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Synthesis of Rare Earth (Oxo)nitridocarbonates by Employment of **Supercritical** Carbon Dioxide, Single-source Precursor, Solid-State and Ion Exchange Reactions

Sandro Pagano,^[a] Martin Zeuner,^[a] Ulrich Baisch^[a,b] Wolfgang Schnick^{[a]*}

Keywords: Lanthanides; Solid-state reactions; Luminescence; Molecular precursor; Oxonitridocarbonates



Abstract

Novel synthetic approaches to rare earth nitrido- and oxonitridocarbonates are described. Dioxy mono-carbodiimides ($\text{Ln}_2\text{O}_2\text{CN}_2$) from the second half of the lanthanide series are accessible by insertion of supercritical CO_2 into lanthanide amido compounds (e.g. $[(\text{Cp}_2\text{ErNH}_2)_2]$), forming single-source precursors. Ammonolysis of amorphous carbamate compounds affords phase pure $\text{Ln}_2\text{O}_2\text{CN}_2$, which are also accessible via the crystalline carbamate compound $[\text{Ln}_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-OC(O}t\text{Bu)NH}\}\text{Cp}_4]$ ($\text{Ln} = \text{Y, Ho, Er, Yb}$). Urea complexes and homoleptic cyanates of europium and strontium have been synthesized by solid-state reaction of urea with the respective metals. Subsequent thermal treatment (160 - 240 °C) results in formation of solvent-free homoleptic cyanates. The Eu^{2+} -doped compounds $[\text{Sr}(\text{OCN})_2(\text{urea})]:\text{Eu}^{2+}$ and $\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$ as well as the respective pure Eu-compounds exhibit strong broad band emissions due to $4f^65d^1-4f^7$ transitions in the bluish green region. Furthermore, rare earth dicyanamides $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ as well as $\text{Ln}[\text{N}(\text{CN})_2]_3$ with $\text{Ln} = \text{Eu, Tb, Gd}$ have been prepared by ion exchange in aqueous solution, followed by evaporation of the solvent at room temperature. Condensed nitridocarbonates

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3 such as rare earth tricyanomelaminates $[\text{NH}_4]\text{Ln}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7\cdot\text{H}_2\text{O}$ with Ln = La-Nd, Sm-
4 Dy have been obtained through ion exchange reactions. The luminescence properties of the
5 europium and terbium dicyanamides as well as the tricyanomelaminates have been explored
6 in detail.
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33 Introduction

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35 Over the last decades, inorganic rare earth compounds have emerged from chemical **oddities**
36 to advanced functional materials. Classical application areas of lanthanide complexes as well
37 as solid-state compounds are homogeneous and heterogeneous catalysts,^[1-3] magnetic
38 devices^[4] and materials for light conversion (phosphors).^[5] Oxidic and nitridic rare earth
39 compounds play an important role for the development of new materials.
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45 We have focused on the synthesis of reactive lanthanide nitrido-precursors and new solid-
46 state compounds based solely on the elements Ln/O/C/N. The first well-established
47 compound in this system was characterized by Hashimoto et al. in 1995. The series of
48 lanthanide dioxy mono-carbodiimides ($\text{Ln}_2\text{O}_2\text{CN}_2$, Ln = La - Gd) was originally synthesized
49 by reacting the respective oxides with a stream of NH_3 at 950 °C in a graphite crucible.^[6,7]
50 $\text{Ln}_2\text{O}_2\text{CN}_2$ are **built** up from $[\text{Ln}_2\text{O}_2]^{2+}$ layers interconnected by carbodiimide (CN_2^{2-}) ions.
51 Owing to the structural affinity to rare earth oxysulfides, which are of significant interest as
52 phosphors for CRT and X-ray scintillators, doped lanthanide dioxy mono-carbodiimides have
53 been investigated thoroughly.^[8-16] However, the synthesis of the heavy rare earth lanthanide
54 dioxy mono-carbodiimides (Ln = Tb - Lu) has not been reported until recently.^[13,15,16] Due to
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3 the high thermal stability of binary rare earth oxides, carbides and nitrides specific synthesis
4 routes are inevitable to expand the field of lanthanide (oxo)nitridocarbonates. Metathesis
5 reactions between lanthanide halides and lithium cyanamide studied by Meyer et al.^[17] gave
6 access to various rare earth carbodiimide compounds characterized in the last years:
7 $\text{La}_2\text{O}(\text{CN}_2)_2$,^[18] $\text{Ln}_2(\text{CN}_2)_3$ (Ln = Y, La - Lu);^[19] $\text{Ce}_3(\text{CN}_2)_3\text{N}$,^[20] $\text{LiEu}_2(\text{CN}_2)_3$,^[21] EuCN_2 .^[22]
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9 Compared to the rapidly growing field of carbodiimide chemistry other rare earth
10 (oxo)nitridocarbonates such as cyanates, dicyanamides or carbamates have been rarely
11 mentioned in the literature.^[23-26] To avoid formation of the thermodynamically favored binary
12 oxides, carbides and nitrides a varied chemistry of rare earth (oxo)nitridocarbonates is
13 strongly dependent on the development of inventive reaction strategies. Consequently, we
14 have focused on low temperature approaches towards other rare earth (oxo)nitridocarbonates
15 including carbamates, carbodiimides, cyanates, dicyanamides and tricyanomelaminates.
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19 The following research report is structured by the respective synthesis strategy – starting with
20 tailor-made precursors, reactions in supercritical CO_2 and ammonolysis to afford
21 nanocrystalline LnN and heavy rare earth $\text{Ln}_2\text{O}_2\text{CN}_2$. Subsequently, the utilization of urea as
22 cyanate donor for the controlled synthesis of $\text{M}(\text{OCN})_2$ (M = Sr, Eu) is described. Ion
23 exchange reactions for rare earth dicyanamides and tricyanomelaminates will be discussed at
24 the end of this report.
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27 28 29 30 31 32 33 34 35 36 37 38 39 40 **Reactive Lanthanide Nitride Materials**

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42 Novel synthetic approaches targeting binary or ternary nitrogen-containing compounds are of
43 general interest, especially in solid-state chemistry, in which basic compounds are often
44 obtained in a higher purity by non-classical reaction routes. Binary lanthanide nitrides are rare
45 earth materials of fundamental interest. There are, however, only a few successful synthetic
46 approaches known for the synthesis of such simple compounds with defined composition. Our
47 general interest to target new nitride containing materials with molecular-precursor
48 syntheses,^[27,28] led us to utilize organolanthanide molecular precursors for solid-state
49 synthesis of highly activated rare earth nitrido compounds (Scheme 1). On this background
50 molecular precursor compounds with ligands exhibiting an adequate thermal lability for
51 subsequent pyrolysis reactions were targeted.^[29]
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In the 1960s, Wilkinson^[30] and Fischer^[30-33] synthesized the first rare earth metallocenes and
observed their ability to bind ammonia. During our search for reactive lanthanide nitride

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3 materials we have extensively studied the reaction of Cp₃Ln complexes (**1**, Ln = Sm, Dy, Ho,
4 Er, Yb) with liquid ammonia yielding sublimable ammine complexes (**2**).^[34] Other lanthanide
5 metallocenes (Ce, Nd, Eu) also reacted with NH₃, but did not show thermal stability.
6 Structural analysis, carried out for the first time for [Cp₃LnNH₃] compounds, showed that the
7 Ln–N distances do not increase linearly from Er to Gd. The Gd complex showed surprisingly
8 long Ln–NH₃ bonds, and structural analysis of [Cp₃SmNH₃] remains problematic, because of
9 the difficulties to obtain suitable **single crystals**. Geometry optimizations and calculations of
10 the Gibbs free energies for the ammine products suggested little difference in behavior.
11 Therefore, intermolecular effects during the crystallization process are considered to be
12 responsible for the stabilization of the NH₃ group for **2** with Ln = Sm - Yb. Thermal treatment
13 of these ammine complexes yielded the respective dimeric amido complexes **[Cp₂LnNH₂]₂** **3**
14 (Ln = Dy, Ho, Er, Yb; Scheme 1). In contrast, **2** **with** Ln = Sm, Gd sublime before decompo-
15 sition to the amido complex occurs. X-ray data of amido-cyclopentadienyl-lanthanide(III)
16 complexes were collected for the first time and proved the formation of a dimeric species.
17 DFT calculations performed for the respective monomers showed that decomposition to the
18 amide at higher temperatures changes significantly from [Cp₃DyNH₃] (1.60 kcal·mol⁻¹) to
19 [Cp₃SmNH₃] (5.83 kcal·mol⁻¹), and confirmed the experimental results.^[34]

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34 Further pyrolysis of **2** or **3** with inorganic bases (e.g. LiNH₂) resulted in the formation of
35 reactive nanocrystalline lanthanide nitride powders **4** with an estimated particle size of about
36 40 - 90 nm. LiCp was observed as a by-product and was separated easily by using organic
37 solvents or sublimation in vacuo. Only traces of carbon remained in the product after
38 evacuation and thus, a brownish solid LnN was obtained after pyrolysis. The formation of
39 nitride material LnN was monitored by temperature programmed high-temperature in situ X-
40 ray diffraction experiments, which proved the formation of LnN at temperatures less than
41 300 °C. Scanning electron microscopy (SEM) indicated the formation of agglomerated bulky
42 material (Figure 1a, b), whereas transmission electron microscopy (TEM) measurements of
43 the crude product revealed particle sizes between 80 and 100 nm (Figure 1c). Electron
44 diffraction (ED) experiments on these particles proved the crystallinity of the product and
45 confirmed the formation of LnN (Figure 1d).^[34]

Precursor Approach to Lanthanide Dioxy Mono-Carbodiimides

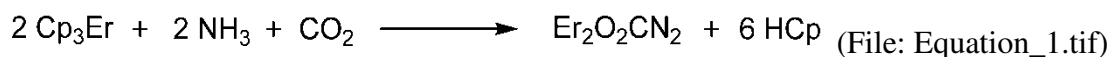
Lanthanide metallocenes were observed to be reasonably stable against thermal treatment under inert gas atmosphere. On the other hand they represent a highly reactive molecular precursor species under CO₂ atmosphere at temperatures above 200 °C. During our studies on the reactivity of lanthanide amine and amido complexes towards CO₂, a number of O/C/N-containing precursors was discovered.^[23] Carbon dioxide was used as a pre-organized C/O source forming labile carbamate intermediates. These compounds turned out to be excellent starting materials for the synthesis of hitherto unknown species in the system Ln/O/C/N. The absorption of CO₂ and the resulting amorphous products have been studied by IR spectroscopy, elemental analysis, and temperature programmed in situ mass spectrometry (MS) studies.^[16]

Two organometallic pathways towards phase-pure synthesis of the heavy lanthanide dioxy mono-carbodiimides have been elaborated. The first involves insertion of CO₂ into the amido complex **3** [(Cp₂ErNH₂)₂] to form the single-source precursor [(Er₂(O₂CN₂H₄)Cp₄)] (**5**). To provide a deeper insight into the structural characteristics of the carbamate precursor, the second approach targeted the synthesis of a crystalline carbamate complex (**6**) which has been fully characterized. After ammonolysis, the precursor approach yielded the hitherto unknown dioxy mono-carbodiimides of Y, Er, Ho and Yb (**7**; Scheme 1).^[16]

