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Luminescent Coordination Polymers for the VIS and NIR Range Constituting from LnCl₃ and 1,2bis(4-pyridyl)-ethane

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A series of 14 lanthanide containing coordination polymers $LnCl_3$ of with 1,2-bis(4-pyridyl)ethane (bpe) was synthesized from either thiazole or pyridine. Depending on the ligand content, a structural diversity from 3D-frameworks ${}^3_{\infty}[LnCl_3(bpe)_2]$ ·thz, Ln = Ce-Lu, to 1Dstrands ${}^1_{\infty}[La_2Cl_6(bpe)_2(thz)_6]$ and ${}^1_{\infty}[LnCl_3(bpe)(py)_2]$ ·(bpe/py), Ln = Gd, Er, were obtained and characterized by X-ray single crystal diffraction, powder diffraction, differential thermal analysis and thermogravimetry (DTA/TG), IR-spectroscopy and photoluminescence spectroscopy. The compounds exhibit a variety of luminescence properties and different phenomena. This includes ligand centred fluorescence, metal-centred 5*d*-4*f*/4*f*-4*f* emission in the visible and the NIR range, antenna effects via Dexter and Förster energy transfer mechanisms, excitation dependent emission with a correlating shift of the chromaticity coordinates and inner filter effects by combined re-absorption/emission.

Introduction

In the last decade, coordination polymers (CPs) and metal organic frameworks (MOFs) have been of growing scientific interest due to their wide variety of possible applications.^[1] One feature, which makes them particularly attractive, is the extraordinary broad variety of photoluminescence (PL) properties, e.g. in lanthanide containing coordination polymers.^[2] In addition to ligand- and metal-centred luminescence, energy transfer processes are remarkable, for example to circumvent the low light absorption of Ln^{3+} ions^[3]. The latter can be circumvented by the so called antenna effect ^[4] by means of inserting suitable organic linker molecules with high absorption coefficients and suitable energetic states for a following energy transfer from the linker to the lanthanide ions. In this report the linker ligand 1,2-bis(4-pyridyl)ethane (bpe) proves to function as a suitable sensitizer due to the pyridyl π systems. The option of effective antenna effects for Ln³⁺ ions in the visible and the NIR range is well known [5] and results in typical 4f-emission spectra with respective chromaticity based on 4f-4f transitions and sharp line emissions.^[6] As an exception of trivalent lanthanide ions, the photoluminescence of Ce³⁺ can utilize 5d-4f transitions resulting in broad emission bands.^[7] The participation of 5d orbitals the luminescence results in a dependence of the chemical surrounding of the Ce³⁺ ion on the luminescence and the emission maximum can be shifted from the UV to the visible area, as shown for coordination polymers such as ${}_{\infty}^{2}$ [Ce₂Cl₆(bipy)₄] py, bipy = 4,4'-bipyridine, and ${}_{\infty}^{3}$ [Ce(Tz)₃], Tz⁻ = 1,2,3-triazolate (UV to blue), or Ce-YAG (yellow) as laser and for pc-LEDs to generate white light.^[8,7]

For the ligand bpe various coordination compounds are known, in which bpe functions as linker between metal centres: For example, in the dinuclear complexes $[Sn_2Cl_2(bpe)Ph_6]^{[9]}$, in one-dimensional coordination polymers with tetrahedrally coordinated metal ions ${}^{1}_{\infty}$ [MCl₂(bpe)] with M = Co^[10], Ni^[11], or in ${}^{1}_{\infty}[\text{FeCl}_{2}(\text{bpe})(\text{dmp})_{2}]^{[13]}$ (dmp = 3,5- $Zn^{[12]}$ dimethylpyridine) with octahedral coordination of the metal centre. Further structural condensation can be observed in the luminescent 2D-network ${}^{2}_{\infty}$ [Ag₃Cl₃(bpe)₂]^[14] or in combination with the carboxyl ligands in ${}^{3}_{\infty}[Zn_2Cl(dcb)(bpe)]^{[15]}$ (dcb = 1,4dicarboxybenzene). Lanthanide containing compounds with bpe coordination are rather rare. Exemplary compounds are the complex $[Nd(tta)_3(bpe)]^{[16]}(tta = thenoyltrifluoroacetone)$ or the coordination polymer $[bpeH]^{1}_{\alpha}[La(bpe)(H_{2}O)(NO_{3})_{4}]^{[17]}$ based on bpe connected hydrated lanthanum nitrate units.

In the following, we present a series of fourteen threedimensional networks and single strands based on LnCl₃, the linker bpe and the co-ligands thiazole and pyridine that exhibit a large variety of luminescence properties.

Results and Discussion

Synthesis

All compounds were synthesized using a solvothermal reaction pathway either in thiazole or pyridine. Hereby, the

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corresponding anhydrous LnCl₃ is reacted within pyridine or thiazole in addition to the linker ligand 1,2-bis(4-pyridyl)ethane (bpe). As bpe itself did not prove to be sufficiently reactive, we use the ability of pyridine and thiazole to act as chemical scissors, breaking up the anhydrous LnCl₃ structure by the formation of lewis-acid base adducts. Solvent complexes such as $[LnCl_3(thz)_4] \cdot 0.5thz$, with Ln = Sm, Eu, Gd, Tb, Dy,^[18] $[LnCl_3(py)_4] \cdot 0.5py_{,}^{[19]}$ with Ln = Y, La, Er, Yb, or $[La_2(\mu_2 - \mu_3)]$ $Cl_{2}Cl_{4}(py)_{8}$ can be formed a room temperature. The addition of the liker ligand bpe, increasing reaction temperature and a shift of the molar ratio of the organic compounds to the bpe ligand leads to the formation of coordination polymers with bpe. Solvothermal reaction parameters cause a connection of lanthanide-chloride building units with bpe molecules, due to the thermodynamically favourite displacement of solvent molecules by linker molecules. We have already applied this reaction route for the synthesis of the series of complexes $[Ln_2Cl_6(bipy)(py)_6]$ for Ln = Pr, Nd, Sm-Yb, bipy = 4,4'bipyridine.^[21] Different from bpe, bipy was shown to be sufficiently reactive without the formation of precursor complexes with py or thz, e.g. in solvent-free reactions yielding MOFs and coordination polymers in the presence of anhydrous metal-chlorides.[22]

Crystal structures of ¹/_∞[La₂Cl₆(bpe)₂(thz)₆](1)

 ${}_{\infty}^{1}$ [La₂Cl₆(bpe)₂(thz)₆](1) crystallizes in the centrosymmetric space group PT as a one-dimensional coordination polymer. The corresponding crystallographic data and interatomic distances are given in table 1 and table S1.

