STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 77 (2021)

Supporting information for article:

Octamolybdate isomers concomitance in metastable crystal structures isolated using homoleptic Co(II)/(III)-complexes as structuring directing templates

Reinaldo Atencio, Alexander Briceño, Julia Bruno-Comenarez, Pedro Silva, Laura Rodríguez, Eleida Sosa, Erick Limones, Yesenia Pacheco, Julio Cáceres and Joel Vielma

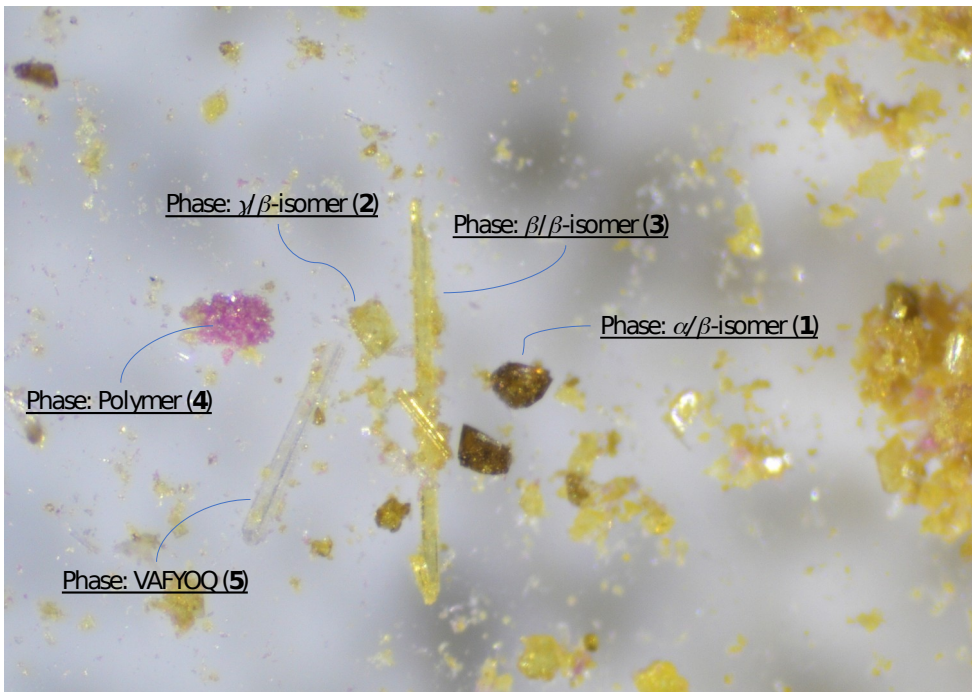

Phase: γ/β-isomer (2)
Phase: β/β-isomer (3)
Phase: α/β-isomer (1)
Phase: Polymer (4)
Phase: VAFYOQ (5)

Figure S1 Photo of the solid obtained using 1:6 Co:Mo molar ratio at 160 °C, in which phases **1**-**5** are identified by SC-XRD takin into account different morphology and color.

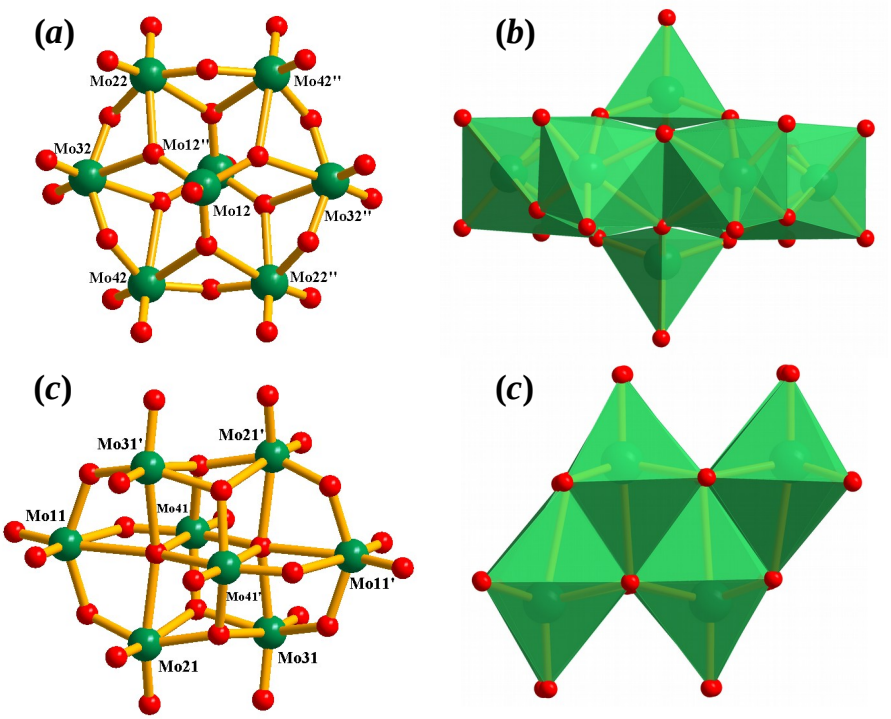


Figure S2 Graphical representation for octamolybdate isomers found in the crystal structures of **1**. Ball-and-stick model of the α- (a) and β-isomer (c). Polyhedral models that display an evident difference between the geometry forms of the α- (b) and β-isomer (d).

