

A Rigid Angular Bidentate Ligand for the Design of a New Class of Coordination Polymers Based on Silver(I) Salts – Influence of the Anion on Coordination Assemblies

Christophe Desmarets,^{*,[a]} Iban Azcarate,^[a] Geoffrey Gontard,^[a] and Hani Amouri^{*,[a]}

Keywords: Coordination chemistry / Coordination polymers / Silver / Ligand design / Self-assembly

The synthesis of a new family of coordination polymers $[\text{AgL}^2\text{X}]_n$ (**1a**, X = CF_3SO_3^- ; **1b**, X = BF_4^- ; **1c**, X = NO_3^- ; **1d**, X = PF_6^-) using 5-methoxy-1,3-bis(pyridin-3-ylethynyl)benzene (**L**²) as the self-assembling ligand is described. All compounds have been fully characterized by spectroscopic techniques and elemental analysis. In particular the X-ray molecular structures of **1a** and **1b** are reported and confirm the formation of 1D silver(I) chains. Their arrangements are described as a function and the nature of the anion. The supra-

molecular product **1a** exhibits argentophilic $\text{Ag}\cdots\text{Ag}$ interactions to afford infinite double chains. Additionally, $\eta^1\text{-Ag}^1\text{-}\pi$ interactions lead to the formation of a network of stacked layers of double chains. In contrast, **1b** lacks metal-counterion bonding and is constituted of infinite coordination polymers, which are held together by $\pi\text{-}\pi$ interactions. The pivotal role of the counteranions on the overall packing arrangement of the polymers is presented and discussed.

Introduction

The design of polymeric organic–inorganic materials is of current interest in the field of coordination chemistry.^[1–3] These new metal-containing materials attract attention not only due to their structural diversity but also because of their potential applications in electrical conductivity, magnetism, host–guest chemistry, luminescence and catalysis.^[4–15] Their topology and properties are determined by several factors such as the metal coordination environment, the topology of spacer ligands employed to connect the metal nodes and weak intermolecular interactions (hydrogen bonding, π -stacking, etc) that stabilize the overall framework. Furthermore, self-assembly has evolved to become an elegant and efficient methodology for the construction of elaborate architectures.^[16]

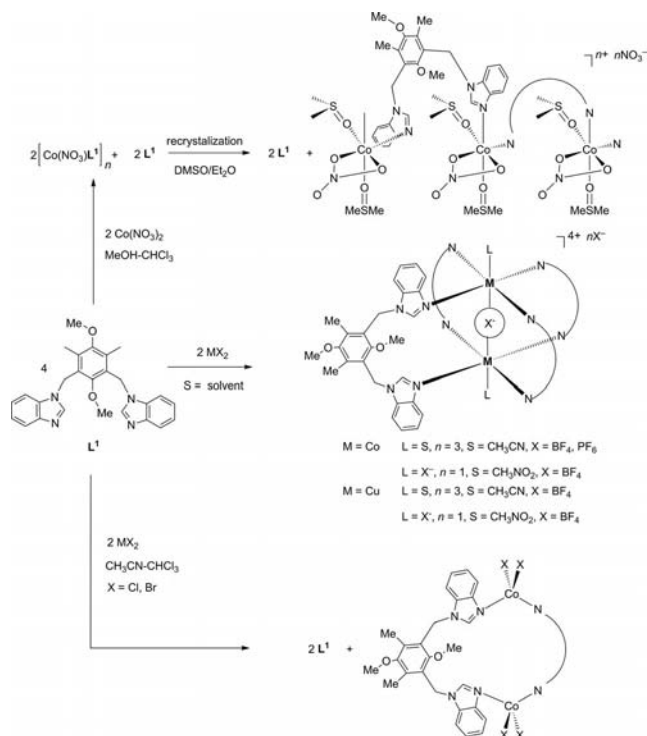
Among the several kinds of linkers used, those that contain ethynyl spacers in their backbones have been found to be suitable to design a range of assemblies with potential applications in optical electronics.^[17,18] In particular, *N*–*N'*-bridging ligands built from the 4-pyridylethynyl group have been successfully exploited to construct a variety of nano-sized architectures such as rectangles, cages, coordination polymers and host–guest assemblies.^[19–26] Surprisingly, despite this fact, examples of 1,3-bis(pyridin-3-ylethynyl)benzene compounds remain relatively scarce. For instance, efforts to prepare 3D architectures such as molecular

