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Two novel lineal d10 metal-organic frameworks with a ditopic flexible linker: Structures, blue luminescence and thermal stability

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ABSTRACT

Two novel supramolecular Ag(I) complexes, $\{[\mathrm{AgL}]\mathrm{NO_3}\}_n$ **(1)**, and $\{[\mathrm{AgL}]\mathrm{CF_3SO_3}\}_n$ **(2)**, **(L)** = ethane-1,2-diyl bis(pyridine-3-carboxylate) have been prepared by self-assembly of Ag(I) salts with ethane-1,2-diyl bis (pyridine-3-carboxylate) **(L)** in THF/H_2O system. The IR, TGA and elemental analysis have been recorded and both complexes were structurally characterized by X-ray crystallography confirming that complexes **(1)** and **(2)** are one-dimensional coordination polymers with lineal and helical chain motifs respectively. Solid emission spectra at room temperature of **(1)** and **(2)** show interesting blue phosphorescence with maximum intensity at 414 and 411 nm respectively, which are assigned to (LLCT) transition.

Luminescent organic and Metal–Organic Frameworks (MOFs) have been an active research area for decades because of their various potential applications in materials sciences. Recently, the applications of novel blue fluorescent materials in blue light emitting devices (LEDs) remain an ongoing interest in materials science [1]. Luminescent metal complexes with pyridine-containing ligand have attracted much attention due to high luminescent efficiency. The d^{10} metal complexes with nitrogen-containing ligand have been synthesized and their luminescent behavior studied [2–5]. Ligand-based emission, where closed-shell metal ions act to stabilize an intrinsically luminescent organic, is less common. A few hybrid structures showing this type of ligand-centered luminescence have been described [5]. Other factors related to luminescent properties, are the closed-shell metal ion interactions which have received much attention, due to the existence of photoluminescence in linearly coordinated complexes of monovalent ions such silver and gold [6–8].

To achieve full-color electroluminescent display, three color components, i.e., green, blue, and red, must be available. Stable blue luminescent compounds that are useful in electroluminescent devices are still scarce and very challenging to prepare [9].

Compared to the pure organic materials used in LED and electroluminescent (EL) devices, the major advantages of the MOF compounds are that the properties of this class of compounds, such as volatility, stability and luminescent properties can be modified readily by manipulating the coordination environment around the central atom as well as counter-ion and solvent [10].

We herein describe a full account on the preparation and structural characterization of two Ag(I) complexes containing flexible ditopic ligand ethane-1,2-diyl bis (pyridine-3-carboxylate) which were found to exhibit blue photoluminescence.

The reaction of the flexible ligand, ethane-1,2-diyl-bis-(pyridyl-3-carboxylate), **(L)** and $AgNO_3$, and $AgCF_3SO_3$ salts, under same experimental conditions leads to the formation of two coordination polymers with different motifs: $\{[\mathrm{Ag(L)(NO_3)}]\}_n$ **(1)** and $\{[\mathrm{Ag(L)(CF_3SO_3)}]\}_n$ **(2)**. As shown in Figs. 1 and 2 each Ag^I center is coordinated by two N atoms from **(L)** symmetry-related in a slightly distorted linear fashion to form linear chains for **(1)** and helical chains for **(2)**. Ag—N bond distances are in the range from 2.157(3) to 2.204(3) Å, typical values for Ag^I—N_{py} coordination distances [11–13]. The bond angles N—Ag—N 158.02(15) and 168.95(11)° for **(1)** and **(2)** respectively are indicative of presence of a distortion from linearity in both compounds. Ag···Ag separations across **(L)** are 14.917(8) and 11.795(9) Å for **(1)** and **(2)**. The helical chain is connected to another one, (symmetry code: 2 − x, 1 − y, 1 − z) through Ag—Ag interactions, with Ag—Ag = 3.1937(4) Å, which is shorter than the van der Waals radii of two silver atoms (3.44 Å) comparable with similar distances reported [13]. Consequently, H-shaped dimeric units are generated. The pyridine rings on the side of the Ag—Ag bond are almost co-planar, forming a dihedral angle of 14.7(2)°, Fig. 3. In both compounds, there are also weak Ag···C interactions with Ag···C distances in the range from 3.071(3) to

