

Triplet-excited State Fusion as a Tool to Photostimulate Vertically-configured Organic Photodetectors

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Photon energy up-conversion via triplet-triplet annihilation (TTA-UC) is a particularly attractive wavelength-shifting tool to enable photoactuation *i.e.* the sensitization of organic solar cells (OSCs) or the photo-stimulation of optogenetic platforms. Essentially, TTA-UC refers to the photophysical process where the energy level of an emissive excited state is prepared by the synergetic effects of lower energy photons via triplet-triplet annihilation photochemical reactions. The TTA-UC phenomenon occurs in multicomponent systems comprising a triplet-excited sensitizer mixed with a ground state activator. Typical activators include a large set of acene-based aromatic hydrocarbons and π -conjugated polymers, whereas the sensitizers are organic phosphorescent dyes with long-lived triplet excited states, *e.g.* transition-metal-containing complexes. Encouraging results have been presented recently on the photoluminescence quantum yield (PLQY) of the archetypical TTA-UC system of the 9,10 di-phenyl anthracene (DPA) emitter mixed with the (2,3,7,8,12,13,17,18-octaethyl-porphyrinato) platinum^{II} (PtOEP) metallorganic sensitizer; a green-to-blue PLQY_{TTA-UC} as high as 8% was reported for solution-processable solid-state DPA:PtOEP films [1]. Nevertheless, the binary nature of the DPA:PtOEP composite film introduces severe implications in terms of device engineering aspects, and the incorporation of the DPA:PtOEP up-converting interlayers in OSC devices with vertically-stacked geometries is hard to achieve.

Herein we present a simple methodology for incorporating a photon absorbing layer of the PtOEP sensitizer, as a self-TTA annihilator medium in a vertically stacked photodiode device structure. The participation of the fusion process in the mechanism of charge photogeneration manifests in the supralinear dependence of the short-circuit current density on the incoming photoexcitation intensity [2]. At low-power illumination, the PtOEP photodiode exhibits photocurrent generation via the fusion of optically-induced PtOEP excited states and it develops an open-circuit voltage as high as 1.15 V. The structural and spectroscopic characterization of the nanostructured PtOEP photoactive layer in combination with electronic structure calculations identify PtOEP dimer species as the annihilating excited state responsible for the formation of charges. Building on this insight, the PtOEP annihilator is further utilized for stimulating the response of UV-only organic photodetector with visible light. These findings propose that triplet-excited annihilator species are valuable photoactive components to be deployed in smart light-management applications.

References

- [1] S. Raišys, S. Juršenai, K. Kazlauskas, Sol. RRL **6**, 2100873, (2022).
- [2] G. Antoniou, P. Yuan, L. Koutsokeras, S. Athanasopoulos, D. Fazzi, J. Panidi, D. G. Georgiadou, T. Prodromakis, P. E. Keivanidis, J. Mater. Chem. C, **10**, 7575, (2022).

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