Supplementary Information

Tetranuclear Zn(II) macrocycles as catalysts for copolymerisation of cyclohexene oxide and CO_2

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1. General procedures and instrumentation

All manipulations of the air- and moisture-sensitive Zn compounds were carried out under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques or a Vacuum Atmospheres glovebox. The solvents *d*$_8$-THF and *d*$_6$-benzene were refluxed over potassium metal overnight, trap-to-trap distilled and three times freeze-pump-thaw degassed prior to use. The solvents used in synthesis (toluene, hexanes and THF) were nitrogen-purged and dried by passage through Vacuum Atmospheres drying towers and then stored over 4 Å molecular sieves. Toluene used in catalysis was dried by refluxing over sodium metal prior to storage under a N_2 atmosphere. Cyclohexene oxide (CHO) was dried over CaH_2 and fractionally distilled under nitrogen. Research grade carbon dioxide was dried over molecular sieves before using for the polymerization studies. For synthesis, *n*-hexanol was dried by stirring over magnesium metal (previously activated by iodine vapour and washed with hexanes) at 150 ^{o}C for 6 hours, and then trap-to-trap distilled, freeze-pump-thaw degassed three times, and finally stored under N_2 over 4 Å molecular sieves until use. Iso-propanol was dried over three sets of freshly activated 4 Å molecular sieves, and stored under N_2. Phenol was dried and purified by vacuum sublimation, by heating the bottom of a pencil ampoule, fitted with a Young's tap, at 100 ^{o}C under vacuum; dry, sublimed phenol was then recovered from the walls of the ampoule. 2,6-di-*tert*-butyl phenol was dried by heating at 100 ^{o}C under vacuum in a Schlenk flask.

For characterisation of the Zn(II) complexes, ^{1}H NMR spectra were recorded on a Bruker AVA-400 spectrometer operating at 399.90 MHz, or on Bruker AVA-500 and Bruker PRO-500 spectrometers operating at 500.12 MHz. ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AVA-400 spectrometer operating at 376.47 MHz or on a Bruker PRO-500 spectrometer operating at 470.59 MHz. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual solvent resonances (C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm; *d*$_8$-THF: δ_H = 1.73 ppm, δ_C = 25.37 ppm) calibrated against an external standard ($SiMe_4$, $\delta_{H,C}$ = 0 ppm). ^{19}F{^{1}H} NMR chemical shifts are referenced to an external standard (CCl_3F, δ_F = 0 ppm). All NMR spectra were measured using Young's tap fitted NMR tubes.

X-ray crystallographic data were collected at 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-Kα radiation equipped with an Eos CCD detector (λ = 0.71073 Å). Structures were solved using SHELXT-2015 direct methods and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-2008. All programs are used within the Olex2 suite. All non-hydrogen atoms refined with anisotropic displacement parameters and H-parameters were constrained to parent atoms and refined using both geometric and riding models.

Elemental analysis was carried out by Mr. Stephen Boyer, London Metropolitan University.

Characterisation of the polymers by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy were carried out on a Bruker AVA-400 instrument. A Shimadzu LC-20AD instrument was used to characterise the molecular weights and dispersity, using a Wyatt MALLS detector, with two Mixed Bed PSS SDV linear S columns and THF as the eluent, at a flow rate of 1.0 mL min^{-1} at 30 °C. Near monodisperse polystyrene standards were used to calibrate the instrument. The polyesters were dissolved in SEC grade THF and filtered prior to analysis.

2. Synthetic procedures for isolated compounds

The tetranuclear Zn-alkyl complexes $Zn_4Et_4(L^1)$, **1**, and $Zn_4Et_4(THF)_4(L^2)$, **2**, were synthesised according to their published procedures.[1]

2.1 Synthesis of $Zn_4(OC_6H_{13})_4(L^1)$, 3

To a brown/yellow solution of **1** (500 mg, 0.38 mmol) in THF (5 cm^{3}) was added *n*-hexanol (182 µL, 1.4 mmol, 3.8 eq) at room temperature, using a microlitre syringe. The solution warmed instantly and gentle effervescence was observed. The solution was stirred for 3 h before the solvent was removed under vacuum; the resulting dark yellow solid was washed twice with hexanes and then dried at 70 ^{o}C under vacuum. Isolated yield: 360 mg (84 %). Elemental analysis calculated for $C_{74}H_{82}F_{10}N_8O_4Zn_4$ (M_r = 1599.0 g mol^{-1}): C, 55.58; H, 5.17; N, 7.01. Found: C, 55.33; H, 5.32; N, 6.93. ^{1}H NMR (C_6D_6, 300 K): δ_H / ppm: 8.07 (s, 4H, imine), 7.02 (d, 4H, $^{3}J_{HH}$ = 5 Hz, pyrrole β-H), 6.94 (s, 4H, Ar C-H), 6.38 (s, 2H, *meso*-H), 6.17 (broad s, 4H, pyrrole β-H), 3.83 (t, 4H, $^{3}J_{HH}$ = 7.5 Hz, Zn-$OC\underline{H}_2C_5H_{11}$), 3.70 (t, 4H, $^{3}J_{HH}$ = 7.5 Hz, Zn-$OC\underline{H}_2C_5H_{11}$), 2.01 (s, 12H, Ar C-$CH_3$), 1.83 – 0.62 (multiple resonances, Zn-$OCH_2C_5\underline{H}_{11}$). ^{19}F{^{1}H} ($C_6D_6$, 300 K): δ_F / ppm: -154.7 (t, Ar^{F} *para*-F), -161.6 (broad s, Ar^{F} *meta*-F).