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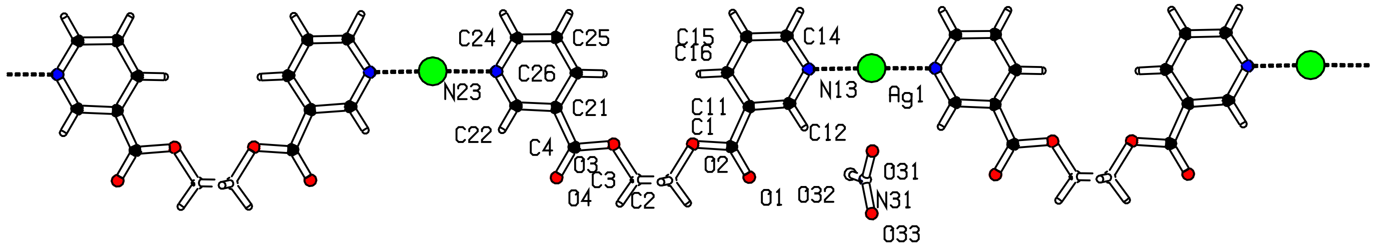

Fig. 1. Linear chain structure of (**1**).

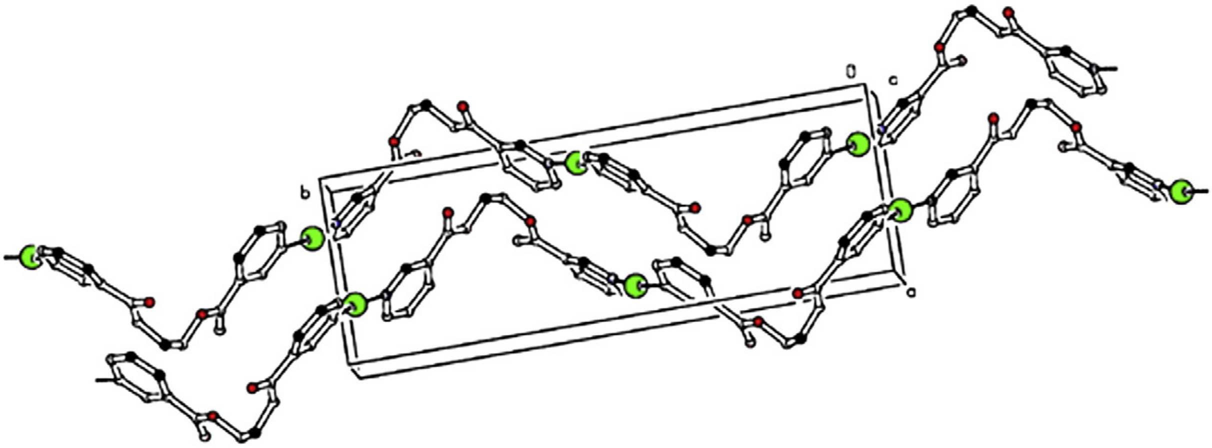

Fig. 2. Parallel arrangement of helical chains structure of (**2**). Triflate anion and H atoms are omitted for charity.

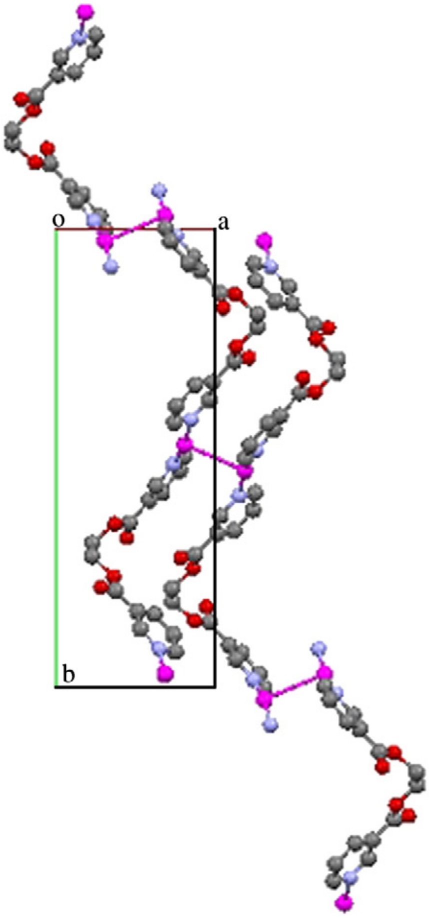

Fig. 3. A view of the H-shaped dimeric units.

