Electronic Supplementary Information (ESI)

A Silver(I) Coordination Polymer with Sodium 3,5-dimethyl-4-sulfonate pyrazolate: a nice example of PXRD structure solution and time-driven crystallization

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Figure S1 Infrared spectrum of **1** (nujol).

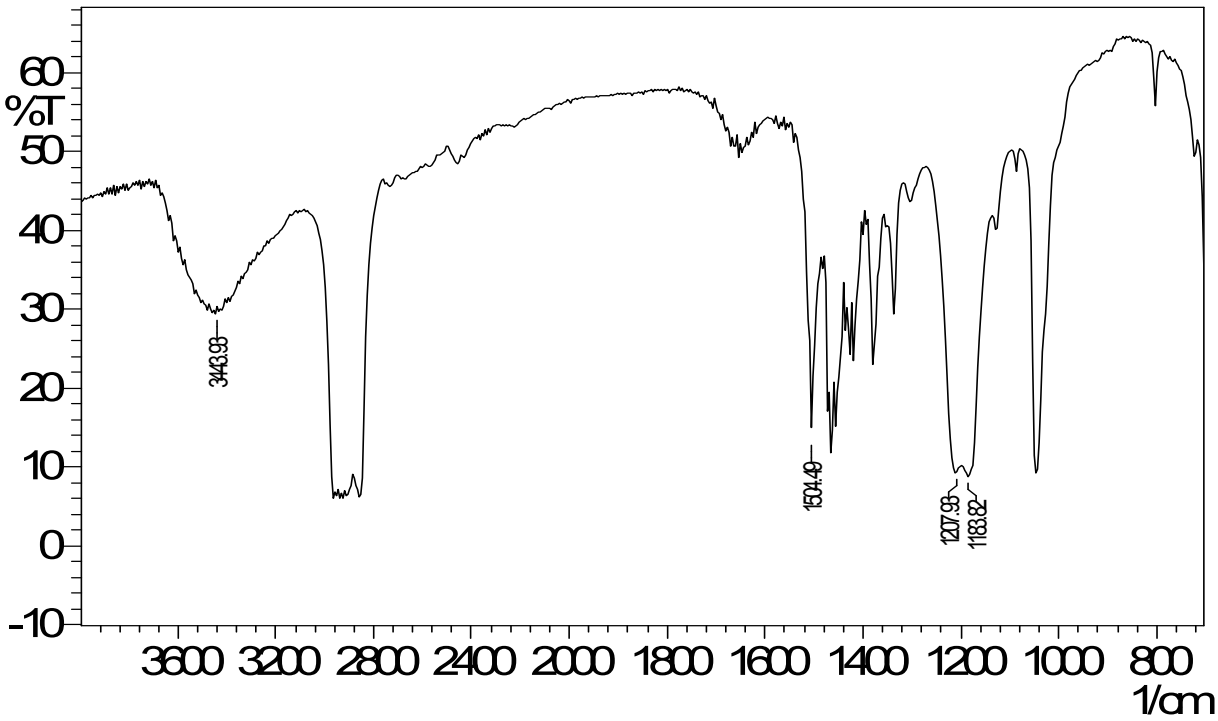
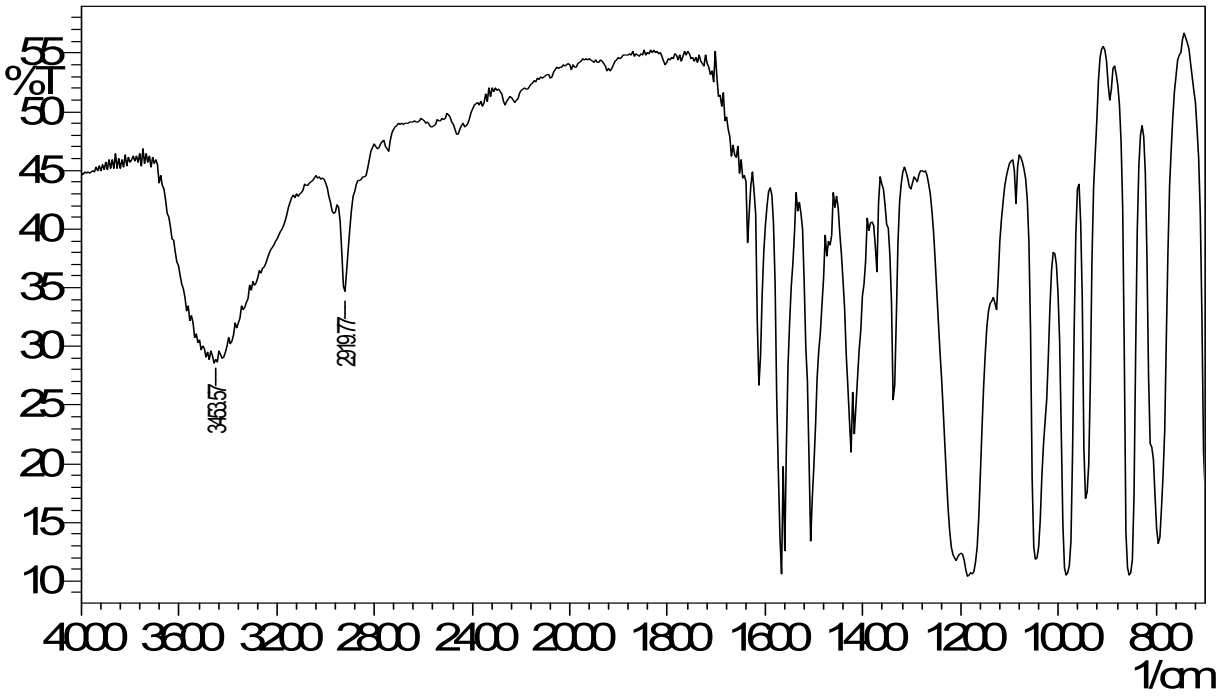