prisms, metallomacrocycles or cages have been reported.^[27–30] In the area of coordination of silver(I) cations, coordination polymers that adopt different conformations in response to the nature of the anion bound has been described using ligands containing hydrophilic dendritic side groups.^[31,32] Very recently, Crowley et al have synthesized and characterized a family of planar disilver(I) metallomacrocycles.^[33]

In this context, we have developed the use of semirigid bidentate 1,3-(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene (**L**¹, Scheme 1) affording a variety of appealing structures such as coordination polymers, macrocycles and cages. For example, extended polymeric chains formed by complexation with silver(I) cations can be obtained.^[34] The pivotal role of the anion on templating silver(I) metallomacrocycles and networks was also studied.^[35] Recently, we have developed the synthesis of some discrete self-assembled metallosupramolecular 3D capsules of the type M_2L_4 based on Co^{II} and Cu^{II} , which can encapsulate weakly coordinated anions.^[36–39] Remarkably, they are perfectly designed to house BF_4^- and PF_6^- . As part of our continuing research program, we sought to introduce a highly rigid ligand in our systems that is more coordinating to the metal to investigate whether it was possible to form new cages in which the encapsulation is not only limited to weakly coordinating anions. This work describes our initial results with this bidentate ligand.

In this paper we report the preparation of a new family of coordination polymers $[\text{AgL}^2\text{X}]_n$ (**1a**, X = CF_3SO_3^- ; **1b**, X = BF_4^- ; **1c**, X = NO_3^- ; **1d**, X = PF_6^-) using 5-methoxy-1,3-bis(pyridin-3-ylethynyl)benzene (**L**²) including the structural characterization of **1a** and **1b**. The influence of the

[a] Institut Parisien de Chimie Moléculaire, UMR CNRS 7201, Université Pierre et Marie Curie Paris-6, 4 place Jussieu, Case 42, 75252 Paris Cedex 05, France
E-mail: hani.amouri@upmc.fr
christophe.desmarets@upmc.fr

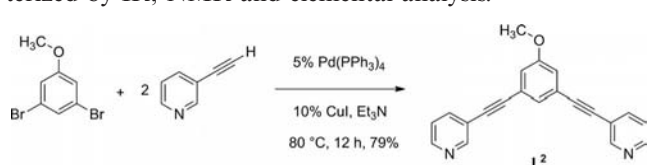


Scheme 1. Representation of **L**¹ and its coordination properties towards Co^{II} and Cu^{II} salts.

anions and intermolecular aromatic interactions on the secondary solid-state structures of **1a** and **1b** are presented and discussed.

Results and Discussion

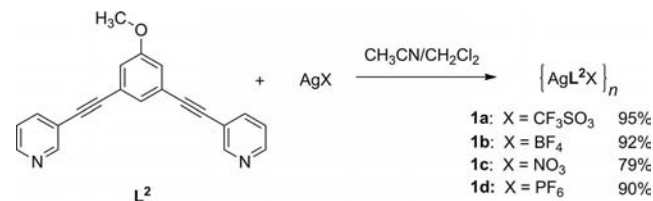
Bidentate **L**² contains two peripheral pyridine groups symmetrically *meta*-connected to a central benzene unit by two ethyne groups. Its topology leads to rigidity along the alkyne axis and rotation of the pyridines is possible. **L**² was synthesized using a Pd/Cu-catalyzed Sonogashira cross-coupling reaction between 3,5-dibromoanisole and 3-ethynylpyridine (Scheme 2). Under these reaction conditions, **L**² was obtained in high yield (79%) and was fully characterized by IR, NMR and elemental analysis.



