ChemComm

Check for updates

Facile access to efficiently luminescent Ln³⁺ phosphonic ester coordination polymers (Ln = Eu, Tb, Dy)†‡

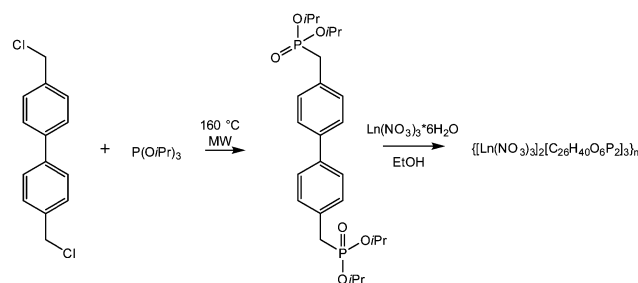Kristijan Krekić, Dieter Klintuch and Rudolf Pietschnig [ID] *

Efficiently luminescent coordination polymers containing lanthanide ions (Eu³⁺, Tb³⁺, Dy³⁺) can be easily obtained using a suitable bisphosphonic ester from which a heterometallic version can be elaborated showing white light emission.

Owing to their remarkable photophysical properties, lanthanide ions are unique for applications in lighting, sensing and display technologies.[1–3] In recent years coordination polymers turned out to be a suitable scaffold for accommodating isolated lanthanide centers.[4–6] While the most frequently employed binding sites in coordination polymers or metal–organic frameworks are carboxylates or nitrogen bases,[7,8] phosphonates[9,10] and organophosphates have been used as ligands as well.[11] By contrast, the use of phosphonic esters for this purpose is less explored and just started to emerge.[12,13] The special benefit of the P⁽ⱽ⁾=O units as ligands towards lanthanide ions is their property to increase quantum yields of complexes compared to their carboxylic acid counterparts. The vibrational frequency of *e.g.* phosphonates is much lower than that of the respective carboxylates, which suppresses vibrational relaxation of excited states at the coordinated metal, thus increasing the quantum yield of emissive processes.[14] Aiming at high rigidity, mainly aryl bonded oxophosphorane units have been employed as ligands so far, which are accessible *via* metallation reactions under inert conditions only, imposing some synthetic challenges with respect to organofluorine functionalities.[15,16]

For alkyl bonded phosphonic acids the Michaelis–Arbuzov rearrangement provides a well-established access offering large structural variety.[17] A disadvantage of this reaction are usually very long reaction times and sometimes very poor yields following classical procedures.[18] By contrast, microwave irradiation allows

uniform heating and higher temperatures which has been demonstrated for phosphonates with small organic substituents at phosphorus.[19,20]

In combining the beneficial features of the aryl and the alkyl based phosphonate ligands we set out to explore the microwave driven preparation of a biphenyl based bisphosphonate. Here we report a novel synthetic access to $(C_6H_4PO(OiPr)_2)_2$ under solvent free conditions in high yield, and its use as ligand for the construction of efficiently photoluminescent coordination polymers involving Eu, Tb, Dy cations along with their non-emissive Y analog. The combination of these metals in heterotrimetallic combinations will be addressed as well, with respect to white light emitting coordination polymers. The use of $(C_6H_4PO(OiPr)_2)_2$ (**L**) as ligand has been limited by its synthetic availability so far. It has been mentioned in the literature several decades ago, but only with very limited characterization with its ligand properties remaining unexplored till now.[21] Starting from 4,4′-dichloromethylbiphenyl and triisopropyl phosphite we have been able to prepare compound **L** on a multigram scale in excellent yield using microwave heating (Scheme 1). The ³¹P NMR spectrum in solution shows a signal at 24 ppm split to a characteristic multiplet with a triplet of triplet like pattern owing to P–H coupling. Solid **L** shows two IR bands characteristic for phosphonates[13] at 1232 and 1105 cm⁻¹.

