

Supplementary Material

Chiral 1-D coordination polymer chains featuring 1,1'-binaphthyl

Hui Min Tay^{A,B}, Shannon Thoonen^{A,C} and Carol Hua^{A,*}

^ASchool of Chemistry, The University of Melbourne, Parkville, Vic. 3010, Australia

^BDepartment of Chemistry, University of Oxford, Oxford, OX1 3TA, UK

^CSchool of Chemistry, Monash University, Clayton, Vic. 3800, Australia

*Correspondence to: Email: carol.hua@unimelb.edu.au

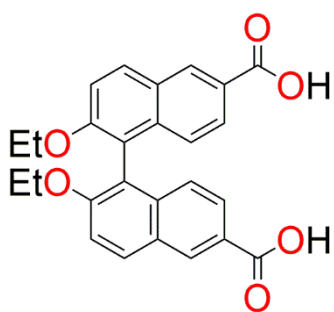
Additional ligand synthesis details

Protection of the alcohol group

Protection of the alcohol group with an ethoxy group was conducted using a literature method.¹ The binaphthol starting material was added to a solution of sodium iodide (0.1 eq), potassium carbonate (5 eq.) and bromoethane (6 eq.) in acetone (~0.1 mM). The reaction mixture was heated to reflux and stirred overnight before being cooled to room temperature and filtered. The solvent was removed from the filtrate and the residue washed with hexane before being air dried to yield the product.

(R)-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene. Obtained as a cream solid in 83% yield. ¹H NMR (CDCl₃, 400 MHz) 7.99 (br s, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.24 (d, *J* = 8 Hz, 1H) 6.93 (d, *J* = 8 Hz, 1H), 4.02 (q, *J* = 8 Hz, 2H), 1.04 (t, *J* = 8 Hz, 3H) ppm.

(S)-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene. Obtained as a cream solid in 84% yield. ¹H NMR (CDCl₃, 400 MHz) 7.98 (br s, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.23 (d, *J* = 8 Hz, 1H) 6.94 (d, *J* = 8 Hz, 1H), 4.01 (q, *J* = 8 Hz, 2H), 1.04 (t, *J* = 8 Hz, 3H) ppm.



(S)-6,6'-dicarboxyl-2,2'-diethoxy-1,1'-binaphthalene was synthesised according to literature methods.^{2,3} (S)-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene (2.0 g, 4.0 mmol) was dissolved in dry THF (50 mL) and cooled to -78°C in a dry ice/acetone bath. ⁿBuLi (5.2 mL, 1.5-M solution in cyclohexane, 8.2 mmol) was added dropwise to yield a colour change from pale yellow to orange before a few small chunks of dry ice (~1 g) were added. The reaction mixture (a white suspension) was allowed to gradually warm to room temperature before being quenched by the careful addition of HCl (1 M, ~5 mL) which

resulted in bubbling of the reaction mixture and a pale yellow solution. The organic layer was separated and the product extracted using ethyl acetate (2 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered and the solvent removed to yield a white solid that was further purified by column chromatography (3:1 EtOAc: hexane with 5% acetic acid)

(S)-6,6'-dicarboxyl-2,2'-diethoxy-1,1'-binaphthalene. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.60 (s, 2H), 8.63 (br s, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 7.71–7.66 (m, 4H), 6.98 (d, *J* = 9.0 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 4H), 1.00 (t, *J* = 7.0 Hz, 6H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 172.1, 167.6, 155.9, 135.5, 131.2, 127.7, 126.5, 125.6, 124.8, 118.5, 115.9, 64.2, 14.7 ppm.

Table S1. Crystallographic parameters for the 1-D chains **1–4**.

