

Supplementary Material for

Nanoscale coordination polymers obtained in ultrasmall liquid droplets on solid surfaces and its comparison to different synthetic volume scales

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S1. Synthesis and characterization of complex 1 in different solvents

Different synthetic procedures were done to obtain the polymeric complex **1** by mixing two equivalent of 4,4-bpy (0.080 g, 0.50 mmol) with one equivalent of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.062 g, 0.25 mmol) in diverse solvent (DMF, DMSO, EtOH, Acetonitrile) containing or not between 2-5% of glycerol. In all the cases, the obtaining precipitate after 3h of reaction was filtered and washed with water and EtOH, and dried under vacuum. The characterization by Elemental Analysis, FT-IR and XRD demonstrated that in all the synthesis the resulting compounds was the same, independently of the solvent and presence/absence of glycerol.

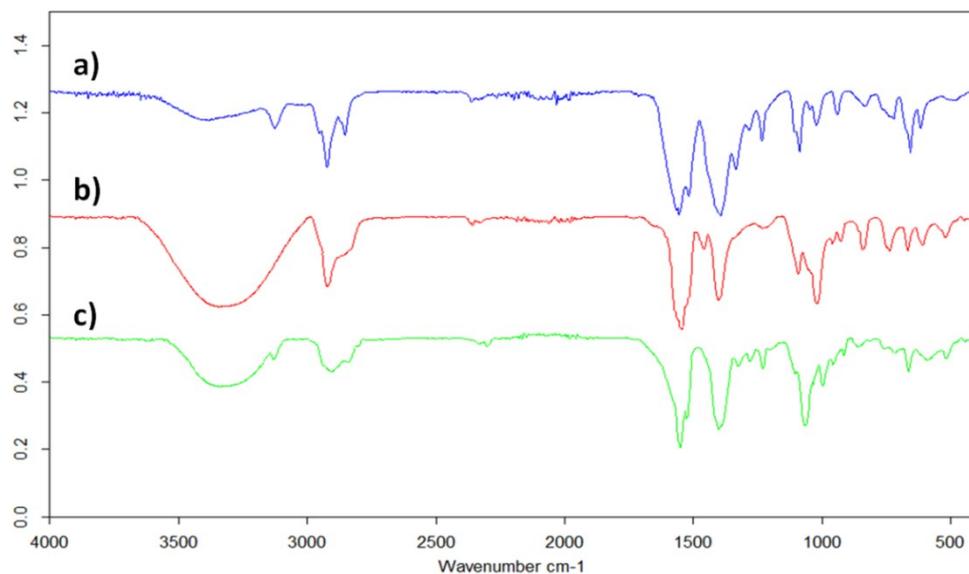


Figure S1. FT-IR spectra of complex **1** obtained in different solvents: a) DMF, b) DMF + 2% glycerol, and c) EtOH.

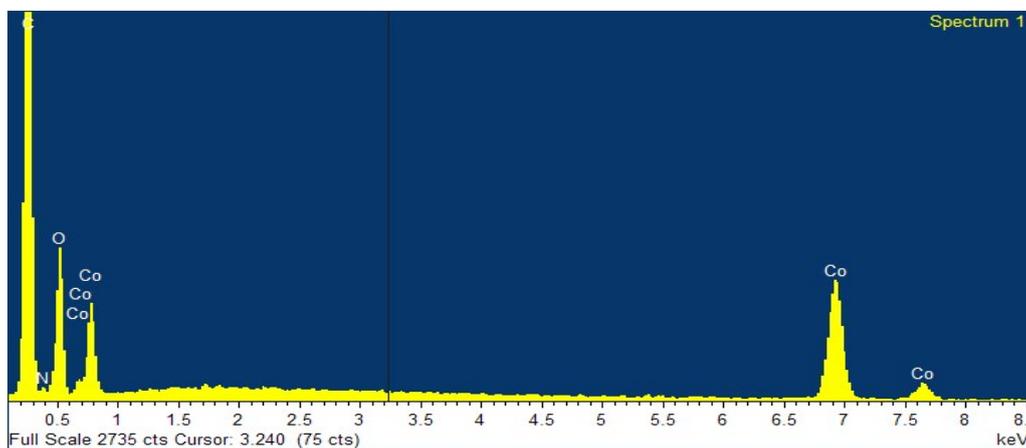


Figure S2. EDX analysis of complex **1** showing the major elements that compose the metal-organic polymeric material.

