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Supplementary Material

Salen-Based Metal Complexes and the Physical Properties of their Porous Organic Polymers

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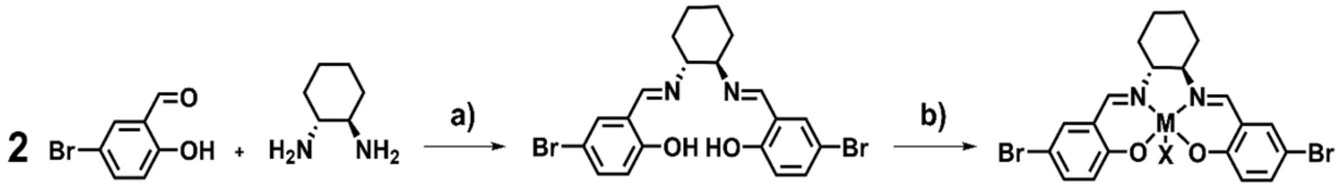
Table of Contents

Synthesis Scheme



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Scheme S1. The synthesis of 2, 2'-[(1*R*,2*R*)-1,2-cyclohexanediyl bis(nitrilomethylidine)] bis[4-bromo-phenol] (**1**) and its family of metal complexes **a)** solvent: MeOH, 80 °C, 2 h, **b)** metal salt (1.1 eq.), NaOMe, solvent: EtOH, 80 °C, 2 h.

Physical Properties of salen-containing POPs

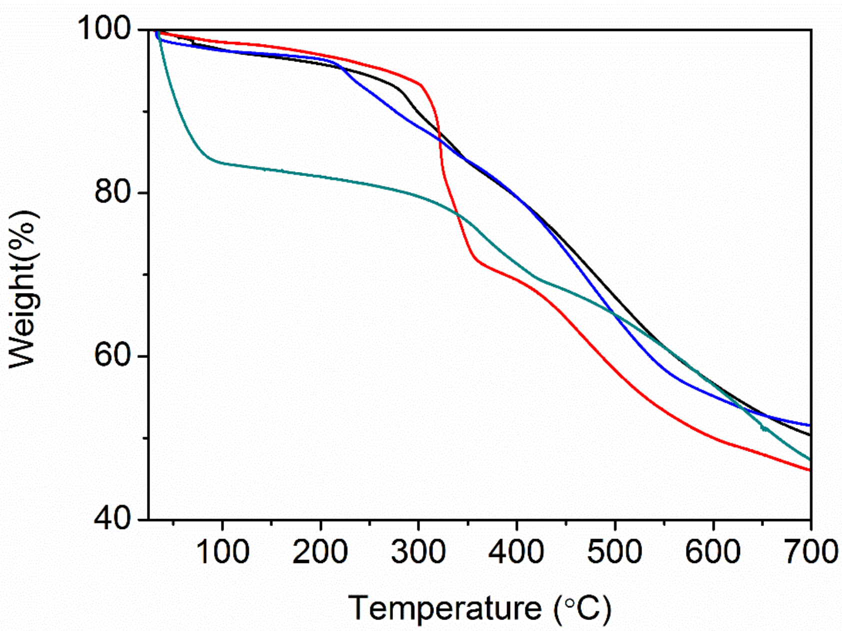

Figure S1. TGA of **POPMn** (black), **POPNi** (red), **POPFe** (blue) and **POPPd** (cyan) taken from 25 to 700 °C. The temperature was ramped at 1 °C min^{-1}.

