

JOURNAL OF SCIENCE



SAKARYA UNIVERSITY

Sakarya University Journal of Science

ISSN 1301-4048 | e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University |
<http://www.saujs.sakarya.edu.tr/>

Title: Triplet-Triplet Annihilation Based Energy Upconversion Mechanism: Cyanine7 Dye Doped with Super Yellow and Rubrene Hosts

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Received: 2019-03-12 15:56:18

Accepted: 2019-10-02 09:21:00

Article Type: Research Article

Volume: 24

Issue: 1

Month: February

Year: 2020

Pages: 55-59

How to cite

Murat Aydemir; (2020), Triplet-Triplet Annihilation Based Energy Upconversion Mechanism: Cyanine7 Dye Doped with Super Yellow and Rubrene Hosts. Sakarya University Journal of Science, 24(1), 55-59, DOI: 10.16984/saufenbilder.538797

Access link

<http://www.saujs.sakarya.edu.tr/tr/issue/49430//538797>

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Triplet-Triplet Annihilation Based Energy Upconversion Mechanism: Cyanine7 Dye Doped with Super Yellow and Rubrene Hosts

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Abstract

In this work, two case studies for energy upconversion mechanisms are presented; one *via* two photon absorption and the other one *via* triplet fusion mechanism. These are strongly required photophysical mechanisms in conjugated organic molecules, due to enhance the efficiency of organic electronic devices. During the investigations, Cyanine7 (Cye7) molecule is used as a sensitizer and for the host molecules rubrene and super yellow molecules are preferred due to their comparatively close locally excited triplet energy levels. The results show that upconverted delayed fluorescence arises from triplet-triplet annihilation mechanism in those particular sensitizer-host systems which gives rise to enhance the internal quantum efficiencies by populating the locally excited singlet states. Consequentially, for the first time Cye7 (near infrared) dye is used as a sensitizer in an energy upconversion experiment, and also two photon absorption mechanisms are reported in ppv based 'super yellow' polymer which has two photon absorption cross-section at 780 nm

Keywords: Cyanine7 dye, delayed fluorescence, energy up-conversion, rubrene, super yellow

1. INTRODUCTION

Energy upconversion process is observed in organic dye systems and widely used in biophysical investigations [1]. Recently, studies on energy up-conversion *via* triplet fusion have been reported, which is a photophysical process results in up-converted delayed fluorescence from a singlet state [2-4]. Energy upconversion *via* triplet fusion could be used in upconverting the near infrared energy spectra of solar radiation to higher energy light and directed onto organic solar cells which absorb primarily at visible wavelengths [5]. Reports have appeared with observations of energy upconversion via triplet

fusion in biomolecules as well [6]. This could pave the way for this type of energy upconversion into biophysical applications as well as fluorescence imaging [6]. Indeed, much lower threshold is needed to achieve upconversion *via* triplet fusion in comparison with that of two photon absorption and this is a promising way to upconvert photons [6]. In an ideal upconversion mechanism, the energy consumption must be minimum during the triplet-triplet energy transfer process, which is a strong requirement to get high efficiency from the system. Using the heavy metal complexes as sensitizers can strongly enhance the spin-orbit coupling, therefore, intersystem crossing (ISC) rate between the locally excited

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singlet and triplet state should be in near unity as well as having long triplet lifetimes, which appears as a driving force for the triplets to diffuse further distances. These result in an increase in collision probability between the triplets of the sensitizer and the acceptor during the triplet-triplet energy transfer process. Actually, this energy transfer is a Dexter-type energy transfer, which requires close proximity between the encounters. Therefore, the working mechanism of this particular system depends on physical interactions (collisions) of the triplets of the sensitizer and the acceptor, for that, the triplets from both of the states must potentially exist in the solution at the same time. In this case, exchange interactions occur as a result of spatial overlaps between the wave functions of the resonating sensitizer and the acceptor triplet states. As a result of collisions, upconverted delayed fluorescence occurs and emits from locally excited singlet state. In this work, energy upconversion mechanism is presented using commercial molecules, where the origin of delayed fluorescence is determined.