Supercritical CO₂ (scCO₂) allows reactions to be carried out in “liquid” carbon dioxide under mild reaction conditions. The mild temperature conditions (50 °C, 220 bar) are of special interest for these precursor compounds because the latter can be carboxylated before thermal degradation of the Cp ligands occurs.^[35-37] Employment of scCO₂ allows the controlled synthesis of Ln/O/C/N containing single-source precursors by absorption and fixation of CO₂. Elemental analysis of the carboxylation product obtained in scCO₂ at 50 °C indicated an atomic ratio Er/O/C/N/H = 2/2/21/2/24 corresponding to the formula [Er₂(O₂CN₂H₄)Cp₄] (**5**). This result corroborates the insertion of one carbon dioxide molecule per dimeric amido complex forming a carbamate moiety. In contrast, the elemental analysis of the carboxylation product obtained in scCO₂ at 150 °C exhibits an atomic ratio of Er/O/C/N/H = 2/10/25/2/24. The resulting formula [Er₂(O₂CNH₂)₂(CO₂)₃Cp₄] corresponds to five CO₂ molecules per dimeric complex. This extensive coordination at the metal center results in an oxygen-rich

product which can be transformed into Er_2O_3 by pyrolysis. These results demonstrate that the amount of CO_2 inserted into the complexes is predominantly dependent on the reaction temperature if the pressure is held constant. Furthermore, the findings highlight the importance of adding at least one equivalent of CO_2 per amido complex in order to obtain useful carbamate precursors and to avoid the formation of lanthanide oxides during subsequent pyrolysis reactions. Ammonolysis of **5** at $700\text{ }^\circ\text{C}$ under NH_3 atmosphere in LiCl/KCl flux yielded highly crystalline and phase-pure dioxy mono-carbodiimide $\text{Er}_2\text{O}_2\text{CN}_2$, whose crystal structure was refined based on XRPD data by the Rietveld method.^[16]

The overall yield of $\text{Ln}_2\text{O}_2\text{CN}_2$ obtained in four reaction steps based on Cp_3Ln as starting material (Scheme 1) is $> 25\text{ mol } \%$. With this synthetic approach it was possible to synthesize pure lanthanide dioxy mono-carbodiimides starting from NH_3 and CO_2 and the well-known Cp_3Ln complexes. The oxophilic character of the lanthanides is the driving force for the reaction.



For the synthesis of a crystalline carbamate complex, *t*-butyl carbamate was considered as an appropriate ligand as it is easily available and exhibits an unprotected amine moiety. As illustrated in Scheme 1, Cp_3Ln ($\text{Ln} = \text{Y, Ho, Er, Yb, Lu}$) reacts with one equivalent of *t*-butyl carbamate in toluene to give **6**, as determined by X-ray crystal structure analysis. Comparing the IR data of **6** and **5** add another piece of evidence for formation and characterization of carbamate compounds by insertion of CO_2 into lanthanide amido complexes (**3**). Ammonolysis of **6** in analogy to **5** afforded phase-pure and crystalline $\text{Ln}_2\text{O}_2\text{CN}_2$ ($\text{Ln} = \text{Y, Ho, Er}$), as proven by elemental analysis and FTIR spectroscopy. The PXRD pattern of $\text{Ln}_2\text{O}_2\text{CN}_2$ ($\text{Ln} = \text{Y, Ho, Er, Yb}$) was indexed using similar lattice constants and the same space group as for $\text{Ln}_2\text{O}_2\text{CN}_2$ with $\text{Ln} = \text{Ce} - \text{Gd}$.^[7] The structures were refined in the space group $P\bar{3}m1$ by the Rietveld method.^[16] Their structure is built up from trigonal $[\text{Ln}_2\text{O}_2]^{2+}$ layers interconnected by carbodiimide ions. The Ln^{3+} -ions are coordinated by four oxygen and three nitrogen atoms (Figure 2).

Our studies revealed that the well known Cp_3Ln complexes can be utilized to bind gaseous reactants such as CO_2 or even NH_3 and thus use them for tailor-made precursor design in the synthesis of solid-state materials to form compounds which are not accessible by standard routes. Nitridic lanthanide materials are of particular interest in materials chemistry of optically active or semiconducting compounds. The reactivity studies of these precursor

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3 compounds towards CO₂ reported herein enlarge the potential of amorphous O/C/N-
4 containing solids as future starting materials for the synthesis of new functional materials.
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7 Urea Route to Homoleptic Cyanates

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10 Employment of urea to generate alkali metal cyanates starting from alkali salts (oxides,
11 hydroxides, carbonates) is a common synthetic approach. Nevertheless only a few reports^[38,39]
12 are known about alkaline earth and lanthanide cyanates and to the best of our knowledge
13 neither systematic investigations nor any structural information has been published for
14 homoleptic cyanates of the latter elements. The decomposition of urea at approximately
15 130 °C, yielding isocyanic acid and ammonia, can be utilized to oxidize electropositive metals
16 such as Eu or Sr.^[40,41] The reaction of three equivalents of urea with Sr or Eu metal in closed
17 ampoules yields [M(OCN)₂(urea)] (M = Sr, Eu), whereas the thermal treatment under vacuum
18 at temperatures of 160 - 240 °C affords evaporation of urea and subsequent formation of
19 solvent-free homoleptic cyanates of Sr and Eu, respectively (see Scheme 2). To avoid
20 oxidation of Eu²⁺ to Eu³⁺ all manipulations were conducted under inert gas atmosphere. For
21 all compounds a phase-pure synthesis was developed and the compounds were fully
22 characterized by means of spectroscopic, magnetic, thermal and crystallographic methods.
23 According to single-crystal X-ray diffraction the isotypic complexes [M(OCN)₂(urea)] (M =
24 Eu, Sr) exhibit a layer-like arrangement of urea and OCN⁻. The structure is built up from Eu²⁺
25 centered chains of face-sharing square antiprisms (Figure 3). These chains are connected by
26 cyanate ions to form layers parallel to (100). The C(NH₂)₂-backbones of urea are filling the
27 space between the layers and exhibit H-bonding to adjacent cyanato anions. The distance
28 between the adjacent Eu²⁺ atoms (Eu1-Eu1: 3.8969(8) Å) is slightly shorter than the sum of
29 their van-der-Waals radii. No magnetic interactions between the Eu atoms have been detected
30 in the temperature range between 1.8 and 300 K by magnetic measurements. The thermal
31 behavior of [M(OCN)₂(urea)] was investigated by TG/DTA measurements and high-
32 temperature in situ X-ray diffractometry (HT-PXRD). The TG/DTA measurements indicate
33 the onset of the decomposition at 160 °C accompanied by an X-ray amorphous state above
34 150 °C. In accordance with HT-PXRD the crystalline, homoleptic cyanates of Sr and Eu
35 M(OCN)₂ are formed above 200 °C and they are stable up to 500 °C. Further heating to
36 700 °C results in the formation of β-SrCN₂^[42] for [Sr(OCN)₂(urea)] and Eu₂O₂CN₂ for
37 [Eu(OCN)₂(urea)];^[7] for the latter unknown phases are also observed in the PXRD of the
38 residue. In contrast to the respective thiocyanates of Eu and Sr, cyanates are more temperature
39 sensitive and decompose without melting.^[43] The PXRD pattern of M(OCN)₂ was indexed
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3 using a similar unit cell setting as that of $\text{Sr}(\text{N}_3)_2$. Subsequently, starting from the structural
4 model of $\text{Sr}(\text{N}_3)_2$ ^[44] the crystal structures of $\text{Sr}(\text{OCN})_2$ and $\text{Eu}(\text{OCN})_2$ were refined in space
5 group *Fddd* by the Rietveld method.^[40] The structure consists of one metal site coordinated by
6 8 cyanate molecules forming square antiprisms. Consequently, each cyanate ion is
7 coordinated to four metal centers (Figure 4). The polyhedra are connected to each other by
8 four common edges. The face-sharing of Eu^{2+} polyhedra in $[\text{M}(\text{OCN})_2(\text{urea})]$ is converted
9 into exclusive corner-sharing in $\text{M}(\text{OCN})_2$.

10 Both compounds $[\text{Eu}(\text{OCN})_2(\text{urea})]$ and $\text{Eu}(\text{OCN})_2$ show strong green to blue emission at low
11 temperatures when irradiated with a UV lamp. However, luminescence is fully quenched at
12 room temperature. A similar behavior has been observed for $\text{M}(\text{SCN})_2:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr},$
13 Ba).^[45] To investigate the luminescence properties of the cyanate compounds in detail we
14 prepared the Eu compounds as well as the Eu-doped Sr compounds $[\text{Sr}(\text{OCN})_2(\text{urea})]:\text{Eu}^{2+}$
15 and $\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$ (doping rate 0.5 % Eu^{2+}). Excitation and emission spectra at different
16 temperatures from 10 K to RT have been collected. The luminescence properties of these
17 compounds and $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ are summarized in Table 1. Comparison of the luminescent
18 properties of $\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$ to those of $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ is advantageous due to the similarity
19 of the cation coordination polyhedra.^[45] The emission curves of all spectra appear nearly in
20 Gaussian shape. This is in accordance with the structural analysis where only one Eu^{2+} site
21 has been located. The excitation spectra represent broad bands without any fine structure. The
22 assignment of the maxima of the lowest excited $5d^14f^7(^7F_0)$ states, which is necessary for the
23 determination of the Stokes shift, is rather difficult because of these broad bands. For all
24 compounds no luminescence spectra could be detected at temperatures above 170 K (T_{quench}).
25 The temperature at which the intensity of signal is half of that at 10 K is between 35 and 65 K
26 ($T_{1/2}$). The emission bands for the urea adducts are located in the green region at 513 nm for
27 $[\text{Eu}(\text{OCN})_2(\text{urea})]$ and at 501 nm for $[\text{Sr}(\text{OCN})_2(\text{urea})]:\text{Eu}^{2+}$, whereas signals for homoleptic
28 cyanates are shifted to remarkably higher energies (Table 1); the emission maxima are located
29 at 475 nm for $\text{Eu}(\text{OCN})_2$ and 457 nm for $\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$. Additionally, the Stokes shift for the
30 homoleptic cyanates is much smaller. This can be explained by the fact that the structure of
31 the homoleptic cyanates is much more rigid and prevents a large increase of the Eu^{2+} ion
32 distance in the excited states. The emission maxima of the urea adducts are similar to
33 $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ in the green region, whereas the homoleptic cyanates exhibit a strong blue
34 shift. This can be explained by the larger covalency of the host lattice caused by the urea
35 ligand. It shifts the center of gravity of the excited $5d^14f^6$ states to lower energy
36 (nephelauxetic effect). The red shift of the Eu^{2+} emission of homoleptic thiocyanates versus
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3 cyanates can be expected because of the formal replacement of oxygen by sulfur and thus, the
4 more covalent environment around Eu^{2+} in thiocyanates. Compared to the emission maxima
5 of nitrides ($\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$: 590 nm)^[46] and simple oxides ($\text{SrO}:\text{Eu}^{2+}$: 625 nm)^[47] signals of the
6 cyanate compounds are significantly shifted towards higher energy.
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10 11 12 13 14 **Luminescent Rare Earth Dicyanamides**

