THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCC Article

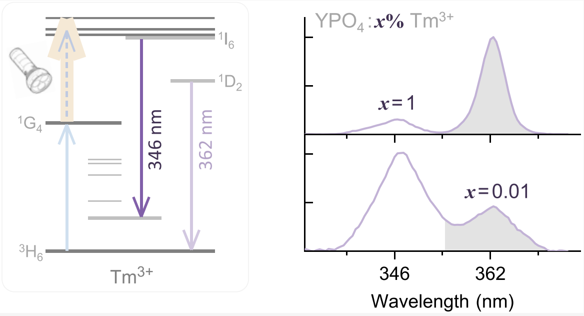
Extended Excitation Approach for Ultraviolet Phosphors via the White-to-Ultraviolet Upconversion

Chengrui Wang, Feng Liu,* Hao Wu, Liangliang Zhang, Jiahua Zhang, Xiao-jun Wang, and Yichun Liu

Cite This: *J. Phys. Chem. C* 2023, 127, 18213−18218 **Read Online**

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: The development of ultraviolet light-emitting materials is attracting increased attention due to their important applications in many technological fields involving light mediated treatment and disinfection. Despite progress, further advancements in these materials have been hindered by the limited availability of excitation light sources. In this work, we utilize a convenient white flashlight as an excitation source to explore the upconverted emission performance of a series of ultraviolet phosphors, involving Tm^{3+}, Er^{3+}, Ho^{3+}, Nd^{3+}, or Pr^{3+} ion activated systems. As an illustration, we demonstrate that a Tm^{3+}-doped yttrium phosphate ($YPO_4:Tm^{3+}$) exhibits ultraviolet emissions peaking at 289, 346, and 362 nm upon exposure to the flashlight. Spectroscopic investigations reveal that both energy-transfer upconversion and excited-state absorption schemes contribute to the excitation. Considering the widespread use of flashlights, white-light excitability presents a promising avenue for broadening the scope of functional ultraviolet phosphors.



■ INTRODUCTION

In developing upconverting phosphors, the vast majority of studies are focusing on visible or infrared emissions,[1−4] which exhibit fundamental and practical perspectives in many fields, such as anticounterfeiting, bioimaging, theragnostics, and temperature sensing.[5−12] In contrast, there is a relative lack of research on the shorter-wavelength ultraviolet emission.[13−17] Considering the important applications of ultraviolet light in various technological fields that involve light-mediated treatment and disinfection,[18,19] upconverting ultraviolet phosphors holds great promise.

Recently, there is increasing attention paid to the development of upconverting ultraviolet phosphors, in which the excitation is generally achieved by sequentially absorbing multiple infrared photons.[20−26] For instance, when illuminated with a 980 nm laser at a very large excitation power density (e.g., tens of W cm^{-2}), ultraviolet emissions have been achieved in $Yb^{3+}-Tm^{3+}$ or $Yb^{3+}-Ho^{3+}$ codoped material systems, in which four or five photons are involved in the excitation process.[20−22] Moreover, the introduction of Gd^{3+} to the $Yb^{3+}-Tm^{3+}$ or $Yb^{3+}-Ho^{3+}$ codoped materials can generate additional ultraviolet emission from the Gd^{3+} ion through nonlinear excitation,[23−26] which is crucial for the development of compact ultraviolet devices. Despite the progress made, it is preferable for practical applications that the upconverting ultraviolet phosphors can be easily excited with a relatively low excitation power. Therefore, a visible-to-ultraviolet upconversion scheme involving two-photon excitation is highly anticipated.

Among the various upconverting ions, Tm^{3+}, Er^{3+}, Ho^{3+}, Nd^{3+}, and Pr^{3+} ions are considered as candidate activators in phosphors to achieve visible-to-ultraviolet upconversion luminescence because of their ladder-like energy levels in the visible region, as well as their emitting levels in the ultraviolet.[27−31] The reported ultraviolet phosphors that can be excited by visible lasers include $LaF_3:Tm^{3+}$, $NaYF_4:Tm^{3+}$, $CsMgCl_3:Er^{3+}$, $BaGd_2ZnO_5:Er^{3+}$, $Y_2O_3:Ho^{3+},Gd^{3+}$, $Y_2SiO_5:Pr^{3+}$, $BaGd_2ZnO_5:Pr^{3+}$, $YBO_3:Pr^{3+}$, and $Li_2CaGeO_4:Pr^{3+}$.[27−36] Besides the excitations with monochromatic light, the energy-level schemes of these activators in phosphors also suggest that the upconversion processes may also occur when excited by white light. Therefore, an incoherent white light source such as a flashlight is preferred to excite upconverting ultraviolet phosphors, as the flashlight is more accessible and less hazardous than lasers.

