



Click-chemistry-based bis-triazolylpyridine diphosphonate ligand for the sensitized luminescence of lanthanides in the solid state within the layers of γ -zirconium phosphate

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ABSTRACT

The synthesis by means of 'click' chemistry of a new ligand bearing the bis-triazolylpyridine motif and pendant phosphonate groups is described. The topotactic phosphate/phosphonate exchange of the ligand into gamma-zirconium phosphate led to an organic–inorganic-layered material which revealed an excellent matrix to achieve the efficient sensitization of emitting lanthanides.

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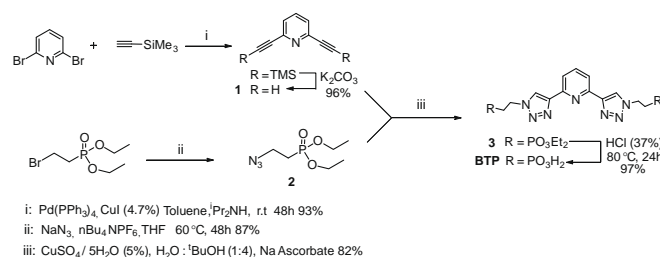
The preparation of *phosphors* or luminescent powders may find immediate applications in many technological areas (telecommunications, solar energy, artificial photosynthesis, lighting, displays, photo-signaled molecular recognition, biotechnology, medical diagnostics, bio-imaging, etc.) related to the broad concept of *photonics*, the science and technology for mastering the interaction of light with matter.¹ To this effect, the sharp and intense luminescence of lanthanides, due to their *ff* electronic transitions, has lots of basic and applied research implications,^{2,3} yet direct lanthanide excitation produces weak emission owing to the metal's low molar absorptivity. Significantly emission enhancement can in turn result when the lanthanide metals chelate with organic ligands that efficiently take the light in and effectively transfer the absorbed energy to the metal. Over the years, our group has succeeded in the development of a large body of organic molecules based on different chromophores which exerted the so-called *antenna effect* with outstanding quantum yields.⁴ On the other hand, we are currently involved in the building of organic–inorganic scaffolds rendering insoluble, thermally stable solids for a variety of applications. The inorganic part is zirconium phosphate in its γ form (γ -ZrP) which has revealed a very versatile carving board where organic phosphonates and other phosphorous functions can be covalently attached by topotactic exchange.

Previous work published by us evidences that pillared γ -ZrP with polyethylenoxygenated chains may constitute a good accommodation for the sensitized emission of lanthanides by suitable chromophores, thus paving the way to the synthesis of highly luminescent solids for applications in optical devices, the sensitive detection of lanthanides, or other chemical species among other applications.⁵ In this Letter we describe the incorporation into γ -ZrP of a new chromophore, {2,2-[4,4-(pyridine-2,6-diyl)]bis(1H-

1,2,3-triazol-1,4-diyl)bis(ethane-1,2-diyl) bis-phosphonic acid; **BTP**}, synthesized by 'click-chemistry' procedures. The resulting material will be tested as a solid host to efficiently sensitize the emission of lanthanide ions.

The synthetic route for the **BTP** ligand is depicted in Scheme 1. 2,6-Diethynylpyridine (**1**) was synthesized from 2,6-dibromopyridine by Sonogashira coupling according to the literature procedures,⁶ followed by hydrolysis with potassium carbonate in THF/methanol.⁷ The azido ethylphosphonate derivative **2** was synthesized from commercial diethyl 2-bromoethylphosphonate and sodium azide in the presence of tetrabutylammonium hexafluorophosphate in THF.⁸ The coupling of 2,6-diethynylpyridine and the azido phosphonate by means of typical click-chemistry⁹ rendered the bis-triazolylpyridine derivative **3**¹⁰ which was finally hydrolyzed to the bis-phosphonic acid ligand **BTP** in 71% overall yield from 2,6-dibromopyridine.¹¹

One of the strongest points of layered γ -ZrP is its use as 2D template to build 3D materials with aprioristic knowledge of its structure, following a synthetic rationale similar to that practiced by



Scheme 1. Synthetic route for **BTP** ligand. Reagents and conditions: (i) Pd(PPh₃)₄, CuI (4.7%), toluene, ¹Pr₂NH, rt, 48 h 93%; (ii) NaN₃, nBu₄NPF₆, THF 60 °C, 48 h, 87%; (iii) CuSO₄/5H₂O (5%), H₂O:tBuOH (1:4), Na ascorbate 82%.

