

Supporting Information for:

***Synthesis and Catalytic Hydrogenation Reactivity of a Chromium
Catecholate Porous Organic Polymer***

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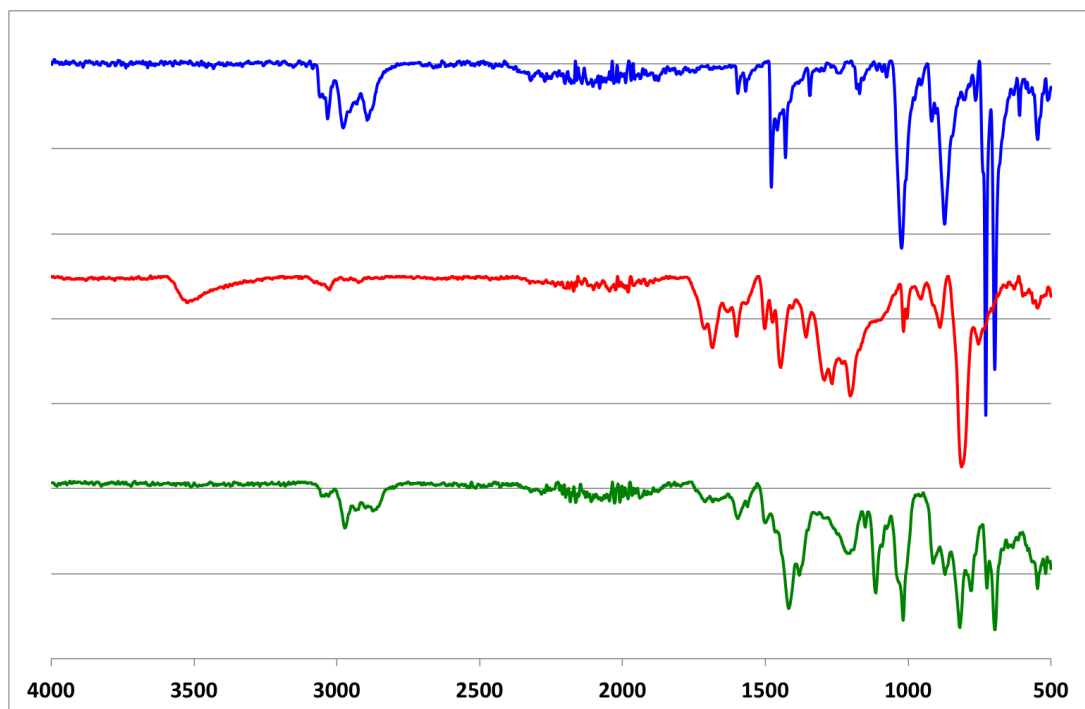


Figure S1. Infrared spectra of [CrPh₃(THF)₃] **1** (blue), catPOP A₂B₁ **2** (red) and [(catPOP)CrPh(L)] (green), **3**.

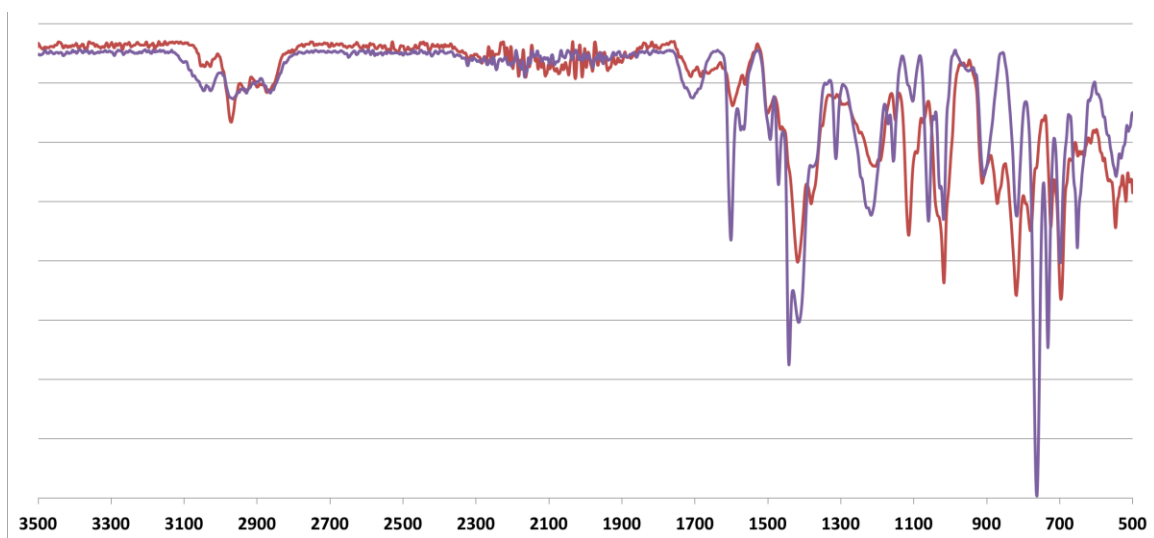


Figure S2. Infrared spectra of [(catPOP)CrPh(L)], **3** (red) and [(catPOP)CrPh(Bipy)], **5** (purple).