2.2 Synthesis of $Zn_3(\mu^2\text{-}O^iPr)_2(\mu^3\text{-}O^iPr)(HL^1)$, 4

Prepared as for **3**, reacting **1** (360 mg, 0.28 mmol) in THF (4 cm^{3}) with *iso*-propanol (80 µL, 1.04 mmol, 3.8 eq). Slow vapour-diffusion of hexanes into a concentrated benzene solution in a sealed vial, over two weeks, afforded very large block crystals of **4**, which were isolated by decanting the supernatant and subsequently washed with hexanes. Crystal yield: 160 mg, 45 %. Elemental analysis calculated for for $C_{59}H_{52}F_{10}N_8O_3Zn_3$ (M_r = 1371.5 g mol^{-1}): C, 54.21; H, 4.01; N, 8.57. Found: C, 54.12; H, 3.97; N, 8.46. Whilst the X-ray crystal structure and elemental analysis shows that the obtained crystalline material consists of a single compound, two compounds were observed after dissolving **4** in d_8-THF for NMR analysis, which is attributed to the reaction of **4** with adventitious water. The NMR data for the major compound (consistent with **4**) is given, along with the NMR data for the minor compound, and these compounds appear in a 3:1 ratio.

Major compound, 4: ^{1}H NMR (d_8-THF, 330 K): δ_H / ppm: 8.36 (broad s, 4H, imine), 7.07 (broad s, 4H, Ar C-H), 6.74 (d, 4H, $^3J_{HH}$ = 4 Hz, pyrrole β-H), 6.25 (broad s, 4H, pyrrole β-H), 6.12 (broad s, 2H, *meso*-H), 4.11 (broad s, 3H, ^{i}Pr *ipso*-H), 2.24 (s, 12H, Ar-CH_3), 1.02 (broad s, 18H, ^{i}Pr CH_3). ^{1}H NMR (d_8-THF, 213 K): δ_H / ppm: 11.98 (s, 1H, pyrrole N-H), 8.86 (s, 1H, imine), 8.68 (s, 1H, imine), 8.48 (s, 1H, imine), 8.40 (s, 1H, imine), 7.56 (s, 1H, Ar C-H), 7.35 (s, 1H, Ar C-H), 7.29 (s, 1H, Ar C-H), 7.04 (s, 2H, Ar C-H and pyrrole β-H), 6.97 (s, 1H, pyrrole β-H), 6.90 (s, 1H, pyrrole β-H), 6.80 (s, 1H, pyrrole β-H), 6.54 – 6.37 (multiple resonances, 4H, pyrrole β-H), 6.22 (s, 1H, *meso*-H), 5.97 (s, 1H, *meso*-H), 4.29 (broad s, 3H, ^{i}Pr *ipso*-H), 2.22 (s, 12H, Ar C-CH_3), 1.45 (s, 3H, ^{i}Pr CH_3), 1.23 (s, 3H, ^{i}Pr CH_3), 1.03 (s, 3H, ^{i}Pr CH_3), 0.90 (s, 3H, ^{i}Pr CH_3), 0.88 (s, 3H, ^{i}Pr CH_3), 0.66 (s, 3H, ^{i}Pr CH_3). $^{19}F\{^1H\}$ NMR (d_8-THF, 330 K): δ_F / ppm: -135.49 (broad s, Ar^F *ortho*-F), -158.82 (broad s, Ar^F *para*-F), -164.07 (broad s, Ar^F *meta*-F).

Minor compound: ^{1}H NMR (d_8-THF, 330 K): δ_H / ppm: 8.17 (s, 4H, imine), 6.90 (s, 4H, Ar C-H), 6.58 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole β-H), 6.12 (s, 4H, pyrrole β-H), 5.99 (s, 2H, *meso*-H), 2.21 (s, 12H, Ar C-CH_3). ^{1}H NMR (d_8-THF, 213 K): δ_H / ppm: 8.24 (s, 4H, imine), 7.02 (s, 4H, Ar C-H), 6.59 (s, 4H, pyrrole β-H), 6.02 (s, 2H, *meso*-H), 3.85 (s, 2H, iPr *ipso*-H), 2.22 (s, 12H, Ar C-CH_3), 1.06 (d, 12H, $^3J_{HH}$ = 5 Hz, ^{i}Pr CH_3), 0.11 (s, 2H, pyrrole N-H). Note that one resonance for the macrocycle is not observed in the aromatic region, at 213 K only, and is likely to be obscured by the resonances of the major compound.

3. Attempted protonolysis reactions of 1

3.1 Protonolysis of 1 with phenol

In a vial, a brown/yellow solution of **1** (20 mg, 15 µmol) in C_6D_6 (*ca.* 0.7 cm^3) was added to phenol (5 mg, 59 µmol, 3.8 eq) and mixed well using a pipette. ^{1}H NMR (C_6D_6, 300 K): δ_H / ppm: 11.73 (broad s, 1H, pyrrole N-H), 8.06 (s, 4H, imine), 6.88 – 6.33 (multiple resonances, doublet and triplet multiplicities; Zn-phenoxides and unreacted phenol, unable to assign individually), 6.80 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole β-H), 6.61 (s, 4H, Ar C-H), 6.17 (s, 2H, *meso*-H), 5.82 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole β-H), 1.85 (s, 12H, Ar C-CH_3).

3.2 Protonolysis of 1 with 2,6-di-*tert*-butyl phenol

In a vial, a brown/yellow solution of **1** (20 mg, 15 µmol) in C_6D_6 (*ca.* 0.7 cm^3) was added to 2,6-di-*tert*-butyl phenol (12 mg, 59 µmol, 3.8 eq) and mixed well, using a pipette. The ^{1}H NMR spectrum was unchanged after mixing at room temperature, and the solution was heated at 90 °C for 24 hours. ^{1}H NMR (C_6D_6, 300 K): δ_H / ppm: 7.81 (s, 4H, imine), 7.32 (d, 4H, $^3J_{HH}$ = 10 Hz, Zn-OAr *meta*-H), 6.97 (s, 2H, *meso*-H), 6.91 (t, 2H, $^3J_{HH}$ = 10 Hz, Zn-OAr *para*-H), 6.82 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole β-H), 6.75 (s, 4H, Ar C-H), 6.42 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole β-H), 2.01 (s, 12H, Ar C-CH_3), 1.60 (s, 36H, Zn-OAr tBu), 1.08 (t, overlapping, $^3J_{HH}$ = 10 Hz, Zn-Et CH_3), 0.55 (q, 4H, $^3J_{HH}$ = 10 Hz, Zn-Et CH_2).

