Supplementary Materials: A Zn(II) Metallocycle as Platform to Assemble a 1D + 1D → 1D Polyrotaxane via π···π Stacking of an Ancillary Ligand

Marzio Rancan, Giada Truccolo, Alice Carlotto, Silvio Quici and Lidia Armelao

Single Crystal X-Ray Diffraction

The data were collected using an Oxford Diffraction Gemini E diffractometer (Oxford Diffraction, Oxfordshire, England), equipped with a 2K × 2K EOS CCD area detector and sealed-tube Enhance (Mo) and (Cu) X-ray sources. The single crystals of compounds were fastened on the top of a Lindemann glass capillary. The data were collected by means of the ω-scans technique using graphite-monochromated radiation. The detector distance was set at 45 mm. The diffraction intensities were corrected for Lorentz/polarization effects as well as with respect to the absorption. The empirical multi-scan absorption corrections using equivalent reflections were performed with the scaling algorithm SCALE3 ABSPACK. The data reduction, finalization and cell refinement were carried out through the CrysAlisPro software (1.171.38.46, Rigaku Oxford Diffraction, Rigaku Corporation, Oxford, UK). The accurate unit cell parameters were obtained by least squares refinement of the angular settings of the strongest reflections, chosen from the whole experiment. The structures were solved with *Olex2* [1] by using *ShelXT* [2] structure solution program by Intrinsic Phasing and refined with the *ShelXL* [3] refinement package using least-squares minimization. In the last cycles of refinement, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculated positions, and a riding model was used for their refinement. In $\{[Zn_2L_2(MeOH)_2] \cdot 2(CHCl_3)\}$ and $\{[Zn_2L_2(EtOH)_2] \cdot 2(CHCl_3)\}$, the two $CHCl_3$ molecules were heavily disordered. Their contribution to the residual electron density was removed using the *Olex2* [1] mask routine. For $\{[Zn_2L_2(MeOH)_2] \cdot 2(CHCl_3)\}$, the program calculated a total solvent accessible volume/cell of 322.6 $Å^3$ (21.1%) and a total electron-count/cell of 113 electrons. Such value is in perfect agreement with the presence of two $CHCl_3$ molecules (116 electrons). For $\{[Zn_2L_2(EtOH)_2] \cdot 2(CHCl_3)\}$, the program calculated a total solvent accessible volume/cell of 263.5 $Å^3$ (17 %) and a total electron-count/cell of 107 electrons. Such value is in good agreement with the presence of two $CHCl_3$ molecules (116 electrons).

Powder X-Ray Diffraction (PXRD)

PXRD pattern was collected with a Bruker D8 Advance diffractometer, in Bragg−Brentano geometry, using Cu Kα X-ray source. The patterns were acquired in the 7−30° 2θ range (0.03°/step and 10 s/step). Powder pattern indexing has been performed with the N-TREOR [4] program in the framework of EXPO2014 [5].

[Zn₂L₂(EtOH)₂] (3)

(a)

(b)

