

Recycling of Singlet Excitons in Organic Bilayers

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Exciton dynamics are studied in C₆₀/Rubrene bilayers with 2D time-resolved photoluminescence. Triplet energy transfer from C₆₀ to rubrene, triplet upconversion in rubrene, and back singlet energy transfer from rubrene to C₆₀ are demonstrated, which leads to repopulation of the C₆₀ singlets pool and increasing C₆₀ fluorescence lifetime.

Effective organic solar cells rely on the ability to split photogenerated excitons at the interface between donor- and acceptor-type materials. Usually, only singlet excitons are harvested while triplet excitons do not contribute to the photocurrent. On the other hand, in many organic materials extremely efficient singlet-to-triplet conversion occurs thereby making a significant fraction of singlets lost for device operation. Therefore, there is a necessity in materials and/or methods to utilize the triplet excitons via either their direct splitting to charges [1] at the interface or back conversion to the singlets.

Here we use 2D time- and spectrally-resolved photoluminescence (PL) to demonstrate singlet exciton recycling in amorphous rubrene (20 nm)/C₆₀ (45 nm) vacuum-deposited bilayers. We show that due to the specific energy alignment, triplet excitons from C₆₀ undergo energy transfer to triplets in rubrene (Fig 1a) [2]. This process causes rubrene PL after C₆₀ photoexcitation in the region of rubrene transparency, which implies formation of high energy rubrene singlets via an up-conversion process [2]. Furthermore, the reverse process also occurs: the relatively short C₆₀ PL decay time increases in the bilayer structure (Fig 1b) because of the C₆₀ singlets pool back-feeding by the energy transfer from rubrene to C₆₀. The nature of the processes are confirmed by 2D mapping of the excitation wavelength-dependent PL (Fig 1c). The results obtained demonstrate the possibility of utilizing the C₆₀ triplet excitons via their back-conversion to singlets through a “buffer” rubrene layer, which is favorable for the charge collection in organic solar cells.

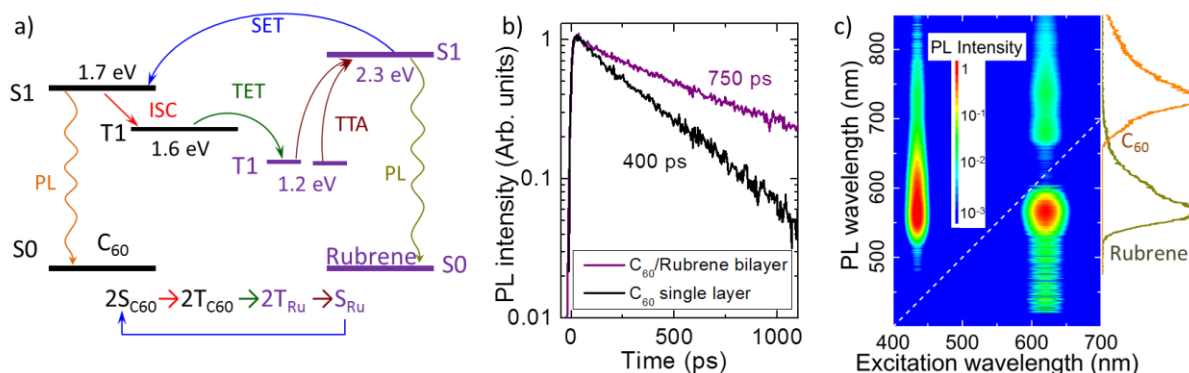


Fig.1 (a) Processes in C₆₀/Rubrene layer after C₆₀ excitation. PL is shown by orange and yellow arrows, intersystem crossing (ISC) in red, triplet energy transfer (TET) in green, singlet energy transfer (SET) in blue and triplet-triplet annihilation (TTA) in brown. The summary of the singlet recycling is shown in the bottom. (b) C₆₀ fluorescence with (purple) and without (black) rubrene layer after 620 nm excitation. (c) 2D map of the excitation wavelength dependent PL. The spectra for each excitation wavelength are integrated over the whole time range, normalized by C₆₀ PL maxima and convoluted with the excitation profile. Rubrene PL after 620 nm excitation (below the diagonal) originates from up-converted singlets formed via consequent TET and TTA processes. Normalized rubrene and C₆₀ PL spectra after 440 nm excitation are shown to the right for comparison.

[1] R. Schueppel *et al.*, ChemPhysChem **8**, 1497 (2007)

[2] A. K. Pandey, Sci. Rep. **5**, 7787 (2015); C. Xiang *et al.*, Small **11**, 5439 (2015)