Electronic Supplementary Information

Trinuclear zinc calix[4]arenes: Synthesis, structure, and ring opening polymerization studies†

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Crystallography

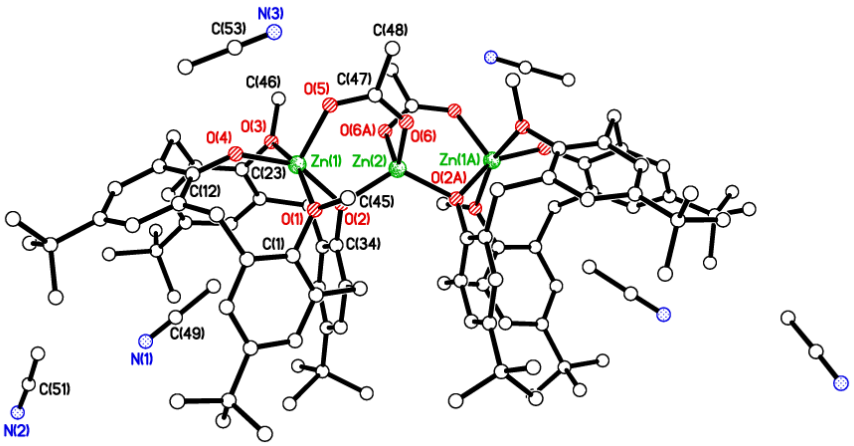


Figure S1. Molecular structure of $[Zn_3(O_2CCH_3)_2(L(O)_2(OMe)_2)_2]\cdot 6MeCN$ H atoms and minor disorder components omitted for clarity. **1'**·6MeCN. Selected bond lengths (Å) and angles (°): Zn(1)-O(1) 2.2204(17), Zn(1)-O(2) 1.9963(18), Zn(1)-O(3) 2.2373(17), Zn(1)-O(4) 1.8919(19), Zn(2)-O(2) 1.9540(17), Zn(2)-O(6) 1.968(2); Zn(1)-O(2)-Zn(2) 107.97(9), O(2)-Zn(2)-O(2A) 121.68(11). Symmetry operator A = –*x*+0.5, *y*, –*z*.

In **1'**·6MeCN, the Zn(1) centre is 5-coordinate and is approximately trigonal bipyramidal as indicated by a structural index parameter of τ = 0.20 [7]. The central Zn(2) is 4-coordinate tetrahedral and is much less distorted than the central zinc centres found in **2** and **3**. One MeCN sits in each calixarene cavity and there are four others that lie *exo* to the molecule.

