Bright Photon Upconversion on Composite Organic Lanthanide Molecules through Localized Thermal Radiation

Huanqing Ye, Viktor Bogdanov, Sheng Liu, Saumitra Vajandar, Thomas Osipowicz, Ignacio Hernández, and Qihua Xiong

Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore
Chemistry Department, M. V. Lomonosov Moscow State University, Leninskie Gory, 1-3, 119991, Moscow, Russia
Centre for Ion Beam Applications, Department of Physics, Faculty of Science, National University of Singapore, 2 Science Drive 3, 117542 Singapore
Chemistry Department, M. V. Lomonosov Moscow State University, Leninskie Gory, 1-3, 119991, Moscow, Russia
Materials Research Institute and School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom
Dpto. CITIMAC, Facultad de Ciencias, Universidad de Cantabria, Avda. Los Castros, s/n 39005 Santander, Spain
NOVITAS, Nanoelectronics Center of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798 Singapore
MajuLab, CNRS-UNS-NUS-NTU International Joint Research Unit, UMI 3654, Singapore

Supporting Information

ABSTRACT: Converting low-energy photons via thermal radiation can be a potential approach for utilizing infrared (IR) photons to improve photovoltaic efficiency. Lanthanide-containing materials have achieved great progress in IR-to-visible photon upconversion (UC). Herein, we first report bright photon, tunable wavelength UC through localized thermal radiation at the molecular scale with low excitation power density (<10 W/cm²) realized on lanthanide complexes of perfluorinated organic ligands. This is enabled by engineering the pathways of nonradiative deexcitation and energy transfer in a composite of ytterbium and terbium perfluorimidodiphosphinates. The IR-excited thermal UC and wavelength control is realized through the terbium activators sensitized by the ytterbium sensitizers having high luminescence efficiency. The metallic molecular composite thus can be a potential energy material in the use of the IR solar spectrum for thermal photovoltaic applications.

The solar spectrum contains a large portion of infrared (IR) photons that are below the band gap of most photovoltaic (PV) semiconductor materials. Thus, they cannot be absorbed by a single-junction PV device. Converting IR photons to visible photons the energies of which are above the PV material band gap would be a solution.1,2 Lanthanide-based materials are mostly used for photon UC through excited-state absorption (ESA) or energy transfer upconversion (ETU).3,4 ETU is termed as cooperative energy transfer (CET) if simultaneous sensitization is achieved in one activator from two sensitizers.5–7 However, the problems of weak lanthanide absorption and weakly doped concentration give only weak UC brightness. Thermal radiation-induced photon UC has been recently demonstrated in weakly lanthanide-doped inorganic oxides as a bright alternative.8,9 This mechanism occurs as a consequence of the IR absorption heating the materials through nonradiative multiphonon relaxation results in substantial thermal (blackbody type) radiation. Then, the extracted high-energy photons are emitted in a range that can be absorbed by commercial PV devices, potentially delivering cost-effective thermal PV devices to exceed the efficiency limit.10,11 However, nonradiative processes with the potential to heat materials are reduced in lanthanide-based inorganics with long lanthanide emission lifetimes of a few milliseconds. Hence, thermal radiation-induced UC requires high excitation power density over 200 W/cm².9 Moreover, for eliminating thermal loss, low thermal conductivity of the inorganics must be used, but the material choices are quite limited and the bulk inorganic crystals have to be cracked,8,9,12 implying difficulty in developing them into realistic thermal PV devices.

Organic lanthanide materials would have important advantages: Organic lanthanide molecules reduce the ion trapping centers, thus increasing the lanthanide doping concentration. Intense organic ligand vibrations, which in fact prevent typically any use in UC-related applications, provide diverse nonradiative relaxation channels to deexcite the lanthanide excitations.13,14
Organic materials usually have lower thermal conductivity [<1 \text{ W/(m-K)}] than many oxides.\textsuperscript{15} The interplay among them makes it interesting to consider organic lanthanide materials as a possibility in obtaining high-energy photons through thermal UC. However, difficulties will arise in the control of nonradiative channels, material stability, wavelength control, etc.

Herein, we first realize bright photon UC on organic lanthanide molecules through thermal and photoluminescence (PL) emission processes. We demonstrate that near-infrared (NIR)-emitting ytterbium (Yb) sensitizers that are chelated with perfluorinated organic ligands and the internal quantum yield (IQY) of Yb PL approaching unity cause terbium (Tb)-based molecule activators to incandesce brightly in the visible without significant losses. Moreover, the existence of a superimposed Tb UC permits a channel to further control the emission wavelength.