4. Catalysis procedures

4.1 Low Pressure Copolymerization Reactions

Distilled and dried cyclohexene oxide, catalyst and hexanol were placed in a Schlenk flask. The reaction mixture was degassed and then heated to 80 °C, at 1 bar CO_2 pressure. After 24 h, the mixture was quenched by exposure to air and a ^{1}H NMR spectrum of the crude mixture was recorded. Then, the cyclohexene oxide was removed, under vacuum, to yield the polycarbonate, which was purified by dissolving in THF and precipitating it with MeOH.

4.2 High Pressure Copolymerization Reactions

A Parr reactor was dried for 20 h at 140 °C and purged with CO_2 three times and allowed to cool to 25 °C. Then, the catalyst and hexanol were dissolved in cyclohexene oxide and added to the Parr reactor. After sealing the reactor, 30 bar of CO_2 was added whilst the reaction mixture was stirring at a low-frequency in order to facilitate CO_2 dissolution. This step was repeated several times until the CO_2 dissolution reached equilibrium and the headspace pressure remained constant. The vessel was heated to the appropriate temperature and stirred for 24 h before a ^{1}H NMR spectrum of the crude reaction mixture was recorded. The mixture was then taken up in methylene chloride and evaporated to dryness. The polymer was purified by dissolving in THF and then precipitating it with MeOH.

5. NMR Spectra

5.1 NMR spectra of the isolated Zn(II) complexes

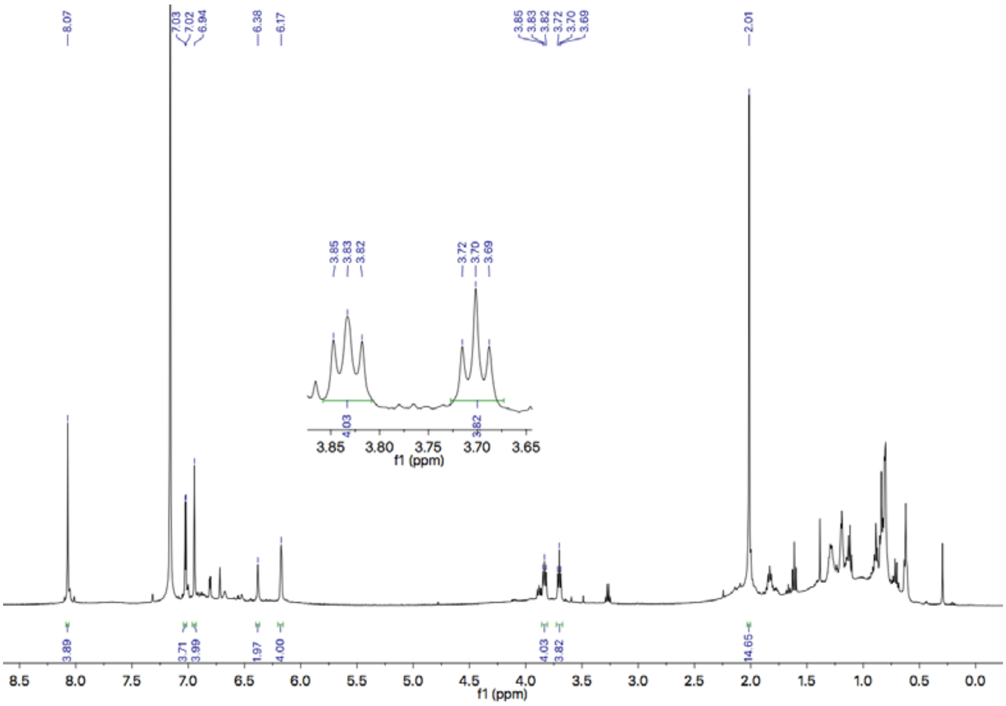

Figure S1. ^{1}H NMR spectrum of **3**, measured at 300 K in C_6D_6. Insert highlights the two inequivalent methylene resonances for the bridging hexanoxide ligands.

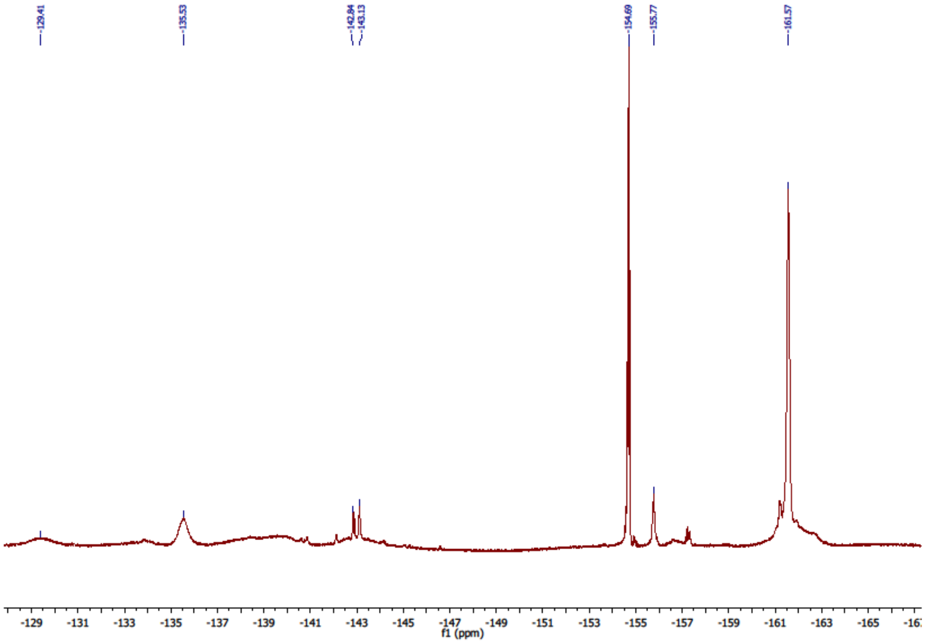

Figure S2. $^{19}F\{^1H\}$ NMR spectrum of **3**, measured at 300 K in C_6D_6. The resonance for the *ortho*-F, which is broadened severely due to hindered rotation of the C_6F_5-group in the tetranuclear complex, can be seen around -136 ppm.

