Electronic Supporting Information for:

Luminescent double helical gold(I)-thiophenolate coordination polymer obtained by hydrothermal synthesis or by thermal solid-state amorphous-to-crystalline isomerization

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Figure S1. PXRD patterns of $[Au(SPh)]_n$ coordination polymers synthesized in hydrothermal conditions at 150 °C **1a** (black) and 120 °C **1b** (red) for 18 h.



Figure S2. View of the double helices of $[Au(SPh)]_n$ coordination polymer along the *b* axis. Red dot bonds correspond to the shortest gold-gold interactions with a length of 3.331(3) Å and the blue Au-Au interactions are of 3.369(3) Å. Hydrogen atoms have been omitted for clarity.



Figure S3. View of the double helices of $[Au(SPh)]_n$ coordination polymer along the *b* axis. Red and blue dot bonds correspond to the C-H··· π interactions of 3.221(1) and 3.763(1) Å and C-H··· π angles of 107.62(2) and 92.62(2) °, respectively. Black speheres represent the centroid of phenyl groups.



Figure S4. View of the packing of the double helices in [Au(SPh)]_n coordination polymer along the b axis. Pink, yellow and grey spheres are gold, sulfur and carbon atoms, respectively. Hydrogen atoms have been omitted for clarity



Figure S5. TGA carried out under air at 10 °C/min of 1a (black) and 1b (red).



Figure S6. Infra-red spectrum of [Au(SPh)]_n compound (1b).



Figure S7. 3D map of the excitation and emission spectra of **1b** carried out at room temperature and in the solid-state.



Figure S8. $[Au_6(SPh)_8]^{2-}$ fragments from the experimental structure (left) and from theoretical model (right).

Table S1. Au-Au distances	† (Å) f	from the e	experimental	structure	and	from	theoretical	model
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	1-2	1-3	1-4	1-5	1-6	2-3	2-4	2-5	2-6	3-4	3-5	3-6	4-5	4-6	5-6
Exp.	3.32	5.66	4.53	3.60	3.37	3.60	3.33	4.03	3.60	3.37	3.33	4.53	3.60	5.66	3.32
Theo.	3.66	6.13	5.27	3.38	3.16	3.66	3.31	3.33	3.38	3.39	3.31	5.27	3.66	6.13	3.66

⁺ See figure S7 for gold atoms assignments.



Figure S9. Calculated $[Au_6(SPh)_8]^{2-}$ fragment showing the Au-Au and C-H… π distances.



Figure S10. Powder X-ray diffraction of compound 2.



Figure S11. TGA and DTA of compound **2** carried out at 10 °C/min under air (red) and nitrogen (black).



Figure S12. Infra-red spectra of 2 (grey) and compound 2 heated at 230 °C at 2 °C/min for 1s (black).



Figure S13. XPS survey scan of compound 2.



Figure S14. XPS analysis of compound 2 from Au4f binding energy.



Figure S15. XPS analysis of compound 2 from S2p binding energy.



Figure S16. XPS analysis of compound 2 from C1s binding energy.



Figure S17. Absorption spectra of **1b** (grey) and **2** (black) coordination polymers. Experiments carried out at room temperature and in the solid-state.



Figure S18. SEM picture of compound 2 heated at 230 °C at 2 °C/min for 1s.



Figure S19. Powder X-Ray diffraction of compound **2** (black) as the starting material and after been heated at 5 °C/min up to 214 °C (blue) and at 216°C (red), which corresponds to the maximum and the end of the first cristallization peak in the DSC experiment, respectively. The grey PXRD pattern is from compound **1b**. The stars correspond to the reflections of bulk gold present as impurities.



Figure S20. Arrhenius plot from the maximum peak position of the crystallization of compound **2** followed by DSC experiments.

According to the Arrhenius behavior, the heating rate can be given by:

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right)$$

Where k is the effective heating rate (K/min), A is a constant (K/min), E_a is the activation energy (J/mol), R is ideal gas constant (8.31446 J/K/mol) and T is the absolute temperature (K). E_a is determined from the slope of the graph, which is plotted ln k = f(1/T).



Figure S21. Emission spectra (λ_{ex} = 340 nm) at room temperature and in the solid-state of thermally induced solid-state crystallization of [Au(SPh)]_n compounds.



Figure S22. Luminescence lifetime of calcined **2** at [210-2-1] after excitation at 379 nm (black) in the solid-state and room temperature. The luminescence decay was fitted to tetraexponential decay (red).



Figure S23. Emission spectra of luminescent $[Au(SPh)]_n$ compound measured at different temperatures from 213 °C to room temperature. Emission appears only from T < 100 °C due to a thermal quenching. Experiments are carried out in the solid-state with λ_{exc} = 340 nm.



Figure S24. Emission spectra starting from the amorphous compound **2** and heated at 200 °C at a heating rate of 10 °C/min and with different times. Experiments are carried out in the solid-state at 40 °C with λ_{exc} = 340 nm.

Luminescence quantum yield was estimated by comparing the sample $[Au(SPh)]_n$ to a porous silicon standard under the same geometrical conditions of complete excitation/emission mappings as described previously.¹ The intensity for the sample and the standard porous silicon sample in the region were they are in saturation of absorption are used as reference number for the quantum yield. The quantum yield of the porous silicon sample has been measured by two independent teams and is 3.2% (Figure S23).²



Figure S25. Quantum yield (QY) deduced from the difference in intensity observed for the crystalline [Au(SPh)]_n sample and the porous Si reference.

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