2. EXPERIMENTAL PROCEDURE

The materials commercially bought from the companies, super yellow polymer (SY) from Merck, rubrene from Aldrich and Cy7 from Lumiprobe. Then the solutions prepared after dissolving in chlorobenzene stirring overnight prior to mixing solutions together. Rubrene at 10^{-2} M concentration was doped with Cy7 ($1.5 \cdot 10^{-4}$ M), SY at 3mg/ml concentration was doped with Cy7 ($1.5 \cdot 10^{-4}$ M) for upconversion measurements. These samples were thoroughly degassed using at least 3 freezes though cycles. Nanosecond gated luminescence and lifetime measurements were made using a system consisting of a 1.63 eV dye laser pumped with high energy pulsed YAG laser emitting at 2.33 eV (EKSPLA). The resolution of the system is ~ 1 ns. Samples were excited at 45° angle to the substrate plane. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics). Decay measurements were performed by logarithmically increasing gate and delay times.

3. RESULTS AND DISCUSSION

In this work, commercial Cyanine7 (Cy7) is used as a sensitizer, and dope it into two different hosts, super yellow (SY) polymer and rubrene (fluorescence and absorption spectra in Fig. 1a). SY has higher singlet and triplet levels (figure 1b) than rubrene, whereas Cy7 singlet level is lower than both hosts, its triplet level is expected to be higher than that of rubrene and lower than of SY. Further the Q band absorption is at 760 nm where neither rubrene nor SY absorbs, making this complex excellent sensitizer (figure 1a). The fluorescence decay lifetime of SY is <1 ns,[7] and rubrene 16.4 ns,[8] whereas fluorescence decay of Cy7 is <1 ns.

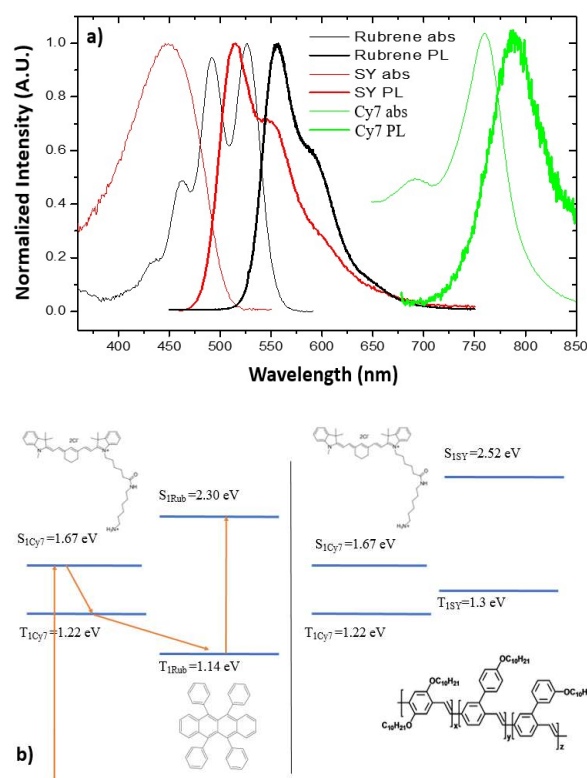


Figure 1. a) Fluorescence and absorption spectra of rubrene, super yellow (SY) and Cy7 in chlorobenzene solution. b) Jablonski diagram, where the singlet, triplet levels and molecular structures of materials are shown. Singlet levels are taken as crossing between absorption and fluorescence emission from Figure 1a. Rubrene triplet level is taken from refs [9,10], SY from ref. [11]

To determine if upconversion occurs using this sensitizer, a degassed solution of highly concentrated rubrene (10^{-2} M) doped with Cy7

($1.5 \cdot 10^{-4}$ M), exciting at 760 nm (30 μ J/pulse) into the absorption band of Cy7, where rubrene does not absorb. As shown in figure 2a inset, in such a case upconverted emission from rubrene is observed. It is proposed that after excitation to the Cy7 singlet level, very efficient intersystem crossing to the sensitizer triplet level takes place. From there, triplets are transferred to the triplet manifold of rubrene where they annihilate resulting in delayed rubrene fluorescence emission. Indeed, two experiments support this crossing pathway. Firstly, the decay of this delayed emission is recorded as 21 μ s, which is much longer than natural fluorescence lifetime of rubrene (16.4 ns). If this arises *via* triplet fusion, it should depend on triplet concentration time evolution which is governed by a rate equation;