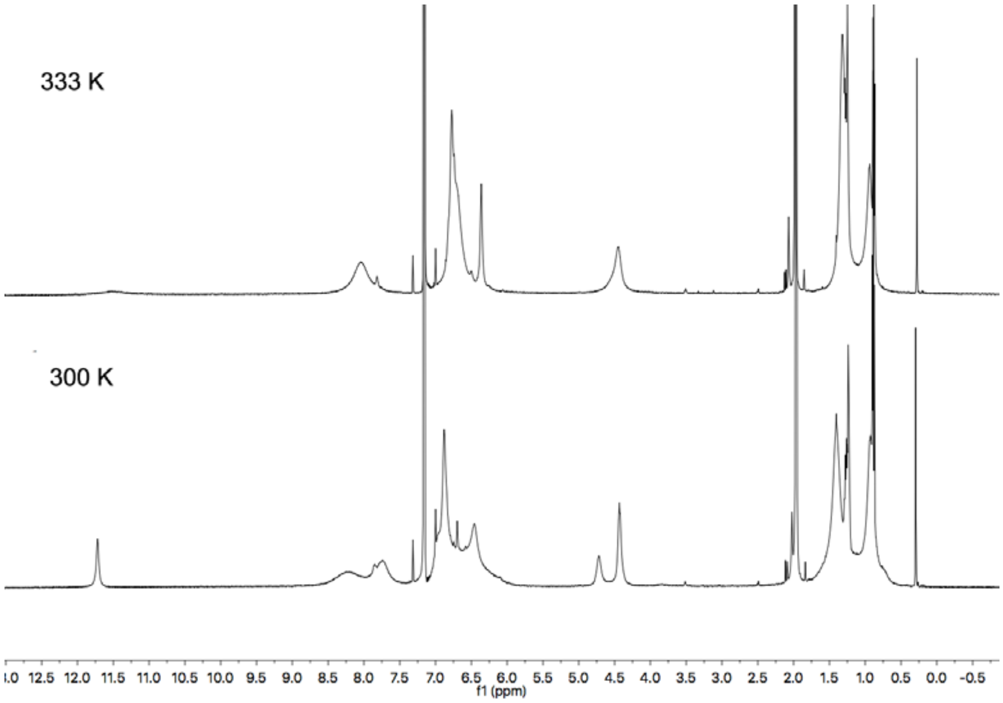

Figure S3. ^{1}H NMR spectra for **4** (crystalline material), measured at 300 and 333 K in C_6D_6, highlighting breadth of the resonances in that solvent, even at elevated temperature.

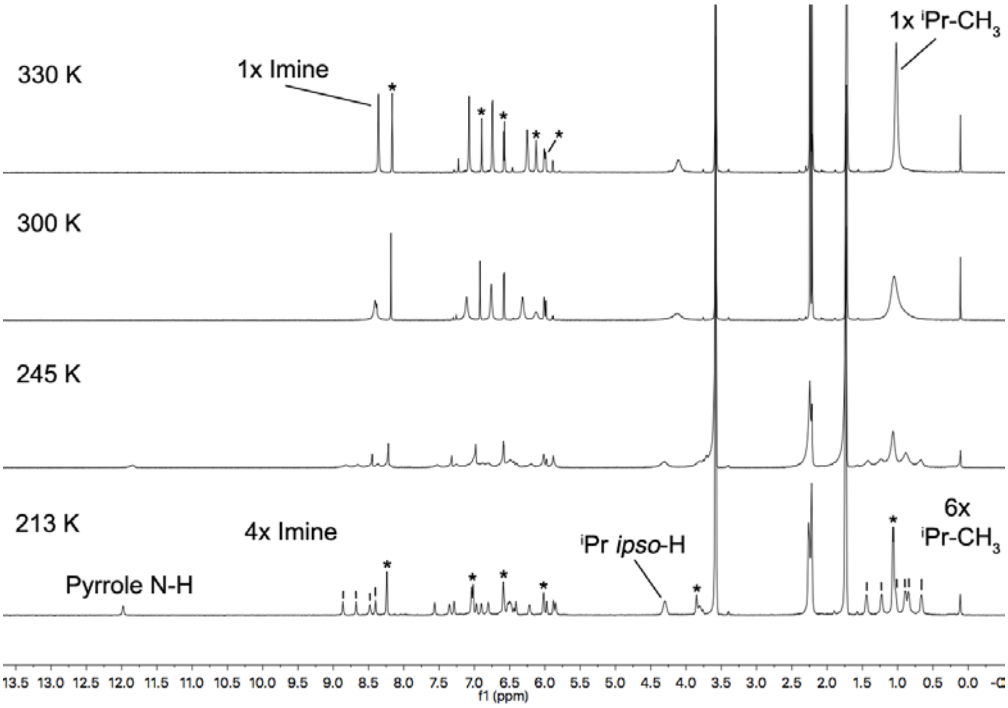

Figure S4. ^{1}H NMR spectra for **4**, measured in *d*$_8$-THF at 213 K, 245 K, 300 K and 330 K. A symmetric structure is observable at 330 K, and an asymmetric structure is observable at 213 K, but at intermediate temperatures, the spectra are broad and uninformative. Asterisks denote resonances assigned to the minor compound, and the vertical strokes in the 213 K spectrum denote the 4 imine resonances and 6 ^{i}Pr CH_3 resonances as labelled.

