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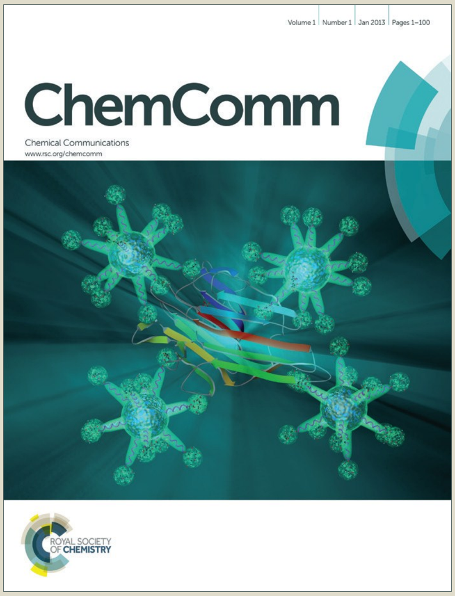

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Highly emissive, solution-processable and dynamic Eu(III)-containing coordination polymers

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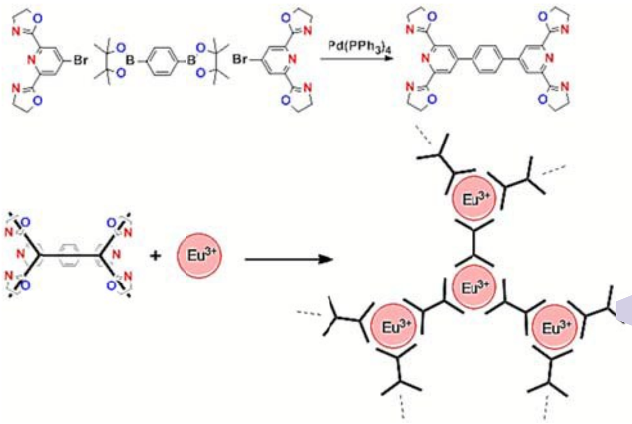
A new class of soluble Eu(III) coordination polymers based on a tridentate ditopic pybox ligand has been developed displaying high metal emission quantum yields of up to 73% as well as a unique dynamic behaviour in solution.

During the last few decades significant progresss has been made in the area of supramolecular polymers.[1,2,3] These type of polymers, where the monomers are held together by non-covalent interactions, shows a wide range of applications such as optical,[4] biomedical,[5] as well as for stimuli-responsive,[6,7] and self-healing materials.[8,9] In particular, the formation of macromolecular assemblies by employing a metal-ion induced self-assembly process in solution is of significant interest.[10,11,12,13,14] These supramolecular metallo-polymers combine common features of traditional covalently bound polymers with the unique characteristics introduced by metal ions such as magnetic,[15] catalytic,[16] self-repairing,[17] spin-crossover,[18] and optical properties.[19,20] So far, the research in this area has mainly focused on the metal-induced self-assembly of d-block metals, such as Ru^{2+}, Zn^{2+}, Co^{2+} and ditopic tridentate organic ligands. A metal-induced self-assembly with organic ligands can also be achieved with lanthanide metal ions. However, the focus within that area mainly focusses on the preparation of lanthanide-based coordination polymers in the solid state,[21,22] or on self-assembled supramolecular metallogels.[23] The use of lanthanides for the preparation of soluble coordination polymers has received far less attention.[24] In the case of solution-phase lanthanide coordination polymers up to three tridentate ligands can be coordinated to the metal centre, leading to a more branched metallo-supramolecular network rather than a 1-dimensional polymeric chain.[25,26] Additionally in the case of using lanthanide ions, the rigidity of the organic ligand becomes an important factor. If the coordinating sites of the ditopic ligand are connected by a flexible chain then the formation of rings rather than a more extended network is observed.[26] The outstanding luminescent properties of Ln(III) complexes, especially of Eu(III) and Tb(III), such as long excited state lifetimes, large antenna-generated shifts, narrow emission bands and high emission quantum yields are well known.[27] However, to date, no extensive studies on the photophysical properties of soluble Ln(III)-based coordination polymers incoorporating ditopic organic ligands have been carried out. One reason for this gap in this field is the lack of appropriate ditopic ligands which are able to serve as efficient sensitizers for Ln(III) emission. In this communication we present the synthesis of a new ditopic-based pybox ligand and its consequent complexation to Eu(III) to form soluble dynamic coordination polymers. To the best of our knowledge this is the first lanthanide soluble coordination polymer based on a rigid dumbbell-shaped ditopic tridentate ligand.



