Self-Assembly of 1-D Coordination Polymers Using Organometallic Linkers and Exhibiting Argentophilic Interactions $Ag^{I}\cdots Ag^{I}$

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Treatment of the organometallic linkers [Cp*M(η^4-benzoquinone)] [M = Rh, L^{Rh}, (**1a**); M = Ir, L^{Ir} (**1b**)] with excess AgOTf provided the novel 1-D coordination polymers of the formula $\{[Ag_3(L^M)_2(CH_3CN)_2(OTf)][L^M](OTf)_2\}_n$ (**2a**,**b**). Single-crystal X-ray diffraction studies carried out on **2a** and **2b** showed that these polymers exhibit, as an outstanding feature, the presence of $d^{10}\cdots d^{10}$ argentophilic interactions between the silver atoms.

The design and self-assembly of coordination frameworks exhibiting original architectures[1] and with potential applications as molecular wires,[2] in catalysis,[3] and ion encapsulation[4] offer exciting new prospects for researchers working in the area of material science.[5] Generally, coordination polymers are formed by self-assembly of organic spacers and transition metal ions of different geometrical structures.[6] In this work, we wish to report the 1-D coordination polymers $\{[Ag_3(L^M)_2(CH_3CN)_2(OTf)][L^M](OTf)_2\}_n$ (**2a**,**b**), based on silver coordination chemistry and using [Cp*M(η^4-benzoquinone)] [M = Rh, L^{Rh} (**1a**); M = Ir, L^{Ir} (**1b**)[7]] as organometallic linkers. Interestingly these coordination polymers **2a**,**b** display, as nodes, three silver ions in close proximity with Ag···Ag contacts of 3.3–3.7 Å (Figure 1).

Prior to this work the self-assembly of 1–3-D networks, was reported using the only known organometallic linker [(η^4-benzoquinone)Mn(CO)$_3$][Na].[8] However, none of these polymers contained silver cations. Thus, our 1-D polymers **2a**,**b** are the first coordination polymers with the neutral organometallic linkers [Cp*M(η^4-benzoquinone)] [M = Rh, L^{Rh} (**1a**); M = Ir, L^{Ir} (**1b**)] to be reported.[7] The current compounds differ completely in coordination and properties than those reported previously.

Treatment of [Cp*M(η^4-benzoquinone)] [M = Rh (**1a**); M = Ir (**1b**)] with excess $AgCF_3SO_3$ in CH_2Cl_2 provided a suspension, the solvent was removed under vacuum and the residue was recrystallized from CH_3CN/Et_2O to give golden crystals of **2a** and off-white crystals of **2b** in good yields (see Exp. Sect.). The spectroscopic data of **2a**,**b** are very similar. Thus, the IR spectra of **2a** and **2b** show the presence of two strong bands at 1266 and 1030 cm^{-1} and at 1267 and 1031 cm^{-1}, respectively, which are assigned to the triflate anions; furthermore, two absorptions are visible at 1593 and 1573 cm^{-1} for **2a** and at 1599 and 1580 cm^{-1} for **2b** which are attributed to the C=O groups of the coordinated benzoquinone. The ^{1}H NMR spectrum of **2a** recorded in [D$_6$]acetone shows the presence of two singlets at δ = 3.76 ppm assigned to the diene protons and at δ = 2.05 ppm attributed to the methyl protons of the (η^5-Cp*)Rh moiety, while **2b** shows the presence of a singlet at δ = 5.00 ppm for the diene protons and at δ = 2.06 ppm for the (η^5-Cp*)Ir moiety.

To ascertain the identity of these complexes **2a**,**b**, a single-crystal X-ray diffraction study was undertaken (Figure 2).[9] The structures of **2a** and **2b** show the formation of a 1-D coordination polymer. For example, **2b** consists of trimetallic silver nodes of formula $[Ag_3(L^{Ir})_2(CH_3CN)_2(OTf)]^{2+}$ which are linked through linear η^4-benzoquinone ligand L^{Ir} (**1b**). In this linear coordination polymer the trimetallic silver clusters constitute so-called secondary building units (SBUs) (Figure 1).[5] In each SBU, all silver atoms have tetrahedral configurations, the central silver atom Ag2, lies in a plane of symmetry, is coordinated to a triflate anion and to three quinone oxygen atoms while the other two silver atoms, which are symmetrically related, are linked to three quinone oxygen atoms and coordinated to CH_3CN (Figure 1). The Ag2···Ag1 distance between the central silver atom and the peripheral ones is 3.37 Å, indicative of an interatomic contact (sum of van der Waals radii of silver is 3.44 Å[10]), while the peripheral Ag1···Ag1 distance is 3.71 Å suggesting a weak interaction. Interestingly, the organometallic linker L^{Ir} adopts a boat conformation in **2b** with the quinone carbon atoms bent out of the diene plane while acting as a pentadentate ligand, and connecting five silver atoms such that one quinone oxygen atom is biden-