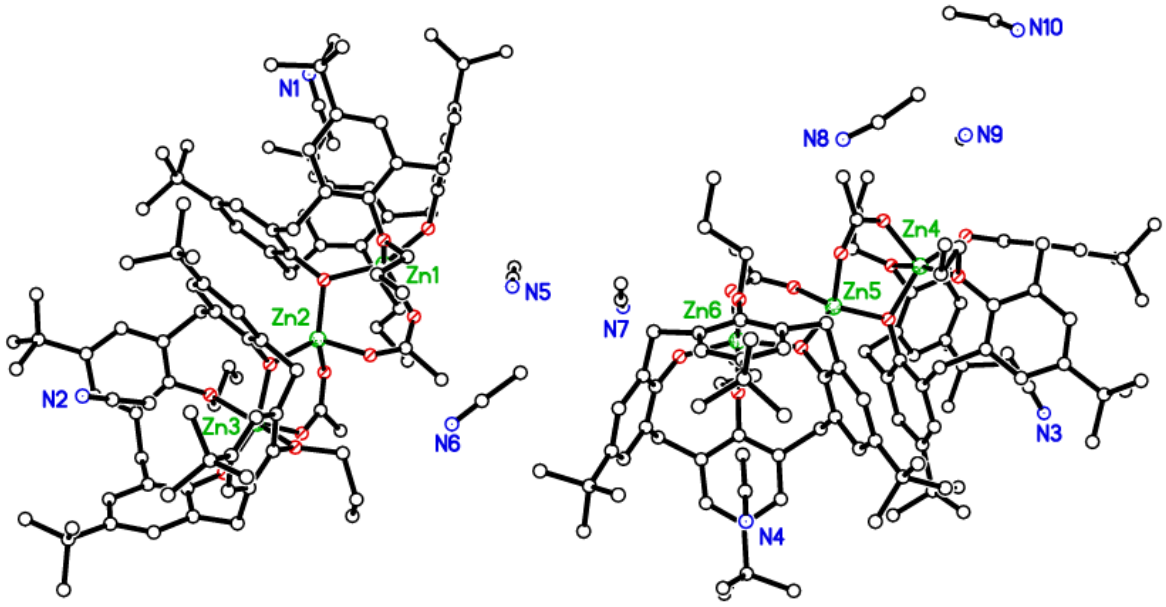


Figure S2. Alternative view of **2**·5MeCN showing the full asymmetric unit but with H atoms and minor disorder components omitted for clarity.

In separate experiments conducted in an attempt to form **3**·8MeCN, two different polymorphs of L(OH)$_2$(O*n*-pentyl)$_2$·MeCN were isolated.

In the first structure, the crystal system is monoclinic and the asymmetric unit comprises α-L(OH)$_2$(O*n*-pentyl)$_2$·MeCN with Z' = 1, and we have reported this structure previously. [S1] Since the data quality are considerably improved on this occasion, we present here the improved results in Table S1.

Table S1. Crystal structure data for α-L(OH)$_2$(Opentyl)$_2$.

Compound	**α-L(OH)$_2$(O*n*-pentyl)$_2$·MeCN**
Formula	$C_{56}H_{79}NO_4$
Formula weight	830.20
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	19.6259(2)
b (Å)	11.52628(9)
c (Å)	23.5831(3)
α (°)	90
β (°)	110.1060(13)
γ (°)	90
V (Å^3)	5009.70(10)
Z	4
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Calculated density (g cm^{-3})	1.101
Absorption coefficient (mm^{-1})	0.52

Crystal size (mm^3)	0.24 × 0.10 × 0.08
ϑ(max) (°)	68.3
Reflections measured	46943
Unique reflections	9146
Reflections with $I > 2\sigma(I)$	7991
R_{int}	0.028
Number of parameters	571
R_1 [$F^2 > 2\sigma(F^2)$]	0.052
wR_2 (all data)	0.147
GOOF, S	1.02
Largest difference peak and hole (eÅ^{-3})	0.43 and –0.25

The second, new, triclinic polymorph is non-merohedrally twinned via a 180° rotation about direct space 1 0 0 and has Z' = 2. The two twin components have a ratio of 0.518:0.482(2), and data data quality is fairly poor. The crystal data are presented in table 2 in the main manuscript.

As for the monoclinic polymorph, one of the pentyl groups lies across the top of the calixarene and forms weak C–H···O interactions with one of the phenol oxygens. This is true for both independent molecules.

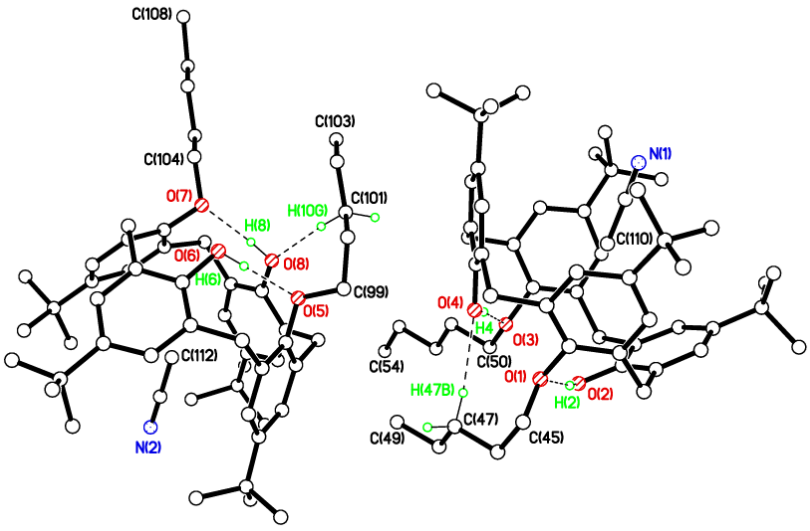


Figure S3. Molecular structure of the triclinic polymorph of β-L(OH)$_2$(O*n*-pentyl)$_2$·MeCN showing the full asymmetric unit comprising two formula units. Most H atoms omitted for clarity.