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16 Investigating the luminescence properties of rare earth dicyanamides is of particular interest
17 as the dicyanamide ion can be regarded as a hybrid between an inorganic ion and a C/N-
18 ligand. However, in the field of lanthanide dicyanamides, most of the solids reported until
19 now are metal-organic dicyanamide complexes such as $[\text{Ln}[\text{N}(\text{CN})_2]_3(2,2'\text{-bipy})_2(\text{H}_2\text{O})]$ with
20 $\text{Ln} = \text{La}, \text{Sm}, \text{Gd}$.^[48] We have been able to synthesize hydrated $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ ($\text{Ln} =$
21 $\text{Eu}, \text{Gd}, \text{Tb}$)^[49,50] by ion exchange reactions in aqueous solutions. Evaporation of H_2O at
22 elevated temperatures was followed by the formation of the non-hydrated $\text{Ln}[\text{N}(\text{CN})_2]_3$ ($\text{Ln} =$
23 $\text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$)^[24,49] species. The crystal structures of hydrated
24 $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ have been determined using single-crystal X-ray diffractometry. The
25 hydrated compounds are isostructural and are built up from irregular quadratic antiprismatic
26 LnN_6O_2 polyhedra connected to each other by three crystallographically independent
27 dicyanamide ($[\text{N}(\text{CN})_2]_3^-$) ions. There are two water molecules completing the coordination
28 sphere of the lanthanide ion (Figure 5). The arrangement of six dicyanamide groups around
29 the lanthanide ion causes a two-dimensional sheet arrangement (Figure 6). The metal ions in
30 two adjacent sheets are approximately 8 Å apart from each other. These layers interact
31 through π - π stacking as well as through hydrogen bonding. The thermal stability of
32 $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Eu}$) has been studied using thermogravimetric and/or
33 differential thermal analysis (TG/DTA). The dehydration of the compound occurs at 150 °C,
34 leading to the formation of anhydrous $\text{Ln}[\text{N}(\text{CN})_2]_3$, and the rearrangement of dicyanamide
35 groups. The coordination number rises from 8 to 9 because the dicyanamide ion is undergoing
36 two different Ln-N coordination modes: i) $\text{Ln} \cdots \text{N}-(\text{CN})_2$ and ii) $\text{Ln} \cdots \text{NC}-\text{N}-\text{CN}$ (Figure 7). The
37 non-hydrated species are isostructural and have been structurally characterized from powder
38 samples.^[24,49]
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58 Figure 8 shows the room-temperature excitation and emission spectra of hydrated
59 $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ and non-hydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$. The emission spectrum of
60 $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$, recorded at $\lambda_{\text{exc}} = 365 \text{ nm}$, shows red luminescence. The typical Eu^{3+}

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3 intra-4f⁶ emission lines were observed, which can be assigned to transitions between the first
4 excited state (⁵D₀) and the ground multiplets (⁷F₀₋₄). The excitation spectrum, monitored at
5 $\lambda_{\text{em}} = 612$ nm is the most intense emission line of Eu³⁺. It exhibits a large broad band between
6 260 and 420 nm, with a maximum at around 335 nm, superimposed with sharp peaks centered
7 at wavelengths extending from 390 to 550 nm. The sharp peaks can be attributed to inner 4f
8 shell ⁷F₀₋₅L₆ (395 nm), ⁷F₀₋₅D₃ (417 nm), ⁷F₀₋₅D₂ (465 nm), ⁷F₀₋₅D₁ (525 nm), and ⁷F₁₋₅D₁
9 (538 nm) transitions of Eu³⁺.^[51] The full width at half-maximum (8000 cm⁻¹) of the broad Eu-
10 N charge-transfer band is comparable with that of the Eu-O charge-transfer band in oxide
11 lattices. However, the position of the Eu-N charge-transfer band is significantly shifted to
12 lower energies compared to that of the oxo compounds (nephelauxetic effect). The excitation
13 spectrum of the non-hydrated Eu[N(CN)₂]₃ shows features similar to those of the spectrum of
14 the hydrated compound except for a slight shift (~10 nm) of the excitation maximum towards
15 a longer wavelength (348 nm), indicating that excitation mechanisms are essentially the same
16 for both the hydrated and non-hydrated phases. The slight shift towards the longer wavelength
17 can be attributed to the formal replacement of two O-donors by three more covalent N-donors
18 in the crystal structure of non-hydrated europium(III) dicyanamide. Figure 9 shows the
19 excitation and emission spectra of Tb[N(CN)₂]₃ · 2H₂O and Tb[N(CN)₂]₃. The excitation
20 spectrum of Tb[N(CN)₂]₃ · 2H₂O, monitored at Tb³⁺ green emission at 545 nm (⁵D₄-⁷F₅),
21 mainly consists of a broad band from 250 to 400 nm with a maximum at 300 nm and super-
22 imposed with sharp lines around 370 nm. The sharp lines originate from intra-4f transitions of
23 Tb³⁺. Excitation into the 4f⁸-4f⁷5d transition of Tb³⁺ at 300 nm yields the characteristic ⁵D₄-
24 ⁷F_J (J = 3-6) emission of Tb³⁺, with ⁵D₄-⁷F₅ green emission as the most intense one ($\lambda_{\text{max}} =$
25 545 nm). Similarly to Eu[N(CN)₂]₃, non-hydrated Tb[N(CN)₂]₃ shows a red shift (~10 nm) in
26 the excitation maximum compared to hydrated Tb[N(CN)₂]₃ · 2H₂O. This can be explained by
27 the different local environment of Tb³⁺ in the hydrated and non-hydrated compounds. The
28 formation of two different crystal structures in turn affects the energy of the d orbital,
29 resulting in excitation maxima at longer wavelengths. The CIE (Commission Internationale
30 d'Eclairage) color coordinates (x, y) of Ln[N(CN)₂]₃ · 2H₂O and Ln[N(CN)₂]₃ with Ln = Eu,
31 Tb are comparable to those of commercial red- and green-emitting phosphors (Table 2).^[46,52]
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55 The quantum efficiencies were measured for both hydrated and non-hydrated phases under
56 monitoring wavelength of 365 nm to compare these phosphors with standard lamp phosphors.
57 The QE study clearly shows that the hydrated phases exhibit comparatively lower efficiencies
58 than the corresponding non-hydrated phases. It is well-known that the non-radiative effect of
59 the OH oscillators of the H₂O molecule affects the luminescence features of trivalent
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lanthanides.^[53] Therefore, comparatively low quantum efficiencies of hydrated dicyanamides can be explained with non-radiative losses by multiphonon emission involving the coordinated water molecules.

Rare Earth Tricyanomelaminates

Even more complex nitridocarbonates such as tricyanomelaminates ($[\text{C}_6\text{N}_9]^{3-}$) can be introduced into the coordination sphere of trivalent rare earth ions by ion exchange reactions. Tricyanomelaminates (TCM) can be regarded as the formal trimerization product of the dicyanamide ion. Depending on the pH value there are reports of non protonated, mono-protonated and diprotonated TCM complexes.^[54-56] Starting from ammonium tricyanomelamine and $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$ an isostructural series of nine lanthanide tricyanomelaminates, $[\text{NH}_4]\text{Ln}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy}$) was obtained by ion exchange reactions.^[57] The structure was found to be built up of La^{3+} and two crystallographically independent monohydrogentricyanomelamine ions $[\text{HC}_6\text{N}_9]^{2-}$, ammonium ions, and crystal water molecules (Figure 10). The monoprotonated $[\text{HC}_6\text{N}_9]^{2-}$ moieties in LaTCM form parallel layers perpendicular to [100] with an interlayer stacking distance of approximately 3.6 Å (Figure 11). The hydrogen atoms H1 and H10 are bound to the triazine ring nitrogen atoms N1 and N10, respectively. In the crystal structure of LaTCM, each La^{3+} ion is surrounded by two nitrogen atoms from two different tricyanomelamine moieties and seven oxygen atoms from crystal water molecules, forming nine-coordinated heptagonal-bi-pyramidal LaN_2O_7 polyhedra. The $[\text{HC}_6\text{N}_9]^{2-}$ ions are coordinated to La^{3+} through their terminal nitrogen atoms N5 and N16. In the crystal structure of LaTCM, intermolecular hydrogen bonds are observed between the protonated ring atoms and the cyanamide side-arms of adjacent $[\text{HC}_6\text{N}_9]^{2-}$ moieties (N1-H1...N15 and N10-H10...N6), giving rise to an eight-membered ring-type arrangement, and thereby forming a tricyanomelamine dimer (Figure 11). Because of the similarity of the X-ray powder patterns, the structures of the other eight rare earth tricyanomelaminates, LnTCM ($\text{Ln} = \text{Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy}$) were assumed to be isotopic and were refined by the Rietveld method, using the lattice parameters and the atomic coordinates of LaTCM as starting values.

The protonated TCM ligand has been assigned from the La compound by solid-state ^1H , ^{13}C , and $^{15}\text{N}\{^1\text{H}\}$ crosspolarization (CP) MAS NMR and advanced CP experiments such as crosspolarization combined with polarization inversion (CPPI) depicted in Figure 12. The ^1H 2D double-quantum single-quantum homonuclear correlation (DQ SQ) spectrum and the $^{15}\text{N}\{^1\text{H}\}$ 2D CP heteronuclear correlation (HETCOR) spectrum have revealed the hydrogen-

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3 bonded (N-H...N) dimer of monoprotonated tricyanomelaminato moieties as well as H-
4 bonding through [NH₄]⁺ ions and H₂O molecules.
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8 Figure 13 shows the excitation and emission spectra of EuTCM. The excitation spectrum
9 monitored at 615 nm shows a series of sharp lines between 300 and 550 nm attributable to
10 Eu³⁺ intra-4f transitions.^[58] Unlike other Eu³⁺ compounds, EuTCM does not show the typical
11 Eu-N charge-transfer band in the excitation spectrum.^[49] This indicates that the Eu-N charge-
12 transfer band in EuTCM might be situated at much higher energy such that it cannot
13 participate in the excitation process. The emission spectrum of EuTCM, recorded at
14 $\lambda_{\text{exc}} = 397$ nm, is composed of the typical Eu³⁺ intra ⁴f₆ emission lines, which can be assigned
15 to transitions between the first excited state (⁵D₀) and the ground multiplets (⁷F₁₋₄).^[58]
16 Furthermore, the ⁵D₀-⁷F₁ line is known to originate from a magnetic dipole transition, while
17 the ⁵D₀-⁷F₂ line originates from an electric dipole transition.^[59]
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29 The excitation spectrum of TbTCM, monitored at the Tb³⁺ green emission at 545 nm (⁵D₄-
30 ⁷F₅), mainly consists of a wide band between 240 and 400 nm with a maximum at 300 nm,
31 superimposed with sharp lines at around 370 and 380 nm, and a further sharp line at 488 nm
32 (Figure 14). The diffuse reflectance spectrum also shows a sharp absorption at 488 nm and a
33 broad band at 300 nm. The sharp lines originate from intra-4f transitions of Tb³⁺. The broad
34 band can be assigned to the ⁴f₈-⁴f₇5d transition of Tb³⁺.^[58] In fluoro and oxo compounds, the
35 ⁴f₈-⁴f₇5d transition of Tb³⁺ is generally observed at higher energy. In the present case, a shift
36 of the f-d transitions to lower energies can be expected due to the nephelauxetic effect.
37 Excitation of the ⁴f₈-⁴f₇5d transition of Tb³⁺ at 300 nm yields the characteristic ⁵D₄-⁷F_J (J = 3-
38 6) emission of Tb³⁺, with ⁵D₄-⁷F₅ green emission as the most intense band ($\lambda_{\text{max}} = 545$ nm).
39 The CIE color coordinates (x, y) of EuTCM and TbTCM as well as quantum efficiencies are
40 summarized in Table 2.
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56 **Conclusion**

