Enantioselective chiral sorption of 1-phenylethanol by homochiral 1D coordination polymers

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Supporting Information

1. X-Ray Crystallography

1.1 Crystallographic Data

Compound reference	**1**	1-PE⊂**1**	**2**
Empirical formula	$C_{126}H_{124}Co_4N_{26}O_{41}$	$C_{128}H_{125.5}Co_4N_{26}O_{40.75}$	$C_{53}H_{60}Cl_2Co_2N_{13}O_{11.5}$
Formula weight	2894.22	2915.76	1251.9
Temperature/K	100.15	100	100.15
Crystal system	triclinic	triclinic	orthorhombic
Space group	*P*1	*P*1	$P2_12_12_1$
a/Å	13.779(3)	13.742(3)	15.344(3)
b/Å	14.632(3)	14.707(3)	18.543(4)
c/Å	19.730(4)	19.765(4)	20.358(4)
α/°	83.04(3)	83.45(3)	90
β/°	81.57(3)	81.70(3)	90
γ/°	62.69(3)	63.22(3)	90
Volume/Å^3	3489.6(15)	3523.5(15)	5792(2)
Z	1	1	4
ρ_{calc}g/cm^3	1.377	1.374	1.436
μ/mm^{-1}	0.556	0.551	0.736
F(000)	1498	1510	2596
Crystal size/mm^3	0.04 × 0.01 × 0.01	0.08 × 0.03 × 0.01	0.04 × 0.02 × 0.01
Radiation	Synchrotron (λ = 0.71088)	Synchrotron (λ = 0.71076)	Synchrotron (λ = 0.71088)
2Θ range/°	2.09 to 49.998	3.106 to 62.688	2.972 to 54.996
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -23 ≤ l ≤ 23	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28	-19 ≤ h ≤ 19, -24 ≤ k ≤ 24, -26 ≤ l ≤ 26
Reflections collected	65545	175375	183909
Independent reflections	23430 [R_{int} = 0.1255, R_{sigma} = 0.1194]	39847 [R_{int} = 0.0750, R_{sigma} = 0.0414]	13298 [R_{int} = 0.2071, R_{sigma} = 0.0634]
Data/restraints/ parameters	23430/103/1673	39847/53/1874	13298/1/738
GOOF on F^2	0.997	1.042	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0937, wR_2 = 0.2450	R_1 = 0.0544, wR_2 = 0.1614	R_1 = 0.1157, wR_2 = 0.3045
Final R indexes [all data]	R_1 = 0.1508, wR_2 = 0.2892	R_1 = 0.0632, wR_2 = 0.1728	R_1 = 0.1297, wR_2 = 0.3143
Largest diff. peak/hole / e Å^{-3}	1.07/-0.80	0.62/-0.64	1.41/-1.09
Flack parameter	0.103(13)	0.003(3)	0.064(7)

Table S1. Crystallographic and refinement parameters for all compounds. + Data treated using the SQUEEZE routine of PLATON.[1] *Data treated using the BYPASS routine of Olex2.[2]

