



HAL
open science

Bringing upconversion down to the molecular scale

Loïc J. Charbonnière

► **To cite this version:**

Loïc J. Charbonnière. Bringing upconversion down to the molecular scale. Dalton Transactions, 2018, 47 (26), pp.8566-8570. 10.1039/c7dt04737a . hal-02396004

HAL Id: hal-02396004

<https://hal.science/hal-02396004>

Submitted on 10 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Bringing upconversion down to the molecular scale

Loïc J. Charbonnière

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract. After solid state and nanoparticles, discrete molecular and supramolecular systems displaying upconversion (UC) in solution have recently emerged in the literature. This frontier article intends to recall the roots of molecular UC and will try to draw perspectives to improve the actual state of the art.

Dedicated to Pr Nicolaas Bloembergen (1920-2017)¹

Since the theoretical description of the phenomenon of two photon absorption by Maria Göppert-Meyer in 1931,² and that of excited state absorption by Nicolaas Bloembergen in 1958,³ upconversion (UC) has been experimentally established for non-linear optical processes,⁴ or for successive linear processes such as excited state absorption (ESA)⁵ or energy transfer upconversion (ETU).⁶ But until recently, observation of upconversion was essentially restricted to bulk solid or crystalline⁷ or amorphous materials.⁸ However, the very end of the last century has witnessed the emergence of nanoparticles (NPs) as promising UC materials for bio-analytical applications,⁹ their detailed synthesis as stable colloidal suspension,¹⁰ and their surface functionalisation.¹¹ This first downscaling step is now illustrated by numerous examples in the literature with applications to bio-labelling, imaging or bio-analytical applications.¹² But the next step towards miniaturization in this top to the bottom approach, downscaling to the molecular level in solution, is still almost unexplored.

In the case of bulk solids and NPs, the choice of the host lattice is of paramount importance as phonons, defined as quasi-particles having the energy of a vibration of the lattice,¹³ can have a dramatic impact on the luminescence properties, affording non-radiative deactivation pathways.¹⁴ Host materials having low phonon energies such as fluoride (LaF₃) and vanadate (YVO₄)¹⁵ are preferred as the probability of non-radiative multi-phonon relaxation processes decrease with the

number of overtones necessary to fill the energy gap between the ground and the excited states. For molecular devices, the question of phonon assisted processes becomes even more crucial as the ligands used for Ln coordination generally bear vibrational absorption bands of high energy such as O-H, N-H or C-H oscillators between 3000 and 3500 cm⁻¹, which have long been known as efficient luminescence quenchers.¹⁶ Probably more important, the solvent itself plays a crucial role in quenching phenomena and the repelling of solvent molecules as far away from the emitting center is of primary importance to get an efficient luminescence.¹⁷

This frontier article is intended to survey the very first examples of molecular upconversion, i.e. bi- or polyphotonic absorption processes leading to UC in discrete molecular compounds. Noteworthy, processes such as triplet-triplet annihilation (TTA),¹⁸ or frequency upconversion luminescence (FUCL)¹⁹ will not be considered here. In the first case, if the annihilation process occurs between two discrete entities, it is generally resulting from the energy diffusion through multiple chromophores and cannot be considered as a molecular process *stricto sensu*. In the case of FUCL, the anti-Stokes process is the result of a thermal population of higher excited state after the absorption of a single photon

One of the very first report of UC in solution was obtained for an Er doped laser liquid.²⁰ It consisted in a 0.2 M solution of ErCl₃ dissolved in a mixture of POCl₃:SnCl₄. Such liquid matrix present the advantage to lack high vibrational energy bonds, i.e. high phonons. Upon 500 mW excitation at 800 nm in the ⁴I_{15/2} → ⁴I_{9/2} absorption band of Er, an UC emission band of Er at 550 nm could be measured in the emission spectrum of the solution. The UC process was unambiguously proved by the quadratic dependence of the emitted intensity as a function of the input pump power and the mechanism was proposed to be an excited state absorption one.

