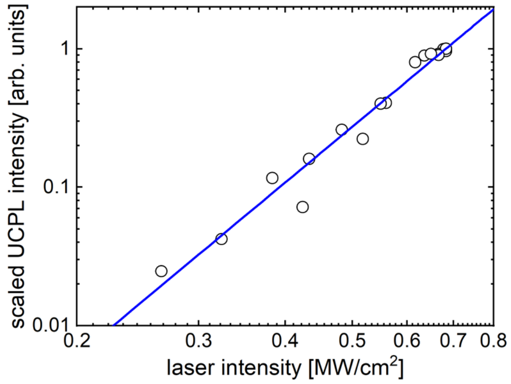


Figure 2. Dependence of the UCPL signal intensity on the excitation laser intensity at an excitation wavelength of 821 nm. Signals were scaled to compare results from multiple samples. Open circles are raw data, and the blue line is a fit of the laser intensity dependence to the experimental data. Laser excitation at 769 nm and 890 nm shows very similar intensity dependence (Figure S7). The exponents from the fit of the data are 4.16 ± 0.20 for 769 nm, 4.16 ± 0.22 for 821 nm, and 3.73 ± 0.30 with a fit up to 1 MW/cm^2 for 890 nm excitation.

Rubrene powders used as purchased without further purification (at 99.99% nominal purity) qualitatively show the same UCPLE spectrum as twice sublimed rubrene crystal samples (Figure S5) with similar overall UCPL signal intensities, so the presence of a chemical impurity causing UCPL is very unlikely. Rubrene can undergo reactive changes when exposed to light in the presence of oxygen. However,

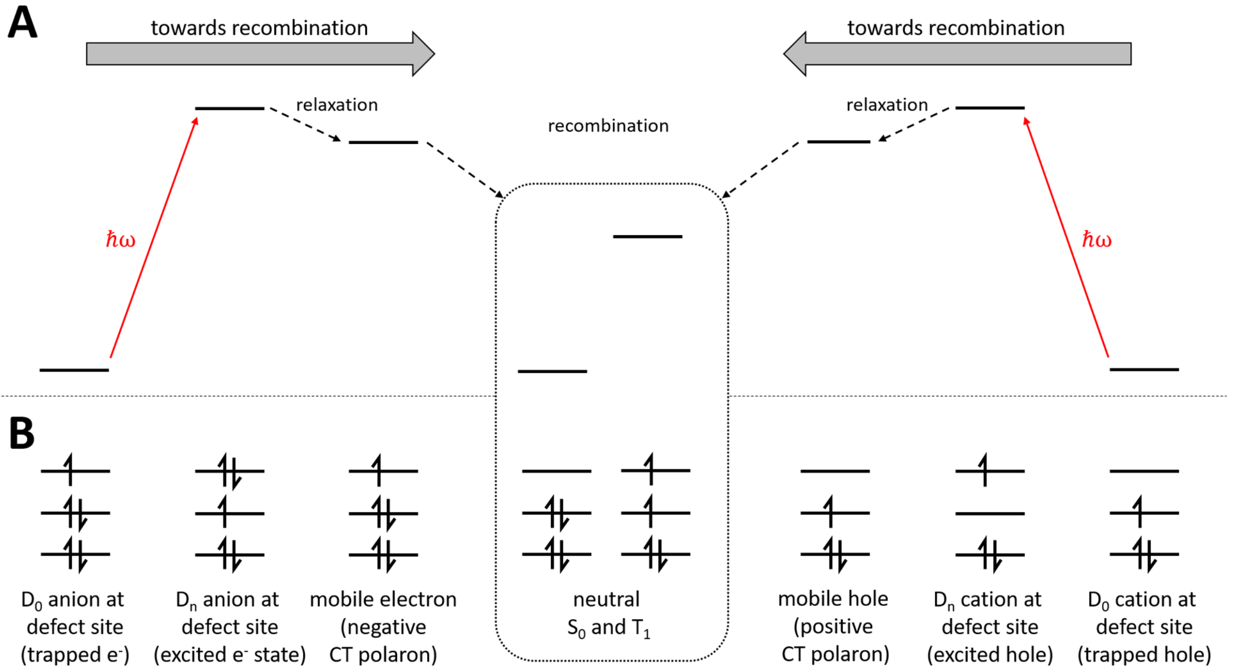


Figure 3. (A) Qualitative reaction diagram showing the recombination of electrons and holes in the proposed mechanism of UCPL from the excitation of trapped electrons (left) and holes (right) through relaxation processes in the crystal to the generation of a triplet exciton (center). (B) Schematic electron configurations in the reaction mechanism. Ground- and excited-state electron configurations of rubrene ions have been determined using TDDFT (see the Supporting Information).

