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Cooperative Infrared to Visible Up Conversion in Tb³⁺, Eu³⁺, and Yb³⁺ Containing Polymers

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The conversion of IR photons to higher energies is widely employed in lasers, imaging, and biology. Mechanisms based on nonlinear properties of the interaction between matter and radiation[1] are longstanding techniques to achieve this, but usually require very high excitation powers. Up-conversion (UC) processes, which occur when IR-excited centers populate a higher-energy emitting state,[2] represent a promising linear Hamiltonian alternative. This process can be extremely efficient and allows a number of photonic and solar cell applications,[3] all of them currently based on inorganic materials. Consequently there are difficulties with their processability, which, together with the low concentration of emitters required to avoid inter-ion quenching of the luminescence,[4] present serious operational limits. Here, we present and analyze the design rules for the observation of intense cooperative UC[5] in simple, inexpensive, and easily synthesized perfluorinated organolanthanide polymers containing Tb³⁺ and Eu³⁺ as emitters and Yb³⁺ as a sensitizer. These compounds allow for fine control of the ion concentration, casting into thin films, and the possibility of combination with light-harvesting units to achieve greatly improved performance.

The discovery of organic materials with nonlinear interactions with incident radiation, such as harmonic generation and multiphoton processes, has strongly impacted the field of IR to visible conversion and, although it requires high power densities, has allowed new and improved applications.[6] Parallel to this, the optical properties of lanthanides in organic matrixes have been the object of extensive research,[7,8] but few examples of organolanthanides with conversion of IR into visible have been found and the soundest ones are based on ligand-related nonlinearities of Tb complexes.[9] UC reports include excited-state absorption in Nd³⁺ complexes[10] and proposed transfer processes in a family of mixed Yb³⁺–Er³⁺ hybrids.[11] However, it is important to note that Nd³⁺ and Er³⁺, both organic visible emitters, have extremely low efficiency even for direct excitation.[7]

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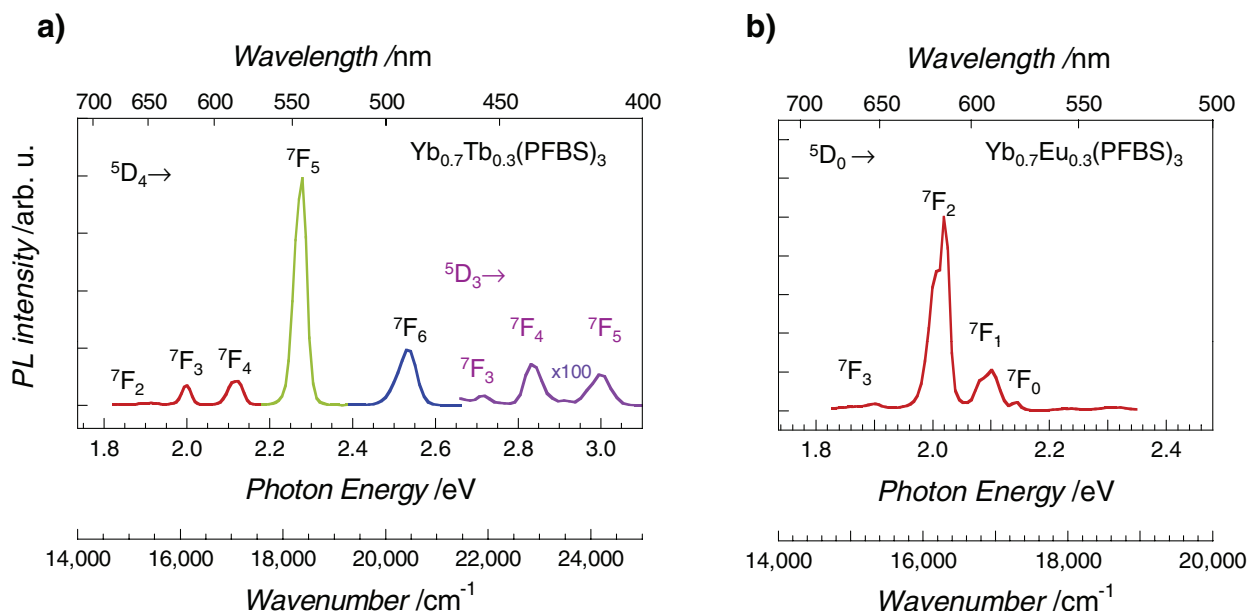Queen Mary University of London
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The main reason for the low UC efficiency in organic compounds containing trivalent lanthanides is the strong nonradiative quenching of the lanthanide excitation by the O–H, C–H, and N–H units usually present in these systems.[12] Multiphonon relaxation of the excited states due to their interaction with the high energy oscillators[13] associated with these groups competes with and overwhelms the possibility of energy transfer and other radiative processes. Thus, the overall efficiency is greatly reduced and so is the applicability of the organolanthanides for UC. Ligands bearing minimal numbers of high frequency oscillators are critical, but are not the only factor to obtain an increase of the desired IR to visible or UV conversion. Given that the multiphonon de-excitation probability increases when the gap to the lower lying states is small in comparison to the energy of the molecular vibrations (so called gap law),[13] efficient organic emitters require lanthanides with no intermediate states close in energy to the ones involved in the radiative or transfer processes.