1.2 Bond Tables

Bonds and long contacts with Co^{II}			Bond angles			
Atom 1	**Atom 2**	**Length (Å)**	**Atom 1**	**Atom 2**	**Atom 3**	**Angle (˚)**
Co1	O7	1.997(11)	O7	Co1	O31[1]	97.0(5)
Co1	O8	2.514(17)	O7	Co1	N3	103.9(6)
Co1	O31[1]	2.059(11)	O7	Co1	N7	107.3(5)
Co1	O32[1]	2.421(15)	N3	Co1	O31[1]	110.8(7)
Co1	N3	2.027(16)	N7	Co1	O31[1]	101.5(6)
Co1	N7	2.018(14)	N7	Co1	N3	131.3(7)
Co2	O9	2.024(12)	O9	Co2	O17	100.3(5)
Co2	O10	2.923(16)	O9	Co2	O18	161.2(6)
Co2	O17	2.104(10)	O17	Co2	O18	61.0(5)
Co2	O18	2.332(13)	N6	Co2	O9	104.9(6)
Co2	O24	2.831(12)	N6	Co2	O17	112.6(5)
Co2	N6	2.023(16)	N6	Co2	O18	83.2(6)
Co2	N10	1.993(17)	N10	Co2	O9	104.1(6)
			N10	Co2	O17	106.7(6)
			N10	Co2	O18	84.0(6)
			N10	Co2	N6	125.1(7)
Co3	O15	2.047(12)	O15	Co3	O16	58.2(5)
Co3	O16	2.377(12)	O15	Co3	C59	29.6(7)
Co3	O23	2.009(11)	O16	Co3	C59	28.7(6)
Co3	O24	2.831(12)	O23	Co3	O15	100.1(5)
Co3	N15	2.035(13)	O23	Co3	O16	157.9(5)
Co3	N19	2.037(12)	O23	Co3	N15	107.2(5)
Co3	C59	2.507(14)	O23	Co3	N19	103.7(5)
			O23	Co3	C59	129.6(7)
			N15	Co3	O15	102.6(5)
			N15	Co3	O16	84.0(4)
			N15	Co3	N19	126.8(6)
			N15	Co3	C59	93.1(5)
			N19	Co3	O15	113.4(5)
			N19	Co3	O16	83.2(5)
			N19	Co3	C59	99.3(6)
Co4	O1[2]	2.068(11)	O1[2]	Co4	O2[2]	57.1(4)
Co4	O2[2]	2.408(11)	O25	Co4	O1[2]	101.1(5)
Co4	O25	2.034(13)	O25	Co4	O2[2]	158.2(5)
Co4	O26	2.721(14)	N18	Co4	O1[2]	103.8(5)
Co4	N18	2.029(14)	N18	Co4	O2[2]	81.6(5)
Co4	N22	2.014(14)	N18	Co4	O25	107.5(5)
			N22	Co4	O1[2]	107.7(5)
			N22	Co4	O2[2]	84.7(5)
			N22	Co4	O25	102.5(5)
			N22	Co4	N18	130.6(6)

[1]-2+X,-1+Y,-1+Z; [2]2+X,1+Y,1+Z

Table S2. Bond lengths (left) and bond angles (right) of atoms with bonds or long contacts to Co^{II} centres for *poly*-$[Co_4(AlaPmDI)_4(bix)_4]\cdot 2DMF\cdot 7H_2O$ (**1**).

Bonds and long contacts with Co^{II}			Bond angles			
Atom 1	**Atom 2**	**Length (Å)**	**Atom 1**	**Atom 2**	**Atom 3**	**Angle (˚)**
Co1	O7	2.068(3)	O7	Co1	O8	58.84(13)
Co1	O8	2.385(4)	O31[1]	Co1	O7	100.13(13)
Co1	O31[1]	2.004(3)	O31[1]	Co1	O8	158.63(12)
Co1	O32[1]	2.763(4)	O31[1]	Co1	N3	106.03(15)
Co1	N3	2.028(3)	O31[1]	Co1	N7	102.97(14)
Co1	N7	2.035(4)	N3	Co1	O7	102.88(13)
			N3	Co1	O8	84.14(15)
			N3	Co1	N7	128.44(14)
			N7	Co1	O7	112.82(14)
			N7	Co1	O8	83.91(14)
Co2	O9	2.023(3)	O9	Co2	O17	99.25(12)
Co2	O10	2.619(4)	O9	Co2	O18	157.90(12)
Co2	O17	2.065(3)	O9	Co2	N6	106.19(13)
Co2	O18	2.406(3)	O9	Co2	N10	101.31(14)
Co2	N6	2.038(3)	O17	Co2	O18	58.72(10)
Co2	N10	2.052(3)	N6	Co2	O17	103.46(13)
			N6	Co2	O18	82.68(12)
			N6	Co2	N10	134.39(14)
			N10	Co2	O17	107.20(14)
			N10	Co2	O18	85.25(13)
Co3	O15	2.059(3)	O15	Co3	O16	58.81(13)
Co3	O16	2.389(4)	O23	Co3	O15	97.45(14)
Co3	O23	2.034(3)	O23	Co3	O16	156.02(13)
Co3	O24	2.523(5)	O23	Co3	N19	105.87(15)
Co3	N15	2.026(4)	N15	Co3	O15	108.7(2)
Co3	N19	2.042(4)	N15	Co3	O16	82.5(2)
			N15	Co3	O23	104.2(2)
			N15	Co3	N19	132.92(17)
			N19	Co3	O15	102.34(15)
			N19	Co3	O16	84.35(16)
Co4	O1[2]	1.998(4)	O1[2]	Co4	O25	101.56(14)
Co4	O2[2]	2.858(4)	O1[2]	Co4	O26	160.84(13)
Co4	O25	2.062(3)	O1[2]	Co4	N18	102.57(18)
Co4	O26	2.362(3)	O1[2]	Co4	N22	104.57(18)
Co4	N18	2.022(4)	O25	Co4	O26	59.39(11)
Co4	N22	2.034(4)	N18	Co4	O25	112.39(14)
			N18	Co4	O26	84.70(15)
			N18	Co4	N22	127.26(15)
			N22	Co4	O25	105.26(14)
			N22	Co4	O26	84.06(15)