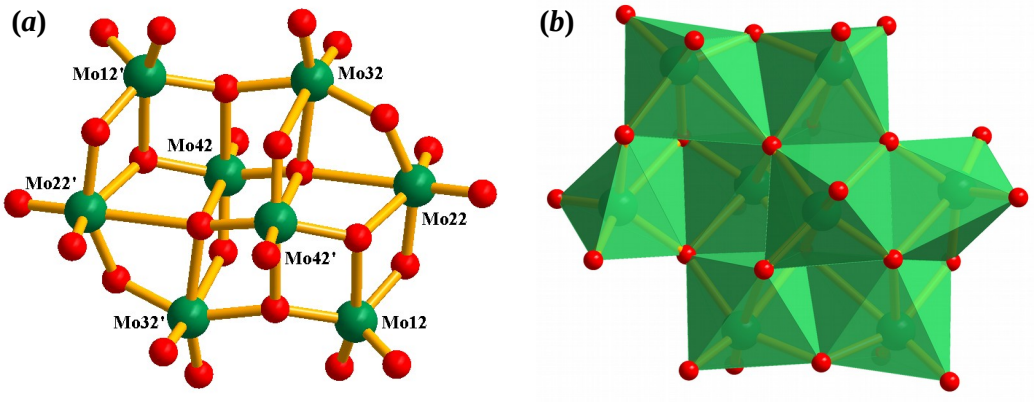


Figure S3 (a) Ball-and-stick and (b) polyhedral representation for the *γ*-isomer found in the crystal structures of **2**.

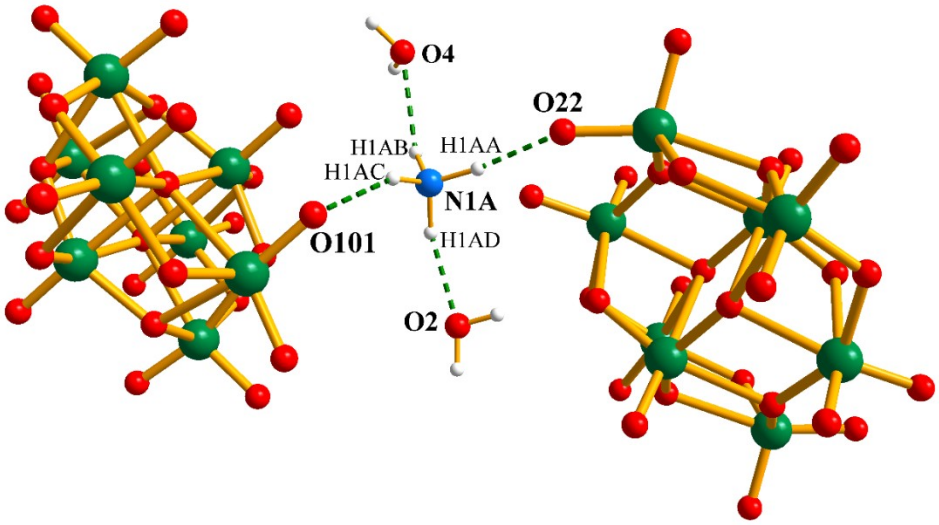


Figure S4 *Pseudo*-tetrahedral site where NH_4^+ is hosted in the crystal structure of **2**. Formed hydrogen bonds agree well with the local site. N1A─H1AA···O22: 1.83 Å and 142.6°. N1A─H1AB···O4: 2.13 Å and 142.6°. N1A─H1AC···O101: 2.01 Å and 155.2°. N1A─H1AD···O2: 1.91 Å and 150.4°.

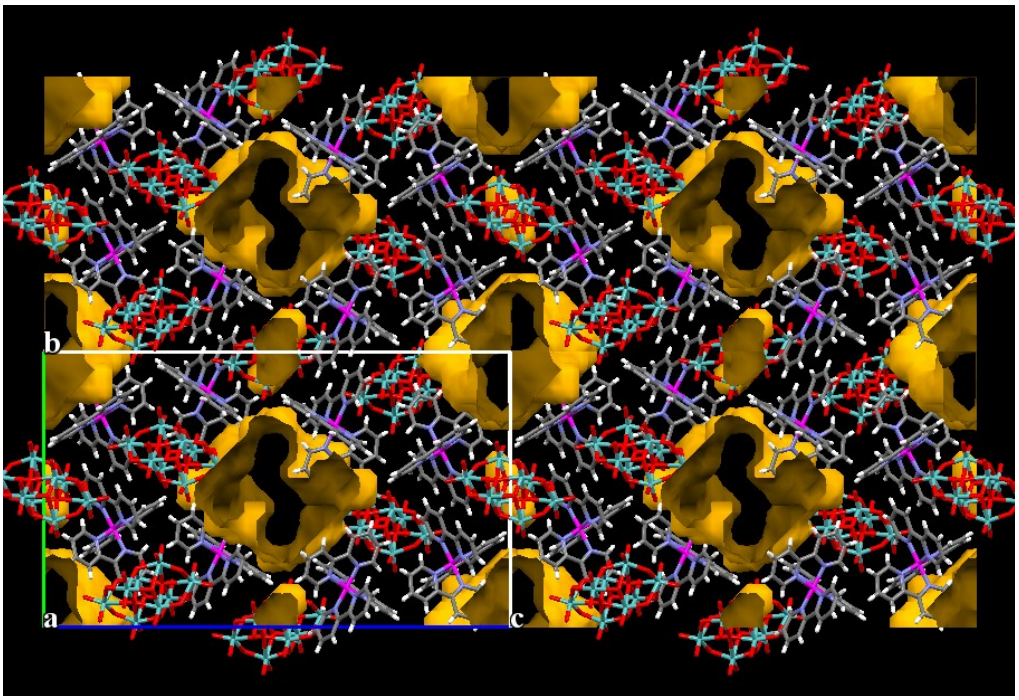


Figure S5 Graphical representation of the crystal structure of **3**, showing channels parallel to the *a*-direction where most of the crystallization water molecules are accommodated.