Both polymorphs form layered structures, with both types of unique molecule within the same layer, and with hydrophobic & hydrophilic zones.

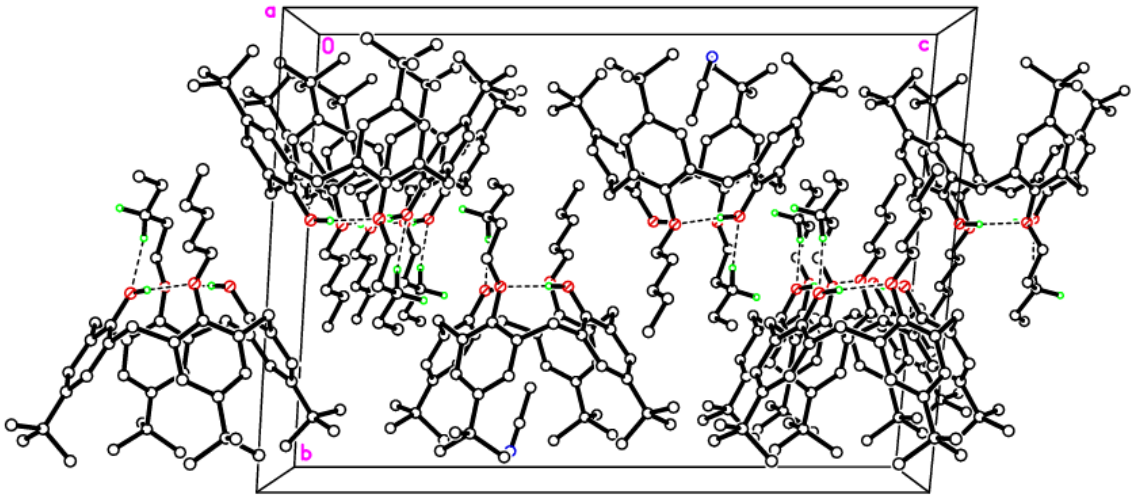
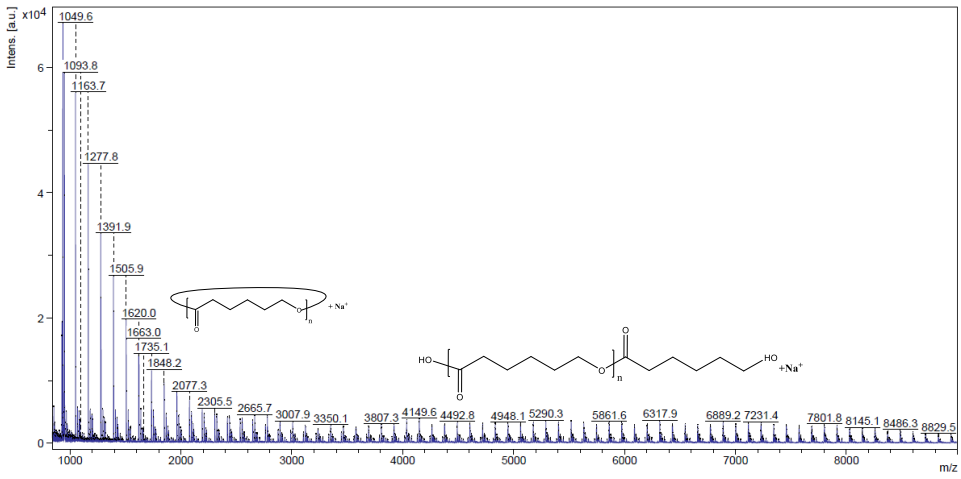
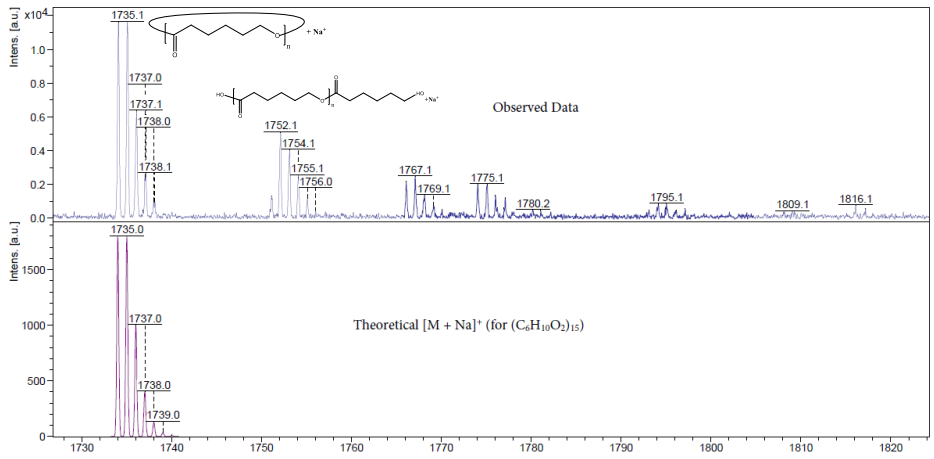