5.2 NMR spectra from attempted protonolysis reactions

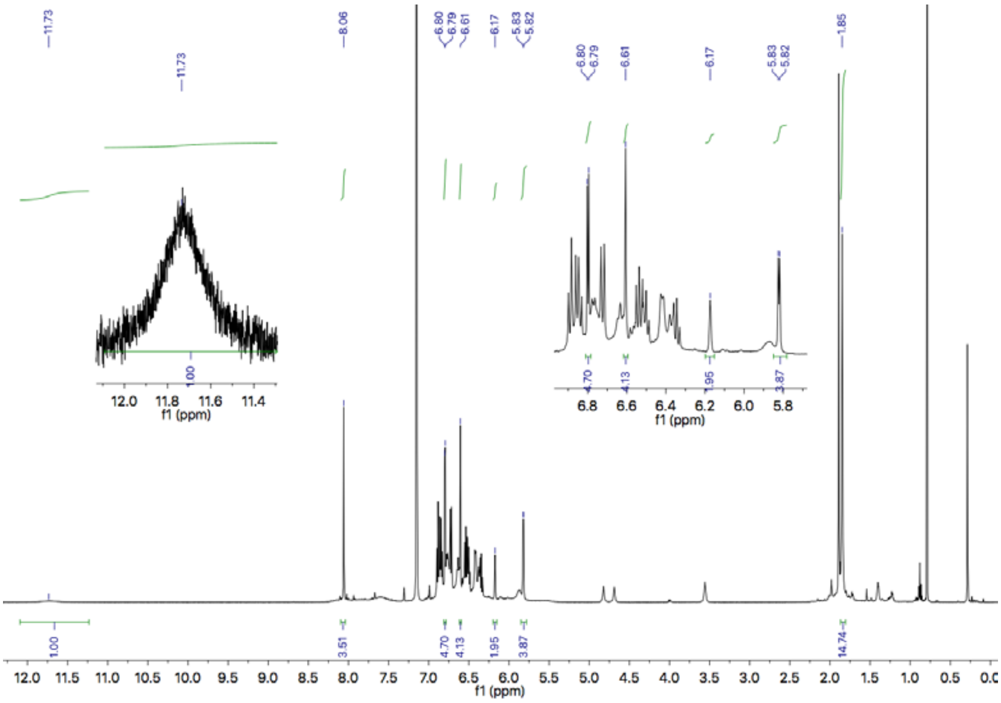

Figure S5. ^{1}H NMR spectrum from the reaction of **1** with 4 equivalents of phenol, measured in C_6D_6 at 300 K. Expanded views of the pyrrole N-H resonance and of the aromatic region are inset.

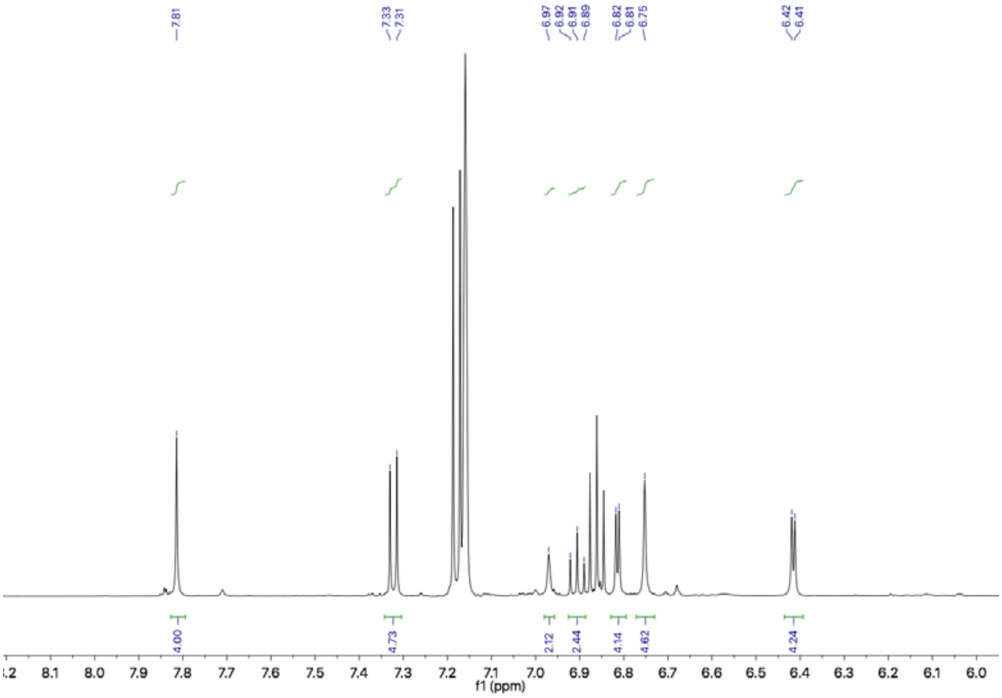

Figure S6. Aromatic region of the ^{1}H NMR spectrum from the reaction of **1** with 4 equivalents of 2,6-di-*tert*-butyl-phenol, after heating at 90 °C for 24 hours, showing clean formation of a single macrocyclic product with two phenoxide ligands.