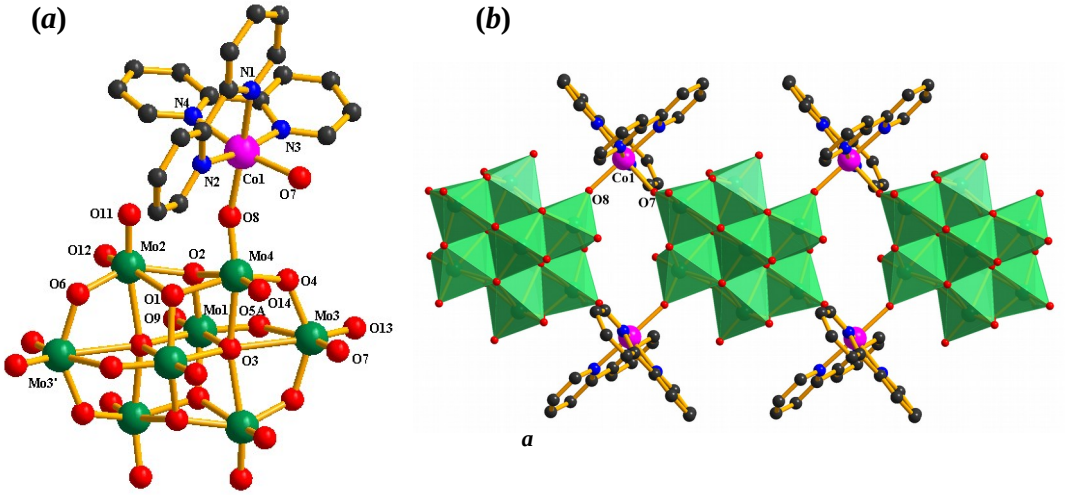


Figure S6 (a) Building block observed in the crystal structure of **4**, including labeling. (b) 1D-polymer running parallel to the *a*-axis found in **4**.

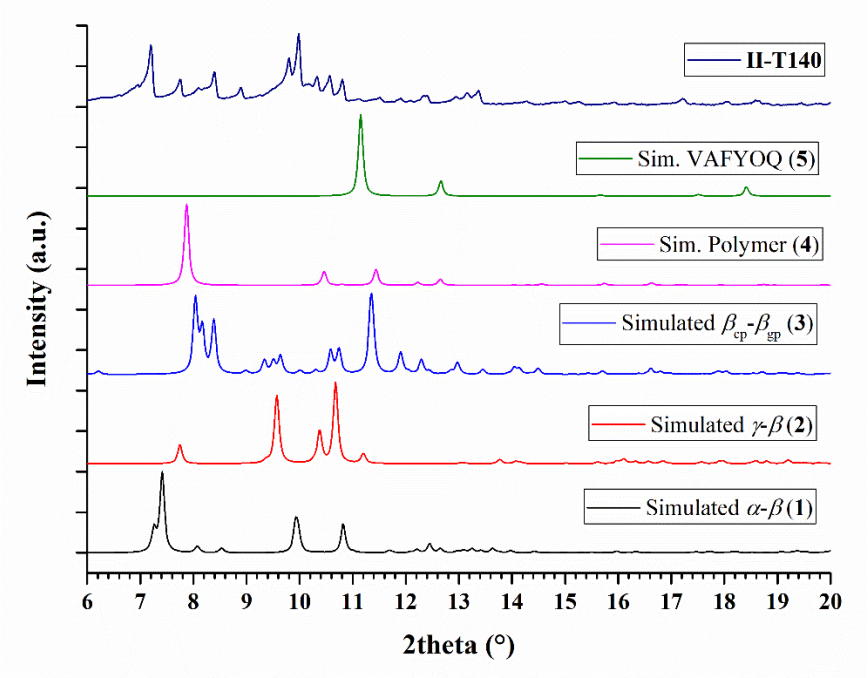


Figure S7 Comparison between P-XRD pattern from solid II-T140 (obtained at 140 °C and Co:Mo ratio: 1.8) and those simulated from SC-XRD of α-β (**1**), γ-β (**2**) and β_{cs}-β_{gp} (**3**), Polymer **4**, and Polymer **5** (VAFYOQ).