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organic chemists. In short, laminar γ -ZrP contains two different kinds of phosphates, one internal which sustains the integrity of the layers (by being bonded to four different zirconium atoms through each of its four oxygen atoms) and the other in the lamellae surface pointing to the interlayer region and using only two oxygen atoms to bond two zirconium atoms. These surface phosphates are the ones which can be exchanged by mild hydrothermal processes with other phosphorous functions topotactically, that is, maintaining the layered structure intact.¹² Layered γ -ZrP was the first to be exfoliated in order to make its interlayer region accessible to phosphonic acids, that is, **BTP**. This can be easily achieved by colloiddally suspending γ -ZrP in 1:1 water–acetone at 80 °C for several minutes. The suspension was treated with the appropriate amount of **BTP** leading to material γ -ZrP-BTP. Figure 1 shows its solid state MAS ³¹P NMR, which exhibits three signals at chemical shifts –27.0 (PO₄), –14.5 [O₂P(OH)₂], and 13.1 [O₂P(OH)-R-P(OH)O₂] ppm. The relative integrals (100:68:30) of these signals in one hand and the weight losses observed in the thermogravimetric analysis (TGA; Fig. 2) in the other allowed for the calculation of γ -ZrP-BTP molecular formula as ZrPO₄(H₂PO₄)_{0.64} (C₁₃H₁₅N₇P₂O₆)_{0.18}·2H₂O, in reasonable accordance with the elemental analysis (calcd: C, 7.78; H, 2.23; N, 4.89; found: C, 7.32; H, 2.35; N, 5.33).

Therefore, experimental data indicates that the topotactic exchange occurred by the replacement of ca. 36% of the surface phosphonate groups by diphosphonates, that is, there are 18 organic chains interspersed in the interlayer region of γ -ZrP per 100 Zr atoms or, what is the same, per 100 surface phosphate/phosphonate positions. Figure 4 shows an idealized model of a portion of the material of the aforementioned molecular formula where two consecutive opposing layers of 25 + 25 surface phosphate/phosphonate groups are set at the experimental interlayer distance, obtained from powder DRX (Fig. 3). The model strongly supports that the inorganic interlayer space is perfectly able to comfortably house the 9 required **BTP** chains between the modeled lamellae containing 50 surface phosphorous sites in opposing faces.

A solid material capable of hosting lanthanides and sensitizing their emission by the *antenna effect* should comprise three simple but stringent conditions: (i) a complex chelating environment to fulfill the high demanding coordination sphere of lanthanide ions; (ii) the presence of a suitable chromophore able to transfer the absorbed photons to the metal ions; (iii) transparency of the inorganic network at the excitation wavelength. The layered γ -ZrP salt is a good candidate for this purpose, since it does not absorb much visible or UV light. The achievement of the first two conditions may be fulfilled by the afore-synthesized material.

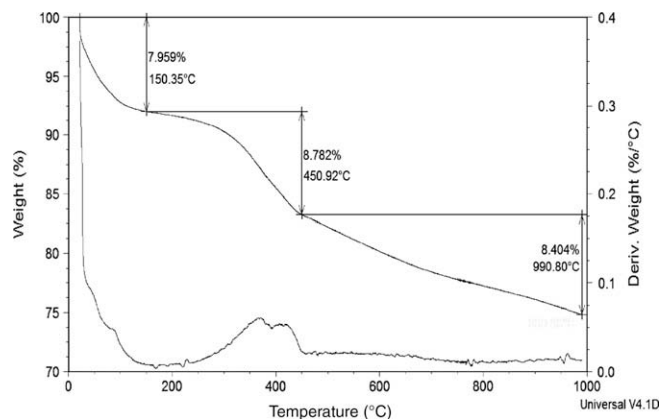


Figure 2. Thermogravimetric profile of material γ -ZrP-BTP.

