

## Upconversion

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## Near-IR to Near-IR Upconversion Luminescence in Molecular Chromium Ytterbium Salts

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**Abstract:** Upconversion photoluminescence in hetero-oligonuclear metal complex architectures featuring organic ligands is an interesting but still rarely observed phenomenon, despite its great potential from a basic research and application perspective. In this context, a new photonic material consisting of molecular chromium(III) and ytterbium(III) complex ions was developed that exhibits excitation-power density-dependent cooperative sensitization of the chromium-centered  $^2E/{}^2T_1$  phosphorescence at approximately 775 nm after excitation of the ytterbium band  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  at approximately 980 nm in the solid state at ambient temperature. The upconversion process is insensitive to atmospheric oxygen and can be observed in the presence of water molecules in the crystal lattice.

## Introduction

Metal-based upconversion (UC) transforming low-energy photons into an anti-Stokes-shifted luminescence is a very attractive non-linear process for fundamental studies as well as for future applications. Examples are solid inorganic host matrices with low-phonon energies doped with transition metal or lanthanoid cations, either as bulk materials<sup>[1]</sup> or, more recently, as nanocrystalline systems.<sup>[2]</sup> UC was long considered to be impossible in discrete metal-organic com-

plexes<sup>[3]</sup> due to the pronounced non-radiative deactivation of the excited metal states by high-frequency oscillators present in organic ligands like -OH, -NH or -CH groups.<sup>[4]</sup> In the past few years, however, many advances have been achieved in implementing metal-based UC in molecular complex species, some even at ambient temperature and in solution.<sup>[5]</sup> This includes metal chelate-organic chromophore combinations,<sup>[6]</sup> mononuclear metal complexes,<sup>[7]</sup> and hetero-oligometallic sensitizer-activator architectures.<sup>[8,9]</sup> The latter have shown to hold the greatest potential for efficient UC, especially for energy transfer upconversion (ETU) but also for cooperatively sensitized upconversion (CSU). For both UC schemes, sensitizer metal centers (S) with appropriate energy levels and sufficiently long luminescence lifetime are necessary to successfully populate an activator (A) excited state with approximately twice the energy of the excited sensitizer state at relatively low excitation power densities. Among the best sensitizing metal centers are  $\text{Yb}^{3+}$  ( ${}^2F_{5/2}$  at  $\approx 10250\text{ cm}^{-1}$ ,  $\approx 976\text{ nm}$ ) and  $\text{Cr}^{3+}$  (octahedral geometry:  ${}^2E/{}^2T_1$  at  $\approx 15000\text{--}12400\text{ cm}^{-1}$ ,  $\approx 665\text{--}805\text{ nm}$  depending on the ligand field). This has been demonstrated for several emissive UC activators in molecular systems, for example the lanthanoids  $\text{Er}^{3+}$  and  $\text{Tb}^{3+}$ .<sup>[8,9]</sup> The earth-abundant metal  $\text{Cr}^{3+}$  has also gained renewed interest as downshifting luminophore/sensitizer,<sup>[10]</sup> on one hand because of the recently developed class of “molecular ruby” emitters which show very high luminescence quantum yields of the  ${}^2E/{}^2T_1$  phosphorescence of up to 30% at room temperature in solution in the absence of oxygen,<sup>[11]</sup> and on the other hand as successful antenna moieties for the downshifting sensitization of near-IR lanthanoid luminescence.<sup>[12,13]</sup>