In this work, we investigate the upconverted excitability of ultraviolet phosphors by using a convenient white flashlight as an excitation source. We center our discussion on a Tm^{3+}-doped yttrium phosphate ($YPO_4:Tm^{3+}$) among a series of ultraviolet phosphors that we developed. Our measurements confirm that the material produces upconverted ultraviolet

Received: July 11, 2023
Revised: August 14, 2023
Published: September 6, 2023

https://doi.org/10.1021/acs.jpcc.3c04664
J. Phys. Chem. C 2023, 127, 18213−18218

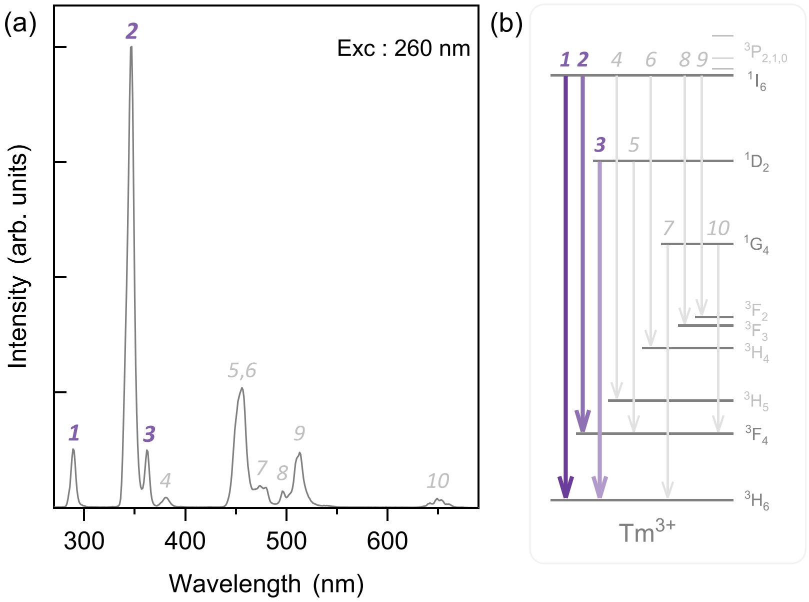


Figure 1. (a) Emission spectrum of the $YPO_4:Tm^{3+}$ phosphor under 260 nm excitation. (b) Assignment of the emission transitions. The labeled peaks in part a correspond to the assigned transitions in part b.

luminescence when exposed to a white flashlight. Subsequently, we investigate the excitation mechanism behind the white-light excitability and reveal the existence of energy-transfer upconversion and excited-state absorption processes during the excitation. Besides the ultraviolet emission from the Tm^{3+} ion, we extend the upconverted emission wavelength by introducing Gd^{3+} ion into the $YPO_4:Tm^{3+}$ combination. The white-light excitability as well as the extended ultraviolet emissions may serve as a conceptual optical tagging for object identification in ambient lighting.

METHODS

All of the phosphor compositions were made by a routinely used solid-state synthesis method. For the Tm^{3+}-doped YPO_4 phosphor material, the starting materials Y_2O_3, $(NH_4)_2HPO_4$ (50% excess) and Tm_2O_3 were blended and finely ground. The mixture was then calcined for 1 h at 800 °C. After an additional grinding process, the mixture was pressed into a disk shape and sintered for another hour at 1300 °C to produce a sample suitable for spectral measurement. Here we have concentrated on the $YPO_4:1\%Tm^{3+}$ formula (hereafter referred to as $YPO_4:Tm^{3+}$, unless stated otherwise). Apart from the phosphate, other phosphors, involving $LaMgGa_{11}O_{19}:Er^{3+}$, $NaYF_4:Ho^{3+}$, $YF_3:Nd^{3+}$ and $Lu_2SiO_5:Pr^{3+}$ were prepared by mixing and grinding the raw chemicals according to a specific stoichiometry and were sintered at 1400 °C (for gallate), 600 °C (for fluorides), and 1450 °C (for silicate), respectively.

All of the emission spectra were measured using the PTI QuantaMaster spectrofluorometer (model 8075−11) at room temperature. The excitation light sources included a filtered xenon lamp, a 473 nm laser, a 589 nm laser, and a commercial white flashlight (Ledlenser, MT18). When the flashlight was used for measurement, the phosphor was illuminated with a continuous light beam. Ultraviolet emissions from the phosphors were collected by utilizing an ultraviolet bandpass filter (Asahi Spectra USA, XUV0400-SP), which allowed the ultraviolet light between 245−400 nm to pass through. The ultraviolet image of the phosphor was captured using an ultraviolet-B camera (OFIL, Scalar), which had sensitivity in the range of 310−320 nm. To present the image, a red, false color highlighted ultraviolet image was overlaid onto a true color image.