Scheme 2. Synthesis of **L**².

Treatment of **L**² (1 equiv.) with AgCF₃SO₃ in CH₃CN/CH₂Cl₂ gave a white precipitate after 4 h. The white precipitate was isolated in high yield (95%) and identified as a 1D coordination polymer **1a** by single-crystal X-ray diffraction (Scheme 3). Elemental analysis of **1a** was consistent with a 1:1:1 ligand:silver:anion ratio. The IR spectrum shows the presence of coordinating triflate anions at 1282 cm⁻¹ and reveals the alkyne stretching vibration at 2216 cm⁻¹. More-

over, **1a** appeared to be stable both in the solid state and in solution in absence of light. The complex is soluble in common polar solvents such as acetone, acetonitrile and methanol, and the ¹H NMR spectrum was recorded in CD₃CN. The spectroscopic data of **1a** show only minimal changes in proton environments by comparison to those of **L**². This is not surprising and is attributed to an equilibrium between the free ligand and the Ag^I salt in the deuterated coordinating solvent and has also been reported previously.^[33] The nature of the species present in solution was investigated by recording an ES-MS of **1a** in acetonitrile solution. The ES-MS was dominated by several peaks that correspond to [HAgL²CF₃SO₃]⁺ (*m/z* = 556.8), [Ag₂L²CF₃SO₃]⁺ (*m/z* = 674.9), [Ag₂(L²)₂CF₃SO₃]⁺ (*m/z* = 984.6) and [Ag₃(L²)₂(CF₃SO₃)₂]⁺ (*m/z* = 1240.5) fragments verified by comparison of the isotopic pattern of the observed peak with theoretical patterns. The presence of these fragments is in agreement with the existence of oligomeric species in solution from the fragmentation of the polymer during the dissolution process. To ascertain the structure of **1a** an X-ray structural determination was undertaken. Crystals of **1a** were grown by vapour diffusion of diethyl ether into a solution of the complex in CH₃CN. Complex **1a** crystallizes in the monoclinic space group *P*2₁/*c*. The structure shows the formation of 1D coordination polymer **1a** in which the silver nodes are linked through the pyridyl arms of **L**² (Figure 1). In addition, each silver centre adopts a T-shaped geometry. All silver(I) ions are coordinated to two nitrogen atoms from two discrete **L**² ligands and one oxygen atom from the triflate anion. The Ag^I-N bond length lies in the range 2.156–2.182(3) Å, typical for a pyridyl-Ag^I bond length.^[40–42] The N1-Ag1-N4 angle of 169.6° is in agreement with the preference of silver(I) to adopt a linear coordination with bipyridyl donor ligands. The Ag-O bond lengths are in the range 2.75–2.78(3) Å, which is comparable to those reported for triflate anions bonded to Ag^I ions.^[43,44] Moreover each Ag^I exhibits an argentophilic Ag...Ag interaction (3.15 Å), which is shorter than the van der Waals radii (3.44 Å) but longer than the Ag...Ag distance in silver metal (2.85 Å).^[45–47] This interaction binds two adjacent 1D coordination polymers to afford an infinite double chain.



Scheme 3. Synthesis of **1a–d**.

Of interest, we note further weak η¹-Ag^I-π interactions between each Ag^I of a double chain and the π electronic system from the -C≡C- bond of **L**² to generate a 2D network constituted of stacked double silver(I) coordination chains. Indeed, this Ag-C contact lies in the range of 3.17–3.24(35) Å indicating a weak η¹-Ag^I-π interaction. Although the average distance of similar interactions is typi-