As for bulk solids or NPs it is not surprising to observe that most of the cases of molecular upconversion are concerning lanthanide complexes. Thanks to their ladder like energy level diagrams with the presence of numerous possibilities of NIR transitions²¹ and their long excited state lifetimes,²²

Laboratoire d'Ingénierie Moléculaire Appliquée à l'Analyse (LIMAA), Institut Pluridisciplinaire Hubert Curien (IPHC), UMR 7178 CNRS/Université de Strasbourg, ECPM, Bâtiment R1N0, 25, rue Becquerel, 67087 Strasbourg Cedex 2, France. E-mail: l.charbonn@unistra.fr

lanthanide cations can provide adequate properties for UC, even at the molecular level. This was the motivation for Güdel and Reinhardt to look for the possibility of UC in Yb, Er and Tm complexes of tris-dipicolinic acid.²³ Unfortunately, they could not observe any UC in these systems, despite their thorough investigation. Interestingly, only three years after this study, a following work²⁴ on Er, Tm and Nd complexes with polyaminoacetic acids (EDTA, DTPA, DOTA and tris-dipicolinic acid) prepared as 0.02 M solutions in H₂O and D₂O demonstrated the possibility of UV (Nd) and visible (Tm and Er) UC for some of the complexes, among which the Er and Tm complexes of dipicolinic acid previously studied by Güdel.²³ In this case, excitation was performed by a combination of two pulsed lasers adjusted to the energy gaps for the first and the second excitation steps. For each laser, the power was quite high, with peak powers reaching 10⁶ kW.cm⁻². Was this observation the result of the double excitation, or was the study of Güdel prone to some quenching process such as concentration quenching in the solid state, is not clear at that time. Whatever the case, this allowed Xiao and co-workers to claim that they were the first to demonstrate UC at the molecular scale in an "aqueous phase", although it was not clearly stated if UC was observed in D₂O or H₂O.

Piguet, Hauser and co-workers were the first to try to tackle the question of molecular UC using supramolecular chemistry in controlled heteropolynuclear assemblies using ETU.²⁵ In their pioneering work, the authors designed a heterotritopic ligand L containing two lateral bidentate sites surrounding a central tridentate one. In the presence of a

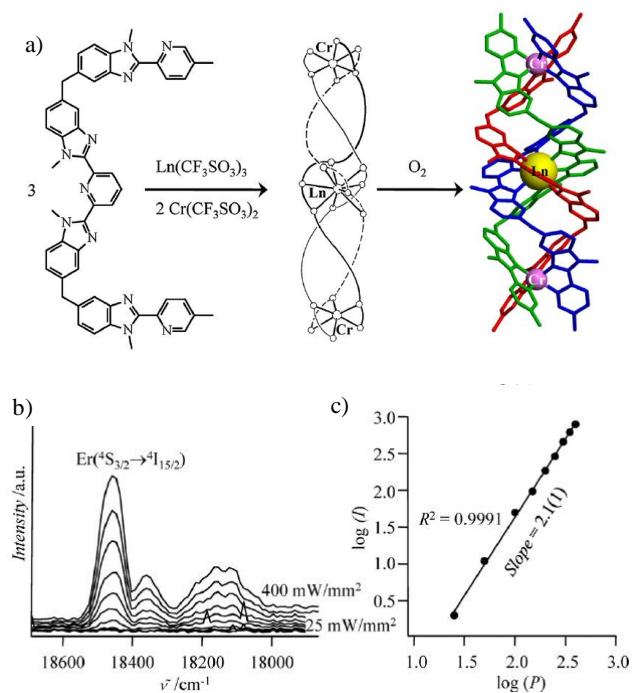


Figure 1. Self assembly process leading to the formation of the [CrErCrL₃]⁹⁺ heterotrimeric triple helix (a) affording visible Er emission upon 750 nm excitation into Cr (b) and the quadratic dependence of the UC process (c). Adapted with permission from reference 25b. Copyright 2017 Elsevier.