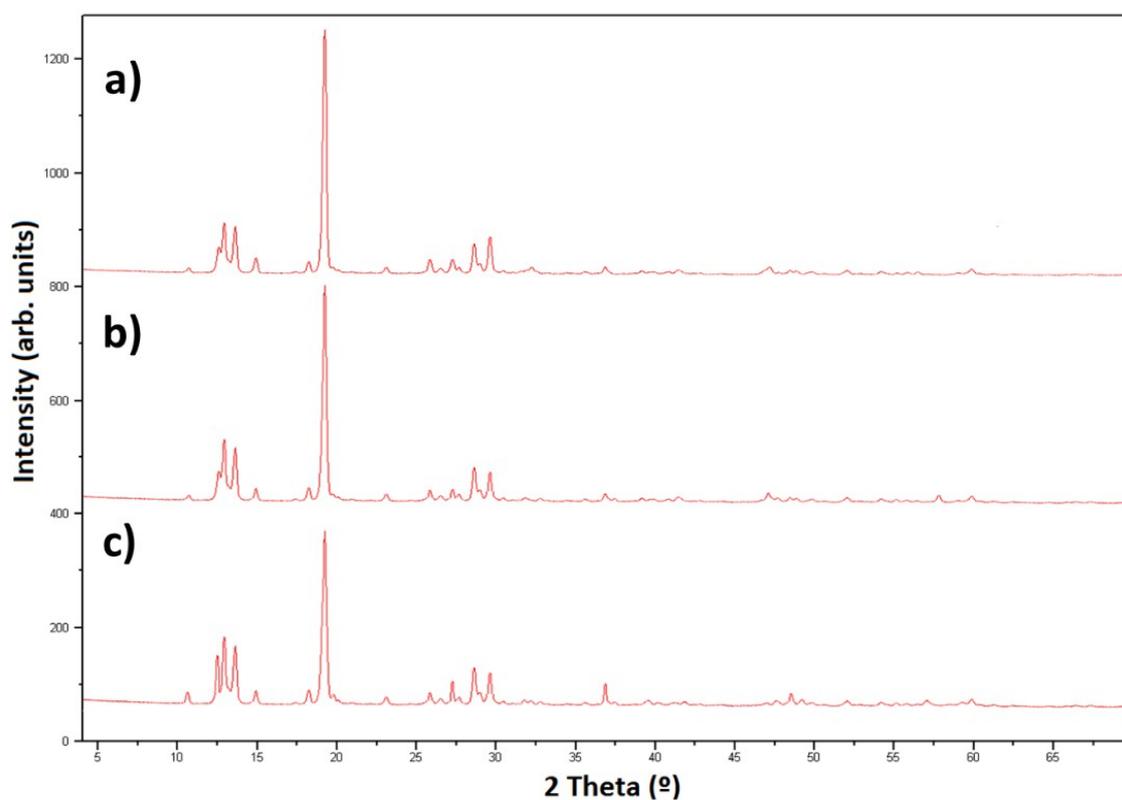


Figure S3. XRD spectra of complex **1** obtained in different solvents: a) DMF, b) DMF + 2% glycerol, and c) EtOH.

