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New Lanthanide Metalloligands and Their Use for the Assembly of Ln-Ag Bimetallic Coordination Frameworks: Stepwise Modular Synthesis, Structural Characterization, and Optical Properties

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Abstract
Stepwise self-assembly processes using new lanthanide metalloligands (Ln-MLs) and silver salts have been successfully applied to isolate 4f-4d heterometallic coordination networks of four different structural types. In particular, the new lanthanide tetrakis-chelate complexes NET₄[Ln(L¹)₄] [HL¹ = 1,3-bis(4′-cyanophenyl)-1,3-propanedione; Ln = Eu (1a), La (1b), Nd (1c), Tb (1d)] and NET₄[Ln(L²)₄] (HL² = 1,3-bis(4′-pyridyl)-1,3-propanedione; Ln = Eu (1e), Nd (1f)] have been synthesized, characterized and reacted with different silver salts. The use of NET₄[Ln(L¹)₄] allowed then to isolate and characterize i) neutral one-dimensional ladder-like species of formula [Ln(L¹)₄Ag] [Ln = Eu (2a), La(2b), Nd(2c), Tb(2d)] and ii) their supramolecular isomers [Ln(L¹)₄Ag] [Ln = Eu (3a), La (3b), Nd (3c), Tb (3d)] showing a very unstable 2D network structure, iii) the cationic 2D species [Ln(L¹)₄Ag₂]X [Ln = Eu, X = PF₆⁻, CF₃SO₃⁻, ClO₄⁻ (4a–4c); Ln = Tb, Nd, La X = PF₆⁻ (4d–4f)] and, only for lanthanum, iv) a fourth 2D species of formula [LaL¹₄(H₂O)Ag] (5) and sql topology. Of the eight nitrile groups on the MLs potentially coordinating, only a partial number is used for networking with Ag(I), that is, only two in families 2 and 3, and four in family 4 and in network 5. Finally, the four structural types are rationalized in terms of a new “pincer-like” Secondary Building Unit (SBU) consisting of a silver cation coordinating two central carbon atoms (γ carbon) of two different diketone ligands on the same ML. Therefore, it is shown that compounds 5, 4 and 2–3 contain, respectively, none, one or two of such pincer-like SBUs. The luminescence properties of the Ln-MLs and some of their polymeric species have been also investigated in solution and in the solid state.

1 Introduction
Metal-organic frameworks (MOFs), a class of crystalline porous materials built up by linking together metal cations or clusters and organic ligands, have attracted great and increasing attention from the scientific community in the last decades mainly for their inherent incredible versatility. Their structures, in fact, can be easily engineered by using the SBU approach and the principles of reticular chemistry to get specific network topologies and tailored properties. 1–4 Their application has been proposed in a wide variety of fields including, among others, ion exchange, 5 catalysis, 6 sensing, 7 magnetism, 8 light emitting and display devices, 9, 10 gas adsorption and reversible storage, 11, 12 taking often advantage from the possibility to develop multifunctional MOFs. 13 In this exciting and very lively context heterometallic f-d metal-organic frameworks (HMOFs), containing lanthanide ions together with transition metal ions as nodes, represent a very important family thanks to the peculiar and unique photophysical properties of f-block-based materials. 14, 15 Their very distinguishable and narrow emission, ranging from UV to NIR, grants the possibility to obtain high quantum yield and brightness (depending from the metal cation environment) and also to use them in technologically relevant devices. Moreover, these lanthanide ions usually show
coordination numbers ranging from 6 to 12 allowing for the preparation of more versatile building blocks in comparison with the transition metal ions, even if less predictable during the design step. In recent times great interest in the crystal engineering of HMOFs has been especially focused on the step-by-step synthetic strategy based on the use of metalloligands.\textsuperscript{16–19} Preformed and sometimes also independently characterized metalloligand complexes (MLs), as self-existing entities, have been employed with different metal ions for the assembly of frameworks exhibiting interesting and useful topologies; by this way a better control of the building up process is expected. However, while many cases have been reported of f-d arrays (both extended or finite molecular entities), constructed either using transition metal metalloligands\textsuperscript{20–22} or following some kind of one-pot synthetic route with mixed hard/soft Lewis base ligands,\textsuperscript{23–25} a very limited number of Ln-metalloligands used in the preparation of HMOFs have been described until now.

One of the first examples was reported by Shimizu et al.,\textsuperscript{26–28} who synthesized the luminescent complex \([\text{Ln}(4,4'\text{-disulfo}-2,2'\text{-bipyridine }N,N'\text{-dioxide})_3(H_2O)_2] \) (Ln = Sm, Eu, Gd, Tb, Dy) and reacted it in situ with Ba(II) to obtain an isostructural series of microporous luminescent HMOFs. More recently, the stepwise strategy based on the lanthanide ML \([\text{Ln}(3\text{-TPyMNTB})_2]ClO_4 \) (Ln = Eu, Gd; 3-TPyMNTB = tris((pyridin-3-ylmethyl)benzimidazol-2-ylmethyl)amine) has been successfully used to assemble Eu-Ag and Gd-Ag HMOFs. Particularly interesting is the europium derivative that shows white light emitting properties.\textsuperscript{29} The same strategy has been also successfully used to assemble Ln-Cd HMOFs, not easily accessible by other way, utilizing the complex \([\text{Ln(ODA)}_3]_3\) (H_2ODA = oxydiacetic acid) as ML.\textsuperscript{30–33} A mixed Gd-Co HMOF has been recently synthetized by a stepwise reaction between the Ln-ML \([\text{Gd(H_2CAM)}_3] \cdot 5/2H_2O \) (H_2CAM = chelidamic acid) and cobalt nitrate.\textsuperscript{34}

Combination of lanthanide metalloligands and transition metal ions in one metal-organic framework could represent a suitable way for isolating new convenient materials with interesting luminescent properties for different applications. We previously employed the metalloligand approach to assemble heterometallic MOFs of different transition metals by developing new M(II) and M(III) tris-chelate complexes of 1,3-functionalized β-diketone ligands (HL\textsuperscript{1} = 1,3-bis(4'-cyanophenyl)-1,3-propanedione and HL\textsuperscript{2} = 1,3-bis(4'-pyridyl)-1,3-propanedione). In particular, HL\textsuperscript{1} based MLs when reacted with AgX salts afforded a rich family of porous 3D heterometallic networks with the same 6-fold interpenetrated pcu topology and interesting reversible anion-exchange properties.\textsuperscript{35} On the other hand, by the same approach the ML \([\text{Fe(L_2)_3}]\) allowed to isolate 2D and 3D polymeric networks with structures depending on the nature of the counter-anions.\textsuperscript{36}

Here we examined the possibility to obtain new Ln-metalloligands using the previously described functionalised β-diketone ligands HL\textsuperscript{1} and HL\textsuperscript{2} (Scheme 1) as the first step for the synthesis of novel f-d HMOFs. We had the parallel aims to explore a new and convenient synthetic approach and to investigate the influence of different environments on the possible emissive properties of these materials.

**Scheme 1. Structure of the two ligands HL\textsuperscript{1} and HL\textsuperscript{2}**

We report here the preparation and structural characterization of two tetrakis-chelate metalloligands \([\text{Ln(L_1)_4}]^+ \) (Ln = Eu, La, Nd, Tb) and \([\text{Ln(L_2)_4}]^-\) (Ln = Eu, Nd), that were successively reacted with a variety of metal salts (Scheme 2). At present, crystalline products were obtained and investigated only by using the \([\text{Ln(L_1)_4}]^+\) metalloligands with silver salts of different anions (X\textsuperscript{−}). Four different types of heterometallic polymeric frameworks were isolated, depending on the counter-anion and/or
the reaction conditions. These include (i) a series of 1D polymers with formula \([\text{Ln}(L^1)_4\text{Ag}]\), (ii) a family of unstable 2D networks with the same composition \([\text{Ln}(L^1)_4\text{Ag}]\), i.e. supramolecular isomers, (iii) a family of 2D cationic frames \([\text{Ln}(L^1)_4\text{Ag}_2]X\) with different \(\text{Ln}\) and/or \(X\) counterion and (iv) the 2D polymer \([\text{La}(L^1)_4(\text{H}_2\text{O})\text{Ag}]\). The characterized structures show the variable donor ability of the metalloligands that, interestingly, can provide for networking with silver ions not only the nitrile donor groups but also the central carbon atoms (\(\gamma\) carbon) of their diketonate ligands.