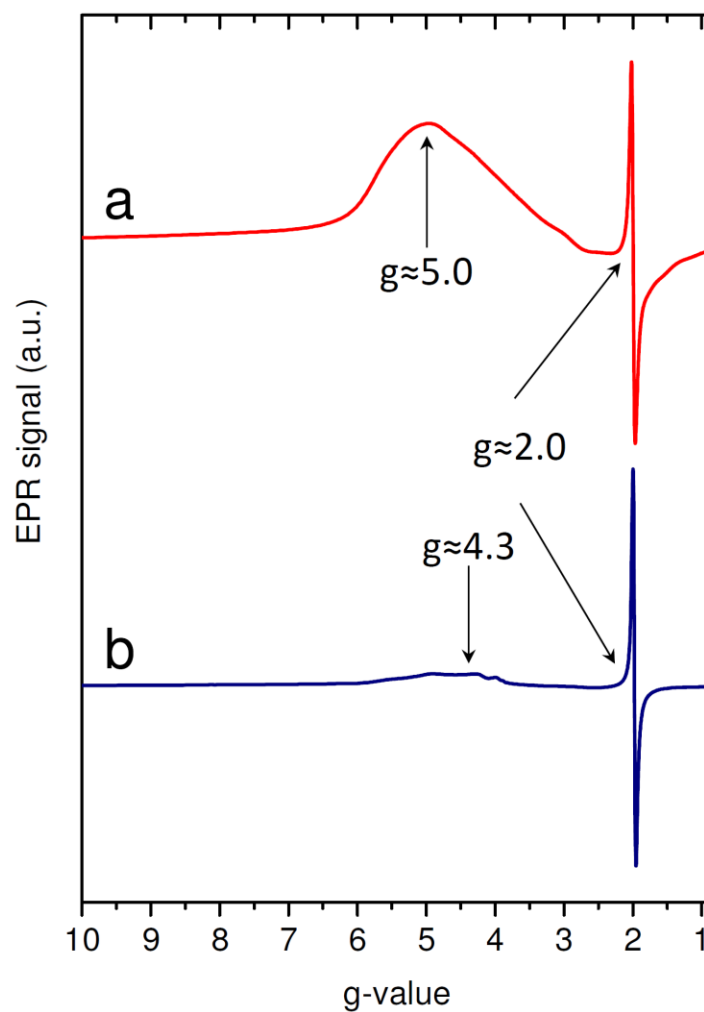


Figure S3. X-band EPR spectra of chromium in: **a** – [(catPOP)CrPh(L)] **3**; **b** – reported [Cr(catPOP)]; Arrows indicate low- and high-field features of the Cr(III) spectra. All spectra were recorded at $T = 10$ K.

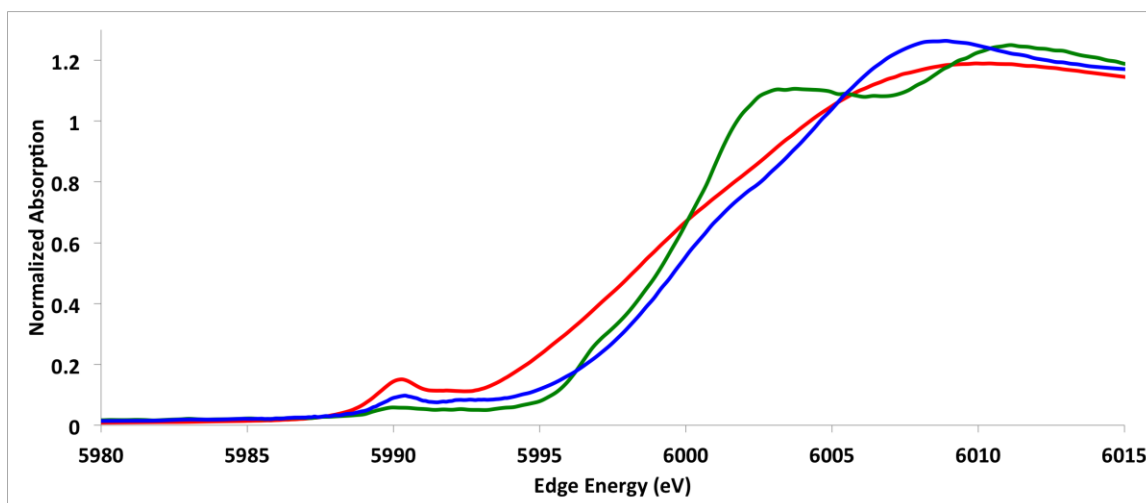


Figure S4. XAS spectra of $[\text{CrPh}_3(\text{THF})_3]$ **1** (green), $[(\text{catPOP})\text{CrPh}(\text{L})]$ **3** (red) and $[(\text{catPOP})\text{CrPh}(\text{Bipy})]$ (blue) **5**.