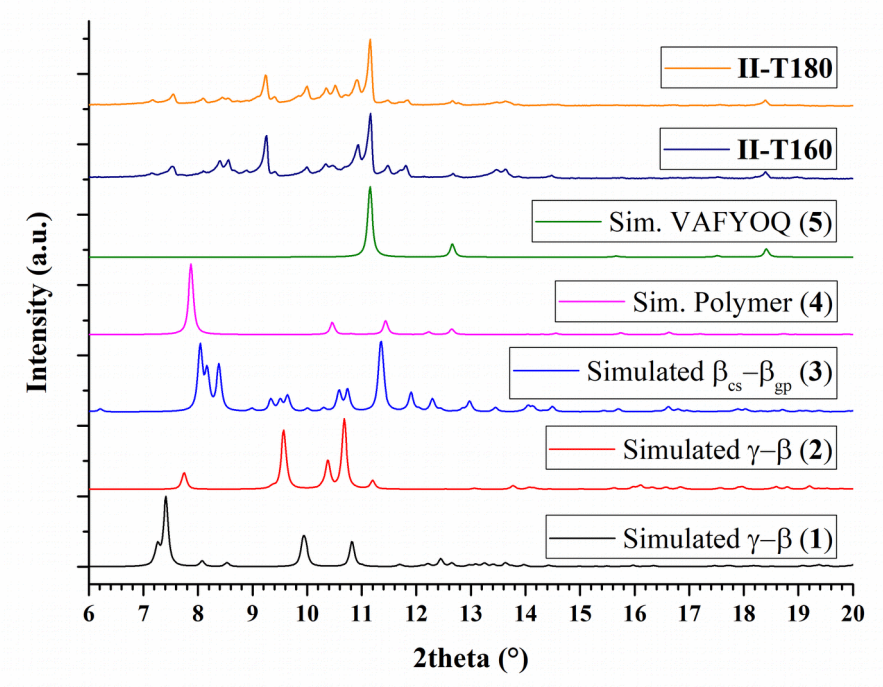
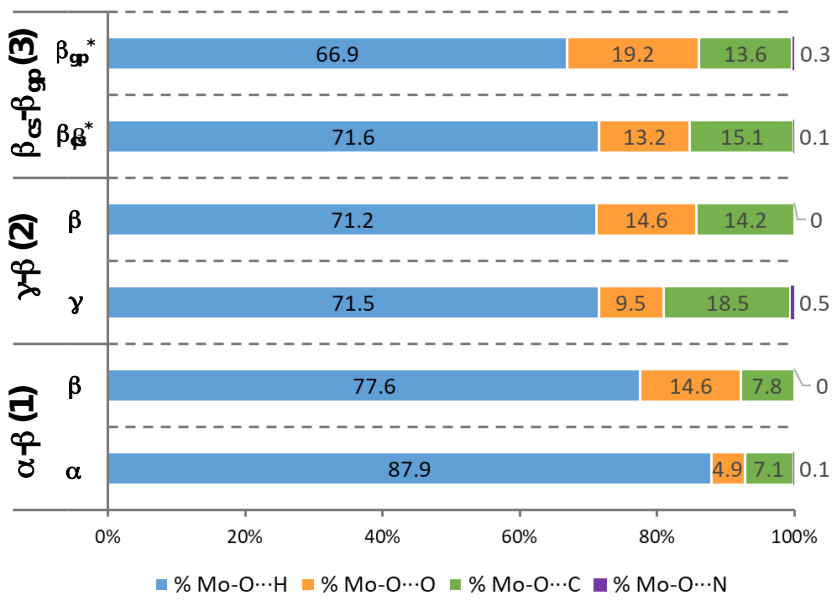


Figure S8 Comparison between P-XRD pattern from solid II-T160 (obtained at 160 °C and Co:Mo ratio: 1.8) and II-T180 (obtained at 160 °C and Co:Mo ratio: 1.8) and those simulated from SC-XRD of **1**-**5**.



* β_{cs} and β_{gp} correspond to the β-isomers located on a center of symmetry and on a general position in the crystal structure of **3**, respectively.

Figure S9 Relative contributions of each intermolecular contact as calculated from HS analysis of each octamolybdate found in α-β (**1**), γ-β (**2**), and β_{cp}-β_{gp} (**3**).

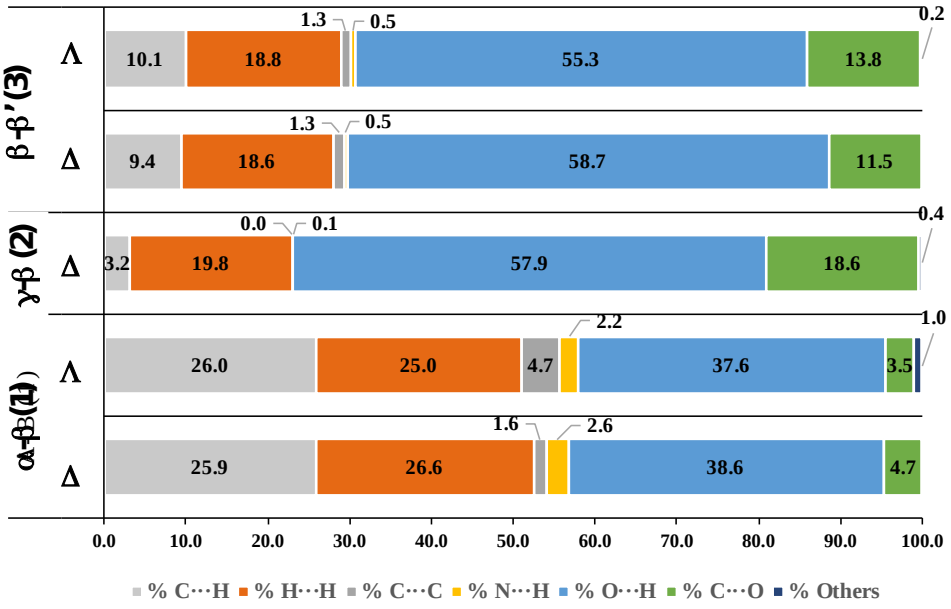


Figure S10 Relative contributions of intermolecular contacts as calculated from HS analysis of cations $[Co(bpy)_3]^n$ (n= 2 or 3) found in the crystal structures of **1-3**. Δ or Λ correspond to the configuration of the isomer observed in its respective asymmetry units for each crystal structure.