Figure S2 Infrared spectrum of **1** (hexachlorobutadiene).



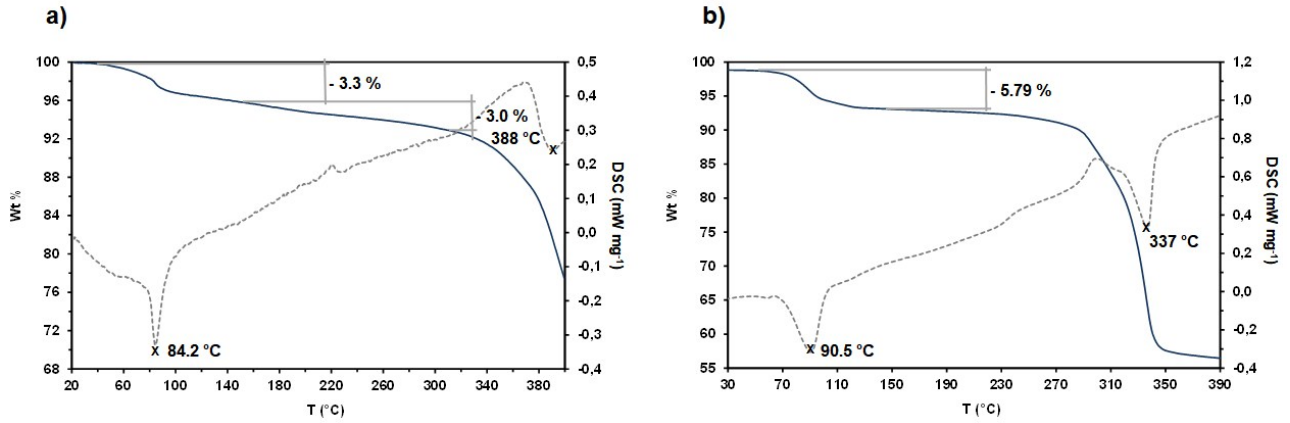


Figure S3. Simultaneous Thermal Analysis for a) **1**, as-synthetized sample and b) **1a**, the one-year old sample. Both analyses have been done in N_2 atmosphere and heating rate 4 K/min. Blue line: TGA; dotted grey line: DSC.