2 Experimental section

2.1 General procedures

All employed commercial reagents and solvents (Sigma-Aldrich) were of high-grade purity and used as supplied, without further purification. The ligands \(HL^1\) and \(HL^2\) were prepared according to published procedures.\(^{35,36}\) All manipulations were performed under aerobic conditions unless standard Schlenk techniques were required. Anhydrous tetrahydrofuran was freshly distilled under nitrogen from sodium/benzophenone. NMR spectra were recorded on Bruker AC300 or AC400 instruments; \(\delta\) values are given in ppm relative to tetramethylsilane. Infrared spectra were collected on a PerkinElmer PARAGON 1000 FT-IR spectrometer. Thermogravimetric analysis (TGA) were performed on a PerkinElmer TGA 7 instrument under dynamic nitrogen (total flow rate 20 cm\(^3\)/min) with a ramp rate of 10°C/min in the range 30–650°C. X-ray powder diffraction (PXRD) patterns were recorded on a Philips PW1820 diffractometer (Cu K\(\alpha\) radiation, \(\lambda = 1.5418\) Å), in the 5–35° 2\(\theta\) range (0.02° and 2.5 s per step). Elemental analyses were carried out at the Microanalytical Laboratory of the University of Milan with a PerkinElmer 2400 instrument.

2.2 Photophysical Measurements

Photochemical experiments were carried out at room temperature in solutions and in solid phase and at 77 K in liquid nitrogen. Solid phase spectra were recorded on samples prepared inserting the solid powders or crystals between two square thin microscope glasses sealed with some double-sided tape while a common quartz cuvette (1 cm optical path) for samples in solution. A UV/VIS spectrophotometer PerkinElmer Lambda 650 was used to measure absorption spectra. Emission spectra were recorded with an Edinburgh FLS920 equipped photomultiplier Hamamatsu R928P and the same instrument connected to a PCS900 PC card was used for the Time Correlated Single Photon Counting (TCSPC) experiments to measure fluorescence lifetimes. Phosphorescence lifetimes were recorded with a PerkinElmer LS-55. Luminescence quantum yields (uncertainty, ±20%) were obtained by SPHEREOPTICS general purpose integration sphere 4”, spectraflect coating 1 baffle 0+/90*, following the De Mello method to record and process data. Fluorescence intensities were corrected, when required, for inner filter effects according to standard methods.\(^{37}\)

2.3 Synthesis of \(\text{NEt}_4[\text{Ln}(L^1)_4]\) [\(\text{Ln} = \text{Eu} (1a, 1a\*), \text{La} (1b), \text{Nd} (1c), \text{Tb} (1d)\)]

Complexes \(1a–1d\) were synthesized with similar procedures on using the corresponding lanthanide salts. Only the synthesis of \(1a\) is here reported in detail. The ligand \(HL^1\) (500.0 mg, 1.82 mmol) was suspended under stirring in 50 mL of ethanol and treated with \(\text{NEt}_4\text{OH}\) (35% aqueous solution, 908.5 mg, 2.159 mmol). After slow addition of \(\text{Eu(NO}_3)_3\cdot5\text{H}_2\text{O}\) (196.4 mg, 0.459 mmol) dissolved in 15 mL of ethanol, a yellow solid starts immediately to precipitate. The reaction mixture was left to stir at room temperature for 16 h. Compound \(1a\) was recovered as a yellow solid after filtration, washing with ethanol, and drying in air. Yield: 82.6%. Elemental Analysis (%): Calcd for \(\text{C}_{76}\text{H}_{56}\text{EuN}_6\text{O}_6\): C 66.37, H 4.10, N 9.17; Found: C 64.31, H 4.01, N 9.42. IR (KBr, cm\(^{-1}\)) v: 3068 (w), 2985 (w), 2226 (s), 1596 (vs), 1546 (s), 1520 (vs), 1488 (vs), 1457 (vs), 1393 (s), 1306 (s), 1294 (s), 1276 (sh), 1218 (m), 1173 (w), 1105 (m), 1056 (m), 1016 (m), 839 (w), 859 (s), 779 (s), 695 (m), 671 (w), 643 (w),
580 (m), 547 (m), 470 (m). 1H NMR (300 MHz, d6-acetone) δ: 8.00 (d, 16 H), 7.70 (d, 16 H), 6.21 (s, 4 H), 3.54 (q, 8 H), 1.43 (t, 12 H).

1b: Yield 82.0%. Elemental Analysis (%): Calcd for C76H56LaN8O8: C 67.01, H 4.14, N 9.25; Found: C 66.29, H 4.25, N 9.26. IR (KBr, cm−1): v: 3062 (w), 3042 (w), 2988 (w), 2227 (s), 1595 (vs), 1546 (vs), 1518 (vs), 1487 (vs), 1456 (vs), 1393 (vs), 1305 (s), 1292 (s), 1272 (sh), 1217 (s), 1174 (m), 1105 (m), 1053 (m), 1016 (s), 1000 (m), 938 (w), 857 (s), 817 (s), 779 (s), 752 (sh), 694 (m), 670 (m), 642 (w), 578 (m), 546 (s), 467 (m). 1H NMR (300 MHz, d6-acetone) δ: 8.23 (d, 16 H), 7.76 (d, 16 H), 6.82 (s, 4 H), 3.51 (q, 8 H), 1.41 (t, 12 H).

1c: Yield 70.6%. Elemental Analysis (%): Calcd for C76H56N8NdO8: C 66.75, H 4.13, N 9.22; Found: C 64.56, H 4.26, N 9.52. IR (KBr, cm−1) 3065(w), 3042(w), 2990(w), 2227(s), 1595(vs), 1547(vs), 1519(vs), 1487(vs), 1457(vs), 1398(vs), 1308(s), 1293(s), 1217(s), 1174(m), 1111(m), 1055(m), 1016(s), 1005(m), 940(w), 852(s), 819(s), 779(s), 694(m), 670(m), 643(w), 578(m), 542(s), 463(m).

1d: Yield 73.6%. Elemental Analysis (%): Calcd for C76H56N8NdO8Tb: C 66.04, H 4.08, N 9.12; Found: C 68.19, H 3.96, N 8.98. IR (KBr, cm−1) 3066(w), 3044(w), 2988(w), 2227(s), 1594(vs), 1545(vs), 1518(vs), 1487(vs), 1456(vs), 1395(vs), 1305(s), 1298(s), 1278(sh), 1215(s), 1174(m), 1101(m), 1054(m), 1016(s), 1013(m), 936(w), 857(s), 817(s), 785(s), 698(m), 674(m), 642(w), 578(m), 546(s), 467(m).

Single crystals of 1a and 1a* were obtained by slow diffusion into dichloromethane solutions of 1a of liquid or vapors of hexane, respectively. PXRD patterns of the bulk solids are comparable to those of the corresponding ground single crystals. They differ from the patterns calculated on the bases of the single-crystal structures possibly as a consequence of structural changes induced by the loss of chlatrated solvents (Figures S1 and S2).

2.4 Synthesis of NET4[Ln(L2)4] [Ln = Eu (1e), Nd (1f)]

Compounds 1e and 1f were obtained by the same procedure using the proper lanthanide nitrate salt. Only the synthesis of 1e is here reported in detail. The ligand HL2 (201.2 mg, 0.889 mmol) was suspended in 5.5 mL of ethanol and treated with NET9OH (35% aqueous solution, 423.3 mg, 1.006 mmol). 3 mL of an ethanol solution of Eu(NO3)3·5H2O (94.2 mg, 0.220 mmol) were slowly added to the mixture which was left under stirring for 3 h. The addition of 14 mL of ethyl acetate causes the precipitation of compound 1e as a yellow solid which was recovered by filtration, washed with water, and dried in air. Yield: 62.9%. Elemental Analysis (%): Calcd for C69H55EuN9O14: C 60.91, H 4.77, N 10.65; Found: C 62.13, H 4.71, N 11.11. IR (KBr, cm−1) v: 3060 (s), 3032 (s), 2984 (s), 2952 (s), 2892 (m), 1654 (sh, s), 1602 (vs), 1560 (s), 1540 (vs), 1522 (vs), 1458 (vs), 1430 (vs), 1384 (vs), 1320 (s), 1284 (s), 1218 (s), 1184 (s), 1172 (s), 1134 (m), 1082 (m), 1060 (s), 998 (s), 944 (s), 880 (w), 850, 772 (s), 720 (s), 690 (s), 664 (m), 610 (s), 522 (m), 458 (w), 432 (w). 1H NMR (300 MHz, d6-acetone) δ: 8.47 (d, 16 H), 7.67 (d, 16 H) 6.05 (s, 4H) 3.55 (q, 8H) 1.44 (t, 12H).