We have obtained a strong blue/green and red cooperative UC from the mixed lanthanide systems: $Yb_{1-x}Tb_x(PFBS)_3$ and $Yb_{1-x}Eu_x(PFBS)_3$, respectively, where PFBS is perfluorobutanesulfonate (**Figure 1**). Cooperative UC takes place when two excited states simultaneously combine their energies and excite a higher state,[2,5] which subsequently radiates at a higher energy than originally absorbed. This is advantageous, as it allows the excitation of different centers with wide gaps as shown in **Figure 2**.

We recently showed indirectly how cooperative UC processes could potentially take place in concentrated long-lived organolanthanide complexes forming nanofibers.[14] Consistently, our choice of lanthanides leading to the observation of UC in this work is based on the absorption energy and relatively large cross-section of the Yb³⁺ centers along with the wide energy gap for the emitting $^5D_4$ and $^5D_0$ states of Tb³⁺ and Eu³⁺, respectively. Once these states are sensitized all de-excitation branches are radiative, which is the reason why Tb³⁺ and Eu³⁺-based materials are amongst the most used lanthanides in organic emitters in the visible range.[7,8] Moreover, by employing perfluorinated ligands with relatively low energy phonons, we reduce nonradiative de-excitation rates for the $^2F_{5/2}$ excited state of Yb³⁺ (sensitizer), which is an essential condition for the energy transfer to be significant. Perhalogenation is a well-known approach to enhance the efficiency in visible and IR-emitting lanthanide(III) complexes.[8,9,14,15]

Perfluorobutanesulfonate was the preferred ligand due to the great solubility of the tris- complexes in a number of solvents, allowing for spin-coating into thin films, and also because of its size. Perfluoroalkanesulfonates are well-known, inexpensive, and commercially available ligands[16] and fine control of the

Figure 1. a) UC spectrum of $Yb_{0.7}Tb_{0.3}(PFBS)_3$ for 980 nm excitation. b) UC spectrum of $Yb_{0.7}Eu_{0.3}(PFBS)_3$ for 980 nm excitation. The intensity is much reduced in comparison to the case of $Yb_{0.7}Tb_{0.3}(PFBS)_3$. The labels at the corresponding peaks stand for the assignment of the involved radiative de-excitation processes in terms of the intraconfigurational f–f transitions, which arise from the electronic configurations of Tb^{3+} and Eu^{3+}. The colors employed for plotting the peaks represent the apparent color to the eye of the corresponding fraction of the spectrum.