RESULTS AND DISCUSSION

Achievement of Visible-to-Ultraviolet Upconversion Luminescence. To learn the luminescence performance and emission character of the $YPO_4:Tm^{3+}$ phosphor, we first measured its conventional photoluminescence emission spectrum. Figure 1a shows that under 260 nm excitation (Tm^{3+} $^3H_6 \rightarrow {}^3P_2$ transition), the phosphor exhibits sharp-line emission covering the ultraviolet and visible regions. In the ultraviolet range, three distinct emission peaks with maxima at 289, 346, and 362 nm are identified and assigned to the $4f^{12} \rightarrow 4f^{12}$ inner-configurational transitions from the $^1I_6$ level ($^1I_6 \rightarrow {}^3H_6$ transition peaking at 289 nm and $^1I_6 \rightarrow {}^3F_4$ at 346 nm) and the $^1D_2$ level ($^1D_2 \rightarrow {}^3H_6$ at 362 nm), respectively, as illustrated in Figure 1b.

Besides the conventional downshifting luminescence, the upconversion luminescence of the $YPO_4:Tm^{3+}$ phosphor under excitation with a monochromatic visible laser has also been examined. Under 473 nm laser excitation (power density, 3 W cm^{-2}), the phosphor exhibits ultraviolet emission peaking at 289, 346, and 362 nm, as shown in the emission spectrum of Figure 2a. Villanueva-Delgado et al. have attributed the excitation mechanism of the 362 nm emission ($^1D_2 \rightarrow {}^3H_4$ transition) in the $NaYF_4:Tm^{3+}$ material system to an energy-transfer upconversion scheme.[32] However, for the emissions at 289 and 346 nm from the $^1I_6$ level, it appears that the $^1I_6$ emitting level is also populated through an energy-transfer upconversion excitation. This is because there is no pathway for excited-state absorption when only excited by 473 nm. Please note that the energy difference between $^1G_4$ and ^3P_J is not in resonance with the wavelength of 473 nm. In addition to the direct argument, the energy-transfer upconversion can also be confirmed by a decay measurement shown in Figure S1. To illustrate this, let us consider the 346 nm emission ($^1I_6 \rightarrow {}^3F_4$ transition) displayed on the right-hand side of Figure 2a, where an energy-transfer upconversion scheme is proposed to explain

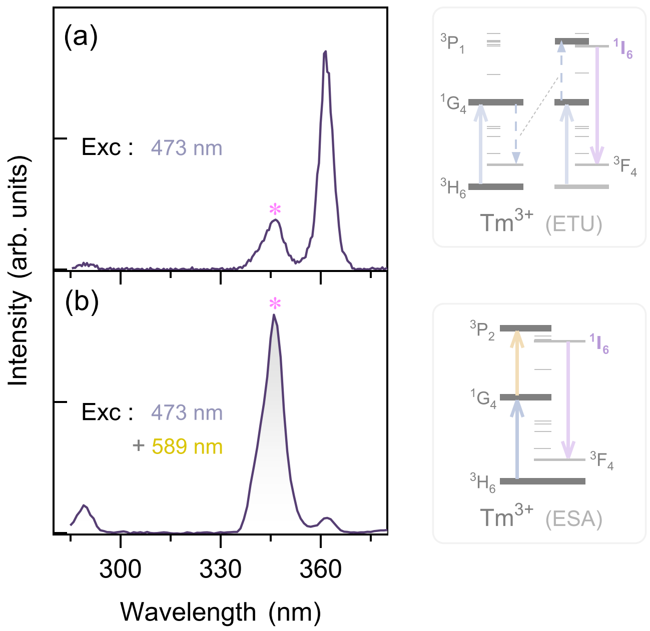


Figure 2. (a) Upconversion luminescence of the YPO$_4$:Tm^{3+} phosphor under 473 nm excitation (3 W cm^{-2}). On the left-hand side, the emission spectrum is shown. On the right, a schematic illustration of the energy-transfer upconversion (ETU) process responsible for the 346 nm emission is provided. (b) Upconversion luminescence of the phosphor upon exposure to combined excitation with a 473 nm laser (1 W cm^{-2}) and a 589 nm laser (2 W cm^{-2}). The emission spectrum is shown on the left-hand side, while the right-hand side illustrates a schematic illustration of the excited-state absorption (ESA) process responsible for the 346 nm emission.

the excitation mechanism. Even so, upon exposure of the phosphor to other excitation light sources, it cannot be excluded that excited-state absorption is responsible for the excitation of the 346 nm emission.

Subsequently, to confirm the presence of excited-state absorption in the excitation of the $^1I_6$ level, we utilized a combined excitation with two lasers, a 473 nm laser (1 W cm^{-2}) and a 589 nm laser (2 W cm^{-2}), to illuminate the YPO$_4$:Tm^{3+} phosphor. It is important to note that while the 589 nm wavelength is out of resonance with the ground-state absorption transition of Tm^{3+}, it may resonate with the Tm^{3+} $^1D_2 \rightarrow$ $^3P_2$ transition. In our measurement, we maintained a relatively low output power density of the 473 nm laser (i.e., 1 W cm^{-2}), which is close to the threshold for nonlinear excitation of the phosphor. As shown in Figure S2, the phosphor exhibits a barely detectable intensity upon the low-power 473 nm excitation alone, but the emission intensity is remarkably enhanced under the combined excitation (473 and 589 nm lasers), indicating a two-step excitation based on the excited-state absorption scheme. Figure 2b gives the emission spectrum of the phosphor as well as a schematic illustration of the upconversion upon the combined excitation. Consequently, our experiment provides evidence that, in addition to an energy-transfer upconversion scheme, excited-state absorption plays a role in the population of the $^1I_6$ emitting level.