Scheme 1: Ligand synthesis and schematic presentation of the preparation of soluble dynamic Eu(III) coordination polymers with pybox-related ditopic ligands.

The new ditopic pybox ligand was synthesized via a palladium catalyzed Suzuki coupling reaction between 4-bromopyridine-2,6-bis(oxazoline) and 1,4-benzenediboronic acid in over 80% yield, and was purified by crystallization from a chloroform/ether solution. The purity of the ligand was verified using NMR, ESI, and elemental analysis characterization (ESI†). Subsequently, the coordination of the ditopic ligand to Eu(III) in a chloroform/acetonitrile solvent mixture in different ligand to metal ratios was investigated. It should be noted that in the case of using the monotopic pybox ligand up to three ligands can coordinate to the Eu(III) metal centre.[28] However, if as herein a ditopic ligand is used two metal ions can coordinate to one ligand and therefore form a coordination network structure in solution. The degree of the network formation strongly depends on the ligand to metal ratio used. Due to the nine coordinating sites available around the Eu(III) metal ions and six binding sites on the ligand, the lowest expected ligand to metal ratio, where all coordinating sites on the metal centre are saturated, is 1.5:1 (Scheme 1). The coordination of more ligand would lead to the formation of individual complexes and a break-down of the network structure. The coordination behaviour for different ligand to metal ratios was firstly investigated using UV-vis absorption spectroscopy (Fig. 1).

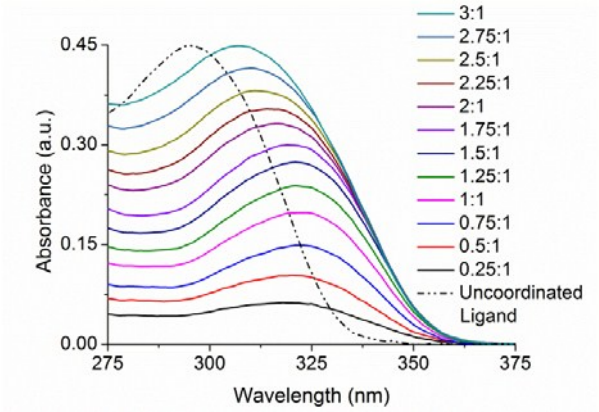


Fig.1: Absorption spectra of a solution containing $Eu(NO_3)_3$ and the ditopic ligand in chloroform / acetonitrile in different ligand to metal ratios, 0.25:1 – 3:1.

The free uncoordinated ligand shows an absorption maximum at around 295 nm. At ligand to metal ratios ranging from 0.25:1 to 1.5:1 the absorption maximum is located at about 320 nm. A further increase of the ligand to metal ratio of up to 3:1 leads to a broadening of the spectra and a constantly increasing shift of the absorption maxima towards lower wavelengths. These spectral changes can be interpreted as the following. At low ligand to metal ratios of up to 1.5:1, all of the ligand is coordinated and experiences a bathochromic shift resulting in similar absorption spectra. The shift of the absorption maxima towards lower wavelengths at higher ligand to metal ratios than 1.5:1 can be explained by the contribution of non-coordinated ligand in the solution. To further justify this conclusion we subtracted the absorption spectrum at a ligand to metal ratio of 1.5:1 (where all ligand is coordinated) from the absorption spectra at ligand to metal ratios of 1.75:1 up to 4:1 (ESI†). The resulting differences result in a similar absorption spectrum as the free non-coordinated ligand. In the absorption measurements described above the concentration of metal ions was kept constant while the ligand was added in variable amounts. Performing the absorbance measurements under Job plot conditions, where the total concentration of ligand and metal ions was kept constant, gave the same result that the highest possible ligand to metal ratio is 1.5:1 (ESI†),

The corresponding excitation spectra (ESI†) correlate very well with the absorption spectra up to a ligand to metal ratio of 1.5:1. A further addition of ligand did not result in changes of the excitation spectra. Since only coordinated ligand contributes to the metal emission this result confirms that at ligand to metal ratios higher than 1.5:1 the additional ligand added above this ratio does not coordinate to the metal.