Two decades ago, Güdel et al. reported an interesting UC Scheme for the generation of  ${}^2E$  UC emission for solid state hosts such as  $\text{Y}_3\text{Ga}_5\text{O}_{12}$  co-doped with  $\text{Yb}^{3+}$  as sensitizer and  $\text{Cr}^{3+}$  as activator.<sup>[14]</sup> These compounds operate via CSU where two excited  $\text{Yb}^{3+}$  cooperatively transfer the energy from their  ${}^2F_{5/2}$  states to an excited quartet state of  $\text{Cr}^{3+}$  ( ${}^4T_2/{}^4T_1$ ) which subsequently populates the emissive  ${}^2E$  state by intersystem crossing (ISC) (Figure 1). This Scheme is particularly interesting because both, excitation and UC emission, are in the near-IR spectral window, increasingly used for bioimaging.<sup>[15]</sup> In molecular systems, near-IR to near-IR upconversion is unknown and the few systems utilizing the couple Yb/Cr reported so far exhibited UC only at very low temperatures (usually below 100 K) in extended solid inorganic matrices. In the past, however, reports on efficient downshifting energy transfer (EnT)  ${}^2E(\text{Cr}^{3+}) \rightarrow {}^2F_{5/2}(\text{Yb}^{3+})$ ,<sup>[12,13]</sup> that led to deactivation of the UC-emissive  ${}^2E$  state, made the successful

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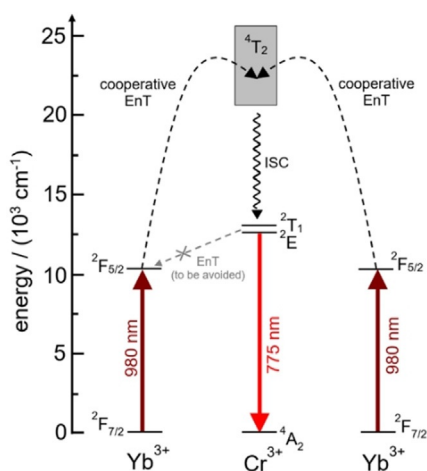
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**Figure 1.** Schematic partial energy-level diagram of the energy levels of  $\text{Yb}^{3+}$  and  $\text{Cr}^{3+}$  (energies given for  $\text{mer}[\text{Cr}(\text{ddpd})_2]^{3+}$ ) relevant for cooperatively sensitized UC involving two  $\text{Yb}^{3+}$  centers absorbing 980 nm light and sensitizing the emission of the  $\text{Cr}^{3+}$  activator.

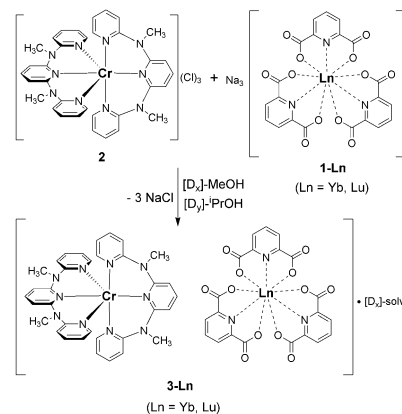
implementation of this attractive UC Scheme unlikely. Especially  $\text{Cr}^{3+}/\text{Yb}^{3+}$ -architectures with highly efficient Dexter EnT (here total angular momentum allowed for  $\Delta J = 1$ )<sup>[16]</sup> in hexacyanidochromate- and oxalato-bridged coordination compounds<sup>[13a-c]</sup> seemed unsuitable for this purpose. On the other hand, dipole-dipole EnT (Förster)  $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$  in oligometallic molecular systems also showed unfavorably high EnT efficiencies of up to ca. 50% despite being forbidden by the total angular momentum selection rule ( $\Delta J = 2, 4, 6$ ).<sup>[13a, 16]</sup>

With these challenges of the  $\text{Cr}^{3+}/\text{Yb}^{3+}$  pair in mind, we revisited the design concept for molecular Yb-Cr-UC. This led to a new photonic material composed of easily accessible  $\text{Cr}^{3+}$  and  $\text{Yb}^{3+}$  complex ions which shows  ${}^2\text{E}/{}^2\text{T}_1$  UC at room temperature already at relatively low excitation power densities.