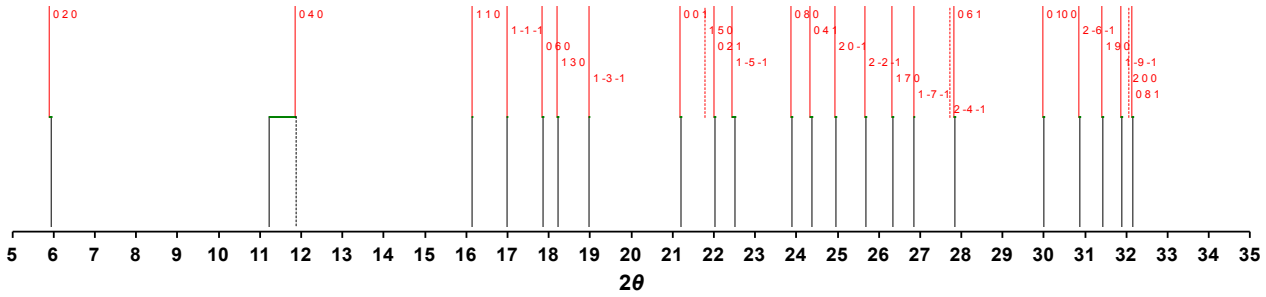


Figure S4 Indexing plot for **1**. Black lines, experimental peaks positions; red lines, calculated peaks positions. Dashed black line: unindexed experimental peak. Gof(20) = 23.5.

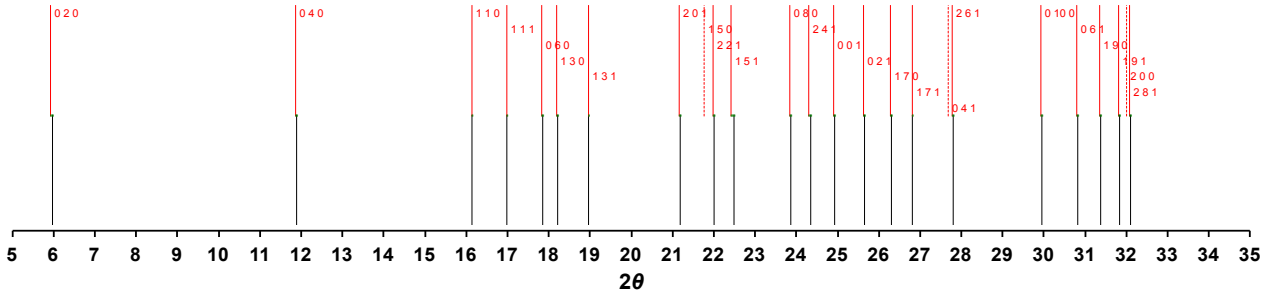


Figure S5 Indexing plot for **1**, without taking into account the small peak at 11.235 2θ. Black lines, experimental peaks positions; red lines, calculated peaks positions. Dashed black line: unindexed experimental peak. Gof(20) = 70.52.