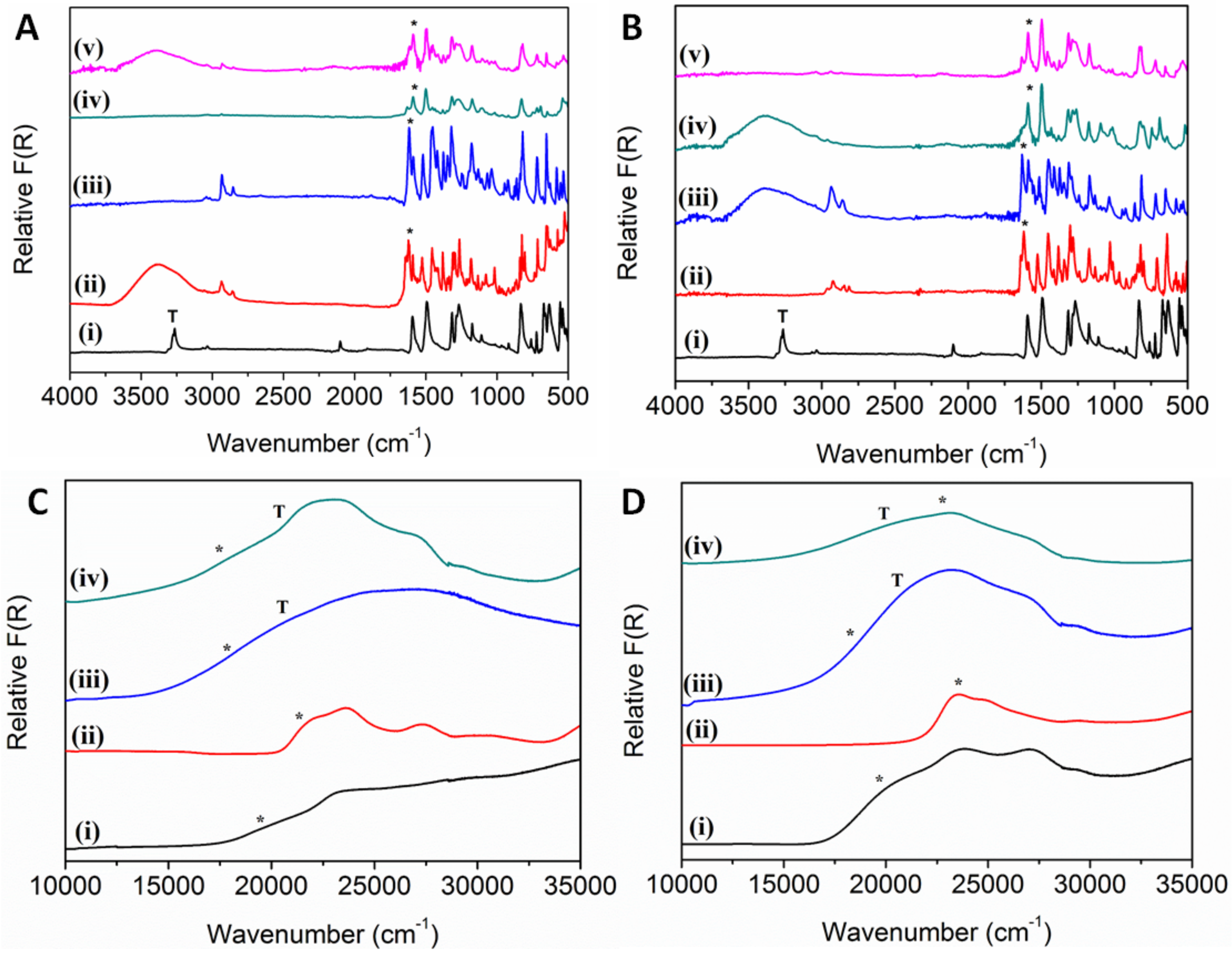

Figure S2. Solid State ATR-IR measurements of **A (i) TPA (ii) Mn1 (iii) Ni1 (iv) POPMn (v) POPNi B (i) TPA (ii) Fe1 (iii) Pd1 (iii) POPFe (iv) POPPd.** * denotes the shift in the $\nu_{C=N}$ stretch from the discrete complexes to the POPs, while the **T** denotes the band that appears from the **TPA** co-ligand. Solid State UV-Vis-NIR measurements of **B (i) Mn1 (ii) Ni1 (iii) POPMn (iv) POPNi D (i) Fe1 (ii) Pd1 (iii) POPFe (iv) POPPd.** * denotes the shift in bands from the discrete complexes to the POPs, while the **T** denotes the band that appears from the **TPA** co-ligand.

