

Room-Temperature Linear Light Upconversion in a Mononuclear Erbium Molecular Complex

GOLESORKHI, Bahman, *et al.*

Reference

GOLESORKHI, Bahman, *et al.* Room-Temperature Linear Light Upconversion in a Mononuclear Erbium Molecular Complex. *Angewandte Chemie: International Edition*, 2018, vol. 57, no. 46, p. 15172-15176

DOI : 10.1002/anie.201810022

Available at:

<http://archive-ouverte.unige.ch/unige:111516>

Disclaimer: layout of this document may differ from the published version.



**UNIVERSITÉ
DE GENÈVE**

Publication: Angew. Chem. Int. Ed. 2018, 57, 15172-15176. DOI: 10.1002/anie.201810022.

Room-Temperature Linear Light Upconversion in a Mononuclear Erbium Molecular Complex **

*Bahman Golesorkhi, Homayoun Nozary, Laure Guénée, Alexandre Fürstenberg and Claude Piguet**

[*] Mr B. Golesorkhi, Dr A. Fürstenberg, Dr H. Nozary, Prof. Dr C. Piguet

Department of Inorganic, Analytical and Applied Chemistry

University of Geneva, 30 quai E. Ansermet

CH-1211 Geneva 4 (Switzerland)

Email: Claude.Piguet@unige.ch

Dr L. Guénée

Laboratory of Crystallography.

University of Geneva, 24 quai E. Ansermet

CH-1211 Geneva 4 (Switzerland)

[**] This work was supported through grants of the Swiss National Science Foundation.

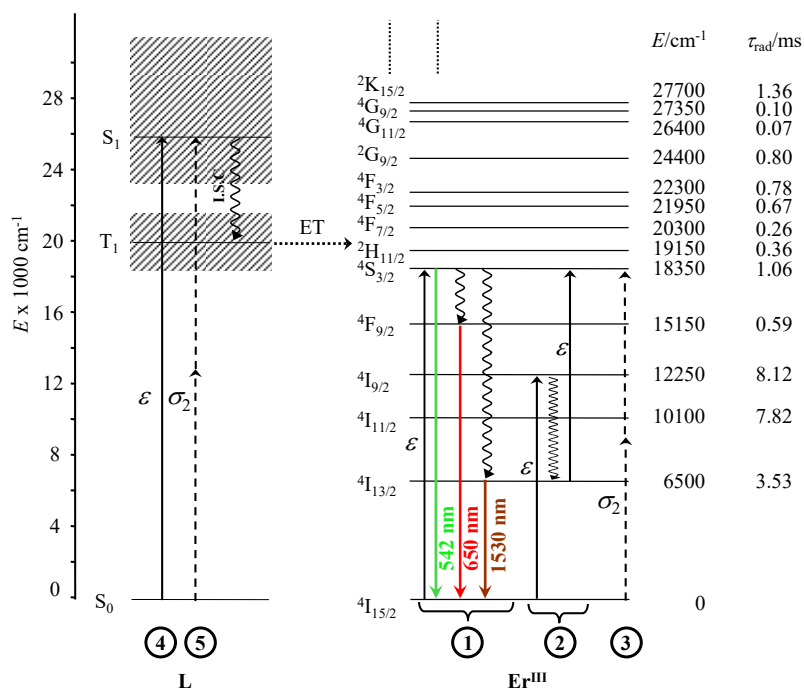
§ Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/>

Keywords: molecular upconversion, erbium complex, excited state absorption.

ABSTRACT

Up to now, the piling up of successive photons of low energies (near-infrared = NIR) using a single lanthanide center and linear optics in order to ultimately produce upconverted visible emission was restricted to low-phonon solid materials and nanoparticles. We show here that the tight helical wrapping of three terdentate *N*-donor ligands around a single nine-coordinate trivalent erbium cation provides favorable conditions for a mononuclear molecular complex to exhibit unprecedented related upconverted emission. Low power NIR laser excitations into the metal-centered transitions $\text{Er}(^4\text{I}_{11/2} \leftarrow ^4\text{I}_{15/2})$ at 801 nm or $\text{Er}(^4\text{I}_{13/2} \leftarrow ^4\text{I}_{15/2})$ at 966 nm result in upconverted blue-green emissions, where two, respectively three photons are successively absorbed by a molecular lanthanide complex possessing high-energy vibrations.