Nonlinear Excitation upon Illumination with the Flashlight. According to the energy-level scheme of Tm^{3+} in phosphors, as well as the spectral feature of the incoherent white light source, the upconversion process upon illumination with a white flashlight is predictable. Subsequently, we experimentally testify the upconversion of YPO$_4$:Tm^{3+} phosphor using a powerful white flashlight (1.37 W cm^{-2}) as the excitation source, whose spectral composition has been presented in Figure S3. By measuring the dependence of the upconverted emission intensity on the power of the flashlight, as illustrated in Figure S4, we confirm a two-step excitation process. To testify the contribution of energy-transfer upconversion or excited-state absorption, we prepare YPO$_4$:Tm^{3+} samples with varying Tm^{3+} content x, ranging from 0.01 to 5 (where x is defined as YPO$_4$:x%Tm^{3+}). Upon excitation by the flashlight, these phosphors exhibit ultraviolet emissions from the $^1I_6$ and $^1D_2$ levels, respectively.

Figure 3a shows that the 346 nm emission intensity reaches its maximum when x equals 1 and then declines with a higher Tm^{3+} content due to concentration quenching. Figure 3b plots the intensity ratio between the 346 and 362 nm peaks as a function of the Tm^{3+} concentration, showing that the ratio decreases at a high concentration of Tm^{3+}. This suggests that different upconversion schemes may be involved in the excitations of the ultraviolet emission depending on the Tm^{3+} concentrations. Notably, although the intensity ratio is

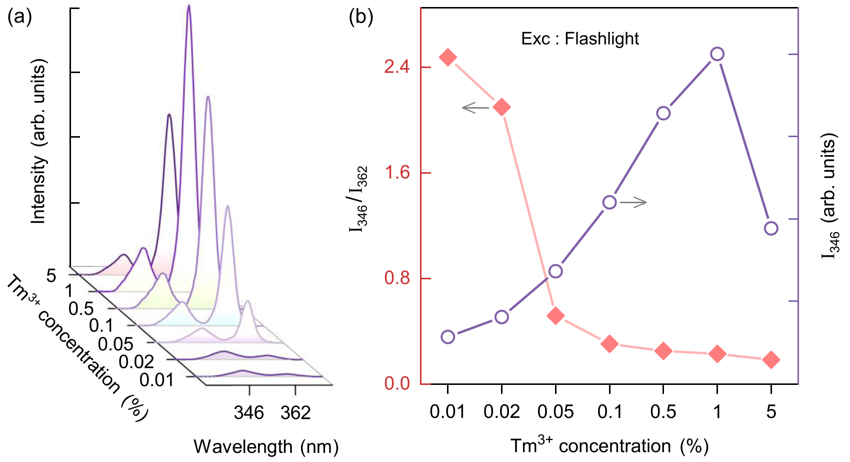


Figure 3. (a) Upconverted emission spectra of YPO$_4$:x%Tm^{3+} (x = 0.01−5) recorded upon illumination with a high-power white flashlight (1.37 W cm^{-2}). (b) Dopant concentration dependence of the emission intensity ratios between the 346 and 362 nm peaks. The 346 nm emission intensities are also presented as a function of the Tm^{3+} concentration.