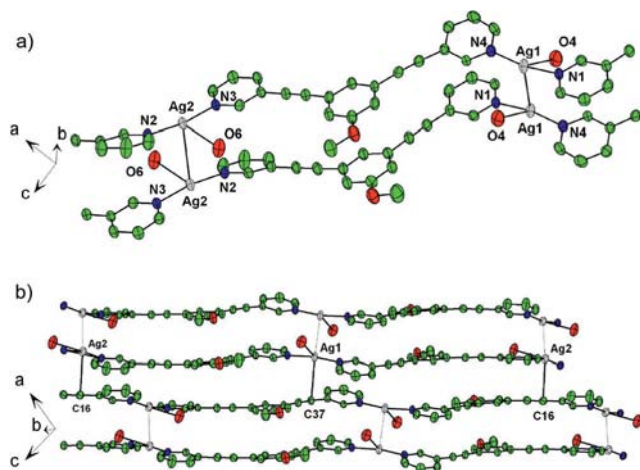


Figure 1. X-ray crystal structure of **1a** showing a) Ag⁺...Ag⁺ interactions resulting in the formation of double chains b) 2D structure formed by η^1 -Ag^I- π carbon-carbon triple bond interactions. (C green, O red, N blue, Ag grey; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–N1 2.156(3), Ag1–N4 2.167(3), Ag2–N2 2.178(3), Ag2–N3 2.182(3), Ag1–O4 2.7538(26), Ag2–O6 2.799(3), Ag1–Ag1 3.1500(8), Ag2–Ag2 3.1505(87), Ag1–C16 3.168(35), Ag1–C37 3.243(35), N1–Ag1–N4 169.6, N2–Ag2–N3 169.8(13).

cally 2.4–2.9 Å,^[48–50] we note that a silver(I) coordination polymer with similar planar geometry assembled with 2,2'-bipyridine exhibiting an Ag–C interaction of 3.3 Å has been reported.^[51] It is noteworthy that such supramolecular Ag⁺...Ag⁺ and η^1 -Ag^I- π interactions may represent an essential driving force for the supramolecular structure formation.

We decided to examine the role of the anion on the formation of this coordination polymer. Thus similar reaction conditions were applied by treating **L**² with other silver(I) salts, AgX (X = BF₄, PF₆, NO₃), instead of AgCF₃SO₃. Similarly, white complexes precipitated from solution in high to excellent yield (79–92%, Scheme 3) and elemental analysis confirmed the formulations of **1a**, **1b**, **1c** and **1d**. The IR spectra of these compounds revealed the presence of BF₄[−], NO₃[−] and PF₆[−] anions for **1b**, **1c** and **1d**, respectively. The ¹H NMR spectra (300 MHz) of **1b**, **1c** and **1d** were recorded in CD₃CN at room temperature and were analogous to that of **1a**. These identical spectroscopic data suggest the formation of homologous 1D coordination polymers. In order to determine whether the anion alters the arrangement in the solid state of these species, we examined the crystallization of **1b**, **1c** and **1d**.

Unfortunately, repeated attempts to crystallize **1c** and **1d** resulted only in the precipitation of amorphous solids. Gratifyingly, vapour diffusion of diethyl ether into an acetonitrile solution of **1b** provided X-ray quality crystals. Complex **1b** crystallizes in the monoclinic space group *P*2₁/*c*. The structure shows the formation of **1b** in which each silver(I) ion is connected to two different **L**² units and leading to a linear geometry (Figure 2). The Ag^I–N bond lengths lie in the range of 2.117–2.127 Å, and the N1–Ag1–N2 angle is 171.57° to afford a zigzag chain. Interestingly, compared to

