# Tuning the 1D-2D dimensionality upon ligand exchange in silver

## thiolate coordination polymers with photoemission switch

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#### Characterization techniques.

**Routine PXRD.** Routine powder X-Ray diffraction (PXRD) was carried out on a Bruker D8 Advance A25 diffractometer using Cu K $\alpha$  radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). X-Ray scattering was recorded between 4° and 90° ( $2\vartheta$ ) with 0.02° steps and 0.5 s per step (28 min for the scan). Divergence slit was fixed to 0.2° and the detector aperture to 189 channels (2.9°).

Synchrotron Powder diffraction. The patterns of [Ag(*p*-SPhF)]<sub>n</sub> (1) and [Ag(*p*-SPhCl)]<sub>n</sub> (2), collected at the Synchrotron Soleil facility (Gif-Sur-Yvette, France) at the CRISTAL beamline, served to index and solve their crystal structures. Each compound was introduced in a glass capillary with a diameter of 0,7 mm and mounted on goniometer head. Data were collected using a monochromatic wavelength ( $\lambda = 0.72844$  Å for 1 and  $\lambda = 0.67122$  Å for 2) at room temperature using the MYTHEN 2 Detector in about 5 minutes. In both cases, the instrumental function was extracted using LaB<sub>6</sub>. The indexation of the powder patterns was performed using the X-cell algorithm implemented in the Reflex program<sup>1</sup> of the Materials Studio software (BIOVIA). The structure solution of the structures was found using the FOX program<sup>2</sup> by introducing a silver free atom and the thiolate molecule under the form of a Z-matrix. The final Refinement using the Rietveld method was performed by the Fullprof\_suite package (Fig. S3 and S4).<sup>3</sup> Table S1 gathers the crystal data and structure refinement parameters for 1 and 2. CCDC-2245604 and CCDC-2245602 contain the supplementary crystallographic data of [Ag(*p*-SPhF)]<sub>n</sub> (1) and [Ag(*p*-SPhCl)]<sub>n</sub> (2), respectively.

**FT-IR spectroscopy.** The Fourier Transform Infrared (FT-IR) spectra were obtained from a Bruker Vector 22 FT-IR spectrometer with KBr pellets at room temperature and registered from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. **Computational details.** The calculations have been conducted using density functional theory (DFT) as implemented in the VASP (Vienna Ab initio Simulation Package).<sup>4</sup> For the exchange-correlation functional, the Perdew, Burke and Ernzerhof (PBE)<sup>5</sup> formulation of the generalized gradient approximation (GGA) was used, together with an energy cut-off of 500 eV for the plane wave basis set and a centered k-mesh with a grid step of 0.25 Å<sup>-1</sup>. The total energy was converged until the total energy difference between two electronic steps became smaller than 10-7 eV. The crystal cell parameters were contrained to the corresponding experimental value, but the atoms were allowed to relax freely until forces became smaller than 5.0 x  $10^{-3}$  eV.Å<sup>-1</sup>. The vibration frequencies and the corresponding intensities were obtained by density-functional perturbation theory (DFPT), as implemented in VASP. The electronic band gap has been calculated by using the HSE06 hybrid functional.

**TGA.** Thermo-gravimetric analyses (TGA) were performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 2 mg of sample was heated at a rate of 10 °C.min<sup>-1</sup>, in a 70  $\mu$ L alumina crucible, under air atmosphere (20 mL.min<sup>-1</sup>). The final residue was characterized as bulk silver.

**Elemental analysis.** C, H, S and O elemental analyses have been carried out with a FlashEA 1112 analyzer from Thermo Scientific.

**UV-vis.** UV-visible absorption spectra were carried out with a LAMBDA 365 UV/Vis Spectrophotometer from Perkin Elmer in solid state with KBr at room temperature.

**SEM.** Scanning Electron Microscopy (SEM) images were obtained with FEI Quanta 250 FEG scanning electron microscope. Samples were mounted on stainless pads and sputtered with carbon to prevent charging during the observation.

Photoemission spectra measurements. Measurements of solid state emission of 1 and 2 with the temperature from 20 to -180°C were performed on a homemade apparatus at Institut Lumière Matière, University of Lyon. The sample was illuminated by an EQ99X laser driven light source filtered by a Jobin Yvon Gemini 180 monochromator. The exit slit from the monochromator was then reimaged on the sample by two 100m focal length, 2 inch diameter MgF2 lenses. The whole apparatus has been calibrated by means of a Newport 918D Low power calibrated photodiode sensor over the range 190-1000 nm. The emitted light from the sample is collected by an optical fiber connected to a Jobin-Yvon TRIAX320 monochromator different long pass filter can be chosen in order to eliminate the excitation light. The resolution of the detection system is 2 nm. Temperature control over the sample was regulated with a THMS-600 heating stage with T95-PE temperature controller from Linkam Scientific Instruments.