1f: Yield 59.7%. Elemental Analysis (%): Calcd for C69H55NdN9O14: C 61.31, H 4.80, N 10.72; Found: C 64.16, H 4.99, N 11.23. IR (KBr, cm−1) v: 3056 (s), 3034 (s), 2983 (s), 2951 (s), 2892 (m), 1654 (sh, s), 1602 (vs), 1560 (s), 1540 (vs), 1522 (vs), 1458 (vs), 1430 (vs), 1384 (vs), 1320 (s), 1281 (s), 1217 (s), 1184 (s), 1174 (s), 1145 (m), 1083 (m), 1061 (s), 700 (s), 944 (s), 883 (w), 856, 773 (s), 721 (s), 667 (s), 664 (m), 612 (s), 523 (m). 1H NMR (300 MHz, d6-acetone) δ: 8.64 (d, 16 H), 8.15 (d, 16 H) 7.70 (s, 4H) 3.47 (q, 8H) 1.35 (t, 12H).

Single crystals of 1e and 1f suitable for X-ray diffraction analyses were grown by slow diffusion of ethyl ether into a dichloromethane solution of the corresponding compound.

2.5 Synthesis of 1D [Ln(L1)4Ag] [Ln = Eu (2a), La (2b), Nd (2c), Tb (2d)]

Microcrystalline samples of 2a–2d were obtained by the same procedure using compounds 1a–1c as starting reagents. Only the synthesis of 2a is here reported in detail. Silver tosylate (10.6 mg, 0.0380 mmol) was dissolved in 6 mL of ethanol/water (5:1 v/v) mixture and added drop by drop over 15
minutes to an acetonitrile solution (5 mL) of 1a (50.8 mg, 0.0369 mmol). The mixture was left under stirring at room temperature for 15 h. A yellow solid formed which was collected on a Büchner funnel, washed with ethanol, and dried in air to give compound 2a. Yield 60.3%. Elemental Analysis (%): Calcd for C$_8$H$_6$AgEuN$_8$O$_6$: C 60.37, H 2.68, N 8.28; Found: C 59.83, H 2.64, N 8.42. IR (KBr, cm$^{-1}$) v: 3088 (w) 3070 (w), 2981 (w), 2228 (s), 1595 (vs), 1547 (vs), 1519 (vs), 1488 (vs), 1447 (vs), 1394 (s), 1293 (s), 1276 (sh), 1218 (s), 1178 (w), 1105 (m), 1056 (m), 1018 (m), 938 (w), 857 (s), 781 (s), 697 (m), 670 (w), 643 (w), 584 (m), 547 (m), 471 (m). Thermogravimetric analysis of 2a is reported in Figure S3.

2b Yield 73%. Elemental Analysis (%): Calcd for C$_8$H$_6$AgLaN$_8$O$_6$: C 60.96, H 2.71, N 8.36; Found: C 58.97, H 2.61, N 8.20. IR (KBr, cm$^{-1}$) v: 3068 (w), 3048 (sh), 2228 (s), 1594 (vs), 1545 (vs), 1518 (vs), 1487 (vs), 1442 (vs), 1392 (vs), 1306 (s), 1293 (s), 1272 (sh), 1218 (s), 1178 (w), 1106 (m), 1054 (m), 1017 (s), 936 (w), 857 (s), 780 (s), 696 (m), 673 (w), 643 (w), 582 (m), 547 (s), 469 (m).

2c Yield 40.6%. Elemental Analysis (%): Calcd for C$_8$H$_6$AgNdN$_8$O$_6$: C 60.72, H 2.70, N 8.33; Found: C 62.11, H 2.78, N 8.04. IR (KBr, cm$^{-1}$) v: 3075 (w), 3050 (sh), 2227 (s), 1594 (vs), 1545 (vs), 1518 (vs), 1488 (vs), 1442 (vs), 1391 (vs), 1306 (s), 1293 (s), 1218 (s), 1174 (w), 1088 (m), 1054 (m), 1015 (s), 936 (w), 853 (s), 780 (s), 696 (m), 666 (w), 643 (w), 583 (m), 547 (s), 473 (m).

2d Yield 41.5%. Elemental Analysis (%): Calcd for C$_8$H$_6$AgNdN$_8$O$_6$: C 60.06, H 2.67, N 8.24; Found: C 57.46, H 2.58, N 8.05. IR (KBr, cm$^{-1}$) v: 3073 (w), 3044 (sh), 2228 (s), 1595 (vs), 1545 (vs), 1517 (vs), 1490 (vs), 1444 (vs), 1393 (vs), 1306 (s), 1295 (s), 1272 (sh), 1218 (s), 1173 (w), 1116 (m), 1054 (m), 1017 (s), 936 (w), 856 (s), 782 (s), 695 (m), 670 (w), 643 (w), 585 (m), 547 (s), 470 (m).

Single crystals of 2a–2d suitable for X-ray analysis were obtained by slow diffusion of an acetonitrile/water (5:1 v/v) solution of silver tosylate in an acetonitrile solution of the proper MLs (1a–1d) in 3 days. PXRD patterns of the bulk solids are comparable to the patterns calculated on the bases of the corresponding single-crystal structures, taking into account the limited crystallinity of the samples (Figure S4).

### 2.6 Synthesis of 2D [Ln(L^1)$_4$Ag] [Ln = Eu (3a), La (3b), Nd (3c), Tb (3d)]

Microcrystalline samples of polymers 3a–3d were obtained by the same procedure using compounds 1a–1d as starting reagents. Only the synthesis of 3b is here reported in detail. A solution of silver tosylate (20.5 mg, 0.074 mmol) in water (10 mL) was added drop by drop in a period of 1 h to a solution of 1b (100.2 mg, 0.074 mmol) dissolved in acetonitrile (10 mL). The mixture was left under stirring for 3 h. A yellow solid formed which was collected by filtration on a Büchner funnel, washed with ethanol, and dried in air to give compound 3b. Yield 79.3%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$LaN$_8$O$_8$: C 60.96, H 2.71, N 8.36; Found: C 60.97, H 2.58, N 8.44. IR (KBr, cm$^{-1}$) v: 3097 (w), 3073 (w), 2933 (vw), 2227 (s), 1596 (vs), 1547 (vs), 1519 (vs), 1488 (vs), 1451 (vs), 1434 (sh, vs), 1393 (s), 1305 (m), 1295 (s), 1277 (sh, m), 1216 (m), 1178 (w), 1107 (m), 1055 (m), 1017 (M), 943 (w), 857 (m), 782 (s), 700 (m), 671 (w), 645 (w), 583 (w), 547 (m), 469 (m).

3a Yield 78.2%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$EuN$_8$O$_8$: C 60.37, H 2.68, N 8.28; Found: C 59.35, H 2.64, N 8.56. IR (KBr, cm$^{-1}$) v: 3090 (w), 3071 (w), 2929 (vw), 2228 (s), 1596 (vs), 1547 (vs), 1519 (vs), 1488 (vs), 1451 (vs), 1432 (sh, vs), 1393 (s), 1307 (m), 1295 (s), 1277 (sh, m), 1217 (m), 1178 (w), 1109 (m), 1056 (m), 1017 (m), 938 (w), 857 (m), 783 (s), 697 (m), 671 (w), 643 (w), 583 (w), 547 (m), 471 (m).

3c Yield 84%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$AgN$_8$NdO$_8$: C 60.72, H 2.70, N 8.33; Found: C 63.61, H 2.60, N 8.29. IR (KBr, cm$^{-1}$) v: 3082 (w), 3073 (w), 2922 (vw), 2226 (s), 1596 (vs), 1547 (vs), 1519 (vs), 1488 (vs), 1451 (vs), 1432 (sh, vs), 1393 (s), 1306 (m), 1295 (s), 1276 (sh, m), 1215 (m), 1178 (w), 1107 (m), 1056 (m), 1017 (m), 939 (w), 857 (m), 785 (s), 697 (m), 671 (w), 646 (w), 584 (w), 546 (m), 470 (m).