3.141(5) Å and fall in the secondary bonding range (the sum of the van der Waals radii of Ag and C is 3.42 Å) [14]. Some polymeric silver (I) compounds have been reported with similar Ag···C interactions, ranging 2.80–3.34 Å [12,15]. Therefore, these interactions are very important for the packing in the solid state, for the compounds under study.

In (**1**), Ag^I cation is six coordinated in a distorted trigonal prismatic square geometric by two N atoms from symmetry-related, two O atom from symmetry-related and two O atom from a single nitrate anion, Fig. 4. The bond angles around Ag^I are ranging from 53.76(11) to 162.82(10)°. This non-lineal angle at the silver cations is due to the asymmetric coordination of the nitrate anions. The crystal structure consists of one-dimensional Ag^I–L chains, which are further extended by μ_2-κ^2 O:O nitrate anions into a two-dimensional (4,4) sheet, Fig. 5. The Ag—O bond lengths are comparable to those in related compounds [16,17].

In (**2**), Ag^I cation is four-coordinated and adopts a saw-horse geometry to two N atoms from symmetry-related and two O atom from a triflate anion, Fig. 6. The N—Ag—N is 168.95(10) and the O—Ag—O is 111.27(8)°. The N—Ag—O ranges from 85.28(7) to 104.31(8)°. The crystal structure consists of one-dimensional Ag^I–L helical chains, which are further extended by triflate anions into a two-dimensional sheet, Fig. 7. The Ag—O bond lengths are comparable to those in related compounds [16–18]. In both compounds, the ligand, (**L**) acts in a μ_2-N:N′-bidentate fashion to link Ag^I cations to form a linear and helical chain motif along [010] for (**1**) and [111] for (**2**). The ethylene moiety of (**L**) retains the gauche conformation [19]. The dihedral angles between the two pyridyl rings are 22.4(2) and 78.9(2)° for (**1**) and (**2**) respectively.

Metal–organic frameworks constructed from d^{10} metal centers and conjugated organic linkers are promising candidates for hybrid photo-active materials with potential applications such a light-emitting diodes (LEDs) [20]. Since Ag(I) d^{10} configuration prevents stabilization of excited states via the ligand field, LMCT and LLCT transitions dominate the photophysics of these compounds. In majority of cases,

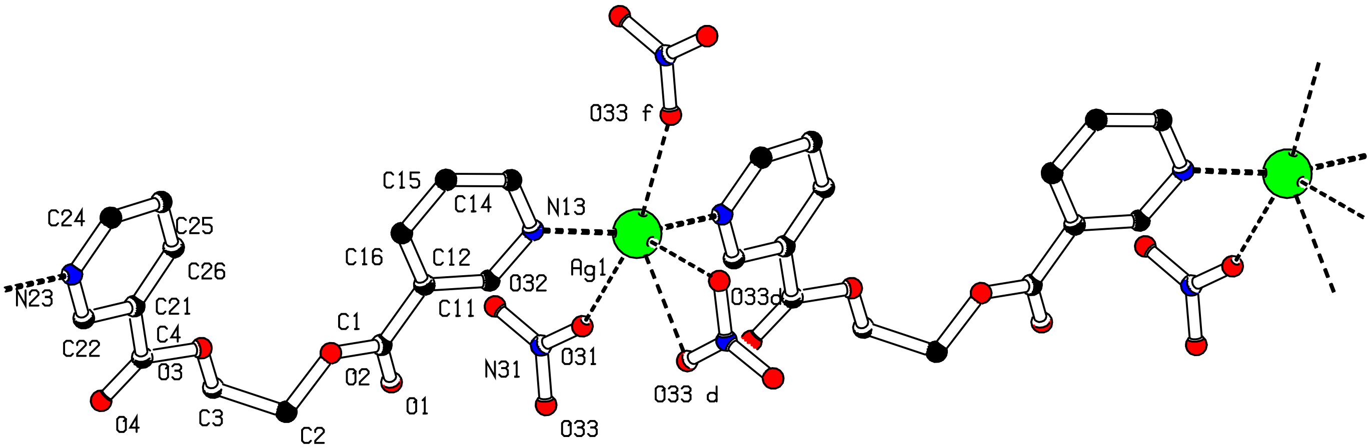

Fig. 4. Ag(I) coordination environment in compound **(1)** (symmetry codes: (O31 and O33 (d) 3/2-x, 1/2+y, 1/2-z; x, y+1, z).

