Self-assembly of *bis*-**β**-diketone-based $[M_2L_2]$ dinuclear platforms into 2-dimensional coordination polymers.

A. J. Brock[a,b], John C. McMurtrie[b] and J. K. Clegg[a*]

School of Chemistry and Molecular Biosciences, The University of Queensland, St. Lucia, QLD, Australia 4072.

School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, 2 George Street, Brisbane, QLD, Australia 4000

Electronic Supplementary Information (ESI)

S1. SCXRD refinement tables and details

	H_2L^1	$[Pd_2L^1_2]$
Empirical formula	$C_{19}H_{25}NO_4$	$C_{38}H_{46}N_2O_8Pd_2$
Formula weight	331.40	871.57
Temperature/K	190	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\text{-}1$
a/Å	6.2281(5)	5.7610(12)
b/Å	19.4672(19)	9.921(2)
c/Å	15.2664(13)	16.902(3)
α/°	90	75.20(3)
β/°	95.993(8)	88.40(3)
γ/°	90	74.52(3)
Volume/Å^3	1840.8(3)	899.2(4)
Z	4	1
ρ_{calc}g/cm^3	1.196	1.609
μ/mm^{-1}	0.677	1.055
F(000)	640	444
Crystal size/mm^3	0.5 × 0.2 × 0.2	0.05 x 0.2 x 0.2
Radiation	CuKα (λ = 1.54184)	synchrotron (λ = 0.7108)
2Θ range for data collection/°	7.384 to 130.312	4.41 - 52.746
Index ranges	$-7 \le h \le 6$, $-22 \le k \le 18$, $-17 \le l \le 17$	$-7 \le h \le 7$, $-11 \le k \le 12$, $-10 \le l \le 21$
Reflections collected	5919	3298
Independent reflections	3073 [R_{int} = 0.0255, R_{sigma} = 0.0426]	3298 [R_{int} = 0.0316]
Data/restraints/parameters	3073/74/294	3298/213/252
Goodness-of-fit on F^2	1.051	1.214
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1489	R_1 = 0.1386, wR_2 = 0.4017
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1692	R_1 = 0.1391, wR_2 = 0.4018
Largest diff. peak/hole / e Å^{-3}	0.34/-0.20	3.53/-4.36

	$\{[Zn_2L^1_2]_n \cdot dmf_n\}$	$\{[Cu_2L^1_2]_n \cdot dmf_n\}$
Empirical formula	$C_{38}H_{44}N_2O_8Zn_2$	$C_{38}H_{46}Cu_2N_2O_8$
Formula weight	787.36	785.85
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	16.584(3)	16.234(3)
b/Å	11.077(2)	11.130(2)
c/Å	12.668(3)	12.499(3)
α/°	90	90
β/°	107.26(3)	105.22(3)
γ/°	90	90
Volume/Å^3	2222.3(8)	2179.1(8)
Z	4	2
ρ_{calc}g/cm^3	1.177	1.198
μ/mm^{-1}	1.123	1.021
F(000)	820	820
Crystal size/mm^3	0.5 × 0.5 × 0.5	0.1 × 0.05 × 0.02
Radiation	synchrotron (λ = 0.7108)	synchrotron (λ = 0.7108)
2Θ range for data collection/°	4.488 to 52.744	4.49 to 54.208
Index ranges	$-20 \le h \le 20$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-20 \le h \le 20$, $-14 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	30449	31832
Independent reflections	4349 [R_{int} = 0.1110, R_{sigma} = 0.0516]	4471 [R_{int} = 0.0372, R_{sigma} = 0.0209]
Data/restraints/parameters	4349/0/284	4471/0/264
Goodness-of-fit on F^2	1.075	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0851, wR_2 = 0.1892	R_1 = 0.0318, wR_2 = 0.0870
Final R indexes [all data]	R_1 = 0.1072, wR_2 = 0.2078	R_1 = 0.0325, wR_2 = 0.0876
Largest diff. peak/hole / e Å^{-3}	0.86/-0.75	0.41/-0.42

Specific Refinement Details

[$Pd_2\mathbf{L}^1{}_2$]

The crystals obtained were very small plates which were difficult to manually separate. Synchrotron radiation was required to obtain suitable diffraction data and because of the instrument design we were limited to a single 360 ° phi scan. The diffraction pattern obtained, however, was still significantly broadened indicative of some degree of twinning and the structure was refined as a two component twin (180 ° rotation about 0 0 1) with approximate twin fractions of 0.57 and 0.43. After refinement, however, there still remains some evidence of further unresolved twinning indicated by large residual peaks in chemically unreasonable positions, which result in higher than ideal statistics. A number of rigid bodies and restraints were required to facilitate realistic modelling particularly in the pyridyl ring and the disordered tertiary butyl group. The connectivity of the structure is unambiguous.