mixture composed of one equivalent of Ln(CF₃SO₃)₃ salts and two equivalents of Cr(II) salts in solution a self-assembly process took place leading to the formation of the heterotrimeric triple helix [CrLnCrL₃]⁷⁺, which is subsequently rendered kinetically inert by air oxidation of Cr(II) into Cr(III) leading to [CrLnCrL₃]⁹⁺ (Figure 1). Using Er as a central Ln cation in the [CrErCrL₃]⁹⁺ species, excitation into the Cr(²E ← ⁴A₂) transition at 750 nm (13 333 cm⁻¹) allowed observation of the Er ⁴S_{3/2} → ⁴I_{15/2} emission band at 542 nm (18 400 cm⁻¹) in acetonitrile frozen solution at 30.6 K or in the solid state at 4 K. Here again, the quadratic dependence of the emitted intensity as a function of the laser power unambiguously established the occurrence of a two photons process through an ETU mechanism.

Since then, these authors have thoroughly studied the different parameters governing this UC phenomenon. Various heteropolynuclear systems have been studied to ascertain the Cr and Er energy levels, using for example Ga surrogates, or through the comparison with heterodinuclear Cr-Er triple helices,²⁶ and they recently demonstrated that the UC process can be observed in 10% solid solutions in which the [CrErCrL₃]⁹⁺ complex is doped at 10% in an optically silent [GaYGaL₃]⁹⁺ matrix at r.t.²⁷

In 2012,²⁸ Sørensen, Faulkner and coworkers reported on the direct two photon excitation of Eu, Tb and Sm salts as 10 mM solutions of Ln(CF₃SO₃)₃ salts in deuterated DMSO at r.t. When considering the Tm salt, they noticed the occurrence of bands in the multi-photon excitation spectra which were not related to two photon excitation and proposed them to be the result of two successive excitation steps through an excited state absorption (ESA) mechanism.²⁹

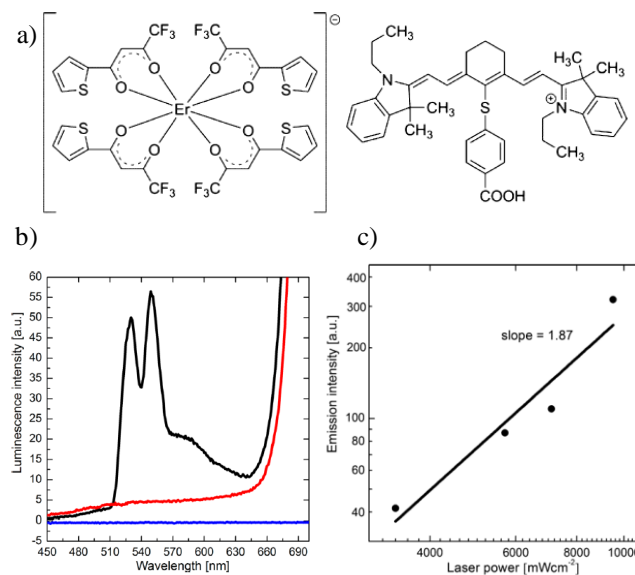


Figure 2. Structure of the [Er(TTA)₄] complex associated to the NIR-806 dye (a), UC spectra obtained upon 808 nm excitation of a 100 μM in CDCl₃ (b) and Log I vs Log P plot showing the quadratic dependence of the UC emission. Adapted with permission from reference 28. Copyright 2017 American Chemical Society.

Two years later, Hyppänen and co-workers reported the preparation of an ion associated Er compound composed of a negatively charged $[\text{Er}(\text{TTA})_4]^-$ complex (TTA stands for 2-thenoyltrifluoroacetate) associated to a positively charged IR-806 positively charged cyanin based counter ion, strongly absorbing in the NIR domain around 806 nm (Figure 2).³⁰ At r.t. for a 100 μM solution in CDCl_3 , excitation in the absorption band of the cyanin resulted in the observation of two emission bands at 510–540 nm and 540–565 nm corresponding to the Er centred $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ emission.