The trivalent lanthanum is positioned on one crystallographic site and is coordinated in a distorted double-capped prism by four chlorine atoms and four nitrogen atoms, which belong to three thiazole molecules and one bpe molecule, giving a C.N of eight. Two of the chlorine atoms are linked to an adjacent lanthanide centre which results in a dinuclear unit (see Fig. 1 and S1). The La-Cl and La-N distances are in the range of 2.8212(11) to 2.9263(11) Å and 2.710(2) to 2.816(2) Å, respectively. These distances are in good accordance to in the MOF respective interatomic distances, e.g. ${}_{00}^{3}$ [La₂Cl₆(bipy)₅]·4bipy^[22b] with La-Cl = 2.760-2.964 Å and La-N 2.750-2.818 Å as well as in the complex [La2(µ- $Cl_{2}Cl_{4}(py)_{8}$ ^[20] with La-Cl = 2.778-2.929 Å and La-N 2.722-2.789 Å. The dimeric unit La₂Cl₆ is interconnected to two other dimers by one bridging bpe molecule forming a single strand. Due to the alternating coordination of the bpe ligand within the dimeric unit, zigzag chains result. These chains are shifted against each other by the length of one bpe molecule within the ac-plane.

Crystal structures of ${}^{3}_{\infty}$ [LnCl₃(bpe)₂]·thz with Ln = Ce(2), Pr(3), Dy(8), Yb(11)

The three-dimensional (3D) framework structure of ${}_{\infty}^{3}$ [LnCl₃(bpe)₂] thz is found for compounds 2 – 12 and was in particular supported by single crystal structure analysis for Ln = Ce(2), Pr(3), Dy(8), Yb(11), which are istopypic and crystallize in the monoclinic space group C2/c.



Figure 1. Top: Coordination sphere of ${}^{1}_{\alpha}[La_{2}Cl_{6}(bpe)_{2}(thz)_{6}](1)$, thermal ellipsoids in this and all following figures depict 50 % of the probability level of the atoms, symmetry operations: I 1-x,2-y,-z; II x-1, 1+y, z-1; III 2-x, 1-y, 1-z. Bottom: Depiction of the parallel stacking of the one-dimensional zig-zag strands of ${}^{1}_{\alpha}[La_{2}Cl_{6}(bpe)_{2}(thz)_{6}](1)$.

Further crystallographic information and interatomic distances are given in table 1 and table S1. The trivalent lanthanide ions, which again occupy only one crystallographic site, are 7-fold coordinated by four nitrogen and three chlorine atoms, forming a pentagonal-bipyramidal coordination polyhedron (see Fig. 2 and S2). The nitrogen atoms belong to four different bpe molecules spanning a plane with one chlorine atom, the other two chlorides are in axial positions. The interatomic distances for Ce-Cl with 2.7373(7)-2.744(7) pm and Yb-Cl with 2.5609(11)-2.6002(13) pm are in good accordance to the corresponding distances in $[CeCl_2(\mu-Cl){py-(R,R)-chxn}]_2$ (py-(R, R)-chxn = N, N'-bis(2-pyridyl-methylidene)-1,2-(R, R)cyclohexanediamine)^[23], [CeCl₃ (CH₃OH)₄]^[24], YbCl₃(py)₄,^[25] and [Yb₂Cl₆(µ-bipy)(py)₆]^[21]. The Ln-N distances are also in the reported range.^[23, 25, 26] They match with the lanthanide contraction, beginning with the shortest distance for Yb-N (2.473(3)-2.509(3) pm, followed by Dy-N (2.522(3)-2.571(4) pm), and Ce-N (2.653(2)-2.693(2) pm). The crystal structure analysis reveals a layered 2D structure with a honeycomb-like topology interconnected by bpe molecules to a 3D structure with dia topology (Fig. 2). The honeycomb-like sheets are interconnected by bpe molecules and are shifted in the ac-plane to one another by the length of half a comb. Additionally, one thiazole molecule is intercalated in pores of the framework structure.

Crystal structures of ${}^{1}_{\infty}$ [LnCl₃(bpe)(py)₂]·(bpe/py) with Ln = Gd(13) and Er (14)

The one-dimensional coordination polymers ${}^{1}_{\infty}$ [LnCl₃(bpe) (py)₂]·(bpe/py) with Ln = Gd(13) and Er(14) crystallize in the

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triclinic space group PT. Crystallographic data and selected interatomic distances are listed in table 1 and table S1.



Figure 2. Top: Coordination sphere of $\frac{3}{\infty}$ [PrCl₃(bpe)₂]·thz(**3**), symmetry operations: $\frac{1}{2}$ -x, y- $\frac{1}{2}$, 3/2-z; $\frac{11}{2}$ -x, $\frac{1}{2}$ +x, $\frac{1}{2}$ -x, $\frac{1}{2}$ -x,

In the structure, the trivalent lanthanide ions are positioned on one crystallographic independent site and coordinated by three terminal chloride anions and four nitrogen atoms of bpe and pyridine (Fig. 3 and S3). The coordination polyhedron is constituted by a distorted pentagonal-bipyramid with two chloride ions in axial position and one chloride ion and four nitrogen atoms in equatorial position, giving a C.N. of seven. The Ln-Cl distances are in the range of 2.6330(12)-2.6864(13) Å for Gd(13) and 2.5822(7)-2.6460(7) Å for Er(14), the Ln-N distances are in the range of 2.570(3)-2.582(3) Å for Gd(13) and 2.520(2)-2533(2) Å for Er(14) for the nitrogen atoms of the pyridine ligands and 2.542(3)-2.594(3) Å and 2.548(2)-2.584(2) Å for the nitrogen atoms of the bpe ligand. All atomic distances are in good accordance with their equivalents in the dinuclear complexes [Ln₂Cl₆(bipy)(py)₆],^[21] Ln = Gd, Er with Gd-Cl 2.6301-2.6785 Å, Er-Cl 2.5834-2.6471 Å, Gd-N 2.558-2.616 Å and Er-N 2.4807-2.576 Å. The chloride ions are positioned in a t-shape form around the Ln³⁺ ions with an Cl-Ln-Cl angle for the axial chlorine atoms of 171.74(3)° for Gd(13) and 172.98(2)° for Er(14), indicating ta certain distortion from the ideal coordination polyhedron with 180°. The lanthanide ions are again connected via bridging bpe molecules to one-dimensional strands. The strands of the onedimensional coordination polymer are arranged parallel to one another (see Fig. S4) and shifted by half of the elemental cell along c-axis. In addition, one non-coordinating bpe and one py molecule are intercalated in the structure. The py molecule exhibits a rotational disorder along the perpendicular line through the barycenter of the pyridyl ring.



Figure 3. Top: Coordination sphere of $\frac{1}{\alpha}[GdCl_3(bpe)(py)_2] \cdot (bpe/py)(13)$. The intercalated pyridine molecule is described with a benzene molecule, due to rotational disorder effects, Symmetry operations: ${}^{1}x,y,z-1$; ${}^{11}1-x,1-y,2-z$; ${}^{11}1-x,-y,1-z$. Bottom: The crystal structure of 13 with a view along [100].