RT emission of  $[Ag(o-SPhCO_2Me)]_n$  was measured with the FS5 Spectrofluorometer from Edinburgh Instruments and using the solid state SC-10 sample holder.

SHG signal. The Second Harmonic Generation (SHG) signals were detected with a Ti:Sa laser from Spectra Physics (Hurricane model) delivering pulse of 100 fs at 800 nm (1 kHz). The SHG was collected at 400 nm with a streak camera C7700 from Hamamatsu coupled with a spectrometer from Princeton instrument. Potassium dihydrogenphosphate (KDP) as a pellet is first measured as a reference. Then one experiment is done on the powder of [Ag (*p*-SPhCl)]<sub>n</sub> (**2**) in the same conditions as KDP and with more gain to enhance the detected signal.

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#### Syntheses of the coordination polymers

**Chemicals and materials.** Silver nitrate (AgNO3,  $\geq$  99.0 %) was purchased from Alfa Aesar. 4-Fluorothiophenol (*p*-HSPhF, 98 %), 4-Chlorothiophenol (*p*-HSPhCl, 97 %) and Methyl thiosalicylate (*o*-HSPhCO<sub>2</sub>Me, 97%) were purchased from Sigma Aldrich. Ethanol, Methanol and DMF were purchased from VWR Chemicals. All reagents and solvents were used as received.

Synthesis of [Ag (*p*-SPhF)]  $_{n}$  (1): AgNO<sub>3</sub> (100 mg, 0.59 mmol, 1 eq.) was dissolved in 10 ml of water in a 20 ml glass vial. Then, 4-Fluorothiophenol (75 mg, 62.3 µL, 0.59 mmol, 1 eq) was introduced to the solution. The vial is sealed and the reaction was let to proceed for 2 h at RT. White precipitate was obtained and washed with 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 63 % (87 mg). Chemical Formula: AgSC<sub>6</sub>H<sub>4</sub>F. Molecular Weight: 235.03 g.mol<sup>-1</sup>. Silver content from TGA (calc.) in wt%: 46.70 (45.90). Elemental analysis: exp. (calc.) %: C, 31.34 (30.66); H, 1.76 (1.72); S, 15.16 (13.64).

Synthesis of [Ag (*p*-SPhCl)] <sub>n</sub> (2): a solution of 4-Chlorothiophenol (85.3mg, 0.59 mmol, 1eq) in MeOH (5ml) was added to AgNO<sub>3</sub> (100 mg, 0.59 mmol, 1 eq) dissolved in H<sub>2</sub>O (5 mL). The reaction was let to proceed for 2 h at RT in a 20 ml sealed vial. White precipitate was obtained and washed with 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 75 % (110 mg). Chemical Formula: AgSC<sub>6</sub>H<sub>4</sub>Cl. Molecular Weight: 251.48 g.mol<sup>-1</sup>. Silver content from TGA (calc.) wt%: 42.11 (42.8). Elemental analysis: exp. (calc.) %: C, 29.44 (28.66); H, 1.57 (1.60); S, 14.02 (12.75).

Chemical, grinding and calcination stability tests.

Stability tests of 1:

In a reducing medium: 20 mg of 1 were dispersed without stirring in 2 ml solution of  $LiBH_4$  in THF (2 M) in a 20 ml vial, at RT for 0.5 h.

In an oxidant medium: 20 mg of 1 were dispersed without stirring in 2 ml solution of  $H_2O_2$  in water (0.01 M) in a 20 ml vial, at RT for 48 h.

In an acidic medium: 20 mg of 1 were dispersed without stirring in 2 ml solution of  $H_2SO_4$  (1 M) in a 20 ml vial and heated at 120°C for 24 h.

In an aqueous medium: 20 mg of  ${\bf 1}$  were dispersed without stirring in 2 ml solution of  $H_2O$  in

a 20 ml vial and heated at 120°C for 24 h.

In a basic medium: 20 mg of 1 were dispersed without stirring in 2 ml solution of NaOH (1 M) in a 20 ml vial and heated at 120°C for 24 h.

Grinding: 20 mg of 1 were manually ground in a mortar for 0.5 h.

Calcination: 20 mg of 1 were heated in an oven under air at 200°C for 1 h.