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59 During the six year funding period by the DFG Schwerpunktprogramm „Lantha-
60 noidspezifische Funktionalitäten in Molekül und Material“ (SPP 1166, project SCHN
377/10), a variety of inventive synthetic strategies targeting new (oxo)nitridocarbonates was

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3 elaborated. The reaction of Cp_3Ln complexes with NH_3 and CO_2 was studied in detail and
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5 metalorganic intermediates like $[Cp_3LnNH_3]$, $[Cp_2LnNH_2]_2$ and carbamates were investigated
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7 by means of crystallographic and spectroscopic methods. The amine and amido complexes
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9 could be transferred into nanocrystalline LnN powders, whereas the carboxylation reactions
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11 with supercritical CO_2 yielded amorphous lanthanide carbamate compounds. These carbamate
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13 complexes could be utilized by means of pyrolysis reaction to obtain the hitherto unknown
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15 dioxy mono-carbodiimides of the smaller lanthanide ions (Y, Ho-Yb). With this novel
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17 synthetic approach we were able to synthesize phase-pure $Ln_2O_2CN_2$ starting from NH_3 and
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19 CO_2 by employing the well-known Cp_3Ln complexes as molecular precursors. Utilizing urea
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21 as O/C/N donor for the synthesis of new oxonitridocarbonates led to the discovery of both
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23 urea complexes as well as homoleptic cyanates of Sr^{2+} and Eu^{2+} . The reaction of Sr and Eu
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25 metal with urea at 130 °C and subsequent thermal treatment afforded the respective cyanates
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27 phase-pure and in nearly quantitative yields. The luminescence properties of all Eu containing
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29 compounds ($[Eu(OCN)_2(OC(NH_2))]$, $[Sr(OCN)_2(OC(NH_2))]:Eu^{2+}$, $Eu(OCN)_2$, $Sr(OCN)_2:Eu^{2+}$)
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31 were studied in detail from RT to 10 K. In addition to precursor and solid-state approaches
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33 metathesis reaction via ion exchange in aqueous solutions were performed. Starting from
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35 lanthanide chlorides and sodium dicyanamide, hydrated $Ln[N(CN)_2]_3 \cdot 2H_2O$ as well as non-
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37 hydrated dicyanamides $Ln[N(CN)_2]_3$ of the lanthanides could be structurally characterized.
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39 Ion exchange reaction of lanthanide chlorides with ammonium tricyanomelaminates (TCM)
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41 afforded the series of nine isostructural lanthanide tricyanomelaminates
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43 $[NH_4]Ln[HC_6N_9]_2[H_2O]_7 \cdot H_2O$ ($Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy$). The Eu^{3+} and the
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45 Tb^{3+} compounds of both the dicyanamides as well as the tricyanomelaminates exhibit strong
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47 red/green luminescence, respectively. The luminescence was studied in detail comprising
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49 color coordinates, quantum yields, furthermore the electronic transitions have been assigned.
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51 The luminescence properties of all investigated compounds are still far from being suitable for
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53 industrial application, but as both oxidic and nitridic lanthanide doped host lattices play an
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55 important role for the development of new luminescence materials,^[5] the comprehensive
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57 investigations in oxygen and nitrogen coordinating (oxo)nitridocarbonates might provide
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59 fundamental knowledge for the understanding of the correlation between luminescence
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61 properties and the crystallographic structure. In addition, the obtained compounds are
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63 promising precursors for the synthesis of new oxidic as well as nitridic materials, as some of
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65 them are easy to synthesize from line chemicals (e.g. urea).

Acknowledgments

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6 **Scheme 1.** Reaction pathways to lanthanide nitridic material and lanthanide dioxy mono-
7 carbodiimides starting from homoleptic cyclopentadienyl complexes. 1 Ln = Y, Sm, Gd, Dy,
8 Ho, Er, Yb, Lu; 2 Ln = Sm, Gd, Dy, Ho, Er, Yb; 3 Ln = Dy, Ho, Er, Yb; 4 Ln = Sm, Gd, Dy,
9 Ho, Er, Yb; 5 Ln = Er; 6 Ln = Y, Ho, Er, Yb, Lu; 7 Ln = Y, Ho, Er, Yb.
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13 **Scheme 2.** Reaction of metals M = Sr, Eu with urea.
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Table 1. Luminescence properties of $[\text{Eu}(\text{OCN})_2(\text{urea})]$, $[\text{Sr}(\text{OCN})_2(\text{urea})]:\text{Eu}^{2+}$, $\text{Eu}(\text{OCN})_2$, $\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$, and $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$.^[45]

	$[\text{Eu}(\text{OCN})_2(\text{urea})]$	$[\text{Sr}(\text{OCN})_2(\text{urea})]:\text{Eu}^{2+}$	$\text{Eu}(\text{OCN})_2$	$\text{Sr}(\text{OCN})_2:\text{Eu}^{2+}$	$\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ ^[45]
$\lambda_{\text{emmax}} / \text{nm}^{[a]}$	513	501	475	457	508
$\nu_{\text{emmax}} / \text{cm}^{-1[a]}$	19480	19960	21040	21900	19685
FWHM / cm^{-1} (nm) ^[a]	1935 (51)	2180 (55)	1870 (42)	2115 (44)	1550 (40)
$\lambda_{\text{excmax}} / \text{nm}^{[a]}$	454	425	422	421	426
$\nu_{\text{excmax}} / \text{cm}^{-1[a]}$	22000	23500	23700	23770	23474
Stokes Shift / cm^{-1} (nm) ^[a]	3500 (59)	4500 (76)	2660 (53)	1870 (36)	3789 (82)
$T_{\text{quench}} / \text{K}$	140	170	140	160	220
$T_{1/2} / \text{K}$	60	65	35	65	157

[a] at 10 K

Table 2. Luminescence properties of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, $\text{Ln}[\text{N}(\text{CN})_2]_3$ and $[\text{NH}_4]\text{Ln}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$ (Ln = Eu, Tb).

phase	CIE color coordinates		QE / % ($\lambda_{\text{exc}} = 365 \text{ nm}$)	reference
	x	y		
$\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$	0.633	0.359	6	perylene dye (BASF)
$\text{Eu}[\text{N}(\text{CN})_2]_3$	0.638	0.356	10.5	perylene dye (BASF)
$\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$	0.319	0.509	18	$\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ (Philips)
$\text{Tb}[\text{N}(\text{CN})_2]_3$	0.334	0.568	25.4	$\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ (Philips)
$[\text{NH}_4]\text{Eu}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$	0.618	0.362	6	perylene dye (BASF)
$[\text{NH}_4]\text{Tb}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$	0.325	0.575	18	$\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ (Philips)

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7 **Figure 1.** a, b) SEM image of ErN showing the bulky nitride powder. c) TEM image of ErN
8 crystallites. d) Corresponding ED pattern showing the ErN phase.^[34]
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13 **Figure 2.** Crystal structure of $\text{Ln}_2\text{O}_2\text{CN}_2$ (Ln = Ce - Gd; Ho, Er, Yb). Left along [001] and
14 right along [010], Ln big gray, O small gray, C black, N white.
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19 **Figure 3.** Left, view along the [100] direction of $[\text{Eu}(\text{OCN})_2(\text{urea})]$; right, view along the
20 [010] direction. Eu-N/O polyhedra gray, O white, C black, N black/white, H atoms have been
21 omitted for clarity. Ellipsoids at 50 % probability level.^[40]
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26 **Figure 4.** Left, representation of the $\text{M}(\text{OCN})_8$ polyhedra; right, view of the $\text{M}(\text{OCN})_2$
27 structure along [100], disregarding that every polyhedron is further connected to four
28 neighboring polyhedra.^[40]
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33 **Figure 5.** The coordination sphere of Ln^{3+} in $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$; Ln = Eu, Gd, Tb.^[49]
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37 **Figure 6.** Polyhedral representation of the structure of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ along [100]. Ln
38 big white, C black, N gray, O small white and H small black spheres.^[49]
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42 **Figure 7.** Coordination sphere of Ln^{3+} in $\text{Ln}[\text{N}(\text{CN})_2]_3$ with Ln = La, Ce, Pr, Nd, Sm, Eu, Gd,
43 Eu.
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48 **Figure 8.** Excitation ($\lambda_{\text{em}} = 616 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 365 \text{ nm}$) spectra of
49 $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ (solid line) and $\text{Eu}[\text{N}(\text{CN})_2]_3$ (dotted line).^[49]
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54 **Figure 9.** Excitation ($\lambda_{\text{em}} = 545 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 365 \text{ nm}$) spectra of
55 $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2 \text{H}_2\text{O}$ (solid line) and $\text{Tb}[\text{N}(\text{CN})_2]_3$ (dotted line).^[49]
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59 **Figure 10.** Representation of one formula unit of the unit cell of
60 $[\text{NH}_4]\text{La}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$. The hydrogen atoms of the $[\text{NH}_4]^+$ group and water mole-
cules have been omitted.^[57]

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6 **Figure 11.** Views along the *a* axis (a), showing hydrogen bonding between two
7 tricyanomelaminates, and along the *c* axis (b) of the unit cell of
8 $[\text{NH}_4]\text{La}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$, showing the parallel stacking of $[\text{HC}_6\text{N}_9]^{2-}$
9 moieties perpendicular to the *a* axis. The hydrogen atoms of the $[\text{NH}_4]^+$ group and water molecules
10 have been omitted.^[57]
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15 **Figure 12.** ^{13}C and ^{15}N chemical shifts observed for $[\text{NH}_4]\text{La}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$.^[57]
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22 **Figure 13.** The diffuse reflectance (REF), excitation (EXC), and emission (EM) spectra of
23 $[\text{NH}_4]\text{Eu}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$ at room temperature. The excitation and emission spectra
24 were recorded at $\lambda_{\text{em}} = 615$ nm and $\lambda_{\text{exc}} = 397$ nm, respectively.^[57]
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29 **Figure 13.** The diffuse reflectance (REF), excitation (EXC), and emission (EM) spectra of
30 $[\text{NH}_4]\text{Tb}[\text{HC}_6\text{N}_9]_2[\text{H}_2\text{O}]_7 \cdot \text{H}_2\text{O}$ at room temperature. The excitation and emission spectra
31 were recorded at $\lambda_{\text{em}} = 545$ nm and $\lambda_{\text{exc}} = 310$ nm, respectively.
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References