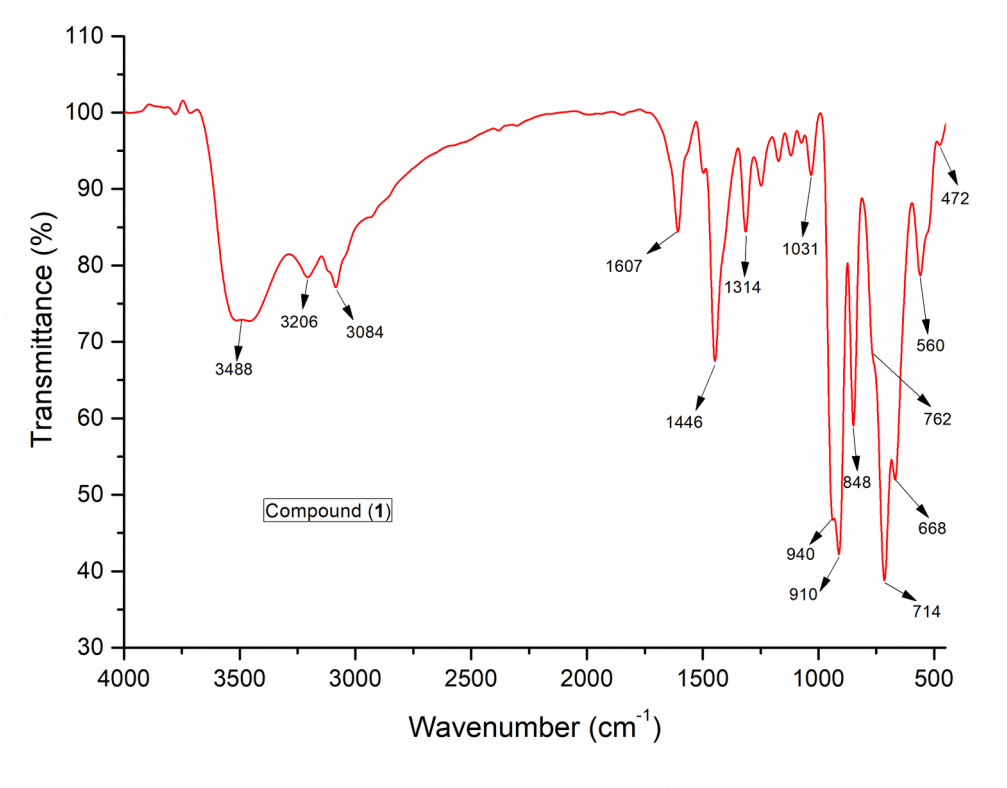


Figure S11 FT-IR for compound **1**.

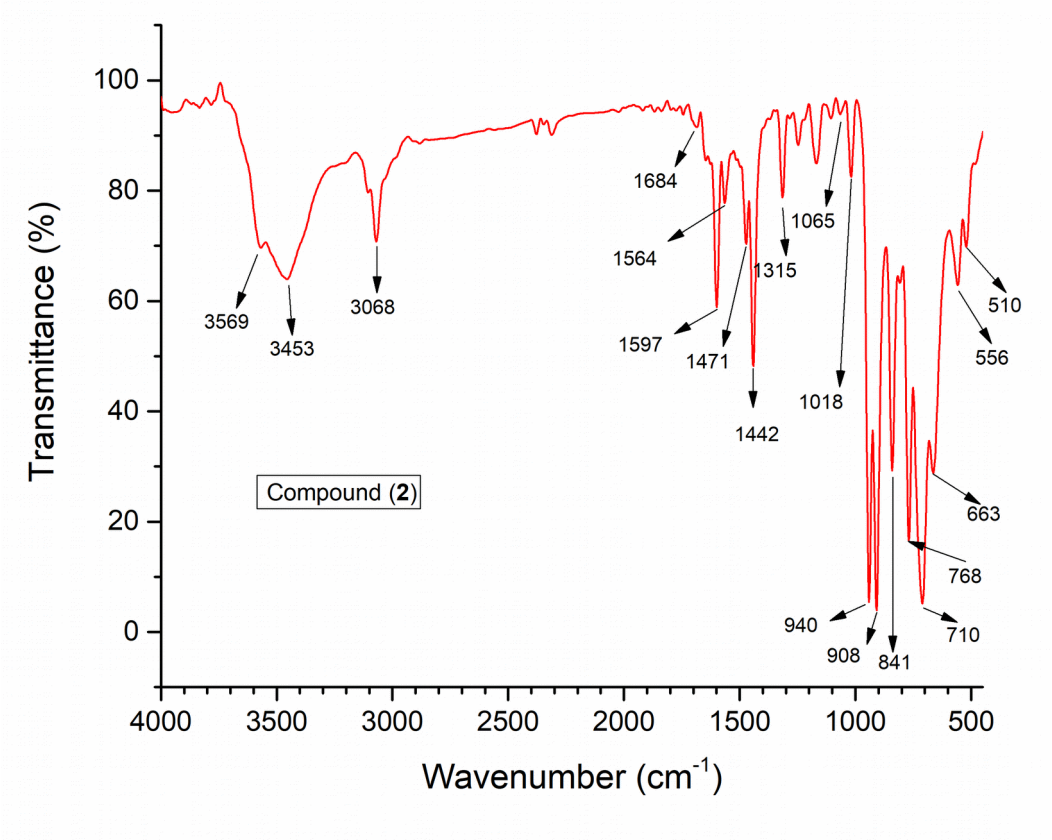


Figure S12 FT-IR for compound **2**.