### Stability tests of 2:

In a reducing medium: 20 mg of 2 were dispersed without stirring in 2 ml solution of LiBH4 in THF (2 M) in a 20 ml vial, at RT for 0.5 h.

In an oxidant medium: 20 mg of **2** were dispersed without stirring in 2 ml solution of  $H_2O_2$  in water (0.01 M) in a 20 ml vial, at RT for 48 h.

In an acidic medium: 20 mg of **2** were dispersed without stirring in 2 ml solution of  $H_2SO_4$  (1 M) in a 20 ml vial, and heated at 120°C for 24 h.

In an aqueous medium: 20 mg of **2** were dispersed without stirring in 2 ml solution of  $H_2O$  in a 20 ml vial, and heated at 120°C for 24 h.

In a basic medium: 20 mg of 2 were dispersed without stirring in 2 ml solution of NaOH (1 M) in a 20 ml vial, and heated at 120°C for 24 h.

Grinding: 20 mg of 2 were manually ground in a mortar for 0.5 h.

### **Exchange reactions.**

Synthesis of  $[Ag(o-SPhCO_2Me)]_n 3'_{(1)}$ :  $[Ag (p-SPhF)]_n (1) (100 mg, 0.425 mmol, 1 eq.)$ was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, methyl thiosalicylate (2337 µL, 17 mmol, 40 eq) was added to the solution. The reaction was let to proceed for 18 h at 120°C. A mixture of yellow and white precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air.

Synthesis of  $[Ag(o-SPhCO_2Me)]_n 3_{(1)}$  from  $3'_{(1)}$  : 40 mg of  $3'_{(1)}$  was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, Methyl thiosalicylate 1170 µL was added to the solution. The reaction was let to proceed for 18 h at 120°C. Yellow precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Chemical Formula: AgSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>3</sub>. Molecular Weight: 275.07. Silver content from TGA (calc.) wt%: 40.6 (39.2). Elemental analysis: exp. (calc.) %: C, 33.78 (34.93); H, 1.22 (2.57); S, 11.38 (11.66); O, 14.79 (11.63).

Synthesis of  $[Ag(o-SPhCO_2Me)]_n 3_{(1)}$  from 1:  $[Ag (p-SPhF)]_n (1)$  (50 mg, 0.212 mmol, 1 eq.) was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, Methyl thiosalicylate (2337µL, 17 mmol, 80 eq) was added to the solution. The reaction was let to proceed for 48 h at 120°C. Yellow precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 68 % (40 mg). Synthesis of  $[Ag(o-SPhCO_2Me)]_n 3_{(2)}$  from 2:  $[Ag(p-SPhCI)]_n (2)$  (50 mg, 0.199 mmol, 1 eq.) was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, methyl thiosalicylate (2500 µL, 18 mmol, 90 eq) was added to the solution. The reaction was let to proceed for 48 h at 120°C. Yellow precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 33 % (18 mg). Chemical Formula: AgSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>3</sub>. Molecular Weight: 275.07. Silver content from TGA (calc.) wt%: 40 (39.2). Elemental analysis: exp. (calc.) %: C, 34.26 (34.93); H, 2.40 (2.57); S, 12.05 (11.66); O, 11.98 (11.63).

Synthesis of  $[Ag(p-SPhF)]_n 1'_{(3)}$  from  $3_{(1)}$ :  $[Ag(o-SPhCO_2Me)]_n 3_{(1)}$  (50 mg, 0.18 mmol, 1 eq.) was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, *p*-HSPhF (1500 µL, 14.4 mmol, 80 eq) was added to the solution. The reaction was let to proceed for 5 min at 120°C. White precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 40 % (17 mg).

Synthesis of  $[Ag(p-SPhF)]_n \mathbf{1}_{(3)}$  from  $\mathbf{3}_{(1)}$ :  $[Ag (o-SPhCO_2Me)]_n \mathbf{3}_{(1)}$  (50 mg, 0.18 mmol, 1 eq.) was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, *p*-HSPhF (1500 µL, 14.4 mmol, 80 eq) was added to the solution. The reaction was let to proceed for 48 h at 120°C. White precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 47 % (20 mg).

Synthesis of  $[Ag(p-SPhCl)]_n 2_{(3)}$  from  $3_{(2)}$ :  $[Ag(o-SPhCO_2Me)]_n 3_{(2)}$  (38 mg, 0.14 mmol, 1 eq.) was dispersed in 10 ml of methanol in a 20 ml sealed vial. Then, *p*-HSPhCl (1619 mg, 11.2 mmol, 80 eq) was added to the solution. The reaction was let to proceed for 1 h at 120°C. White precipitate was obtained and washed by 20 mL of ethanol for 3 times. The powder was collected by centrifugation at 10000 rpm. The product was dried in air. Yield: 14 % (5 mg).