Trivalent erbium, with its open-shell electronic configuration $[\text{Xe}]4f^{11}$, is famous for displaying a series of regularly spaced $^{2S+1}L_J$ spectroscopic levels with long radiative lifetimes (right part of Scheme 1). Hence, one-photon excitation in low-phonon solid materials usually leads to multiple downshifted emission (see ① in Scheme 1).^[1]

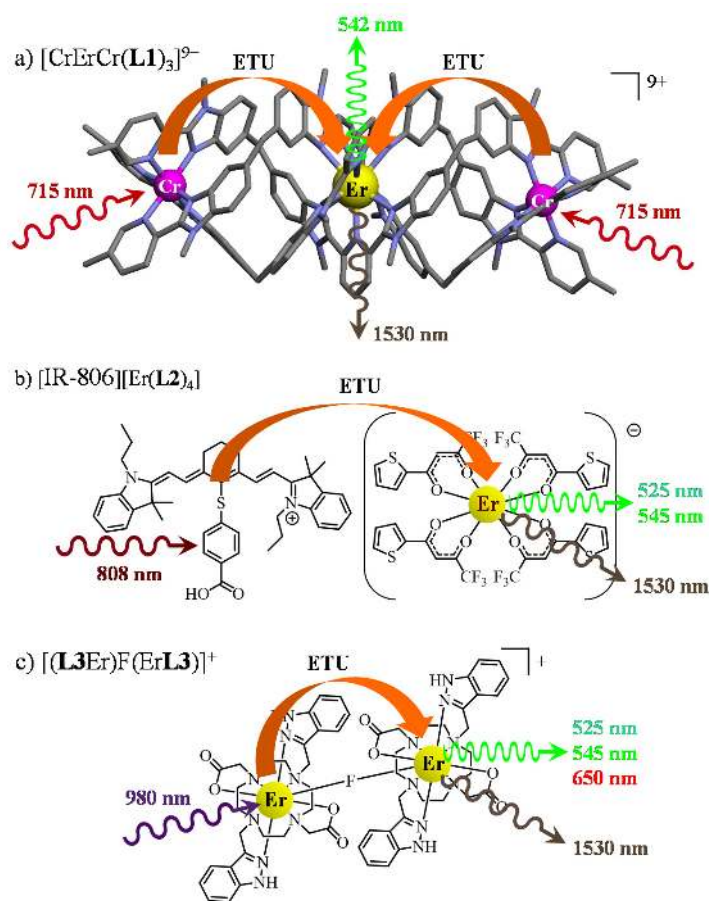


Scheme 1. Energy-level diagrams for an aromatic ligand sensitizer **L** (left) located close to an Er^{3+} ion (right) illustrating ① linear one-photon excitation followed by multiple luminescence, ② linear successive two-photon excitation (excited-state absorption: ESA), ③ non-linear two-photon absorption, ④ linear one-photon indirect sensitization and ⑤ non-linear two-photon indirect sensitization (ISC = intersystem crossing, ET = energy transfer). The reported energies and radiative lifetimes given as an example are those found for Er^{3+} doped into yttrium orthoaluminate YAlO_3 .^[2]

Taking advantage of the existence of long-lived intermediate excited states as relays, successive one-photon absorptions using linear optics, often referred to as upconversion via excited-state absorption (ESA, see ② in Scheme 1), may become competitive with relaxation processes, and the piling of up to five near-infrared photons (980 nm) onto an Er^{3+} cation prior to the emission of a single visible blue photon (410 nm) has been reported in doped YF_3 .^[3] The ESA strategy and the closely related energy transfer upconversion mechanism (ETU), where absorption is performed by peripheral