- [1] F. T. Edelmann, *Chem. Soc. Rev.* **2009**, 38, 2253-2268.
- [2] C. Meermann, K. W. Toernroos, W. Nerdal, R. Anwander, *Angew. Chem.* **2007**, 119, 6628-6633; *Angew. Chem., Int. Ed.* **2007**, 46, 6508-6513.
- [3] N. S. Babu, R. Sree, P. S. S. Prasad, N. Lingaiah, *Energy Fuels* **2008**, 22, 1965-1971.
- [4] J. Fidler, D. Suess, T. Schrefl, *Handbook of Magnetism and Advanced Magnetic Materials* **2007**, 4, 1945-1968.
- [5] R.-J. Xie, N. Hirosaki, *Sci. Technol. Adv. Mater.* **2007**, 8, 588-600.
- [6] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, *J. Solid State Chem.* **1995**, 114, 592-594.
- [7] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, *J. Solid State Chem.* **1996**, 125, 37-42.
- [8] E. Saeilynoja, M. Lastusaari, J. Hoelsaea, P. Porcher, *J. Lumin.* **1997**, 72, 201-203.
- [9] J. Holsa, R.-J. Lamminmaki, M. Lastusaari, P. Porcher, E. Sailynoja, *J. Alloys Compd.* **1998**, 275-277, 402-406.
- [10] J. Holsa, R.-J. Lamminmaki, M. Lastusaari, E. Sailynoja, P. Porcher, P. Deren, W. Streck, *Spectrochim. Acta, Part A:* **1998**, 54, 2065-2069.
- [11] M. Takahashi, Y. Hashimoto, S. Kikkawa, H. Kobayashi, *Zairyo* **2000**, 49, 1230-1234.
- [12] T. Takeda, N. Hatta, S. Kikkawa, *Chem. Lett.* **2006**, 35, 988-989.
- [13] M. Li, W. Yuan, J. Wang, C. Gu, H. Zhao, *Powder Diffr.* **2007**, 22, 59-63.
- [14] J. Sindlinger, J. Glaser, H. Bettentrup, T. Jüstel, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2007**, 633, 1686-1690.
- [15] M. Lei, H. Z. Zhao, H. Yang, B. Song, L. Z. Cao, P. G. Li, W. H. Tang, *J. Alloys Compd.* **2008**, 460, 130-137.
- [16] M. Zeuner, S. Pagano, W. Schnick, *Chem. Eur. J.* **2008**, 14, 1524-1531.
- [17] J. Glaser, H.-J. Meyer, *Angew. Chem.* **2008**, 120, 7658-7661; *Angew. Chem., Int. Ed.* **2008**, 47, 7547-7550.
- [18] R. Srinivasan, S. Tragl, H. J. Meyer, *Z. Anorg. Allg. Chem.* **2005**, 631, 719-722.
- [19] J. Glaser, L. Unverfehrt, H. Bettentrup, G. Heymann, H. Huppertz, T. Juestel, H. J. Meyer, *Inorg. Chem.* **2008**, 47, 10455-10460.
- [20] L. Unverfehrt, M. Stroebale, J. Glaser, H. J. Meyer, *Z. Anorg. Allg. Chem.* **2009**, 635, 1947-1952.

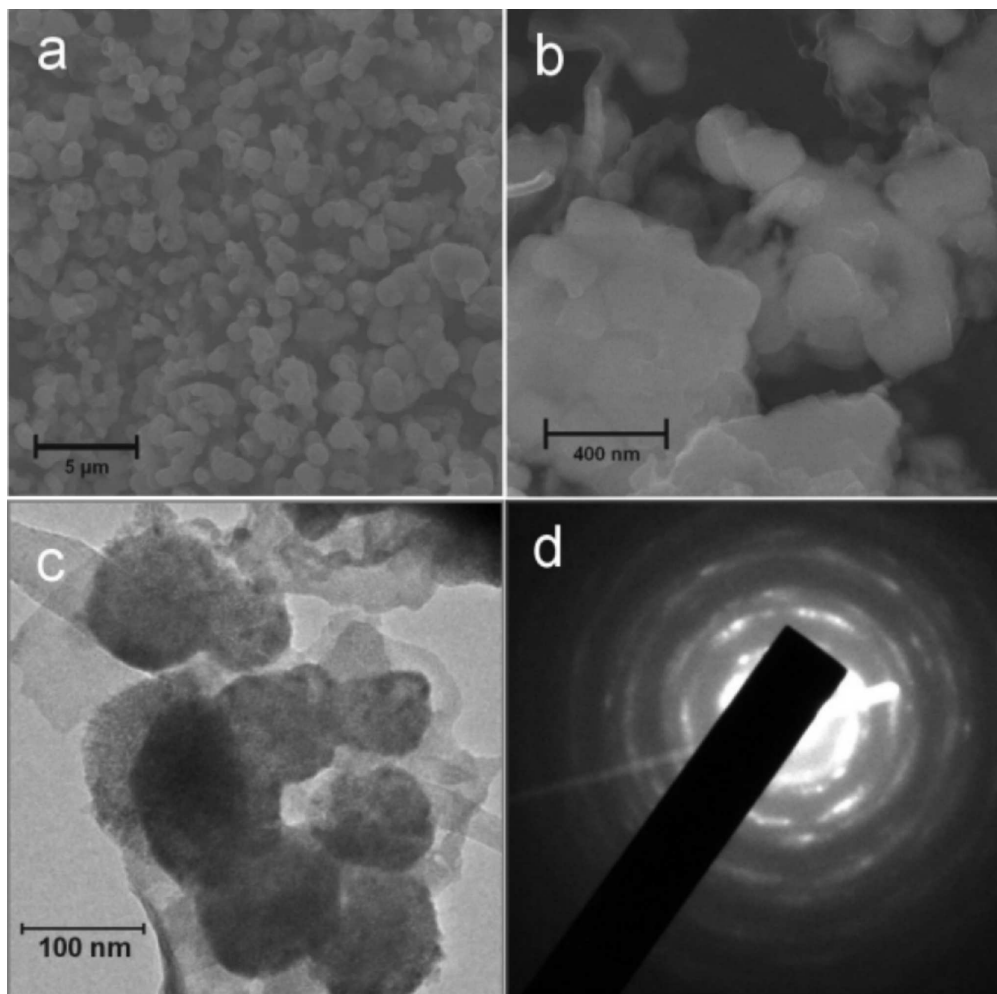
- 1
2
3 [21] W. Liao, C. Hu, R. K. Kremer, R. Dronskowski, *Inorg. Chem.* **2004**, *43*, 5884-5890.
4
5 [22] O. Reckeweg, F. J. DiSalvo, *Z. Anorg. Allg. Chem.* **2003**, *629*, 177-179.
6
7 [23] U. Baisch, S. Pagano, M. Zeuner, W. Schnick, *Eur. J. Inorg. Chem.* **2006**, 3517-3524.
8
9 [24] B. Juergens, E. Irran, W. Schnick, *J. Solid State Chem.* **2005**, *178*, 72-78.
10
11 [25] M. S. Wickleder, *Chem. Rev.* **2002**, *102*, 2011-2087.
12
13 [26] J. Liu, E. A. Meyers, J. A. Cowan, S. G. Shore, *Chem. Commun.* **1998**, *18*, 2043-2044.
14
15 [27] W. Schnick, R. Bettenhausen, B. Götze, H. A. Hoeppe, H. Huppertz, E. Irran, K.
16 Koellisch, R. Lauterbach, M. Orth, S. Rannabauer, T. Schlieper, B. Schwarze, F.
17 Wester, *Z. Anorg. Allg. Chem.* **2003**, *629*, 902-912.
18
19 [28] W. Schnick, *Angew. Chem.* **1999**, *111*, 3511 –3512; *Angew. Chem. Int. Ed.* **1999**, *38*,
20 3309 –3310.
21
22 [29] U. Baisch, S. Pagano, M. Zeuner, J. Schmedt auf der Günne, O. Oeckler, W. Schnick,
23 *Organometallics* **2006**, *25*, 3027-3033.
24
25 [30] J. M. Birmingham, G. Wilkinson, *J. Am. Chem. Soc.* **1956**, *78*, 42-44.
26
27 [31] E. O. Fischer, H. Fischer, *J. Organomet. Chem.* **1966**, *6*, 141-148.
28
29 [32] R. D. Fischer, H. Fischer, *J. Organomet. Chem.* **1965**, *4*, 412-414.
30
31 [33] H. Fischer, *Doctoral thesis*, Technische Hochschule München, Germany, **1965**.
32
33 [34] U. Baisch, S. Pagano, M. Zeuner, N. Barros, L. Maron, W. Schnick, *Chem. Eur. J.*
34 **2006**, *12*, 4785-4798.
35
36 [35] J. A. Behles, J. M. DeSimone, *Pure Appl. Chem.* **2001**, *73*, 1281-1285.
37
38 [36] P. Raveendran, Y. Ikushima, S. L. Wallen, *Acc. Chem. Res.* **2005**, *38*, 478-485.
39
40 [37] M. Solinas, J. Jiang, O. Stelzer, W. Leitner, *Angew. Chem.* **2005**, *117*, 2331-2335;
41 *Angew. Chem. Int. Ed.* **2005**, *44*, 2291-2295.
42
43 [38] H. A. Baskin, U.S. Patent 19.620.711, **1963**.
44
45 [39] D. O. De Pree, K. L. Lindsay, U.S. Patent 2.801.154, **1957**.
46
47 [40] S. Pagano, G. Montana, C. Wickleder, W. Schnick, *Chem. Eur. J.* **2009**, *15*, 6186-
48 6193.
49
50 [41] G. Meyer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 201-222.
51
52 [42] W. Liao, R. Dronskowski, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*,
53 i124.
54
55 [43] C. Wickleder, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1693-1698.
56
57 [44] O. Reckeweg, A. Simon, *Z. Naturforsch., B: Chem. Sci.* **2003**, *58*, 1097-1104.
58
59 [45] C. Wickleder, *Chem. Mater.* **2005**, *17*, 1228-1233.
60