As for other systems, the LogI/LogP plot evidenced a quadratic dependence resulting from a two photons mechanism. The proposed mechanism rely on a two steps excitation of Er through the IR-806 triplet state. This very singular system demonstrated that the antenna effect, by which Ln excitation is indirectly obtained through the sensitization of organic ligand may be of interest within the frame of molecular UC and the resulting UC emission could be observed for rather lower excitation power radiance of 5–6 $\text{W}\cdot\text{cm}^{-2}$.

As a demonstration of the detrimental influence of the OH, NH and CH oscillators on the luminescence properties of the UC devices in solutions, all examples mentioned above were observed at low temperatures,²⁵ or for high concentrations of Ln salts with very excitation powers for ESA mechanisms,^{24,29} or in deuterated organic solvents.³⁰ Taking advantage of the supramolecular approach, we reported in 2016 a first example of UC in a fluoride bridged Er dimer in D_2O .³¹ The Er cation was embedded into the cavity formed by a DOTA like ligand (Figure 3).

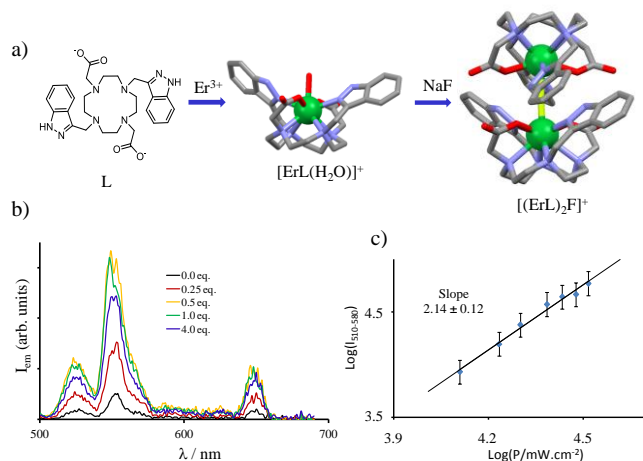


Figure 3. Supramolecular formation of the fluoride bridged Er dimer (a), evolution of the UC emission spectra upon fluoride addition ($\lambda_{\text{exc}} = 980$ nm, b), and LogI/LogP plot evidencing the two photons mechanism.²⁹

A $[\text{ErL}(\text{H}_2\text{O})]^+$ complex was obtained, containing a water molecule at the apical position to fulfil the first coordination sphere. In the presence of fluoride anions in aqueous solutions, a supramolecular dimer formed, assembled through the concomitant weak interactions provided by the bridging fluoride anion, π - π aromatic stacking interactions and hydrogen bonding.³² At r.t. with a millimolar concentration of the complex in D_2O , a very weak UC emission could be

observed upon excitation at 980 nm in the $\text{Er } ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ absorption band, which is attributed to an ESA mechanism. Addition of fluoride to the D_2O solution resulted in a large increase of the UC emission intensity as a result of the formation of the fluoride bridged dimer.

Among the interests of the supramolecular approach, the possibility to direct the formation of heteropolynuclear assemblies by a kinetic and/or thermodynamic control of the reaction conditions appears as a very promising approach. Within the frame of the ETU approach, which requires the gathering of an energy acceptor with one or more energy donors, the energy transfer efficiency is strongly distance dependent. Taking advantage of this approach, we recently demonstrated that polyphosphonated ligands could be very interesting building blocks for the formation of homo- and heteropolynuclear Ln complexes.³³