Compound	[Ni(<i>R</i>)- L ₁) ₂ (H ₂ O) ₂] (1)	[Cu(<i>R</i>)- L ₁) ₂ (H ₂ O) ₂] (2)	[Cu ₂ (<i>S</i>)- L ₂) ₂ (DMF) ₂]·2H ₂ O (3)	[Ag(<i>R</i>)-L ₁] (4)
Formula	C ₆₈ H ₆₀ N ₄ NiO ₆	C ₆₈ H ₅₀ CuN ₄ O ₆	C ₅₈ H ₅₃ Cu ₂ N ₂ O ₁₄	C ₃₄ H ₂₈ AgN ₂ O ₂
Formula Weight	1087.91	1082.66	1129.10	604.45
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2	<i>I</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	12.954(3)	12.662(3)	19.2270(4)	9.1110(18)
<i>b</i> (Å)	16.633(3)	16.357(3)	25.6841(3)	21.143(4)
<i>c</i> (Å)	18.387(4)	18.472(4)	13.9888(2)	33.432(7)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
Cell Volume (Å ³)	3961.7(14)	3825.8(13)	6908.06(19)	6440(2)
<i>Z</i>	2	2	4	8
ρ _{calc} (g cm ⁻³)	0.912	0.940	1.086	1.247
μ mm ⁻¹	0.286	0.328	1.204	0.655
F(000)	1144.0	1126.0	2340.0	2472.0
Crystal size mm ⁻³	0.1 × 0.08 × 0.03	0.18 × 0.18 × 0.17	0.195 × 0.079 × 0.075	0.21 × 0.15 × 0.05
Radiation	Synchrotron (λ = 0.710750)	Synchrotron (λ = 0.710750)	CuKα (λ = 1.54178)	Synchrotron (λ = 0.710755)
Reflections collected	73001	65954	30378	55345
Independent reflections	12179	11389	12824	8573
Data/restraints/parameters	[R _{int} = 0.0298, R _{sigma} = 0.0170]	[R _{int} = 0.0832, R _{sigma} = 0.0471]	[R _{int} = 0.0416, R _{sigma} = 0.0476]	[R _{int} = 0.1040, R _{sigma} = 0.0684]
GooF	12179/0/348	11389/0/348	12824/118/656	8573/0/355
GooF	1.055	0.936	1.086	0.992
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0719, <i>wR</i> ₂ = 0.2388	<i>R</i> ₁ = 0.0867, <i>wR</i> ₂ = 0.2531	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.1453	<i>R</i> ₁ = 0.0887, <i>wR</i> ₂ = 0.2573
<i>R</i> ₁ , <i>wR</i> ₂ (all)	<i>R</i> ₁ = 0.0818, <i>wR</i> ₂ = 0.2583	<i>R</i> ₁ = 0.1297, <i>wR</i> ₂ = 0.2967	<i>R</i> ₁ = 0.0683, <i>wR</i> ₂ = 0.1695	<i>R</i> ₁ = 0.1029, <i>wR</i> ₂ = 0.2708
Largest diff. peak/hole/eÅ ⁻³	0.56/−0.97	0.80/−0.62	0.91/−0.97	1.06/−1.01
Flack parameter	0.013(5)	−0.002(11)	−0.006(13)	−0.005(17)