We have chosen tetrakis(pentafluorophenyl)imidodiophosphinimidic (F-TPIP\textsuperscript{2−}) ligand (L) to obtain Yb, Tb, and Y complexes that are vacuum compatible to make integrated optic devices and can be incorporated in composite systems. The detailed material-related information can be found in the Supporting Information. In Figure 1a, the pristine YbL\textsubscript{3} absorption merely gives the peak at 975 nm wavelength, corresponding to the Yb 2F\textsubscript{7/2} → 2F\textsubscript{5/2} transition with no organic ligand absorption observed in the region. PL consists of an emission band from 780 to 1150 nm wavelengths, where the refractive index in the solid (section 4 of the Supporting Information). The inset displays the corresponding Yb emission decays for \([\text{YbL}_3]_x[\text{YfL}_3]_{1-x}\) (x = 0.1, 0.5, 0.7) films and YbL\textsubscript{3} powder. (c) AFM topography of a 200 nm thick \([\text{YbL}_3]_x[\text{YfL}_3]_{1-x}\) film surface on a sapphire substrate in a 1 × 1 μm\textsuperscript{2} area.

![Figure 1](image_url)

**Figure 1.** (a) Absorption in solution and solid and PL spectrum for YbL\textsubscript{3} powder, where L is F-TPIP\textsuperscript{2−}. The wavelength region from 940 to 1050 nm was recorded at 910 nm excitation. The wavelength region from 700 to 900 nm shows the onset of Yb anti-Stokes emission at 975 nm excitation. (b) Time dependence of Yb PL using a 5 ns pulse at 975 nm excitation. The red dots for YbL\textsubscript{3} film emission in vacuum and the black solid is the fitting curve with a single-exponential function (details in the Supporting Information). The gray dots represent the spectrum data for the film emission exposed in air. The inset displays the corresponding Yb emission decays for \([\text{YbL}_3]_x[\text{YfL}_3]_{1-x}\) (x = 0.1, 0.5, 0.7) films and YbL\textsubscript{3} powder. (c) AFM topography of a 200 nm thick \([\text{YbL}_3]_x[\text{YfL}_3]_{1-x}\) film surface on a sapphire substrate in a 1 × 1 μm\textsuperscript{2} area.

The acquisition of the radiative lifetime and the PL lifetime gives a direct measurement of the internal quantum yield (IQY) of Yb emission. Given this, we estimate IQY = \(\tau_{\text{rad}}/\tau_{\text{exc}}\) within the experimental error with a value approaching unity (>50% in air, > 86% in vacuum). The high IQY implies that direct vibrational quenching by the organic ligands is reduced. This elimination can be rationalized regarding the low phonon energies in the perfluorinated complex, and no evident vibration frequencies or overtones are detected >1650 cm\textsuperscript{-1} in the Fourier transform infrared spectrum of the complex (Figure S3).

To harvest Yb IR excitations, we chose the Tb ion as the activator. This choice is critical to realize bright UC because the Tb ion has no intermediate energy levels from the \(^{7}\text{F}_{0,7}\) levels (<5000 cm\textsuperscript{-1}) to the \(^{5}\text{D}_{4}\) level (~20 000 cm\textsuperscript{-1}), and their energy gap \(\Delta E \geq 15\ 000\ \text{cm}^{-1}\) widely exceeds the F-TPIP-vibrational energies (>1650 cm\textsuperscript{-1}), while the intermediate \(\Delta E\) among \(^{7}\text{F}_{0,7}\) levels are well resonant with the organic vibrational energies. We employ \([\text{YbL}_3]_{0.7}[\text{TbL}_3]_{0.3}\) with the mixture ratio giving a Yb/Tb ratio of 2, which was reported to provide the most efficient CET UC in a Yb–Tb mixed system.\textsuperscript{17–18} CET-induced Tb-based UC takes place with continuous-wave (CW) 975 nm excitation when the complex powder in vacuum (Figure S7), as allowed by the long Yb excited-state lifetime.
We then use high vacuum (\( \sim 10^{-5} \) mbar) to further eliminate the permeated gas molecules, particularly trace \( \text{H}_2\text{O} \) and \( \text{N}_2 \), to reduce the thermal loss in the materials. This method is shown to be effective because Figure 2a shows a bright thermal UC for the sample in high vacuum, while the brightness decreases with the vacuum decreased. In high vacuum, the visible fraction rises when \( \text{CW} \ 975 \text{ nm excitation power increases from 2.5 to 10.0 W/cm}^2 \) and gradually overwhelms the Tb UC (left inset to Figure 2a). Corresponding blackbody temperature (\( T_{\text{BB}} \)) can be obtained using the emission region (450–800 nm) by Planck’s law fit, and the power dependence of the laser-induced \( T_{\text{BB}} \) is shown in Figure 2b. We found \( T_{\text{BB}} \) increases up to \( \sim 1300 \) K at 10 W/cm\(^2\), while the \( T_{\text{BB}} \) and the spectral radiance (SR) intensity starts to drop after \( \sim 12.0 \text{ W/cm}^2 \) due to the rapid material decomposition or evaporation.