typical amounts of photooxidation products at the surface of rubrene crystals handled at normal conditions are rather small.[33] In addition, the conjugation in rubrene is broken in all common degradation products. As a result, one would expect that the degradation products have larger HOMO−LUMO gaps and $S_0 \rightarrow S_1$ transition energies that are higher than for rubrene itself. This expectation is consistent with results from time-dependent density functional theory (TDDFT) calculations of the lowest-energy excitations of the known degradation products (TDDFT results and optimized geometries can be found in the Supporting Information, sections S1.10 and S1.11).[34,35] This all but eliminates degradation products as the sensitizing species.

We can turn to other luminescence processes in rubrene to guide our search for the mechanism for UCPL. The mechanism for electrochemiluminescence of rubrene in solution involves the recombination of a rubrene radical cation and a rubrene radical anion, producing an excited triplet and a ground state, both neutral molecules.[36−38] A similar mechanism could be at work in UCPL of solid rubrene. If the presence of both excited anions and cations is necessary to observe UCPL, then the UCPLE spectrum of rubrene should be proportional to the product of cation and anion absorption spectra:

$$Y_{\mathrm{UCPL}}(\omega) \propto \alpha_{+}(\omega)\cdot\alpha_{-}(\omega) \tag{1}$$

where $Y_{\mathrm{UCPL}}(\omega)$ is the upconversion yield and $\alpha_{+}(\omega)$ and $\alpha_{-}(\omega)$ are the absorption coefficients of the rubrene radical cation and radical anion, respectively. Figure 1 shows a comparison of the experimental data and the product of the absorption spectra of the radical ions, taken from the work of Tagawa and co-workers.[32] The overall shape of the UCPLE spectrum agrees quite well with the product of the ion spectra, strongly suggesting that the excitation of both cations and anions is necessary for the observation of UCPL in rubrene. Deviations between our experimental results and the product of the ion absorption spectra are likely due to the fact that the ion absorption spectra were measured in solution whereas our measurements were performed on solid crystals.[32] These deviations are in all cases less than ca. 200 cm^{-1}, which is a reasonable expectation for shifts due to solvatochromic and crystal effects.

Because recombination of radical anions and cations in solution results in the formation of two neutral molecules, one in the ground state and the other in the T_1 triplet state,[37,38] a mechanistic picture emerges that explains the shape of the UCPLE spectrum in solid rubrene, as well as the quartic intensity dependence of the process (see Figure 3). Because it is unlikely that NIR radiation itself will produce charge carriers in rubrene, let us for the moment assume that we start with intrinsically present charge carriers.[18] Electrogenerated chemiluminescence in rubrene solutions through the formation of a triplet is observed without prior photoexcitation,[37,38] so the question arises why the observed UCPL process in solid rubrene requires excitation. A likely explanation is that while mobile anionic or cationic charge carriers (i.e., free electrons and holes) will readily undergo recombination, and will not be available for UCPL, anionic and cationic charge carriers localized on strongly bound defect sites (i.e., trapped electrons and holes) will be long-lived, because they do not have nearby reaction partners to undergo recombination. We therefore propose that the starting species for the observed UCPL process are localized, immobile negatively and positively charged defects that can be described in a molecular picture as rubrene anions and cations. Photoexcitation of these charge carriers results in the population of excited states that can couple to mobile interband states, i.e., leading to the formation of charge transfer (CT) polarons, similar to CT excitons,[39−41] enabling the charge carriers to move through the crystal. The lifetimes of such CT polarons in crystalline rubrene have not

Table 1. Parameters Used in the Kinetic Model

σ_{CTe}, σ_{CTh} (cm^2)[a]	k_R ($cm^3\ s^{-1}$)[a]	k_L (s^{-1})[a]	k_A ($cm^3\ s^{-1}$)[b]	k_{SF} (s^{-1})[b]	k_Q (s^{-1})[b]	k_{PL} (s^{-1})[b]
10^{-21}–10^{-15}	10^{-15}–10^{-9}	10^5–10^6	10^{-12}	5×10^{10}	1.67×10^4	6.25×10^7

[a] Range of parameters tested in the present work that produce quartic intensity dependence. [b] Values taken from Table 2 in ref 28.

been measured to our knowledge. Assuming that the relaxation dynamics are similar to those for $S_1 \rightarrow S_0$ in neutral rubrene, we estimate these relaxation processes to occur on the 100 ps to 100 ns time scale,[42] converting available excess energy into phonon excitations. Recombination of a cationic and an anionic charge carrier can produce two neutral molecules, one in the triplet state and one in the ground state (see Figure 3), similar to the processes leading to electrochemiluminescence in rubrene solutions.[36,38] The triplet excitons formed this way can then combine to undergo TTA, resulting in the emission of a photon from an excited singlet state.