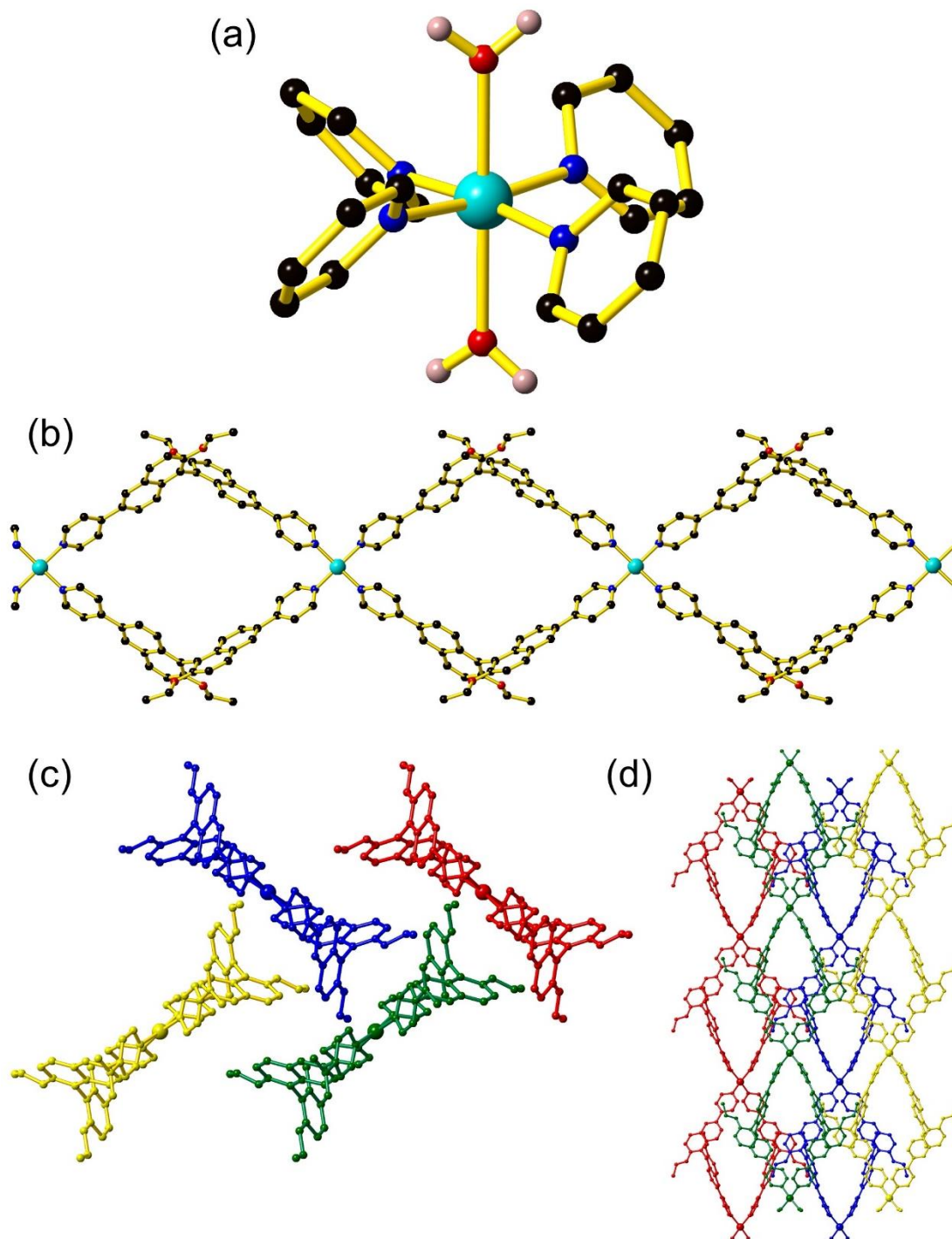


Figure S1. Crystal structure of $[\text{Cu}((R)\text{-L}_1)_2(\text{H}_2\text{O})_2]$ (**2**) showing (a) the coordination environment around Cu^{II} , (b) the 1-D chain, stacking of the 1-D chain as viewed down the (c) c axis and (d) b axis.

Table S2. Analysis of the possible coordination geometries using the SHAPE program for the 6-coordinate M^{II} centres in frameworks **1–2**.

Geometry	Symmetry	1 (Ni)	2 (Cu)
HP-6	D _{6h}	32.666	32.349
PPY-6	C _{5v}	28.366	27.224
OC-6	O _h	0.116	1.056
TPR-6	D _{3h}	15.418	15.618
JPPY-6	C _{5v}	31.940	30.169

HP-6, Hexagon; PPY-6, Pentagonal pyramid; OC-6, Octahedron; TPR-6, Trigonal prism; JPPY-6, Johnson pentagonal pyramid 32. The minima values are indicated in bold.

Table S3. Analysis of the possible coordination geometries using the SHAPE program for the 5-coordinate Cu^{II} centres in frameworks **3**.

Geometry	Symmetry	3 (Cu)
PP-5	D _{5h}	32.498
vOC-5	C _{4v}	0.652
TBPY-5	D _{3h}	5.148
SPY-5	C _{4v}	0.453
JTBPY-5	D _{3h}	7.980

PP-5, Pentagon; vOC-5, Vacant octahedron; TBPY-5, Trigonal bipyramid; SPY-5, Spherical square pyramid; JTBPY-5, Johnson trigonal bipyramid J12. The minima value is indicated in bold.