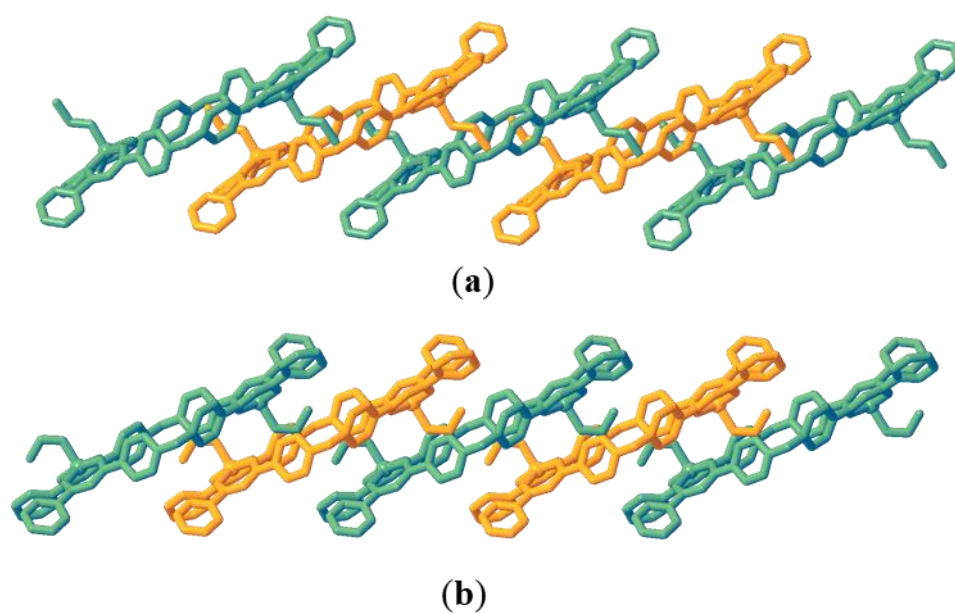**Figure S1.** H-bond supported 1D chain highlighting the two different orientation of the coordinated EtOH molecules.
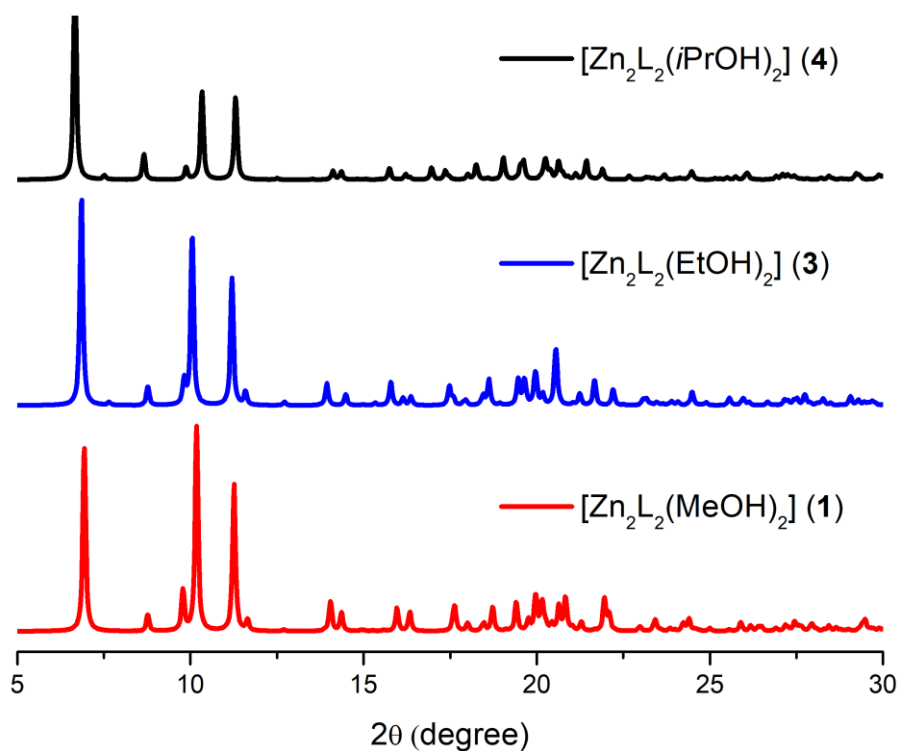
[Zn₂L₂(iPrOH)₂] (4)