[1]-2+X,-1+Y,-1+Z; [2]2+X,1+Y,1+Z

Table S3. Bond lengths (left) and bond angles (right) of atoms with bonds or long contacts to Co^{II} centres for *poly*-{[Co_4(AlaPmDI)$_4$(bix)$_4$]·2DMF·0.25PE·6.5H_2O} (1-PE ⊂ **1**):

Bonds and long contacts with Co^{II}			Bond angles			
Atom 1	**Atom 2**	**Length (Å)**	**Atom 1**	**Atom 2**	**Atom 3**	**Angle (˚)**
Co1	Cl1	2.291(4)	O7	Co1	Cl1	109.2(3)
Co1	O7	1.959(9)	O7	Co1	N7	112.5(4)
Co1	O8	2.702(9)	O7	Co1	N3	110.1(4)
Co1	N7	2.008(10)	N7	Co1	Cl1	104.3(3)
Co1	N3	2.014(13)	N7	Co1	N3	119.5(5)
			N3	Co1	Cl1	99.9(4)
Co2	Cl2	2.283(4)	$O1^1$	Co2	Cl2	106.7(3)
Co2	$O1^1$	2.013(10)	$O1^1$	Co2	N10	109.8(4)
Co2	$O2^1$	2.412(10)	$O1^1$	Co2	N6	106.3(4)
Co2	N10	2.027(11)	N10	Co2	Cl2	97.7(4)
Co2	N6	2.031(11)	N10	Co2	N6	129.7(5)
			N6	Co2	Cl2	104.2(4)

^{1}+X,+Y,-1+Z; ^{2}+X,+Y,1+Z

Table S4. Bond lengths (left) and bond angles (right) of atoms with bonds or long contacts to Co^{II} centres for *poly*-$[Co_2(AlaPmDI)(bix)_2Cl_2] \cdot 2DMF \cdot 2H_2O$ (**2**),

1.3 Additional Crystallographic Refinement Details

poly-[Co_4(AlaPmDI)$_4$(bix)$_4$]·2DMF·7H_2O (**1**):

The data is of low quality (as seen by high R_{int} and wR_2 values), but was the best data that could be obtained using synchrotron radiation. Due to poor diffraction to high angle, the dataset was truncated to 2Θ = 50°. Better quality data of the same structure with 1-phenylethanol was obtained. However, this dataset of the structure without 1-phenylethanol is included for completeness. A number of restraints were required for bond lengths and displacement ellipsoids, primarily those associated with the imidazole rings, as shown in the information embedded in CIF file. Electron density within voids that could not be sensibly modelled had its contribution to the diffraction data accounted for using the SQUEEZE feature within PLATON[1] (results discussed in main manuscript).

poly-{[Co_4(AlaPmDI)$_4$(bix)$_4$]·2DMF·0.25PE·6.5H_2O} (1-PE ⊂ **1**):