1a, the structure showed no Ag⁺...Ag⁺ interactions resulting in a different packing arrangement of the infinite chains. Indeed, **1b** displays a π - π interaction between the central phenylene ring and the pyridine ring of two adjacent chains with an interplane distance of 3.511 Å, with $a_1 = 19.71^\circ$ and $a_2 = 18.04^\circ$ (the two aromatic rings are not exactly parallel $\alpha = 5.2^\circ$). This weak interaction is observed throughout the infinite chain. A comparison of **1a** and **1b** allows us to attribute their structural differences as a function of the nature of the counteranion (Scheme 4). Using the same reaction conditions, **L**² gives different motifs of chain stacking. The presence or absence of Ag^I...anion interactions may play a pivotal role and define the overall packing arrangement. Due to the coordination of the anion to the metal centre, the effective positive charge at each Ag^I ion is reduced and allows the cations to approach each other more closely and consequently to form Ag⁺...Ag⁺ interactions. Conversely, when the anion is not coordinated to the metal as in **1b**, the Ag^I...Ag^I distance between two chains is longer. Although solid state X-ray structures could not be obtained for **1c** and **1d** so far, we feel that they might have similar packing as those observed for **1a** and **1b**, respectively. We speculate that the PF₆[−] anion should exhibit a similar effect to BF₄[−] anion, whereas NO₃[−], a more coordinating anion, may provide a similar packing to that observed with the triflate anion. Moreover, we note that silver coordination polymers in which the coordination of the anion to the metal influences the packing have been previously reported.^[52]

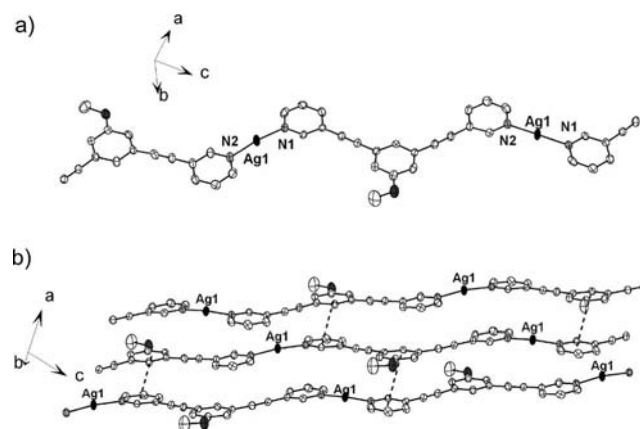
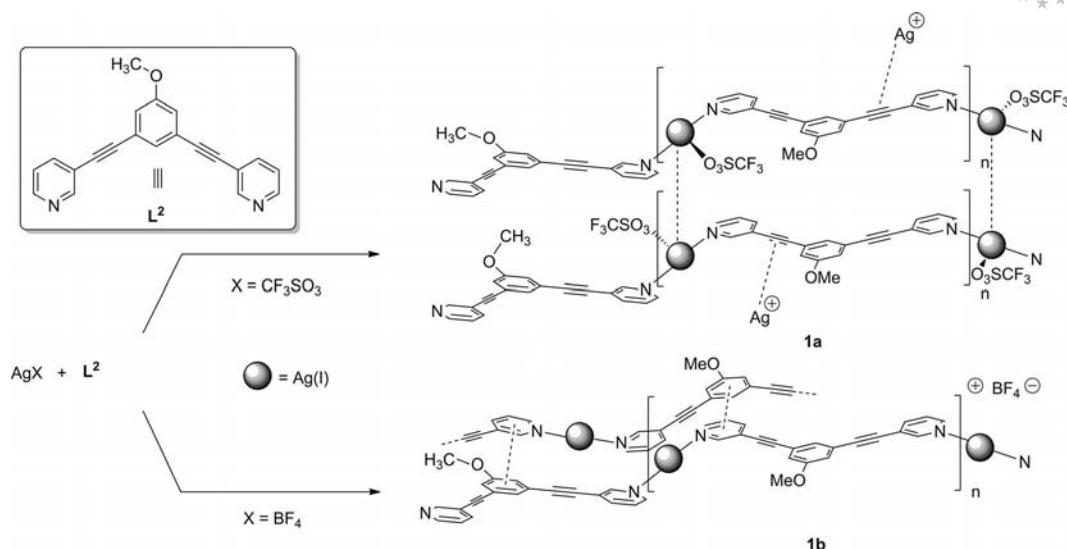


Figure 2. X-ray crystal structure of **1b**. a) View of the cationic chain b) π - π interactions between two adjacent 1D coordination polymers. (C white, O dark grey, N grey, Ag black; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–N1 2.117, Ag1–N2 2.121, N1–Ag1–N2 171.6.

