Elucidating the Role of Structure and Spin in Photon Upconversion via Triplet-Triplet Annihilation

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Introduction

Photon upconversion—combining two or more low energy photons to generate a higher energy excited state—is an intriguing strategy for increasing the maximum theoretical solar cell efficiencies from 33% to >43%. It is well known that inorganic nanoparticles and organic small molecule triplet-triplet annihilation (TTA) pairs can promote photon upconversion (UC). Of the two, molecular TTA-UC (see **Fig.1**) is particularly appealing because UC efficiencies >40% have been demonstrated for some of these systems and, in contrast to inorganic UC, is achievable even under low intensity, non-coherent, solar irradiation [1]. The key to realizing efficient TTA-UC is to gain a fundamental understanding of how the structure and interaction between acceptor molecules dictates the rate and efficiency of the TTA event. Unfortunately, we lack a fundamental understanding of how the acceptor orientation and spin interactions influence the TTA. This knowledge is necessary to design new and efficient TTA-UC systems.

Experimental

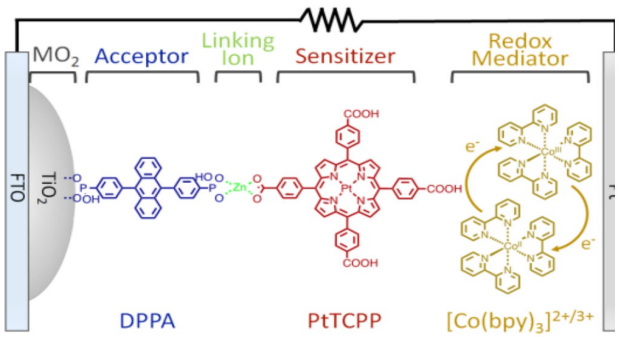

Fig.1 Schematic representation of the self-assembled bilayer TTA-UC solar cell.

We have performed electron paramagnetic resonance (EPR) measurements at 240 GHz as a function of temperature and under steady state irradiation for samples composed of sensitizer only (ZrO_2-PtTCPP), and the TTA-UC bilayer (ZrO_2-DPPA-Zn-PtTCPP), and the ZrO_2 only. We have used the multi-frequency heterodyne quasi-optical spectrometer equipped with a 12.5 T SC magnet at the NHMFL in Tallahassee, which allows for optical excitation access, as well as in situ irradiation using light emitting diodes. A variable temperature flow cryostat was used for the experiments in the range from room temperature to liquid helium temperature. EPR measurements were done by using field modulation, while excitation dependent signals were detected via double modulation of field-modulated EPR and amplitude modulation of the excitation light.

Results and Discussion

The EPR signature at 240 GHz of the investigated samples is dominated by impurities in the ZrO2, mostly related to Mn^{2+}. At low temperature the zero-field splitting and strain broadened m_S = -5/2 to m_S = -3/2 and m_S = -3/2 to m_S = -1/2 transitions of the S = 5/2 Mn^{2+} which led to a 0.5 Tesla wide background signal with a narrower peak from the m_S = -1/2 to m_S = +1/2 transition around g = 2 (see **Fig.2**). With a LED irradiating the bilayer at low temperatures a hint of a signal is observed, but with the current excitation intensity we cannot make any definite statements about its origin.

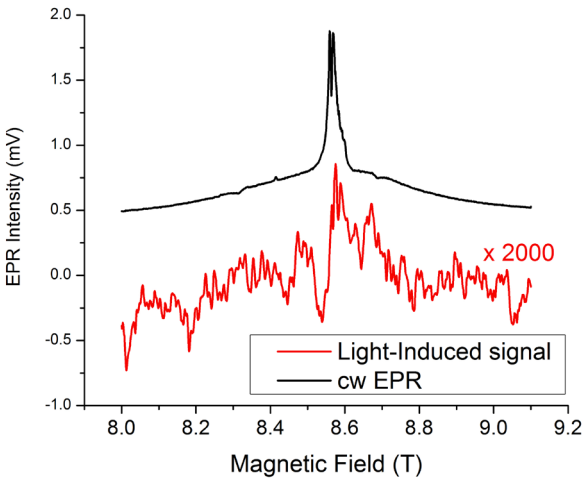

Fig.2 EPR and light induced EPR in a self-assembled bilayer at 10 K.

Conclusions

The initial experiments show that even at low temperature the steady state population of paramagnetic excited states that is generated with the current cw optical excitation of the bilayer material is insufficient for the detection sensitivity.

Acknowledgements

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References

[1] Dilbeck, T., *et al.*, J. Phys. Chem. C, **121**, 19690 (2017).