- 1
2
3 [46] R. Mueller-Mach, G. Mueller, M. R. Krames, H. A. Höpfe, F. Stadler, W. Schnick, T.
4 Juestel, P. Schmidt, *Phys. Status Solidi A* **2005**, *202*, 1727-1732.
5
6
7 [47] N. Yamashita, *J. Lumin.* **1994**, *59*, 195-199.
8
9 [48] A. -Q. Wu, F. -K. Zheng, W. -T. Chen, L. -Z. Cai, G. -C. Guo, J. -S. Huang, Z. -C.
10 Dong, Y. Takano, *Inorg. Chem.* **2004**, *43*, 4839-4845.
11
12 [49] A. Nag, P. J. Schmidt, W. Schnick, *Chem. Mater.* **2006**, *18*, 5738-5745.
13
14 [50] A. Nag, W. Schnick, *Z. Anorg. Allg. Chem.* **2006**, *632*, 609-614.
15
16 [51] D. H. Dieke, *Spectra and Energy Levels of Rare-Earth Ions in Crystals*, Interscience
17 Publishers; New York, 1968.
18
19 [52] M. Zeuner, F. Hintze, W. Schnick, *Chem. Mater.* **2009**, *21*, 336-342.
20
21 [53] R. M. Supkowski, W. D. Horrocks Jr., *Inorg. Chim. Acta* **2002**, *340*, 44-48.
22
23 [54] E. Irran, B. Juergens, W. Schnick, *Solid State Sci.* **2002**, *4*, 1305-1311.
24
25 [55] B. F. Abrahams, S. J. Egan, B. F. Hoskins, R. Robson, *Chem. Commun.* **1996**, 1099-
26 1100.
27
28 [56] B. F. Abrahams, S. J. Egan, B. F. Hoskins, R. Robson, *Acta Crystallogr., Sect. C:*
29 *Cryst. Struct. Commun.* **1996**, *52*, 2427-2429.
30
31 [57] A. Nag, B. V. Lotsch, J. Schmedt auf der Günne, O. Oeckler, P. J. Schmidt, W.
32 Schnick, *Chem. Eur. J.* **2007**, *13*, 3512-3524.
33
34 [58] G. Blasse, B. C. Grabmeier, *Luminescent Materials*, Springer, Berlin, **1998**.
35
36 [59] C. Görller-Walrand, K. Binnemans, *Handbook on the Physics and Chemistry of Rare-*
37 *Earths, Vol. 25*, (Eds. : K. A. Gschneider, Jr. , L. Eyring), North Holland, Amsterdam,
38 **1998**, Chapter 167.
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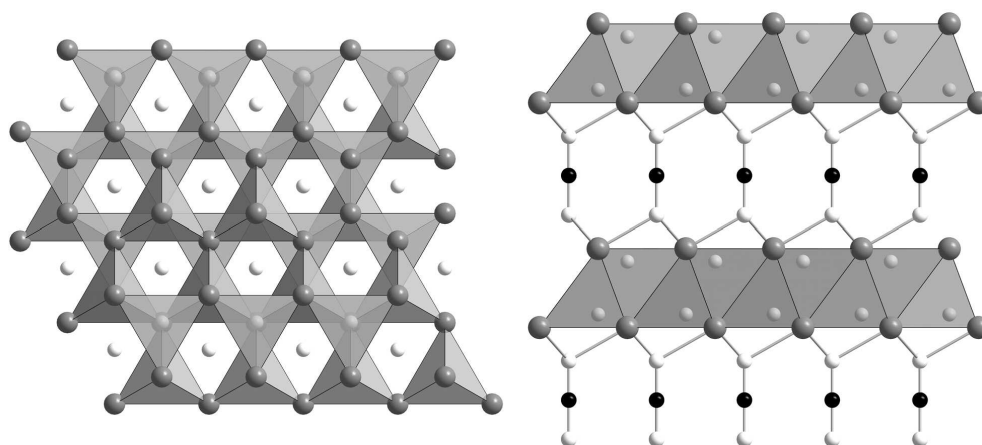


Equation_1
5x0mm (600 x 600 DPI)

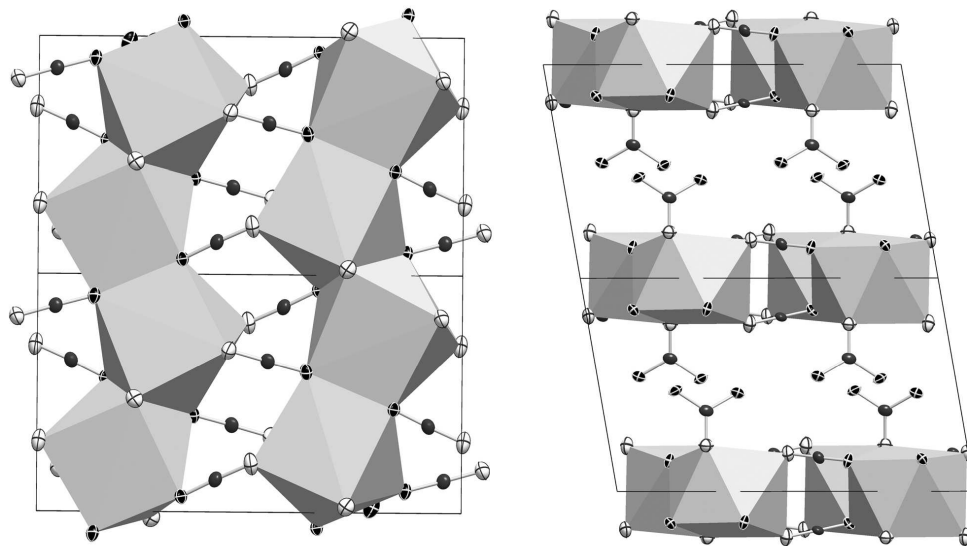
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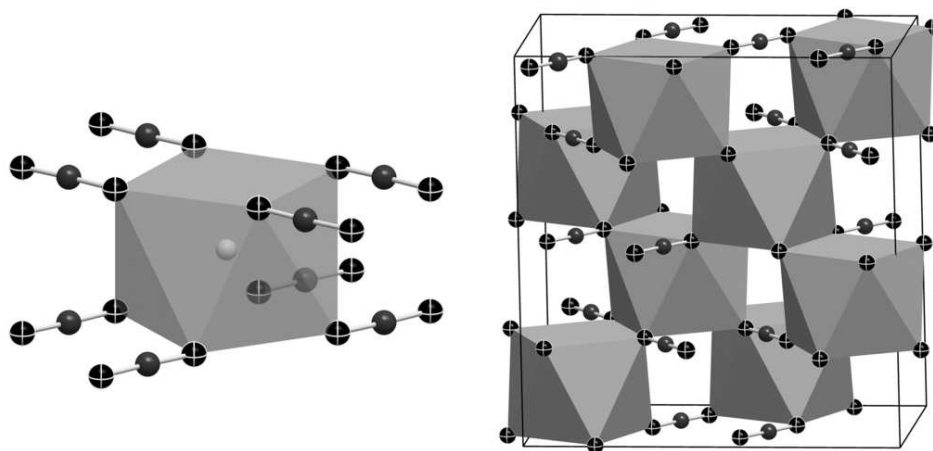
Figure_1
85x85mm (600 x 600 DPI)



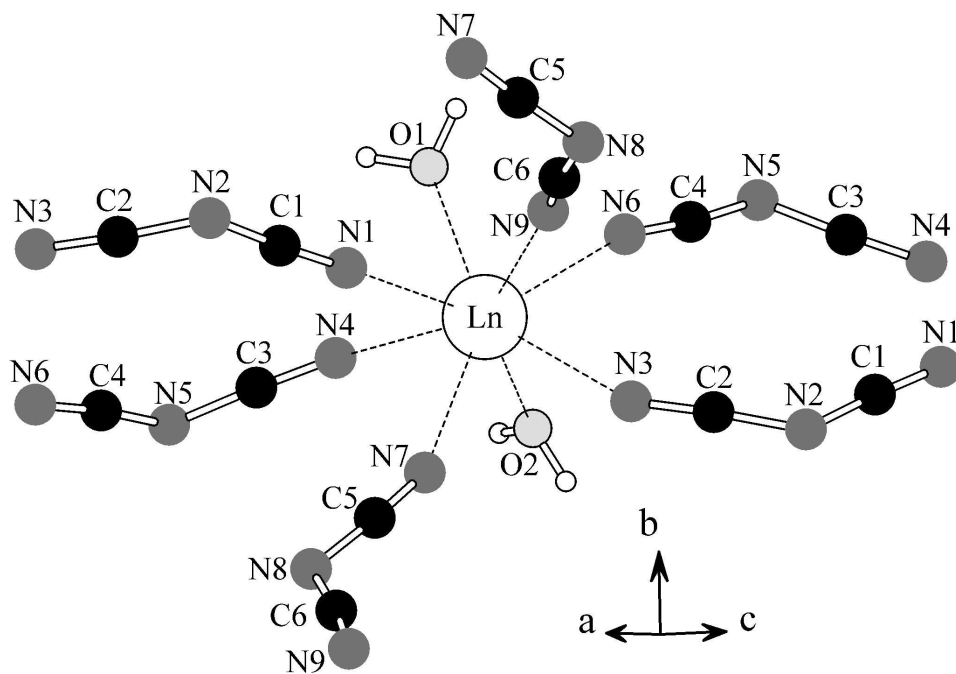
Figure_2
83x37mm (600 x 600 DPI)



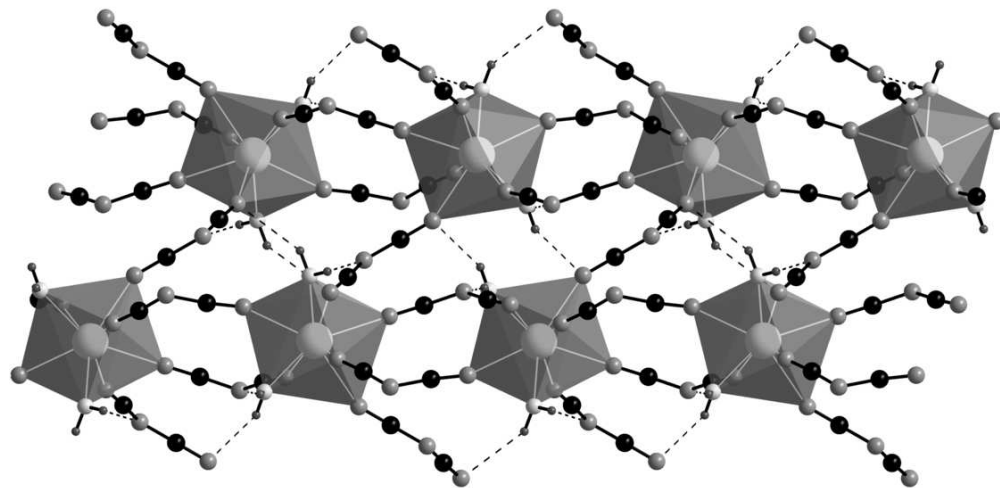
Figure_3
85x50mm (600 x 600 DPI)



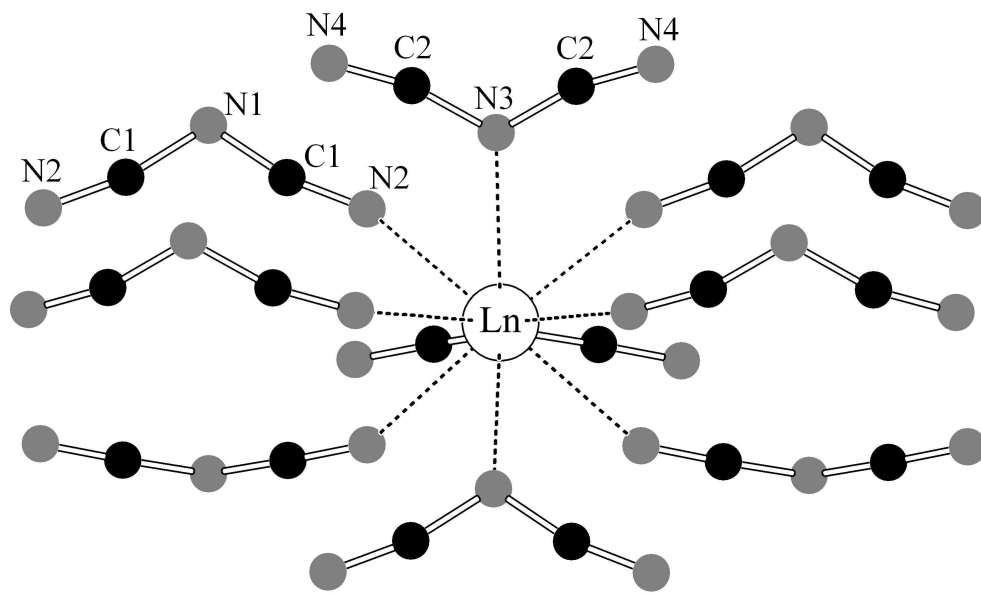
Figure_4
45x24mm (600 x 600 DPI)