sensitizers prior to being transferred onto the erbium activator, are currently the subject of intense optimization in upconverting nanoparticles.^[4] The largest reported quantum yields reach the 1-5 % range, which is compatible with innovative applications for imaging biological tissues through transparent biological optical windows,^[5] and for enhancing solar cell efficiency via the collection of additional NIR photons that are not accessible to silica-based technologies.^[6] Despite the obvious advantages that the toolkit of molecular chemistry could bring to the design of these upconverting probes in terms of tuning, processability and reproducibility, the implementation of upconversion in molecular complexes has been so far unambiguously evidenced only for a very few number of sophisticated multi-center devices, which exploit the indirect ETU mechanism (Scheme 2).^[7] To the best of our knowledge, molecular-based upconversion using the ESA mechanism is currently unknown in mononuclear systems, and it has even been predicted to be unworkable.^[8] It is however fair to mention that near-infrared-to-visible upconversion was previously reported for the direct pumping of Er^{3+} bound to standard chelating ligands in solution,^[9] but the required, extremely high 100 kW peak laser powers focused to a spot size of 100 μm in diameter ($\approx 10^9 \text{ W/cm}^2$) are reminiscent of the conditions of operation of non-linear optical two-photon absorption processes (see ③ in Scheme 1). Later, Sorensen and Faulkner indeed irradiated simple solutions of lanthanide salts and of coordination complexes using powerful pulsed femtosecond pulsed NIR lasers and confirmed the primacy of non-linear optical processes in these conditions.^[10] On the other hand, the binding of trivalent lanthanide cations into polyaromatic organic ligands offers valuable perspectives for improving indirect metal sensitization with the help of the antenna effect. According to this mechanism, the ligand-centered excited states are initially populated by efficient linear (see ④ in Scheme 1)^[11] or non-linear (see ⑤ in Scheme 1)^[12] excitation processes prior to undergoing intersystem crossing (ISC) and energy transfer (ET), which ultimately populate the erbium-centered excited states. However, the binding of Er^{3+} to molecular polyaromatic ligands brings the activator in close proximity to high-energy oscillators (C-C, C-N, C-H), which usually provide efficient non-radiative energy relaxation pathways. The resulting Er^{3+} -centered excited-state lifetimes are reduced

to such an extent that (i) only a single and weak emission band can be detected for erbium coordination complexes ($\text{Er}({}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2})$ at 1530 nm in the near infrared)^[13] and (ii) successive photon absorption (ESA) has no chance to compete with the fast relaxation.^[8] Nonetheless, the unexpected dual visible green $\text{Er}({}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2})$ and near-infrared $\text{Er}({}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2})$ luminescence identified in the triple helical complex $[\text{CrErCr}(\text{L1})_3]^{9+}$ cast the first doubts on these generally admitted guidelines.^[14] This result was later confirmed by related multiple erbium-centered luminescence detected in fluorinated tetrakis-betadiketonates $[\text{Er}(\text{L2})_4]^-$ ^[15] and fluorine-bridged macrocyclic dimers $[(\text{L3Er})\text{F}(\text{ErL3})]^+$ (Scheme 2).^[16]



Scheme 2. Erbium-based coordination complexes exhibiting linear upconversion processes following the ETU mechanism. The X-ray crystal structure is shown for $[\text{CrErCr}(\text{L1})_3](\text{CF}_3\text{SO}_3)_9$ ^[14] and chemical structures deduced from spectroscopic data recorded in solution are depicted for $[\text{IR-806}][\text{Er}(\text{L2})_4]$ ^[15] and $[(\text{L2Er})\text{F}(\text{L2Er})]^+$.^[16]

The ‘long-lived’ $\text{Er}({}^4\text{I}_{13/2})$ excited states in the latter complexes were exploited as intermediate relays for the piling up of a second photon provided by energy transfer (ETU mechanism) to reach the high-

energy $\text{Er}(^4\text{S}_{3/2})$ and $\text{Er}(^2\text{H}_{11/2})$ levels, from which the first lanthanide-centered upconverted signals could be observed in molecular complexes using reasonable incident excitation power intensities (10–100 W/cm^2 , Scheme 2).^{[14],[15],[16]} A possible competition between multi-center ETU and single-center ESA mechanisms was suggested to occur in $[(\text{L}3\text{Er})\text{F}(\text{ErL}3)]^+$ in order to rationalize the residual upconverted signal detected at low concentration of fluoride anions.