Institute of Chemistry and Center for Interdisciplinary Nanostructure Science and Technology, University of Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany. E-mail: pietschnig@uni-kassel.de; Fax: +49 561 804 4649; Tel: +49 561 804 4458

† Dedicated to Prof. Dr. László Nyulászi on the occasion of his 60th birthday.
‡ Electronic supplementary information (ESI) available: Experimental and synthetic details, spectral and analytical data. CCDC 1562260–1562264 and 1569994. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc06621j
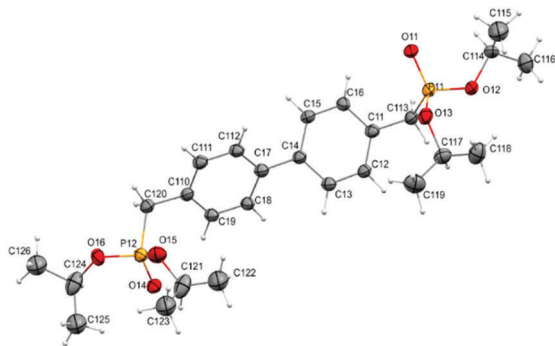

Scheme 1 Synthesis of **L** and coordination polymers **1a–e** containing Eu (a), Tb (b), Dy (c), Y (d) or Eu₀.₁₅Tb₀.₇₀Y₀.₁₅ (e).

Fig. 1 Solid state structure of ligand **L**. Ellipsoids are drawn at 30% probability level.
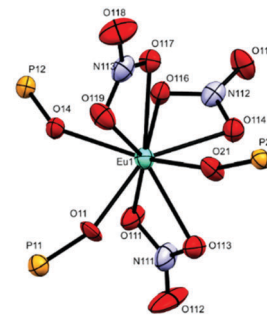

Fig. 2 Coordination sphere around the europium ion in **1a**. Thermal ellipsoids are drawn at 30% probability level.

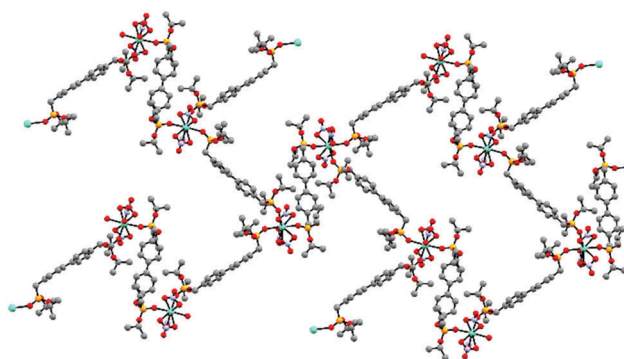Fig. 3 Repeating unit of **1a**. Hydrogen atoms are omitted for clarity.

Ligand **L** crystallizes in a $P2_1/n$ space group. In the asymmetric unit one molecule of ligand is present showing twisted phenyl rings (Fig. 1). The P=O bond lengths range between 1.455(5) and 1.476(5) Å and are within standard bond lengths for such systems.[12,22] The angles around P11 cover a range between 103.8(3) and 114.9(3)°. The other phosphorus atom (P12) has angles within a range of 102.5(4) to 115.5(4)°. Both atoms show slight deviation from tetrahedral environment probably owing to steric interactions of the bulky substituents. The arrangement of the biphenyl system deviates from coplanarity with an inter-planar angle of 43.7(3)°.

The formation of coordination polymers **1a–e** can be achieved by slow evaporation of an ethanol solution of the respective $Ln(NO_3)_3$ salt (Ln = Eu, Tb, Dy, Y) and an excess of the ligand **L** at room temperature (Scheme 1). Ethanol proved to be the best solvent to grow crystals suitable for single crystal X-ray analysis while other alcohols usually gave only microcrystalline powders. Polymers **1a–e** are all isostructural which was further confirmed by powder diffraction for **1e** as bulk material. Besides single crystal X-ray diffraction, compounds **1a–e** were characterized by elemental analysis and IR spectroscopy. All polymers **1a–e** show two nearly identical bands for the coordinated ligand at 1165 and 1097 cm^{-1} shifted to lower wave numbers compared with uncoordinated **L**. Out of the polymers **1a–e** only the structure of europium based **1a** will be discussed as representative structure of the series. The polymer crystallizes in space group $P2_1/n$. The asymmetric unit contains one $Eu(NO_3)_3$ unit with 1.5 eq. of ligand **L** suggesting a formula for the repeating unit of polymer as $[[Eu(NO_3)_3]_2L_3]$. This composition of the coordination polymer is further confirmed by elemental analysis. In the solid state structure each europium ion is coordinated by three bidentate nitrate anions and three monodentate ligands adding up to a coordination number of 9 (Fig. 2). The bond lengths from europium to nitrate oxygen atoms are in the range of 2.418(7) to 2.479(7) Å and do not deviate significantly from similar complexes.[13] The bond lengths of europium to oxygen atoms belonging to the phosphonic ester ligand are slightly shorter compared with those of a nitrate and are in the range of 2.313(5) to 2.347(5) Å. The polymer forms a zig-zag chain in a two dimensional sheet like arrangement (Fig. 3). These sheets are stacked in an alternating AB packing. Interestingly Π–Π stacking between biphenyl rings is not observed, due to