The 1-phenylethanol present was found from the electron density peaks, and is modelled at fixed 0.25 occupancy. An AFIX66 constraint was applied to the benzene ring in 1-phenylethanol to model it as a rigid hexagon, alongside DELU and SIMU restraints. The modelling of 1-phenylethanol was attempted with both (R) and (S)-1-phenylethanol, and gave similar R_{int} values. The final model includes 1-phenylethanol as the (R) enantiomer, for consistency with results from the enantioselective chromatographic separations experiments. Electron density within voids that could not be sensibly modelled had its contribution to the diffraction data accounted for using the BYPASS routine within Olex2.[2]

poly-[Co_2(AlaPmDI)(bix)$_2Cl_2$] ·2DMF·2H_2O (**2**):

A DFIX restraint was added to a long carbonyl bond on a DMF solvent molecule.

2. Powder X-Ray Diffraction (PXRD)

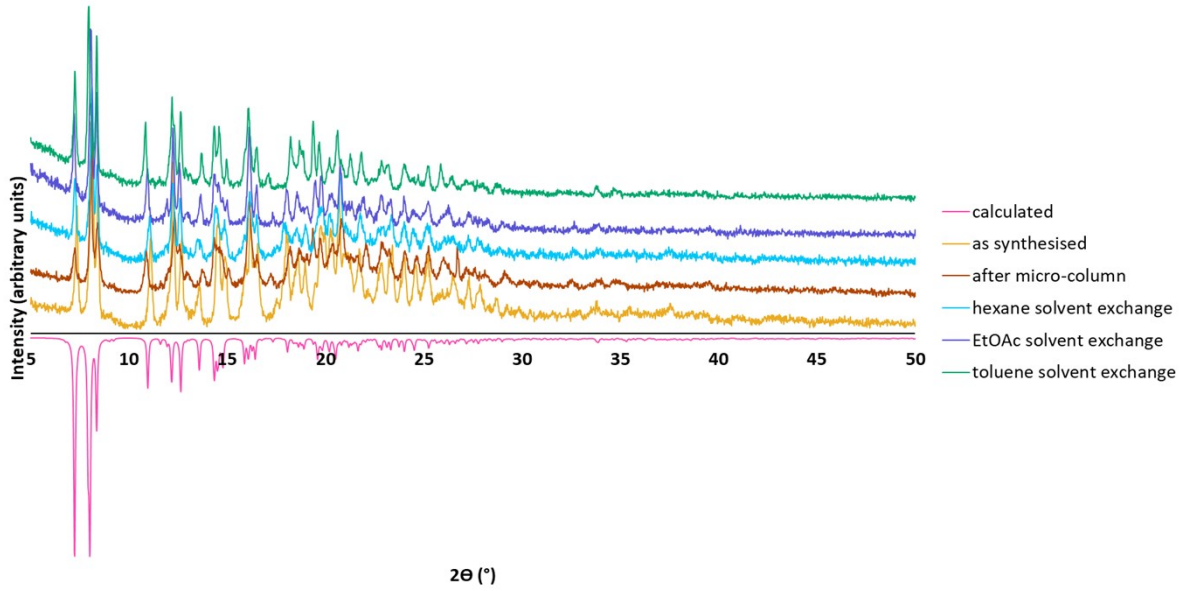

Figure S1. Comparison of calculated (100 K) and experimental (298 K) PXRD patterns for *poly*-[Co(AlaPmDI)(bix)]·2DMF·7H_2O (**1**).