inter-ion distance can be obtained by selecting the appropriate alkyl chain length. Another way to achieve such control of the distance between lanthanide ions is to include transparent complexes, such as $Y(PFBS)_3$ or $La(PFBS)_3$, which decrease the overall concentration of active ions in the solid. Interestingly, compounds thus prepared still provided UC for dilutions of the starting materials in up to 50% of the transparent ion complexes. This may be necessary if light-harvesting molecules are
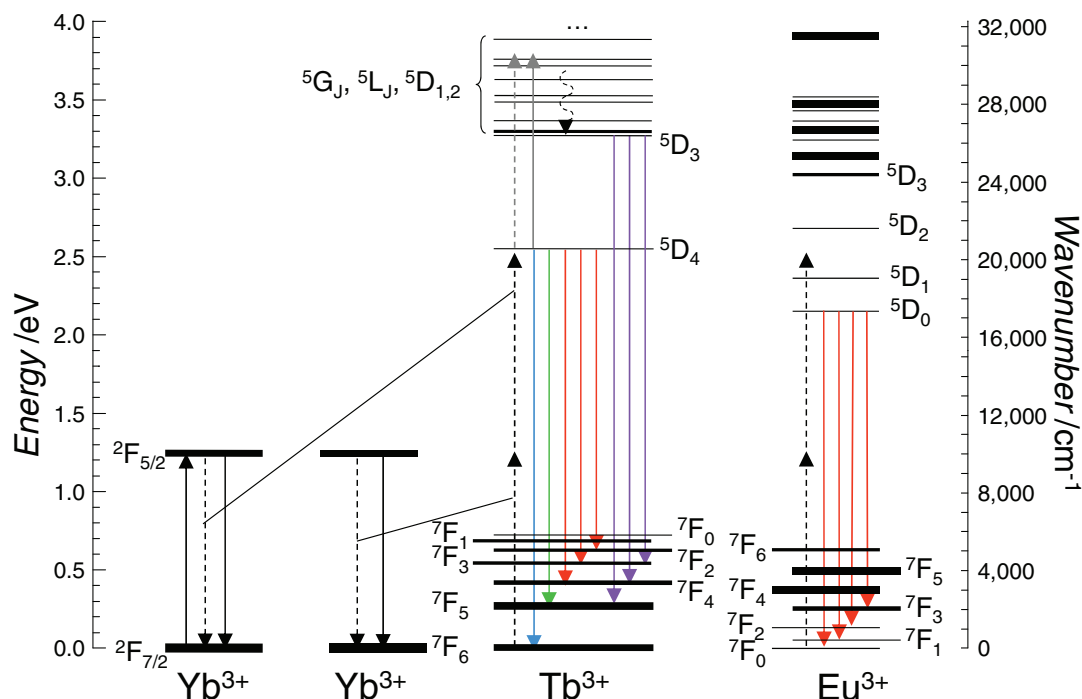

Figure 2. Cooperative UC processes Yb^{3+}–Tb^{3+} and Yb^{3+}–Eu^{3+} systems showing resonant or nonresonant transfer of energy absorbed in the IR range by the Yb^{3+} complexes. The dotted arrows represent nonradiative energy transfer and curled arrows represent multiphonon decays; black/grey and colored solid arrows represent absorption and emission of photons, respectively.

to be introduced because they would imply longer average distances between the UC sensitizing and emitting complexes.

Figure 1a shows the associated spectrum of the $Yb_{0.7}Tb_{0.3}(PFBS)_3$ photoluminescence (PL) at 1.265 eV (980 nm) excitation. A corresponding picture is shown in the Supporting Information, Figure 1. This sample provides the most intense UC along the $Yb_{1-x}Tb_x(PFBS)_3$, $0.1 < x < 0.5$ series. In order to rule out the possibility of multiphoton absorption from the Tb^{3+} complexes, the ytterbium was replaced by yttrium and we observed that $Y_{0.7}Tb_{0.3}(PFBS)_3$ was not luminescent in the visible range under IR excitation. The blue (2.529 eV), green (2.275 eV), and red (2.120 eV, 1.996 eV, 1.909 eV) components of the spectrum correspond to the emission from $^5D_4$ to the lower excited states (Figure 1a and 2). Thus, cooperative energy transfer from two neighboring Yb^{3+} ions in the $^2F_{5/2}$ excited state to Tb^{3+} $^5D_4$ (Figure 1a), or equivalently the trimer transition $[Yb^{3+}\ ^2F_{5/2},\ Yb^{3+}\ ^2F_{5/2},\ Tb^{3+}\ ^7F_6] \rightarrow [Yb\ ^2F_{7/2},\ Yb\ ^2F_{7/2},\ Tb^{3+}\ ^5D_4]$, is the main mechanism providing visible UC at room temperature.[17,18] The spectrum also reveals the presence of much reduced UV components in the region 2.7–3.1 eV, which can be due to further transfer from Yb^{3+} or excited state absorption of Tb^{3+} in the $^5D_4$ state and emissions from $^5D_3$ (see Figure 2).