It should be emphasized that we have previously reported the influence of various anions on the self-assembly of supramolecular structures with **L**¹ and with silver(I) salts.^[35] Our results show that CF₃SO₃[−] anions are more coordinating than BF₄[−] anions and more recently we have demonstrated that they undergo anion- π interactions with neutral organometallic metal-arene complexes.^[53]



Scheme 4. Schematic representation of the preparation of coordination silver(I) chain polymers **1a** and **1b**.

Conclusions

5-Methoxy-1,3-bis(pyridin-3-ylethynyl)benzene (**L**²) has been synthesized as a bidentate self-assembling ligand and its coordination properties toward silver salts, AgX (X = CF₃SO₃, BF₄, NO₃, PF₆), were investigated. The resulting architectures were identified and characterized as 1D coordination polymers [AgL²X]_n (**1a**, X = CF₃SO₃; **1b**, X = BF₄; **1c**, X = NO₃; **1d**, X = PF₆) by comparing their spectroscopic data and elemental analyses. In particular, the single-crystal X-ray structures of **1a** and **1b** were determined. This work illustrates the influence of the anion in determining the final packing arrangement of the polymers: with coordinating triflate anions Ag⁺⋯Ag interactions provide a layered structure of double chains, whereas with BF₄[−], a 2D network of 1D coordination polymers held together by π–π interactions is created. Efforts to construct new discrete 3D supramolecular nanocapsules with **L**² involving other metals are currently underway.

Experimental Section

General Methods: All solvents used were reagent grade or better. Commercially available reagents were used as received. All experimental manipulations were carried out under argon using Schlenk techniques. IR spectra were recorded with a Bruker Tensor 27 equipped with a Harrick ATR. Elemental analyses were performed at the Microanalytical Laboratory of the Université Pierre et Marie Curie Paris-6. NMR experiments were carried out with a Bruker Avance 300 MHz spectrometer operating at 300 K with chemical shifts referenced to residual solvent peaks. Chemical shifts are reported on parts per million (ppm) and coupling constants (*J*) in Hertz (Hz).

5-Methoxy-1,3-bis(pyridin-3-ylethynyl)benzene (L**²):** To an oven dried two neck round-bottomed flask equipped with a magnetic stirrer was added [Pd(PPh₃)₄] (112 mg, 0.097 mmol, 0.1 equiv.), which was solubilized in argon-degassed Et₃N (45 mL) freshly distilled with CaH₂. The red solution was heated to 80 °C. 3,5-Dibromoanisole (516.1 mg, 1.94 mmol, 1 equiv.), 3-ethynylpyridine

(600 mg, 5.83 mmol, 3 equiv.) and CuI (36.9 mg, 0.194 mmol, 0.2 equiv.) were successively added to the reactor. The reaction mixture was maintained under argon with stirring for 20 h at 80 °C. The solvent was removed under vacuum and the residue was chromatographed twice on silica gel (AcOEt/hexane, 50:50) to afford **L**² as a white solid; yield 79%. M.p. 104 °C. IR (ATR): $\tilde{\nu}$ = 2210, 1731, 1582, 1561, 1477, 1417, 1362, 1254, 1228, 1184, 1140, 1053, 1021, 854, 799, 700 cm^{−1}. ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.75 (d, *J* = 1.5 Hz, 2 H, py-H), 8.56 (dd, *J* = 4.8, 1.5 Hz, 2 H, py-H), 7.89 (dt, *J* = 8.1, 2.1 Hz, 2 H, py-H), 7.38 (ddd, *J* = 8.1, 5.0, 0.9 Hz, 2 H, py-H), 7.34 (t, *J* = 1.5 Hz, 1 H, Ar-H), 7.17 (d, *J* = 1.5 Hz, 1 H, Ar-H), 3.85 (s, 3 H, OMe) ppm. C₂₁H₁₄N₂O (310.35): calcd. C 81.27, H 4.55, N 9.03; found C 81.35, H 4.52, N 7.53.