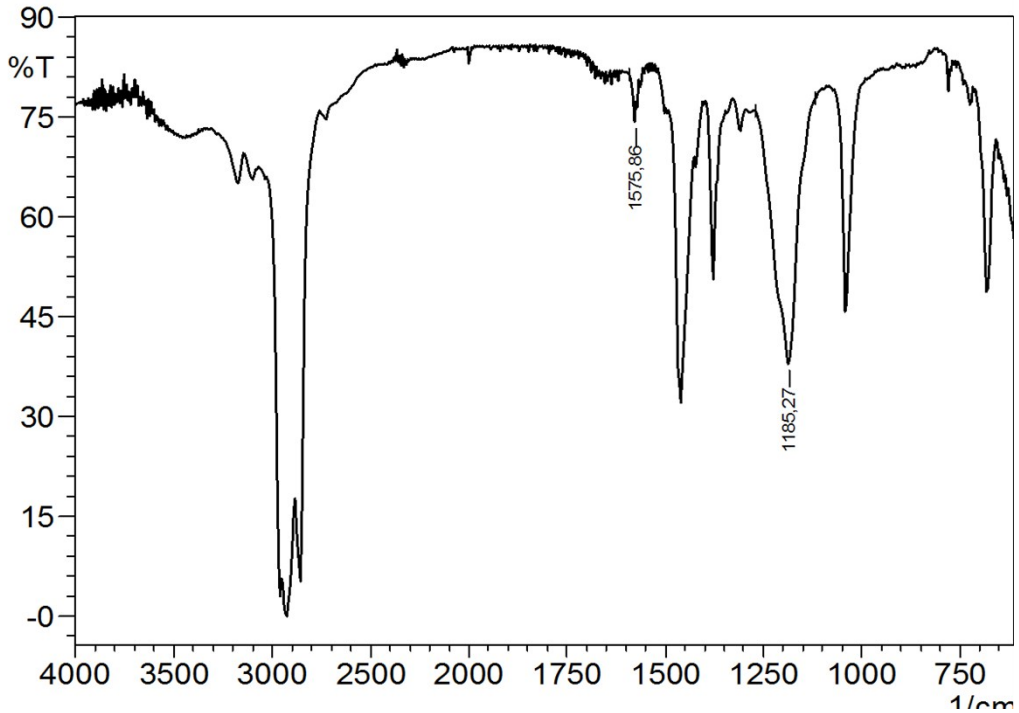


Figure S6 Infrared spectrum of **1_HT** (nujol).

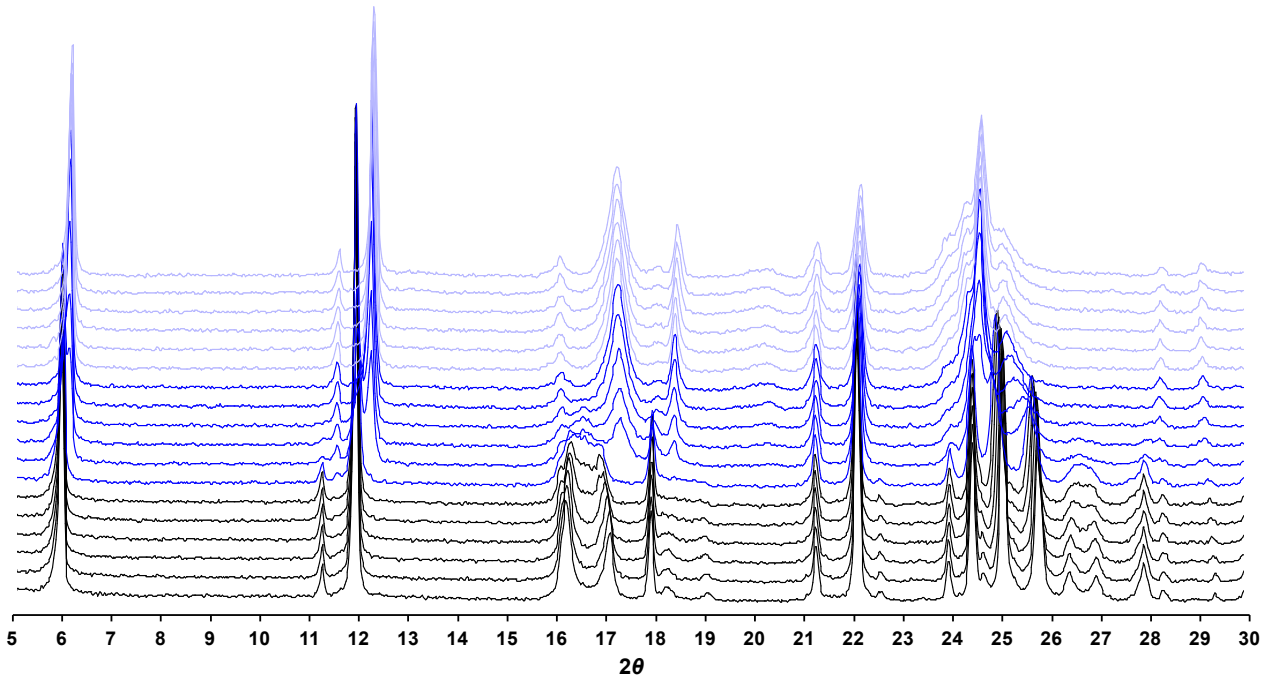


Figure S7 Collection of the diffractograms of **1** from room temperature (black, bottom) to 250 °C (light blue, upper).