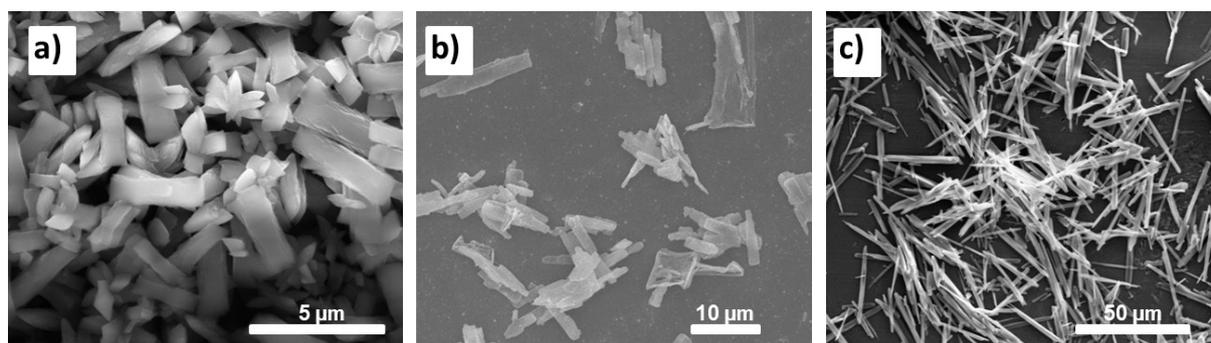


Figure S4. SEM images of complex **1** morphology obtained for the samples synthesized in bulk in different solvents: a) DMF, b) DMF + 2% glycerol, and c) EtOH

S2. Structures of complex 1 obtained upon drop casting of a cobalt acetate and bpy (molar ratio 1:2) DMF solution on Si/SiO₂