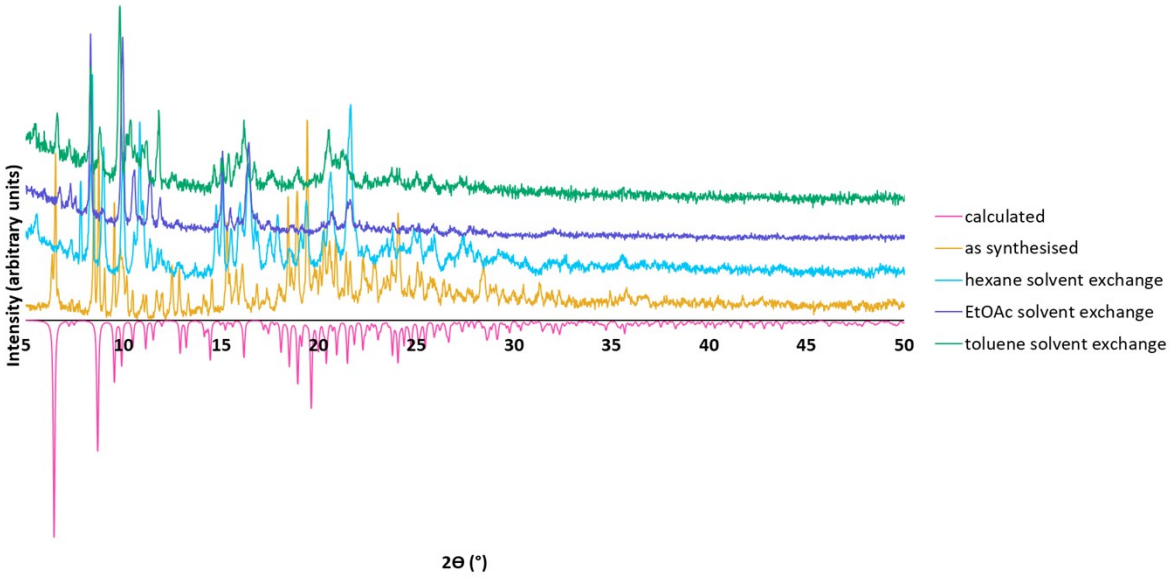

Figure S2. Comparison of calculated (100 K) and experimental (298 K) PXRD patterns for *poly*-[Co_2(AlaPmDI)(bix)$_2Cl_2$] ·2DMF·2H_2O (**2**).

3. Separation Studies

3.1 Chiral GC-FID

Analyte solutions were injected into an Agilent 7820A GC coupled with flame ionisation detection (FID). The detector temperature was 300 °C. Data were collected at 20 Hz. Data acquisition and analysis was performed using Agilent software. The conditions for each analyte were as follows:

Toluene (100 ppm toluene in *n*-hexane):

The oven temperature program started at 40 °C (held for 4 min), ramped to 60 °C at 5 °C/min, and then ramped to 160 °C at 40 °C/min (held for 0.5 min). Nitrogen was used as carrier gas at a flow rate of 1.4 mL/min, and the inlet temperature was 230 °C. A β-DEX™ 110 column of 30 m × 0.25 mm × 0.25 µm film thickness was used with autosampler injection (1 µL, split ratio 10:1).

Ethyl acetate (100 ppm ethyl acetate in *n*-hexane):

The oven temperature program started at 40 °C (held for 3 min), ramped to 125 °C at 30 °C/min (held of 0.5 min). Nitrogen was used as carrier gas at a flow rate of 1.4 mL/min, and the inlet temperature was 200 °C. A Supelco wax column of 30 m × 0.32 mm × 0.25 µm film thickness was used with manual syringe injection (0.5 µL, split ratio 10:1).

1-Phenylethanol:

A β-DEX™ 110 column of 30 m × 0.25 mm × 0.25 µm film thickness was used with autosampler injection (1 µL). Soaking samples: The oven temperature program started at 80 °C (held for 1 min), ramped to 140 °C at 4 °C/min, and then ramped to 205 °C at 20 °C/min (held for 1 min). Nitrogen was used as carrier gas at a flow rate of 1.4 mL/min, and the inlet temperature was 230 °C. Injection split ratios of 5:1, 10:1, and 50:1 were used for the 10 ppm, 100 ppm, and 1000 ppm solutions respectively. Micro-column samples: The oven temperature program started at 80 °C (held for 1 min), and ramped to 205 °C at 50 °C/min (held for 3 min). Nitrogen was used as carrier gas at a flow rate of 1.2 mL/min, and the inlet temperature was 200 °C. The injection split ratio was 5:1.