Table S1. ICP-OES results for metallated polymers. The term in brackets denotes the metal that

POP	Calculated metal content assuming no homocoupling (%)	Calculated metal content assuming single homocoupling (%)	Experimental Metal Content Found (%)	Other Metal Content Found (%)
POPMn	7.57 (Mn)	5.40 (Mn)	5.31 (Mn)	0.42(Pd), 0.11(Cu)
POPNi	8.45 (Ni)	5.95 (Ni)	4.07 (Ni)	0.31(Pd), 0.14(Cu)
POPFe	7.16 (Fe)	5.48 (Fe)	4.70 (Fe)	0.60(Pd), 0.09(Cu)
POPPd	14.34 (Pd)	10.30 (Pd)	9.13 (Pd)	0.17 (Cu)

*The robust nature of the polymers meant that only partial degradation of the polymer was achieved, prior to analysis. This should have, in principle, leached the entire metal content.

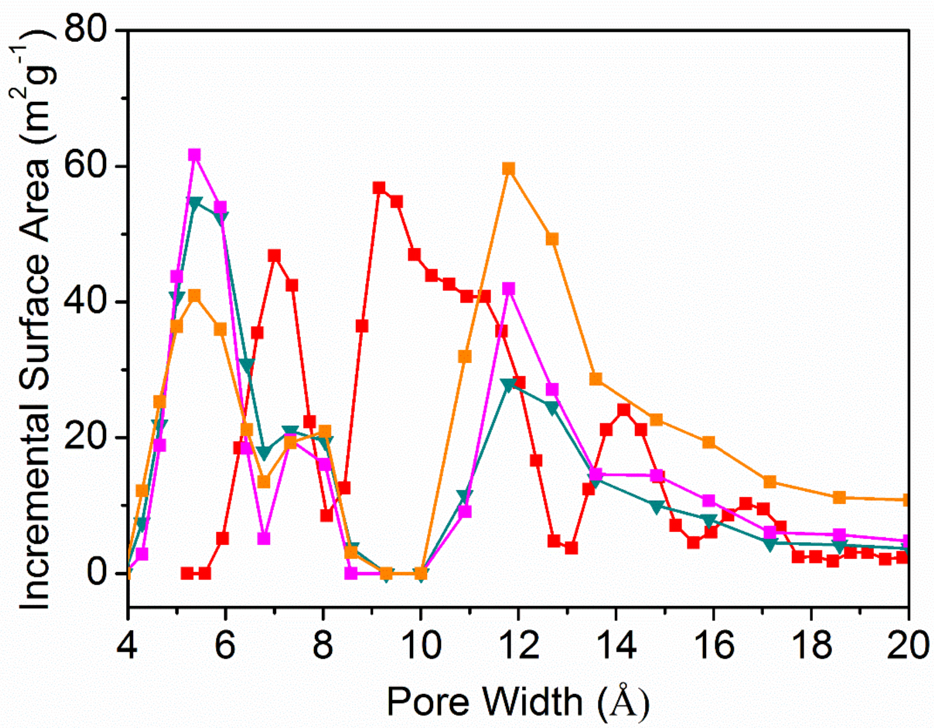

Figure S3. DFT pore size distributions for **a) POPPd** (red), **POPMn** (green), **POPNi** (magenta) and **POPFe** (orange).