3d Yield 90.1%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$AgN$_8$O$_8$: C 60.06, H 2.67, N 8.24; Found: C 60.00, H 2.55, N 8.07. IR (KBr, cm$^{-1}$) v: 3088 (w), 3077 (w), 2943 (vw), 2228 (s), 1595
(vs), 1546 (vs), 1520 (vs), 1488 (vs), 1469 (vs), 1395 (s), 1394 (s), 1309 (s), 1296 (s), 1276 (sh, s), 1223 (m), 1179 (w), 1106 (m), 1056 (w), 1016 (m), 938 (w), 837 (sh, s), 851 (s), 781 (s), 698 (m), 670 (w), 586 (w), 558 (m), 548 (m), 472 (w).

Yellow needle-shaped crystals of 3b used for X-ray analysis were obtained by slow diffusion of an acetonitrile solution of 1b into a water solution of [Ag(CH$_3$CN)$_4$]BF$_4$ in 3 days.

Despite the good agreement between the patterns collected for the powders of 3a–3c, the comparison with the pattern calculated from the partial data collected for the single crystal of 3b is very lacking (Figure S5). This result can be safely attributed to the highly unstable nature of the structure of 3, that did not allow a complete single-crystal structural characterization even at low temperature.

2.7 Synthesis of 2D [Ln(L$_1$)$_4$Ag$_2$]X [Ln = Eu, X = PF$_6$, ClO$_4$, CF$_3$SO$_3$ (4a–4f); Ln = La, Nd, Tb, X = PF$_6$ (4d–4f)]

Microcrystalline samples of polymers 4a–4f were obtained by the same procedure using compounds 1b–1c as starting reagents and the proper silver salts. Only the synthesis of 4a is here reported in detail. A solution of hexafluorophosphoric acid (19.2 mg, 0.076 mmol) in ethanol (8 mL) was added drop by drop in a period of 15 minutes to a solution of 1a (51.2 mg, 0.037 mmol) dissolved in dichloromethane (8 mL). The mixture was left under stirring for 3 h. A yellow solid formed which was collected by filtration on a Büchner funnel, washed with ethanol, and dried in air to obtain compound 4a. Yield 93%. Elemental Analysis (%): Calcd for C$_{547}$H$_{34}$O$_{29}$P$_{2}$F$_{12}$: C 50.86, H 2.26, N 6.98; Found: C 52.00, H 2.32, N 6.95. IR (KBr, cm$^{-1}$) ν: 3096 (w), 3071 (w), 2976 (w), 2247 (sh, m), 2230 (m), 1595 (vs), 1546 (vs), 1520 (vs), 1488 (vs), 1449 (vs), 1394 (s), 1309 (m), 1296 (s), 1276 (sh, s), 1223 (m), 1179 (w), 1106 (m), 1056 (w), 1016 (m), 938 (w), 837 (sh, s), 851 (s), 781 (s), 698 (m), 670 (w), 644 (w), 586 (w), 558 (m), 548 (m), 172 (w).

4b Yield 95%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$O$_{20}$F$_{12}$: C 52.35, H 2.32, N 7.18; Found: C 50.56, H 2.33, N 7.13. IR (KBr, cm$^{-1}$) ν: 3095 (w), 3070 (w), 2974 (w), 2230 (s), 1595 (s), 1546 (vs), 1521 (vs), 1487 (s), 1449 (s), 1394 (s), 1308 (s), 1296 (s), 1277 (sh), 1223 (s), 1168 (m), 1015 [s, ν(Cl–O), ClO$_4$], 1057 (m), 1017 (m), 938 (w), 859 (m), 780 (s), 698 (m), 645 (m), 583 (w), 547 (m), 472 (m).

4c Yield 91%. Elemental Analysis (%): Calcd for C$_{69}$H$_{38}$O$_{20}$F$_{12}$: C 51.48, H 2.25, N 6.98; Found: C 49.52, H 2.21, N 8.30. IR (KBr, cm$^{-1}$) ν: 3093 (w), 3069 (w), 2974 (w), 2230 (s), 1595 (vs), 1546 (vs), 1521 (vs), 1489 (vs), 1451 (vs), 1394 (s), 1308 (s), 1295 (s), 1278 (sh), 1260 (sh, ν(C–F), CF$_3$SO$_3$), 1225 (s), 1168 (m), 1106 (m), 1057 (m), 1017 (m), 938 (w), 859 (m), 780 (s), 698 (m), 671 (w, δ(C-F), CF$_3$SO$_3$), 641 (m), 583 (w), 548 (m), 472 (m).

4d Yield 92%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$O$_{20}$F$_{12}$: C 51.28, H 2.28, N 7.04; Found: C 52.15, H 2.38, N 7.16. IR (KBr, cm$^{-1}$) ν: 3096 (w), 3071 (w), 2976 (w), 2247 (sh), 2230 (s), 1595 (vs), 1545 (vs), 1519 (vs), 1488 (vs), 1445 (vs), 1392 (vs), 1308 (s), 1295 (s), 1276 (sh), 1222 (s), 1179 (w), 1106 (m), 1054 (m), 1016 (m), 936 (w), 850 (s), 838 (sh), 780 (s), 698 (m), 644 (w), 583 (w), 558 (m), 548 (m), 470 (m).

4e Yield 93%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$O$_{20}$F$_{12}$: C 52.35, H 2.32, N 7.18; Found: C 53.14, H 2.24, N 6.67. IR (KBr, cm$^{-1}$) ν: 3096 (w), 3073 (w), 2974 (w), 2247 (sh, m), 2230 (m), 1595 (vs), 1545 (vs), 1520 (vs), 1488 (vs), 1449 (vs), 1395 (s), 1310 (m), 1296 (s), 1276 (sh, s), 1223 (m), 1179 (w), 1106 (m), 1056 (w), 1016 (m), 938 (w), 837 (sh, s), 851 (s), 781 (s), 698 (m), 670 (w), 644 (w), 586 (w), 558 (m), 548 (m), 472 (w).

4f Yield 95%. Elemental Analysis (%): Calcd for C$_{68}$H$_{36}$O$_{20}$F$_{12}$: C 50.64, H 2.25, N 6.95; Found: C 50.56, H 2.27, N 7.01. IR (KBr, cm$^{-1}$) ν: 3095 (w), 3072 (w), 2974 (w), 2247 (sh, m), 2230 (m), 1595 (vs), 1546 (vs), 1520 (vs), 1488 (vs), 1450 (vs), 1396 (s), 1309 (m), 1296 (s), 1276 (sh, s), 1223 (m), 1179 (w), 1106 (m), 1056 (w), 1016 (m), 938 (w), 837 (sh, s), 851 (s), 781 (s), 698 (m), 670 (w), 644 (w), 586 (w), 558 (w), 552 (w), 472 (w).

Thermogravimetric analyses of 4a–4d are reported in Figure S6. Yellow plate-shaped crystals of 4a and 4b suitable for X-ray analysis were obtained by slow diffusion of an ethanol solution of AgPF$_6$
or AgClO₄ into a CH₂Cl₂ solution of 1a in 5 days. PXRD patterns of the bulk solids are comparable to the patterns calculated on the bases of the corresponding single-crystal structures, taking into account the limited crystallinity of the samples (Figures S7 and S8).

### 2.8 Synthesis of 2D [La(L¹)₄(H₂O)Ag] (5)

A solution of silver tosylate (20.8 mg, 0.075 mmol) in water (10 mL) was added drop by drop in about 30 seconds to a solution of 1b (101.0 mg, 0.074 mmol) dissolved in acetonitrile (10 mL). The mixture was left under stirring for 3 h. A yellow solid formed which was collected by filtration on a Büchner funnel, washed with water and acetonitrile, and dried in air. Yield: 95.2%. Elemental Analysis (%): Calcd for C₆₈H₃₈AgLaN₈O₉: C 60.15, H 2.82, N 8.25; Found: C 61.23, H 2.71, N 8.10.

IR (KBr, cm⁻¹): 3093 (w), 3077 (w), 2924 (w), 2250 (s), 2228 (s), 1598 (vs), 1546 (vs), 1514 (vs), 1489 (vs), 1428 (vs), 1389 (s), 1306 (s), 1293 (s), 1270 (s), 1222 (s), 1175 (m), 1108 (s), 1052 (m), 1014 (s), 936 (w), 861 (sh, s), 856 (s), 788 (s), 777 (sh, s), 758 (m), 692 (s), 678 (m), 643 (w), 578 (m), 551 (m), 546 (m), 535 (m), 475 (s).

Thermogravimetric analysis of 5 is reported in Figure S9. Yellow needle-shaped crystals of 5 suitable for X-ray analysis were obtained by slow diffusion of an acetonitrile solution of [Ag(CH₃CN)₄]BF₄ into a water solution of 1b in 1 month. PXRD pattern of the bulk solid is comparable to the pattern calculated on the bases of the corresponding single-crystal structure (Figure S10).