## Results and Discussion

The main idea was to avoid Dexter EnT from  ${}^2\text{E}(\text{Cr}^{3+})$  to  ${}^2\text{F}_{5/2}(\text{Yb}^{3+})$  and opt for a system, where  $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$  EnT was only possible by a less efficient Förster mechanism. Therefore, we utilized spatially separated metal centers in discrete coordination environments. For the realization of this design, we chose the complex  $\text{mer}[\text{Cr}(\text{ddpd})_2]^{3+}$  (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-ylpyridine-2,6-diamine). This  $\text{Cr}^{3+}$  complex shows a very high phosphorescence quantum yield  $\Phi$  of up to 30% in argon-saturated  $\text{CD}_3\text{CN}$  solution at room temperature (298 K) and even remains quite emissive in air-saturated water with  $\Phi = 2.1\%$ .<sup>[11c,d]</sup> Despite earlier reports on the complex  $[\text{Yb}(\text{dpa})_3]^{3-}$  (dpa = 2,6-pyridine-dicarboxylate) and the only moderately long lifetime of its excited  ${}^2\text{F}_{5/2}$  energy level in the solid state (solid **1-Yb** at 295 K:  $\tau = 2.9 \mu\text{s}$ ),<sup>[3, 13c]</sup> we chose this anion as counterpart for the  $\text{Cr}^{3+}$  complex because of its straightforward synthetic accessibility and its good match with  $[\text{Cr}(\text{ddpd})_2]^{3+}$  in terms of comparable size and opposite charge. The latter parameters were ex-

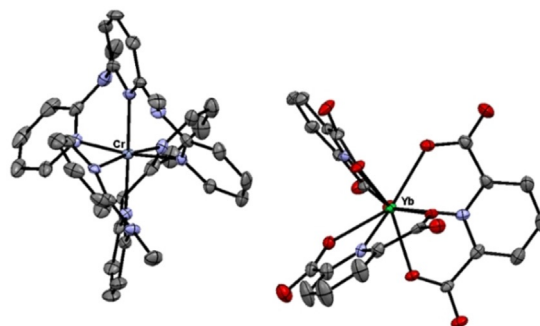
pected to facilitate the crystallization of the desired Cr/Yb ionic solid, where only intermolecular  $\pi$ - $\pi$ -stacking interactions between the different ions occurs. The synthesis of our novel photonic material **3-Yb** was achieved by mixing  $\text{Na}_3[\text{Yb}(\text{dpa})_3] \cdot 6\text{H}_2\text{O}$  (**1-Yb**)<sup>[17]</sup> with  $[\text{Cr}(\text{ddpd})_2]\text{Cl}_3$  (**2**, see SI for details) in an alcoholic solution (Scheme 1). We also prepared



**Scheme 1.** Synthesis of the chromium-lanthanoid salts **3-Ln**.

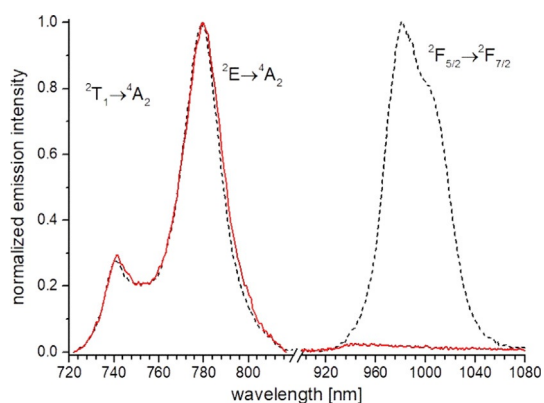
the reference compound **3-Lu** as a structural analogue of **3-Yb**, thereby utilizing the photoinactive nature of  $\text{Lu}^{3+}$  with its  $4f^{14}$  electronic configuration. **3-Yb** and **3-Lu** were obtained as bright yellow solids in good to excellent yields (57–88%). Both, complex anion and cation,<sup>[18]</sup> are chiral but were used as racemates. Elemental analysis of both compounds revealed large amounts of lattice water and methanol in the material (see SI for details). To suppress potentially severe non-radiative deactivation of both the  ${}^2\text{E}/{}^2\text{T}_1$  and  ${}^2\text{F}_{5/2}$  excited states via multiphonon relaxation by C-H and O-H oscillators,<sup>[4]</sup> the syntheses were also repeated with  $[\text{D}_4]\text{-MeOH}/[\text{D}_8]\text{-iPrOH}$ . The X-ray structural analysis of single crystals of **3-Ln** grown from MeOH/*i*PrOH mixtures confirmed that all salts are isostructural, racemic mixtures of the complex ions (Figure 2, see also Table S1 and Figure S1 in the SI).<sup>[19]</sup>

