Letter

Kinetics of near-infrared-to-visible upconversion in rubrene: An initial excitation of triplets

Pushpendra Kumar*
Max-Planck Institute of Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Durga Prasad Kandel and Rajendra Adhikari
Department of Physics, Kathmandu University, Box:6250, Kavre, Nepal

Ahibur Rahaman*
Department of Organic Chemistry, Arrhenius Laboratory Stockholm University, Svante Arrhenius vag 16C, 10691 Stockholm, Sweden

Khadga J. Karki†
Guangdong Technion-Israel Institute of Technology, 241 Daxue Road, Shantou, Guangdong Province 515603, People's Republic of China

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Upconversion (UC) in a molecular system is a process in which excitons produced by a multiple absorption of low-energy photons at long wavelengths undergo fusion to produce high energy excitons that consequently recombine to emit anti-Stokes shifted photons. Molecular systems for UC typically require a sensitizer. However, recent experiments show that UC in rubrene occurs even without the presence of the sensitizer. In this system, intermediate states are assumed to absorb photons at near-infrared wavelengths, which either absorb additional photons to populate the emissive singlet state or undergo fusion to generate triplets. The triplets can again undergo fusion to populate the excited singlet state. The final emission is around 600 nm. These models have been tested against the intensity dependence of the UC emission. Here, we have measured the kinetics of UC in rubrene by using intensity modulated photoexcitation at 800 nm to better understand the underlying mechanism. The models of UC that have been proposed so far do not agree with our measurements. Our results show that the yield of UC lags behind excitation significantly, indicating that triplet states are directly excited from the ground state, and their fusion, which depends on the population, becomes prominent after a certain build up time. While the intermediate states could form dynamically after the UC has been initiated and enhance the process, further sensitive absorption measurements are necessary to understand the role of the intermediate states in the process. Our results are important in finding new routes to enhance UC in pristine organic semiconductors for applications in photovoltaics, lasers, bioimaging, optical devices, and lighting.

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I. INTRODUCTION

Upconversion (UC) in molecular systems proceeds via the fusion of two triplet excitations. As the direct excitation of triplet states from a typical singlet ground state is spin forbidden, it is common to use sensitizers for the initial excitation. The overall mechanism involves excitation of the sensitizer, which undergoes intersystem crossing to populate the triplet states followed by the energy transfer to the triplet states of the molecules of interest. Diffusion mediated fusion of two such molecular excitations leads to a simultaneous excitation of a high lying singlet state in one of the molecules and de-excitation in the other [1–4]. This process is also commonly known as triplet-triplet annihilation (TTA) [5,6]. The molecules that have been excited to the singlet state undergo radiative recombination emitting photons with higher energies compared to the photons initially absorbed by the sensitizer. A simple scheme of the UC in a typical molecular system is given in Eq.(1):

$$S_{1s}^{*} \rightarrow T_{1s}^{*} \rightarrow T_{1m}^{*} : T_{1m}^{*} + T_{1m}^{*} \rightarrow S_{1m} \rightarrow S_{0m} + \text{photon}, \quad (1)$$

where S_{1s} and T_{1s} are the first singlet and triplet states of the sensitizer, S_{1m} and T_{1m} are the first singlet and triplet states of the chromophore and S_{0m} is the corresponding ground state. One of the advantages of TTA based UC is the availability of a huge array of molecular systems that can upconvert photons from ultraviolet (UV) to near-infrared (NIR) wavelength [7]. UC has been observed in different classes of chromophores including anthracene [3], tetracene [4], pyrene, and perylene [8] and diimide based derivatives [9]. UC in these systems have found numerous applications in lasers, [10] optical devices, [11,12] bioimaging, [13–15] photovoltaics, and lighting [16–18].

While the initial excitation of the singlet state of the sensitizer is essential for the efficient absorption of low energy photons in a typical molecular system for UC, recent measurements have shown an exception in rubrene where the

*Chemical Physics, Department of Chemistry, Lund University, Box 120, SE-221 00 Lund, Sweden.
†khadga.karki@gtiit.edu.cn