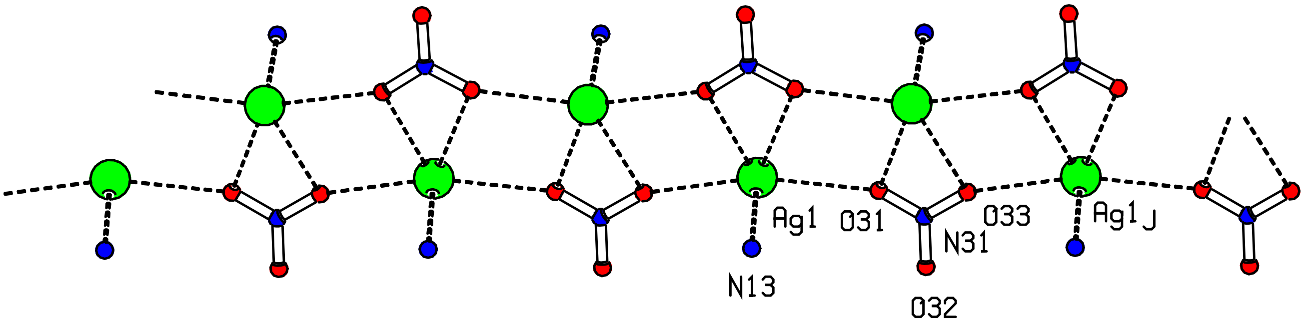

Fig. 5. Coordination of NO_{3-} with Ag(I) in **(1)** forming two-dimensional (4,4) sheet.