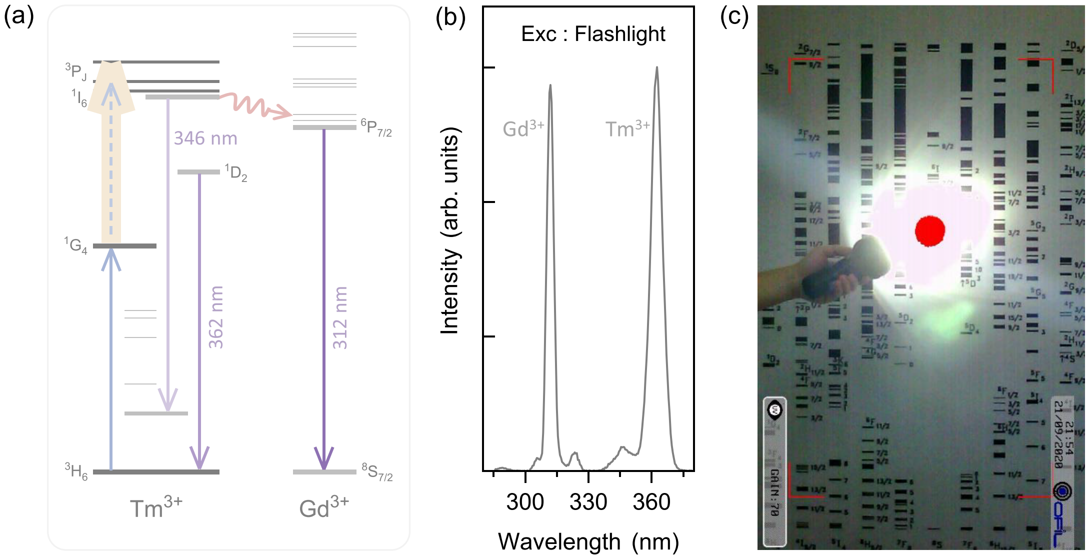


Figure 4. (a) Schematic illustration of upconversion luminescence in the $Y_{0.4}Gd_{0.6}PO_4:Tm^{3+}$ phosphor when illuminated by a white flashlight. (b) Upconverted emission spectrum of the phosphor, which is exposed to a powerful white flashlight with an intensity of 1.37 W cm^{-2}. (c) Ultraviolet imaging of the phosphor under excitation with the flashlight using an OFIL Scalar camera. In the picture, the ultraviolet-B signal is highlighted through a red false color overlay.

relatively high in the diluted Tm^{3+} system (e.g., $x < 0.05$), the absolute intensity of the 346 nm ultraviolet peak is low in compositions like these. The increase in emission intensity, as shown in Figure 3b, with dopant concentration implies that the effect of cross-relaxation on the population of the $^1I_6$ level can be ruled out. Such an evolution of emission intensity is quite understandable since the excitation is less efficient via excited-state absorption in diluted Tm^{3+} compositions compared to an energy-transfer upconversion scheme at high Tm^{3+} concentration. As a consequence, one can deduce that both energy-transfer upconversion and excited-state absorption are involved in the excitation of the ultraviolet emission in $YPO_4:Tm^{3+}$.

Extension of the Ultraviolet Emission Wavelengths. Besides the ultraviolet emission from Tm^{3+}, the upconverted emission can also be extended to other wavelengths by introducing the Gd^{3+} ion into the $YPO_4:Tm^{3+}$ system. According to the energy-level schemes of lanthanide ions, Tm^{3+} has an emitting level that is nearly resonant with the excited level of Gd^{3+}.[23] This means that after excitation into the Tm^{3+} $^3P_J/^1I_6$ levels via the upconversion an energy transfer from the Tm^{3+} $^1I_6$ to the excited level of Gd^{3+} is possible, followed by an ultraviolet emission from the $^6P_{7/2}$ of Gd^{3+} (see Figure 4a). The assumed energy transfer and the associated ultraviolet emission have been experimentally verified in $Y_{1-z}Gd_zPO_4:Tm^{3+}$ (z = 0.2, 0.4, 0.6, 0.8, 1) phosphors upon exposure to the high-power flashlight (Figure S5). As an example, Figure 4b gives the upconverted emission spectrum of the $Y_{0.4}Gd_{0.6}PO_4:Tm^{3+}$ phosphor composition, which consists of ultraviolet emission peaks at 312 nm (from Gd^{3+}), 346 and 362 nm (from Tm^{3+}). Taking into account the white-light excitability and ultraviolet emission performance of the phosphor, a realization of ultraviolet-B tagging for object identifying in indoor lighting environment is expected. In Figure 4c, we demonstrate the use of an ultraviolet B-tagging patch ($Y_{0.4}Gd_{0.6}PO_4:Tm^{3+}$ composition) in ambient lighting. When exposed to a flashlight, the phosphor surface generates an ultraviolet-B emitting spot, producing clear imaging via an ultraviolet-B camera (OFIL, Scalar). The results described here indicate that the upconverting phosphor, containing Tm^{3+} and Gd^{3+} ions, could function as a new type of optical tag.

The above results fully demonstrate that the Tm^{3+}-activated phosphate phosphors can be excited by white light through white-to-ultraviolet upconversion. To further validate the upconverted excitability of various ultraviolet phosphors, we have developed a series of materials, including $LaMgGa_{11}O_{19}:Er^{3+}$, $NaYF_4:Ho^{3+}$, $YF_3:Nd^{3+}$, and $Lu_2SiO_5:Pr^{3+}$. When these phosphors are excited by a powerful flashlight, they exhibit ultraviolet luminescence. Figure 5 displays the