The dynamics of the Yb^{3+} and Tb^{3+} PL were measured (**Figure 3**). The decay curves show an extremely long lifetime for the majority of ions but also short lifetime components, the latter being related to the presence of remaining water molecules in the coordination sphere of a fraction of the lanthanide ions (it is estimated that this was the case for less than 5% of the complexes). The lifetime of the Yb^{3+} IR emission in the water-free environment ($\tau_{YbTb(IR)} \approx 1.2$ ms) is remarkably long, meaning

that radiative and nonradiative de-excitation pathways are limited, which we believe is the key for the observation of UC in the presence of Tb^{3+}. By comparison of the Yb^{3+} IR emission long component lifetime with that of the $Yb_{0.7}Y_{0.3}(PFBS)_3$, $\tau_{YbY(IR)} \approx 1.7$ ms and, assuming that cooperative transfer to Tb^{3+} is the only additional contribution to de-excitation, the UC probability per unit time was estimated to be[19,20] $\tau_{Yb\rightarrow Tb(UC)}^{-1} = \tau_{YbY(IR)}^{-1} - \tau_{YbTb(IR)}^{-1} \approx 250$ s^{-1}. This implies a comparable efficiency to that obtained in fluoride-based glasses synthesised by sol-gel methods, but is smaller than in those based on silica.[20,21]

The UC PL decay (Figure 3, inset) is a multi-exponential decay with a long component approximating the conventional Tb^{3+} emission lifetime, $\tau_{Tb} \approx 3.5$ ms. The fact that it is not purely exponential can be related to the fact that that some sensitized Tb^{3+} ions can accept more transfers from nearby Yb^{3+} ions (or absorb an IR photon), which leads to the observation of UV emission from higher states, or they could transfer the energy back to Yb^{3+} neighbors. The occurrence of the second mechanism is established by the observation of a broad Yb^{3+} luminescence at 1.265 eV upon excitation at 2.529 eV (corresponding to the $^7F_6 \rightarrow ^5D_4$ absorption of Tb^{3+}, Supporting Information, Figure 2) and suggests that the reverse transfer mechanism proving quantum-cutting down conversion[22] is also possible in these systems. A reliable determination of the corresponding quantitative influence of these mechanisms could not be made on the basis of a dynamical study[23,24] due to the uncertainties caused by the contribution of the water-perturbed centers.

The UC luminescence intensity shows an unexpected dependence upon laser power. A log-log plot slope of the order of two[25] is anticipated for the Tb^{3+} visible UC needing two photons absorbed by two Yb^{3+} ions and a slope three for the UV (implying three photons absorbed by three centers). However, we observe slopes of 4.7 and 6.9 in the explored power density ranges (Supporting Information, Figure 3). It must be noted that although the slopes are not 2 and 3 for the visible and UV UC processes, their ratio is still close to 2:3. Slow avalanche processes are usually responsible for high slopes in UC systems above a critical pumping rate.[26] These processes imply low absorption of the laser-pumped level plus an enhanced absorption cross-section of an intermediate excited state that can be fed additionally though cross-relaxation.[2,26] Similar looped mechanisms have also been proposed, even in the case of strong absorption.[27] Our system has no intermediate states involved in the transfer (see Figure 2) that can be responsible for avalanche-like behavior; instead we ascribe the obtained discrepancy to the contribution of laser-heating[28] of our micrometric (1–5 µm) samples. Indeed, we believe that laser heating may be a common feature in thermally insulated or poorly conducting nano- and micrometer-sized materials and we emphasize that the measurement of the power dependence of cooperative UC in systems with no intermediate states is a good test before stating the occurrence of avalanche or looping mechanisms. Our samples were all measured in a vacuum environment in order to avoid hydration. Thus, long exposure to the laser raises their temperature, which favors PL.[29,30] This explanation is supported by the observaton that cooling of the sample under constant excitation power results in a decrease in the UC PL. Moreover, the excitation spectrum of the Yb-Y PFBS analog shows that the absorption peak of Yb^{3+} in these systems
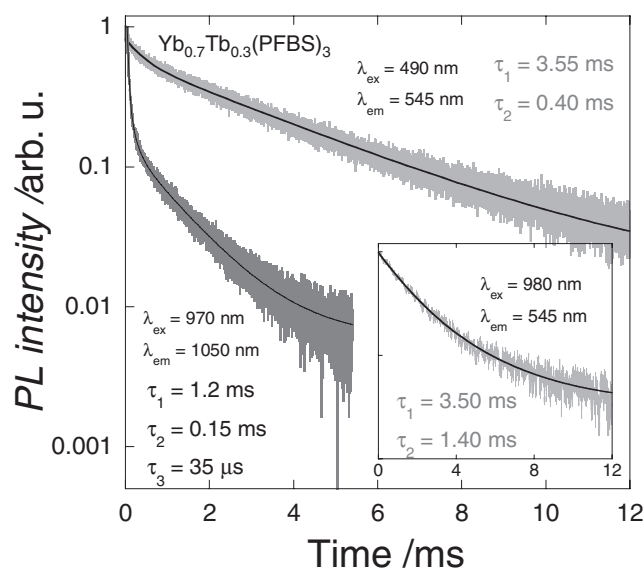