Our preliminary results show that the goal of finding ways to introduce lanthanide ions into a suitable solid material while keeping them brightly luminescent and the solid scaffold intact¹³ has been achieved in γ -ZrP-BTP. The organic ligand **BTP** showed in acetonitrile solution (10^{-6} M) absorption bands at 210 and 290 nm, the latter being quite intense ($\epsilon = 4 \times 10^4$ M⁻¹cm⁻¹) and probably the most useful one to sensitize the lanthanides. In fact, the simple suspension of the solid γ -ZrP-BTP for 48 h at rt in a 0.1-M aqueous solution of LnCl₃ (Ln = Tb³⁺ or Eu³⁺) followed by centrifugation, water washing, and drying at 100 °C for 3 h rendered a new material containing ca. 20 Ln³⁺ ions per 100 Zr atoms, as measured by X-ray fluorescence.

The luminescence measurements of these materials in the solid state (Fig. 5) did show the typical structured emission of Ln³⁺, and the excitation spectrum displayed bands at 300–310 nm close to that belonging to the free organic ligand, strongly supporting that the bis-triazolylpyridine chromophore performs the purported *antenna effect* when covalently bonded to the galleries of γ -ZrP.

With the limited data at hand it is not possible to exactly know where the lanthanides are located within the material. Yet it is noteworthy that the number of lanthanide atoms accepted per 100 Zr (20) almost matches the number of the organic chains, suggesting that entering of the metal ions is somewhat conditioned by the chelating chromophore. In the case of europium, the splitting of the ground state levels hints the Eu³⁺ local symmetry.¹⁴ The emission spectrum of Eu³⁺ γ -ZrP-BTP (Fig. 5B) shows single peaks for the ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ transitions and low intensity for

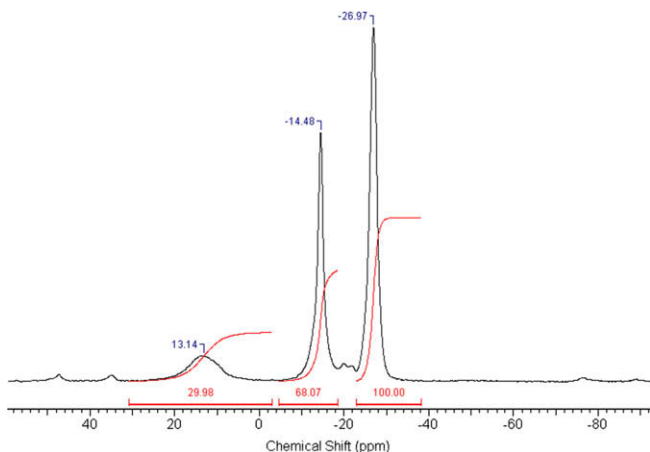


Figure 1. Solid-state MAS (10 kHz) ³¹P NMR spectrum of material γ -ZrP-BTP.

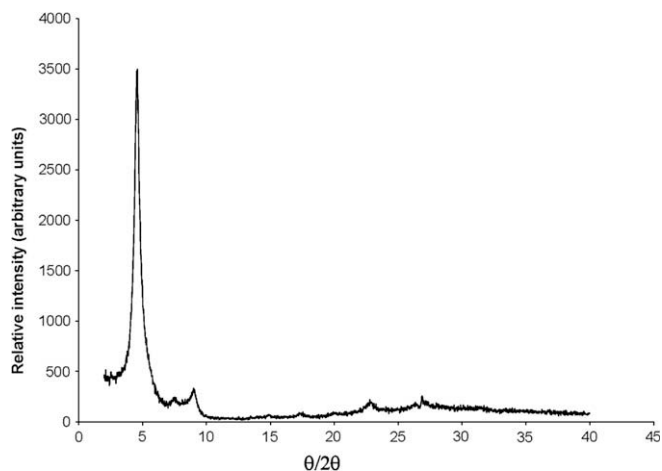


Figure 3. Powder X-ray diffraction pattern of material γ -ZrP-BTP.