the perpendicularity of neighboring phenyl rings. A minor difference between the molecular structures of **1a–e** affects the dihedral angles of the phenyl rings of the biphenyl unit which deviates slightly from coplanarity. The deviation for **1a** is slightly (*ca.* 2°) larger than for **1b–e** which are identical within the limits of precision. Also the cell volume is smaller in case of **1a** (by *ca.* 200 Å^3). Nevertheless such tiny structural features can be decisive for physical properties as in related cases.[23]

Owing to the paramagnetic nature of the metal ion, NMR spectroscopy is unsuitable to get an insight into the polymer formation in solution. However, with mass spectrometry some information could be obtained right after mixing the reactants. With MALDI-MS the formation of dimers of the type $[(Eu_2(NO_3)_5)L_2]^+$ (m/z = 1634.28) and trimers $[(Eu_3(NO_3)_8)L_3]^+$ (m/z = 2438.30) could be observed which suggests a step wise growth mechanism.

The study of the photophysical properties of ligand **L** in the solid state revealed a remarkable emission quantum yield of 89% at the excitation wavelength of 350 nm with an emission maximum at 410 nm (Fig. 4). Coordination of **L** to a non-emissive metal center like yttrium such as in **1d** leads to similar yet slightly red shifted (11 nm in excitation, 4 nm in emission) excitation and emission spectra with a still high emission quantum yield of 60%. By comparison, the excitation spectrum of coordination polymer **1a** shows a hypsochromic shift of the ligand based excitation at 330 nm. The europium based excitation of **1a**, however, remains almost unchanged as compared to the spectra obtained for solid $Eu(NO_3)_3$ used as reference
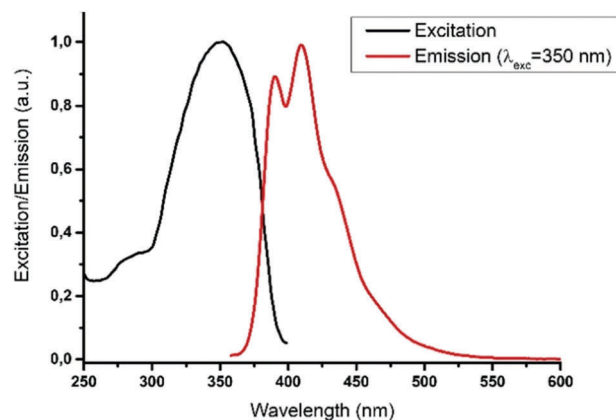
Fig. 4 Normalized ligand excitation and emission spectrum of solid **L**.

besides being the starting material in the preparation of **1a**. Based on these findings, we performed excitation experiments with wavelengths adapted to either the ligand transitions or the metal transitions for comparison.