Figure 3. Photoluminescence decay curves for the IR and green emissions of $Yb_{0.7}Tb_{0.3}(PFBS)_3$. The extremely long lifetimes achieved for the Yb^{3+} photoluminescence $\tau > 1.2$ ms are essential for achieving UC in the presence of Tb^{3+}. Lines represent fits to multi-exponential dependences. When more than one exponential was needed to fit the experimental data, the process was done iteratively, adjusting the fast and long components separately from measurements on shorter and longer timescales. The occurrence of short components relates to the presence of coordinated water molecules in a fraction of the complexes. The inset shows the green up-conversion decay.

lies around 975 nm while our diode excites at 980 nm. We interpret the increase in PL due to laser heating of the poorly heat-dissipating sample in terms of a thermal enhancement of the excitation at the wavelengths and energies used. Apart from its role in the Yb^{3+} absorption,[29] temperature can also increase the overlap between the density states of the involved levels due to the larger population of vibrational modes.[30]

We have also detected UC PL in $Yb_{0.7}Eu_{0.3}(PFBS)_3$ (Figure 1b) when the Yb^{3+} ions are excited to $^2F_{5/2}$ by the IR laser. The red PL from $^5D_0$ is notably less intense than in the case of Tb^{3+}, as expected due to the lack of resonance of the process: $[Yb^{3+}$ $^2F_{5/2}, Yb^{3+} \, ^2F_{5/2}, Eu^{3+} \, ^7F_0] \rightarrow [Yb^{3+} \, ^2F_{7/2}, Yb^{3+} \, ^2F_{7/2}, Eu^{3+} \, ^5D_1$ or $^5D_2]$.[19,31] The corresponding long component of the Yb^{3+} lifetime, $\tau_{YbEu(IR)} = 1.38$ ms, provides an estimate of $\tau_{Yb \rightarrow Eu(UC)}^{-1} \approx 110 \, s^{-1}$, bearing a smaller efficiency than those of the Tb^{3+} analogue and Yb^{3+}-Eu^{3+} processed silica glass[19] but comparable with sol-gel fluoride glasses.[20]

The strong visible emission obtained for mixed lanthanide perfluorobutanesulfonates upon IR excitation suggests that cooperative energy transfer occurs from Yb^{3+} organic complexes to neighbouring Tb^{3+} and Eu^{3+} complexes if nonradiative de-excitation processes are kept low. The estimated efficiencies are within the range of those measured fluoride glasses obtained by sol-gel methods. These results open up a new path for a number of exciting biological and photonic applications requiring conversion of IR radiation into visible at moderate and low powers.