Interestingly, the spectrum in the IR region from \( 1010 \) to \( 1300 \) nm wavelengths primarily exhibits the Yb emission of being much more intense than the IR fraction of the thermal radiation. Integrating Yb emission from 1010 to 1200 nm with \( \tau_{\text{Yb(IR)}} \) (zoom in, left inset). The lifetimes of the excited state are slightly shorter than the pristine \( \tau_{\text{Yb(YR)}} \) with \( \sim 0.07 \) ms lifetime (5 ns pulse excitation) into the Tb \( 5\text{D}_4 \) level, while \( \text{Tb} \) 550 nm emission peak shows a lifetime of \( \sim 1.32 \pm 0.07 \text{ ms} \) (Figure 3) with the direct excitation (5 ns pulse excitation) into the Tb \( 5\text{D}_4 \) level, which could reduce the thermal dissipation from beforehand-excited Tb units to Yb units to heat the materials to \( T_{\text{BB}} \). Nevertheless, it is likely that the thermal dissipation among molecular clusters is disrupted because of the \( \sim 20 \) nm vacuum space between grains, which can reduce the thermal loss from the high-temperature centers to the neighboring ones. This might explain the rise time being much shorter than those (from seconds to minutes) in crystalline or nanocrystalline oxides, which have higher thermal conductivity benefitting thermal dissipation over bulky hosts. Our discovered phenomena thus are distinct from the conventional lanthanide-based UC.\(^8,20\) Low excitation power implies less solar concentration technology is required.

Figure 3 shows the time evolution of the dynamics and the energy migration routes. Yb PL decay trace in \( \{\text{YbL}_3\}_{0.7}\{\text{TbL}_3\}_{0.3} \) with 0.79 \( \pm 0.06 \) ms lifetime (5 ns pulse excitation) in vacuum becomes shorter than the pristine lifetime \( T_{\text{BB(YR)}} \) of \( \sim 1.1 \) ms, giving a CET rate estimate of \( r_{\text{Yb(Tb)}(\text{IR})} = r_{\text{Yb(YR)}}^{-1} - r_{\text{Yb(UC)}}^{-1} \approx 356 \text{ s}^{-1} \), \( \text{Tb} \) 550 nm emission peak shows a lifetime of \( \sim 1.22 \pm 0.07 \text{ ms} \) with quasi-CW (38 ms square pulse) 975 nm excitation in vacuum. This might be due to the phonon-assisted energy migration between Tb ions enhanced by the laser-induced heating. Particularly, the interion interaction for the Tb ions could be dominant because the Tb emission lifetime is shorter than the reported one for TbL\(_3\) dissolved in deuterated solvents.\(^22\) The thermal UC has a rise time (20–45 ms) (Figure S10) longer than the one for Tb UC, which implies a thermal dissipation from beforehand-excited Tb units to Yb units to heat the materials to \( T_{\text{BB}} \). Nevertheless, it is likely that the thermal dissipation among molecular clusters is disrupted because of the \( \sim 20 \) nm vacuum space between grains, which could reduce the thermal loss from the high-temperature centers to the neighboring ones. This might explain the rise time being much shorter than those (from seconds to minutes) in crystalline or nanocrystalline oxides, which have higher thermal conductivity benefitting thermal dissipation over bulky hosts.\(^9,12\)
the high geometric symmetry of the complex molecule could make the metallic complex such as copper phthalocyanine in vacuum. The stability of the organic materials containing aromatic rings up to multiphonon-relaxation from Tb to organic vibrations. Tb3+:5D4 and the stable organic ligands. The temperature dependence between the sensitizers and activators in the composite is first demonstrated, giving a normalized QE of 1.33 × 10−4 cm2/W at 1300 K, which is comparable to those achieved in the UC of inorganics. The stability of the organic materials containing aromatic rings up to the ~1200 K has been reported even in a hydrogenated organic metallic complex such as copper phthalocyanine in vacuum. Also, perfluorinated materials are known to have much higher thermal stability in general.6,24 In our studied complexes, the overall effect of the coordinated perfluorinated aromatic rings of −(C6F5)−, the ring configuration of −(O−P−N−P−O)−, and the high geometric symmetry of the complex molecule could further enhance the thermal stability. In fact, investigating the time-stability of the thermal radiation in [YbL4]0.5[TbL4]0.5 powder: Yb PL (gray dots) for 975 nm excitation using a square 38.0 ms pulse at 975 nm excitation. The time values resulted from the fit of the exponential functions. Jablonski diagram (below) detailing the energy-transfer processes among Yb, Tb, and organic vibrations. Dashed arrows represent nonradiative processes, and colored solid arrows represent the absorption and emission of photon. The red dashed arrows represent the CET from Yb3+:2F5/2 to Tb3+:5D4, and multiphonon-relaxation from Tb to organic vibrations. The black dashed arrows represent nonradiative deactivations in Tb3+ transitions.