Similar results were obtained using NMR titration measurements of diamagnetic La(III) ions with the uncoordinated ligand (ESI†). The changes in the NMR spectra are best visible by comparing the triplets of the CH_2 protons on the ligand oxazoline rings. Upon addition of ligand to the La(III) ions up to a ligand to metal ratio of 1:1, the formation of a first soluble species with two distinct triplets located at 4.83 ppm (for CH_2O) and 4.28 ppm (for CH_2N) respectively. Compared to the uncoordinated ligand (triplets located at 4.54 ppm (for CH_2O) and 4.12 ppm (for CH_2N)) both values are shifted downfield. Further addition of ligand up to a ligand to metal ratio of 1.5:1 results in a diminishing of the first species and the appearance of a second species displaying two new broad triplet signals located at 4.77 ppm and 3.95 ppm. This result is in agreement with previous findings from NMR titrations for the monotopic pybox ligand where more addition of ligand to the La(III) metal centre results in a significant upfield shift of the closest to the metal lying CH_2N signals.[28] The broadening of the proton signals upon increasing the ligand to metal ratio itself can be seen as an indication for the formation of larger structures in solution.[26] Starting at a ligand to metal ratio of 1.75:1 more addition of ligand does not result in further coordination to the La(III) metal ions. Instead the presence of uncoordinated ligand can be seen in the NMR spectra, which confirms the findings made by UV-vis absorption spectroscopy. To confirm the formation of higher molecular weight structures two-dimensional diffusion ordered NMR spectra (DOSY) were obtained for the free uncoordinated ligand as well as for the sample where both of the above described species are present (ESI†). The obtained spectra clearly show significant differences in the diffusion constants for the uncoordinated ligand (8.6×10^{-10} m^2/s), the first species (5.6×10^{-10} m^2/s) as well as the second species (3.1×10^{-10} m^2/s) indicating that the second species is considerably bigger than the first species. We therefore conclude that the second species corresponds to the formation of the soluble coordination network while the first to smaller polymeric chains or oligomeric structures.

ESI mass spectra (ESI†) of our samples showed a major peak corresponding to $[(Eu(DitopicPyboxPh)Eu)(2NO_3)]^{4+}$ but no peaks, presumably due to the instability of coordination network during the ionization process, for a higher degree polymeric structure were observed. We, among other groups, have found that further detailed structural characterization of these types of coordination polymers in solution is rather difficult to ascertain, due to the dynamic behaviour of the coordination bond.[20] However, the results from the UV-vis absorption spectra as well as NMR titrations and DOSY experiments indicate that the highest possible ligand to metal ratio without the presence of free uncoordinated ligand is 1.5:1 which is in agreement with previous findings from the literature and suggests the formation of a coordination network in solution herein.[24,26] Based on these results and taking into account the high binding affinities of pybox-related ligands to Ln(III) ions,[29,28] we conclude that a high mass coordination network assembly is formed between the new ditopic pybox ligand and Eu(III) metal ions.

The photophysical properties were further investigated by steady state and time-resolved emission measurements. Upon UV-excitation of the ditopic pybox ligands at 355 nm, emission peaks located at 579, 592, 616, 650, and 689 nm are seen which can be assigned to the typical Eu(III) $^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 4$) emission peaks (ESI†).[27] For all the emission spectra measured a single symmetrical peak at 579 nm, corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition, can be seen, indicating that only one major emitting species is present in solution (ESI†).[30] Furthermore, the presence of this transition suggests that Eu(III) is a non-centrosymmetric site.[31] The $^5D_0 \rightarrow {}^7F_1$ transition (592 nm) is an allowed magnetic dipole transition and is independent of the symmetry around the Eu(III) metal centre. In comparison, the intensity of the more prominent hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (616 nm), which is responsible for the bright red emission of all samples, is symmetry dependant. Therefore, differences in the site symmetry around the Eu(III) metal ions can be calculated from the intensity ratios (R) of the emission lines corresponding to the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions.[32] Herein the obtained emission intensity ratio (ESI†) slightly decreases with increasing concentration of ligand of up to a ligand to metal ratio of 1:1, indicating that the order of the symmetry around the Eu(III) metal centre increases.[33]

The emission decay lifetimes for all the samples (ESI†) are in the ms time range, which is consistent for pybox-related Eu(III) coordination compounds.[28] All emission decay curves can be fitted by mono-exponential functions, indicating that only one major emitting species is present is solution. However, the lifetimes show significant changes upon changing the ligand to metal ratio (Fig. 2).