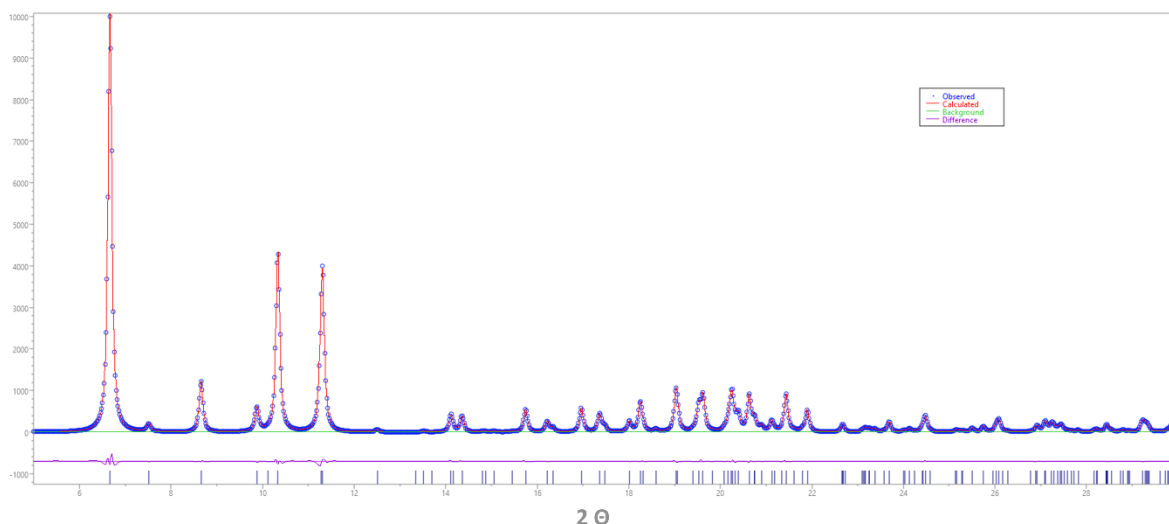**Figure S2.** PXRD patterns of [Zn₂L₂(MeOH)₂] (**1**), [Zn₂L₂(EtOH)₂] (**3**) and [Zn₂L₂(*i*PrOH)₂] (**4**).

Figure S3. Powder pattern indexing of [Zn$_2$L$_2$(iPrOH)$_2$]. Color code: observed data, blue circle; calculated pattern, red line; background, green line; difference, purple line.

Table S1. Unit cell of [Zn$_2$L$_2$(*i*PrOH)$_2$].

	Space Group	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	Volume (Å^3)
[Zn$_2$L$_2$(bipy)]$_n$ **PXRD**	P-1	9.780(3)	13.019(3)	14.0608(3)	99.169(2)	102.608(2)	110.764(2)	1577.77(8)

[Zn$_2$L$_2$(bipy)]$_n$
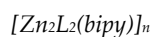
Synthesis

A DMF solution (1 ml) of bipy (4 mg, 0.025 mmol) has been added to a DMF solution (5 ml) of {[Zn$_2$L$_2$](MeOH)$_2$} (16 mg, 0.015 mmol). The instantaneous precipitation of a white solid was observed, and it was recovered by filtration and washed with methanol. Yield: 95 %. Elemental analysis expected for [Zn$_2$L$_2$(bipy)]$_n$: C 71.83 %, H 4.35 %, N 2.33 %. Elemental analysis found C 71.75 %, H 4.43 %, N 2.29 %.