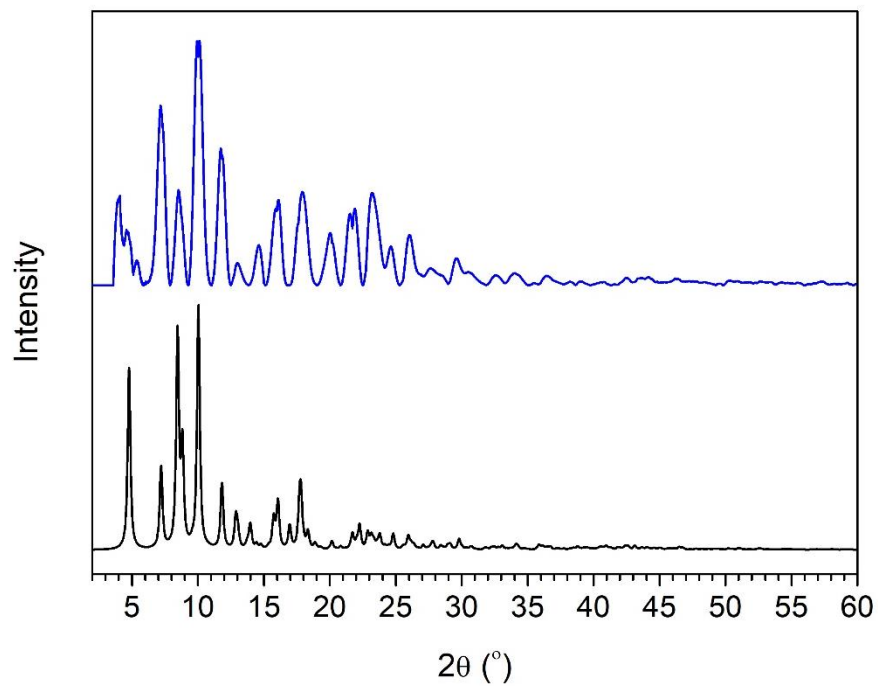


Figure S2. PXRD of [Ni((*R*)-L₁)₂(H₂O)₂] (**1**) (blue) between 5 and 60° 2θ versus the calculated pattern (black).

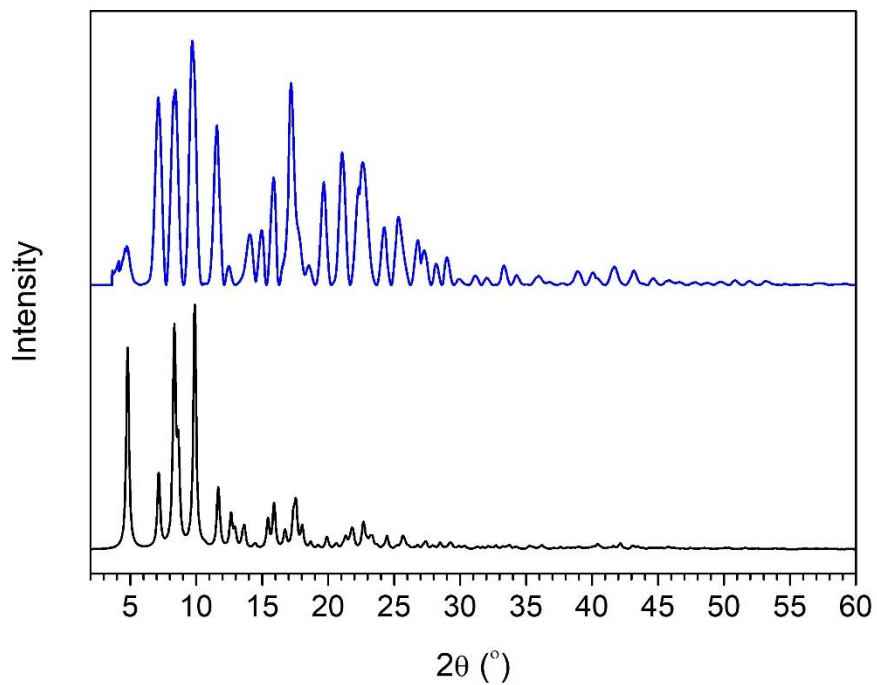


Figure S3. PXRD of [Cu((*R*)-L₁)₂(H₂O)₂] (**2**) (blue) between 5 and 60° 2θ versus the calculated pattern (black).