Using an excitation wavelength at 330 nm (maximum ligand excitation) leads to an increase of quantum yield from 2% in Eu(NO$_3$)$_3$ up to 37% for polymer **1a**. The emission spectra obtained for ligand-centered excitation at 330 nm can be assigned to seven literature known luminescent transitions of europium (Fig. 5)[24] suggesting an antenna like energy transfer from the ligand to the metal. Despite excitation of the ligand, no ligand emission can be observed in turn at any excitation wavelength, suggesting a unidirectional energy transfer from ligand to metal with significant rise of luminescence quantum yield for the metal emission. Using an excitation wavelength at 396 nm (maximum europium excitation) again leads to a drastic increase of quantum yield from 6% in Eu(NO$_3$)$_3$ up to remarkable 70% for polymer **1a**. The latter finding suggests that apart from an antenna effect the rigid matrix of the coordination polymer along with the enhanced vibrational properties of the oxophosphorane donor sites leads to reduced energy dissipation upon metal excitation of **1a** as compared
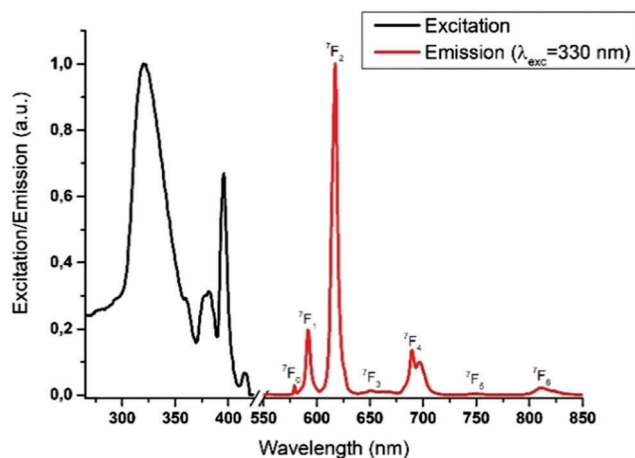
with the corresponding nitrate salt. To exclude the possibility that the quantum yields of the latter are low simply owing to vibrationally active water molecules in the nitrate salt used for comparison, Eu$_2$O$_3$ has been used as an alternative reference giving essentially identical results.

For the terbium based polymer **1b** similar effects can be observed. The organophosphorus ligand in **1b** again causes a strong excitation band located at 318 nm (Fig. 6) resulting in an increased emission quantum yield of 26% for **1b** compared to 5% for Tb(NO$_3$)$_3$. However, addressing the excitation maximum of terbium at 353 nm leads to an identical quantum yield of 26% with no further increase as in the corresponding europium case. This indicates a less efficient ligand to metal energy transfer for terbium than for europium with ligand **L**. Again the emission bands can be assigned to seven literature known metal based transitions.[25]

Moreover, a metal to ligand energy transfer occurs for the Tb based **1b**, which depends on the excitation wavelength. This behavior causes an additional ligand emission observable in the spectra.

In dysprosium based polymer **1c** the ligand to metal energy transfer effects a highly enhanced intensity in the excitation spectrum of dysprosium. Like for **1b** the emission spectrum of **1c** is strongly dependent on the excitation wavelength owing to the competition between metal to ligand energy transfer and direct ligand emission. The combination of metal and ligand emissions raises the luminescence quantum yield from below 2% for Dy(NO$_3$)$_3$ up to 34% for polymer **1c** at 373 nm excitation wavelength. At an excitation wavelength of 399 nm, where no ligand emission occurs, still a quantum yield of 11% can be measured. In the region characteristic for the metal based emission four literature known luminescence transitions can be detected (Fig. 7).[1] The different luminescence behaviour of **1a** compared with the other luminescent metal complexes **1b,c** may be attributed to the higher ion potential of the Tb and Dy ions owing to their smaller size or the torsional difference of the biphenyl system in the corresponding coordination polymers. Moreover, for simple model compounds of these metals it is known from the literature that the f-splitting is slightly larger for
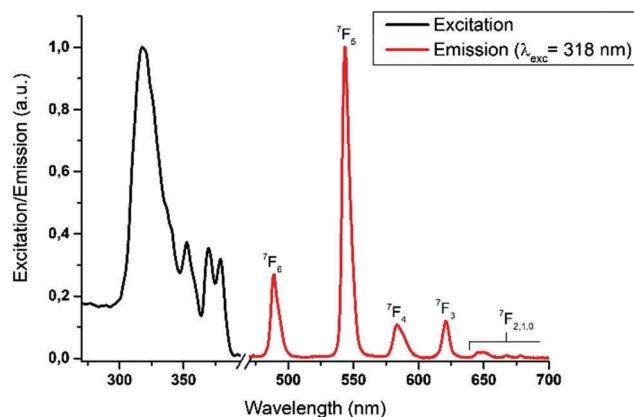
Fig. 5 Normalized excitation and emission spectrum of **1a** at 330 nm excitation wavelength with the observed $^5D_0 \rightarrow {}^7F_n$ transitions.