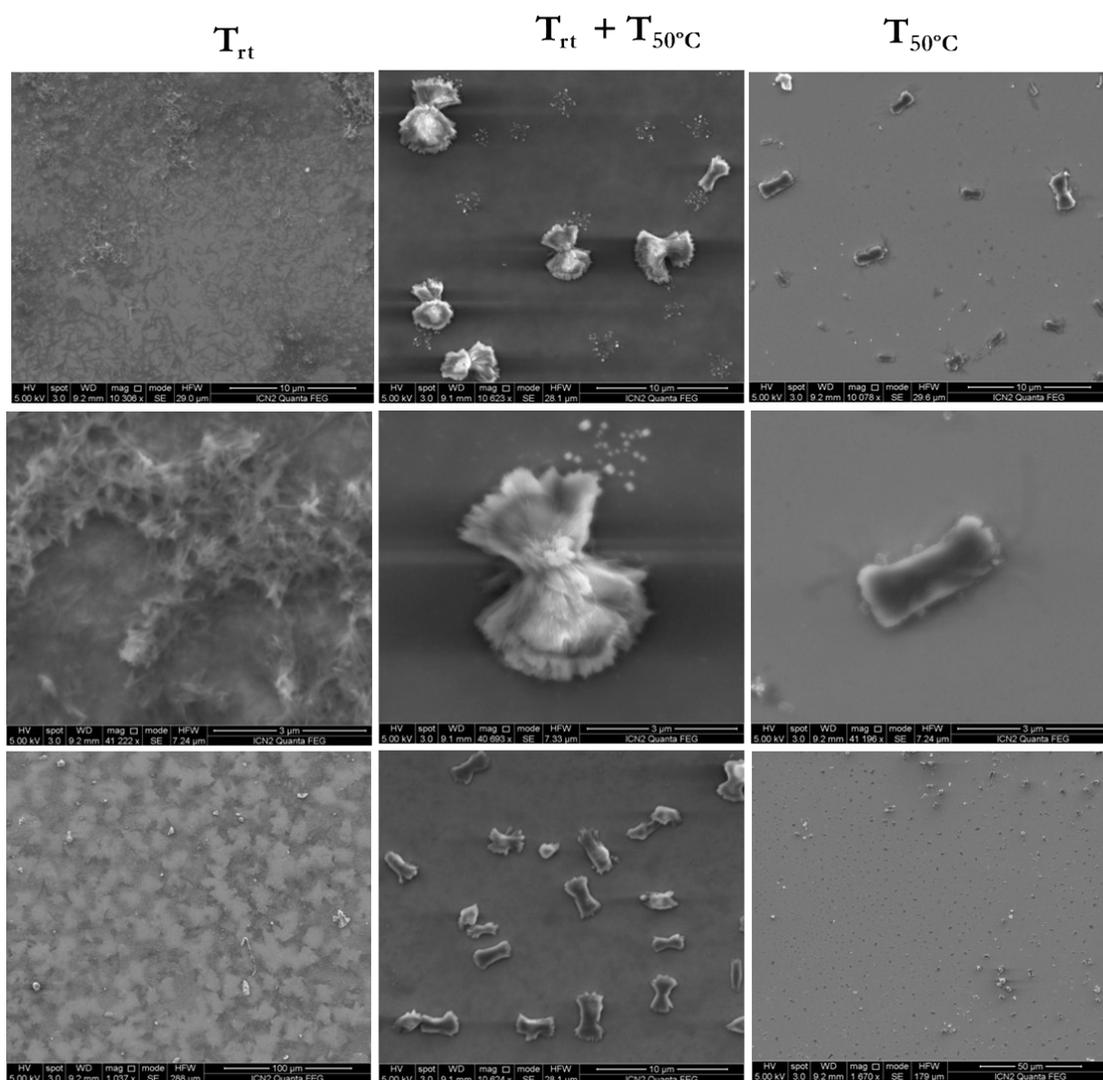


Figure S5. SEM images of complex 1 obtained upon deposition of μL droplets of a cobalt acetate and bpy (molar ratio 1:2) DMF solution deposited on a Si/SiO₂ surface and dried following three different drying conditions: (Column I, T_{rt}) room temperature until complete droplet evaporation; (Column II, $T_{rt} + T_{50^{\circ}C}$) 50 $^{\circ}C$ for four hours; and (Column III, $T_{50^{\circ}C}$) combined drying: 4 h at room temperature and 4 h at 50 $^{\circ}C$.

S3. Structures of complex 1 obtained upon drop casting of cobalt acetate and bpy (molar ratio 1:1) DMF solution on Si/SiO₂