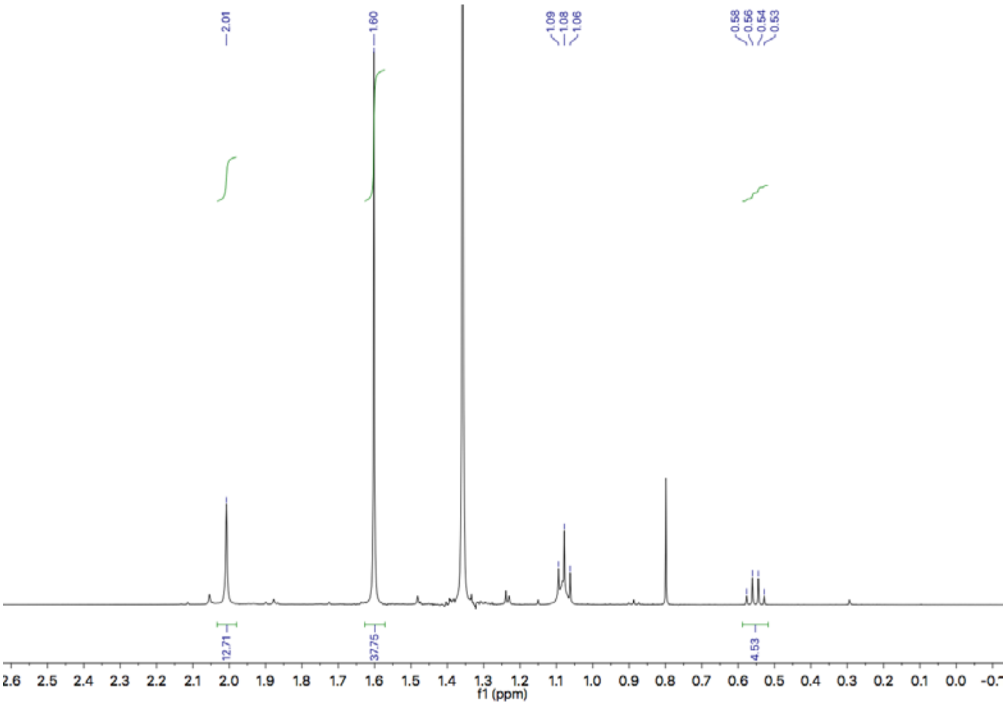

Figure S7. Aliphatic region of the ^{1}H NMR spectrum from the reaction of **1** with 4 equivalents of 2,6-di-*tert*-butyl-phenol, after heating at 90 ^{o}C for 24 hours, highlighting that two ethyl ligands remain in the Zn-phenoxide complex.

5.3 NMR spectra of the isolated polymers

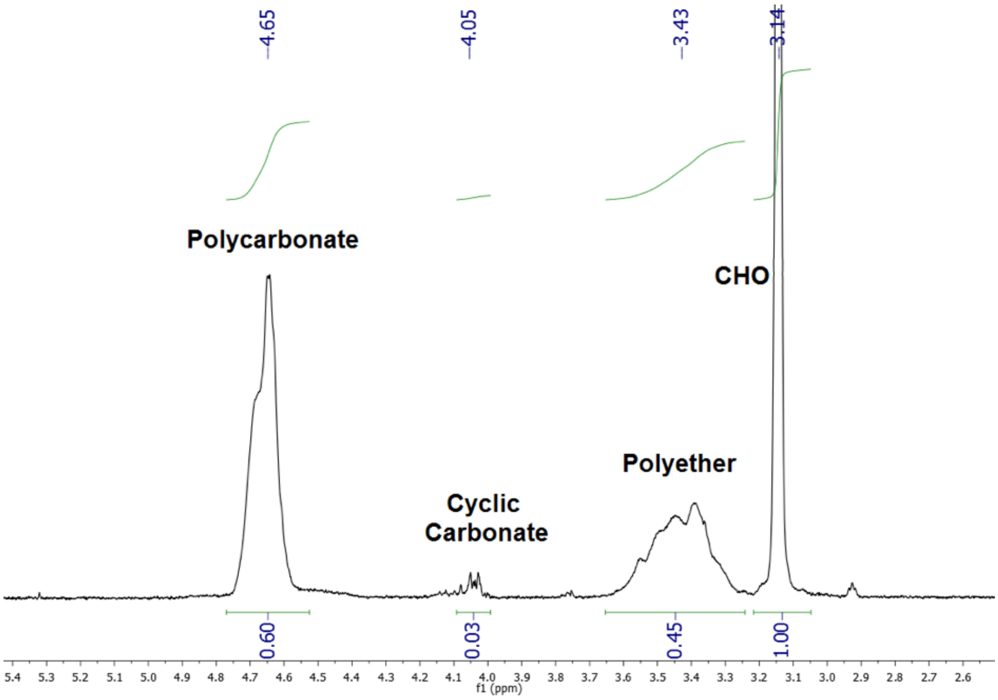

Figure S8. Selected region of the NMR spectrum of the polymer formed from the reaction of neat CHO with 30 atm CO_2, catalysed by **1** (Table 1, entry 3 in the main text). It should be noted that the labels polycarbonate/polyether refer to carbonate/ether linkages in the polymer backbone.