Powder X-ray diffraction (PXRD)

PXRD investigations were performed on all compounds 1-14 to prove the phase purity, the isotypic/isostructural character among the isoconstitutional compounds and to check the single crystal structure determinations. The simulated diffraction patterns of 1(La), 13(Gd) and 14(Er) are in good accordance with the observed ones, indicating correct structure determination and phase purity (Fig. S5 and S6). For the series of the frameworks 2(Ce)-12(Lu) all PXRD investigations revealed similar diffraction patterns (Fig. 4), indicating their isotypic structure and phase purity.

Table 1. Crystallographic data for La(1), Ce(2), Pr(3), Dy(8), Yb(11), Gd(13) and Er(14).

	La (1)	Ce (2)	Pr (3)	Dy (8)	Yb (11)	Gd (13)	Er (14)
Formula	C15H15Cl3LaN4	C27H27Cl3CeN5S	$C_{27}H_{27}Cl_3PrN_5S$	$C_{27}H_{27}Cl_3DyN_5S$	$C_{27}H_{27}Cl_3YbN_5S$	C ₆₁ H ₆₁ Cl ₆ Gd ₂ N ₁	1 C ₆₁ H ₆₁ Cl ₆ Er ₂ N ₁₁
fw / g mol ⁻¹	593.18	700.09	700.88	722.90	733.01	1475.44	1495.46
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	PĪ	C2/c	C2/c	C2/c	C2/c	ΡT	PT
a/Å	9.198(2)	36.032(7)	35.828(2)	35.642(2)	35.641(8)	9.339(2)	9.3175(10)
<i>b</i> /Å	9.727(2)	9.260(2)	9.2397(4)	9.2416(6)	9.257(2)	12.925(3)	12.8780(14)
c/Å	12.425(3)	18.688(4)	18.6155(9)	18.5076(11)	18.512(4)	14.064(3)	13.971(2)
$\alpha /^{\circ}$	77.92(3)	90	90	90	90	103.44(3)	103.280(2)
$eta /^{\circ}$	79.77(3)	108.34(3)	108.312(1)	109.0580(10)	109.781(7)	102.03(3)	102.030(3)
γ/°	79.08(3)	90	90	90	90	101.85(3)	101.880(2)
$V/\text{\AA}^3$	1056.3(4)	5919(2)	5850.5(5)	5762.1(6)	5747(2)	1556.4(6)	1538.0(3)
Z	2	8	8	8	8	1	1
$\rho_{cale}\!/g\!/cm^3$	1.865	1.5711	1.5913	1.657	1.6908	1.573	1.614
μ/cm^{-1}	2.708	1.905	2.036	2.969	3.631	2.417	3.018
T/K	100(3)	100(3)	100(3)	100(3)	167(3)	168(5)	168(5)
data range/°	3.38 to 56.76	2.38 to 56.70	4.48 to 56.64	4.50 to 56.68	2.42 to 56.58	3.86 to 54.18	3.38 to 54.14
X-ray radiation			Μ	10-K α , $\lambda = 0.71073$ Å			
Collected reflections	15684	43306	38871	42289	41295	19153	18949
No. of unique reflections	5201	7360	7282	7149	7146	6810	6716
No of parameters	238	333	333	449	357	361	361
$\begin{array}{l} R_1 \text{ for reflections} \\ F_0 \!\!>\!\! 2\sigma \left(F_0\right)]^a \end{array}$	0.0230	0.0219	0.0274	0.0332	0.0338	0.0369	0.0251
R ₁ (all) ^a	0.0252	0.0320	0.0456	0.0584	0.0583	0.0417	0.0296
wR ₂ (all) ^b	0.0573	0.0518	0.0664	0.0750	0.0813	0.0744	0.0554
S	1.028	1.029	1.051	1.030	1.046	1.208	0.980
Res. electro density (e/Å ³)	^{Dn} 1.04/-0.52	0.79/-0.54	0.83/-1.15	1.13/-2.30	1.96/-2.15	1.31/-1.11	0.86/-0.38

^a $\mathbf{R}_1 = \sum [|\mathbf{F}_0| - |\mathbf{F}_c|] / \sum |\mathbf{F}_0| \cdot \mathbf{B}_2 = [\sum \mathbf{w} (|\mathbf{F}_0|^2 - |\mathbf{F}_c|^2)^2 / \sum \mathbf{w} (|\mathbf{F}_0|^2)^2]^{1/2} \cdot [27]$

However, the presence of a phase transition at low temperatures can be assumed, as the simulated diffraction pattern based on the single-crystal structure investigation at 100 K shows differences in reflection positions compared to the observed powder diffraction patterns recorded at 293 K. The reflections in the range of 15 to 17° and the first three reflections of the simulated pattern are not superimposing the observed powder patterns, indicating minor structural change between the observed single crystal structure at 100 K and the observed bulk

pattern at 293 K. In order to prove this assumption, a cell indexing was carried out for the observed powder pattern of 10(Er) as an exemplary of the room temperature data. It revealed an elemental cell related to the single-crystal indexing with the monoclinic space group C2 and cell parameters of a = 36.626(8)Å. b = 9.344(9)Å, c = 9.443(5)Å. $\beta = 111.42(5)^{\circ}$. Compared to the cell indexed by single-crystal x-ray data, the axis c is halved. We therefore verified our single-crystal diffraction data, which does not allow reduction

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of a cell axis by one half, but confirmed the determination by singe-crystal diffraction based investigations at 100 K for Ce(2), Pr(3), Dy(8), Yb(11). Accordingly, we assume the existence of a phase transition between 100 K and 293 K for Ce(2)-Lu(12).



Figure 4. Comparison of the observed powder X-ray diffraction patterns (Curadiation) of isotypic $\frac{3}{\omega}$ [LnCl₃(bpe)₂]·thz, Ln = Ce(**2**)-Lu(**12**), at RT with the simulated diffraction pattern of the single-crystal X-ray structure determination of Pr(**3**) at 100 K.

Photoluminescence spectroscopy

The series of three-dimensional networks **2-11** and single strands **13-14** reveals six different photoluminescence effects subsequent to excitation with UV-light. Figure 5, 6 and S7/S8 show the recorded emission and excitation spectra of the compounds at room temperature in solid state including the ligands thiazole and bpe (the latter also dissolved in *i*-PrOH).