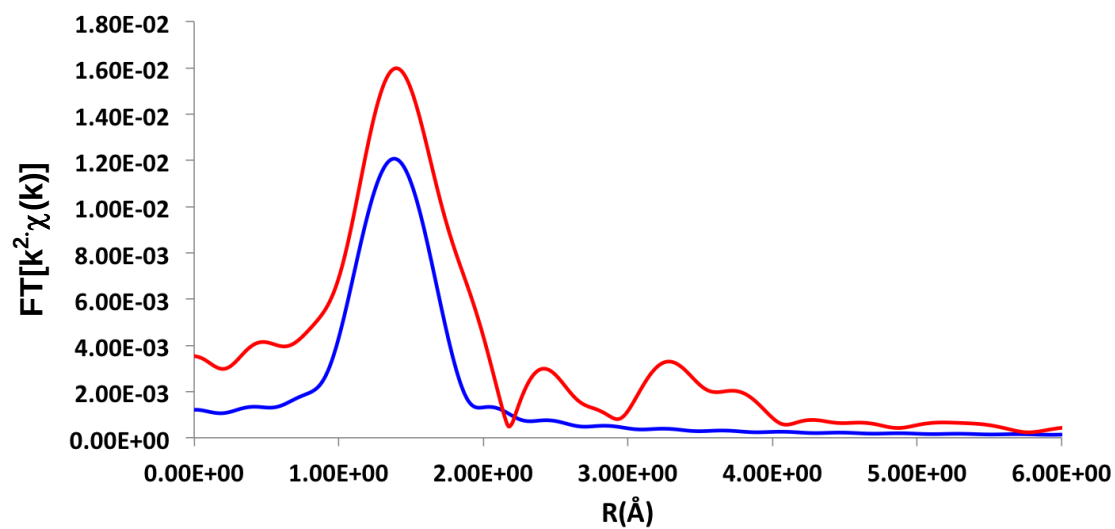


Figure S5. XANES spectra of $[(\text{catPOP})\text{CrPh}(\text{L})]$ **3** (blue) and $[(\text{catPOP})\text{CrPh}(\text{Bipy})]$ **5** (red).

Table S1. Summary of the XANES results

Sample	Treatment	Pre-edge (eV)	Edge energy (E ₀ , eV)	Oxidation State
Cr foil	N ₂ , RT	N.A.	5989.0	0
CrCl ₂	N ₂ , RT	5988.3	5995.2	II
CrCl ₃	He, RT	5990.2	5997.9	III
CrCl ₃ (THF) ₃	N ₂ , RT	5990.2	5996.4	III
Cr(acac) ₃	He, RT	5990.4	5998.0	III
CrO ₃	air, RT	5993.9	6007.8	VI
[(catPOP)CrPh(L)]	N ₂ , RT	5990.3	5998.3	III
[(catPOP)CrPh(Bipy)]	N ₂ , RT	5990.4	5999.7	III

Table S2. Summary of the EXAFS results of Cr-POP

Sample	Treatment		Coordination Number	Bond Distance (Å)	$\Delta\sigma^2$	ΔE_0	Comments
[(C ₆ H ₆) ₂ Cr]	N ₂ , RT	Fit	12.0 (fix)	2.10	0.0046	1.45	
		Crystal Structure	12.0	2.142			<i>Chem. Rev.</i> 1982 , 82, 499
[Cp* ₂ Cr]	N ₂ , RT	Fit	10.0 (fix)	2.12	0.0128	3.87	
		Crystal Structure	10.0	2.15			<i>Organometallics</i> 1996 , 15, 3474
CrCl ₃ (THF) ₃	N ₂ , RT	Fit	Cr-O 3.0	2.02	0.000	2.21	
			Cr-Cl 3.0	2.27	-0.001	-4.85	
[(catPOP)CrPh(L)]	N ₂ , RT	Fit	4.0	1.90	0.006	-3.80	
[(catPOP)CrPh(Bipy)]	N ₂ , RT	Fit	4.8	1.88	0.007	-6.9	