Experimental Section

The synthesis of the mixed metal perfluorobutane-sulfonates was performed in two steps. First, the pure metal complexes were obtained by mixing a 3 M water solution of perfluorobutane-sulfonic acid (99.9%, TCI) and the metal oxide (99.9%, Sigma-Aldrich) in appropriate proportions. Tb_2O_3 was handled in a glove-box to avoid oxidation of Tb^{3+} to Tb^{4+}. Mixing the corresponding percentage of the dry metal complex in de-ionized water yielded the $L_{1-x}M_x(PFBS)_3 \cdot nH_2O$, L,M = Y, Yb, Tb, Eu compounds. Evaporation of the solvent led to white, highly hydrated, waxy materials,[32] which were dried in a tube furnace at 570 K at 10^{-5} Pa for three weeks in order to remove the water molecules coordinated to the trivalent ion. The drying time could be reduced to around 10 days in the presence of cold P_2O_5. The obtained material was hygroscopic and was kept under a vacuum of $\approx 10^{-5}$ Pa during all the measurements. Thin films were obtained by spin-coating a water solution. Fourier transform IR (FTIR) spectra of the dried sample showed the presence of a small fraction of residual water. Electron microscopy and energy dispersive X-ray spectroscopy (EDS) were performed at the Nanovision Centre, Queen Mary University of London to characterize the morphology of the samples as well as to confirm their homogeneity and relative metal concentration.

UC PL was measured using a 980 nm modulated diode laser and a digital lock-in amplifier. The reported powers densities were estimated at the sample. For conventional time-resolved PL and excitation, a tunable Continuum Panther optical parameter oscillator was used. Luminescence was detected using visible or nitrogen-cooled IR photomultiplier tubes. Spectral resolution was better than 3 nm. Time-resolved intensity decay curves, $I(t)$, were recorded using a digital oscilloscope.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, P. S. Pershan, *Phys. Rev.* **1962**, *127*, 1918.

[2] F. Auzel, *Chem. Rev.* **2004**, *104*, 139.

[3] a) W. Lenth, R. M. Macfarlane, *Opt. Photonics News* **1992**, *3*, 8; b) S. Heer, K. Kömpe, H.-U. Güdel, M. Haase, *Adv. Mater.* **2004**, *16*, 2102; c) J. Milliez, A. Rapaport, M. Bass, A. Cassanho, H. P. Jenssen, *J. Display Technol.* **2006**, *2*, 307; d) T. Trupke, A. Shalav, B. S. Richards, P. Würfel, M. A. Green, *Solar Energy Mater. Sol. Cells* **2006**, *90*, 3327; e) T. R. Hinklin, S. C. Rand, R. M. Laine, *Adv. Mater.* **2008**, *20*, 1270; f) M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey, P. N. Prasad, *Nano Lett.* **2008**, *8*, 3834; g) Y. I. Park, J. H. Kim, K. T. Lee, K. S. Jeon, H. B. Na, J. H. Yu, H. M. Kim, N. Lee, S. H. Choi, S. I. Baik, H. Kim, S. P. Park, B. J. Park, Y. W. Kim, S. H. Lee, S. Y. Yoon, I. C. Song, W. K. Moon, Y. D. Suh, T. Hyeon, *Adv. Mater.* **2009**, *21*, 4467.

[4] D. L. Dexter, J. H. Schulman, *J. Chem. Phys.* **1954**, *22*, 1063.

[5] L. D. Livanova, I. G. Saitkulov, A. L. Stolov, *Sov. Phys.– Solid State* **1969**, *11*, 750; translation in *Fiz. Tverd. Tela* **1969**, *11*, 918.

[6] a) W. Denk, J. H. Strickler, W. W. Webb, *Science* **1990**, *248*, 73; b) T. Kaino, S. Tomaru, *Adv. Mater.* **1993**, *5*, 172; c) H. S. Nalwa, *Adv. Mater.* **1993**, *5*, 341; d) M. Albota, D. Beljonne, J. L. Brédas, J. E. Ehrlich, J. Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X. L. Wu, C. Xu, *Science* **1998**, *281*, 1653; e) G. S. He, P. P. Markowicz, T. C. Lin, P. N. Prasad, *Nature* **2002**, *415*, 767.

[7] S. Comby, J. C. G. Bünzli, in *Handbook On The Physics And Chemistry Of Rare Earths*, Vol. 37 (Eds: K. A. Gschneidner, Jr., J. C. G. Bünzli, V. K. Pecharsky), Elsevier, Amsterdam, The Netherlands **2007**, p. 217.