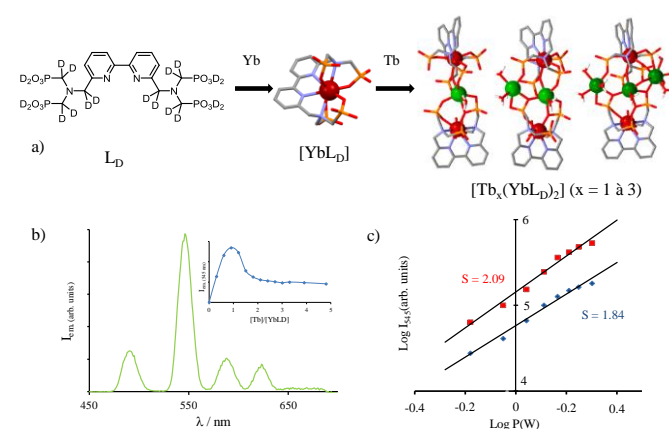


Figure 4. Structure of the perdeuterated tetraphosphonated bipyridyl ligand L_D forming heteropolynuclear $[(\text{YbL}_\text{D})_2\text{Tb}_x]$ ($x = 1$ to 3) species (a), UC emission spectrum showing Tb emission upon Yb excitation at 980 nm (b), and LogI vs LogP plot ascertaining the two photon process (c).³⁴

The careful analysis of the coordination of Ln cations with a tetraphosphonated bipyridine ligand (Figure 4) revealed that the addition of the cations into solutions of the ligand first resulted in the formation of mononuclear $[\text{LnL}]$ species in which the cation is fully coordinated in the octadentate cavity of the ligand. The wrapping of the pyridyl moiety around the metal resulted in a high negative density of charge on one hemisphere of the complex³³ and additional quantity of Ln cations resulted in the formation of $[(\text{LnL})_2\text{Ln}_x]$ polynuclear species ($x = 1$ to 3). By a strict control of the stoichiometry, the mononuclear $[\text{LnL}]$ complexes can be isolated and the addition of a second Ln' cation generated thermodynamically and kinetically stable $[(\text{LnL})_2\text{Ln}'_x]$ heteropolynuclear species. Using Yb/Tb as a Ln/Ln' pair of cations and a perdeuterated version of the ligand (L_D , Figure 4), $[(\text{YbL}_\text{D})_2\text{Tb}_x]$ complexes are formed in solution. Upon excitation into the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ absorption band of Yb at 980 nm, an unprecedented cooperative UC sensitization of Tb is observed, with emission of the typical $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6$ to 3) emission band of Tb in the green and red region.³⁴ The maximum of UC intensity was observed for the $[(\text{YbL}_\text{D})_2\text{Tb}_2]$ complex at r.t. at submillimolar concentrations. If cooperative UC photosensitization was

already observed and studied in the solid state,³⁵ it was expected to be a rather inefficient process as it results from a second order phenomenon. However, the Yb/Tb pair present numerous advantage. With its single ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ electronic transition at *ca* 980 nm ($10\,200\text{ cm}^{-1}$), Yb do not possess too low energy levels in the NIR region. It has recently been demonstrated that perdeuteration of the ligand, associated to deuterated solvents allowed to reach very long luminescence lifetimes of few hundreds μs with excellent luminescence quantum yields.¹⁷ Then, the Tb 5D_4 excited state lies at *ca* 485 nm ($20\,620\text{ cm}^{-1}$), which is almost exactly twice the energy of the Yb emission at 980 nm. Finally, although the central Tb cations are partially coordinated to D_2O molecules, its luminescence is only partially quenched, Tb being the luminescent Ln cation the less affected by OH oscillators.^{16b} The Yb/Tb pair is thus particularly appealing for observing UC at the molecular scale, even if the UC quantum yield (QY) remains still rather low. Comparison with established luminescence references led to QY of the order of 10^{-8} - 10^{-9} in these systems.³⁶ However, the supramolecular approach with polyphosphonated compounds appeared to be extendable to other chemical ligands,³⁶ with important opportunities to improve the UC QY.

Molecular UC: what's next?

From these pioneering studies of the very few groups working in the field some trends can be delineated concerning the possible future of the topic.

The different cases showing UC from an ESA mechanism always require large concentrations and powerful excitation sources. Getting long lived intermediate excited state lifetimes requires forbidden transitions as are the Laporte forbidden f-f transitions or the Cr(III) (${}^2E \leftarrow {}^4A_2$) one. As a consequence, the associated absorption coefficients are very low, thereby requiring high energy to get sufficient population of the excited states. Unless these absorption could be increased, *e.g.* by d-f mixing or with MLCT transitions, it appears elusive to be able to reach efficient molecular UC at concentrations useful for potential analytical applications (μM or less) by the ESA mechanism.