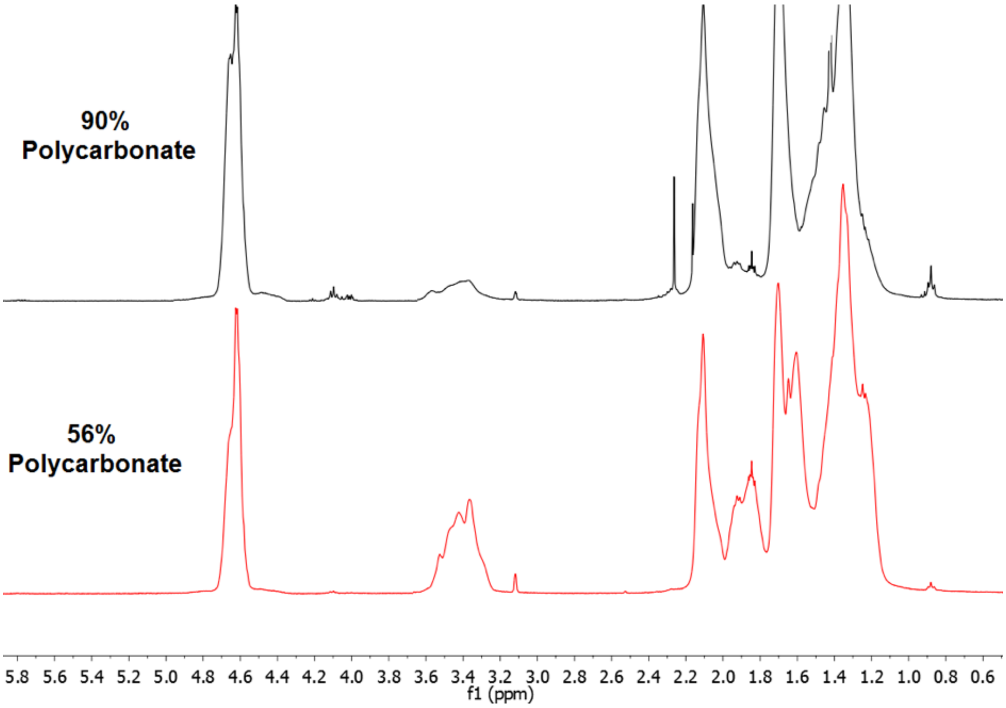

Figure S9. Comparison of NMR spectra for the polymers obtained before and after dilution of CHO in toluene, highlighting improvement in carbonate selectivity. Red spectrum: polymer obtained from the reaction of neat CHO and 30 atm CO_2, catalysed by **1** (Table 1, entry 3 in the main text). Black spectrum: polymer obtained from the reaction of 5 M CHO in toluene and 30 atm CO_2, catalysed by **1** (Table 1, entry 5 in the main text). It should be noted that the labels polycarbonate/polyether refer to carbonate/ether linkages in the polymer backbone.

6. Monitoring of the optimised ROCOP reaction

Table S1. Monitoring of the ROCOP reaction between cyclohexene oxide (CHO) and CO_2, catalysed by 0.2 mol% **1** with 0.8 mol% *n*-hexanol. Reaction conditions: solvent = toluene; $[CHO]_0$ = 5 M; T = 80 °C; $[CO_2]$ = 30 atm. (a) Conversion calculated from the relative ^1H NMR integrals of the methine proton resonances corresponding to CHO, PCHC and PCHO. (b) Selectivity for carbonate calculated from the relative ^1H NMR integrals of the methine proton resonances corresponding to PCHC, PCHO and CHC. (c) TON = (moles epoxide consumed)/(moles catalyst). (d) Both M_n (g mol^{-1}) and Đ determined by size-exclusion chromatography (SEC), using narrow molar-mass polystyrene standards. (e) M_n theor. = (moles epoxide consumed) x 142 / 4.

Entry	Time / h	Conversion / % (a)	Selectivity / % (b)	TOF / h^{-1} (c)	M_n (Đ) (d)	$M_{n\ \text{theor.}}$ (e)
1	2	20	78	50.0	194000 (1.89); 2400 (3.05)	3350
2	4	39	90	49	273000 (1.71); 4800 (3.40)	6922
3	8	59	88	37	226600 (1.87); 7800 (2.42)	10472
4	14	64	89	23	193300 (1.78); 6100 (2.75)	11360
5	24	70	90	15	221700 (2.04); 7900 (2.21)	12425

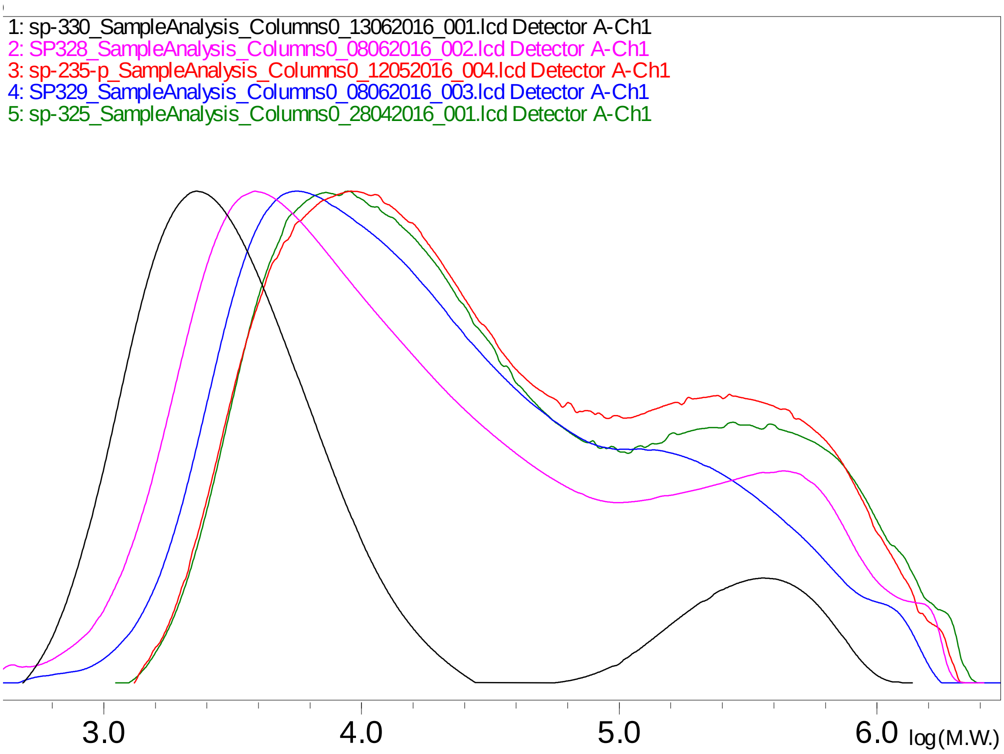

Figure S11: Plots showing the evolution of molecular weight, as determined by GPC, against conversion for entries 1-5 Table S1, respectively.