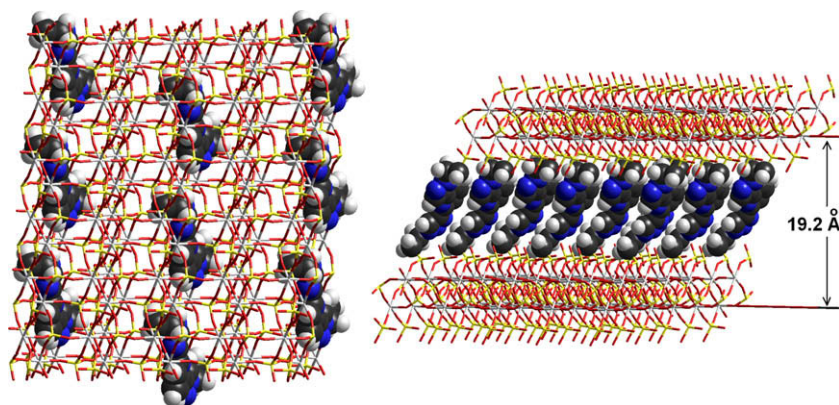


Figure 4. Idealized model for $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)_{0.64} (\text{C}_{13}\text{H}_{15}\text{N}_7\text{O}_6\text{P}_2)_{0.18}$ (see text).

$^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ emissions thus suggesting a distorted D_4 symmetry.¹⁵

The solid state phosphorescence lifetime of materials $\text{Tb}^{3+}\text{C}\gamma\text{-ZrP-BTP}$ and $\text{Eu}^{3+}\text{C}\gamma\text{-ZrP-BTP}$ was 0.7 and 0.3 ms, respectively, time spans which are shorter than those observed for **BTP** complexes in acetonitrile solution (2.5 and 1 ms for Tb^{3+} and Eu^{3+} , respectively) thus suggesting that one or more non-radiative pathways are contributing in the solid state to the deactivation of the metal-centered excited state, leading to the shortening of luminescence lifetimes. This can be easily explained by the weak vibronic coupling that should take place among the lanthanides and the OH oscillators belonging to the phosphate/phosphonate and/or interstitial water.

Summing up, a new ligand based in the bis-triazolypyridine motif with pendant phosphonate groups has been synthesized and topotactic exchanged into $\gamma\text{-ZrP}$. This new material has demonstrated coordination abilities with Eu^{3+} and Tb^{3+} and interesting luminescent properties. Additional work is in progress to avoid the shortcoming of the deleterious influence of the OH oscillators and to measure the quantum yields of emission of $\gamma\text{-ZrP-BTP}$ and related materials in order to improve the properties of these layered hybrid materials for its efficient utilization in optical applications.