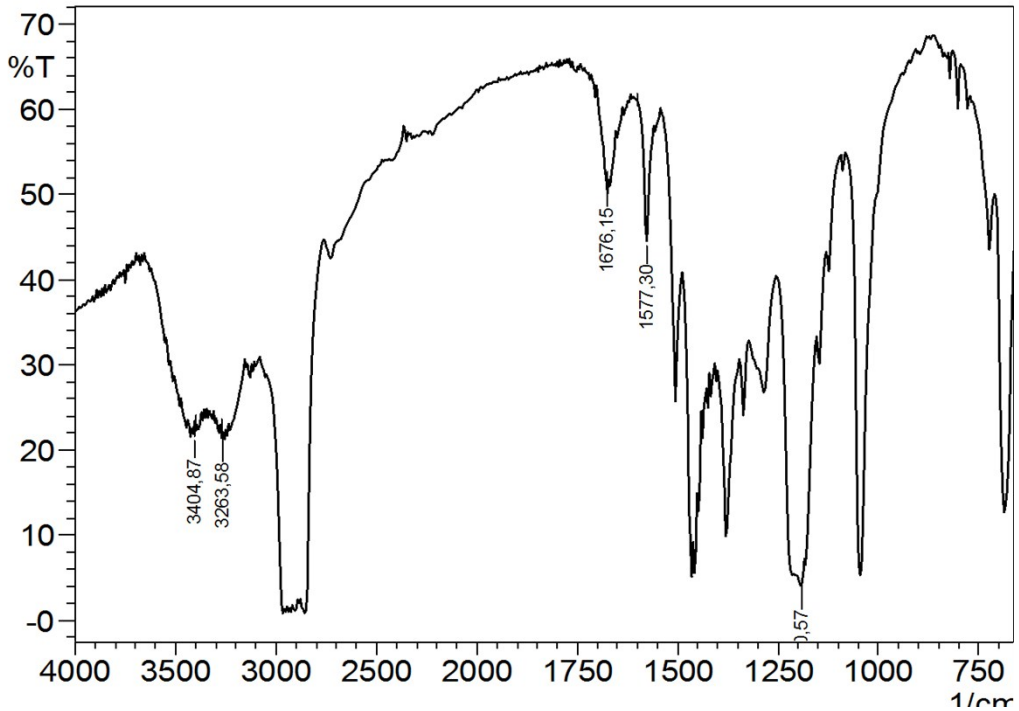


Figure S8 Infrared spectrum of **1a** (nujol).

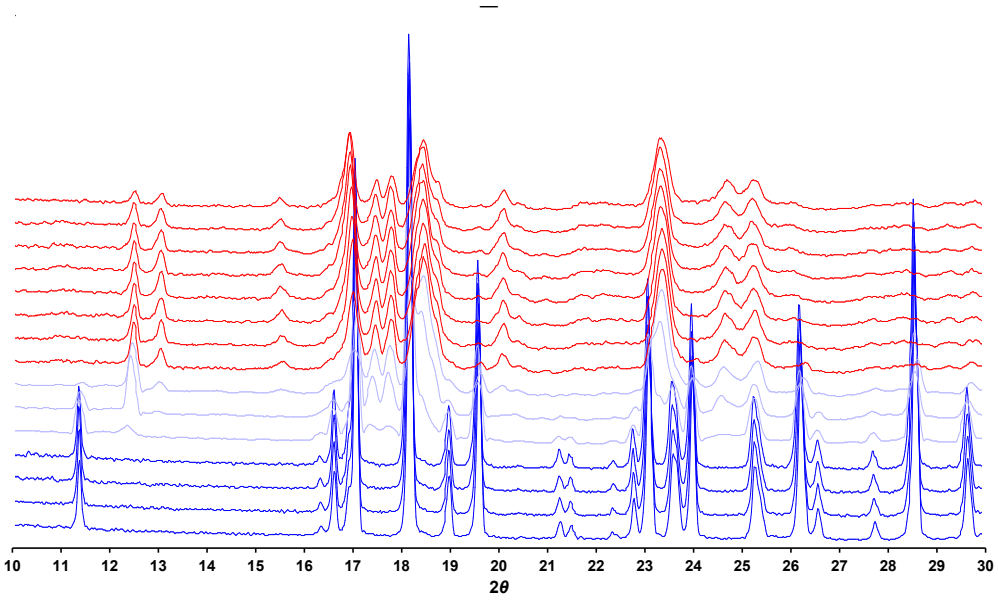


Figure S9 Collection of the diffractograms of **1a** from room temperature (black, bottom) to 290 °C (light blue, upper).