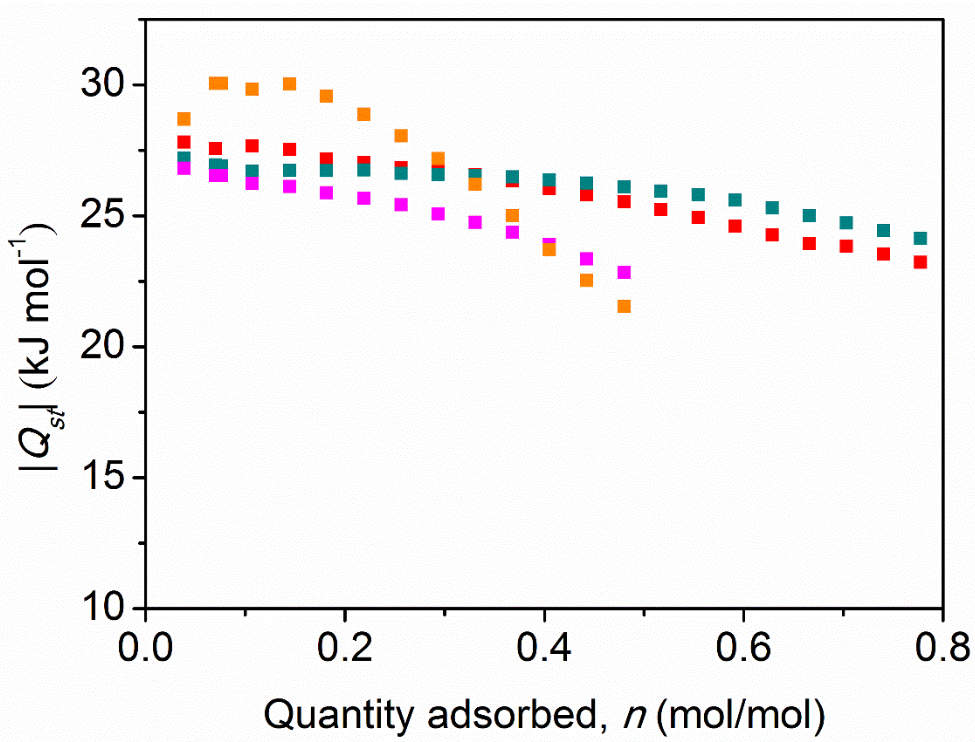

Figure S4. Isosteric heats of adsorption for **POPPd** (red), **POPMn** (green), **POPNi** (magenta) and **POPFe** (orange).