The ETU mechanism or cooperative sensitization seemed to be more appealing for discrete systems composed of an acceptor and one or more energy donors. Whatever the system envisaged, the construction of heteropolynuclear species should take into account some important parameters. The energy transfer steps leading to UC are strongly distance dependent and a close proximity of the energy donors and acceptors is a mandatory parameter for a successful device. Within the frame of Förster's theory of energy transfer,³⁷ the $1/r^6$ distance dependence of the energy transfer efficiency, where r is the donor-acceptor distance, associated to rather short Förster critical radii in the case of Ln/Ln' donor/acceptor pairs,³⁸ point to distances no longer than 6 to 7 Å at maximum, otherwise, the efficiency would rapidly decrease. Still considering the approach of Förster, a second important point to consider is the protection of the NIR Ln donor atoms. These later are the energy tanks feeding the upper excited states

and, considering that the energy transfer efficiency is directly proportional to the donor luminescence QY, the UC efficiency is quadratically related to the donor QY. In that respect, Yb appears again as an unavoidable elemental building block and recent examples have demonstrated the large improvements accessible in the luminescence QY of Yb.^{17,39} However, future works will have to take into account a further parameter: not only does the first coordination sphere of the NIR donors is important, the second and third one are also responsible of a large part of the luminescence quenching. As a simple illustration, partial deuteration of our tetraphosphonated ligand L leading to L_D (Figure 4) allowed for a modest 25 % increase of the Yb luminescent QY, while the use of D_2O in place of H_2O resulted in a 1900 % increase, even though there are no water molecules in the first and second sphere of the Yb cations.

As previously mentioned by Piguet and co-workers,²⁶ a possible trend for UC optimization also lies into the implementation of numerous donors for a single acceptor. Supramolecular chemistry should be of an important help to reach this target.

Finally, the adaptation of the concept of antenna effect to UC systems should also be of interest to increase the pull of Ln donors in the excited state. This approach has been successfully applied recently to UC nanoparticles functionalized with NIR dyes⁴⁰ and it is also at the origin of the observation of Hyppänen and co-workers at the molecular level.³⁰ Interestingly, these authors noticed that only 20 % of the NIR dye luminescence was quenched upon introduction of the $[\text{Er}(\text{TTA})_4]^-$ anion, pointing to large possible UC increase by the optimization of the antenna effect. However, this approach will require a subtle interplay in the matching of the energy levels of the antenna and that of the Ln donor and acceptor. NIR luminescent dyes generally also display non negligible absorption bands in the visible region and it would really be a pity to be able to generate an UC emission signal if this one is quenched by absorption of the organic antenna.

Conclusions

Since the very first reports on UC in the 1960's, the field has witnessed an exponential growth with more than 1500 publications mentioning UC in their title in 2016.⁴¹ But the phenomenon has only recently emerged at the molecular level and examples are still scarce. However, in only one decade, the UC molecules have dramatically evolved, necessitating less and less excitation power and attaining the (deuterated) aqueous phase with conventional NIR laser diodes. If the topic is so exciting, it is probably due to the fact that there remain one of the last holy grail to reach: observing molecular upconversion in water, which would really represent a breakthrough in spectroscopy. Should this objective titillate the spirits and inventiveness of our colleagues, one would undoubtedly see new ideas and new structures appear and possibly some working in water too.

Acknowledgements.

Dr Aline Nonat is gratefully acknowledge for her reading and correction of the paper and for participation for some unpublished results mentioned in the text.

Conflict of interest. There are no conflicts to declare.