[8] K. Binnemans, *Chem. Rev.* **2009**, *109*, 4283.

[9] K. L. Wong, G. L. Law, W. M. Kwok, W. T. Wong, D. L. Phillips, *Angew. Chem. Int. Ed.* **2005**, *117*, 3502.

[10] X. Xiao, J. P. Haushalter, G. W. Faris, *Opt. Lett.* **2005**, *30*, 1674.

[11] C. Y. Sun, X. J. Zheng, X. B. Chen, L. C. Li, L. P. Jin, *Inorg. Chim. Acta* **2009**, *362*, 325.

[12] R. H. C. Tan, M. Motevalli, I. Abrahams, P. B. Wyatt, W. P. Gillin, *J. Phys. Chem. B* **2006**, *110*, 24476.

[13] M. J. Weber, *Phys. Rev.* **1967**, *157*, 262.

[14] I. Hernández, R. H. C. Tan, J. M. Pearson, P. B. Wyatt, W. P. Gillin, *J. Phys. Chem. B* **2009**, *113*, 7474.

[15] Y. Hasegawa, Y. Wada, S. Yanagida, *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 183.

[16] M. G. Shen, C. Cai, W. B. Yi, *J. Fluorine Chem.* **2008**, *129*, 541.

[17] G. M. Salley, R. Valiente, H. U. Güdel, *J. Lumin.* **2001**, *94–95*, 305.

[18] G. M. Salley, R. Valiente, H. U. Güdel, *Phys. Rev. B* **2003**, *67*, 134111.

[19] G. S. Maciel, A. Biswas, P. N. Prasad, *Opt. Comm.* **2000**, *278*, 65.

[20] S. Sivakumar, F. C. J. M. van Veggel, *J. Display Technol.* **2007**, *3*, 176.

[21] I. R. Martín, A. C. Yanes, J. Méndez-Ramos, M. E. Torres, V. D. Rodríguez, *J. Appl. Phys.* **2001**, *89*, 2520.

[22] a) P. Vergeer, T. J. H. Vlugt, M. H. F. Kox, M. I. den Hertog, J. P. J. M. Van Der Eerden, A. Meijerink, *Phys. Rev. B* **2005**, *71*,

014119; b) B. M. van der Ende, L. Aarts, A. Meijerink, *Adv. Mater.* **2009**, *21*, 3073.

[23] R. Martin-Rodriguez, R. Valiente, S. Polizzi, M. Bettinelli, A. Speghini, F. Piccinelli, *J. Phys. Chem. C* **2009**, *113*, 12195.

[24] R. S. Brown, W. S. Brocklesby, W. L. Barnes, J. E. Townsend, *J. Lumin.* **1995**, *63*, 1.

[25] M. Pollnau, D. R. Gamelin, S. R. Luthi, H. U. Güdel, M. P. Hehlen, *Phys. Rev. B* **2000**, *61*, 3337.

[26] M. F. Joubert, *Opt. Mater.* **1999**, *11*, 181.

[27] S. Sivakumar, F. C. J. M. van Veggel, P. S. May, *J. Am. Chem. Soc.* **2007**, *129*, 620.

[28] Y. Qua, X. Kong, Y. Sun, Q. Zeng, H. Zhang, *J. Alloys Compd.* **2009**, *485*, 493.

[29] M. V. D. Vermelho, P. V. dos Santos, M. T. de Araujo, A. S. Gouveia-Neto, F. C. Cassanjes, S. J. L. Ribeiro, Y. Messaddeq, *J. Lumin.* **2003**, *102–103*, 762.

[30] G. M. Salley, R. Valiente, H. U. Gudel, *J. Phys.: Condens. Matter* **2002**, *14*, 5461.

[31] W. Strek, P. J. Deren, A. Bednarkiewicz, Y. Kalisky, P. Boulanger, *J. Alloys Compd.* **2001**, *300 – 301*, 180.

[32] A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandström, S. Lidin, I. Persson, M. Sandström, *Chem.– Eur. J.* **2005**, *11*, 4065.

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