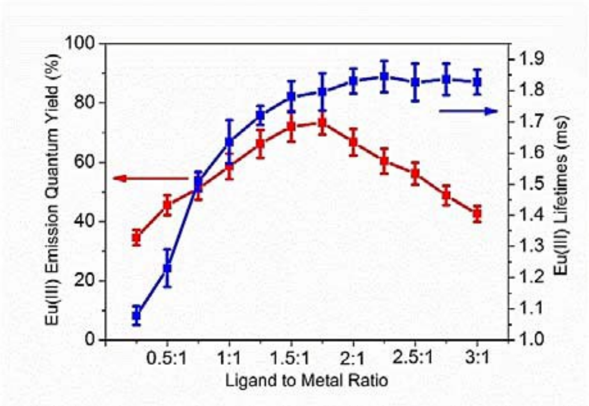


Fig. 2: Relative Eu(III) emission quantum yields (left axes) and Eu(III) emission lifetimes (right axes) for different ligand to metal ratios in chloroform / acetonitrile.

Up to a ligand to metal ratio of 1.5:1 to 1.75:1 the emission lifetime in a chloroform / acetonitrile solvent mixture increases from about 1.0 ms to about 1.8 ms and plateaus upon further ligand addition. These changes in the lifetimes might be due to the coordination of water molecules to Eu(III) which are known to quench the emission.[34] The possible water coordination was investigated by lifetime measurements in chloroform / methanol and chloroform / deuterated methanol from where the number of directly coordinated water molecules (q) to the Eu(III) metal ions can be estimated using Horrock's equation.[35] The lifetimes in chloroform / methanol are slightly shorter but show a similar trend to that in chloroform / acetonitrile while the lifetimes in chloroform / deuterated methanol do not change significantly upon changing in the ligand to metal ratios (ESI†). As a result, the calculated number of coordinated water molecules (q) constantly decreases with an increase of the ligand to metal ratio up to 1.5:1 where it reaches a value close to 0 (ESI†). Relative quantum yields were measured at 279 nm and follow a similar trend as the emission lifetimes at low ligand to metal ratios of up to 1.5:1 (Fig. 2). The quantum yield increases steadily from about 34% to 73% with an increase of the metal to ligand ratio of up to 1.5:1 to 1.75:1. Upon further increasing the ligand to metal ratio to 3:1 the quantum yield significantly drops to about 40%, which can be explained by increasing competitive uncoordinated ligand absorption (as could be seen from Fig. 1). The high quantum yield values reported herein are comparable to a previous reported *para*-thiophene-derived pybox ligand.[29] It was found that electron-withdrawing groups in the *para*-position of the centre pyridine ring of the pybox ligand result in a more favorable triplet state to Eu(III) energy transfer. In the case of our ditopic ligand with a benzene ring connecting the two pybox moieties in the *para*-position, a similar effect for the ligand triplet state energy is expected, which could explain the high values of the quantum yield. Triplet state measurements of the related Gd(III) compounds at 77 K are currently ongoing.

All the data from the photophysical studies (emission intensity ratios, excited state lifetimes, and quantum yields) are consistent and point towards the same conclusion that at a ligand to metal ratio of 1:1.5 to 1:1.75 all coordinating sites of the Eu(III) metal centre are occupied by ligand and that at this stage the degree of the coordination network formation in solution is maximized. At higher ligand to metal ratios the additional amount of ligand will not coordinate and remains as free uncoordinated ligand in solution which does not affect the Eu(III) emission properties. Furthermore, it has been shown that water is coordinated to the Eu(III) metal centre at low ligand to metal ratios of up to 1.25:1. Since the $Eu(NO_3)_3$ source does not give emission, the water coordination must come from partly coordinated Eu(III) metal ions which are not fully saturated by ligand. This leads to the conclusion that if an insufficient amount of ligand is present to form a network, the formation of other structures such as polymeric chains might be more favorable. The concentration dependence of the photophysical properties were investigated by dilution of the sample with a ligand to metal ratio of 1.5:1 (ESI†). It can be seen that Eu(III) lifetimes as well as emission intensity ratios R do not significantly change indicating that the photophysical properties are not concentration dependant. It should be noted that the molar concentrations used for the photophysical studies were in the micro-molar range. At higher molar concentrations in the sub milli-molar range, the formation of an insoluble precipitate was observed when a ligand to metal ratio of 1.5:1 was reached. SEM images of the precipitate show the formation of porous material and XPS elemental analysis showed that the ligand to metal ratio in the solid state is reasonably close (1.75:1) to the highest possible ratio in solution (1.5:1) from where the precipitation occurred (ESI†). From that we conclude that the size of the coordination network is increasing with an increase of the concentration as well as an increase of the ligand to metal ratio of up to 1.5:1.