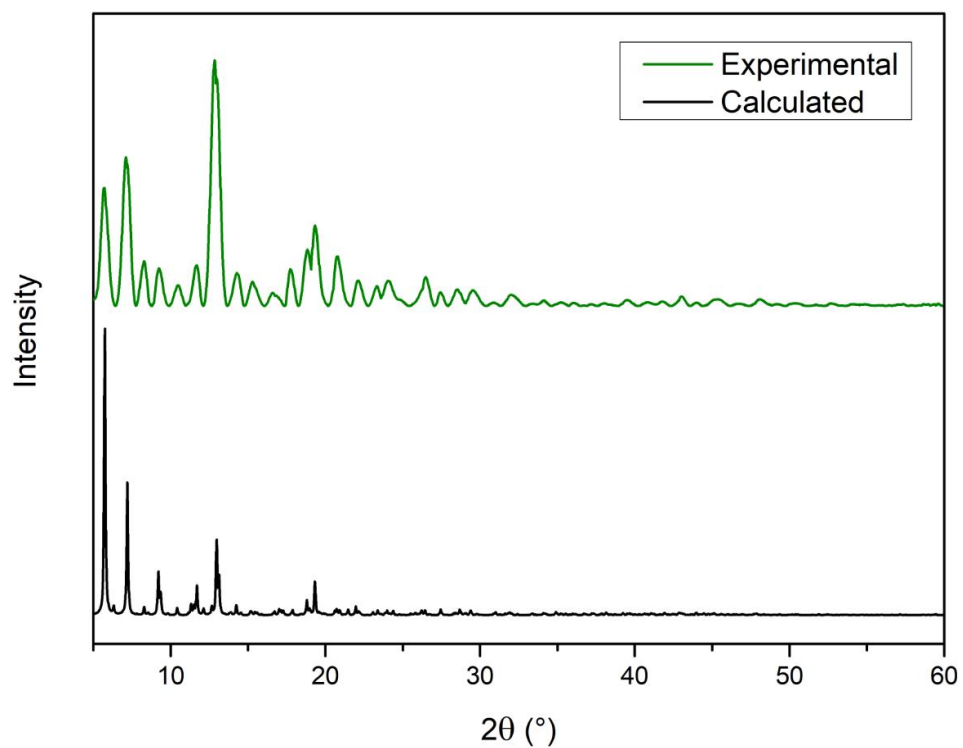


Figure S4. PXRD of $[\text{Cu}_2((S)\text{-L}_2)_2(\text{DMF})_2]\cdot 2\text{H}_2\text{O}$ (**3**) (green) between 5 and 60° 2θ versus the calculated pattern (black).

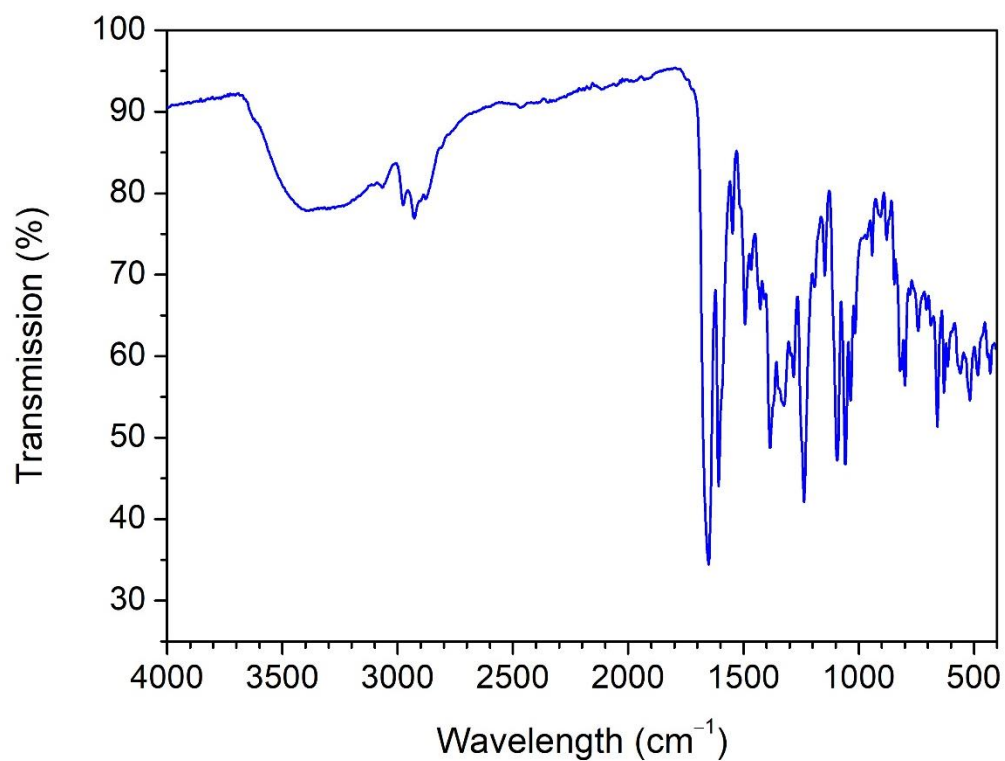


Figure S5. ATR IR spectra of $[\text{Ni}((R)\text{-L}_1)_2(\text{H}_2\text{O})_2]$ (**1**) between 4000 and 400 cm^{-1} .