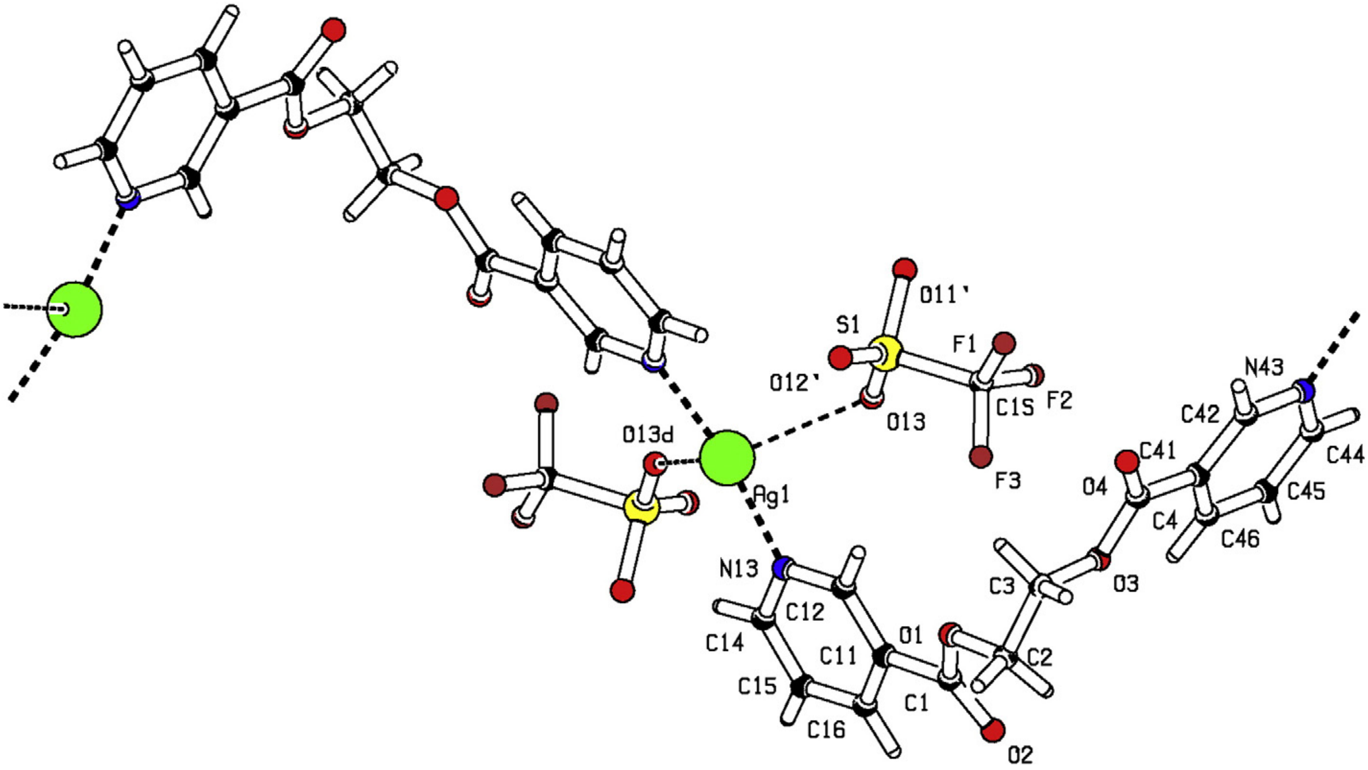

Fig. 6. Ag(I) coordination environment in compound **(2)** (symmetry codes: O13d and N43: 2-x, 1-y, 1-z; 3/2-x, -1/2+y, 1/2-z).

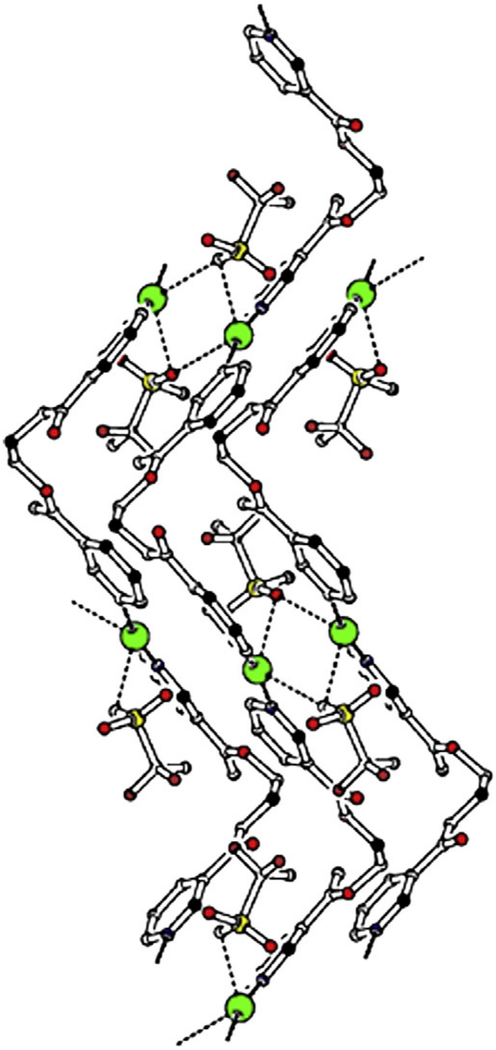

Fig. 7. Part of the crystal structure for **(2)** consists of one-dimensional Ag(I)-L helical chains, which are further extended by triflate anions into a two-dimensional sheet.

emission originates from excited ^{3}LMCT or ^{3}LLCT states (triplet emitters), due to strong spin-orbit coupling induced by heavy atom, consequently, between the HOMO–LUMO states that are lowered, results in a red-shift in the emission wavelength. However, as it is known Ag(I) may emit weak photoluminiscence at low temperature, but room temperature examples are scarce [21–24]. Because single crystals of **(1)** and **(2)** are air-stable and insoluble in common solvents, solid-state emission properties of luminescent complexes **(1)** and **(2)** as well as free ligands **(L)** were investigated at room temperature. The results indicate that the emission properties of **(L)** were affected by their incorporation of metal-containing coordination compounds because there is a red shift displacement in emission maximum of **(1)** and **(2)** with respect to **(L)**. Fig. 8 shows emission and excitation spectra for (**L**) with one maximum at 394 nm upon excitation at 352 nm. Under same experimental conditions the emission and excitation spectra for compounds **(1)** and **(2)** have been studied, compound **(1)** exhibits one emission band at 414 nm while compound **(2)** exhibits one emission maximum at 411 nm upon excitation at 368 and 346 nm respectively. It is hard to propose a correct mechanistic conclusion for their luminescence based only on emission spectra, although the excited state lifetime (τ) measure may be helpful in verifying the photoluminescence mechanism [25]. The lifetime of **(1)** can be well fitted by a single-exponential function with τ at 0.78 ms, which is similar to free ligand **(L)** lifetime ($\tau = 0.74$ ms), in accordance with the similarity of the lifetime, the emission band of **(1)** may be attributed mainly to LLCT transition. Meanwhile the lifetime of **(2)** can be fitted by a double-exponential function with τ_1 and τ_2 at 0.68 and 0.80 ms, respectively; therefore the emission band may be also assigned to LLCT, admix with MC transition, belonging to the Ag(I)—Ag(I) interaction with the presence of the nd$\sigma^* \rightarrow (n+1)p\sigma$ transitions [25,26]. The long lifetime of emissive state in the ms range is probably suggestive of triplet origin and comparable to those in related compounds [28,29]. Therefore, the red-shift of **(1)** and **(2)** compared to **(L)** is due to the stabilization of (^{3}LLCT) state, that shows to significantly affect the energy gap of the frontier orbitals [26]. Furthermore, emission intensity of compound **(1)** is a little weaker than that of the free ligand, which can be attributed to the heavy atom effect [27]. The enhance emission intensity of compound **(2)** can be originated to Ag(I)—Ag(I) interaction, that effectively increases the structural rigidity of metal–organic framework and reduces the loss of energy via vibration motion [10].