In the solid state, the ligand bpe reveals two emission bands in the range of $\lambda = 300-400$ nm ($\lambda_{max} = 347$ nm, $\tau_{obs} < 1$ ns) and $\lambda = 400-650$ nm ($\lambda_{max} = 469$ nm, $\tau_{obs} = 9.9(8)$ ns), which can be assigned to fluorescence. Participation of triplet states is excluded due to the short decay times of the processes. The second band could possibly result from an exciplex formation, as it is not present in any of the products **1-14**. However, by dissolving and freezing bpe in *i*-PrOH, the intensity ratio of the second fluorescent band is significantly reduced but not quenched. The corresponding excitation spectra of bpe exhibit an absorption process with a maximum at $\lambda_{max} = 307$ nm and a side maximum at λ_{max} . = 322 nm in the solid state (*i*-PrOH: λ_{max} . = 292 nm and 306 nm), that can be assigned to excited singlet states. The emission spectra of thiazole shows one broad fluorescence band in the range of λ = 330-460 nm (λ_{max} . = 376 nm, τ_{obs} = 2.1(1) ns) and the excitation spectra reveals an absorption process with a maximum at λ_{max} . < 260 nm and a side maximum at λ_{max} . = 320 nm. The energetic position of the triplet level T₁ was reported at 26045 cm⁻¹ around 380 nm.^[28]



Figure 5. Emission spectra of the compounds **2**, **4-7**, **10**, **11**, **13**, **14** and the ligands bpe in solid state and in *i*-PrOH as well as thiazole at RT ($\lambda_{exc} = 300 \text{ nm}$).

The two Gd³⁺-compounds, **6** and **13** are good examples to observe effects of ligand-centered luminescence in compounds isostructural to other lanthanides without participation of Gd³⁺ in the luminescence, as the respective 4f-transiton at 307nm is not populated. Accordingly, the emission is ligand centred fluorescence (e.g. in **6**: λ_{max} . = 355 nm, $\tau_{obs} < 1$ ns) and derives from the linking bpe molecules with a shoulder of the thz emission. The maxima of the fluorescence band of bpe are shifted slightly to higher wavelengths and energy as result of the coordination as donor ligand. This can be also observed in the compounds Pr(**3**) (Fig. S7) Nd(**4**), Ho(**9**), Yb(**11**) and

Lu(12) (Fig. S7), as the excitation spectra of these compounds resemble the excitation spectrum of bpe (Fig. S8).



Figure 6. Excitation spectra of the compounds **2**, **4-7**, **10**, **11**, **13**, **14** and the ligand bpe in solid state and in *i*-PrOH as well as thiazole at RT.

In contrast, the emission of **2** containing the Ln^{3+} -ion Ce^{3+} results in a broad metal-centred band (λ_{max} . = 550 nm, τ_{obs} = 8.3(1) ns) based on 5*d*-4*f* transitions of Ce^{3+} .^[7,8] No ligand-centred emission is observed, however, as the Ce-centred emission is parity allowed and therefore strong, it cannot substantially be resolved, if the bpe ligand functions as a sensitizer for Ce^{3+} or if the respective ligand-centred emission is too weak compared to Ce^{3+} to be observed. The resulting emission colour (chromaticity) appears as a strong lemon yellow (see TOC). The energetic positions of the emissive excited 5*d*-states of Ce^{3+} are therefore closer to the oxide Ce-YAG (yellow)^[8c] than to $\frac{2}{\infty}[Ce_2Cl_6(bipy)_4]$ py, containing the related ligand 4,4'-bipyridine.^[8b] This shows the complex behaviour and influence of ligand and crystal field splitting influencing the energetic positions of Ln-5*d*-states, which do

not allow a simplified deduction from related bonding partners such as pyridyl ligands.

In the compounds with Sm(5), Tb(7) and Dy(8) the typical visible 4*f*-4*f* transitions are observed in the emission spectra.^[6] The non-centrosymmetric pentagonal-bipyramidal coordination sphere of N and Cl atoms around Ln influences the finestructure and intensities of the 4f-states slightly according to ligand and crystal field.^[6c] Ligand centred emission is also observed, the intensity ratio strongly depending on the intensity of the Ln³⁺-emission (the latter being strongest for Tb³⁺ and less pronounced for Dy³⁺ and Sm³⁺. Only weak 4*f*-excitation is present for the three Ln³⁺. We therefore assume a sensitization of these lanthanide ions by the linker ligand bpe via an antenna effect.^[4] The organic ligand transfers excitation energy to the metal centres, as excited ligand states of the organic linker bpe and the Ln³⁺-4*f*-states have a suitable energetic match for the energy transfer.^[4,21] However, this energy transfer is limited by the short decay times of the excited states of bpe in the nsregion. Besides the antenna effect of the linker bpe via the Dexter energy transfer mechanism, we consider the intercalated thiazole molecules another source for energy transfer to the lanthanide ions via the Förster energy transfer mechanism. Within this mechanism, the ligand (donor) can transmit energy to the lanthanide ion (acceptor) over long distances (up to 1000 pm)^[29]. Thiazole itself can potentially function as another antenna with broad band singlet and triplet excitation and excited states in the correct energetic range to transfer energy on to excited 4f-states of lanthanide ions (see Fig. 6). According to the short lifetimes of excited states of bpe, thiazole, even if intercalated only, can add to sensitizer effects according to the longer decay times of its triplet states. However, as thz is no direct coordination partner for 2-12, energy transfer for this ligand on to lanthanides is likely to happen via space. In order to elaborate the interplay of Dexter and Förster transfer, three-dimensional photoluminescence spectra were recorded for compounds 5 (Sm^{3+} , see Fig. 7), 7 (Tb^{3+}) and 8 (Dy^{3+}) . They show excitation possibilities of bpe and thz next to the typical intra 4f-line emission of the Lnions^[6]. The spectra also illustrate that the emission of the compounds is excitation dependent. Figure 7 shows a 3Dspectrum of the Sm³⁺-compound (5), which is translated into a 2D-height profile of the intensity and the corresponding chromaticity coordinates for selected excitation wavelengths. In the emission spectrum of 5, both, emission of bpe and thz can be found excitation dependent in addition to emission of Sm³⁺. For excitation in the region $\lambda = 260-280$ nm, the emission is dominated by Sm³⁺, and the chromaticity coordinates remain all in the red part of the chromaticity diagram together with weak thz related triplet emission. This indicates that the antenna effect for bpe is effective in this excitation area, as most of the excitation energy of the ligand is transferred to the Sm³⁺-ion, wherefrom it is emitted in the visible red region, whereas the energy transfer from thz is less effective for its excited singlet states. This is in accordance with attributing bpe to Dexter and thz to Förster energy transfer mechanisms for the two ligands. With higher excitation wavelengths, the emission colors move

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to the bluish-white region due to a higher proportion of ligand emission addressed to bpe. The intensity of the metal-centered emission is also increasing for excitation >290nm but not as strong as the emission of bpe. The efficacy of the energy transfer from bpe is partly moved to thz. A possible reason for this observation is the fact that the emission of bpe in this region comes from an aggregation induced effect with decay times in the nanosecond and does not originate from triplet states, whereas thz can populate triplet states in this energetic region. It also illustrates that such an aggregation induced effect is less suitable as sensitizer.