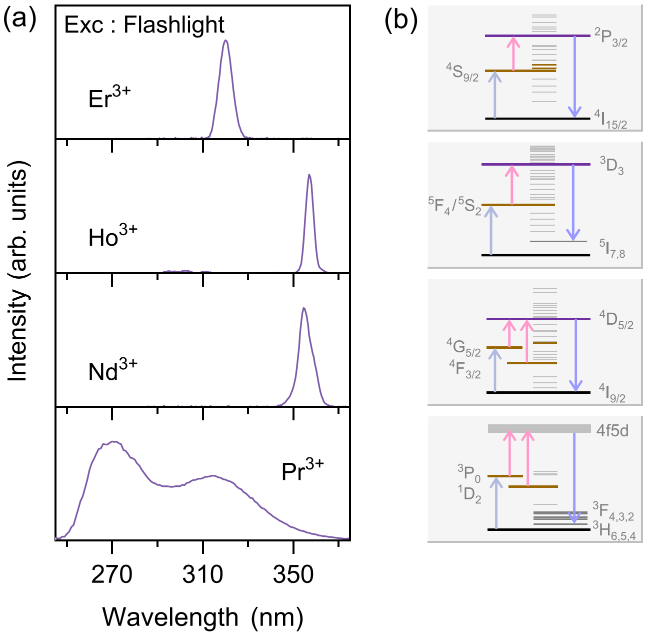


Figure 5. (a) Upconverted emission spectra of $LaMgGa_{11}O_{19}:Er^{3+}$, $NaYF_4:Ho^{3+}$, $YF_3:Nd^{3+}$ and $Lu_2SiO_5:Pr^{3+}$ upon excitation by a flashlight with an intensity of 1.37 W cm^{-2}. (b) Schematic representations of the upconversion luminescence processes.

https://doi.org/10.1021/acs.jpcc.3c04664
J. Phys. Chem. C 2023, 127, 18213−18218

upconverted emission spectra of these phosphors, with the emission maxima at 320, 357, 355, and 270 nm, corresponding to the $4f^{11}(^2P_{3/2}) \rightarrow 4f^{11}(^4I_{15/2})$ transition of Er^{3+}, the $4f^{10}(^3D_3) \rightarrow 4f^{10}(^5I_7)$ transition of Ho^{3+}, the $4f^3(^4D_{5/2}) \rightarrow 4f^3(^4I_{9/2})$ transition of Nd^{3+}, and the $4f5d \rightarrow 4f^2(^3H_4)$ transition of Pr^{3+}, respectively. To evaluate the excitation mechanisms of these phosphors, the spectroscopic approach presented in Figures 2 and 3 may be applicable.

■ CONCLUSIONS

In summary, we have developed a series of ultraviolet phosphors activated by Tm^{3+}, Er^{3+}, Ho^{3+}, Nd^{3+}, or Pr^{3+} ion. These phosphors exhibit white-to-ultraviolet upconversion luminescence when excited with a convenient flashlight. As a proof of concept, we use the $YPO_4:Tm^{3+}$ phosphor to demonstrate the upconverted emission performance when exposed to the flashlight. The $^1I_6$ level of Tm^{3+} in the phosphor is excited by absorbing two visible photons followed by ultraviolet emission. Moreover, by introducing the Gd^{3+} ion into the lattice through an energy transfer design, the emission wavelength of the phosphor can be extended. Consequently, this work provides a novel excitation strategy for achieving multiwavelength ultraviolet emissions, paving the way for broadening the scope of ultraviolet phosphors with upconverted excitability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c04664.

> "(1) Decay curve, (2) upconverted emission upon excited-state absorption, (3) output spectrum of the flashlight, (4) I-P plot upon flashlight illumination, and (5) upconverted emission of $Tm^{3+}-Gd^{3+}$ codoped phosphors (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Feng Liu − *Key Laboratory for UV-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China;* orcid.org/0000-0002-7310-8763; Email: fengliu@nenu.edu.cn

Authors

Chengrui Wang − *Key Laboratory for UV-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China*

Hao Wu − *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China;* orcid.org/0000-0002-8396-7393

Liangliang Zhang − *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China;* orcid.org/0000-0002-9546-8786

Jiahua Zhang − *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China;* orcid.org/0000-0001-5180-7267

Xiao-jun Wang − *Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, United States;* orcid.org/0000-0003-1506-0762

Yichun Liu − *Key Laboratory for UV-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.3c04664

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (11774046, 12074373, 52072361, 51732003) and the Department of Science and Technology of Jilin Province (20230101012JC).

■ REFERENCES

(1) Downing, E.; Hesselink, L.; Ralston, J.; Macfarlane, R. A three-color, solid-state, three-dimensional display. *Science* **1996**, *273*, 1185−1189.

(2) Wang, F.; Deng, R. R.; Wang, J.; Wang, Q. X.; Han, Y.; Zhu, H. M.; Chen, X. Y.; Liu, X. G. Tuning upconversion through energy migration in core-shell nanoparticles. *Nat. Mater.* **2011**, *10*, 968−973.

(3) Haase, M.; Schäfer, H. Upconverting nanoparticles. *Angew. Chem., Int. Ed.* **2011**, *50*, 5808−5829.

(4) Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F. Y. Upconversion luminescent materials: advances and applications. *Chem. Rev.* **2015**, *115*, 395−465.