As intended, in the solid material, downshifting EnT in **3-Yb** should only be possible by the forbidden Förster mechanism. In our crystal, each  $\text{Cr}^{3+}$  activator is surrounded



**Figure 2.** Thermal ellipsoid plot of the asymmetric unit in **3-Yb** (Ortep 3 for Windows,<sup>[20]</sup> 50% probability level). Lattice solvent molecules and hydrogen atoms are omitted for clarity.

by five  $\text{Yb}^{3+}$  sensitizers as nearest neighbors with a distance distribution of  $8.75 \text{ \AA} < r_{\text{Cr-Yb}} < 9.07 \text{ \AA}$  (Figure S2 in the SI). Taking into account the distance relationship for  $\text{S} \rightarrow \text{A}$  EnT ( $k_{\text{EnT}} \propto r^{-6}$ ) and assuming similar contributions from all other parameters (e.g. orientation of the chromophores, dipole moments etc.), similar energy transfer rates to the central  $\text{Cr}^{3+}$  activator were expected for the five nearest sensitizers that should hence only vary by a factor of up to  $(8.75/9.07)^{-6} = 1.24$ . Selective excitation of **3-Ln** at  $\lambda_{\text{exc}} = 435 \text{ nm}$  into the  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$  band<sup>[11c,d]</sup> of  $[\text{Cr}(\text{ddpd})_2]^{3+}$  produces the expected chromium phosphorescence  ${}^2\text{E}/{}^2\text{T}_1$  with an emission maximum around 780 nm. For **3-Yb**, excitation at 435 nm leads not only to the  $\text{Cr}^{3+}$  emission (Figure 3) but also to the appearance of a  $\text{Yb}^{3+}$  luminescence ( ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ ) at around 1000 nm (Figure 3). Since the chromium-free precursor **1-Yb** is not emissive upon excitation at 435 nm (Figure S3), this clearly indicated undesired  $\text{Cr} \rightarrow \text{Yb}$  EnT in **3-Yb**. Further evidence for a downshifting EnT between  $\text{Cr}^{3+}$  and  $\text{Yb}^{3+}$  was obtained by time-resolved luminescence measurements under the same conditions (Table 1).



**Figure 3.** Normalized steady-state emission spectra ( $\lambda_{\text{exc}} = 435 \text{ nm}$ ) of **3-Yb** (dashed black line) and **3-Lu** (solid red line) in the solid state at  $T = 298 \text{ K}$  in air. Excitation was at 435 nm. The relative intensities of the emission spectra of the different  $\text{Cr}^{3+}$  and  $\text{Yb}^{3+}$  emission bands were not comparable.

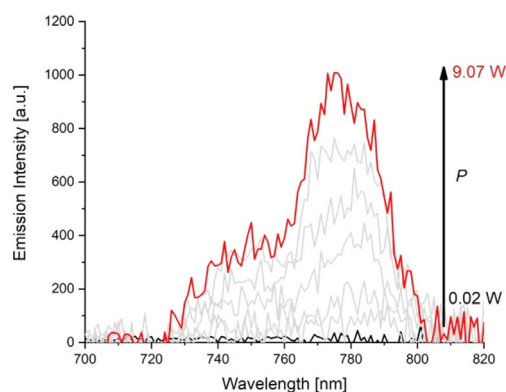
**Table 1:** Luminescence lifetimes  $\tau$  and quantum yields  $\Phi$  of compounds **3-Ln** ( $\text{Ln} = \text{Yb}, \text{Lu}$ ) in the solid state at 298 K for excitation at 435 nm.