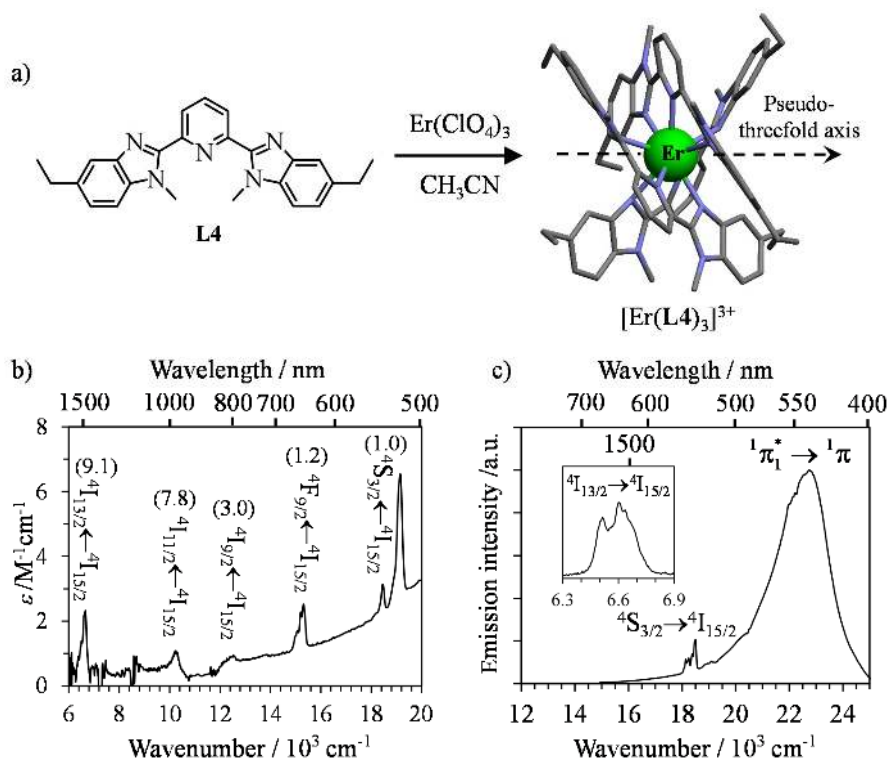


Figure 1. a) Formation and molecular structure of mononuclear triple-helical cation $[\text{Er}(\text{L}4)_3]^{3+}$ as found in the crystal structure of $[\text{Er}(\text{L}4)_3](\text{ClO}_4)_3 \cdot 1.5\text{CH}_3\text{CN}$, and corresponding b) absorption spectrum (3 mM in CH_3CN with radiative lifetime τ_{rad} / ms given in parentheses) and c) emission spectrum (solid state, $\lambda_{\text{exc}} = 370 \text{ nm}$) recorded at room temperature (inset: NIR region of the emission spectrum).^[17]

In order to decipher and program the rare dual Er-centered emission, which is essential for molecular upconversion, the two capping chromium units found in $[\text{CrErCr}(\text{L}1)_3]^{9+}$ were removed. The resulting solution-stable mononuclear chromophore $[\text{Er}(\text{L}4)_3]^{3+}$ was shown to exist as pseudo- D_3 symmetrical triple helical complex, the crystal structure of which displayed pseudo-tricapped trigonal nine-coordinate Er^{3+} sites (Figure 1a), separated from their neighbors by intermetallic distances larger

than 1 nm (Figure S1 in the Supporting Information).^[17] The absorption spectrum (Figure 1b) displays the expected Er-centered transitions with non-negligible (for f-f transitions) molar absorption coefficients ($2 \leq \epsilon \leq 7 \text{ M}^{-1} \cdot \text{cm}^{-1}$), which are still compatible with millisecond-range radiative lifetimes (Figure 1b and Table S1 in the Supporting Information).^[18] The emission spectrum of $[\text{Er}(\mathbf{L4})_3]^{3+}$, recorded upon ligand-centered excitation, displays residual ${}^1\pi^* \rightarrow {}^1\pi$ ligand-centered fluorescence together with dual visible $\text{Er}({}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2})$ and near-infrared $\text{Er}({}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2})$ erbium-centered radiative relaxations as previously observed in the parent $[\text{CrErCr}(\mathbf{L1})_3]^{9+}$ helicate (Figure 1c).^[17] Given that (i) one intermediate Er-centered excited state is sufficiently long-lived to act as a relay ($\tau(\text{Er}({}^4\text{I}_{13/2})) = 5.57(6) \mu\text{s}$ at 298 K)^[17] and (ii) the high-energy $\text{Er}({}^4\text{S}_{3/2})$ excited level is luminescent, $[\text{Er}(\mathbf{L4})_3]^{3+}$ fulfills the minimum requirements for potential Er-centered upconversion via the ESA mechanism.