### 2.9 Crystallography

Crystal data for the metallocigands 1a, 1a*, 1e, and 1f and for the heterometallic MOFs 2a, 2c, 2d, 4a, and 5 are listed in Table S1 (Supporting Information). Data were collected on a Bruker APEXII-CCD diffractometer using Mo Ka radiation (λ = 0.71073 Å). Empirical absorption corrections (SADABS)³⁸ were applied to all data. The structures were solved by direct methods (SIR97)³⁹ and refined by full-matrix least squares on F² (SHELX-2014)⁴⁰ using the WINGX interface.⁴¹ All hydrogen atoms were placed in geometrically calculated positions and subsequently refined using a riding model with Uiso(H) = 1.2 Ueq(C). Anisotropic thermal parameters were assigned to all non-hydrogen atoms, except for the clathrate solvent molecules (1a and 1f: dichloromethane; 1a*: 3 dichloromethane; 1e: water; 2a and 2c: ½ acetonitrile; 2d: ½ acetone) that have been modelled also for the disorder. Further details on the refinements of the observed disordered groups can be found in the cif files. Crystals of 3b proved to be highly unstable and a full refinement was not possible. A model was found and the coordinates are reported in the supplementary materials. All crystals were kept under mineral oil and the data collections were done at 150 K to limit decomposition. For 4a it was difficult to refine a consistent model for the solvent molecules so their contribution was subtracted from the observed structure factors according to the BYPASS procedure⁴² as implemented in PLATON⁴³ with the command SQUEEZE, and the PF⁶⁻ anion was modelled isotropically over two equally occupied position. Crystal data and selected bond distances and angles for all the characterized species are reported in Tables S1–S6. The diagrams were produced using ToposPro⁴⁴ and Mercury⁴⁵ programs. CCDC 1910771–1910779 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
3 Results and discussion

3.1 Syntheses and crystal structures of the lanthanide metalloligands

3.1.1 NEt₄[Ln(L¹)₄] [Ln = Eu (1a, 1a*), La (1b), Nd (1c), Tb (1d)]

Complexes 1a–1d were synthesized in good yields by reacting HL¹, tetraethylammonium hydroxide and the corresponding lanthanide nitrate salts (4:4:1 ratio) in ethanol under stirring overnight at room temperature. The compounds were isolated as yellow microcrystalline solids and were characterized by XRD, IR, and ¹H NMR analyses. Crystallization by slow diffusion of liquid or vapors of hexane into dichloromethane solutions of 1a produced single crystals whose X-ray diffraction analyses revealed to belong to different crystalline forms, namely NEt₄[Eu(L¹)₄]·CH₂Cl₂ (1a) and NEt₄[Eu(L¹)₄]·3CH₂Cl₂ (1a*). Both structures crystallize in the P–1 space group and differ in the number of clathrate dichloromethane molecules. Crystals of 1a and 1a* easily desolvate in the air at room temperature to give microcrystalline materials. Monitoring of such desolvation processes by X-ray powder diffraction show changes in the powder patterns up to the complete removal of clathrate molecules and convergence to similar powder patterns, thus indicating the transformation to the same crystalline phase for desolvated 1a and 1a* (Figure S1). Microcrystalline powders of compounds 1b–1d are similar to desolvated powders of 1a and 1a*, as evidenced by comparison of their respective PXRD patterns (Figure S2).

The asymmetric units of both 1a and 1a* contain one tetrakis-chelate anionic complex, one tetraethylammonium cation and, respectively, one and three dichloromethane molecules. A view of the tetrakis-chelate complex in the crystal structure of 1a is reported in Figure 1. Views with labeling schemes for 1a and 1a* are shown in Figure S11. Europium centers in both compounds coordinate eight oxygen atoms belonging to four crystallographic different β-diketonate ligands (L¹) adopting coordination geometries intermediate between triangular dodecahedron (DD-8) and square antiprism (SAPR-8), the two ideal geometries for coordination number eight.

Figure 1. View of the europium complex in 1a. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% of probability.
Average values for the Eu–O distances (2.38 and 2.39 Å in 1a and 1a*), respectively and for the O–Eu–O bite angles of the diketonate ligands (69.5 and 70.1 in 1a and 1a*, respectively) are very similar in the two pseudopolymorphs. Such Eu–O distance and bite angle values are fully comparable to those of similar tetrakis-chelate β-diketonate europium complexes. In both compounds the six-membered chelate rings are folded along the O···O vector with dihedral angles between the EuO2 plane and the plane of the ligand (defined by the two oxygen atoms and the γ-carbon atom) in the range 4.0(4)–28.6(4)° for 1a and 16.73(13)–25.46(14)° for 1a*. Such values are comparable to those observed in other tetrakis-chelate lanthanide diketonate complexes and differences can be safely attributed to packing effects.

More generally, differences in the europium coordination geometries between 1a and 1a* are not significant and easily ascribable to differences in crystal packing, induced by the different number of clathrate dichloromethane molecules. No particular intermolecular interactions are present in the two crystal structures except for a face to face π−π interaction between phenyl rings belonging to the same ligand of two different adjacent complexes, which are related by an inversion center, found only in 1a* (angle between mean planes of phenyl rings 3.13(17)°, centroid to centroid distance 3.605(2) Å).

Europium complexes, in both structures, are arranged along rows, with the tetaethyl ammonium and the solvent molecules disposed in the inter-row regions (Figure S12).

3.1.2 NEt4[Ln(L2)4] [Ln = Eu (1e), Nd (1f)]

Compounds 1e and 1f were obtained as yellow microcrystalline powders by reacting at room temperature europium or neodymium nitrate with four-fold equivalents of HL2 in ethanol/water mixtures in the presence of excess amounts of tetraethylammonium hydroxide. The two compounds were characterized by XRD, IR, and 1H NMR analyses. Single crystals of 1e and 1f suitable for X-ray diffraction analyses were grown by slow diffusion of ethyl ether into a dichloromethane solution of the corresponding compound. They crystallize in the space group $P_{2_1}/c$ as solvates NEt4[Eu(L2)4]·H2O (1e) and NEt4[Nd(L2)4]·CH2Cl2 (1f). Views of the two lanthanide complexes with labelling schemes are shown in Figure S12.

The asymmetric unit of 1e contains the europium complex, a tetaethylammonium cation and a water molecule. Europium atom is coordinated to eight oxygen atoms of four crystallographically independent chelating ligands adopting a coordination geometry intermediate between DD-8 and SAPR-8. The Eu–O distances average value is 2.38 Å and the average bite angle O–Eu–O of the chelate diketonate ligands is 70.2°, comparable with the values found for 1a and 1a*. The six-chelate rings are folded along the O···O vector, showing dihedral angles in the range 18.60(14)–27.55(14)°.

The asymmetric unit of 1f contains two neodymium complexes, two tetaethylammonium cations and two dichloromethane molecules. Also in this structure all the chelating ligands are crystallographically independent. The two neodymium complexes in the asymmetric unit do not show significant differences and their geometrical parameters are very similar (Table S4). In particular, the average values for the Nd–O distances are 2.43 and 2.44 Å, while the average bite angles O–Nd–O of the chelate diketonate ligands are 69.0 and 69.2°, respectively. Again the six-chelate rings are folded along the O···O vector showing dihedral angles in the range 25.60(12)–33.18(12)°, respectively.

The europium and neodymium anionic complexes in the two crystal structures pack along rows, while the tetaethylammonium cations and the clathrate solvent molecules (water and dichloromethane) are located between these rows. In 1e the water molecule is hydrogen bonded to a pyridyl nitrogen atom (O1w···N8, 2.94 Å).

Lanthanide complexes of pyridyl substituted β-diketonate are uncommon. The complex [Eu(HL2)3(H3L2)]Cl4·EtOH 46 is the only known example of a tetrakis-chelate containing four bispyridyl-β-diketonate ligands, even if in this species three ligands are monoprotonated zwitterions and one is a doubly protonated cation. All other reported examples contain solvent molecules coordinated to the lanthanide metals and less than four chelating ligands. 47–51
3.2 Lanthanides-silver coordination networks assembled with the \([\text{Ln}(L^1)_4]^-\) metalloligands

The reactivity of the NEt₄[Ln(L^1)_4] metalloligands was investigated with different metal salts. In spite of the many attempts, single crystals suitable for X-ray diffraction analysis were isolated only using silver salts of various anions. We have isolated by this way four different families of polymeric Ln-Ag species, with distinct topology, in which the starting metalloligand moieties are essentially preserved. We have also identified the factors that can possibly drive the formation of the different products.