Figure 7. 3D-photoluminescense spectra of $\frac{3}{2}[SmCl_3(bpe)_2]$ ·thz (5) and the corresponding CIE-coordinates for different excitation wavelengths indicating.

The coordination polymers Nd(4), Yb(11) Er(10), and Er(14) reveal a combination of ligand-centred emission in the visible range as well as the 4f-4f emission of the corresponding lanthanide ions in the NIR range.^[6,7] As the excitation spectra show no direct Ln³⁺-excitations, the 4f-4f-transitions for emission are also triggered by antenna effects of the ligands, as described before. The respective NIR-emission is strong for Nd in 4 and Yb in 11, in contrast it is weak for Er in 10 and 14. Instead of high intensity, for Er^{3+} -ions (10 and 14), the so called inner filter effect can be observed.^[8a] The profile of the ligandcentred emission band exhibits indentations that can be attributed to the re-absorption of the emitted fluorescence by direct excitation based on the 4f-4f transitions of the Er³⁺-ions within the same compound. Such effects were observed especially for several Er-containing coordination polymers with N-donor ligands before.^[8a]

Vibrational Spectroscopy

For all compounds La(1)-Er(14), the presence of the free or coordinated ligands bpe, thz and py can be confirmed by IR-spectroscopy investigations, performed for all compounds. The vibration profile of coordinated bpe is related to 1,2-di(4-pyridyl)ethylene coordinated to metal ions in known compounds^[30]. The interconnecting ligand bpe can be identified at the interplanar C-H-bending vibration at 827 cm⁻¹ and the

aromatic v(C-C, C-N) ring vibration at 1594 cm⁻¹. For the compounds La(1)-Lu(12), an energetic shift of the vibration bands to higher energies (829-831 cm⁻¹, 1608-1613 cm⁻¹) can be observed, which confirms the presence of interconnecting bpe.

For the compounds Gd(13) and Er(14), an energetic shift of the vibration bands in combination with signal splitting to higher energies indicates the presence of coordinated and intercalated bpe. Therefore the energies of the bpe vibration bands in the compounds Gd(13) and Er(14) can be observed at a split signal at 831 cm⁻¹ and at two well dividable bands in the range of 1600-1601 cm⁻¹ and 1611-1612 cm⁻¹.

The free ligand pyridine exhibits an intense ω (C-H)-wag vibration at 1439 cm⁻¹, and the non-coordinating ligand thiazole the vibration band δ (C-H) at 1041 cm⁻¹. Coordination to Ln³⁺ ion leads to a shift of the vibrations to higher energy, exhibiting an intense band at 1444 cm⁻¹ for pyridine and 1049 cm⁻¹ for thiazole. The intercalated py molecule can be observed in a band shoulder at 1432 cm⁻¹.

Thermal investigations

In order to obtain information about the thermal properties of the synthesized coordination polymers and networks, exemplarily DTA/TG investigations were performed on the compounds Pr(3), Nd(4), Gd(6), Yb(11) and Gd(13). For the interpretation of results, the thermal properties of the free ligands are: bpe (m_p: 110-111 °C^[31], decomposition: 272-273 °C^[32]), thiazole (b_p = 117-118 °C)^[33] and pyridine (b_p = 114°C).^[34] The corresponding thermal properties are shown in Figures 8 for Pr(3) and Gd(13) (and for Nd(4), Gd(6), Yb(11) in Fig. S9-11)).

For a brief discussion, only one 3D-framework (3) and one 1Dstrand polymer (13) are discussed, here (for further determinations, see Fig. S9-S11). The three-dimensional frameworks all show the release of one equivalent of noncoordinating thiazole in the first mass loss step, which is combined with an endothermic signal around 205 °C. In the compound Pr(3), the endothermic signal 2 at 270°C coincides with a second mass loss step (Pr: 25.5 %) that can be identified with the loss of one equivalent of bpe (theo.: Pr: 26.3 %). The remaining equivalent of bpe is lost thereafter at 400°C (mass loss: Pr: 23.5 %; theo .: Pr: 26.3 %). Based on the difference in measured and theoretical value, it can be assumed that the ligand bpe is not released completely, but rather appears to decompose slightly at temperatures >400°C. This correlates with a further mass loss after the endothermic signal 3 for 3. The theoretical value of the remaining mass of the inorganic salt is 35.3 % for Pr(3), which suits with the actual mass at 800 °C (Pr(3): 33.0 %). Furthermore, black remnants could be observed after measurement, corroborating the partly carbonization of the bpe ligand. A melting point of reformed LnCl₃ could only be observed in the investigated temperature range for Nd(4) at 755 °C (theoretical: $m_p = 770$ °C).^[35] DTA signal 1 of the ladder like coordination polymer $\frac{1}{\omega}[GdCl_3]$ $(bpe)(py)_2$ (bpe/py) (13) is split into three sub signals (1a: 105°C; 1b: 170°C, 200°C) indicating a complex endothermic



release process of 2.5 equivalents of intercalated and coordinated pyridine (Figure 8).

Figure 8. Simultaneous DTA/TG investigation of ${}^{3}_{\infty}$ [PrCl₃(bpe)₂]·thz (3) and ${}^{1}_{\infty}$ [GdCl₃(bpe)(py)₂]·(bpe/py) (13) performed with a heating rate of 10°C/min and a flow rate of 20 ml min⁻¹ Ar and 20 ml N₂ min⁻¹.

The corresponding mass loss of 25.5% corresponds well with the theoretical mass loss of 26.8 %. The combined signals 2a and 2b (290°C) indicate evaporation and partly decomposition of the half equivalent of intercalated bpe. Furthermore, the mass loss of 12.0 % corresponds well to the theoretical mass loss of 12.5 %. With the release of free bpe a possible condensation product "GdCl₃(bpe)" could be formed from **13**. Due to the metal coordination of bpe in **13**, the thermal release temperature for the linking bpe molecules is increased to 455°C. A decomposition of the released bpe ligand is assumed due to differences in mass loss 20.0 %, compared to the theoretical value of a full equivalent of bpe (24.9 %), and black remnants were observed after the investigation.