(5) Yao, W. J.; Tian, Q. Y.; Wu, W. Tunable emissions of upconversion fluorescence for security applications. *Adv. Opt. Mater.* **2019**, *7*, No. 1801171.

(6) Ren, W.; Lin, G. G.; Clarke, C.; Zhou, J. J.; Jin, D. Y. Optical nanomaterials and enabling technologies for high-security-level anticounterfeiting. *Adv. Mater.* **2020**, *32*, No. 1901430.

(7) Wang, F.; Banerjee, D.; Liu, Y. S.; Chen, X. Y.; Liu, X. G. Upconversion nanoparticles in biological labeling, imaging, and therapy. *Analyst* **2010**, *135*, 1839−1854.

(8) Liu, L.; Wang, S. F.; Zhao, B. Z.; Pei, P.; Fan, Y.; Li, X. M.; Zhang, F. Er^{3+} sensitized 1530 to 1180 nm second near-infrared window upconversion nanocrystals for in vivo biosensing. *Angew. Chem., Int. Ed.* **2018**, *57*, 7518−7522.

(9) Li, H.; Tan, M. L.; Wang, X.; Li, F.; Zhang, Y. Q.; Zhao, L. L.; Yang, C. H.; Chen, G. Y. Temporal multiplexed in vivo upconversion imaging. *J. Am. Chem. Soc.* **2020**, *142*, 2023−2030.

(10) Chen, G. Y.; Qiu, H. L.; Prasad, P. N.; Chen, X. Y. Upconversion nanoparticles: design, nanochemistry, and applications in theranostics. *Chem. Rev.* **2014**, *114*, 5161−5214.

(11) Liu, Y. Y.; Meng, X. F.; Bu, W. B. Upconversion-based photodynamic cancer therapy. *Coord. Chem. Rev.* **2019**, *379*, 82−98.

(12) Qiu, X. C.; Zhou, Q. W.; Zhu, X. J.; Wu, Z. G.; Feng, W.; Li, F. Y. Ratiometric upconversion nanothermometry with dual emission at the same wavelength decoded via a time-resolved technique. *Nat. Commun.* **2020**, *11*, 4.

(13) Zhou, B.; Yan, L.; Huang, J. S.; Liu, X. L.; Tao, L. L.; Zhang, Q. Y. NIR II-responsive photon upconversion through energy migration in an ytterbium sublattice. *Nat. Photonics* **2020**, *14*, 760−766.

(14) Su, Q. Q.; Wei, H. L.; Liu, Y. C.; Chen, C. H.; Guan, M.; Wang, S.; Su, Y.; Wang, H. F.; Chen, Z. G.; Jin, D. Y. Six-photon upconverted excitation energy lock-in for ultraviolet-C enhancement. *Nat. Commun.* **2021**, *12*, 4367.

(15) Wang, A. Y.; Liu, Y. C.; Wang, X. J.; Liu, F. White-light flashlight activated up-conversion luminescence for ultraviolet-B tagging. *Opt. Lett.* **2020**, *45*, 2720−2723.

(16) Yan, S. Y.; Liu, F.; Zhang, J. H.; Wang, X. J.; Liu, Y. C. Persistent emission of narrowband ultraviolet-B light upon blue-light illumination. *Phys. Rev. Appl.* **2020**, *13*, No. 044051.

(17) Du, Y. Y.; Ai, X. Z.; Li, Z. Y.; Sun, T. Y.; Huang, Y.; Zeng, X. R.; Chen, X.; Rao, F.; Wang, F. Visible-to-ultraviolet light conversion: materials and applications. *Adv. Photonics Res.* **2021**, *2*, No. 2000213.

(18) Reed, N. G. The history of ultraviolet germicidal irradiation for air disinfection. *Public Health Rep.* **2010**, *125*, 15−27.

(19) Raeiszadeh, M.; Adeli, B. A critical review on ultraviolet disinfection systems against COVID-19 outbreak: applicability, validation, and safety considerations. *ACS Photonics* **2020**, *7*, 2941−2951.

(20) Chen, D. Q.; Wang, Y. S.; Yu, Y. L.; Huang, P. Intense ultraviolet upconversion luminescence from Tm^{3+}/Yb^{3+}:β-YF_3 nanocrystals embedded glass ceramic. *Appl. Phys. Lett.* **2007**, *91*, No. 051920.

(21) Wang, G. F.; Qin, W. P.; Wang, L. L.; Wei, G. D.; Zhu, P. F.; Kim, R. J. Intense ultraviolet upconversion luminescence from hexagonal $NaYF_4$:Yb^{3+}/Tm^{3+} microcrystals. *Opt. Express* **2008**, *16*, 11907−11914.

(22) Wang, X.; Bu, Y.; Xiao, S.; Yang, X.; Ding, J. W. Upconversion in Ho^{3+}-doped YbF_3 particle prepared by coprecipitation method. *Appl. Phys. B: Laser Opt.* **2008**, *93*, 801−807.