Metalloligands \([\text{Ln}(L^1)_4]^-\) possess eight donor nitrile groups that can be potentially employed for networking; however, in the HMOFs prepared only 2 or 4 groups out of the 8 are coordinated to silver. Moreover, as often observed in β-diketonate complexes,\(^{52-55}\) the central carbon atom (methine or γ-carbon) can also form bonds towards external metal ions. We have previously described tris-chelated metalloligands with the same β-diketonate ligands that give networks with silver cations exhibiting Ag–C bonds, with bond distances in the range 2.451(11)–2.531(7) Å.\(^{35}\)

The high flexibility in the stereochemistry of these metalloligands allows for the formation of a new type of Secondary Building Unit (SBU) in the reaction with silver cations. This SBU consists of a “pincer-like” moiety, in which a silver cation coordinates to two central carbon atoms of two different diketonate ligands of the same metalloligand (Figure 2). The different polymeric products could be organized on the basis of the number of these SBUs. Accordingly, species with 0, 1, and 2 “silver-pincers” per ML have been obtained.

![Schematic representation of the silver pincer-like SBUs observed in two polymer families described below. One silver-pincer like SBU (top) is formed by one ML and one silver cation interacting with the central carbon atoms of two diketonate ligands. Such neutral SBU is present in polymeric families 2 and 3. Two silver pincer-like SBUs (bottom) are formed by one ML and two silver cations, each of which interacts with the central carbon atoms of two diketonate ligands. Such cationic SBU is present in polymeric family 4.](image)

Moreover, a relevant distinction to be underlined is related to the dimension of the lanthanide ion. Using MLs of Tb, Eu, and Nd only three different polymers have been obtained, while with the ML of the bigger La cation an additional fourth polymeric species can be obtained (see below). Scheme 2 collects the synthetic experimental conditions used to obtain all of the polymeric products based on the nitrile functionalized Ln-MLs NEt₄[Ln(L^1)_4].
Scheme 2. Experimental conditions for the synthesis of the 1D and 2D polymeric families 2–5

i) CH₃C₆H₄SO₃Ag/1a–1d, stoichiometric ratio 1:1, EtOH/H₂O (5:1)/CH₃CN; ii) CH₃C₆H₄SO₃Ag/1a–1d, stoichiometric ratio 1:1, H₂O/CH₃CN, slow mixing; iii) AgX/1a–1d, stoichiometric ratio 2:1, X = PF₆⁻, ClO₄⁻, CF₃SO₃⁻, EtOH/CH₂Cl₂; iv) CH₃C₆H₄SO₃Ag/1b, stoichiometric ratio 1:1, H₂O/CH₃CN, fast mixing. During the crystallization of 3b and 4b, solvent mediated slow transformations to 5 have been evidenced.

The key factors for the synthesis of these compounds are the Ag:ML ratio and the solvent system used in the different preparations. We will now proceed to analyze in detail the different polymeric products.

3.2.1 1D coordination networks [Ln(L¹)₄Ag] (2a–2d)

The reactions of all the metalloligands with various silver salts (tosylate, triflate, hexafluorophosphate, and tetrafluoroborate) in a stoichiometric ratio of 1:1 and in different solvent systems (mixtures of ethanol, acetonitrile, water, and acetone) generate the species [Ln(L¹)₄Ag] [Ln = Eu, La, Nd, and Tb (2a–2d)]. Though the polymers can be prepared in many different conditions, best results are obtained when the reaction is performed using silver tosylate in ethanol/water (5:1)/acetonitrile as solvent system. In the synthesis of this family of coordination networks, only the stoichiometric ratio ML/Ag of 1:1 and the presence of small amount of water seems to be crucial. All the crystals of the family are isomorphous and belong to the triclinic system, space group P–1. Their structures contain the same ladder-like 1D network depicted in Figure 3 for 2a.
Figure 3. Views of a single molecular ladder motif in 2a, hydrogen atoms have been omitted for clarity. a) Front view and b) lateral view of the ladder running along b, showing the π-π interaction reinforcing the rungs of the ladder. c) Simplified representations of the ladder obtained considering europium and silver atoms as nodes (in grey, the silver pincer is highlighted in pink) and considering the whole SBUs as nodes (in blue).

The main structural features concern the interactions of the silver ions with the Ln metalloligands and the role of the β-diketonate ligands in the networking process. In this structure only one silver-SBU (of the type previously described) per ML is observed. Out of the four β-diketonate ligands of a ML two are involved in the silver-SBU, with Ag–C bonds in the range 2.447(4)–2.486(6) Å. Two adjacent SBUs interconnect via mutual exchange of one CN–Ag link using one of their two diketonate ligands (Figure 3a). These double-bridged centrosymmetric pairs form the rungs of the ladder-like polymeric motif. The rungs show strong reinforcing π-π interactions between the phenyl rings of the ligands (for the two phenyl rings the center-to-center distance is 3.901(10) Å and the stacking distance is 3.35 (12) Å) (Figure 3b). Of the two diketonate ligands not involved in the formation of the SBU, one, outward oriented with respect to the ladder, remains dangling or “free”, while the other employs a CN group to bind a silver ion on a nearest neighboring rung, thus forming the rails of the ladder. The four diketonate ligands belonging to a ML differ in their interactions with the silver cations: the first one uses the central carbon atom and one CN group, the second one only the central carbon atom, the third one a CN group, and the fourth one is completely non-interacting. Surprisingly, only two CN donor groups per ML are involved in bonds to silver, one to build the rails and the other the rungs of the ladder motif.

Each Ag atom is therefore four-connected, with an AgC2N2 environment of distorted tetrahedral geometry; the Ag–N bond lengths are in the range 2.257(5)–2.284(6) Å.

As already observed for the metalloligands 1a–1d, the six-membered chelate rings are folded along the O···O vector with dihedral angles between the EuO2 plane and the plane of the ligand (defined by the two oxygen atoms and the γ-carbon atom) in the range 12.5(3)–26.5(3)°.
The major differences are expected between the two diketonate ligands wrapping the silver atom [with a C–Ag–C angle of 122.3(2)°] with respect to the other two ligands, as a consequence of the partial re-hybridization of the central carbon atom from sp² to sp³ and the consequent decrease of the π-electron delocalization: indeed, the C–C–C bond angles are smaller [120.4(6) and 120.1(6)° vs 123.6(7) and 123.6(8)°] and the C–C bond lengths longer [range 1.423(9)–1.444(9) Å vs range 1.393(9)–1.415(10) Å].

The ladders are packed in a parallel arrangement, running along the b direction.

### 3.2.2 2D coordination networks [Ln(L¹)₄Ag] (3a–3c)

On performing the reactions leading to the family 2a–2d in a different solvent system, replacing ethanol with water, the new family [Ln(L¹)₄Ag] [Ln = Eu, La, and Nd (3a–3c)] can be isolated. Crystals of these species are very unstable and accurate structural determinations could not be accomplished; nevertheless, they were shown to be isostructural by comparing their PXRD patterns (Figure S5). After many attempts, single-crystal diffraction analysis was possible for a sample of 3b, even if the low quality of the data collected allowed to refine the skeleton of the framework only (Table S7). This partial result suffices to establish the supramolecular isomeric relationship existing between the families 2 and 3, sharing the network composition [Ln(L¹)₄Ag]. The structure is illustrated in the top row of Figure 4 and consists of slightly undulated 2D layers with large windows. As for compounds of the family 2, also in these species 3a–3c we observe the presence of only one SBU per ML (Figure 4a–b). All the CN groups of the two diketonate ligands involved in the formation of the SBU with the silver atom remain free, while each of the other two diketonates of the Ln-ML uses one CN group to bind the silver ions of two lateral SBUs. Overall there are two distinct types of diketonates: a pair that uses only the central carbon atom to bind silver, and a second pair that uses one CN donor group. Therefore, also in this case only two CN groups of the ML (out of eight) are employed for networking.

The topology of the layers can be rationalized in two different ways: assuming as nodes the entire SBUs we can idealize these single-edged windows as squares, giving a 4¹-sql topology (as shown in red in Figure 4c), while using both silver and lanthanide atoms as distinct nodes we obtain a honeycomb network (6³-hcb, as shown in blue in Figure 4c).