References

- 1 E. Yablonovitch *Nature*, **2017**, *550*, 458.
- 2 M. Göppert-Meyer *Ann. Phys. (Ger)* **1931**, *401*, 273.
- 3 N. Bloemberger, *Phys. Rev. Lett.* **1959**, *2*, 84.
- 4 W. Kaiser and C.G.B. Barrett *Phys. Rev. Lett.* **1961**, *7*, 229.
- 5 J. Porter, *Phys. Rev. Lett.*, **1961**, *7*, 414
- 6 a) F. Auzel, *C. R. Acad. Sc. (Paris)*, **1966**, *262*, 1016. b) F. Auzel, *C. R. Acad. Sc. (Paris)*, **1966**, *263*, 819
- 7 a) D.R. Gamelin and H.U. Güdel, *Acc. Chem. Res.* **2000**, *33*, 235. b) F. Auzel, *Chem. Rev.* **2004**, *104*, 139.
- 8 I. Hernandez, N. Pathumakanthar, P.B. Wyatt, and W.P. Gillin, *Adv. Mater.* **2010**, *22*, 5356.
- 9 a) H.J.M.A.A. Zijlmans, J. Bonnet, J. Burton, K. Kardos, T. Vail, R.S. Niedbala and H.J. Tanke, *Anal. Biochem.* **1999**, *267*, 30. b) J. Hampl, M. Hall, N.A. Mufti, Y.-M.M. Yao, D.B. MacQueen, W.H. Wright and D.E. Cooper, *Anal. Biochem.* **2001**, *288*, 176.
- 10 a) S. Heer, O. Lehmann, M. Haase, H.-U. Güdel, *Angew. Chem. Int. Ed.* **2003**, *42*, 3179. b) J.-C. Boyer, F. Vetrone, L.A. Cuccia and J. Capobianco, *J. Am. Chem. Soc.* **2006**, *128*, 7444.
- 11 G. Yi, H. Lu, S. Zhao, Y. Ge, W. Yang, D. Chen and L.-H. Guo, *Nano Lett.* **2004**, *4*, 2191.
- 12 a) F. Wang and X. Liu, *Chem. Soc. Rev.* **2009**, *38*, 976. b) G. Chen, H. Qiu, P.N. Prasad and X. Chen, *Chem. Rev.* **2014**, *114*, 5161. c) W. Zheng, P. Huang, D. Tu, E. Ma, H. Zhu and X. Chen, *Chem. Soc. Rev.* **2015**, *44*, 1379.
- 13 I. Bertini, C. Lucchinat, in *NMR of Paramagnetic Molecules in Biological Systems*, 1986, The Benjamin/Cummings Publishing Company, California.
- 14 M. Haase and H. Schäfer, *Angew. Chem. Int. Ed.* **2011**, *50*, 5808.
- 15 R. Diamente, M. Raudsepp, F.C.J.M. van Veggel, *Adv. Funct. Mater.* **2007**, *17*, 363.
- 16 a) W. D. W. Jr Horrocks, D. Sudnick, *J. Am. Chem. Soc.*, **1979**, *101*, 334. b) A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams, M. Woods *J. Chem. Soc. Perkin Trans 2*, **1999**, 493.
- 17 J.-Y. Hu, Y. Ning, Y.-S. Meng, J. Zhang, Z.-Y. Wu, S. Gao and J.-L. Zhang, *Chem. Sci.*, **2017**, *8*, 2702.
- 18 a) P. Duan, N. Yanai, and N. Kimizuka, *J. Am. Chem. Soc.* **2013**, *135*, 19056. b) G. Massaro, J. Hernando, D. Ruiz-Molina, C. Roscini, and L. Latterini, *Chem. Mater.* **2016**, *28*, 738. c) Y. Zeng, J. Chen, T. Yu, G. Yang, and Y. Li, *ACS energy Lett.* **2017**, *2*, 357.
- 19 Y. Liu, Q. Su, X. Zou, M. Chen, W. Feng, Y. Shi, and F. Li, *Chem. Commun.* **2016**, *52*, 7466.
- 20 C. Koeppen, G. Jiang, G. Zheng and A.F. Garito, *Opt. Lett.* **1996**, *21*, 653.
- 21 S.V. Eliseeva and J.-C.G. Bünzli, *Chem. Soc. Rev.* **2010**, *39*, 189.