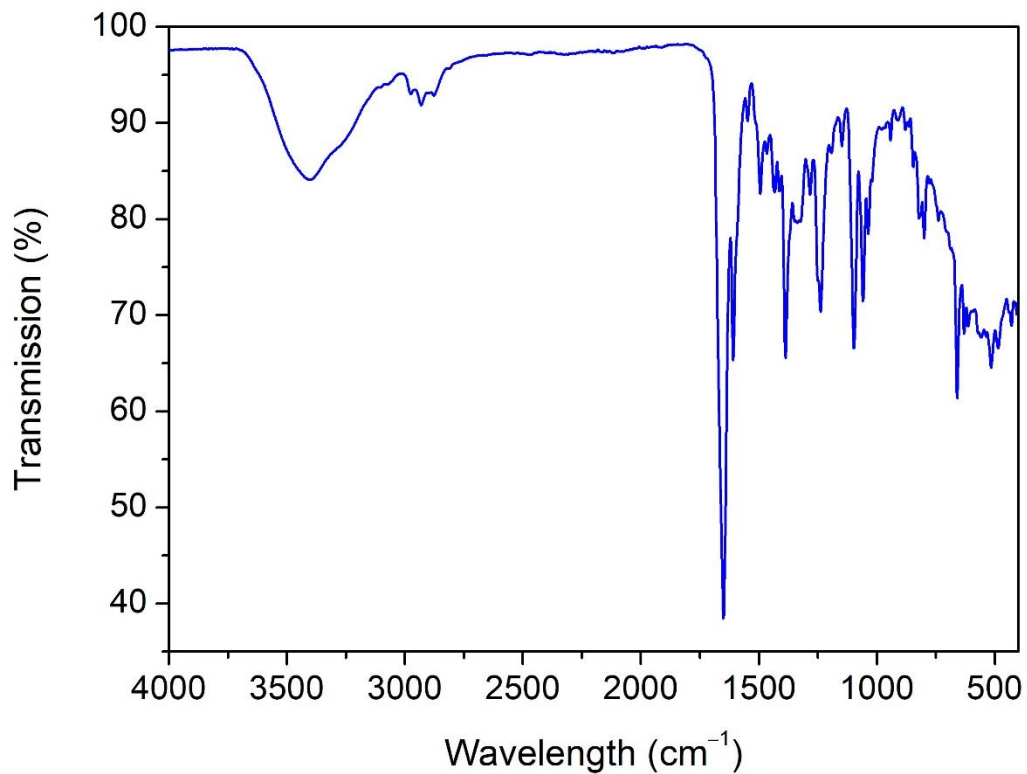


Figure S6. ATR IR spectra of $[\text{Cu}((R)\text{-L}_1)_2(\text{H}_2\text{O})_2]$ (**2**) between 4000 and 400 cm^{-1} .

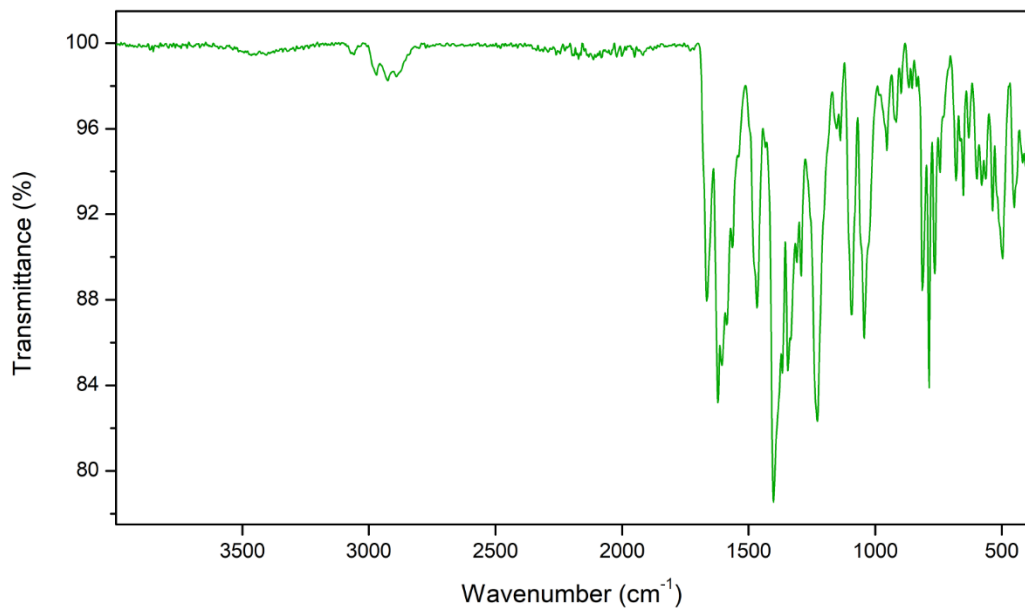


Figure S7. ATR IR spectra of $[\text{Cu}_2((S)\text{-L}_2)_2(\text{DMF})_2] \cdot 2\text{H}_2\text{O}$ (**3**) between 4000 and 400 cm^{-1} .