The main difference between the structures of these supramolecular isomers (families 2 and 3) are related to the orientation of the SBUs in the network (compare Figure 3c and 4b). While sequences of SBUs oriented in alternate directions lead to the 1D ladder, sequences of SBUs oriented all in the same direction lead to the 2D network 3. This latter orientation results in a polar direction in the layers (the polar axis running along b), with adjacent layers showing opposite polarity. Indeed, these layers are stacked down e with an ABAB sequence (Figure S13). The absence of counter-ions and the slight displacement of the stacking layers in this structure generate large 1D channels along the stacking direction, that may be the reason of the instability of 3b.
3.2.3 2D coordination networks [Ln(L\(^1\))\(_4\)Ag\(_2\)]X (4a–4f)

The reactions of all the Ln-MLs with different silver salts (hexafluorophosphate, perclorate, and triflate) in a stoichiometric ratio of 1:2 in CH\(_2\)Cl\(_2\)/EtOH (1:1) generate the species [Ln(L\(^1\))\(_4\)Ag\(_2\)]X [Ln = Eu, X = PF\(_6\)\(^-\), CF\(_3\)SO\(_3\)\(^-\), ClO\(_4\)\(^-\)] (4a–4c); Ln = Tb, Nd, La, X = PF\(_6\)\(^-\)] (4d–4f). Their structure is illustrated in the bottom row of Figure 4. As for the synthesis of the previous species, the structure determining factors are the stoichiometric ratio ML/Ag of 1:2 and the solvent system employed. The nature of the counter-anion of the silver salt seems not to influence the outcome of the reactions. As a consequence, we believe that this family of polymers could include other species with anions of similar shape, such as BF\(_4\)\(^-\), AsF\(_6\)\(^-\), and SbF\(_6\)\(^-\). All the crystals belong to the orthorhombic system, space group \(Pnca\), and their structure contains a 2D network of squares, using the whole SBUs as nodes (Figure 4f, in red) or hexagonal double-edged meshes, using the metal atoms as nodes (Figure 4f, in blue). This framework is unique, being characterized by the presence of two silver-pincer SBUs per ML (Scheme 2).

In this structure, all the four diketonate ligands of the Ln-ML play the same role, i.e. they form each an Ag–C bond via the central carbon atom and use one of their two CN groups to bind the silver ion of a lateral SBU. Overall, four CN groups (out of eight) are employed by each ML for networking. All the edges of the square windows are reinforced by π–π interactions between phenyl rings [for the two phenyl rings the centre-to-centre distance is 4.459(13) Å and the angle between the phenyl rings is 3.37(12)°]. The layers in family 4 are stacked with an ABAB sequence along \(a\) and the disordered counter-anions are located in the channels running in the same direction (Figure S14). The double edges and the disordered
anions obstruct the 1D channels running along the stacking direction, creating isolated voids that add up to 19% of the cell volume.

### 3.2.4 2D coordination network \([\text{La}(L^1)_4(H_2O)Ag]\) (5)

Only with the lanthanum metalloligand 1b a fourth type of polymeric array can be obtained, having formula \([\text{La}(L^1)_4(H_2O)Ag]\) (5). Bulk microcrystalline powders of this species are obtained from the same reaction system leading to 3b by fast addition of an aqueous silver solution to the lanthanum metalloligand 1b dissolved in acetonitrile. Single crystals of 5 are grown slowly, in about one month, after the disappearance of the crystals of 3b initially formed (a solvent mediated process).

![Figure 5. Two views of a single molecular layer of compound 5, down c (top) and [110] (bottom).](image)

The new species shows again a 2D polymeric structure, in which however no silver pincer-like SBUs are present and only the CN groups (4 groups per ML) are involved in the coordination to the silver cations (Figure 5). Since this structure can be obtained only with the La metalloligand, i.e. the species containing the metal with the largest ionic radius, this feature is probably of relevance in driving this
structural type formation. Indeed, the lanthanum cation is 9-coordinated, with an additional water molecule in the inner coordination sphere [La–O 2.712(8) Å], and adopt a monocapped square-antiprismonic geometry (SAPRS-9).

The topological simplification of the 2D network 5, considering the lanthanum and silver atoms as nodes, gives a square layer 4^4-sql with single edges (Figure 6a). However, the structural type is related to that of the red polymorph of PbO (litharge) since it is not flat and the two types of 4-connected nodes are different: the La nodes show a square pyramidal geometry, while the Ag nodes are (slightly) distorted tetrahedral [N–Ag–N angles 101.2(4) and 113.78(19)°]. As clearly evidenced by the simplified representation of the network, the layers are strongly puckered and stacked with interdigitation in an AAA sequence along c. A remarkable resemblance of this network with an egg tray can be noticed (Figure 6b).

Interestingly, a side view of the layer shows that the uncoordinated CN groups are all oriented outwards the two surfaces of the layers (Figure 5b) while, on the other hand, all the La-water vectors are oriented towards the middle section of the layer. The exo-oriented donor groups could in principle allow interactions of the layers with external metal ions. The two types of nitrile groups (coordinated

Figure 6. Views of the simplified network of 5 obtained by considering the metal atoms as nodes (lanthanum in blue and silver in pink). In a) a single layer is presented, showing the position of the water molecules coordinated to the lanthanum ions. In b) the staking of the egg-tray like layers along c is evidenced.
to the silver ions and free), at variance from what observed in all the previously presented complexes, are clearly distinguishable in the IR spectra.

3.3 Luminescence properties

We studied the photophysical properties of the ligands (HL\textsuperscript{1} and HL\textsuperscript{2}) and of their complexes in dichloromethane solution and in the solid state, and of the coordination polymers in the solid state only. The most relevant data are gathered in Table 1. The absorption spectra of the free ligands and of the corresponding europium metalloligands are reported in Figure 7.

HL\textsuperscript{1} presents absorption maxima at 255 and 352 nm, and a large and not structured fluorescence band centered at 405 nm at room temperature (both in solution and in the solid state) with a low emission quantum yield (< 10\textsuperscript{-4}). Because of its energy and excited state lifetime, this band can be attributed to a spin allowed fluorescence transition. HL\textsuperscript{2} presents very similar characteristics but with slightly higher energies in absorption and emission that falls at 400 nm in solution, with a quantum yield similar to that of HL\textsuperscript{1}.

All the monomeric lanthanide complexes NET\textsubscript{4}[Ln(L\textsuperscript{1})\textsubscript{4}] were characterized both at room temperature and at 77 K in dichloromethane solution. Due to their low intrinsic absorption, lanthanide ions can present a high brightness only if an efficient antenna effect through the light excitation of suitable ligands and an efficient energy transfer process to the metal-centered states of the metal ions can be obtained. A first parameter to be observed is thus the energy of the ligand-centered states in the complexes. For this purpose, we carefully characterized the lanthanum complex 1b, since La\textsuperscript{3+}, presenting the close shell electronic configuration of xenon, does not usually have metal-centered (MC) emission bands.\textsuperscript{56} The absorption spectrum of the complex presents the features of the ligand absorption profile but with the band at lower wavelength shifted to 365 nm, as expected upon metal complexation. It is important to mention that the absorption spectrum of 1b is superimposable with those of all the other complexes with HL\textsuperscript{1}, indicating that the ligand experiences similar complexation environments in all the 1a–1d species (Figure S15). The emission spectrum of 1b at room temperature presents a broad fluorescence band at circa 380 nm with a lifetime of 2 ns, while at 77 K it shows also a lower-energy (555 nm) longer-lived (2.2 ms) band attributable to a \textsuperscript{3}LC transition (Figure S16).

It is important to note that, according to these data, the \textsuperscript{3}LC state (19250 cm\textsuperscript{-1}) is lower in energy than the MC \textsuperscript{5}D\textsubscript{4} state of the Tb\textsuperscript{3+} ion, suggesting that the ligand HL\textsuperscript{1} is not able to sensitize the typical MC emission of this ion. In agreement with this consideration, 1d does not present any typical MC emission in solution, not even at low temperature.
### Table 1. Photophysical properties of the ligands, the metalloligands, and the heterometallic coordination networks. 