Direct 801 nm diode laser excitation of the $\text{Er}({}^4\text{I}_{9/2} \leftarrow {}^4\text{I}_{15/2})$ transition in molecular $[\text{Er}(\mathbf{L4})_3](\text{ClO}_4)_3$ complex at room temperature indeed reveals the downshifted near-infrared $\text{Er}({}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2})$ emission (1515 nm) induced by linear one-photon processes (slope $n = 1.14(2)$ for the $\log(I)$ - $\log(P)$ plot, Figures S2-S3),^[19] together with the challenging green upconverted $\text{Er}({}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2})$ emission at 542 nm (Figure 2a). The dependence of the upconverted emission on the incident pump intensity ($\log(I_{\text{up}})$ - $\log(P)$ plot in Figure 2b) returns an average slope of $n = 1.80(8)$, which is typical for the linear successive absorption of two photons obeying the ESA mechanism (Scheme 3a, *vide infra*).^[19] At these reasonable incident power intensities ($1\text{-}30 \text{ W} \cdot \text{cm}^{-2}$), there is no realistic option for the operation of competitive non-linear Er-centered^[10] or ligand-centered two-photon absorption processes.^[12] The latter assertion is further supported by the lack of residual ligand-centered emission following NIR excitation at 801 nm (Figure 2a). Due to the decrease of non-radiative relaxation processes at low temperature, the upconversion mechanism is improved by a factor of five at 30 K (Figure S4), but the square dependence of the upconverted emission intensity on the incident power is maintained at all temperatures (Figure S5).