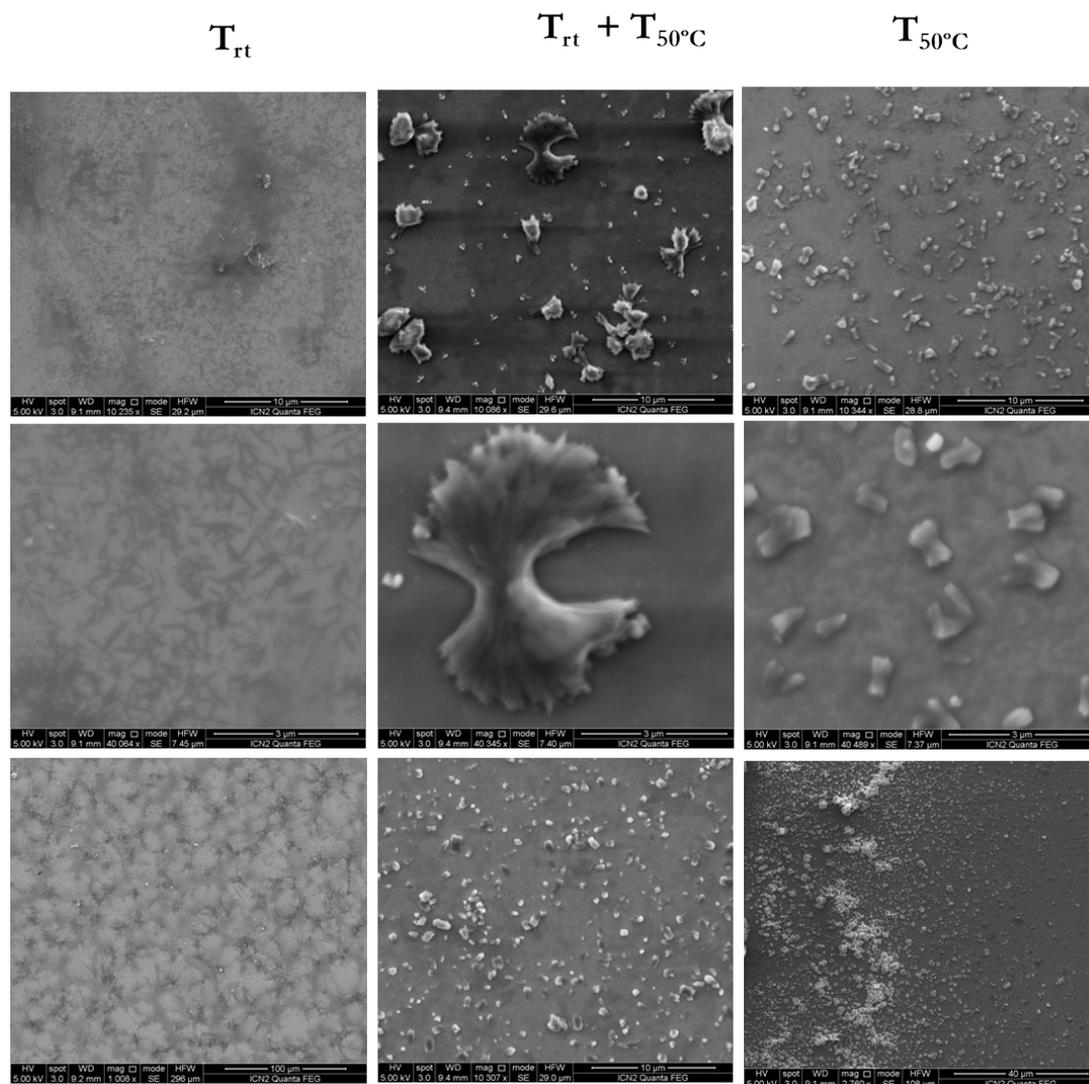


Figure S6. SEM images of complex **1** obtained upon deposition of μL droplets of a of cobalt acetate and bpy (**molar ratio 1:1**) DMF solution deposited on a Si/SiO₂ surface and dried following three different drying conditions: (Column I, T_{rt}) room temperature until complete droplet evaporation; (Column II, $T_{rt} + T_{50^{\circ}C}$) 50 $^{\circ}\text{C}$ for four hours; and (Column III, $T_{50^{\circ}C}$) combined drying: 4 h at room temperature and 4 h at 50 $^{\circ}\text{C}$.

S4. Structures of complex 1 obtained *in situ*, upon the successive drop casting of 2 μL -droplets of a cobalt acetate solution (in DMF) and bpy ligand (in DMF) with a molar ratio 1:2 on Si/SiO_2