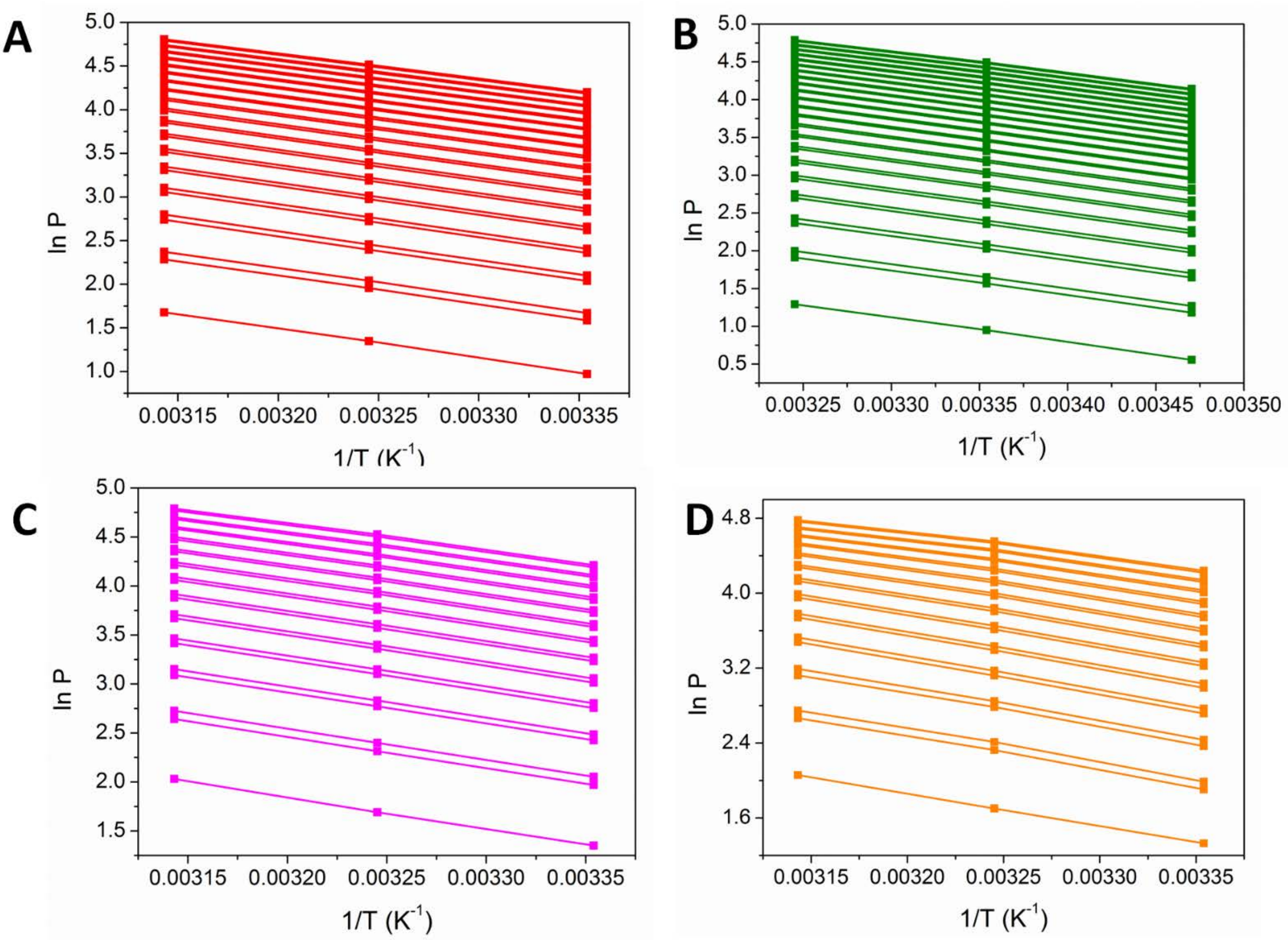

Figure S5. Isosteres of **A POPPd**, **B POPMn**, **C POPNi** and **D POPFe**.

Selected Comparisons of CO_2 selectivity

Table S2. A table of selected comparisons of other POP-materials and their selectivities. Adapted and edited with permission from 1.

Entry	Name	Structure	Selectivity	Reference
1.	TrzPOP-*x* (*x* = 1-3)	Triazine based POPs with phenolic functional groups	S = 27-96 (298 K)	2
2.	TPOP-36 TPOP-33 NPC-*x*-500 (*x* = 1-4)	Triazine based POPs and their porous carbons	S = 33.9 (273 K) S = 25.5 (273 K) S = 15.6-16.8 (273 K)	3
3.	BILP-2 BILP-4 BILP-5 BILP-7	Benzimidazole based POPs	S= 71 (298 K) S = 32 (298 K) S = 39 (298 K) S = 34 (298 K)	4
4.	BIPLP-1	*Bis*(imino) pyridine based POP	S = 16 (298 K)	5
5.	TBILP-1 TBILP-2	Combination of Triazine and benzimidazole co-ligands	S = 63 (298 K) S = 40 (298 K)	6
6.	ALP-*x* (*x* = 1-4)	Azo based POPs	S = 27-35 (298 K)	7
7.	Polymer-*x* (*x* = 1-5)	Hyper cross-linked phosphonium polymers	S = 28-56 (298 K)	8
8.	Network-*x* (*x* = 1,2)	Binaphthol based POPs	S = 16-23 (298 K)	9
9.	PAF-*x* (*x* = 33-35)	Tri(4-ethynylphenyl)amine based POPs with various appended functional groups	S = 19.4-104.3 (298 K)	10
10.	PECONF-*x* (*x* =1-4)	Phosphorus organonitridic frameworks	S = 41-51 (298 K)	11
11.	BDPCMP-*x* (*x* = 1-4)	BODIPY based POPs	S = 31.1-38.6 (273 K)	12
12.	COP-*x* (*x* = 32-37)	POPs containing ester and amide functional groups	S = 13-32 (298 K)	13
13.	MKPOP-*x* (*x* = 1-4)	POPs containing mannitol-based linkers	S= 60-105.2 (273 K)	14
14.	TzTz-POP-*x* (*x* = 1,2)	POPs containing Thiazolothiazolate linkers	S = 35-54 (273 K)	15
This Work	**POP*x* (*x* = Mn, Ni, Fe, Pd)**	**Salen-based POPs**	**S = 16-20**	**-**

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