<table>
<thead>
<tr>
<th>compound</th>
<th>absorption maxima (nm)</th>
<th>emission maxima (nm)</th>
<th>emission lifetime (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL$^1$</td>
<td>255, 352</td>
<td>405</td>
<td>3 ns</td>
</tr>
<tr>
<td>NEt$_4$[Eu(L$^1$)$_4$] (1a)</td>
<td>252, 368</td>
<td>615 (615)</td>
<td>41, 21$_{pw}$ (430)</td>
</tr>
<tr>
<td>1D-[Eu(L$^1$)$_4$Ag] (2a)</td>
<td></td>
<td>615$_{pw}$</td>
<td>20$_{pw}$</td>
</tr>
<tr>
<td>2D-[Eu(L$^1$)$_4$Ag] (3a)</td>
<td></td>
<td>615$_{pw}$</td>
<td>15$_{pw}$</td>
</tr>
<tr>
<td>2D-[Eu(L$^1$)$_4$Ag$_2$]PF$_6$ (4a)</td>
<td></td>
<td>615$_{pw}$</td>
<td>20$_{pw}$</td>
</tr>
<tr>
<td>NEt$_4$[La(L$^1$)$_4$] (1b)</td>
<td>256, 365</td>
<td>380$^b$ (555)</td>
<td>2 ns$^b$ (2.2 ms)</td>
</tr>
<tr>
<td>1D-[Nd(L$^1$)$_4$Ag] (2c)</td>
<td>256, 367</td>
<td>893, 1065</td>
<td>–$^c$</td>
</tr>
<tr>
<td>2D-[Nd(L$^1$)$_4$Ag] (3c)</td>
<td></td>
<td>894$<em>{pw}$, 1070$</em>{pw}$</td>
<td>–$^c$</td>
</tr>
<tr>
<td>NEt$_4$[Tb(L$^1$)$_4$] (1d)</td>
<td>256, 367</td>
<td>390$^b$</td>
<td>2 ns$^b$</td>
</tr>
<tr>
<td>HL$^2$</td>
<td>243, 338</td>
<td>400</td>
<td>5 ns</td>
</tr>
<tr>
<td>NEt$_4$[Eu(L$^2$)$_4$] (1e)</td>
<td>290, 350</td>
<td>615</td>
<td>140, 480$_{pw}$</td>
</tr>
<tr>
<td>NEt$_4$[Nd(L$^2$)$_4$] (1f)</td>
<td>255, 367</td>
<td>890, 1064</td>
<td>–$^c$</td>
</tr>
</tbody>
</table>

$^a$ All the values determined in dichloromethane solution at room temperature, apart from the ones in round brackets, determined at 77 K, and the ones with the subscript “pw”, measured for the microcrystalline powders. $^b$ Data relative to the LC emission. $^c$ Not possible to measure with our instrumentation.

The emission spectrum of compound 1a reveals the typical MC bands of the europium ion (Figure 8) and it is possible to observe the $^0$D$^5$$^→$$^7$F$^J$ transitions with $J$ from 0 to 4. The presence of the forbidden $^0$D$^5$$→$$^7$F$^0$ and $^0$D$^5$$→$$^7$F$^3$ transitions and, above all, the high value of the ratio between the $^0$D$^5$$→$$^7$F$^2$ and $^0$D$^5$$→$$^7$F$^1$ intensities are in line with a low symmetry environment of the Eu$^{3+}$ ion, lacking an inversion center, in agreement with the geometry observed in the crystal structure (Figure 1). The energy of the $^3$LC transition is, in this case, compatible with a good energy transfer from the ligand to the metal center.

![Figure 8](image-url.com) Emission spectra in CH$_2$Cl$_2$ at r.t. of the free ligand HL$^1$ (red, $\lambda_{ex}$ 320 nm) and the complexes NEt$_4$[Eu(L$^1$)$_4$] (1a) (black, $\lambda_{ex}$ 340 nm) and NEt$_4$[Nd(L$^1$)$_4$] (1c) (green, $\lambda_{ex}$ 370 nm).
However, the measurements of its lifetime (Table 1) give quite low values not in line with what expected for similar compounds (lifetimes in the range of hundreds of microseconds), evidencing the presence of favorable non-radiative deactivation pathways. The energy of the MC state is close to the one of the $^3$LC transition, so that the sensitization of the MC state is possible but with the establishment of a thermally activated equilibrium between the two states. The ten-fold increase of the emission lifetime observed at low temperature (77 K) supports this assumption. The neodymium complex 1e is also efficiently populated by the ligand and presents the typical IR bands at 893 and 1065 nm with an interesting emission quantum yield of circa 2%. The two NEt$_4$[Ln(L$^2$)$_4$] complexes 1e and 1f show luminescence spectra very similar to those observed for their L$^1$ homologues, but with a longer lifetime (Table 1, Figure S17), probably due to the higher energy of the $^3$LC state in this case, a condition that would shift the above mentioned equilibrium in favor of the europium MC state.

Figure 9. Emission spectra at r.t. of the solid powders of (a) [Eu(L$^1$)$_4$Ag] (2a), (b) [Eu(L$^1$)$_2$Ag] (3a), and (c) [Eu(L$^1$)$_2$Ag$_2$]PF$_6$ (4a). Insets: enlarged lower intensity peaks.
Due to the lack of luminescence of the lanthanum and terbium complexes, it was possible to characterize only the 1D and 2D polymers containing europium (2a, 3a, and 4a, Figure 9) and neodymium (2c and 3c). As a general remark, results obtained for the microcrystalline powders and the single crystals (data not shown) of the same species were always identical. A comparison of the data obtained for the metalloligands and for the corresponding silver-lanthanide coordination networks allows to observe that the presence of the silver centers did not significantly change the photophysical behavior of this species. This means that the presence of silver pincer-like secondary building units does not add other efficient non-radiative deactivation pathways for the excited states. It has also to be mentioned that the series of 2D structures containing europium and bearing different counter anions (4a–4c) presents again analogous characteristics and, for this reason, the corresponding data are not reported in Table 1.

4 Conclusions

The construction of heterometallic metal-organic framework is generally a difficult task to be accomplished due to the propensity of a given donor group to better coordinate to a specific metal. One of the strategies employed to attain this result involves the use of asymmetric ligands in which different coordinating groups can be directed towards different metal centers. The stepwise metalloligand approach represents a valid alternative that, in addition, allows to exert a better control on the topology of the assembled network prepared. However, this stepwise approach has not been yet fully exploited in the case of HMOF containing lanthanides metalloligands.

In this work we explored the use of two new tetrakis-chelate Ln-MLs, containing the 1,3-disubstituted diketonate ligands HL\textsubscript{1} and HL\textsubscript{2}, in order to prepare HMOFs by reaction with silver cations. It was found that this approach gives good results only using the metalloligands based on the 4-cyanophenyl-substituted diketonate HL\textsubscript{1}, obtaining different families of 1D and 2D HMOFs. On the other hand, the lability in solution of the metalloligands based on the 4-pyridyl-substituted diketonate HL\textsubscript{2} prevents their networking with silver cations.

The structures of the monomeric building blocks and those of four families of lanthanide-silver heterometallic networks has been described, allowing to point out some general features of their synthetic strategy and to ascertain the coordination ability of the starting lanthanide metalloligands. In particular, we found that both the Ln-to-Ag stoichiometric ratio and the solvent employed in the syntheses proved to be crucial in determining the nature of the structures assembled. We also observed that the coordination capabilities of the Ln-MLs could not be fully exploited, due to the high number of cyano groups per ML and to the additional formation of the silver pincer-like SBUs that induce a deformation in the coordination environment of the metal atoms. Both these factors lead to the preferential formation of 1D and 2D networks over 3D ones. Nevertheless, some of the prepared materials are porous and in one of the isolated families (4) the presence of about 20% of free volume can be estimated from the crystallographic data.

The photophysical characterization of the ligands and the metalloligands evidenced that lanthanum and terbium complexes are not emissive while the europium ones present quite low intensities and lifetimes due to similar energies of the MC and \(^3\)LC states that give rise to a thermally activated equilibrium. On the other side, the sensitization of the neodimium complexes is very efficient. The heterometallic coordination networks have similar photophysical behaviour evidencing that, both in 1D and 2D structures, the presence of silver ions does not add other efficient non-radiative deactivation pathways.

The results here presented point out some of the features of the lanthanide metalloligands and of their interaction with silver cations that could be fruitfully employed in the development of new HMOFs with tailored structures and properties.
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website. TGA plots; X-ray powder diffraction patterns; representations of molecular and crystal structures; absorption and emission spectra; tables of crystallographic data.

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Notes
The authors declare no competing financial interest.

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Table of Contents Synopsis
Stepwise self-assembly processes using new lanthanide metalloligands and silver salts have been successfully applied to isolate 4f-4d heterometallic coordination networks of four different structural types. Their structures can be rationalized in terms of a new “pincer-like” secondary building unit consisting of a silver cation coordinating the central carbon atoms of two different diketonate ligands.