[Ag(L²(CF₃SO₃))]_n (1a**):** **L**² (50 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) was added to a solution of AgOTf (40 mg, 0.16 mmol) in CH₃CN (5 mL). The solution was stirred in the dark at room temperature for 4 h, during which time a white precipitate formed. The solid was isolated by filtration, washed with CH₂Cl₂ and diethyl ether and dried under vacuum; yield 95% (91 mg, 0.152 mmol). IR (ATR): $\tilde{\nu}$ = 1282 [ν(C–F)] cm^{−1}. ES-MS (CH₃CN): *m/z* 566.8 [HAgL²CF₃SO₃]⁺ (calcd. 567), 674.9 [Ag₂L²CF₃SO₃]⁺ (calcd. 674.9), 984.6 [Ag₂(L²)₂CF₃SO₃]⁺ (calcd. 985.0), 1240.5 [Ag₃(L²)₂(CF₃SO₃)₂]⁺ (calcd. 1242.8). ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.74 (d, *J* = 1.5 Hz, 2 H, py-H), 8.56 (dd, *J* = 4.8, 1.5 Hz, 2 H, py-H), 7.91 (dt, *J* = 8.1, 2.1 Hz, 2 H, py-H), 7.41 (ddd, *J* = 8.1, 5.0, 0.9 Hz, 2 H, py-H), 7.35 (t, *J* = 1.5 Hz, 1 H, Ar-H), 7.18 (d, *J* = 1.5 Hz, 1 H, Ar-H), 3.85 (s, 3 H, OMe) ppm. [Ag(L²(CF₃SO₃))·0.3Et₂O (589.5): calcd. C 47.27, H 2.91, N 4.75; found C 48.03, H 2.69, N 4.64. X-ray quality crystals were obtained by slow vapour diffusion of diethyl ether into an acetonitrile solution of **1a**.

[AgL²](BF₄)_n (1b**):** **1b** was prepared in a similar way to **1a** using **L**² (50 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) and AgBF₄ (31 mg, 0.16 mmol) in CH₃CN (5 mL); yield 92% (86 mg, 0.147 mmol). IR (ATR): $\tilde{\nu}$ = 1048 [ν(B–F)]. ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.74 (d, *J* = 1.5 Hz, 2 H, py-H), 8.56 (dd, *J* = 4.8, 1.5 Hz, 2 H, py-H), 7.92 (dt, *J* = 8.1, 2.1 Hz, 2 H, py-H), 7.41 (ddd, *J* = 8.1, 5.0, 0.9 Hz, 2 H, py-H), 7.35 (t, *J* = 1.5 Hz, 1 H, Ar-H), 7.18 (d, *J* = 1.5 Hz, 1 H, Ar-H), 3.86 (s, 3 H, OMe) ppm. [AgL²](BF₄)·0.8CH₂Cl₂ (572): calcd. C 45.70, H 2.74, N 4.89; found C 45.77, H

2.92, N 4.39. X-ray quality crystals were obtained by slow vapour diffusion of diethyl ether into an acetonitrile solution of **1b**.

[AgL²NO₃]_n (1c): **1c** was prepared in a similar way to **1a** using **L²** (50 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) and AgNO₃ (27 mg, 0.16 mmol) in CH₃CN (5 mL); yield 79% (65 mg, 0.126 mmol). IR (ATR): $\tilde{\nu}$ = 1302 [ν(N–O)]. ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.73 (d, *J* = 1.5 Hz, 2 H, py-H), 8.56 (dd, *J* = 5.1, 1.5 Hz, 2 H, py-H), 7.89 (dt, *J* = 7.8, 2.1 Hz, 2 H, py-H), 7.41 (ddd, *J* = 8.1, 4.8, 0.9 Hz, 2 H, py-H), 7.35 (t, *J* = 1.2 Hz, 1 H, Ar-H), 7.17 (d, *J* = 1.2 Hz, 1 H, Ar-H), 3.85 (s, 3 H, OMe) ppm. [AgL²NO₃]·0.6CH₂Cl₂ (531): calcd. C 48.84, H 2.88, N 7.91; found C 47.57, H 2.78, N 7.87.