Species	$\tau_{2\text{E} \rightarrow 4\text{A}_2}^{\text{air}}$ (783 nm) [ $\mu\text{s}$ ] <sup>[a]</sup>	$\tau_{2\text{E} \rightarrow 4\text{A}_2}^{\text{argon}}$ (783 nm) [ $\mu\text{s}$ ] <sup>[a]</sup>	$\tau_{2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2}}^{\text{air}}$ (980 nm) [ $\mu\text{s}$ ] <sup>[a]</sup>	$\Phi_{2\text{E} \rightarrow 4\text{A}_2}^{\text{air}}$ [%] <sup>[b]</sup>
<b>3-Yb</b>	390 (100%)	380 (100%)	9 (rise, 2%) 369 (decay, 102%)	5.9
<b>3-Yb</b> (deut.)	160 (15%) 390 (85%)	180 (12%) 370 (88%)	12 (rise, 3%) 373 (decay, 103%)	5.8
<b>3-Lu</b> (deut.)	280 (11%) 660 (89%)	320 (12%) 720 (88%)	n.a.	6.8

[a] Lifetimes are fitted mono- or biexponentially, percentages in parentheses give relative amplitudes of the components, estimated uncertainty of  $\tau \pm 5\%$ . [b] Measured using an integrating sphere setup Quantaaurus-QY C11347-11 (see Supporting Information for details), estimated uncertainty  $\pm 5\%$ .

The decay curve of the  $\text{Cr}^{3+}$ -centered  ${}^2\text{E}/{}^2\text{T}_1$  emission of **3-Yb** exhibited monoexponential decay kinetics with a long lifetime  $\tau = 390 \mu\text{s}$ . The decay profile of the  $\text{Yb}^{3+}$  emission revealed biexponential kinetics with a long luminescence lifetime of 369  $\mu\text{s}$ , uncharacteristic for molecular  $\text{Yb}^{3+}$  species<sup>[4]</sup> which normally show luminescence lifetimes in the low  $\mu\text{s}$ -range. The lifetime of 369  $\mu\text{s}$  closely matches the  ${}^2\text{E}/{}^2\text{T}_1$  lifetime of the  $\text{Cr}^{3+}$  emission of 390  $\mu\text{s}$ . In addition, a noticeable rise time component ( $\tau = 9 \mu\text{s}$ ) was present. These observations are all typical for EnT from the long-lived  ${}^2\text{E}$  state to  $\text{Yb}^{3+}$ .<sup>[13d-f]</sup> As detailed before, this EnT could reduce the efficiency of the  ${}^2\text{E}$  upconversion luminescence by non-radiatively depopulating this state. To quantify the potential loss in efficiency, we determined the quantum yield of the  ${}^2\text{E}/{}^2\text{T}_1$  phosphorescence of **3-Yb** and **3-Lu** upon excitation at 435 nm (Table 1). These measurements yielded  $\Phi$  values of 6.8% and 5.8% for deuterated **3-Lu** and **3-Yb**, respectively, and hence revealed only a moderate decrease of 15%  ${}^2\text{E}$  quantum yield for **3-Yb** relative to **3-Lu**. This is favorably low compared to the loss due to Förster EnT reported for analogous downshifting systems in the literature (ca. 20–50%),<sup>[13d-f]</sup> especially when considering that in our case each  $\text{Cr}^{3+}$  has considerably more next  $\text{Yb}^{3+}$  neighbors (here 5, previously 1 at similar distances  $r_{\text{Cr-Yb}}$ ) as EnT acceptors. Surprisingly, neither the crystallization of **3-Yb** from deuterated solvents nor the presence of oxygen significantly affected the luminescence decay kinetics of  $\text{Cr}^{3+}$  in **3-Yb** and **3-Lu** (Table 1). The decay profile of the  $\text{Cr}^{3+}$   ${}^2\text{E}/{}^2\text{T}_1$  emission in deuterated **3-Lu** in air also showed biexponential decay kinetics and revealed considerably longer lifetimes than observed for **3-Yb** (Table 1). Deuterated **3-Lu**:  $\tau_1 = 660 \mu\text{s}$ , 89% and  $\tau_2 = 280 \mu\text{s}$ , 11%.

