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Investigation of exciton dynamics in triplet dopant blended polymer photovoltaic devices

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It is necessary to use the thicker film of photo-absorbing organic (polymer) layers through the high light absorption for high power-conversion efficiency. However, diffusion length of the singlet excitons (usually 5-10nm), which is strongly dependent on exciton mobility and lifetime, is much shorter than the absorption depth required for efficient light absorption. In this aspect, triplet materials might be excellent candidates because of their excellently longer exciton lifetimes compared to the singlet ones. Therefore, it should be possible to transport triplets to a planar interface where excitons dissociation can occur, without the need of using a distributed heterjunction, due to the very long triplet diffusion range.

It is known that the spin orbital coupling determines the intersystem crossing and consequently the singlet and triplet ratios in polymer (organic) materials. Usually, conjugated polymer (organic) materials with aromatic structure have weak spin-orbital coupling and thus limits the triplet generation under photoexcitation. Modification of singlet and triplet excitons ratio can be made by introducing a heavy-metal complex, which improves the photovoltaic response through the improved light absorption as well as controlling exciton dissociation, exciton-charge reaction and recombination of dissociated charge carriers in organic bulk heterojuction solar cells. Furthermore, this can solve the disadvantage of triplet materials, such as low charge carrier mobility, by increasing charge transport and carrier collection efficiency, leading to a better photovoltaic performance.

Here, we have investigated the triplet exciton dynamics of a conjugated polymer in heavy metal complex blended system.

Figure 1 shows (a) the chemical structure, (b) photoluminescence (PL) spectra of pristine MEH-PPV and 5% PtOEP blended MEH-PPV film at room temperature. MEH-PPV shows two main PL peaks at 576 and 625 nm with a much weaker red shoulder. Three discernible peaks are obviously resolved to provide information about a single electronic state (0 - 0 emission band) and the featureless vibronic structures such as 0-1, 0-2 emission bands upon excitation in the solution state. The PL emission of the PtOEP centered at 650 nm is due to the radiative decay from the

triplet state to the ground state (Fig 1. (b)). When the PtOEP is blended with MEH-PPV, the PL intensity of both MEH-PPV and PtOEP is strongly quenched. It indicates that there is interaction between MEH-PPV and PtOEP. Figure 1 (c) shows the photo-induced absorption (PIA) spectra of pristine MEH-PPV and PtOEP blended MEH-PPV films at 40K, excited with 501 nm where both MEH-PPV and PtOEP absorb. The PIA spectra of PtOEP blended MEH-PPV films at 40K were spectrally same as that of pristine MEH-PPV (900 nm), indicating the same excited species, triplet state of MEH-PPV, is responsible in each case. In the blend, strength of the T_1-T_n absorption of MEH-PPV triplet is increased when the PtOEP doping concentration increases, indicating the presence of an additional population of triplet excitons in the polymer formed by triplet-triplet energy transfer from PtOEP to MEH-PPV or improvement of the intersystem crossing efficiency of MEH-PPV. Figure 1 (d) shows PIA spectra of pristine MEH-PPV and 5% PtOEP blended MEH-PPV films at RT. The PIA spectrum of PtOEP blended MEH-PPV films at RT (840 nm) is spectrally different from pristine MEH-PPV at 40K (900 nm) (No PIA signal of MEH-PPV at RT), which is originated from the polaron between MEH-PPV and PtOEP. The intensity at 840 nm is one order lower than that at 900nm. As a result, we expect PL quenching of MEH-PPV is mainly due to the exciton dissociation between MEH-PPV and PtOEP, not the siglet-singlet or singlet-triplet energy transfer from MEH-PPV to PtOEP.

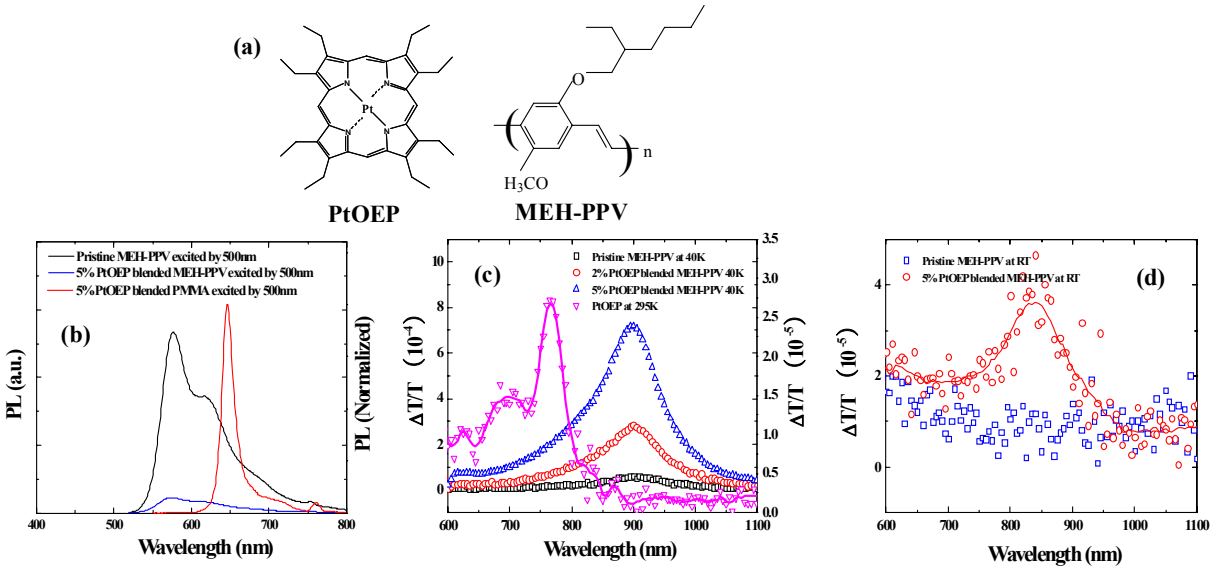

Figure 1. (a) The chemical structure, (b) Photoluminescence spectra of pristine MEH-PPV and 5% PtOEP blended MEH-PPV film, (c) PIA spectra of pristine MEH-PPV and PtOEP blended MEH-PPV film at 40K, excited by 501nm, (d) PIA spectra of pristine MEH-PPV and 5% PtOEP blended MEH-PPV film at RT, excited by 501nm.