3.2 Soaking Studies

	concentration (ppm)	analyte	solvent	average peak area as % of control	standard deviation of measurement (%)
control	100	EtOAc	*n*-hexane	100	1
H_2AlaPmDI	100	EtOAc	*n*-hexane	101	4
1	100	EtOAc	*n*-hexane	96	3
2	100	EtOAc	*n*-hexane	102	3
control	100	toluene	*n*-hexane	100	4
H_2AlaPmDI	100	toluene	*n*-hexane	100	4
1	100	toluene	*n*-hexane	102	4
2	100	toluene	*n*-hexane	98	4

Table S5. Amounts of EtOAc and toluene remaining after soaking the framework materials, **1**, **2**, and H_2AlaPmDI in a 100 ppm solution in *n*-hexane to allow for sorption. Control samples were of the soaking solution without any solid material. The reported peak area is an average of three GC-FID runs. Small changes in concentration occurred during handling and sampling due to solvent loss.

3.3 'Micro-column' Study

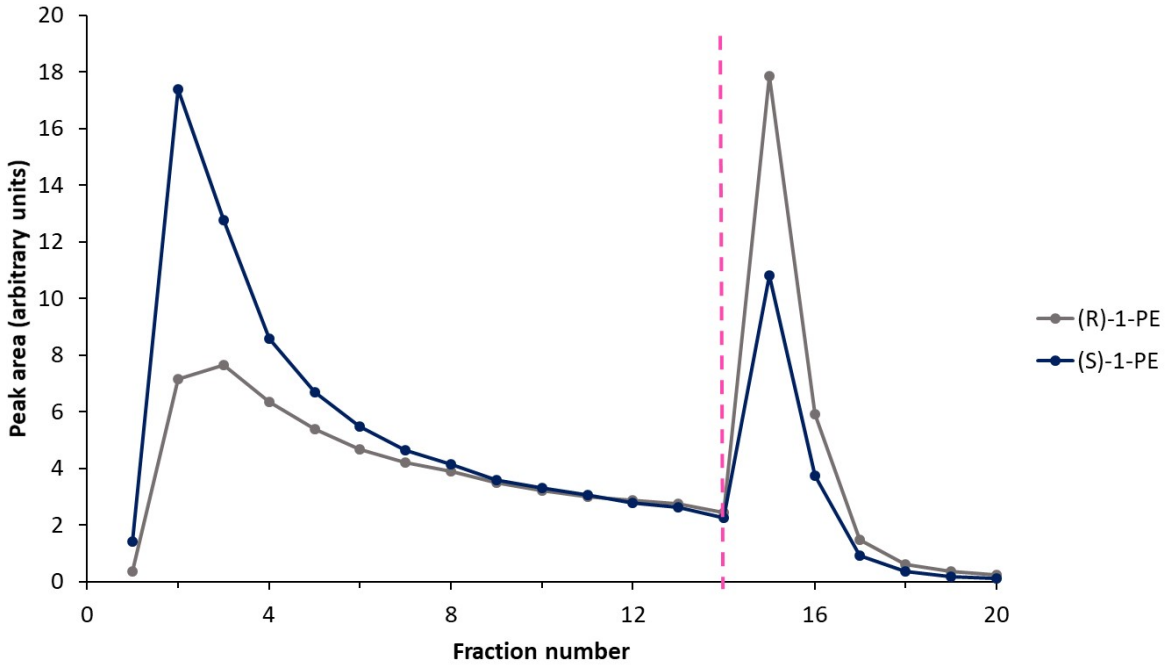

Figure S4. Plots of eluted peak area of (R) and (S)-1-phenylethanol vs. fraction number (100 - 200 µL per fraction) for micro-column packed with **1** as a stationary phase. The eluent was initially 20:1 *n*-hexane:ethyl acetate and was changed to 100% ethyl acetate at fraction 14.