Figure 3. Time evolution of photon emission in [YbL4]0.5[TbL4]0.5 powder: Yb PL (gray dots) for 975 nm excitation using a 5.0 ns pulse. Tb3+:5D4 → Tb3+:5F4 emission (green dots) when directly excited to Tb3+:5D4 level using a 5 ns pulse at 487 nm excitation. Tb3+:5D4 → Tb3+:5F4 emission (green dots, the inset) when excited using a square 38.0 ms pulse at 975 nm excitation. Fitting curves (black lines) are using single-exponential functions (details in the Supporting Information). The thermal UC recorded at 700 nm wavelength (red curve) when excited using a square 38.0 ms pulse at 975 nm excitation. The time values of the exponential functions. Jablonski diagram (below) detailing the energy-transfer processes among Yb, Tb, and organic vibrations. Dashed arrows represent nonradiative processes, and colored solid arrows represent the absorption and emission of photon. The red dashed arrows represent the CET from Yb3+:2F5/2 to Tb3+:5D4, and multiphonon-relaxation from Tb to organic vibrations. The black dashed arrows represent nonradiative deactivations in Tb3+ transitions.

owing to the ultrahigh IQY of Yb emission in the pristine Yb perfluorinated complex. The results imply a novel energy material system allowing for improved convenience and compatibility for integrating a photon UC layer onto thermal PV devices.

■ EXPERIMENTAL METHODS

Details of experimental methods in material synthesis, optical characterization, and data analysis are available in the Supporting Information. In summary, tetraakis(pentafluorophenyl)imidodiphosphinate acid (>98% Changzhou Garde Pharmtech Co. Ltd., China) and the lanthanide chlorides (>99.99% Sigma-Aldrich) are commercially purchased. Materials for purification using vacuum train prior to the use for experiments. Film samples are fabricated using a high-vacuum deposition system. B(λ, T_BB) = \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{h c}{\lambda k T_BB}\right)^2 \left(1 - e^{-\lambda k T_BB}\right) according to Planck’s law was used to fit thermal radiation spectra to yield T_BB with R^2 > 0.99. Exponential functions were used for lifetime fitting. A homemade vacuum chamber was used to place the materials in vacuum.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b02513.

Method to obtain luminescence spectra, thin-film preparation, detailed materials characterization, IQYs calculation methods, data analysis for time-resolved measurements, additional spectral data for UC and thermal radiation, and thermal stability studies (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qihua@ntu.edu.sg.

ORCID

Huanqing Ye: 0000-0002-7737-2676
Ignacio Hernández: 0000-0001-7104-8907
Qihua Xiong: 0000-0002-2555-4363

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Q.X. acknowledges the support from the Singapore National Research Foundation through Investigatorship award (NRF-NRFI2015-03), and the Singapore Ministry of Education via an AcRF Tier 2 grant (MOE2013-T2-1-049) and a Tier 1 grants (2015-T1-001-175 and RG113/16). I.H. acknowledges EU FP7 (MC-CIG Grant 303535) and Spanish MINECO (Grant MAT2016-80438-P).

■ REFERENCES


(9) Soares, M. R. N.; Ferro, M.; Costa, F. M.; Monteiro, T. Upconversion Luminescence and Blackbody Radiation in Tetragonal YSZ Co-Doped with Tb\(^{3+}\) and Yb\(^{3+}\). Nanoscale 2015, 7, 19958–19969.


DOI: 10.1021/acs.jpcl.7b02518