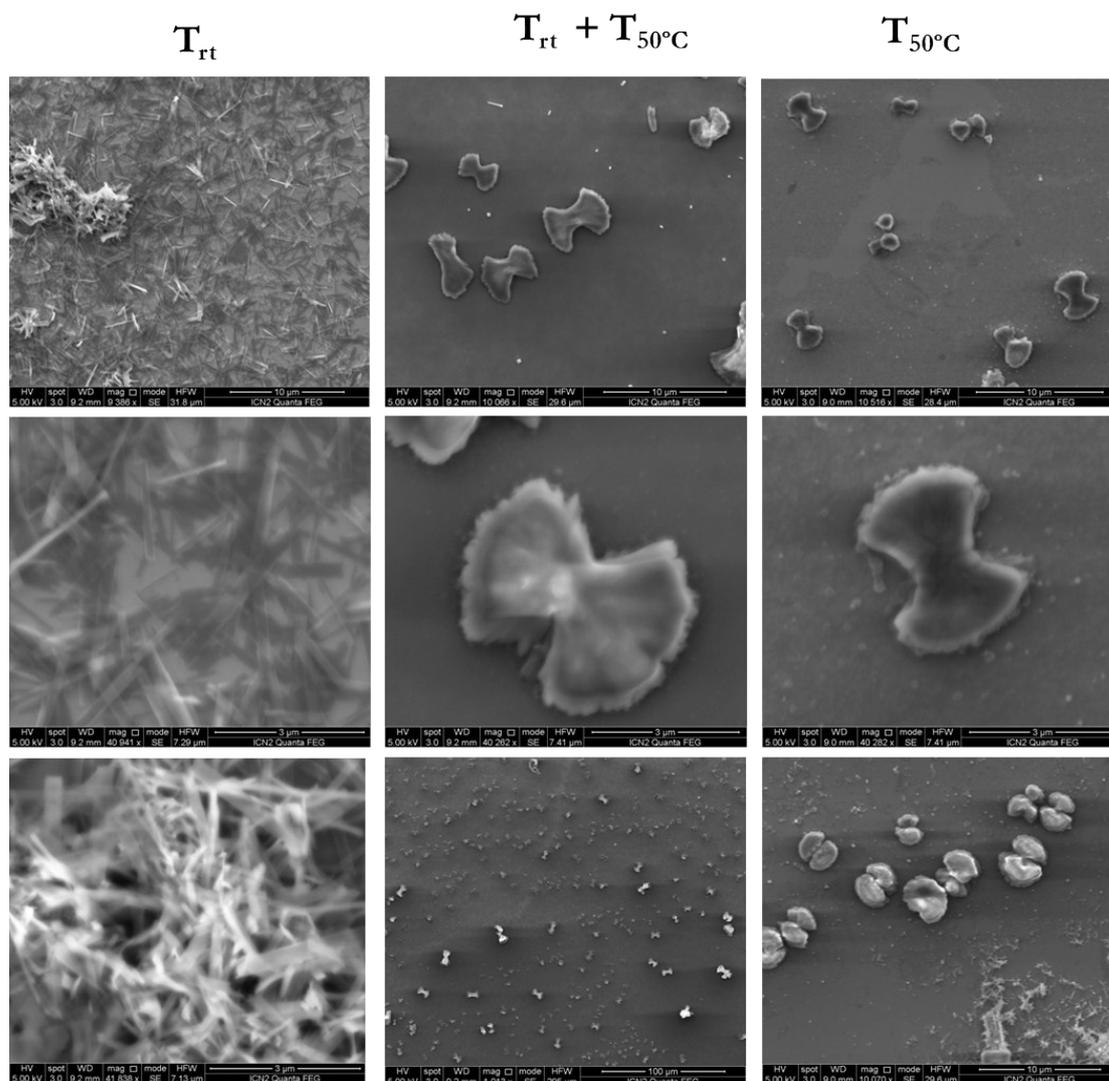


Figure S7. SEM images of complex 1 obtained *in situ*, upon the successive drop casting of 2 μL -droplets of a cobalt acetate solution (in DMF) and bpy ligand (in DMF) with a molar ratio 1:2 on Si/SiO_2 surface and dried following three different drying conditions: (Column I, T_{rt}) room temperature until complete droplet evaporation; (Column II, $T_{rt} + T_{50^\circ\text{C}}$) 50 $^\circ\text{C}$ for four hours; and (Column III, $T_{50^\circ\text{C}}$) combined drying: 4 h at room temperature and 4 h at 50 $^\circ\text{C}$.

S5. Structures of complex 1 obtained *in situ*, upon the successive drop casting of 2 μL -droplets of a cobalt acetate solution (in DMF) and bpy ligand (in DMF) with a molar ratio 1:1 on Si/SiO_2