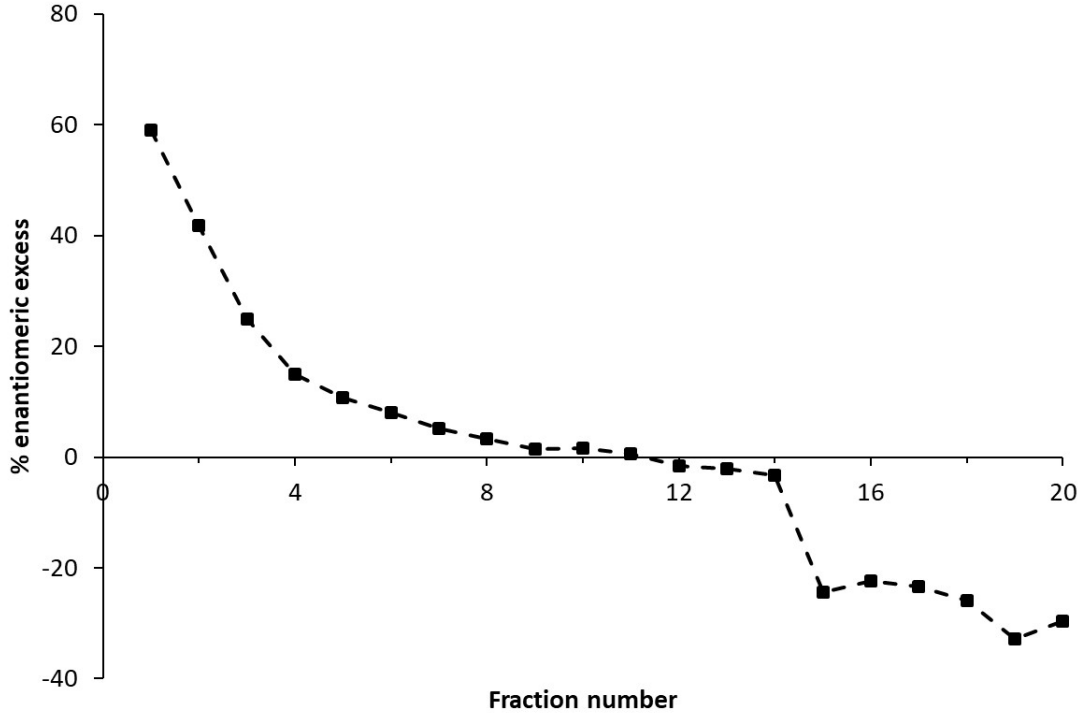

Figure S5. Plot of % enantiomeric excess (% ee) vs. fraction number (100 - 200 µL per fraction) of recovered fractions of 1-phenylethanol eluted from a micro-column packed with **1** as a stationary phase.