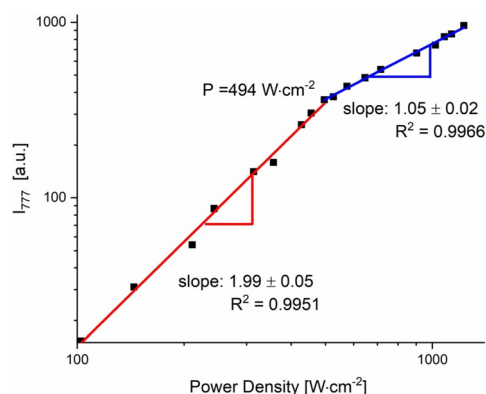
Finally, UC measurements of **3-Yb** and **3-Lu** were performed at 298 K under ambient atmosphere. Expectedly, **3-Lu** did not yield any UC emission upon excitation at 976 nm. In contrast, excitation of the  $\text{Yb}^{3+}$  sensitizers in **3-Yb** produced intense  ${}^2\text{E}/{}^2\text{T}_1$  UC emission of the activator  $\text{Cr}^{3+}$  with a maximum around  $\lambda_{\text{em}} = 780 \text{ nm}$  (Figure 4). Time-resolved studies confirmed successful UC in **3-Yb** and deuterated **3-Yb**, while no luminescence signal was observed for **3-Lu** (Figure S9). For **3-Yb**, excitation power densities ( $P$ )



**Figure 4.** Excitation power-density ( $P$ ) dependence of the UC luminescence ( ${}^2\text{E}/{}^2\text{T}_1 \rightarrow {}^4\text{A}$ ) of **3-Yb** (298 K, solid, air) for  $\text{Yb}^{3+}$  excitation at  $\lambda_{\text{ex}} = 976 \text{ nm}$ .



as low as  $P \approx 67 \text{ W cm}^{-2}$  were sufficient for the observation of UC which is a reasonably low threshold for UC by a normally not very efficient CSU mechanism.<sup>[5]</sup> The  $P$  dependence of the UC emission intensity depicted in Figure 5 shows two distinct regions. Below  $P \approx 494 \text{ W cm}^{-2}$ , the number of excited  $\text{Yb}^{3+}$  is low and UC depends quadratically on  $P$  indicating a biphotonic process (log-log plot: slope or photonic order of 1.99). At higher  $P$ , sensitizer saturation slowly occurs as indicated by a photonic order below 2 which eventually approaches 1 as is typical for a one-photon process (slope or photonic order of 1.05).<sup>[21]</sup>



**Figure 5.** Log–log plot of the upconversion  ${}^2\text{E}$  luminescence ( $\lambda_{\text{em}} = 777 \text{ nm}$ ) versus the incident power density in **3-Yb** ( $\lambda_{\text{ex}} = 976 \text{ nm}$ , 298 K, solid)—gradients obtained by linear fitting for the low (red) and high (blue) power density regimes.

## Conclusion

In conclusion, by carefully revisiting earlier downshifting  $\text{Cr}^{3+}/\text{Yb}^{3+}$  systems, we realized a novel near-IR to near-IR upconversion (UC) material by simply combining  $\text{Cr}^{3+}$  and  $\text{Yb}^{3+}$  complexes in an ionic solid. This expands the small number of molecular UC examples by a new pair of sensitizer/activator metal complexes. Importantly, UC can be realized with synthetically easily accessible non-deuterated/non-halogenated building blocks at room temperature in the presence of oxygen and water molecules. This proof-of-concept study will pave the way to a new class of photonic materials and enable new possibilities for the field of molecular UC.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** chromium · energy transfer · luminescence · upconversion · ytterbium

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