Fig. 6 Normalized excitation and emission spectrum of **1b** at 318 nm excitation wavelength with the observed $^5D_4 \rightarrow {}^7F_n$ transitions.
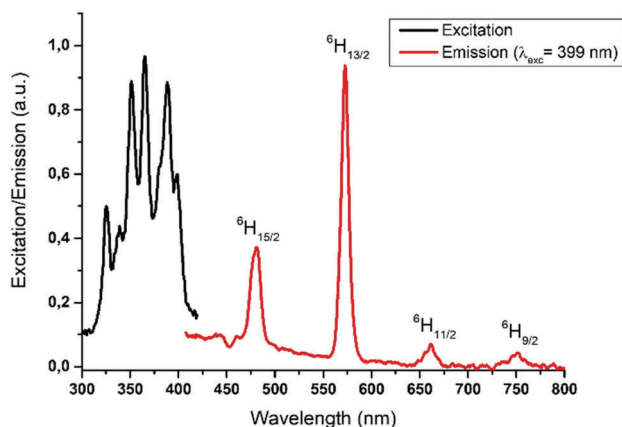
Fig. 7 Normalized excitation and emission spectra (399 nm excitation) of dysprosium based **1c** with the observed $^5F_{9/2} \rightarrow {}^6H_{n/2}$ transitions.

Eu^{3+} than for the two other metal ions.[26,27] A further more specific explanation may arise from the reduced cell volume for **1a** compared to **1b,c** – despite the larger ion size of Eu^{3+} – which should increase the rigidity of the polymeric framework leading to reduced vibrational energy dissipation and consequently higher emission quantum yields.

Since the quantum yields of the metal ions could be enhanced by the combination with the novel organophosphorus ligand **L** we wanted to further explore their suitability for light emitting devices. A mixture of the metal complexes should allow to adjust the emission color just by the choice of the excitation wavelength. Thus, a mixed metal heterotrimetallic version of $[Ln(NO_3)_3]_2L_3$ (**1e**) containing Eu, Tb and Y in a 0.15 : 0.70 : 0.15 ratio shows under standard UV-light at 366 nm the emission of white light with a quantum yield of 26%, where the red part comes from europium, green from terbium and the blue one from the yttrium-**L**-complex (Fig. 8).

As mentioned above, in case of the yttrium complex the metal itself is not emissive but rather ensures a controlled arrangement of the blue emitting ligand. To conclude we have developed a straightforward access to a ditopic bisphosphonate

ligand and explored its ligand properties towards selected f-block metals. The ligand is well suited to transfer energy to the metal centers leading to emissions with quantum yields near 70% for Eu and around 30% for Tb and Dy. By combination of metal ions with different emission colors, mixed hetero-metallic versions can be prepared within this polymer scaffold showing white light emission with 26% quantum yield.

Conflicts of interest

There are no conflicts to declare.
The authors declare no conflicts of interest.