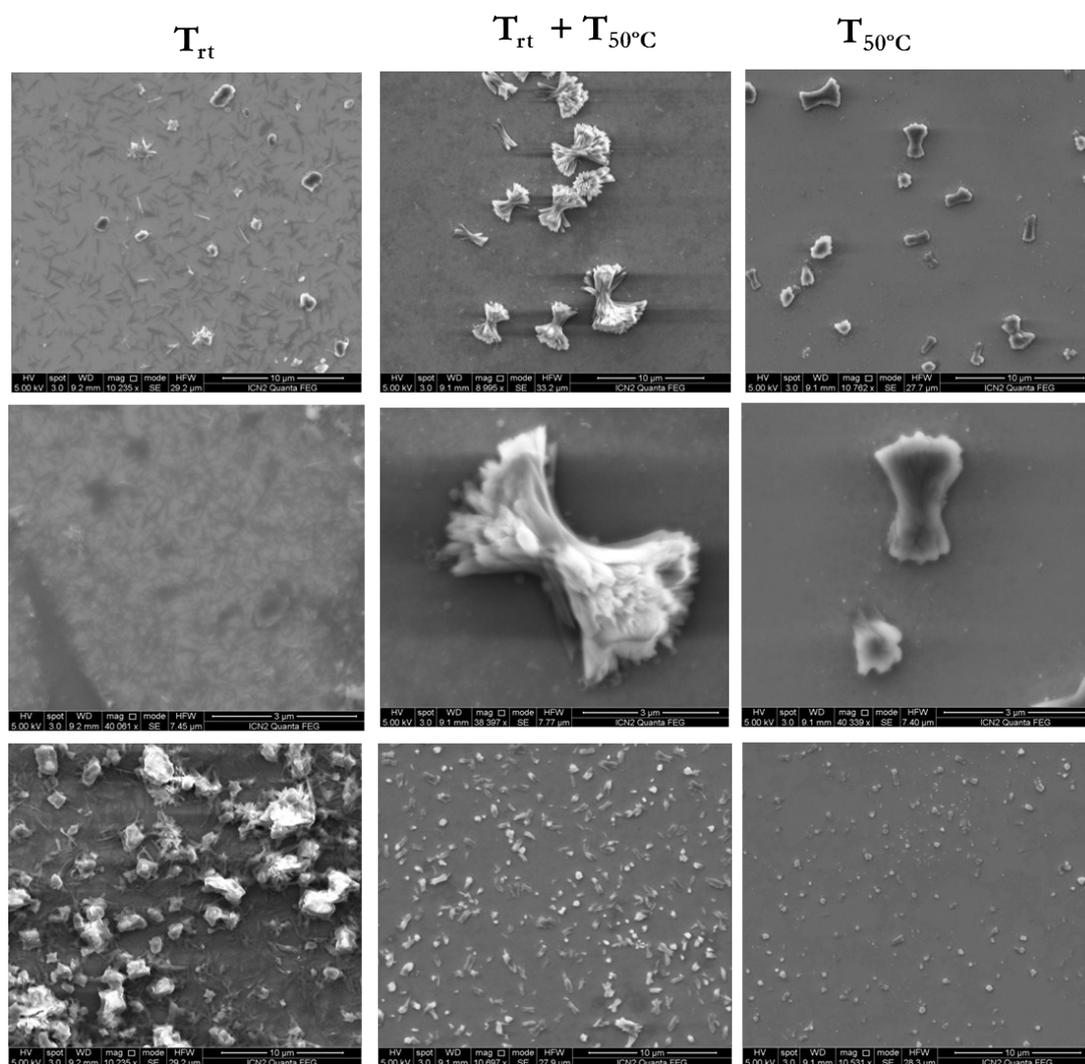


Figure S8. SEM images of complex 1 obtained *in situ*, upon the successive drop casting of 2 μL -droplets of a cobalt acetate solution (in DMF) and bpy ligand (in DMF) with a molar ratio 1:1 on Si/SiO_2 surface and dried following three different drying conditions: (Column I, T_{rt}) room temperature until complete droplet evaporation; (Column II, $T_{\text{rt}} + T_{50^\circ\text{C}}$) 50 $^\circ\text{C}$ for four hours; and (Column III, $T_{50^\circ\text{C}}$) combined drying: 4 h at room temperature and 4 h at 50 $^\circ\text{C}$.

S6. XRPD comparative spectra of complex 1 synthesized by drop casting *in situ* and *ex situ*).