- 22 J.-C.G. Bünzli, *Chem. Rev.* **2010**, *110*, 2729.
- 23 C. Reinhardt and H. Güdel *Inorg. Chem.* **2002**, *41*, 1048.
- 24 X. Xiao, J.P. Haushalter and G.W. Faris, *Opt. Lett.* **2005**, *30*, 1674.
- 25 a) L. Aboshyan-Sorgho, C. Besnard, P. Pattison, K.R. Kittilstved, A. Aebischer, J.-C.G. Bünzli, A. Hauser and C. Piguet *Angew. Chem. Int. Ed.* **2011**, *50*, 4108. b) L. Aboshyan-Sorgho, M. Cantuel, S. Petoud, A. Hauser, and C. Piguet, *Coord. Chem. Rev.* **2012**, *256*, 1644.
- 26 D. Zare, Y. Suffren, L. Guénée, S. V. Eliseeva, H. Nozary, L. Aboshyan-Sorgho, S. Petoud, A. Hauser and C. Piguet, *Dalton Trans.* **2015**, *44*, 2529.
- 27 D. Zare, Y. Suffren, H. Nozary, A. Hauser, and C. Piguet, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14612.
- 28 T. J. Sørensen, O. A. Blackburn, M. Tropiano, and S. Faulkner, *J. Phys. Chem.* **2012**, *541*, 16.
- 29 O. A. Blackburn, M. Tropiano, T. J. Sørensen, J. Thom, A. Beeby, L. M. Bushby, D. Parker, L. S. Natrajan, and S. Faulkner, *Phys. Chem. Chem. Phys.* **2012**, *14*, 13378.
- 30 I. Hyppänen, S. Lahtinen, T. Ääritalo, J. Mäkelä, J. Kankare, and T. Soukka, *ACS Photonics* **2014**, *1*, 394.
- 31 A. Nonat, C.F. Chan, T. Liu, C. Platas-Iglesias, K.-L. Wong, and L.J. Charbonnière, *Nature Commun.* **2016**, *7*, 11978
- 32 T. Liu, A. Nonat, M. Beyler, M. Regueiro-Figueroa, K. Nchimi Nono, O. Jeannin, F. Camerel, F. Debaene, S. Cianféroni-Sanglier, R. Tripier, C. Platas-Iglesias and L.J. Charbonnière, *Angew. Chem. Int. Ed.* **2014**, *53*, 7259.
- 33 N. Souri, P. Tian, A. Lecointre, Z. Lemaire, S. Chafaa, J.-M. Strub, S. Cianféroni-Sanglier, M. Elhabiri, C. Platas-Iglesias, L.J. Charbonnière *Inorg. Chem.* **2016**, *55*, 12962.
- 34 N. Souri, P. Tian, C. Platas-Iglesias, S. Chafaa, K.L. Wong, A. Nonat, and L.J. Charbonnière, *J. Am. Chem. Soc.* **2017**, *139*, 1456.
- 35 see for example G.M. Salley, R. Valiente, and H.U. Güdel, *J. Phys. Condens. Matter* **2002**, *14*, 5461.
- 36 Unpublished results.
- 37 T. Förster, *Disc. Faraday Soc.* **1959**, *27*, 7.
- 38 a) C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 8197. b) J. Shah, *Curr. Sci.* **1980**, *49*, 736. c) D.J. Lewis, P.B. Glover, M.C. Solomons, Z. Pikramenou, *J. Am. Chem. Soc.* **2011**, *133*, 1033. d) D. Sendor, M. Hilder, T. Juestel, P.C. Junk, U.H. Kynast, *New J. Chem.*, **2003**, *27*, 1070. e) A. Nonat, T. Liu, O. Jeannin, F. Camerel, and L. J. Charbonnière, to be published in *Chem. Eur. J.* **2018**.
- 39 C. Doffeck, and M. Seitz, *Angew. Chem. Int. Ed.* **2015**, *54*, 9719.
- 40 W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, and J. C. Hummelen, *Nature Photonics* **2012**, *6*, 560.
- 41 Source: Isiweb of knowledge.