

Lanthanide nanoparticles ignite dark molecular triplets

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Molecular triplets have attracted great interest across multidisciplinary fields of the research ranging from thermally activated delayed fluorescence [1], triplet-triplet annihilation (TTA) upconversion [2], to photodynamic therapy relying on TTA between triplet photosensitizers and surrounding triplet oxygen to generate singlet oxygen species [3]. Molecular triplets are normally ‘dark states’ because of the spin-forbidden nature of direct optical transition from a singlet ground state (S_0) to a triplet excited state (T_1). To circumvent this limitation, triplet dynamics are conventionally controlled *via* the heavy atom effect to enhance intersystem crossing from the singlet to the triplet excited state ($S_n \rightarrow T_n$) [4], or *via* highest occupied molecular orbital-lowest unoccupied molecular orbital engineering to tune the gap between excited singlet and triplet states. However, it remains challenging to break the spin-forbidden rule for accomplishing the direct optical transition from S_0 to T_1 .

Very recently, Han and coworkers [5] have developed a novel approach to control the optical properties of molecular triplets by coupling small molecules to lanthanide nanoparticles (Figure 1(a)). Benefiting from such coupling, direct optical transition from S_0 to T_1 of the molecule occurred. As presented in Figure 1(b), an approximately 200-fold enhancement was observed in the near-infrared (NIR, 700–1,100 nm) absorbance of the NaGdF₄-rubrene blend film compared with the pristine rubrene film. It was found that the enhanced absorption in the NIR region matches well with the calculated triplet levels of an isolated rubrene mo-

lecule (inset of Figure 1(b)). The authors hypothesized that the enhanced triplet absorption could be related to the short-range spin-exchange interaction between the lanthanide ions with unpaired 4f electrons and the coupled molecules. This is supported by the calculations based on density functional theory and the multireference second-order Møller-Plesset perturbation theory. To further experimentally validate their hypothesis, the authors prepared blend films of rubrene with different types of lanthanide nanoparticles, including NaGdF₄, NaYF₄ and NaLuF₄. The enhancement in triplet absorption was observed only in the NaGdF₄-rubrene blend film with seven unpaired 4f electrons of Gd³⁺, while no NIR absorption features could be observed for the Y³⁺- and Lu³⁺-based blend films (Figure 1(b)).

Inspired by the remarkably enhanced absorption of the NaGdF₄-rubrene blend film in the NIR region, the authors carried out excitation toward the NaGdF₄:Yb³⁺-rubrene (or tetracene) hybrid systems in the spectral region of 850–1,020 nm, and observed upconversion emission at all excitation wavelengths. Furthermore, they prepared a series of NaGdF₄:Yb³⁺-tetracene blend films with varying concentration ratios of tetracene to NaGdF₄:Yb³⁺. Intriguingly, an emission characteristic of a single tetracene molecule was obtained when the concentration of tetracene was diluted to 1 molecule per 100 NaGdF₄:Yb³⁺ nanoparticles (Figure 1(c)). In comparison with the conventional lanthanide or TTA-based upconversion, the authors deduced that the lanthanide (Yb³⁺)-triplet excitation fusion (LTF) mechanism accounts for the upconversion process in the NaGdF₄:Yb³⁺-tetracene hybrid systems (Figure 1(d)). In comparison with conven-

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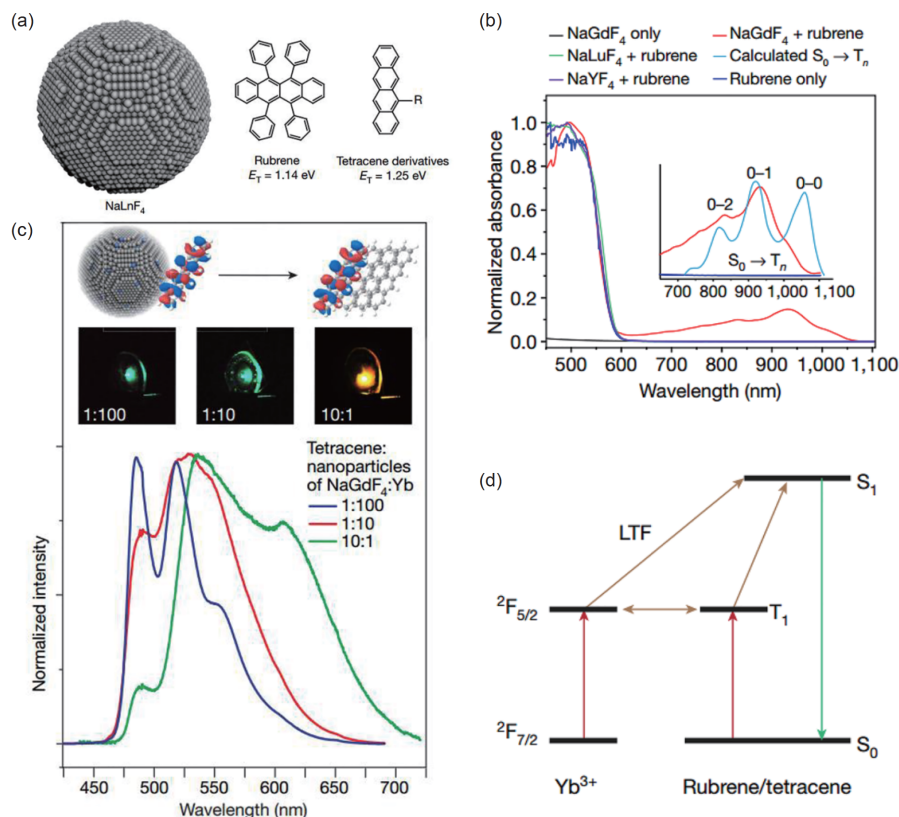


Figure 1 (a) Schematic illustration of a single lanthanide nanoparticle and the organic molecules in this work. (b) Comparison of the photothermal deflection spectroscopy of films of NaGdF₄-rubrene, NaLuF₄-rubrene, NaYF₄-rubrene with pristine rubrene and with NaGdF₄ only. Inset: the calculated absorption spectrum denoting the direct transition from S₀ to T_n. (c) Top: scheme representing the isolated molecule (left) and molecular conjugates (right) when tetracene couples with the NaGdF₄:Yb³⁺ nanoparticles. Note that grey and blue spheres in the nanoparticle refer to Gd³⁺ and Yb³⁺ ions, respectively. Bottom: upconversion spectra and corresponding emission photographs (middle) of NaGdF₄:Yb³⁺-tetracene blend films with varying tetracene-to-nanoparticle ratios (1:100, 1:10 and 10:1). (d) Proposed lanthanide-LTF upconversion mechanism [5] (color online).

tional lanthanide- or TTA-based upconversion, the authors demonstrated that LTF process can largely reduce photon energy loss and yield significantly higher upconversion efficiency.

Despite a huge step forward that has been achieved by this work, there is still plenty of room to make further progress on the triplet control by optimizing the geometry of the inorganic-organic interface between lanthanide nanoparticles and molecules. Further theoretical work is also required to understand the nature of the spin-exchange interaction between the lanthanide ions with unpaired 4f electrons and the coupled molecules. Considering the effective optical harvesting of molecular triplets based on lanthanide nanoparticle-molecule coupling, the outreach of this strategy in multidisciplinary research fields such as triplet energy

transfer, photon upconversion, and biomedicine therapeutics will be anticipated.

Conflict of interest The authors declare no conflict of interest.

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