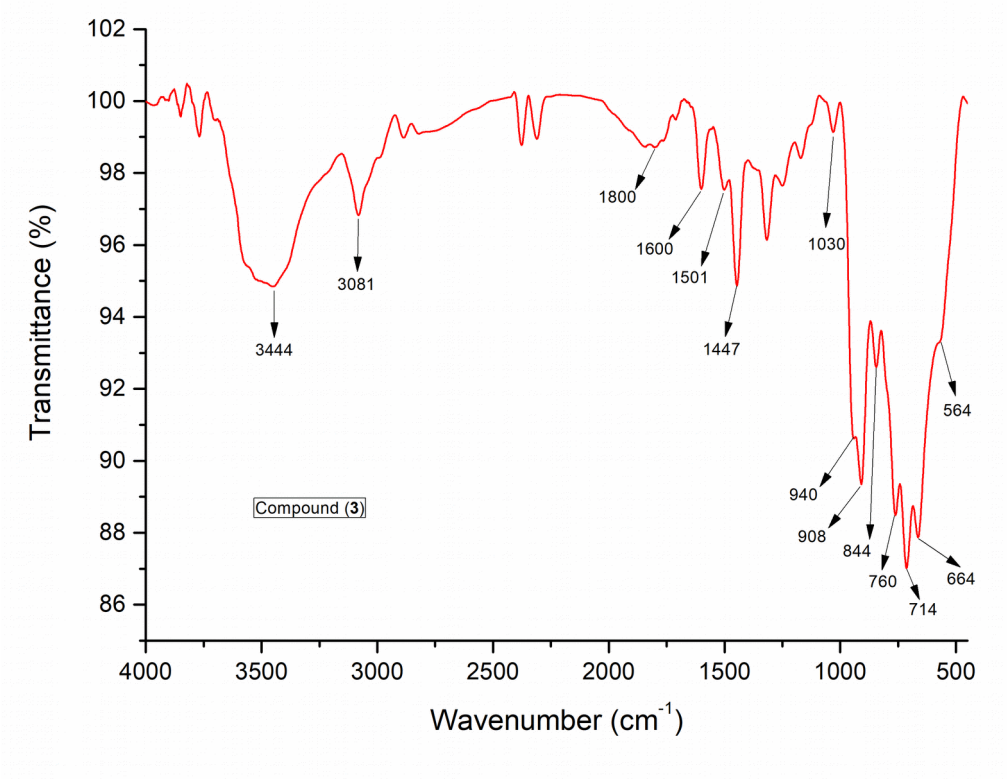


Figure S13 FT-IR for compound **3**.

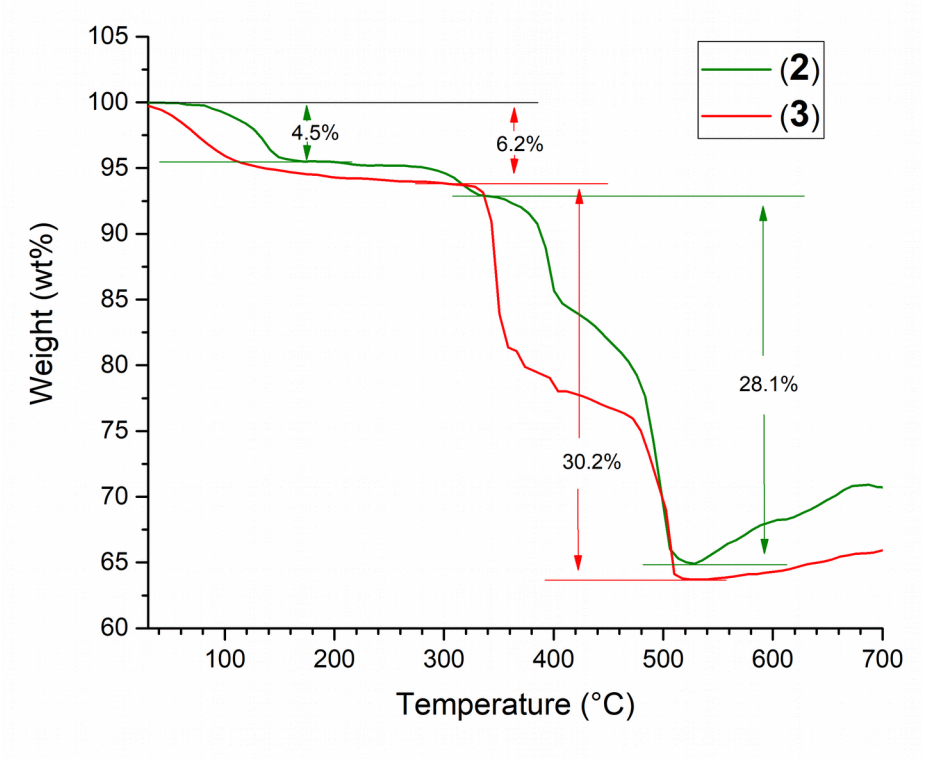


Figure S14 Thermal Gravimetric curves for compounds {$[NH_4^+]$**[Co(bpy)$_3$][(γ-Mo$_8$O$_{26}$)$_{0.5}$(β-Mo$_8$O$_{26}$)$_{0.5}$]}·4H$_2$O (2)** and **{[Co(bpy)$_3$]$_2$[(β-Mo$_8$O$_{26}$)$_{0.5}$(β-Mo$_8$O$_{26}$)]}·12H$_2$O (3).**