7. Gel permeation chromatography data

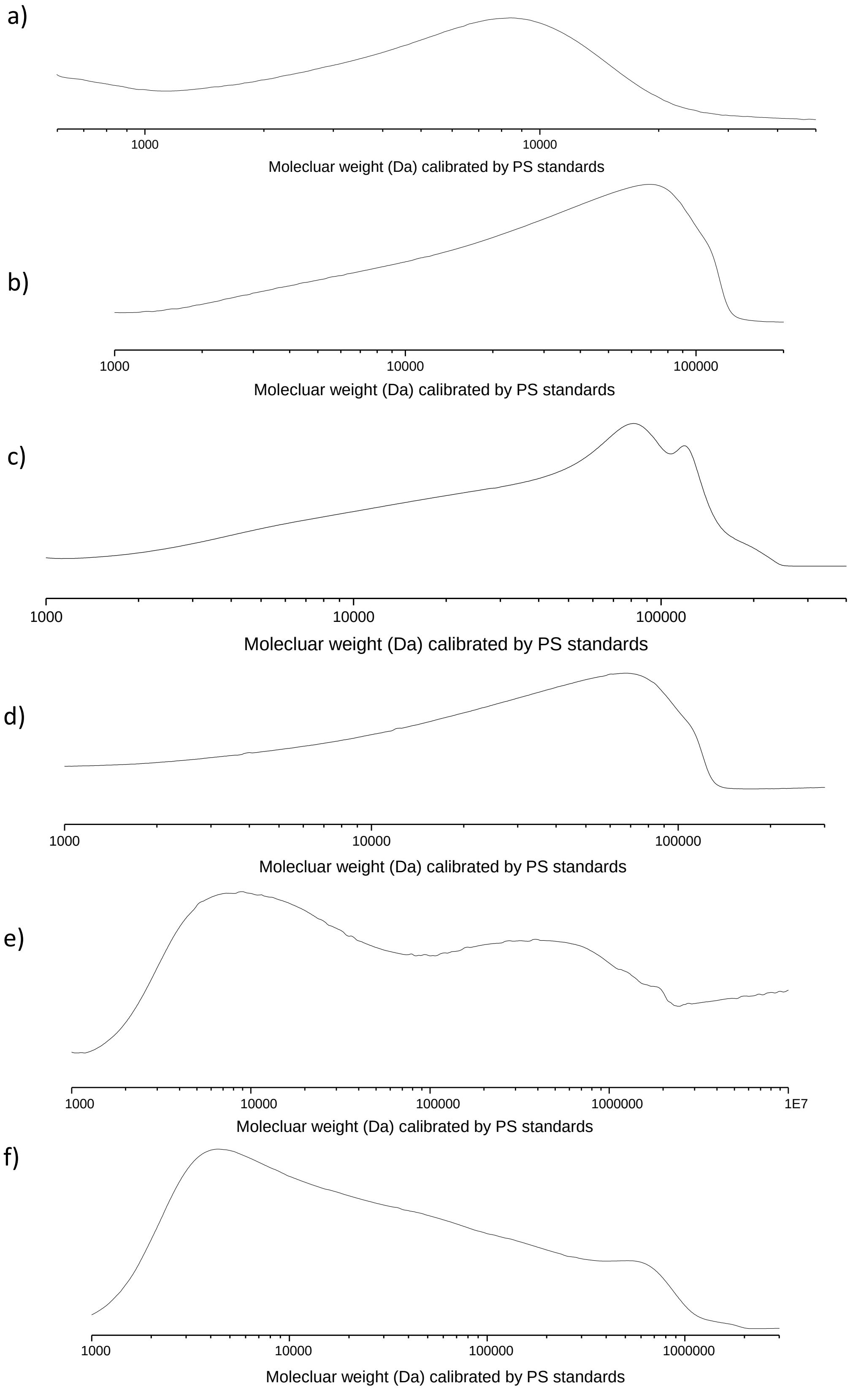

Figure S12. SEC traces of polymers. a) to f) are corresponding to entry 1-5 and 10, respectively, in Table 1.

8. X-ray crystallography data for 4

Table S2. Summary of X-ray crystallography data for the trinuclear *iso*-propoxide complex, **4**.

CCD Number	1509316
Chemical formula	$C_{59}H_{52}F_{10}N_8O_3Zn_3\cdot 3.5(C_6H_6)$
M_r / g mol^{-1}	1580.57
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature / K	170
a, *b*, *c* / Å	13.6817 (3), 17.1958 (4), 17.9104 (4)
a, b, g / deg	105.877 (2), 105.185 (2), 104.788 (2)
V / Å^3	3660.90 (17)
Z	2
Radiation type	Mo *K*α
μ / mm^{-1}	1.06
Crystal size / mm	0.44 × 0.42 × 0.13
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical
T_{min}, T_{max}	0.472, 0.780
No. of measured, independent and observed [I > 2σ(I)] reflections	88885, 13872, 10986
R_{int}	0.063
$(\sin\theta / \lambda)_{\mathrm{max}}$ / Å^{-1}	0.610
$R[F^2 > 2\theta (F^2)]$, $wR(F^2)$, S	0.040, 0.088, 1.04
No. of reflections	13872
No. of parameters	946
No. of restraints	36
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\mathrm{max}}$, $\Delta\rho_{\mathrm{min}}$ / e Å^{-3}	0.55, -0.39

9. References

1. T. Cadenbach, J. R. Pankhurst, T. A. Hofmann, M. Curcio, P. L. Arnold and J. B. Love, *Organometallics*, 2015, **34**, 2608.