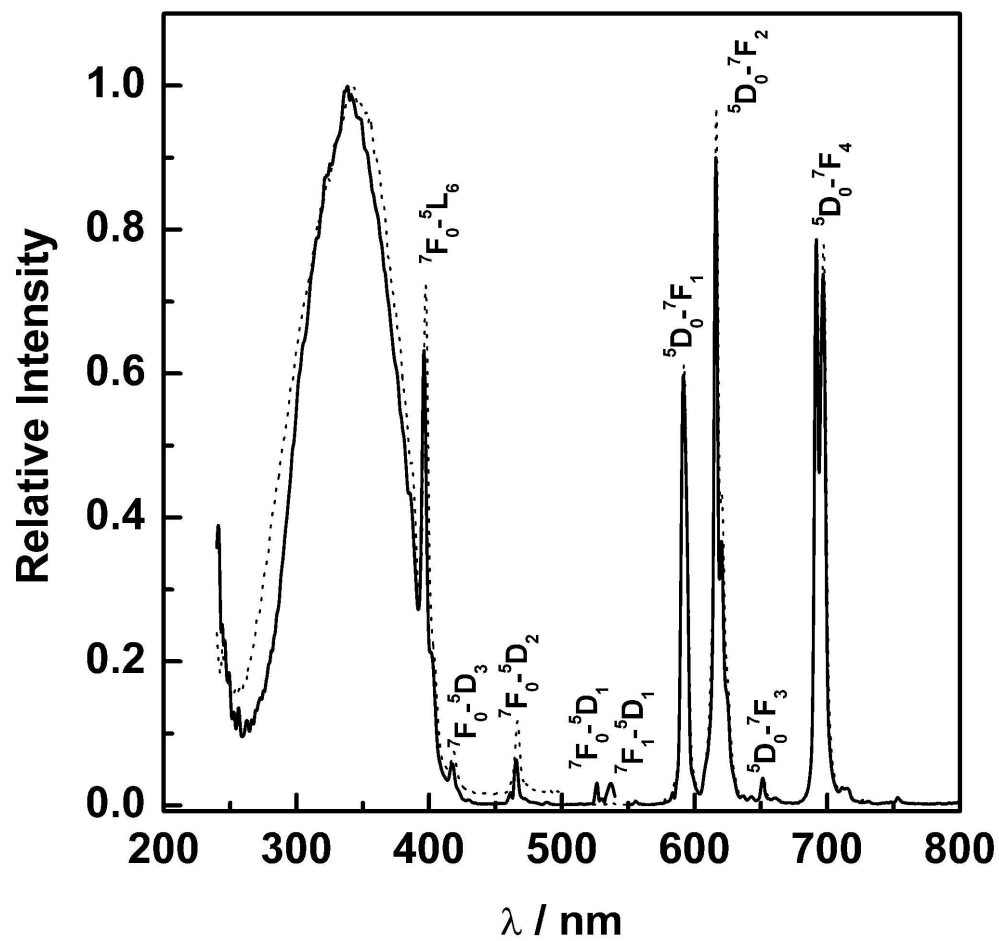
Figure_5



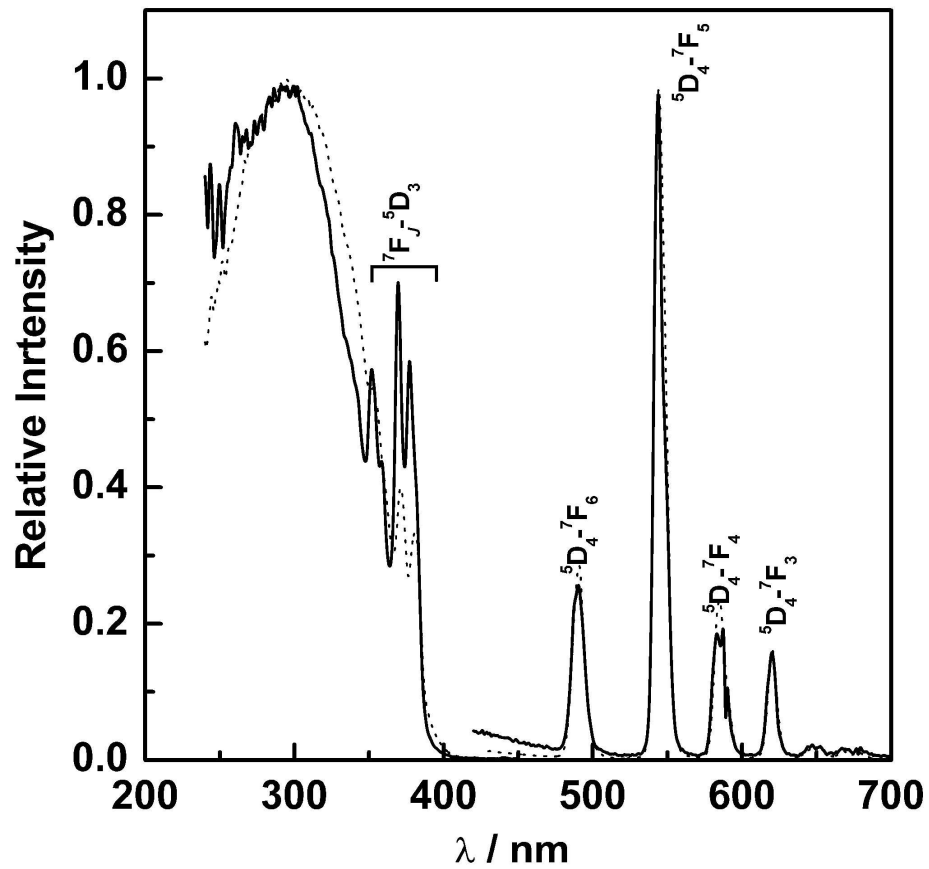
Figure_6
47x26mm (600 x 600 DPI)



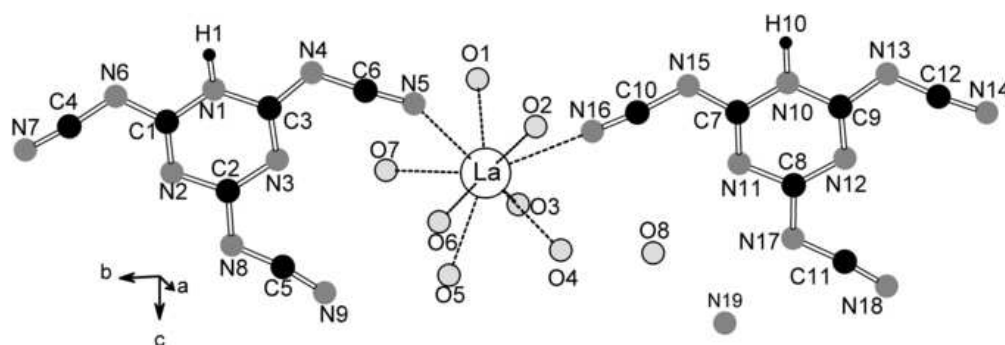
Figure_7



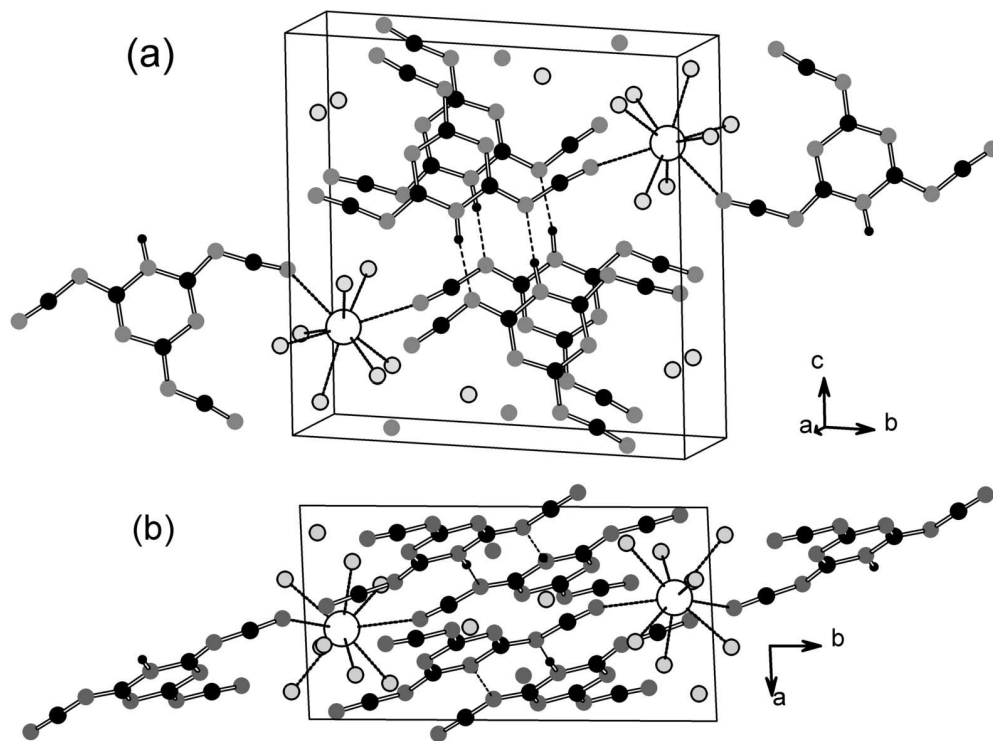
Figure_8
1466x1391mm (72 x 72 DPI)