Notes and references

1 O. Guillou, C. Daiguebonne, G. Calvez and K. Bernot, *Acc. Chem. Res.*, 2016, **49**, 844–856.
2 J.-C. Bünzli, *Nat. Chem.*, 2010, **2**, 696.
3 B. Samson, A. Carter and K. Tankala, *Nat. Photonics*, 2011, **5**, 466–467.
4 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
5 A. Deluzet, W. Maudez, C. Daiguebonne and O. Guillou, *Cryst. Growth Des.*, 2003, **3**, 475–479.
6 D. Kustaryono, N. Kerbellec, G. Calvez, S. P. Freslon, C. Daiguebonne and O. Guillou, *Cryst. Growth Des.*, 2010, **10**, 775–781.
7 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.
8 C. Daiguebonne, N. Kerbellec, O. Guillou, J.-C. Bünzli, F. Gumy, L. Catala, T. Mallah, N. Audebrand, Y. Gérault, K. Bernot and G. Calvez, *Inorg. Chem.*, 2008, **47**, 3700–3708.
9 S. M. F. Vilela, A. D. G. Firmino, R. F. Mendes, J. A. Fernandes, D. Ananias, A. A. Valente, H. Ott, L. D. Carlos, J. Rocha, J. P. C. Tome and F. A. Almeida Paz, *Chem. Commun.*, 2013, **49**, 6400–6402.
10 F. A. A. Paz, S. M. F. Vilela and J. P. C. Tomé, *Cryst. Growth Des.*, 2014, **14**, 4873–4877.
11 S. K. Gupta, S. K. Langley, K. Sharma, K. S. Murray and R. Murugavel, *Inorg. Chem.*, 2017, **56**, 3946–3960.
12 J.-W. Zhang, C.-C. Zhao, Y.-P. Zhao, H.-Q. Xu, Z.-Y. Du and H.-L. Jiang, *CrystEngComm*, 2014, **16**, 6635.
13 L. Zhang, W. Dou, W. Liu, C. Xu, H. Jiang, C. Chen, L. Guo, X. Tang and W. Liu, *Inorg. Chem. Commun.*, 2015, **59**, 53–56.
14 Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka and S. Yanagida, *J. Phys. Chem.*, 1996, **100**, 10201–10205.
15 A. Orthaber, F. Belaj, J. H. Albering and R. Pietschnig, *Eur. J. Inorg. Chem.*, 2010, 34–37.
16 A. Orthaber, C. Seidel, F. Belaj, J. H. Albering, R. Pietschnig and U. Ruschewitz, *Inorg. Chem.*, 2010, **49**, 9350–9357.
17 A. E. Arbuzov, *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 687.
18 A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, 1981, **81**, 415–430.
19 D. Villemin, F. Simeon, H. Decreus and P.-A. Jaffres, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **133**, 209–213.
20 J. J. Kiddle and A. F. Gurley, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2000, **160**, 195–205.
21 V. S. Abramov and N. A. Moskva, *Zh. Obsch. Khim.*, 1967, **37**, 2243–2247.
22 N. Stock, N. Guillou, J. Senker, G. Férey and T. Bein, *Z. Anorg. Allg. Chem.*, 2005, **631**, 575–581.
23 M. Cindrić, G. Pavlović, D. Pajić, K. Zadro, D. Cinčić, T. Hrenar, E. Lekšić, A. Belen Pinar Prieto, P. Lazić and D. Šišak Jung, *New J. Chem.*, 2016, **40**, 6604–6614.
24 K. Binnemans, *Coord. Chem. Rev.*, 2015, **295**, 1–45.
25 S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley & Sons, Ltd, 2006.
26 F. S. Richardson, M. F. Reid, J. J. Dallara and R. D. Smith, *J. Chem. Phys.*, 1985, **83**, 3813–3830.
27 M. Atanasov, C. Daul, H. U. Güdel, T. A. Wesolowski and M. Zbiri, *Inorg. Chem.*, 2005, **44**, 2954–2963.
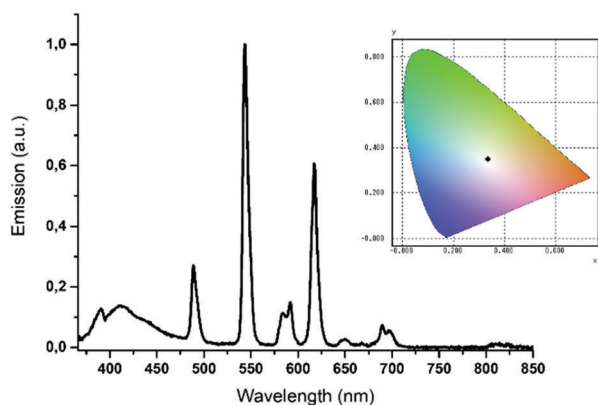

Fig. 8 Normalized emission spectrum of heterotrimetallic **1e** excited with a wavelength of 366 nm with the resulting color of the emitting light shown in the color map (black dot).