{[$Zn_2\mathbf{L}^1{}_2$]$_n$·dmf_n} and *{[$Cu_2\mathbf{L}^1{}_2$]$_n$·dmf_n}*

During the refinement of the crystal structures of {[$Zn_2\mathbf{L}^1{}_2$]$_n$·dmf_n} and {[$Cu_2\mathbf{L}^1{}_2$]$_n$ ·dmf_n} a region of disordered electron density was observed across a point of inversion. Despite many attempts to refine this as a disordered DMF solvent molecule no reasonable model was obtained. The region of electron density was therefore masked using Olex2.[1] For {[$Zn_2\mathbf{L}^1{}_2$]$_n$ ·dmf_n}, the electron density correlated to 73.2 electrons and for {[$Cu_2\mathbf{L}^1{}_2$]$_n$·dmf}$_n$, the electron density correlated to 80.0 electrons. This is in good agreement with the 73 electrons associated with a single full-occupancy DMF molecule.

S2. Topology[2]

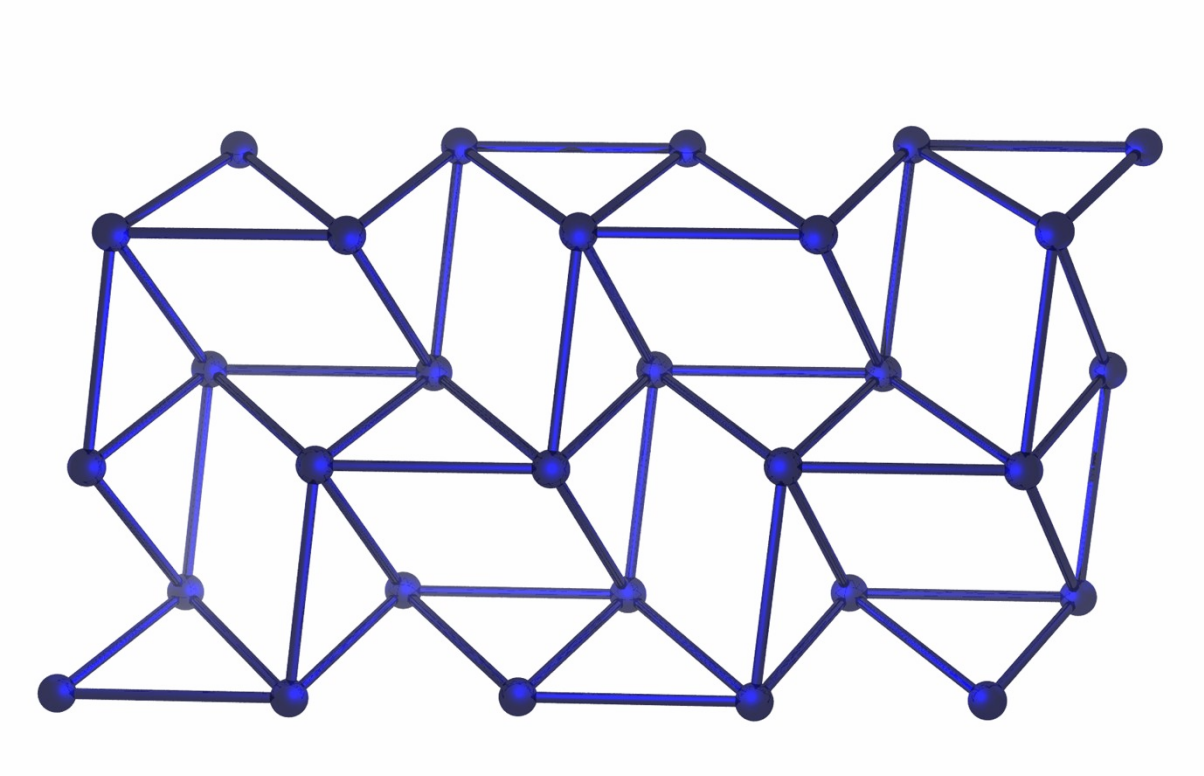

Figure S1. Topological diagram derived from crystal structure of $[Zn_2\mathbf{L^1}]_n$ and $[Cu_2\mathbf{L^1}]_n$, showing **tts** topology. Metal atoms are shown as blue spheres.

S3. References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
2. V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576.