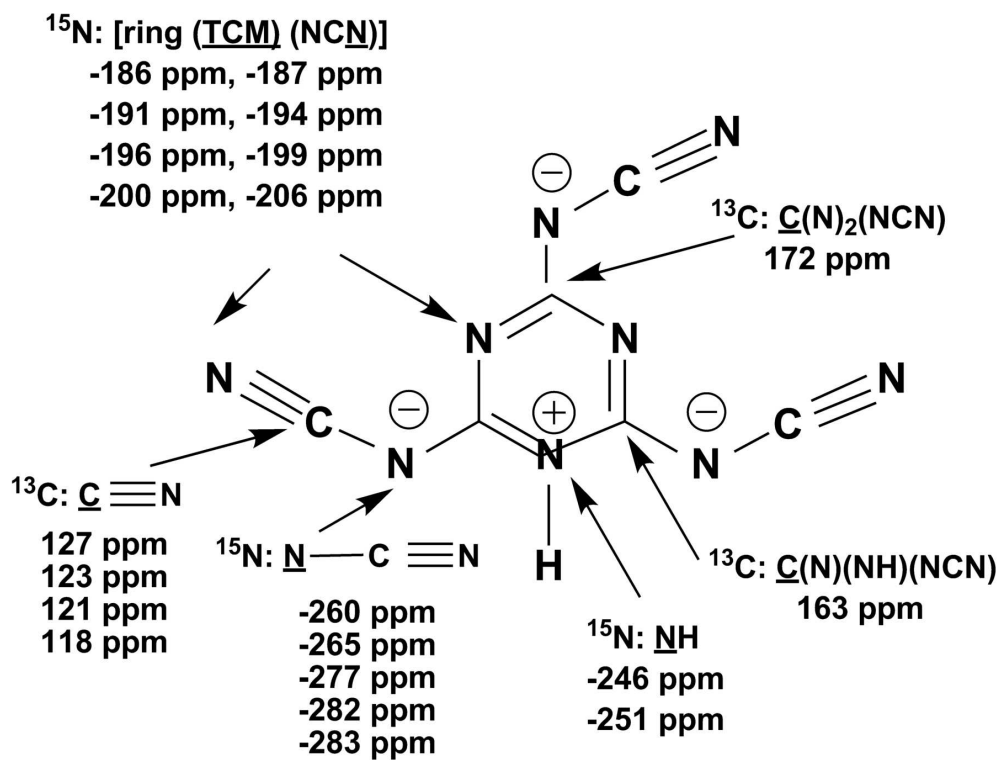
Figure_9
1174x1090mm (96 x 96 DPI)



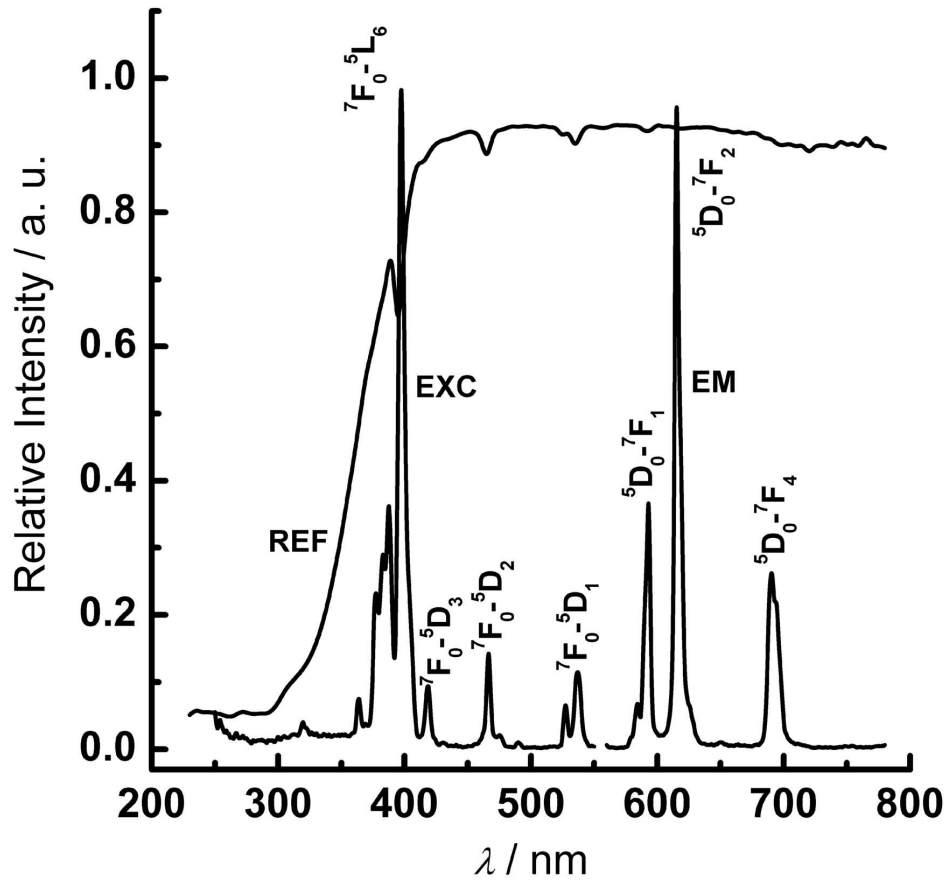
Figure_10
28x9mm (600 x 600 DPI)



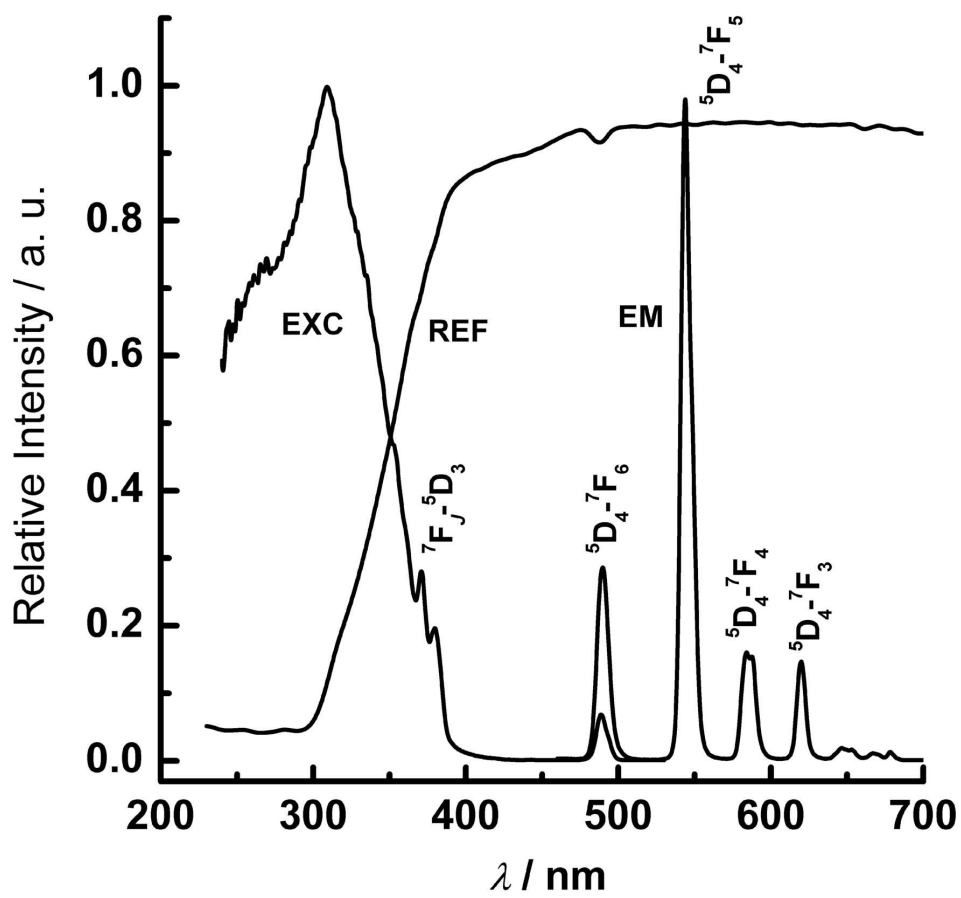
Figure_11
67x53mm (600 x 600 DPI)



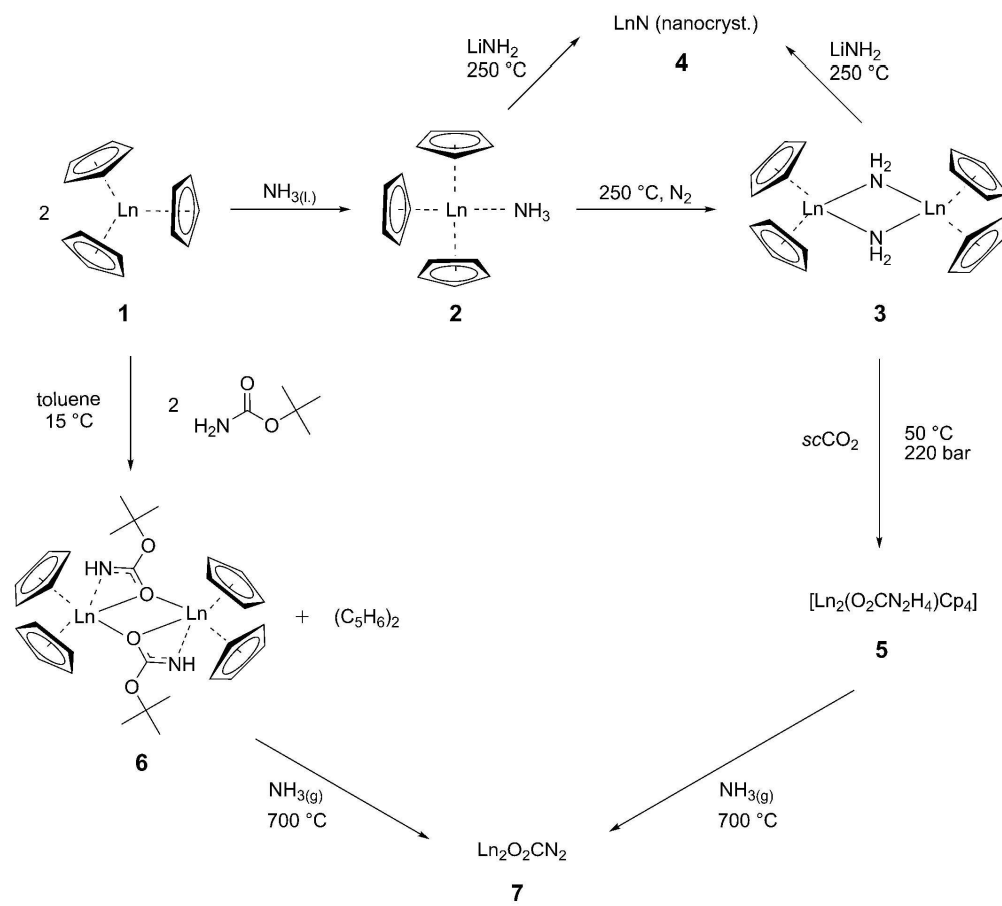
Figure_12
 76x58mm (600 x 600 DPI)



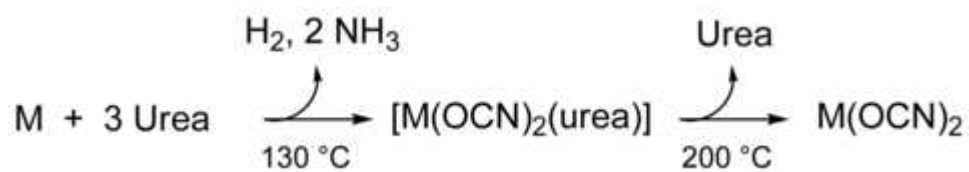
Figure_13
78x72mm (600 x 600 DPI)



Figure_14
78x72mm (600 x 600 DPI)



Scheme_1
180x162mm (600 x 600 DPI)



Scheme_2
20x3mm (600 x 600 DPI)