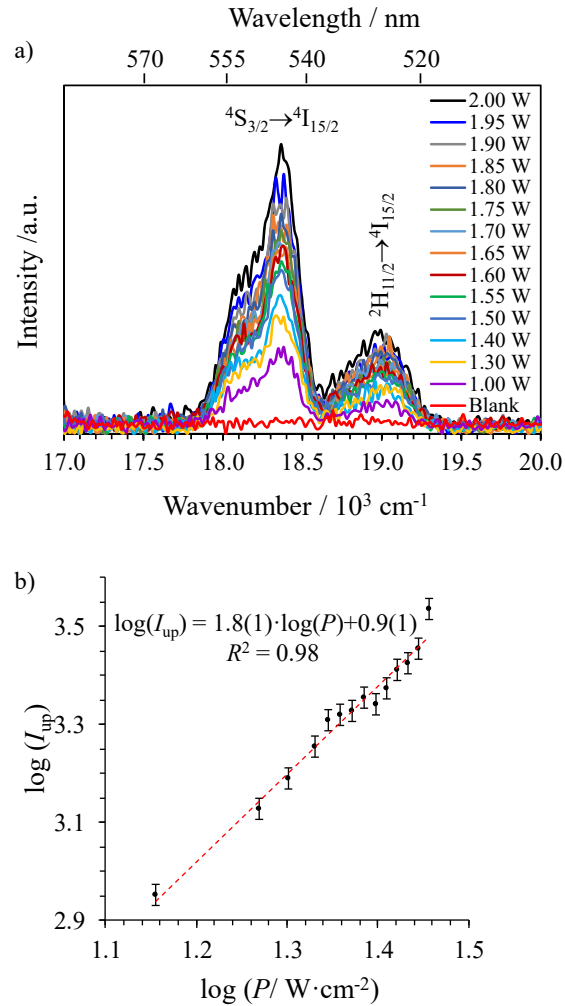


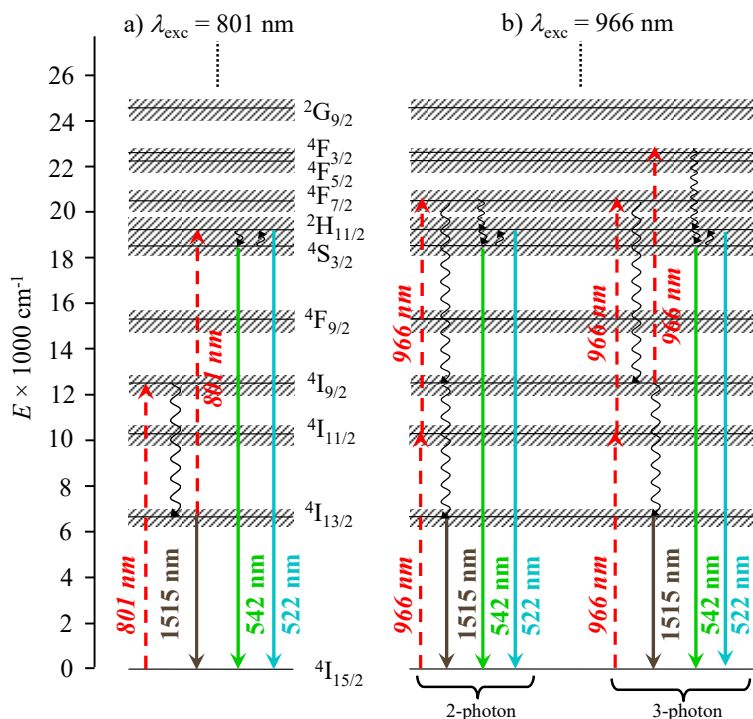
Figure 2. a) Upconverted visible $Er(^2H_{11/2} \rightarrow ^4I_{15/2})$ and $Er(^4S_{3/2} \rightarrow ^4I_{15/2})$ emissions observed for $[Er(L4)_3](ClO_4)_3$ (solid state, 298 K) recorded upon laser excitation of the $Er(^4I_{9/2} \leftarrow ^4I_{15/2})$ transition at $\lambda_{exc} = 801 \text{ nm}$ ($\tilde{\nu}_{exc} = 12284 \text{ cm}^{-1}$) and using increasing incident pump intensities focused on a spot size of $\approx 0.07 \text{ cm}^2$ (the blank (red curve) was recorded upon irradiation of the copper plate support covered with silver glue at maximum intensity $P = 29 \text{ W} \cdot \text{cm}^{-2}$) and b) corresponding log-log plot of upconverted intensities I_{up} as a function of incident pump intensities P (in $\text{W} \cdot \text{cm}^{-2}$).

Careful inspection of the $Er(^4S_{3/2} \rightarrow ^4I_{15/2})$ emission further reveals the presence of a second weak upconverted signal located on the high-energy side of the $Er(^4S_{3/2} \rightarrow ^4I_{15/2})$ transition (Figure 2a). Its energetic location (522 nm, 19150 cm^{-1}) combined with its relative strengthening upon increasing the temperature suggest the operation of thermal equilibrium between the two close $Er(^4S_{3/2})$ and $Er(^2H_{11/2})$ levels (Scheme 3a). This leads to a second thermally-activated upconverted $Er(^2H_{11/2} \rightarrow ^4I_{15/2})$ emission, a phenomenon previously documented for ETU processes operating in

[IR-806][Er(L2)₄]^[15] and [(L3Er)F(ErL3)]⁺.^[16] Direct 966 nm diode laser excitation of the Er(⁴I_{11/2}←⁴I_{15/2}) transition in the molecular [Er(L4)₃](ClO₄)₃ complex at room temperature, but using slightly larger incident power intensities ($35 \leq P \leq 71 \text{ W}\cdot\text{cm}^{-2}$) leads to similar optical signatures (Figures S6-S10 in the Supporting Information) except for the log(*I*)-log(*P*) dependences which now imply a two-photon process for the downshifted Er(⁴I_{13/2}→⁴I_{15/2}) emission (slope $n = 2.07(4)$, Figures S7-S8) and the piling up of up to three successive photons for the upconverted Er(⁴S_{3/2}→⁴I_{15/2}) emission (slope $n = 2.6(1)$, Figures S6b and S10). Again, the upconverted emission becomes stronger at low temperature (Figure S9), while its three-photon character is retained (Figure S10). A detailed investigation of the excited levels and specific relaxation processes responsible for this three-photon ESA process is beyond the scope of this communication. One however notices that the unusual two-photon character of the Er(⁴I_{13/2}→⁴I_{15/2}) downshifted emission observed upon Er(⁴I_{11/2}←⁴I_{15/2}) excitation at 966 nm is a strong argument for the lack of efficient relaxation between the adjacent Er(⁴I_{11/2}) and Er(⁴I_{13/2}) levels, a trend which will contribute to favor excited-state absorption over competitive internal relaxation processes. Moreover, the non-integer slopes of 2.6 (Figure S6b, 298 K) and 2.7 (Figure S10, 52 K) observed for the log(*I*_{up}) versus log(*P*) plots may reflect competitions between two- and three-photon mechanisms (Scheme 3b).