4. Thermogravimetric Analysis Traces

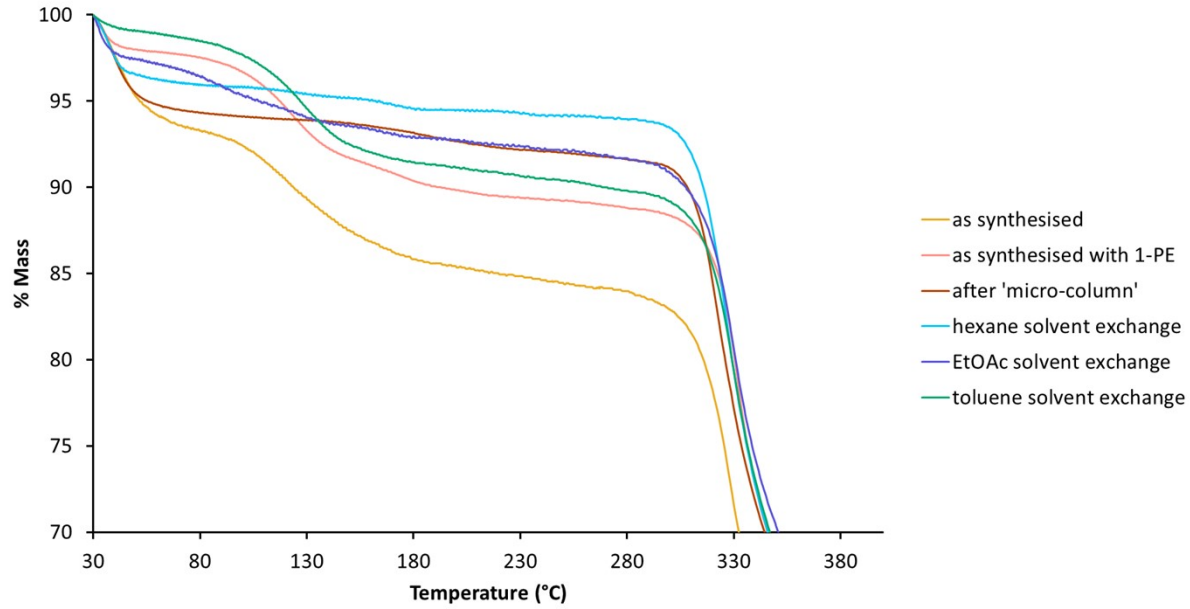

Figure S6. Thermogravimetric analysis trace of *poly*-[Co(AlaPmDI)(bix)]·2DMF·7H_2O (**1**) as synthesised, with and without 1-phenylethanol (1-PE), after 'micro-column', and after soaking in *n*-hexane, EtOAc, and toluene for 24 hours.

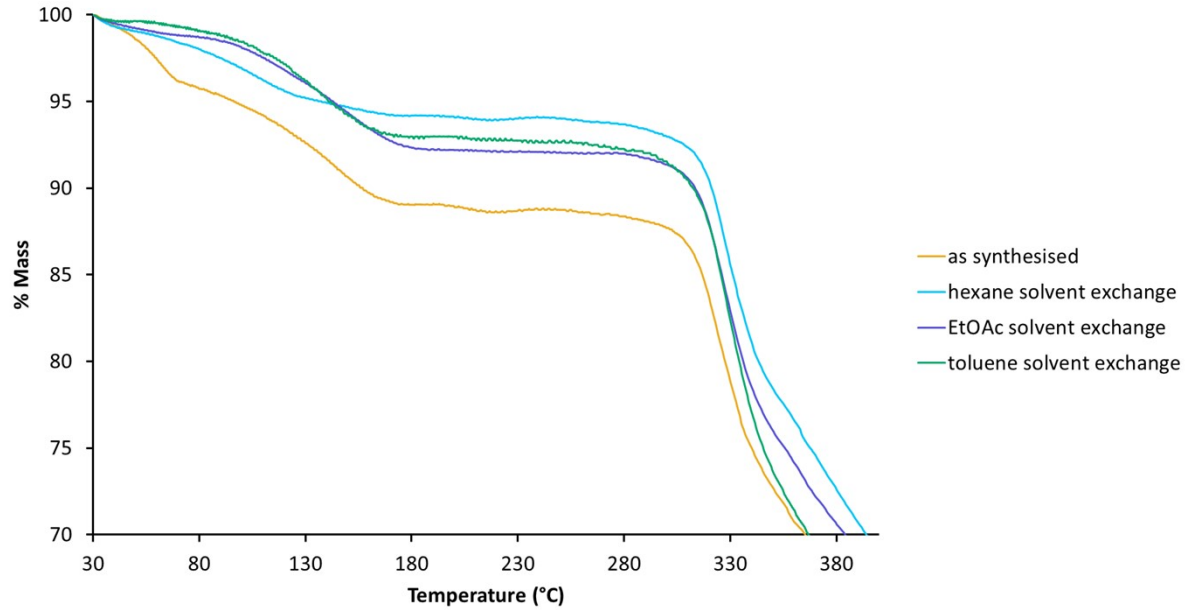

Figure S7. Thermogravimetric analysis trace of *poly*-[Co_2(AlaPmDI)$(bix)_2Cl_2$]·2DMF·2H_2O (**2**) as synthesised, and after soaking in *n*-hexane, EtOAc, and toluene for 24 hours.

5. References

1. A. Spek, PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Cryst. C*, 2015, **71**, 9-18.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.