There are of course loss mechanisms associated with each step in the proposed model, which limit the overall yield of UCPL. The CT polarons can be recaptured into defect sites before they recombine, or they can recombine in a nonradiative process. Finally, the singlet exciton created by TTA may fissure again into two triplets.[28,43]

To test whether the proposed mechanism really can account for the quartic intensity dependence, we can describe it using a system of rate equations. The densities of photogenerated mobile negative and positive charge carriers, N_e and N_h, are governed by

$$\frac{dN_e}{dt} = \Phi(t)N_{e0}\sigma_{CTe} - k_R N_e N_h - k_L N_e \quad (2)$$

and

$$\frac{dN_h}{dt} = \Phi(t)N_{h0}\sigma_{CTh} - k_R N_e N_h - k_L N_h \quad (3)$$

where N_{e0} and N_{h0} describe the densities of the trapped electrons and holes; $\Phi(t)$ is the photon fluence (in photons per cm^2 and s, the time dependence encodes the laser pulse duration), and σ_{CTe} and σ_{CTh} are the mobile charge carrier formation cross sections. The parameter k_R is the charge recombination rate constant, and k_L is the rate constant for loss processes, depleting the mobile charge carriers (set to be the same for negative and positive carriers for simplicity). The density of triplets, N_T, is described by

$$\frac{dN_T}{dt} = k_R N_e N_h - k_A {N_T}^2 + 2k_{SF}N_S - k_Q N_T \quad (4)$$

where N_S is the density of singlet excitons formed by TTA, k_A the TTA rate constant, k_{SF} the singlet fission rate constant, and k_Q a triplet quenching rate constant. Finally, the singlet population is governed by

$$\frac{dN_S}{dt} = k_A {N_T}^2 - k_{PL}N_S - k_{SF}N_S \quad (5)$$

where k_{PL} is the PL rate constant. Several parameters in this model are known from the literature, and we summarize them in Table 1, following the review of these parameters in the work by Bardeen and co-workers.[28] We note that the model described in eqs 2–5 is a minimal model, and many additional (but ultimately unknown) parameters could be added, such as a triplet–triplet quenching reaction or nonradiative singlet exciton relaxation. The unknown parameters in the current model are σ_{CTe}, σ_{CTh}, k_R, and k_L. There is a wide range of these unknown parameters for which the model reproduces the experimentally observed quartic intensity dependence of UCPL (see Table 1), robustly supporting the proposed mechanism.

We note that the source of the initially localized charged defects is not unambiguously clear. The proposed mechanism will result in a depletion of the initially excited, localized charge carriers over irradiation time, as they are lost because of recombination. The depletion of charge carriers over time is consistent with the observation of significant photobleaching (see Figures S10 and S11), which has also been observed by Nienhaus and co-workers in other processes that involve intrinsic charge carriers in rubrene, and has been tied to surface effects.[18] Irradiation with a pulsed excitation source operating at 20 Hz and a time-averaged intensity of 68 mW/cm^2 results in the UCPL signal decaying, reaching 45% of its initial value after ca. 150 s and only slightly decreasing from this value over the course of hours. Upon blocking the light source, the signal returns to close its original value after only a 10 min recovery time (see Figure S10), indicating that in the absence of excitation, an equilibrium develops where the charge carriers are replenished, possibly at the crystal surface.[18]

In conclusion, we propose that the UCPL observed in rubrene crystals and powders is due to the excitation of interband states that correspond to excited states of radical cations and radical anions in the crystal. We measured the rubrene UCPLE spectrum in crystalline samples as well as powders and found that the measured UCPLE features in the NIR are in good agreement with a product of the experimental absorption spectra of the two radical ion species. Excitation of localized, molecular charge carriers results in mobile charge carriers, which can recombine to produce triplet excitons. These triplet excitons can then undergo TTA, resulting in photoluminescence. This model accounts for the features in the UCPLE spectrum, the quartic intensity dependence of the UCPL signal, and the photobleaching of UCPL.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01999.

> Crystal synthesis by physical vapor deposition, XRD analysis, UV–vis absorption of crystals, PL spectra of crystals with different excitation wavelengths, UCPLE spectroscopy details, temperature dependence of UCPL and PL, UCPL bleaching, and calculation details (PDF)

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Notes

The authors declare no competing financial interest.

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