As already suspected in a pioneering study dedicated to molecular-based energy transfer upconversion,^[9] we demonstrate in this work that a judiciously designed mononuclear erbium complex possessing non-negligible oscillating strengths for its f-f transitions combined with the existence of at least two emissive states, one of which operating in the visible part of the electromagnetic spectrum, is a good candidate for exhibiting excited-state absorption (ESA) followed by upconverted emission at the molecular level. The triple helical [Er(L4)₃]³⁺ chromophore fulfills these criteria and indeed provides room-temperature two-photon upconversion upon direct near-infrared (801 nm) excitation into the Er(⁴I_{9/2}←⁴I_{15/2}) transition according to the standard mechanism proposed in Scheme 3a.^[7] The related, but three-photon upconversion process observed upon excitation into the Er(⁴I_{11/2}←⁴I_{15/2}) transition at 966 nm is much more challenging and unexpected

because the large intermolecular Er-Er distances (> 1 nm) is expected to prevent the contribution of Er-Er cross relaxation to the upconversion process.^{[3],[19b]} Scheme 3b proposes a credible mechanistic pathway summarizing the current observations.



Scheme 3. Er-centered energy-level diagrams found for $[\text{Er}(\text{L4})_3](\text{ClO}_4)_3$ highlighting possible mechanisms for a) two-photon ESA upconversion upon 801 nm excitation and b) competition between two- and three-photon ESA upconversion upon 966 nm excitation.

It is however honest to finally mention that these molecular-based upconverted signals, although they can be induced under reasonable incident laser power intensities and recorded using standard detectors, are rather weak and currently not exploitable for accurate estimations of quantum yields and excited-state lifetimes. Nevertheless, the immense intrinsic advantages of chemical formulation, tuning and reproducibility offered by molecular objects over the difficult characterization, and challenging processability and synthetic repeatability of nanoparticles and doped solid materials probably justify future quests for optimizing upconversion in lanthanide coordination complexes.

Acknowledgments

This work is supported through grants from the Swiss National Science Foundation.

Conflict of interest

The authors declare no conflict of interest.