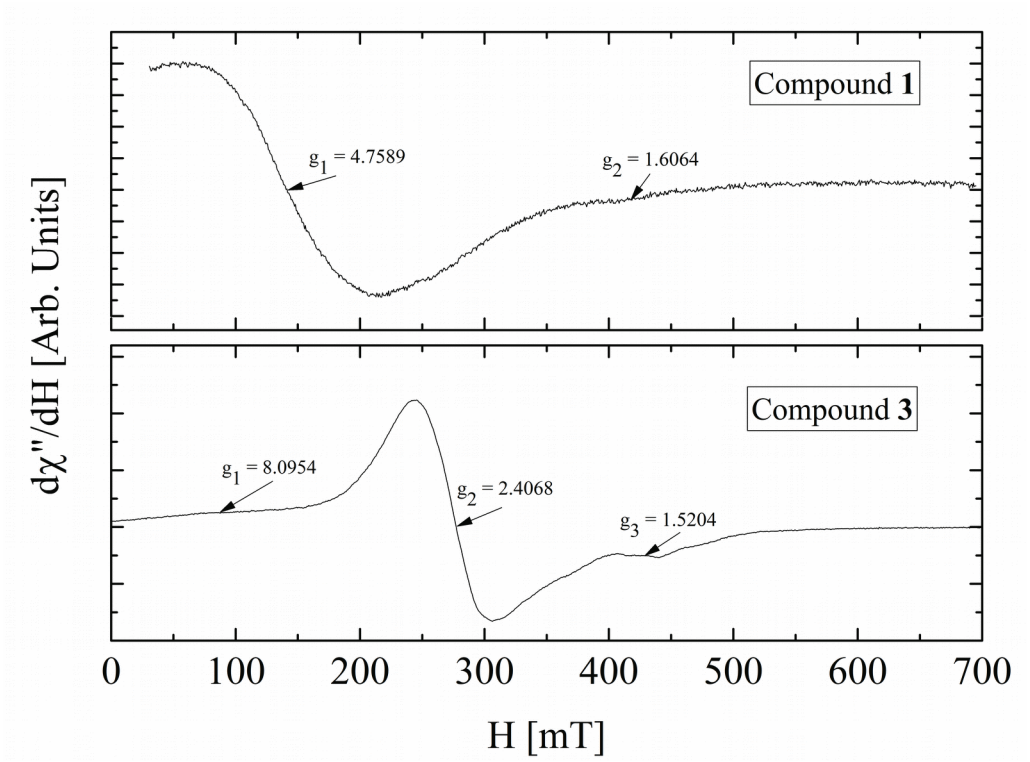


Figure S15 Room temperature EPR spectra for **1** and **3**.

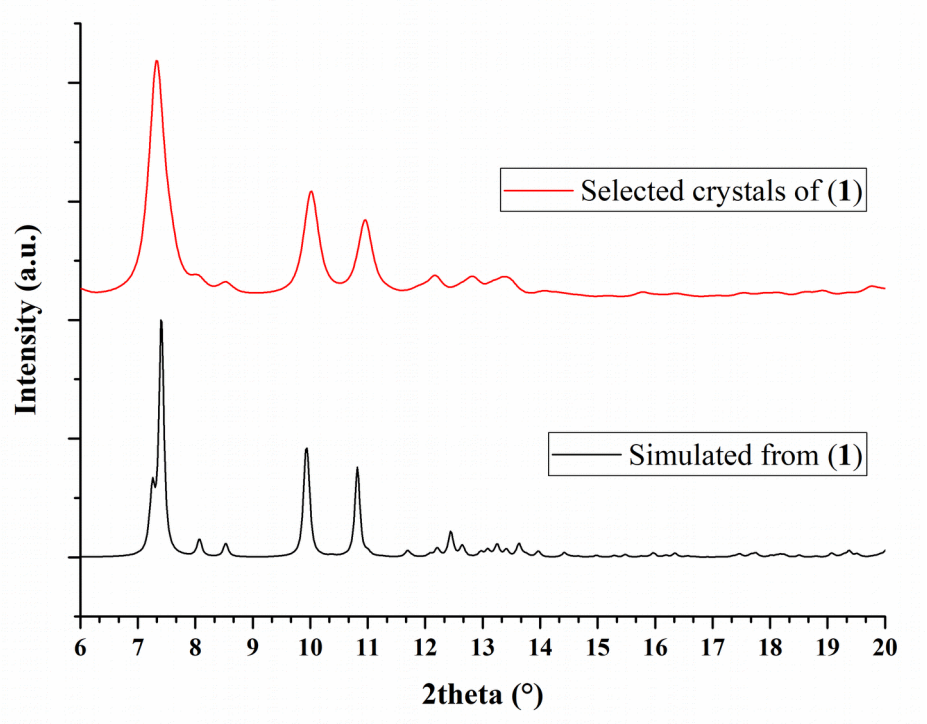


Figure S16 Comparison of P-XRD simulated from SC-XRD of **1** (black) *vs*. P-XRD of selected crystals of **1** (red).