Despite several efforts to grow single crystals suitable for X-ray diffraction studies, only microcrystalline material was obtained. The obtained product was analysed by PXRD and its diffraction pattern compared with the simulated pattern of [Cu$_2$L$_2$(bipy)]$_n$. Despite strong similarities, there are some minor, but important differences that lead to exclude that [Zn$_2$L$_2$(bipy)]$_n$ is isostructural with [Cu$_2$L$_2$(bipy)]$_n$, as confirmed by the comparison of their unit cells.
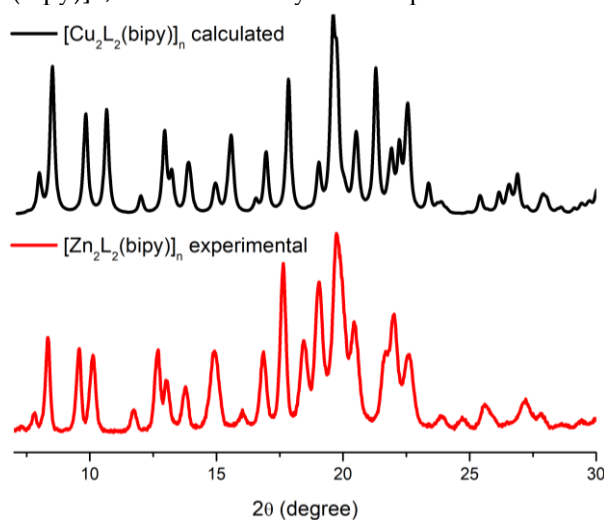
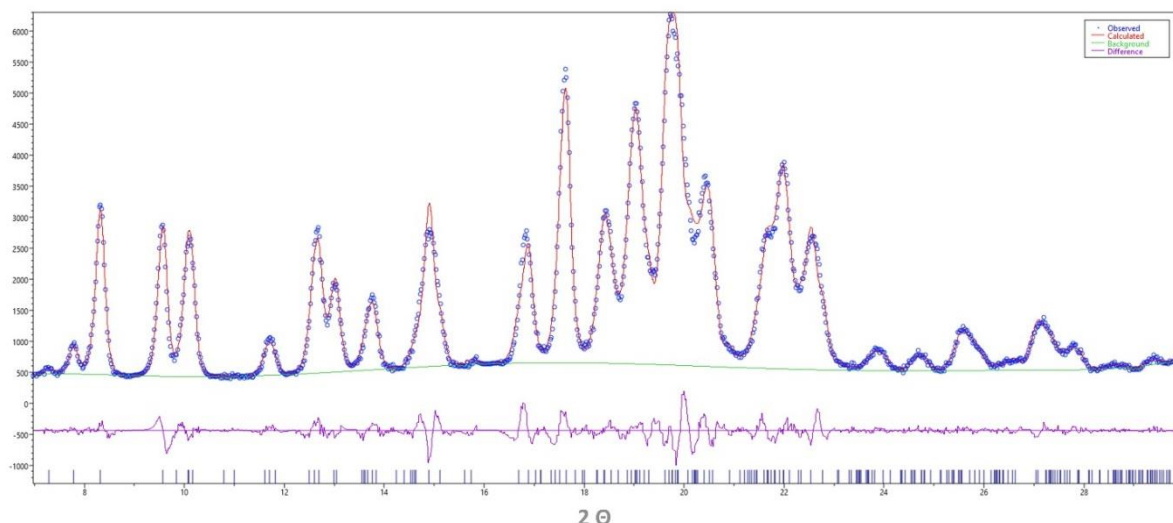**Figure S4.** PXRD patterns of [Zn$_2$L$_2$(bipy)]$_n$ (experimental) and [Cu$_2$L$_2$(bipy)]$_n$ (calculated).

Figure S5. Powder pattern indexing of [Zn$_2$L$_2$(bipy)]$_n$. Color code: observed data, blue circle; calculated pattern, red line; background, green line; difference, purple line.

Table S2. unit cell of [Zn$_2$L$_2$(bipy)]$_n$ and [Cu$_2$L$_2$(bipy)]$_n$.

	Space Group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å^3)
[Zn$_2$L$_2$(bipy)]$_n$ PXRD	P-1	9.673(2)	14.576 (3)	21.616(2)	83.501(1)	100.023(2)	105.065(2)	3148.95(10)
[Cu$_2$L$_2$(bipy)]$_n$ single crystal [7]	P-1	9.7072(5)	12.5827(7)	13.7631(8)	63.589(6)	70.337(5)	76.509(5)	1410.82(16)

References

1. Dolomanov, O. V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *OLEX2* : a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341, 10.1107/S0021889808042726.

2. Sheldrick, G.M.; IUCr *SHELXT*—Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8, 10.1107/S2053273314026370.

3. Sheldrick, G.M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8, 10.1107/S2053229614024218.

4. Altomare, A.; Campi, G.; Cuocci, C.; Eriksson, L.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Werner, P.E. Advances in powder diffraction pattern indexing: N-TREOR09. *J. Appl. Crystallogr.* **2009**, *42*, 768–775, 10.1107/S0021889809025503.

5. Altomare, A.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Corriero, N.; Falcicchio, A. EXPO2013: A kit of tools for phasing crystal structures from powder data. *J. Appl. Crystallogr.* **2013**, *46*, 1231–1235, 10.1107/S0021889813013113.