Figure S4. Packing structure of the triclinic polymorph β-L(OH)$_2$(O*n*-pentyl)$_2$·MeCN.

Ring opening polymerization





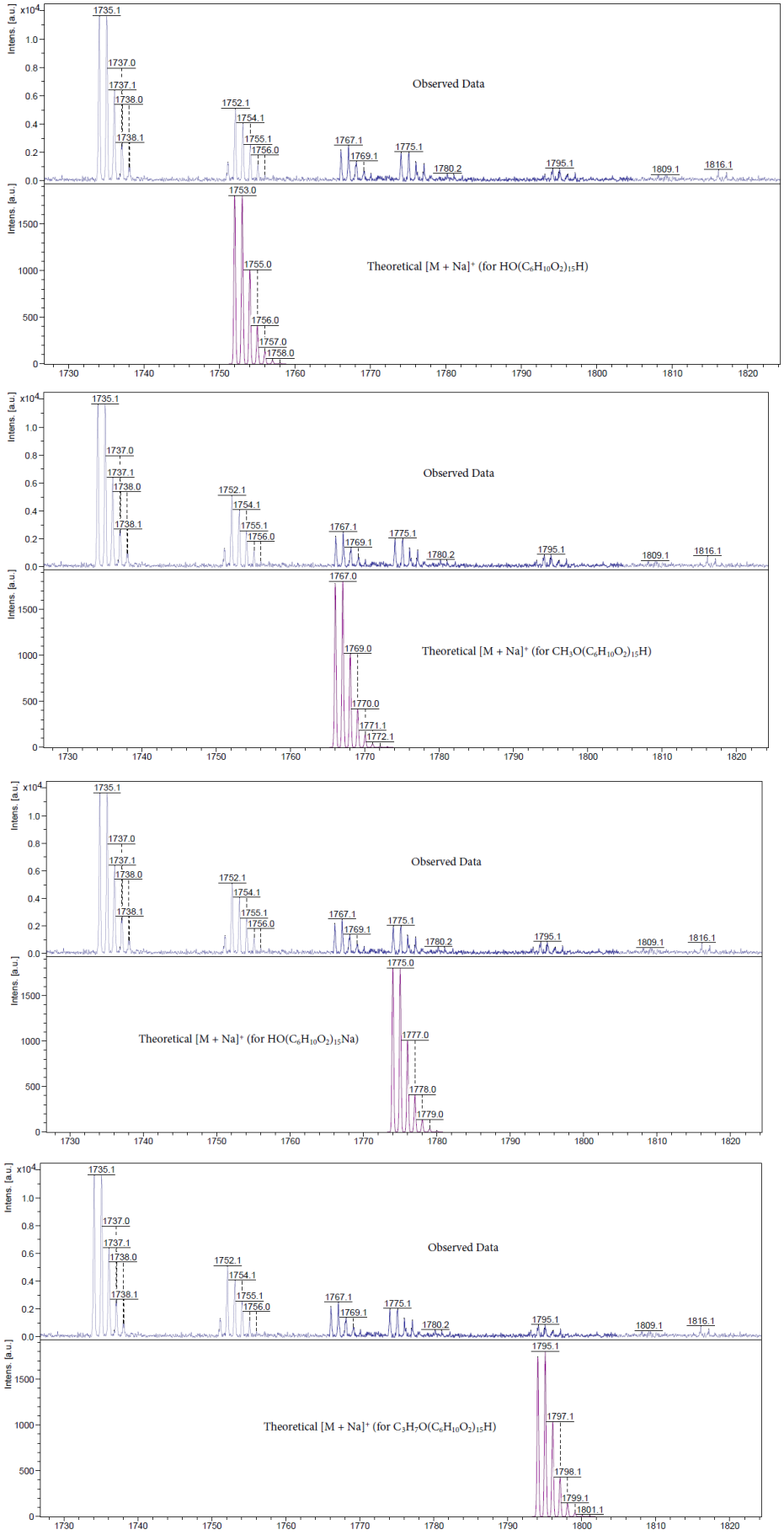
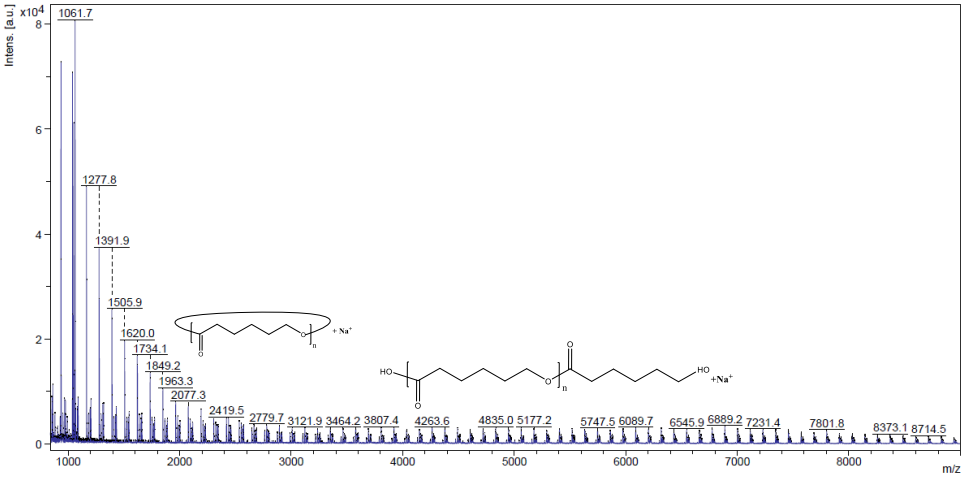
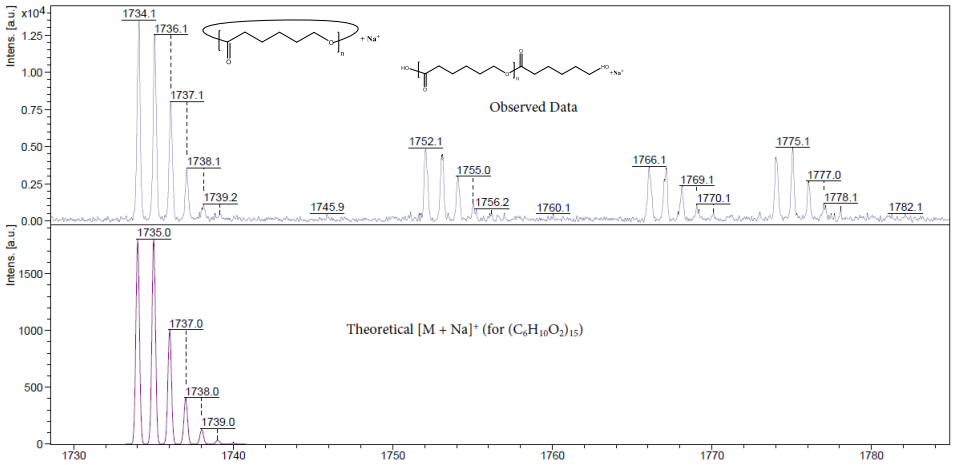
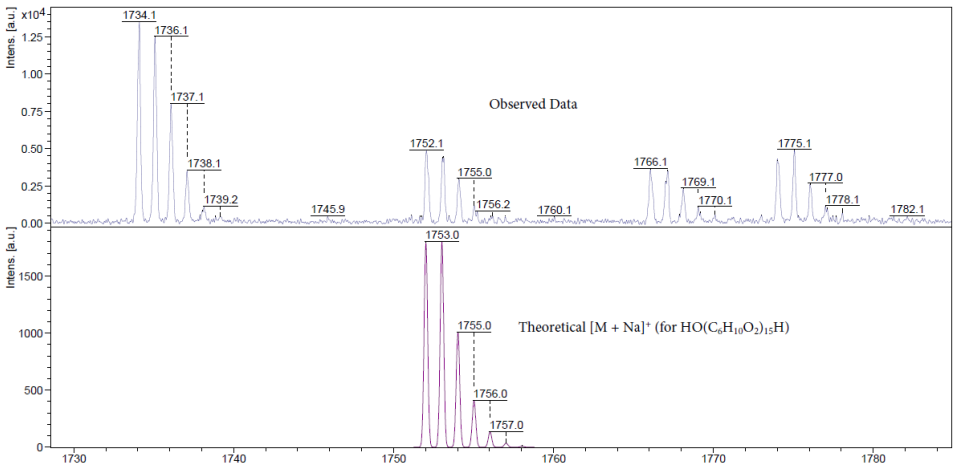