Experimental

General considerations

All experiments were carried out under inert conditions (Argon atmosphere) using glove box (MBraun, LabMaster SP and Innovative technology, Pure Lab), vacuum line, Schlenk and and DURAN[™] ampoule techniques. Heating furnaces based on Al₂O₃ tubes with Kanthal wire resistance heating and NiCr/Ni temperature elements controlled by Eurotherm 2416 control

units were used for experiments in sealed glass ampoules. Anhydrous rare earth chlorides were synthesised according to the ammonium halide route ^[36] using the oxides Er₂O₃, Yb₂O₃, Lu₂O₃ (99.9 %, RC-Nukor), La₂O₃, Nd₂O₃, Sm₂O₃, Tb₄O₇ (99.9 %, Auer-Remy), Pr₆O₁₁, Dy₂O₃ (99.9 %, Serva), Gd₂O₃ (99.9 %, Koch Chemicals), Ho₂O₃ (99.9 %, Strem), HCl solution (10 mol 1^{-1} , reagent grade) and NH₄Cl (99.9 %, Fluka). The anhydrous CeCl₃ was prepared by a modified ammonium halide route, in which high temperature calcined CeO₂ (99.9 %, Auer-Remy) was solubilized by hours-long boiling in various mixtures of concentrated acids HCl (37 %, fuming)/HNO3 (69 %, fuming) and HCl (37 %, fuming)/H₂O₂ (30 %). Colourless, pure Ce(OH)₃ was obtained by alkaline precipitation with concentrated aqueous NaOH solution (37 %). As al alternative, Cerium-hydroxide was also obtained by alkaline treatment of an aqueous Ce(NO₃)₃·6(H₂O) (99 %, Riedel-de Haën) solution. The corresponding precipitates were then dissolved in HCl acid (10 mol l⁻¹, reagent grade) and NH₄Cl (99.9 %, Fluka) was added. For all Ln, the initially trivalent lanthanide-ammonium-chlorides formed were thermally decomposed to LnCl₃ and purified by sublimation under vacuum. 1,2-Bi(4-pyridyl)ethane (bpe, 97 %, Sigma-Aldrich) was dried under vacuum, anhydrous thiazole (thz, ≥ 99 %, Sigma-Aldrich) was dried over molecular sieves and anhydrous pyridine (py, 99 %, Acros) was used as purchased.

Synthesis

The respective lanthanide chlorides, 1,2-bis(4-pyridyl)ethane and thiazole or pyridine were sealed into evacuated (1.10^{-3} mbar) glass ampoules by using Quickfit techniques and degassed by freezing with liquid nitrogen. Subsequently, deliberate heating programs wer used for the syntheses. The heating program for the syntheses of La(1)-Lu(12) consisted of five steps starting with heating to 120°C with a rate of 5°C h⁻¹, then to 160°C at 2°C h⁻¹. The temperature was maintained for 96 h then cooled to 120°C with 2°C h⁻¹ and to room temperature with 1° C h⁻¹. For compounds Gd(13) and Er(14) the heating program included four steps starting with heating to 50°C with a rate of 5 °C h⁻¹, then to 190°C with 1°C h⁻¹. The temperature was maintained for 168 h then cooled down to room temperature with 1°C h⁻¹. All reactions yielded crystalline compounds. For purification, the compounds containing pyridine were washed with 2x 1 ml anhydrous pyridine, removing remaining non-reacted bpe and were dried under vacuum. The thiazole containing compounds were washed with 2x 1 ml anhydrous dichloromethane. All products are air and moisture sensitive.

Synthesis of ${}^{1}_{\infty}$ [La₂Cl₆(bpe)(thz)₆] (1)

LaCl₃ (0.3 mmol; 74 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline product within excess thz. Yield: 62 mg, 35%. Elemental analysis: Anal. calcd. for $C_{30}H_{30}Cl_6La_2N_8S_6$ ($M_r = 1185.55$ gmol⁻¹): C 30.39, H 2.55, N 9.45, S 16.23; Found: C, 30.93; H, 2.68; N, 9.07; S 15.60. IR (ATR): (3088 w, 3050 w, 1608 vssh, 1560 m, 1491 m, 1455 w, 1421 ssh, 1379 s, 1311 s, 1237 m, 1123 vw, 1049 vs, 1006 m, 940 w, 900 s, 872 m, 826 vs, 744 s) cm⁻¹.

Journal Name Synthesis of ${}^{3}_{\infty}$ [CeCl₃(bpe)₂]·thz (2)

CeCl₃ (0.3 mmol; 74 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline product. Yield: 87 mg, 41%. Elemental analysis: Anal. calcd. for C₂₇H₂₇Cl₃CeN₅S ($M_r = 700.08 \text{ gmol}^{-1}$): C 46.32, H 3.89, N 10.00, S 4.58; Found: C, 47.75; H, 4.10; N, 9.66; S 4.52. IR (KBr): (3084 w, 3049 w, 2962 vw, 1609 vssh, 1558 m, 1501 m, 1424 vs, 1379 ssh, 1314 w, 1261 m, 1226 vs, 1104 w, 1070 m, 1043 m, 1010 vs, 862 w, 829 m, 810 s, 736 m, 625 w, 604 m, 536 s, 489 w) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [PrCl₃(bpe)₂]·thz (3)

PrCl₃ (0.3 mmol; 74 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a light greenish crystalline product. Yield: 142 mg, 68%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3PrN_5S$ ($M_r = 700.88 \text{ gmol}^{-1}$): C 46.27, H 3.88, N 9.99, S 4.58; Found: C, 46.69; H, 3.85; N, 9.86; S 3.75. IR (KBr): (3080 w, 3034 w, 2930 vw, 2858 vw, 1610 vssh, 1558 m, 1503 m, 1479 m, 1423 vs, 1379 ssh, 1318 w, 1226 vs, 1120 w, 1071 m, 1040 m, 1011 vs, 878 vw, 861 w, 830 s, 814 s, 728 m, 625 w, 600 m, 537 s, 521 vw, 489 w) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [NdCl₃(bpe)₂]·thz (4)

NdCl₃ (0.3 mmol; 75 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above yielding a light bluish crystalline product. Yield: 138 mg, 65%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3NdN_5S$ (M_r = 704.21 gmol⁻¹): C 46.05, H 3.86, N 9.94, S 4.55; Found: C, 46.48; H, 3.94; N, 9.71; S 4.42. IR (KBr): (3081 w, 3034 w, 2930 vw, 2858 vw, 1611 vssh, 1558 m, 1503 m, 1479 m, 1424 ssh, 1380 m; 1318 w, 122 6vs, 1125 w, 1072 vs, 1042 m, 1012 vs, 878 vw, 861 m, 830 s, 810 s, 729 m, 625 w, 600 m, 537 s, 521 w, 4901 w, 425 m) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [SmCl₃(bpe)₂]·thz (5)

SmCl₃ (0.3 mmol; 77 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline product. Yield: 113 mg, 53%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3SmN_5S$ ($M_r = 710.33$ gmol⁻¹): C 45.65, H 3.83, N 9.86, S 4.51; Found: C, 46.27; H, 3.87; N, 9.83; S 4.52. IR (KBr): (3064 w, 3035 w, 2929 vw, 2859 vw, 1611 vssh, 1558 m, 1503 m, 1480 m, 1424 vs, 1380 m, 1318 m, 1227 vs, 1120 w, 1071 s, 1040 m, 1012 vs, 878 w, 861 m, 831 s, 814 s, 730 m, 701 vs, 625 m, 600 m, 537 vs, 521 w, 491 w) cm⁻¹.

