

Cite this: *J. Mater. Chem. C*,
2024, 12, 18572

Photon upconversion materials collection

Eva Hemmer,^a Nobuo Kimizuka,^b Łukasz Marciniak,^c Lea Nienhaus^d
and Timothy Schmidt^e

DOI: 10.1039/d4tc90183e

rsc.li/materials-c

Photon upconversion generally describes the conversion of low energy photons into higher energy photons, as a result of multi-photon processes, leading to an apparent anti-Stokes shift of the emission. Although the upconversion process has been known for decades, the recent surge in research, as highlighted by this themed collection, has not only enabled a deeper understanding and quantitative

description of the underlying processes but also, more importantly, facilitated its intentional and diverse applications in sensing, imaging and optical device design. This collection covers the different classes of materials capable of undergoing upconversion through different mechanisms. Despite their distinct differences, the similarities are important to highlight – enabling a connection between the fields may be able spark future research directions.

The first avenue to achieve photon upconversion is triplet-triplet annihilation (TTA), a process in which two spin-triplets generate a higher energy spin-singlet in a spin-allowed process. While TTA was first reported over 50 years ago by Parker and Hatchard,¹ the field of sensitized photon upconversion emerged in the early 2000s following seminal work

by Koslov and Castellano.² Since the energy is essentially stored in the long-lived triplet states during TTA, one benefit of this process is that it can become efficient at low power densities. As a result, it may be a pathway toward increasing the power conversion efficiency of conventional photovoltaics by unlocking the sub-bandgap photons which are otherwise not able to be utilized. Despite its promise, there are several hurdles that must be overcome prior to successful integration. More efficient devices must be fabricated; for this, new annihilators must be identified, or the efficiency of existing systems increased. In addition, devices must be fully encapsulated to ensure the absence of oxygen, a triplet quencher. By adding the encapsulation directly to the upconversion system, additional processing steps can be

^a Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie-Curie Street, Ottawa, ON, K1N 6N5, Canada

^b Department of Applied Chemistry, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka, 819-0395, Japan

^c Institute of Low Temperature and Structure Research, Polish Academy of Science, Wroclaw, Poland

^d Department of Chemistry, Rice University, 6100 Main Street, Houston, TX 77005, USA

^e School of Chemistry, UNSW Sydney, NSW 2052, Australia



Eva Hemmer



Nobuo Kimizuka

avoided, possibly resulting in lower device costs.

To identify novel annihilators, the criterion is that the energy of the singlet state must be equal to or lower than twice the energy of the triplet state: $E(S_1) \leq 2E(T_1)$. In addition, it is beneficial that the second triplet excited state T_2 is not accessed during the TTA process. Experimentally determining the triplet energy is an intensive process, hence, the ability to accurately computationally screen triplet energies would be beneficial, as demonstrated by Schmidt and coworkers (<https://doi.org/10.1039/d4tc02241f>) in this themed collection.

In addition to leveraging molecular diffusion in solution, supramolecular strategies that integrate molecular self-assembly and triplet exciton migration hold promise for developing green TTA systems that eliminate the use of organic solvents and are less sensitive to dissolved oxygen in aqueous systems or solid materials. One such approach is

demonstrated by Evans *et al.* (<https://doi.org/10.1039/d4tc00562g>), who employed hybrid organic–inorganic ureasil polymers as the host matrix for TTA which simultaneously acts as an oxygen barrier – enabling upconversion without additional encapsulation requirements.

Upconverting inorganic (nano)materials excel due to their optical properties and corresponding versatile applications that range from optical devices to imaging probes and thermal sensors. This themed collection showcases contributions related to lanthanide-based phosphors, highlighting recent advances from materials design to multimodality and enhanced sensing capabilities. For instance, Lei *et al.* (<https://doi.org/10.1039/D4TC00859F>) designed an upconverting phosphor by triple doping with Ho^{3+} , Er^{3+} , and Yb^{3+} , thereby leveraging the absorbance of the Er^{3+} ion at 1550 nm for excitation. The resultant high color purity luminescent material

has potential for application in the field of display lighting.

The enhancement of lanthanide upconversion is still a major goal and challenge to be addressed by researchers in the field: several of the works in this collection propose strategies to significantly enhance photon upconversion. These include the decoration of a single polystyrene microsphere with upconverting nanoparticles and its location on the center of the annular near-field, boosting the upconversion emission (Wu *et al.*, <https://doi.org/10.1039/D4TC01063A>). Other strategies employ phosphors with negative thermal expansion, such as $\text{Y}_2\text{Mo}_3\text{O}_{12}:\text{Nd}^{3+}, \text{Yb}^{3+}$ (Zhang *et al.*, <https://doi.org/10.1039/D4TC01352B>) or $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Er}^{3+}/\text{Yb}^{3+}$ (Wang *et al.*, <https://doi.org/10.1039/D4TC01673D>), for thermally enhanced near-infrared upconversion fluorescence. Careful materials design is another route when seeking optimization of the optical properties of lanthanide-based phosphors. In this vein, the structure of $\text{GdLaO}_3:\text{Er}^{3+}/\text{Yb}^{3+}/\text{Sc}^{3+}$ allows selective cross-relaxation to occur, ultimately improving the efficiency of energy transfer and, thus, leading to strong red upconversion emission (Li *et al.*, <https://doi.org/10.1039/D4TC01015A>). Thermal sensing using the upconversion emission of lanthanide-based phosphors is one of the avenues these materials might take when it comes to their applications. Hence, interestingly, the above-mentioned materials not only exhibit enhanced upconversion emission but are also promising candidates for



Lukasz Marciniak



Lea Nienhaus



Timothy Schmidt

application in luminescent thermometry. While thermometry based on the luminescence intensity ratio of two emission bands is undoubtedly the most common approach in current lanthanide-based thermometry, lifetime-based thermometers are on the constant rise. In their contribution, Gállico and Murugesu provide new insights into the molecular world of lifetime-based thermometry (<https://doi.org/10.1039/D4TC03204G>).

Last but not least, lanthanide-based phosphors are excellent candidates when it comes to the exploration

of multimodality. For instance, switching of the wavelength of the near-infrared excitation source allows for selective bioimaging or therapy (Jiang *et al.*, <https://doi.org/10.1039/D4TC01535E>), while the combination of upconverting nanoparticles with magnetic FeS₂ opens the door to novel opto-magnetic applications (Runowski *et al.*, <https://doi.org/10.1039/D4TC01117A>).

This themed collection of contributions related to upconversion provides a snapshot of the diverse strategies to boost performance and to leverage application

potential. Control over molecular and material structure provides improved performance and increased understanding of underlying processes. With this, we foresee a bright future for the field of upconverting phosphors, from TTA to upconversion and from molecules to inorganic materials.

References

- 1 C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc., London*, 1962, 386.
- 2 D. V. Kozlov and F. N. Castellano, *Chem. Commun.*, 2004, 2860–2861.