REFERENCES

- [1] a) B. M. van der Ende, L. Aarts, A. Meijerink, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11081-11095. b) C. Piguet, *Nature Chemistry* **2014**, *6*, 370; c) C.-G. Ma, M. G. Brik, D.-X. Liu, B. Feng, Y. Tian, A. Suchocki, *J. Luminesc.* **2016**, *170*, 369-374.
- [2] D. K. Sardar, S. Chandrasekharan, K. L. Nash, J. B. Gruber, *J. Appl. Phys.* **2008**, *104*, 023102.
- [3] F. Auzel, *Chem. Rev.* **2004**, *104*, 139-173;
- [4] a) M. Haase, H. Schäfer, *Angew. Chem. Int. Ed.* **2011**, *50*, 5808-5829; b) S. Han, R. Deng, X. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 11702-11715; c) F. Wang, X. Liu, *Acc. Chem. Res.* **2014**, *47*, 1378-1385; d) D. M. Wu, A. Garcia-Etxarri, A. Salleo, J. A. Dionne, *J. Phys. Chem. Lett.* **2014**, *5*, 4020-4031; e) J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, *Chem. Rev.* **2015**, *115*, 395-465.
- [5] a) Y. Liu, D. Tu, H. Zhu, X. Chen, *Chem. Soc. Rev.* **2013**, *42*, 6924-6958; b) S. Gai, C. Li, P. Yang, J. Lin, *Chem. Rev.* **2014**, *114*, 2343-2389; c) L.-D. Sun, Y.-F. Wang, C.-H. Yan, *Acc. Chem. Res.* **2014**, *47*, 1001-1009; d) J. Zhou, J. L. Leano Jr., Z. Liu, K.-L. Wong, R.-S. Liu, J.-C. G. Bünzli, *Small* **2018**, 1801882.
- [6] a) X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.* **2013**, *42*, 173-201. B) J.-C. G. Bünzli, A.-S. Chauvin, *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 44 (Eds.: J.-C. G. Bünzli, V. K. Pecharsky), Elsevier North Holland, Amsterdam, 2014, pp. 169-281; c) P. Ramasamy, P. Manivasakan, J. Y. Kim, *RSC Adv.* **2014**, *4*, 34873-34895.
- [7] Y. Suffren, B. Goleosorkhi, D. Zare, L. Guénée, H. Nozary, S. V. Eliseeva, S. Petoud, A. Hauser, C. Piguet, *Inorg. Chem.* **2016**, *55*, 9964-9972; b) L. J. Charbonnière, *Dalton Trans.* **2018**, *47*, 8566-8570.
- [8] C. Reinhard, H. U. Güdel, *Inorg. Chem.* **2002**, *41*, 1048-1055.
- [9] X. Xiao, J. P. Haushalter, G. W. Faris, *Opt. Lett.* **2005**, *30*, 1674-1676.

- [10] a) T. J. Sorensen, O. A. Blackburn, M. Tropiano, S. Faulkner, *Chem. Phys. Lett.* **2012**, *541*, 16-20; b) O. A. Blackburn, M. Tropiano, T. J. Sorensen, J. Thom, A. Beeby, L. M. Bushby, D. Parker, L. S. Natrajan, S. Faulkner, *Phys. Chem. Chem. Phys.* **2012**, *14*, 13378-13384.
- [11] E. G. Moore, A. P. S. Samuel, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 542-552.
- [12] a) C. Andraud, O. Maury, *Eur. J. Inorg. Chem.* **2009**, 4357-4371; R. Medishetty, J. K. Zareba, D. Mayer, M. Samoc, R. A. Fischer, *Chem. Soc. Rev.* **2017**, *46*, 4976-5004.
- [13] F. Artizzu, M. L. Mercuri, A. Serpe, P. Deplano, *Coord. Chem. Rev.* **2011**, *255*, 2514-2529.
- [14] L. Aboshyan-Sorgho, C. Besnard, P. Pattison, K. R. Kittilstved, A. Aebischer, J.-C. G. Bünzli, A. Hauser, C. Piguet, *Angew. Chem. Int. Ed.* **2011**, *50*, 4108-4112.
- [15] I. Hyppänen, S. Lahtinen, T. Ääritalo, J. Mäkelä, J. Kankare, T. Soukka, *ACS Photonics* **2014**, *1*, 394-397.
- [16] A. Nonat, C.F. Chan, C. Platas-Iglesias, Z. Liu, W.-T. Wong, W.-K. Wong, K.-L. Wong, L. J. Charbonnière, *Nature Commun.* **2016**, 11978.
- [17] B. Golesorkhi, L. Guénée, H. Nozary, A. Fürstenberg, Y. Suffren, S. V. Eliseeva, S. Petoud, A. Hauser, C. Piguet, *Chem. Eur. J.* **2018**, *24*, 13158-13169.
- [18] a) J.-C. G. Bünzli, A.-S. Chauvin, H. K. Kim, E. Deiters, S. V. Eliseeva, *Coord. Chem. Rev.* **2010**, *254*, 2623-2633; b) Z. Wang, T. Senden, A. Meijerink, *J. Phys. Chem. Lett.* **2017**, *8*, 5689-5694.
- [19] a) M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel, *Phys. Rev.* **2000**, *B61*, 3337-3346; b) M. T. Berry, P. S. May, *J. Phys. Chem. A* **2015**, *119*, 9805-9811.

TOC

The linear piling of two (801 nm) or three (966 nm) photons via excited-state absorption (ESA) leading to upconverted visible emission has been implemented at room temperature into a mononuclear molecular erbium complex possessing high-energy oscillators.