Synthesis of ${}^3_{\infty}$ [GdCl₃(bpe)₂]·thz (6)

GdCl₃ (0.3 mmol; 79 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline product within excess thz. Yield: 132 mg, 62 %. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3GdN_5S$ ($M_r = 717.22 \text{ gmol}^{-1}$): C 45.22, H 3.79, N 9.76, S 4.47; Found: C, 46.10; H, 3.92; N, 9.62; S 4.43. IR (KBr): (3083 w, 3035 w, 2929 vw, 2858 vw, 1612 vssh, 1558 m, 1503 m, 1480 m, 1424 s 1380 w, 1318 m, 1227 vs, 1120 m, 1072 m, 1040 w, 1013 vs, 978 m, 861 vw, 830 vs, 811 s, 728 s, 625 s, 600 w, 537 s, 521 w, 492 m) cm⁻¹.

Synthesis of ${}^3_{\infty}$ [TbCl₃(bpe)₂]·thz (7)

TbCl₃ (0.3 mmol; 80 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above yielding a colourless crystalline product. Yield: 144 mg, 67%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3TbN_5S$ ($M_r = 718.89$ gmol⁻¹): C 45.11, H

3.79, N 9.74, S 4.46; Found: C, 45.90; H, 3.84; N, 9.86; S 4.33. IR (KBr): (3083 w, 3036 w, 2929 vw, 2859 vw, 1612 vssh, 1558 m, 1504 m, 1480 m, 1424 vs, 1380 m, 1318 m, 1227 vs, 1120 m, 1071 vs, 1041 m, 1013 vs, 878 vw, 861 m, 831 s, 811 s, 731 s, 625 m, 600 m, 537 s, 521 m, 491 w) cm⁻¹

Synthesis of ${}^3_{\infty}$ [DyCl₃(bpe)₂]·thz (8)

DyCl₃ (0.3 mmol; 81 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline product. Yield: 154 mg, 71%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3DyN_5S$ ($M_r = 722.47$ gmol⁻¹): C 44.89, H 3.77, N 9.69, S 4.43; Found: C, 44.65; H, 3.76; N, 9.33; S 3.65. IR (KBr): (3086 w, 3038 w, 2919 vw, 2862 vw, 1613 vssh, 1558 m, 1504 m, 1480 m, 1427 vs, 1381 m, 1319 m, 1228 vs, 1115 m, 1072 s, 1035 m, 1013 vs, 878 vw, 860 m, 827 s, 811 s, 726 s, 623 m, 603 m, 533 s, 517 m) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [HoCl₃(bpe)₂]·thz (9)

HoCl₃ (0.3 mmol; 81 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a light pink crystalline product in excess thz. Yield: 147 mg, 67 %. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3HoN_5S$ ($M_r = 724.90 \text{ gmol}^{-1}$): C 44.74, H 3.75, N 9.66, S 4.42; Found: C, 45.56; H, 3.91; N, 9.53; S 4.10. IR (KBr): (3065 w, 3036 w, 2929 vw, 2859 vw, 1613 vssh, 1558 m, 1504 m, 1480 m, 1425 vs, 1380 m, 1318 m, 1228 vs, 1120 m, 1072 s, 1041 w, 1013 s, 878 vw, 861 m, 831 s, 814 s, 733 m, 625 m, 601 m, 537 s, 522 m, 493 w) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [ErCl₃(bpe)₂]·thz (10)

ErCl₃ (0.3 mmol; 82 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. yielding a slightly pink crystalline product within the solvent. Yield: 153 mg, 70 %. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3ErN_5S$ ($M_r = 727.23$ gmol⁻¹): C 44.59, H 3.74, N 9.63, S 4.41; Found: C, 44.42; H, 3.79; N, 9.90; S 4.52. IR (KBr): (3065 w, 3036 w, 2929 vw, 2859 vw, 1613 vssh, 1558 m, 1503 m, 1480 m, 1425 vs, 1380 m, 1318 m, 1228 vs, 1120 m, 1071 s, 1042 m, 1013 vs, 878 vw, 861 m, 831 s, 811 s, 732 m, 625 m, 601 m, 537 s, 522 m, 493 w) cm⁻¹.

Synthesis of ${}^{3}_{\infty}$ [YbCl₃(bpe)₂]·thz (11)

YbCl₃ (0.3 mmol; 84 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above. The reaction yielded a colourless crystalline. Yield: 139 mg, 63 %. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3YbN_5S$ ($M_r = 733.01 \text{ gmol}^{-1}$): C 44.24, H 3.71, N 9.55, S 4.37; Found: C, 44.30; H, 3.73; N, 9.57; S 4.61. IR (KBr): (3066 w, 3032 w, 2926 vw, 2859 vw, 1612 vssh, 1558 m, 1504 m, 1480 m, 1425 vs, 1380 m, 1318 m, 1227 vs, 1120 m, 1071 vs, 1042 m, 1014 s, 878 vw, 861 m, 830 s, 811 s, 731 s, 625 m, 601 m, 546 s, 522 m, 492 w) cm⁻¹

Synthesis of ${}^{3}_{\infty}$ [LuCl₃(bpe)₂]·thz (12)

LuCl₃ (0.3 mmol; 84 mg), bpe (0.6 mmol; 109 mg) and thz (4.5 mmol; 383 mg) were reacted according to the synthesis procedure described above yielding a colourless crystalline product. The obtained product was washed with 2 x 1 ml dichloromethane. Yield: 98 mg, 44%. Elemental analysis: Anal. calcd. for $C_{27}H_{27}Cl_3LuN_5S$ (M_r = 734.94 gmol⁻¹): C 44.13, H 3.70, N 9.53, S 4.36; Found: C, 44.08; H, 3.75; N, 9.27; S 4.15. IR (KBr): (3083 w, 3036 w, 2929 vw, 2859 vw, 1613 vssh, 1557 m, 1503 m, 1480 m, 1424 vs, 1380 m, 1318 m, 1230 vs, 1120 m, 1070 vs, 1041 m, 1015 vs, 878 vw, 861 m, 828 s, 809 s, 731 s, 619 m, 600 m, 537 s, 521 m, 493 w) cm⁻¹.

Synthesis of ${}^{1}_{\infty}$ [GdCl₃(bpe)(py)₂]·(bpe/py) (13)

GdCl₃ (0.5 mmol; 132 mg), bpe (1.5 mmol; 276 mg) and py (1.6 mmol; 126 mg) were reacted according to the synthesis procedure described above yielding a colourless crystalline product within excess py. Yield: 150 mg, 41% Elemental analysis: Anal. calcd for C61H55Cl6GdN11 $(M_r = 1475.44 \text{ gmol}^{-1})$: C 49.66, H 4.17, N 10.44; Found: C, 48.73; H, 4.19; N, 10.18. IR (KBr): (3066 w, 3029 w, 2955 vw, 2927 vw, 2860 vw, 1611 vssh, 1600 vssh, 1558 m, 1504 m, 1488 m, 1444 vs, 1432 vssh, 1417 ssh, 1220 vs, 1154 vw, 1068 vs, 1037 m, 1009 vs, 989 m, 871 vw, 831 vs, 752 s, 701 vs, 623 s, 600 vw, 645 s, 623 m, 600 vw, 545 vs, 532 vs, 487 vw, 425 m) cm⁻¹.