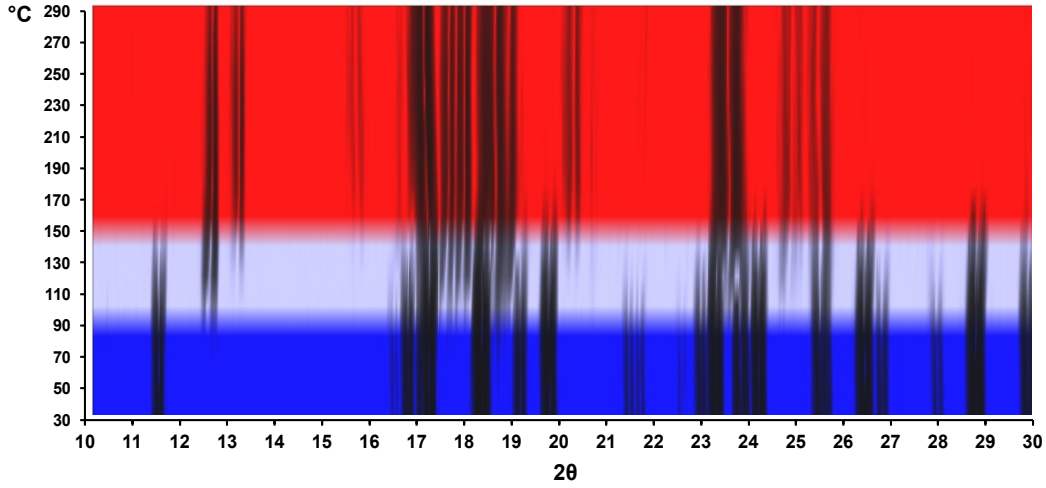


Figure S10 Two-dimensional contour plot as a function of 2θ and temperature for the collection of powder X-ray diffraction patterns measured at elevating temperatures in the range 30-290 °C for **1a**. The region highlighted in the graph between 100 and 150 °C shows the transition from low-temperature to high-temperature phase.