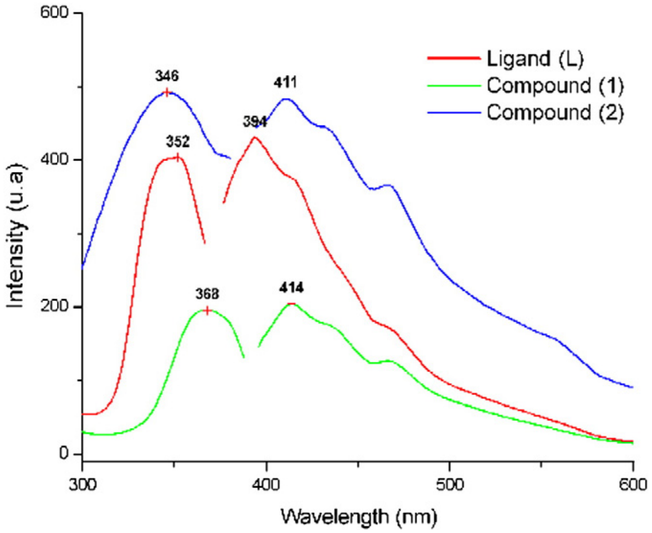

Fig. 8. Emission and excitation spectra for **(L)**, **(1)** and **(2)** compounds.

The thermal stability of both polymers studied using thermal gravimetric analysis (TGA), from 25 to 600 °C under flowing Argon at a heating rate of 10 °C/min (Fig. 9-1 and 9-2) for compounds **(1)** and **(2)** is thermally stable up to 194 °C and 212 °C respectively. Furthermore the TGA curves show that there are no chemical decomposition up to 230 °C for compound (**1**) and 500 °C for compound **(2)**.

The weight loss for compound **(1)** (observed: 63.3%, calculated: 65.5%) occurs from 194 to 221 °C, which is attributable to the complete decomposition of the sample. The residue is $AgNO_2$. For compound **(2)** (observed: 79%, calculated: 79.6%) occurs from 212 to 512 °C, which is attributable to the complete decomposition of the sample. The residue is metallic silver.

Two novel Ag(I) coordination polymers were prepared by a diffusion method between $AgNO_3$ and $AgCF_3SO_3$ with **(L)** = ethane-1,2-diyl bis(pyridine-3-carboxylate), and these structures were characterized by X-ray crystallographic, TGA and IR techniques.

The luminescent properties of the ligand free **(L)** were modified, preparing coordination polymers for diffusion methods between **(L)** and silver salts. The nature of the used anion allows to obtain coordination polymers with different motifs, thermal stabilities and luminescent properties. This should presumably lead to new tuneable materials.

The ligand free was synthesized according to the reported method [19].

Compounds **(1)** and **(2)** were obtained by diffusion method between $AgNO_3$ and $AgCF_3SO_3$ with (**L**) [30]. Single-crystal X-ray diffraction analysis reveals that both compounds crystallize in space group $P2_1/n$ and consist of slightly distorted lineal $[Ag(L)]_n$ chains for **(1)** and helical chains for **(2)** [31].

