STATISTICAL PROBABILITY OF SINGLET EXCITON GENERATION THROUGH TRIPLET-TRIPLET ANNIHILATION IN TES-ADT ANNIHILATOR

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Triplet-triplet annihilation mediated photon upconversion (UC) is a process used to increase the energy of incoherent photons. This phenomenon could be applied in various fields, such as targeted drug delivery, bioimaging, photovoltaics and many others [1]. Each UC system is composed of at least two types of molecules: a sensitizer and an annihilator. The sensitizer is responsible for light absorption, triplet state generation through intersystem crossing (ISC) and triplet energy transfer (TET) to the annihilator. Meanwhile, the annihilator molecules undergo triplet-triplet annihilation (TTA), resulting in the formation of an emissive singlet state. The TTA process can produce quantum states with different multiplicities, however only the singlet ($M = 1$) is beneficial for photon upconversion. Hence, one of the most important parameters of an annihilator is a probability that TTA results in a singlet state, known as the statistical probability factor (f). f value directly impacts the UC quantum yield (Φ_{UC}) and is viewed as a limiting factor in many NIR-to-Vis UC systems. Recent studies show that the f values of many annihilators used in NIR-to-Vis upconversion (e.g., rubrene, diketopyrrolopyrrole derivatives) rarely exceed 20% [2,3]. Therefore, it is crucial to search for new annihilators with higher statistical factor values. The aim of this work is to thoroughly study the f factor of a 5,11-bis(triethylsilylethynyl)anthradithiophene (TES-ADT) annihilator, which could be used in various UC systems.

To evaluate statistical probability factor of the TES-ADT annihiliator, it was paired with a metal-organic palladium phthalocyanine (PdPc) sensitizer. UC solutions in toluene with varying annihilator concentrations, as well as solid state samples, were prepared for this study. After determining the Φ_{UC} and other necessary parameters (TET, TTA and fluorescence quantum yields), the f factor values for each sample were calculated. The results indicate a notable trend: the f value tends to increase with the concentration of the annihilator in UC solutions, reaching up to 84% (Fig. 1 b). Moreover, the statistical factor value is also high in solid-state samples ($f \approx 60\%$). The increasing trend in the statistical probability factor could be attributed to the formation of dimers or larger aggregates, favouring the singlet state generation through TTA. In this work, aspects related to molecular geometry and energy levels are considered to explain the observed tendencies. The obtained results may be useful in the development of novel annihilators for photon upconversion.

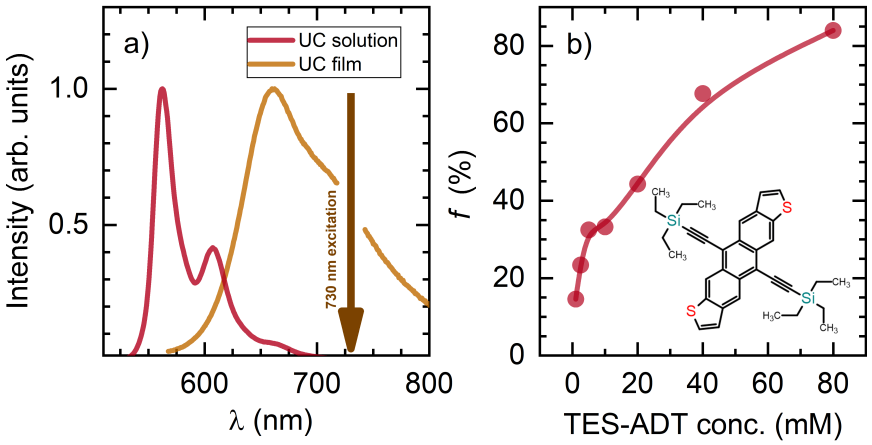

Fig. 1. a) Corrected emission spectra of the UC solution in toluene (1 mM TES-ADT, 15 μM PdPc) and UC film. b) Statistical probability factor f of UC solutions with increasing TES-ADT concentration (c_{PdPc} = 15 μM).

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