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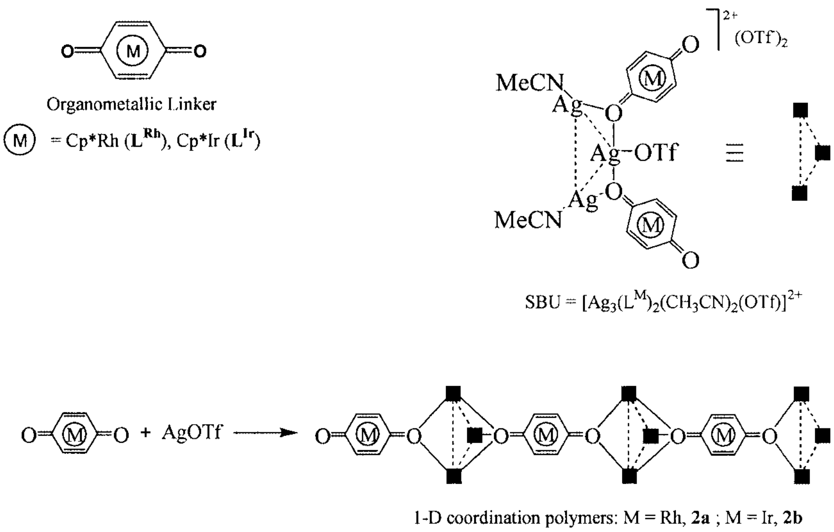

Figure 1. Self-assembly of 1-D polymers **2a**,**b** showing the secondary building units (SBUs) connected by the pentadentate organometallic linkers L^M; M = Rh (**1a**), Ir (**1b**).

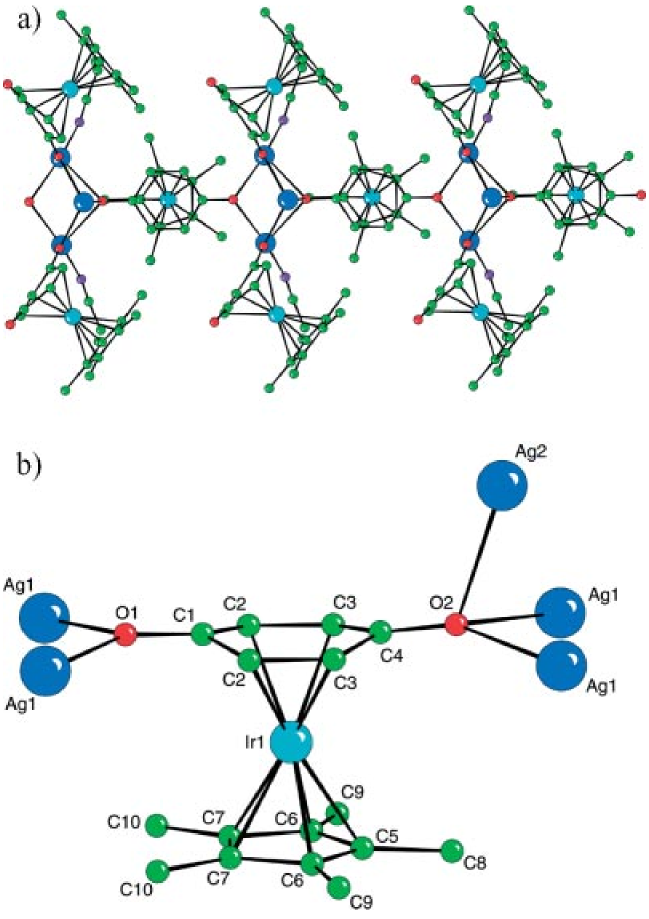

Figure 2. (a) X-ray structure of the 1-D polymer $\{[Ag_3(L^{Ir})_2(CH_3CN)_2(OTf)][L^{Ir}](OTf)_2\}_n$ (**2b**), the triflate anions are omitted for clarity. (b) View of the coordination environment of the pentadentate organometallic linker L^{Ir} in **2b**. Selected bond lengths [Å]: C1–O1 1.293(9), C4–O2 1.281(9), O1–Ag1 2.297(3), O2–Ag1 2.560(4), O2–Ag2 2.508(7), Ir1–C1 2.377(7), Ir1–C2 2.216(5), Ir1–C3 2.220(5), Ir1–C4 2.407(7).

tate (hinge angle θ = 11.85°) and the other one tridentate (hinge angle θ = 11.72°). Such coordination mode has not been reported before (Figure 2b).

Thus, each SBU is connected to the adjacent SBU via a bidentate quinone oxygen atom from one side and through a tridentate quinone oxygen atom from the opposite side, describing a unique architecture for the 1-D coordination polymers $\{[Ag_3(L^M)_2(CH_3CN)_2(OTf)][L^M](OTf)_2\}_n$ (**2a**,**b**).