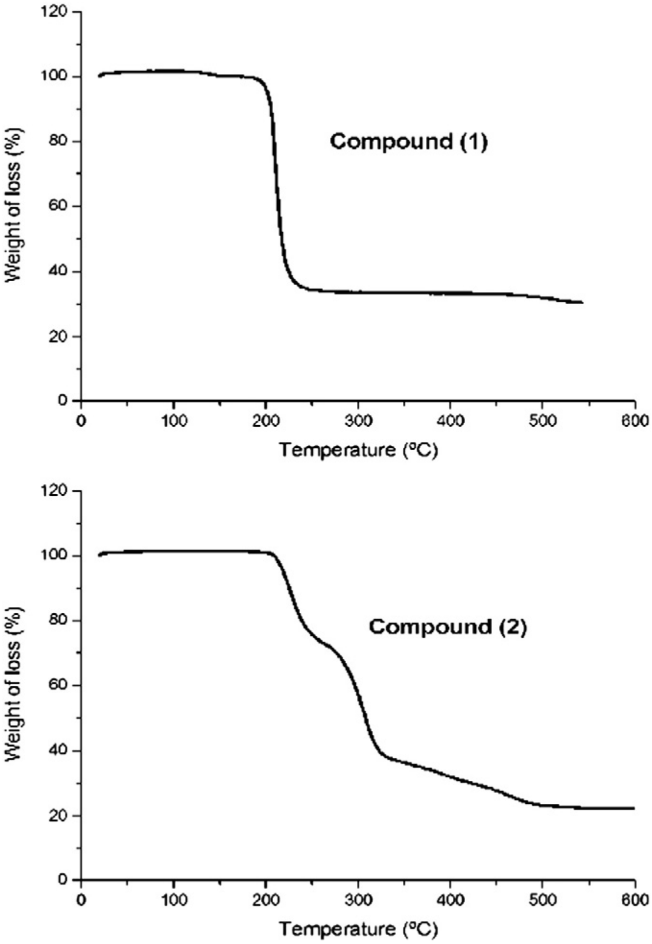

Fig. 9. The TGA curves for (**1**) and (**2**) compounds.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.03.022.

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[30] Compound (1) A solution of AgNO3 (16.9 mg, 0.1 mmol) in water was slowly added to a solution of L (27.2 mg, 0.1 mmol) in THF (4 ml). Colorless single crystals suitable for X-ray were obtained after a few days were obtained in 64%. Anal. Calc. for C14H12N3O7Ag (441.03): C, 38.1; H, 2.72; N, 9.52% Found: C, 38.8, H, 2.81, N, 9.32%. The IR (KBr, cm^{-1}): 1736 s, 1609 m, 1455 m, 1240 s and 635 m. Compound (2): A solution of AgCF3SO3 (25.7 mg, 0.1 mmol) in water was slowly added to a solution of L (27.2 mg, 0.1 mmol) in THF (4 ml). Colorless single crystals suitable for X-ray were obtained after a few days were obtained in 75% yield. Anal. Calc. for C15H12N2O7SF3Ag (528.04): C, 34.09; H, 2.27; N, 5.30%. Found: C, 35.3, H, 2.41, N, 5.23%. The IR (KBr, cm^{-1}): 1727 s, 1605 m, 1424 m, 1278 s and 632 s.
[31] Single crystals analysis were performed at 173(2) K with a STOE IPDS II two-circle-diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω-2θ scan technique. All data were collected for absorption by multi-scan method using [31a]. The program X-area [31b] was applied for integration of the diffraction profiles. The structures were solved with direct method using SHELXS-97 followed by structure refinement on F2 with program SHELXL-97 [31c]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically with isotropic thermal parameters set to 1.2Ueq of the parent atom. Crystal data for (1): C14H12AgN3O7, Mr = 442.14, Monoclinic P21/n, a = 13.0008(8) Å, b = 7.8631(4) Å, c = 14.9166(7) Å, β = 98.301(4)°, V = 1508.90(14) Å3, Z = 4, Dc = 1.946 g cm-3, μ = 1.382 mm-1, F(000) = 880, 21810 reflections measured with 2900 unique reflections, GOF = 0.902. The final [I > 2σ(I) R = 0.0344, wR2 = 0.0754]. The CCDC reference number is 795281. Crystal data for (2): C16H14AgF3N2O7S, Mr = 543.22, Monoclinic P21/n, a = 7.9745(6) Å, b = 10.9040(6) Å, c = 21.8561(13) Å, β = 94.865(5)°, V = 1893.6(2 Å3, Z = 4, Dc = 1.905 g cm^{-3}, μ = 1.248 mm^{-1}, F(000) = 1080, 11865 reflections measured with 3544 unique reflections, GOF = 0.977. The final [I > 2σ(I) R = 0.0330, wR2 = 0.0881]. The CCDC reference number is 795282.
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