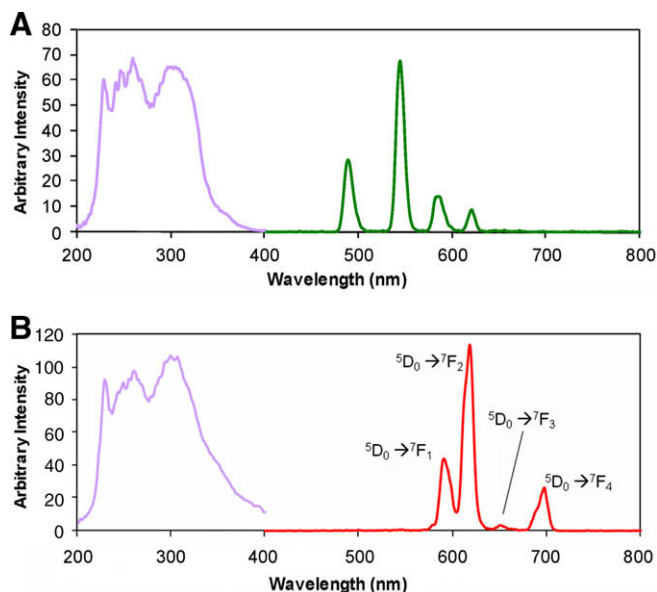


Figure 5. Emission and excitation spectrum of the solid $\gamma\text{-ZrP-BTP}$ containing ca. 20 ions of Tb^{3+} (green) and Eu^{3+} (red) per 100 Zr atoms. $\lambda_{\text{exc}} = 300$ nm.

Acknowledgments

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- Spectroscopic data of compound **1**: Brown solid; ^1H NMR (CDCl_3 , 300 MHz): δ 3.15 (s, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.64 (dd, $J = 0.9, 7.5$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 77.7, 82.1, 127.1, 136.5, 142.7.
- Spectroscopic data of compound **2**: Yellow oil; ^1H NMR (CDCl_3 , 300 MHz): δ 1.32 (dt, $J = 7.07$ Hz, $J_{\text{HP}} = 0.44$ Hz, 6H), 2.04 (dt, $J_t = 7.7$ Hz, $J_{\text{HP}} = 18.6$ Hz, 2H), 3.53 (dt, $J_t = 7.7$ Hz, $J_{\text{HP}} = 12.2$ Hz, 2H), 4.11 (m, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 16.3, (d, $J_{\text{CP}} = 6.1$ Hz), 25.91 (d, $J_{\text{CP}} = 140.8$ Hz), 45.32 (d, $J = 1.92$ Hz), 61.85 (d, $J_{\text{CP}} = 6.4$ Hz); ^{31}P NMR (CDCl_3 , 75.5 MHz): δ 26.90.
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- Spectroscopic data of compound **3**: Brown oil; ^1H NMR (CDCl_3 , 300 MHz): δ 1.30 (t, $J = 7.1$ Hz, 12H), 2.47 (dm, $J = 18.5$ Hz, 4H), 4.10 (m, 8H), 4.71 (dm, $J = 12.1$ Hz, 4H), 7.85–8.08 (m, 3H), 8.28 (s, 1H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 16.25 (d, $J_{\text{CP}} = 3.6$ Hz), 16.33 (d, $J_{\text{CP}} = 3.5$ Hz), 27.16 (d, $J_{\text{CP}} = 141.4$ Hz), 27.7 (d, $J_{\text{CP}} = 141.2$ Hz), 44.61 (d, $J_{\text{CP}} = 1.9$ Hz), 45.31 (d, $J_{\text{CP}} = 2.1$ Hz), 61.89 (d, $J_{\text{CP}} = 6.6$ Hz), 62.16 (d, $J_{\text{CP}} = 6.6$ Hz), 119.17, 122.63, 137.66, 148.26, 149.77; ^{31}P NMR (CDCl_3 , 75.5 MHz): δ 25.53.
- Spectroscopic data of compound **BTP**: Brown solid; ^1H NMR ($\text{D}_2\text{O-TFA}$, 300 MHz): δ 2.24 (dm, $J = 18.7$ Hz, 4H), 4.52 (m, 4H), 7.94–8.27 (m, 3H), 8.58 (s, 1H); ^{13}C NMR ($\text{D}_2\text{O-TFA}$, 75.5 MHz): δ 25.91, 27.73, 44.96, 44.99, 123.15, 126.61, 138.36, 142.58, 146.95; ^{31}P NMR ($\text{D}_2\text{O-TFA}$, 75.5 MHz): δ 23.55; HMRS (MALDI): m/z calcd for $\text{C}_{13}\text{H}_{18}\text{N}_7\text{O}_6\text{P}_2$: 430.08020 ($\text{M}+\text{H}^+$), found 430.07884.
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