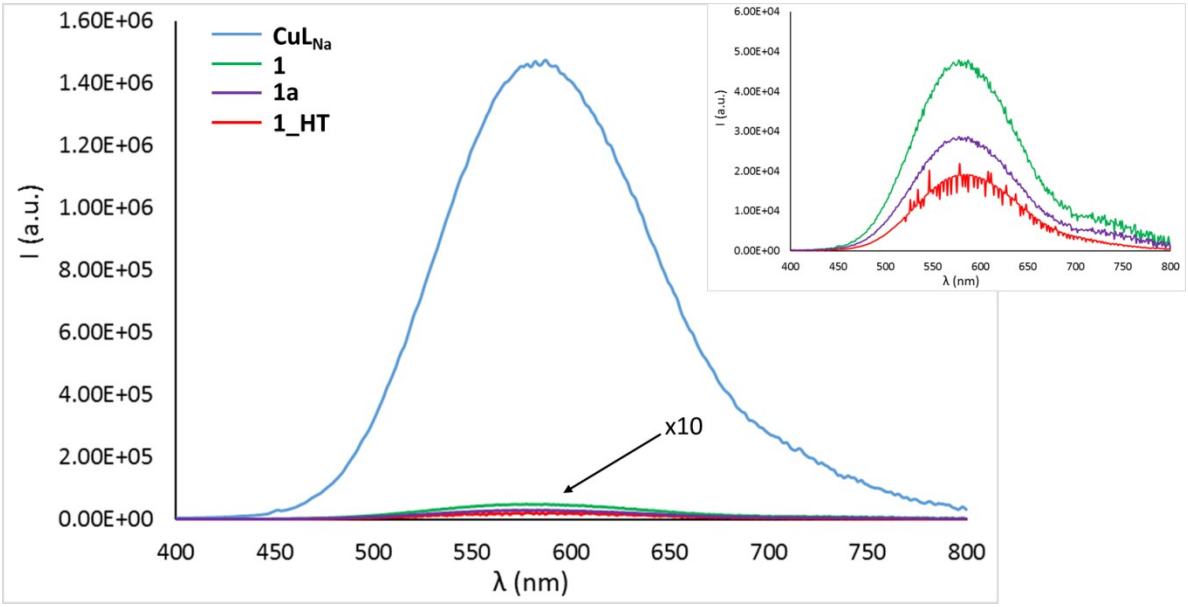


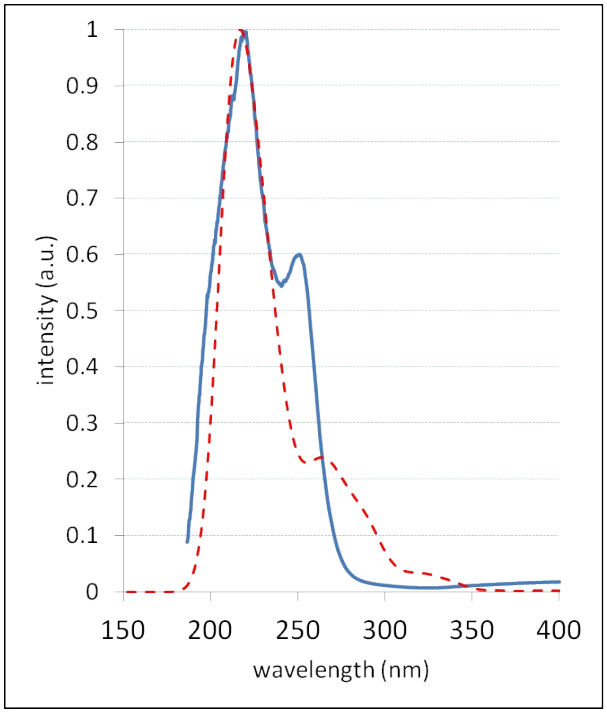
Figure S11 Comparison among the intense phosphorescence shown by complex **CuL$_{Na}$** and the poor emissive properties of the silver derivatives **1**, **1_HT** and **1a** when excited at 265 nm.

Computational details

All calculations were carried out at the density functional (DFT) level of theory with the ADF2017.106 program package.[1] C, H, N, O and S atoms were described through AUG/TZ2P basis sets [triple-ζ Slater-type orbitals (STOs) plus two polarization function and diffuse functions]; the QZ4P basis set (quadruple-ζ STO plus four polarization functions) was used for the Ag atoms. Scalar relativistic effects on silver atoms were treated by applying the zeroth-order regular approximation (ZORA).[2]

TD-DFT calculations were performed on the dimeric $[\mathbf{Ag_2(L_{Na})_3}]^-$ model system built up from the X-ray structure of complex **1** employing the dispersion-corrected PBE functional PBE-D.[3] Na atoms were substituted by H bonded to the oxygen atom of SO_3 moiety.

Figure S12. Comparison between the experimental (blue solid line) UV spectrum of **1** and the one calculated for the model system $[\mathbf{Ag_2(L_{Na})_3}]^-$ (red dotted line).



λ (nm)	Oscillator strength, f
324.92	0.01477
291.63	0.03127
286.18	0.01909
277.97	0.02860
274.61	0.01330
271.92	0.01376
265.56	0.04614
262.91	0.02873
258.28	0.01491
255.48	0.01062
253.37	0.01017
243.49	0.02446
240.92	0.02244
237.71	0.01684
232.50	0.06542
227.63	0.02253
224.96	0.04334
222.65	0.02787
217.53	0.02311
216.43	0.02598
211.27	0.04545
208.82	0.02852

Only transitions with f > 0.01 are reported

[1] (a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comp. Chem.* 2001, **22**, 931-967; (b) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.* 1998, **99**, 391-403; (c) E.J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J.W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, M. Pavanello, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, J.I. Rodríguez, P. Ros, P.R.T. Schipper, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev, ADF2014, SCM, *Theoretical Chemistry*, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[2] (a) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* 1994, **101**, 9783-9792; (b) E. van Lenthe, A. Ehlers, E. J. Baerends, *J. Chem. Phys.* 1999, **110**, 8943-8953.

[3] S. Grimme, *Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction*, Journal of Computational Chemistry 2006, **27**, 1787.