[AgL²PF₆]_n (1d): **1d** was prepared in a similar way to **1a** using **L²** (50 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) and AgPF₆ (40 mg, 0.16 mmol) in CH₃CN (5 mL); yield 90% (81 mg, 0.144 mmol). IR (ATR): $\tilde{\nu}$ = 756 [ν(P–F)]. ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.73 (d, *J* = 1.5 Hz, 2 H, py-H), 8.58 (dd, *J* = 4.8, 1.5 Hz, 2 H, py-H), 7.90 (dt, *J* = 7.8, 2.1 Hz, 2 H, py-H), 7.39 (ddd, *J* = 8.1, 4.8, 0.9 Hz, 2 H, py-H), 7.33 (t, *J* = 1.2 Hz, 1 H, Ar-H), 7.17 (d, *J* = 1.2 Hz, 1 H, Ar-H), 3.85 (s, 3 H, OMe) ppm. [AgL²PF₆]_n·1.5CH₂Cl₂ (690): calcd. C 39.13, H 2.48, N 4.06; found C 38.64, H 2.12, N 4.16.

Data Collection and Structure Refinement: A single crystal of **1a** or **1b** was selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo-K_α radiation. Unit-cell parameter determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs^[54]. Multi-scan absorption correction was applied^[55]. The structure was solved by direct methods using the SIR92 program^[56] and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package^[57].

Crystal Data for 1a: Yellow crystal, C₄₄H₂₈Ag₂N₄F₆O₈S₂, monoclinic, *P*₂₁/*c*, *a* = 8.3889(16), *b* = 18.5773(16), *c* = 29.144(6) Å, *a* = 90, *β* = 98.787(11), *γ* = 90°, *V* = 4488.6(13) Å³, *Z* = 4, *T* = 200(1) K, *μ* = 1.048 mm^{−1}, 48054 reflections measured, 13079 independent (*R*_{int} = 0.0756), 6132 observed [*I* ≥ 2σ(*I*)], 597 parameters, final *R* indices *R*₁ [*I* ≥ 2σ(*I*)] = 0.0474 and *wR*₂ (all data) = 0.1250, GOF(on *F*²) = 0.957, max/min residual electron density 0.832/−1.023 e Å^{−3}.

Crystal Data for 1b: Colourless crystal, C₂₁H₁₅AgN₂F₄BO_{1.5}, monoclinic, *P*₂₁/*c*, *a* = 10.7344(9), *b* = 17.4781(16), *c* = 11.1875(9) Å, *a* = 90, *β* = 103.965(6), *γ* = 90°, *V* = 2036.9(3) Å³, *Z* = 4, *T* = 200(1) K, *μ* = 1.043 mm^{−1}, 16116 reflections measured, 5738 independent (*R*_{int} = 0.0501), 3034 observed [*I* ≥ 2σ(*I*)], 272 parameters, final *R* indices *R*₁ [*I* ≥ 2σ(*I*)] = 0.0567 and *wR*₂ (all data) = 0.1643, GOF(on *F*²) = 1.043, max./min. residual electron density 0.860/−0.836 e Å^{−3}. The BF₄[−] anion and the water molecule are disordered over two positions. Both were refined isotropically to avoid meaningless anisotropic displacement parameters.

CCDC-826115 (for **1a**) and -826116 (for **1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We acknowledge the Université Pierre et Marie Curie Paris-6 and the Centre National de la Recherche Scientifique (CNRS) for supporting this work.

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Received: May 23, 2011

Published Online: August 31, 2011