The dynamic behaviour of the coordination polymers in solution was investigated by titration of the Eu(III) coordination sphere saturated sample in a ligand to metal ratio of 1.5:1 against Tb(III) and Sm(III) metal ions. Upon the addition of Tb(III) ions, the emission intensity of Eu(III) continuously decreases, indicating that Eu(III) is partly replaced by Tb(III) (ESI†). Tb(III) does not give any emission with the ditopic pybox ligand, presumably because the triplet state energy of the ligand lies below the excited $^5D_4$ Tb(III) state (21500 cm^{-1}) and thus no energy transfer to Tb(III) can occur. Sm(III) as another emitting lanthanide ion was therefore chosen to perform similar titration experiments. Again the replacement of Eu(III) by Sm(III) ions can be seen by a decrease of the Eu(III) emission intensity (ESI†). However, because the excited state lifetime of Sm(III) is in the micro-second range compared to a milli-second range lifetime of Eu(III), the mixed metal emission spectra cannot be observed using steady-state spectroscopy, therefore, time-resolved emission spectroscopy was used at a µs scale (Fig. 3).

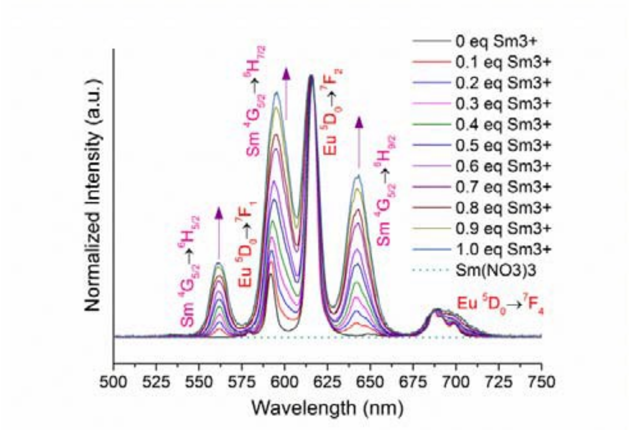


Fig. 3: Time-gated emission spectra of a Eu(III) sample in a ligand to metal ratio of 1.5:1 titrated with Sm(III) metal ions (5µs delay, 10 µs gate width, 1 nm band width).

Upon the addition of Sm(III) ions, the intensity of the distinct Sm(III) emission bands ($^4G_{5/2} \rightarrow {}^6H_{J/2}$, J = 5, 7, 9) increases while the Eu(III) emission intensity decreases. Moreover, the $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ intensity ratios as well as emission decay lifetimes change during the titration (ESI†), indicating that a partial replacement of Eu(III) by Sm(III) leads to a change in the symmetry as well as higher quenching of the Eu(III) metal centre.

In summary, we have synthesized a new rigid ditopic pybox-related ditopic ligand, and shown that this ligand can be used for a self-assembly process in solution to form a soluble coordination network based on Eu(III) metal ions. All photophysical data reported herein point towards the same conclusion that at a ligand to metal ratio of 1.5:1 all coordinated sites on Eu(III) are saturated by ligand which is consistent with the theoretical value for the network formation. The ditopic pybox ligand is an efficient sensitizer for Eu(III) emission displaying high quantum yields of up to 73%. High quantum yields together with the dynamic nature make these materials promising for the preparation of sensing applications, photoactive devices, as well as mixed metal emitting materials.

Notes and references

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† Electronic Supplementary Information (ESI) available: Instrumental and experimental procedures; synthesis and full characterization of the ligand DitopicPyboxPh; photophysical studies of the Eu(III) containing coordination polymers. See DOI: 10.1039/c000000x/

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