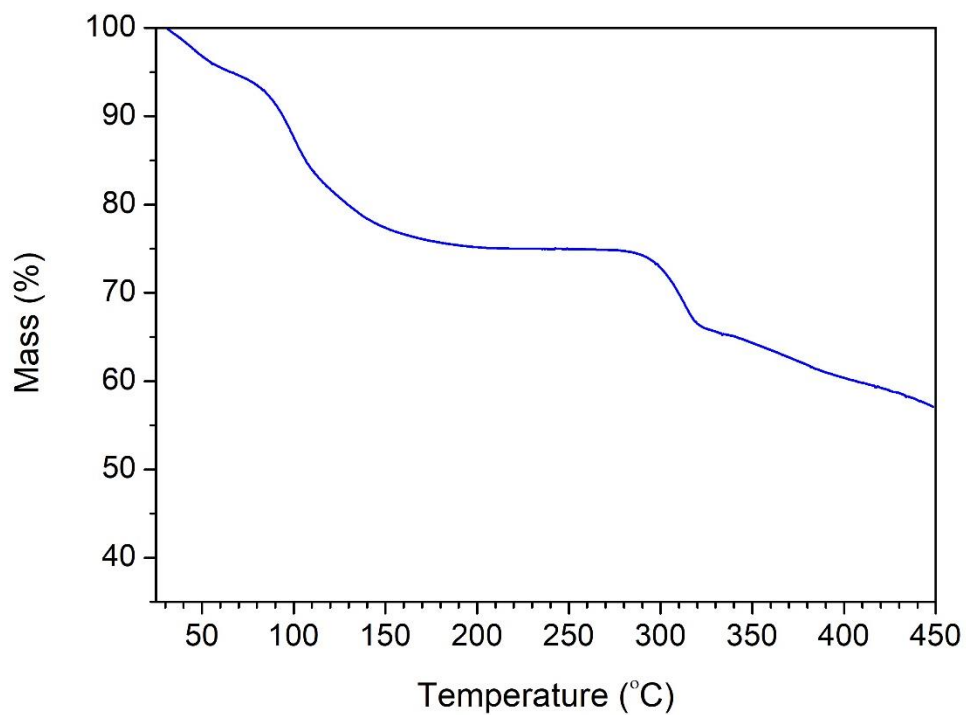


Figure S8. Thermal Gravimetric Analysis of $[\text{Ni}((R)\text{-L}_1)_2(\text{H}_2\text{O})_2]$ (**1**) between 25 and 450°C measured under nitrogen gas with a ramp rate of 5°C/min.