Discrete trimetallic Ag^I complexes with $d^{10}\cdots d^{10}$ Ag···Ag interactions with luminescent properties continue to generate much interest.[11] The short metal–metal contacts found in these complexes are believed to play a dominant role in excited-state properties.[12] Thus, we intend in the near future to study the photophysical properties of our 1-D polymers **2a**,**b**.

In summary, we have reported a novel class of supramolecular coordination polymers with organometallic linkers exhibiting short argentophilic Ag···Ag interactions. These results illustrate successfully the role of the organometallic ligand linkers L^M (M = Rh, Ir) to produce a novel class of supramolecular species when combined with different metal ions of different geometries. The photoluminescence properties of our coordination polymers will be reported in due course.

Experimental Section

General: All experimental manipulations were carried out under argon using standard Schlenk tube techniques. ^1H NMR spectra were recorded with a Bruker AM 300 MHz. IR spectra were recorded as KBr discs with a bio-rad FT-IR spectrometer FTS 165. All solvents were distilled according standard procedures prior to use.

2a: To a suspension of AgOTf (51 mg, 0.2 mmol) in CH_2Cl_2 (15 mL) was added an orange solution of **1a** (35 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The suspension turned yellow immediately and a solid formed; this mixture was stirred at room temperature for 1 h and then the solvent was removed under vacuum, affording a yellow powder which was dried under vacuum and recrystallized by slow diffusion of diethyl ether into a CH_3CN solution to give golden crystals (yield 36 mg, 55%). This compound was identified as $\{[Ag_3(L^{Rh})_2(CH_3CN)_2(OTf)][L^{Rh}](OTf)_2\}_n$. ^1H NMR [300 MHz, $(CD_3)_2CO$]: δ = 2.05 (s, 15 H, Cp*), 3.76 (s, 4 H, benzoquinone) ppm. IR (KBr disc): $\tilde{\nu}$ = 1593, 1572 [ν(C=O)]; 1266 [ν(S–O)]; 1030 [ν(C–F)] cm^{-1}.

2b: To a suspension of AgOTf (80 mg, 0.3 mmol) in CH_2Cl_2 (15 mL) was added a pale yellow solution of **1b** (47 mg, 0.1 mmol). The suspension turned light brown immediately and a solid formed; this mixture was stirred at room temperature for 16 h and then the solvent was removed under vacuum, providing a brown powder which was dried under vacuum and recrystallized by slow diffusion of diethyl ether into a CH_3CN solution to give off-white crystals (yield 45 mg, 60%). This compound was identified as $\{[Ag_3(L^{Ir})_2(CH_3CN)_2(OTf)][L^{Ir}](OTf)_2\}_n$. ^1H NMR (300 MHz, CD_3CN): δ = 2.06 (s, 15 H, Cp*), 5.00 (s, 4 H, benzoquinone) ppm. IR (KBr disc): $\tilde{\nu}$ = 1593, 1572 [ν(C=O)]; 1267 [ν(S–O)]; 1031 [ν(C–F)] cm^{-1}.

Supporting Information: Figures of the coordination polymer **2a**.

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[9] Crystal data: **2a**: $C_{48}H_{57}Ag_3O_6Rh_3\cdot(CF_3O_3S)_3\cdot 2(C_2H_3N)$, orthorhombic, *Cmc*2₁, a = 31.820(3), b = 8.5459(8), c = 23.658(2) Å, V = 6433.3(10) Å^3, Z = 4, T = 250(2) K, μ = 1.835 mm^{-1}, 18201 reflections measured, 7303 independent (R_{int} = 0.0761), 4555 observed [$I > 2\sigma(I)$], 425 parameters, final R indices R_1 [$I > 2\sigma(I)$] = 0.0649 and wR_2 (all data) = 0.1435, Flack parameter η = –0.03(6), GOF on F^2 = 0.946, max./min. residual electron density = 1.31/–1.57 e·Å^{-3}. **2b**: $C_{48}H_{57}Ag_3O_6Ir_3\cdot(CF_3O_3S)_3\cdot 2(C_2H_3N)$, orthorhombic, $Cmc2_1$, a = 31.934(3), b = 8.6198(7), c = 23.842(2) Å, V = 6562.9(10) Å^3, Z = 4, T = 250(2) K, μ = 7.121 mm^{-1}, 30911 reflections measured, 9476 independent (R_{int} = 0.0421), 8048 observed [$I > 2\sigma(I)$], 434 parameters, final R indices R_1 [$I > 2\sigma(I)$] = 0.0318 and wR_2 (all data) = 0.0676, Flack parameter η = 0.078(6), GOF on F^2 = 1.007, max./min. residual electron density = 1.09/–1.57 e·Å^{-3}. A single crystal of the moisture-sensitive compounds **2a** or **2b** was rapidly 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 parameters determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220). The structures were solved by direct methods using the SHELXS-86 program (G. M. Sheldrick, University of Göttingen, **1986**) and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, **1997**). CCDC-270623 (**2a**) and -270630 (**2b**) 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.

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