$$\frac{d[T]}{dt} = -(k_m)[T] - k_{tt}[T]^2 \quad (1)$$

Where k_m is monomolecular decay rate, k_{tt} - bimolecular decay rate, $[T]$ - triplet concentration. If the monomolecular processes are the main mechanism of triplet depletion, then (1) can be solved to give phosphorescence intensity (PH) proportionality;

$$PH \sim [T] = [T_0] \exp(-[k_m]t) \quad (2)$$

T_0 is triplet concentration at time 0 i.e. the triplet population initially formed through intersystem crossing. Delayed fluorescence arising from triplet-triplet annihilation i.e. triplet fusion is proportional to the square of triplet concentration;

$$DF \sim [T]^2 = [T_0]^2 \exp(-2[k_m]t) \quad (3)$$

Hence delayed fluorescence should decay with a rate twice as small as phosphorescence decay. To confirm this, the rubrene DF lifetime recorded by us can be compared with the literature values. Previously, the triplet lifetime of rubrene in acetonitrile solution have been reported to be 82 μ s which is 4 times greater than our value [12]. However, Liu *et al.* fit the data from 150 μ s to 250 μ s whereas the lifetime is up to 150 μ s in here (figure 2 a). From figure 2 in ref [12] it can be

clearly distinguished that up to 150 μ s rubrene decays with a faster lifetime than 82 μ s fitted by these authors, and their data is double-checked and find this faster value to be ~ 40 μ s, exactly twice greater than our DF value. This supports the hypothesis that this upconverted light arises due to triplet fusion on rubrene molecules.

Further, the rubrene delayed fluorescence intensity could be expressed as the integral of the square of the triplet concentration:

$$DF \sim \int_0^{\infty} k_{tt}[T]^2 dt = \int_0^{\infty} k_{tt}[T_0]^2 \exp(-2[k_m]t) dt = \frac{k_{tt}[T_0]^2}{2(k_m)} \quad (4)$$

According to (4) the DF signal should follow a quadratic dependence on initial triplet concentration (or on laser fluence). When the equation (1) is solved considering the high triplet concentration situation, then the first term in equation (1) can be neglected to get;

$$[T] = \frac{[T_0]}{(1 + k_{tt}[T_0]t)} \sim t^{-1} \quad (5)$$

Therefore, it would follow that in at very high triplet concentration the DF intensity follows a linear proportionality on the excitation fluence (initial triplet concentration T_0) and (4) can be rewritten:

$$DF \sim \int_0^{\infty} k_{tt}[T]^2 dt = \int_0^{\infty} k_{tt} \frac{[T_0]^2}{(1 + k_{tt}[T_0]t)^2} dt = \frac{k_{tt}[T_0]^2}{k_{tt}[T_0]} = [T_0] \quad (6)$$

Indeed, previously it was observed that the DF arising due to triplet fusion *via* the sensitization of a metal complex obeys a quadratic dependence at low laser flux, but at high intensity it turns over and follows a linear laser dependence [13,14]. This is also observed in here and the turnover point can be considered to be the energy upconversion *via* triplet fusion efficiency indicator [13,14]. The observation of this turnover point also confirms that DF in rubrene: Cy7 arises due to energy upconversion *via* triplet fusion (figure 2 b)