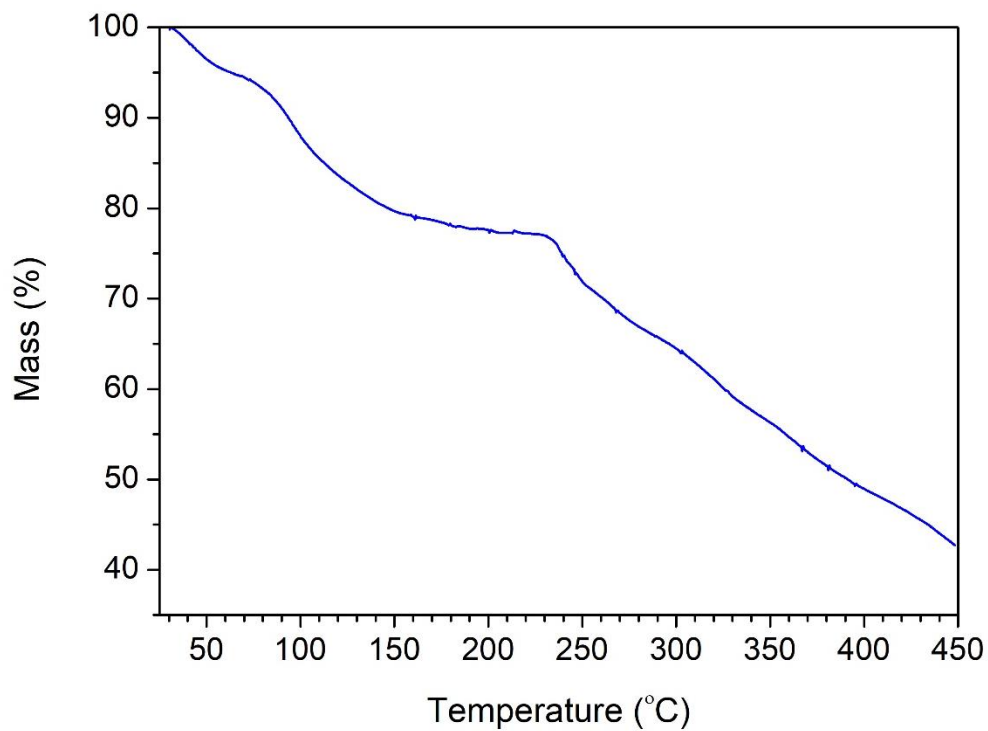


Figure S9. Thermal Gravimetric Analysis of $[\text{Cu}((R)\text{-L}_1)_2(\text{H}_2\text{O})_2]$ (**2**) between 25 and 450°C measured under nitrogen gas with a ramp rate of 5°C/min.

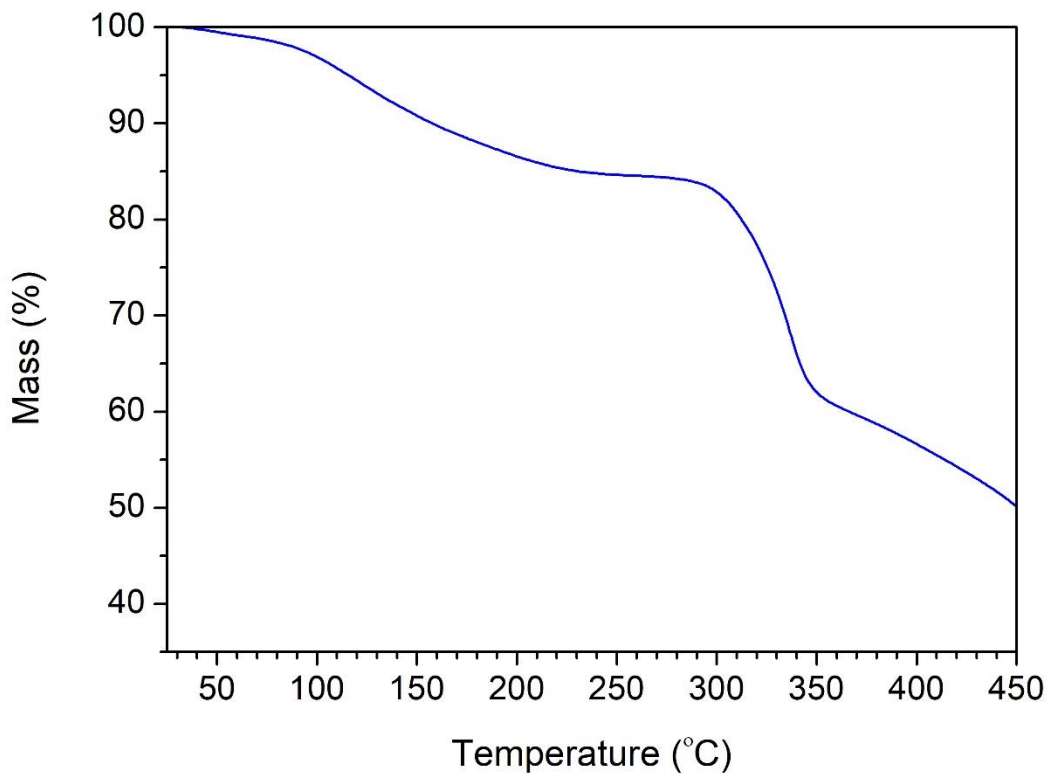


Figure S10. Thermal Gravimetric Analysis of [Cu₂((S)-L₂)₂(DMF)₂·2H₂O (3) between 25 and 450°C measured under nitrogen gas with a ramp rate of 5°C/min.

References

1. Q.-W. Zhang, D. Li, X. Li, P. B. White, J. Mecinović, X. Ma, H. Ågren, R. J. M. Nolte and H. Tian, *J. Am. Chem. Soc.*, **2016**, *138*, 13541-13550.
2. M. Seter, D. Dakternieks and A. Duthie, *Main Group Met. Chem.*, 2012, **35**, 73.
3. V. Alcázar, J. R. Morán and F. Diederich, *Isr. J. Chem.*, **1992**, *32*, 69-77.