(23) Cao, C. Y.; Qin, W. P.; Zhang, J. S.; Wang, Y.; Zhu, P. F.; Wei, G. D.; Wang, G. F.; Kim, R. J.; Wang, L. L. Ultraviolet upconversion emissions of Gd^{3+}. *Opt. Lett.* **2008**, *33*, 857−859.

(24) Yu, Y.; Zheng, Y. D.; Cheng, Z. M.; Wang, D.; Liu, L. X.; Qin, F.; Zheng, C. B.; Zhang, Z. G.; Cao, W. W. Ultraviolet emissions from Gd^{3+} ions excited by energy transfer from Ho^{3+} ions. *J. Lumin.* **2011**, *131*, 347−351.

(25) Wang, L. L.; Lan, M.; Liu, Z. Y.; Qin, G. S.; Wu, C. F.; Wang, X.; Qin, W. P.; Huang, W.; Huang, L. Enhanced deep-ultraviolet upconversion emission of Gd^{3+} sensitized by Yb^{3+} and Ho^{3+} in β-$NaLuF_4$ microcrystals under 980 nm excitation. *J. Mater. Chem. C* **2013**, *1*, 2485−2490.

(26) Galleani, G.; Santagneli, S. H.; Ledemi, Y.; Messaddeq, Y.; et al. Ultraviolet upconversion luminescence in a highly transparent triply-doped Gd^{3+}−Tm^{3+}−Yb^{3+} fluoride−phosphate glasses. *J. Phys. Chem. C* **2018**, *122*, 2275−2284.

(27) Huang, S. H.; Lai, S. T.; Lou, L. R.; Jia, W. Y.; Yen, W. M. Upconversion in LaF_3:Tm^{3+}. *Phys. Rev. B* **1981**, *24*, 59.

(28) Gharavi, A. R.; McPherson, G. L. Ultraviolet emissions from Gd^{3+} ions excited by energy transfer from pairs of photoexcited Er^{3+} ions: upconversion luminescence from $CsMgCl_3$ crystals doped with Gd^{3+} and Er^{3+}. *J. Opt. Soc. Am. B* **1994**, *11*, 913−918.

(29) Qin, F.; Zheng, Y. D.; Yu, Y.; Zheng, C. B.; Tayebi, P. S.; Zhang, Z. G.; Cao, W. W. Ultraviolet upconversion luminescence of Gd^{3+} from Ho^{3+} and Gd^{3+} codoped oxide ceramic induced by 532-nm CW laser excitation. *Opt. Commun.* **2011**, *284*, 3114−3117.

(30) Méndez-Ramos, J.; Abril, M.; Martín, I. R.; Rodríguez-Mendoza, U. R.; Lavín, V.; Rodríguez, V. D.; Núñez, P.; Lozano-Gorrín, A. D. Ultraviolet and visible upconversion luminescence in Nd^{3+}-doped oxyfluoride glasses and glass ceramics obtained by different preparation methods. *J. Appl. Phys.* **2006**, *99*, No. 113510.

(31) Hu, C. H.; Sun, C. L.; Li, J. L.; Li, Z. S.; Zhang, H. Z.; Jiang, Z. K. Visible-to-ultraviolet upconversion in Pr^{3+}: Y_2SiO_5 crystals. *Chem. Phys.* **2006**, *325*, 563−566.

(32) Villanueva-Delgado, P.; Krämer, K. W.; Valiente, R.; de Jong, M.; Meijerink, A. Modeling blue to UV upconversion in β-$NaYF_4$:Tm^{3+}. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27396−27404.

(33) Cates, E. L.; Cho, M.; Kim, J. H. Converting visible light into UVC: microbial inactivation by Pr^{3+}-activated upconversion materials. *Environ. Sci. Technol.* **2011**, *45*, 3680−3686.

(34) Yang, Y. M.; Mi, C.; Su, X. Y.; Jiao, F. Y.; Liu, L. L.; Zhang, J.; Yu, F.; Li, X. D.; Liu, Y. Z.; Mai, Y. H. Ultraviolet C upconversion fluorescence of trivalent erbium in $BaGd_2ZnO_5$ phosphor excited by a visible commercial light-emitting diode. *Opt. Lett.* **2014**, *39*, 2000−2003.

(35) Zhao, X. Y.; Liu, F.; Shi, T. X.; Wu, H.; Zhang, L. L.; Zhang, J. H.; Wang, X. J.; Liu, Y. C. Conceptual ultraviolet-C light source based on up-conversion luminescence. *Adv. Photonics Res.* **2022**, *3*, No. 2200106.

(36) Zhou, X. Q.; Qiao, J. W.; Zhao, Y. F.; Han, K.; Xia, Z. G. Multi-responsive deep-ultraviolet emission in praseodymium-doped phosphors for microbial sterilization. *Sci. China Mater.* **2022**, *65*, 1103−1111.