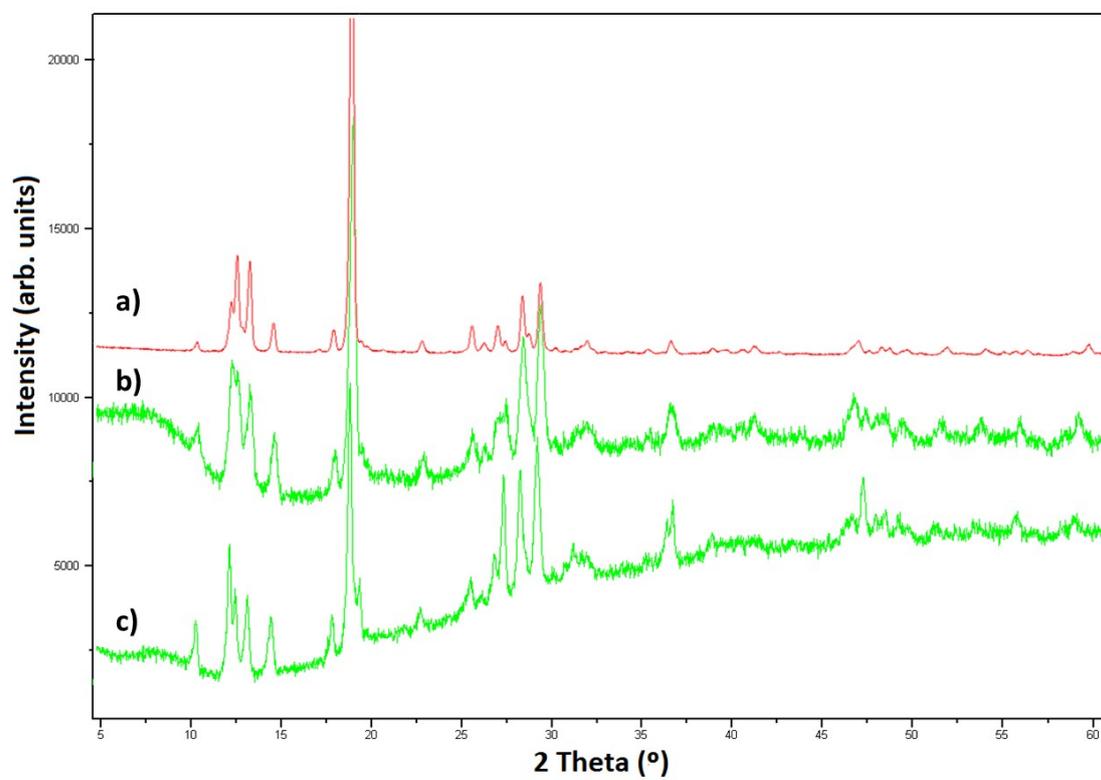


Figure S9. XRPD spectra of complex 1 synthesized by dropcasting *in situ* (b) and *ex situ* (c), and comparison with the bulk material (a).

S7. TEM images of complex 1 deposited on Si/SiO₂ substrates and amorphous carbon-coated TEM grids

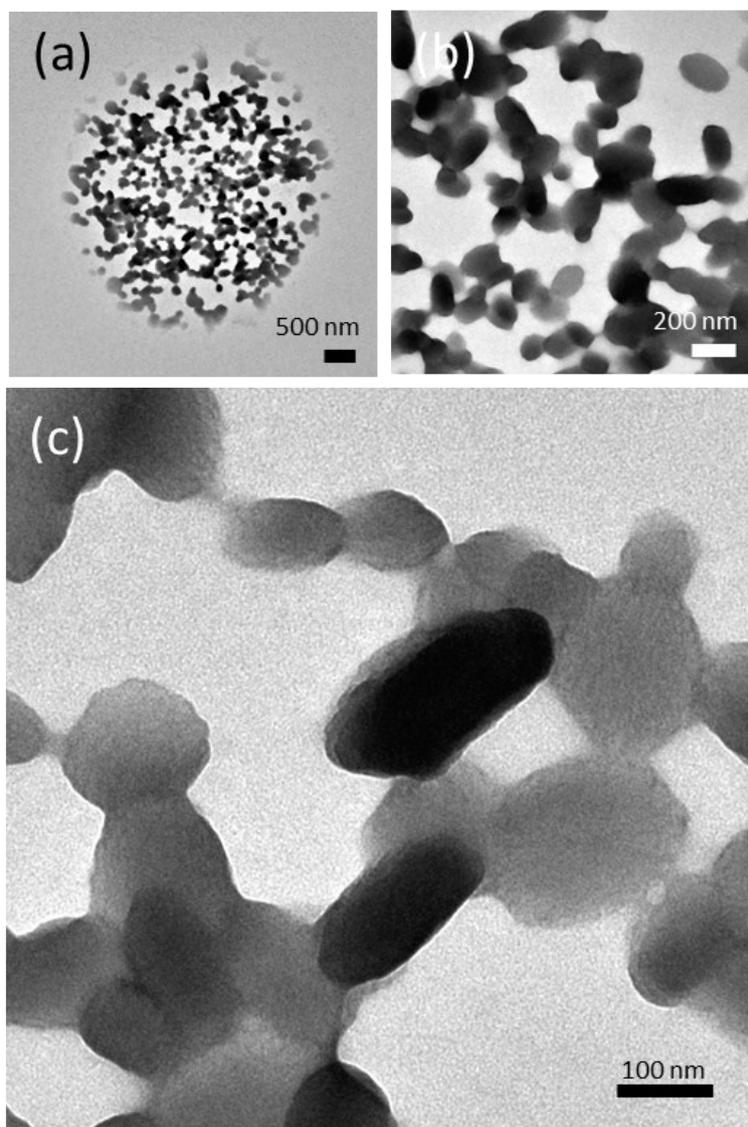


Figure S10. (a-b) HR-TEM characterization of $\text{Co}(\text{CH}_3\text{COO})_2(\mu\text{-}4,4'\text{-bpy})$ (**1**) obtained by AFM-assisted lithography on surfaces through *in situ* deposition method. (c) CP structures seemed to be sensitive to electron beam and the ordering of the crystal was very difficult to visualize.