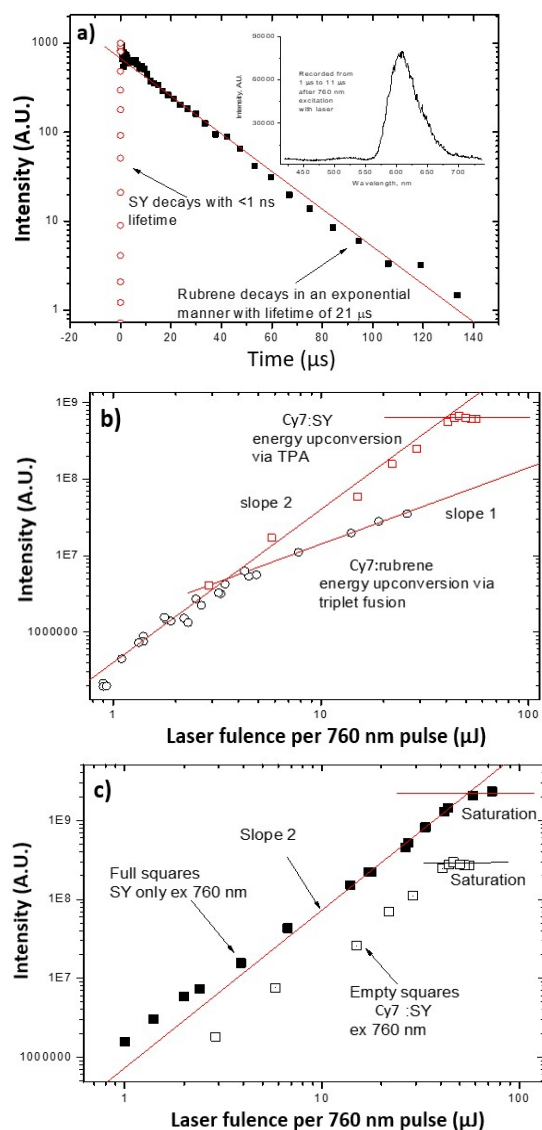


Figure 2. **a)** Decays of rubrene (squares) and SY (open circles) both doped with Cy7 in chlorobenzene, both excited at 760 nm, straight diagonal line is monoexponential fit of 21 μs . Rubrene decay is clearly much longer than SY. In rubrene DF spectrum from Cy7:rubrene solution is depicted recorded 1 μs after excitation, exciting at 760 nm. **b)** Laser fluence dependencies of SY and rubrene emission from Cy7:SY and Cy7:rubrene in chlorobenzene solutions exciting at 760 nm. **c)** Laser fluence dependencies of SY emission from SY only and SY: Cy7 in chlorobenzene solutions. They are clearly different rubrene emission laser fluence dependency from Cy7:rubrene solution as saturation point can be observed in the former and not in the latter.

When Cy7 ($1.5 \cdot 10^{-4}$ M) is doped in SY (3mg/ml) and excited with 760 nm laser pulse (30 μJ per pulse), very different behaviour is observed compared to that described above. This could be

expected mainly due to the fact that Cy7 triplet is lower than the triplet of SY hence no transfer to the super yellow triplet manifold is possible when Cy7 Q band is excited at ~ 760 nm. However when exciting a solution of SY: Cy7 at 760 nm, well below the absorption band of SY, the upconverted emission still can be observed from SY. The SY emission decay is <1 ns, much shorter than that of rubrene emission observed from Cy7:rubrene solution. Indeed, the decay of fluorescence of pure SY is <1 ns [7] and it can be said that two photon absorption is observed. Hence it is proposed that this sensitizer does not have any influence in this case, which is supported by the fact that after excitation of SY only solution at 760 nm under the same conditions, only emission from super yellow is observed. This case is very different from that of Cy7:rubrene, which can be confirmed by the SY emission dependency on laser fluence. A quadratic dependence (figure 2 c) from very low intensities is observed, however, instead of the turnover to the linear dependence as suggested by equations 4 and 6, the saturation of two photon absorption is recorded. Indeed, this is clear proof that energy upconversion via two photon absorption rather than triplet fusion is observed.

4. CONCLUSION

In summary, two cases of energy upconversion are presented. One, in rubrene: Cy7 is based on triplet fusion, whereas the other, SY: Cy7 is based on two photon absorption. It is clearly shown how the two of them can be distinguished. If the upconversion is achieved *via* triplet fusion then 1) the upconverted emission decay will be much longer than it is fluorescence lifetime, and will have a decay rate twice faster than triplet decay of the host; 2) its laser fluence dependency will follow quadratic law initially and later will turn to the linear regime. Whereas if the upconversion is achieved *via* two photon absorption, 1) the upconverted light decay rate will be in the range of its fluorescence lifetime; 2) its laser fluence dependency will follow quadratic dependency up to very high energies and will saturate at some point, however, no linear regime will be observed as in previous case. It is demonstrated for the first time two photon absorption in super yellow

copolymer, and showed that it can be very efficient at weak $<1 \mu\text{J}$ per pulse excitations. Also for the first time Cy7 was used as a sensitizer in energy upconversion *via* triplet fusion with rubrene as a host.

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