Synthesis of ${}^{1}_{\infty}$ [ErCl₃(bpe)(py)₂]·(bpe/py) (14)

ErCl₃ (0.5 mmol; 137 mg), bpe (1.5 mmol; 276 mg) and py (1.6 mmol; 126 mg) were reacted according to the synthesis procedure described above. The reaction yielded a violet crystalline product. Yield: 183 mg, 41%. Elemental analysis: Anal. calcd for $C_{61}H_{55}Cl_6Er_2N_{11}$ (M_r = 1495.46 gmol⁻¹): C 48.99, H 4.11, N 10.30; Found: C, 48.66; H, 4.02; N, 10.05. IR (KBr): (3066 w, 3030 w, 2955 vw, 2928 vw, 2861 vw, 1612 vssh, 1601 vssh, 1558 m, 1505 m, 1488 m, 1444 vs, 1432 vssh, 1417 ssh, 1221 vs, 1155 w, 1069 s, 1038 s, 1012 vs, 990 m, 872 vw, 831 vs, 753 s, 701 vs, 624 m, 601 vw, 545 s, 533 ssh, 489 vw, 428 vw, 408) cm⁻¹

Single crystal X-ray diffraction

 $\int_{\infty}^{1} [La_2Cl_6(bpe)_2(thz)_6]$ Suitable single crystals of (1), ∞^{3} [LnCl₃(bpe)₂] thz with Ln = Ce(2), Pr(3), Dy(8), Yb(11) and ${}^{1}_{\infty}$ [LnCl₃(bpe)(py)₂] (bpe/py) with Gd(13) and Er(14) were selected for X-ray diffraction from the crystalline product from mother-liquor mixed with high viscosity perfluorinated ether (99.9%, ABCR). Data collection for the compounds were carried out on a BRUKER AXS Smart Apex 1 diffractometer at 168 K equipped with a graphite monochromator (Mo-K α radiation; $\lambda = 0.7107$ Å) and on a BRUKER AXS Apex II diffractometer with Helios-mirror at 100 K using either the BRUKER AXS Smart Software package or the BRUKER AXS Apex Suite.^[37] All structure solutions were carried out with direct methods using SHELXS^[27] and the crystal structures were refined using SHELXL^[27] on the graphical platform XSEED^[38] and OLEX2.[39] Integrity of symmetry was checked with the PLATON program.^[40] For all compounds, the non-hydrogen atoms were refined anisotropically by least square techniques, all hydrogen atoms with geometrical constraints regarding their positions. For 1, two thz rings show positional disorder for one C-S bond of the rings and were constrained to mixed C/S-positions in the refinement. Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition numbers CCDC-1414453 (1), 1414454 (2), 1414455 (3), 1414456 (8), 1414457 (11), 1023837 (13), and 1023838 (14) or the names of the authors and the literature citation.

Powder X-Ray diffraction

For powder diffraction, all samples were mortared and sealed in Lindemann glass capillaries (\emptyset 0.3 mm). Diffraction data was collected on a BRUKER AXS D8 Discover powder X-ray diffractometer, equipped with Lynx-Eye detector in transmission

Photoluminescence and vibrational spectroscopy

Excitation and emission spectra were recorded with a HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a 450 W Xe-lamp, double grated excitation and emission monochromators and a photo multiplier tube (R928P) at RT, using the FluorEssence software. Excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. Additionally, both excitation and emission spectra were corrected for the spectral response of the monochromators and the detector using correction spectra provided by the manufacturer. All samples were investigated as solids in spectroscopically pure quartz cuvettes in front face mode at room temperature and 77 K. NIR photoluminescence investigations were performed on a Photon Technology International Quanta Master TM Model QM-2000-4 spectrometer with an InGaAs-NIR detector and a 75 W xenon short arc lamp (UXL-75XE, Ushio). Additional filters for excitation (300 nm banbpess, $\Delta 20$ nm, OD 5, Edmund Optics), as well as an edge filter for emission (GG 650, Reichmann Optics) were used together with quartz cuvettes (Suprasil). For the luminescence decay investigations, an Edinburgh Instruments FLSP920 spectrometer was used equipped with pulsed picosecond laser (375 nm, 5 mW), with double grated excitation and emission monochromators and a PMT (Peltier cooled: -20 °C), and F900 software. *τ*-Decay time investigations were carried out in right angle mode and corrected for the instrument response function. IR-spectra were recorded with a THERMO Nicolet 380 FT-IR spectrometer in transmission mode using OMNIC 32 software. Either, 5 mg of the compounds were mixed with 300 mg of anhydrous KBr and pressed to transparent pellets at 5 kbar, or an ATR unit was used.

Thermal and elemental analysis

Thermal investigations were carried out by simultaneous DTA/TG on a Netzsch STA 409 thermal analyzer using the Proteus Software package on 15-30 mg of the samples. The compounds were investigated in an inert gas atmosphere (50% Ar and 50% N₂) and heated from 20 °C to 900 °C with a heating rate of 10 °C h⁻¹ in a constant gas flow of 20 ml min⁻¹ Ar and 20 ml min⁻¹ N₂. Carbon, nitrogen and hydrogen elemental analysis was performed with a vario micro cube (Elementar Analysensysteme GmbH).

Conclusions

A series of fourteen lanthanide coordination polymers ${}^{1}_{\infty}$ [La₂Cl₆(bpe)₂(thz)₆] (1), ${}^{3}_{\infty}$ [LnCl₃(bpe)₂] thz with Ln = Ce(2),

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Pr(3), Nd(4), Sm(5), Gd(6), Tb(7), Dy(8), Ho(9), Er(10), Yb(11) and Lu(12), $\frac{1}{20}$ [LnCl₃(bpe)(py)₂] (bpe/py) with Gd(13) and Er(14) was obtained from anhydrous halides with the linker 1,2bis(4-pyridyl)ethane and the solvents thiazole or pyridine. The majority of the compounds exhibit a remarkable amount of photoluminescence properties ranging from the VIS to the NIR region that prove the linker bpe as suitable sensitizer for lanthanide emission. Interesting phenomena apply, such as excitation dependent emission with a correlating shift of the chromaticity coordinates, antenna effects by the Dexter and Förster energy transfer mechanisms, ligand centred as well as 5d-4f- / 4f-4f-metal centred emission, and finally the inner filter effect. Furthermore, the coordination polymers were investigated on their thermal properties.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: additional crystal structure images, further crystallographic data such as interatomic distances and angles, X-ray powder patterns, photoluminescence spectra, and results from DTA/TG. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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