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Figure S1. SEM images of 1 (a.) and 2 (b.).



Figure S2. TGA curves of 1 and 2 carried out in air at 10°C/min.



Figure S3. Final Rietveld plot of 1 showing observed (red crosses), calculated (black line), and

difference (blue line) data ( $\lambda$  = 0.72844 Å ). A zoom is shown as inset.



**Figure S4.** Final Rietveld plot of **2** showing observed (red crosses), calculated (black line), and difference (blue line) data ( $\lambda = 0.67122$  Å). A zoom is shown as inset.

1	2
Ag (SC <sub>6</sub> H <sub>4</sub> F)	Ag (SC <sub>6</sub> H <sub>4</sub> Cl)
235.03	251.48
monoclinic	orthorhombic
P21/n	Iba2
4.6917(1)	32.5519(12)
29.3556(6)	7.3734(2)
4.6950(1)	5.8211(1)
100.5301(14)	
635.74(3)	1397.16(7)
4	8
0.72844	0.67122
0.05, 0.08	0.03, 0.05
0.09	0.05
	1 Ag (SC <sub>6</sub> H <sub>4</sub> F) 235.03 monoclinic $P2_1/n$ 4.6917(1) 29.3556(6) 4.6950(1) 100.5301(14) 635.74(3) 4 0.72844 0.05, 0.08 0.09

**Table S1.** Crystallographic data and Rietveld refinement parameters for 1 and 2.

	1	2
Ag-S (Å)	2.56(3)	2.296(9)
	2.59(3)	2.399(9)
	2.64(2)	2.722(11)
	2.68(2)	3.092(1)
Ag-Ag (Å)	3.00 (1)	2.932(13)
Ag-S-Ag (°)	70.0(9)	
	70.2(9)	69.5(5)
	86.6(10)	103.8(3)
	88.2(10)	123.7(5)
	124.2(11)	
	131.4(12)	
S-Ag-S (°)	92.5(11)	92 7(5)
	92.7(11)	52.7(5)
	108.7(13)	119.0(6)
	111.0(14)	131.0(6)
	124.2(15)	
	131.4(16)	
1	1	

Table S2. Selected bonds and angles of 1 and 2.



Figure S5. Types of Halogen…Halogen (X<sub>2</sub>) interactions.

	<b>1</b> (Hal = F)	<b>2</b> (Hal = Cl)
HalHal (Å)	2.965(2)	3.790(9)
HalC (Å)	3.391(5)	5.915(5)
HalH (Å)	2.647(5)	5.363(4)
C-HalHal (°)	109.55(7)	155.5(2), 104.1(1)

Table S3. Distances and angles involving the Halogen atoms in 1 and 2.



Figure S6. SHG signal of [Ag(p-SPhCl)]  $_n$  (2),  $\lambda_{exc}$  = 800 nm.



Figure S7. Experimental and calculated FT-IR of 1 and 2.



Figure S8. Solid state UV-vis absorption spectra in wavelength (left) and the Tauc plots (right)





**Figure S9**. Emission spectra of **1** (left) and **2** (right) from RT to -180°C ( $\lambda_{ex}$  = 246 nm). The large and low intensity bands at 390 nm may originate from intra-ligand charge transfer or from external impurities or defects from the window used in the support.



**Figure S10.** PXRD patterns of **2** treated in acidic, basic, aqueous, oxidant and reducing media and under mechanical conditions. The black star is for bulk silver.



Figure S11. PXRD patterns of products obtained after exchange reactions from 2.



Figure S12. FT-IR spectra of 3(1) and 3(2).



**Figure S13.** TGA curves of  $\mathbf{3}_{(1)}$  and  $\mathbf{3}_{(2)}$  carried out in air at 10°C/min. The experimental values of remaining Ag are 40.6 and 40.0 %, respectively, corresponding to the expected theoretical value (39.2 %).



**Figure S14.** Solid state excitation and emission ( $\lambda_{ex}$  = 320 nm) spectra at RT of **3** obtained by direct synthesis and **3**<sub>(1)</sub> and **3**<sub>(2)</sub> obtained by exchange reactions.



**Figure S15.** Exchange reaction from  $3_{(2)}$  with an excess of *p*-HSPhCl to afford  $2_{(3)}$ .

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