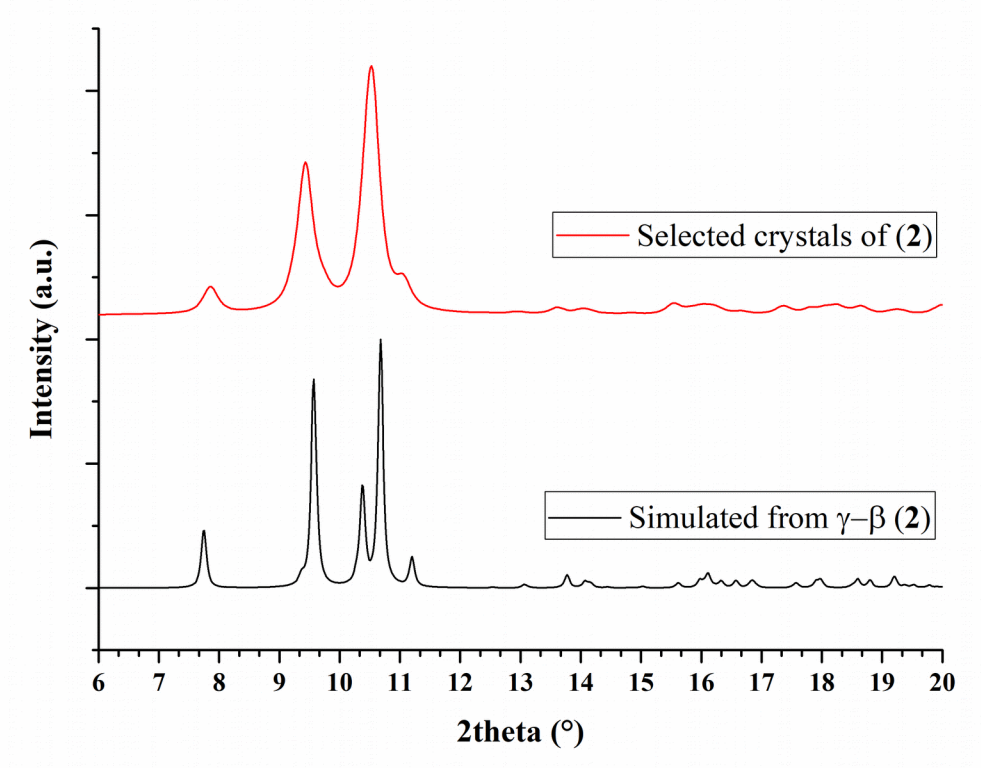


Figure S17 Comparison of P-XRD simulated from SC-XRD of **2** (black) *vs*. P-XRD of selected crystals of **2** (red).

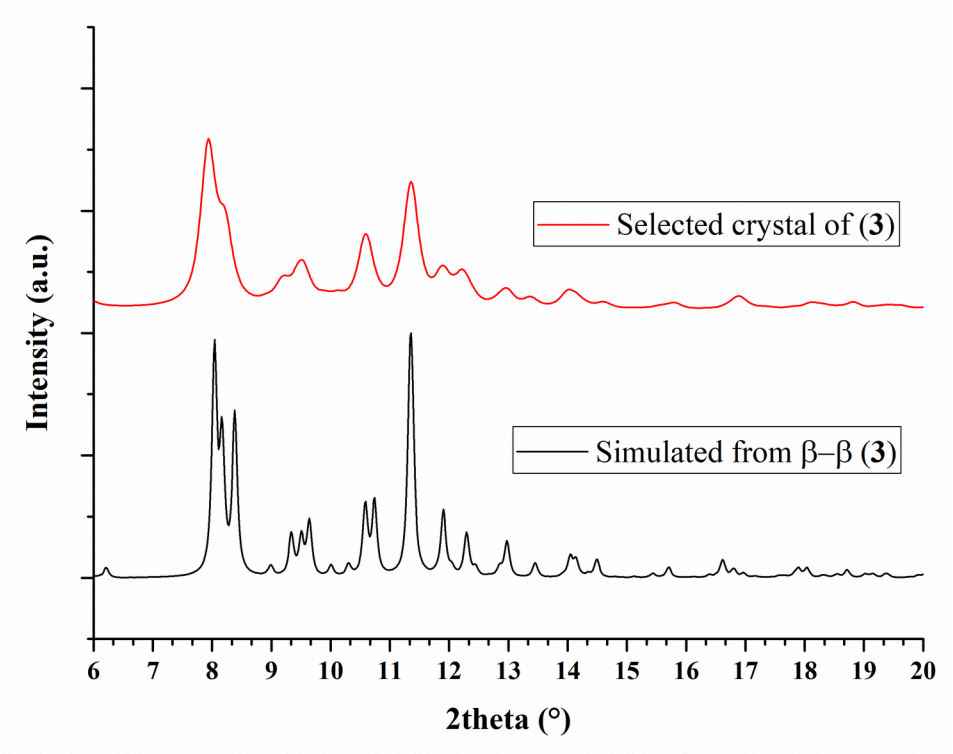


Figure S18 Comparison of P-XRD simulated from SC-XRD of **3** (black) *vs*. P-XRD of selected crystals of **3** (red).