Figure S5. MALTI-TOF spectrum of PCL from **2** (entry 11, table 1). The main polymer are cyclic polymers [M = 22.99 (Na+) + n × 114.14 (CL)] (e.g. peak 1735 = (15 x

114.14)+23) and chain polymer (terminated by 2 OH) [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na+)] (e.g. peak 1753= (15 x 114.14)+23+18).







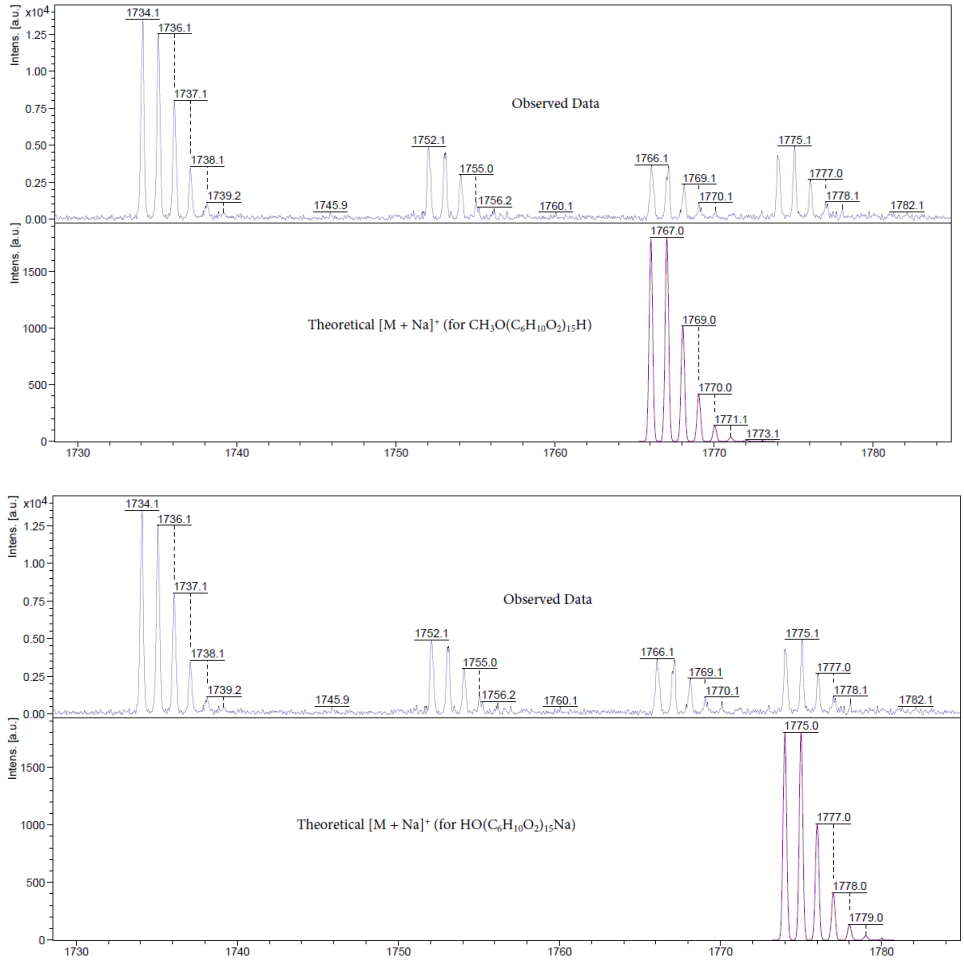
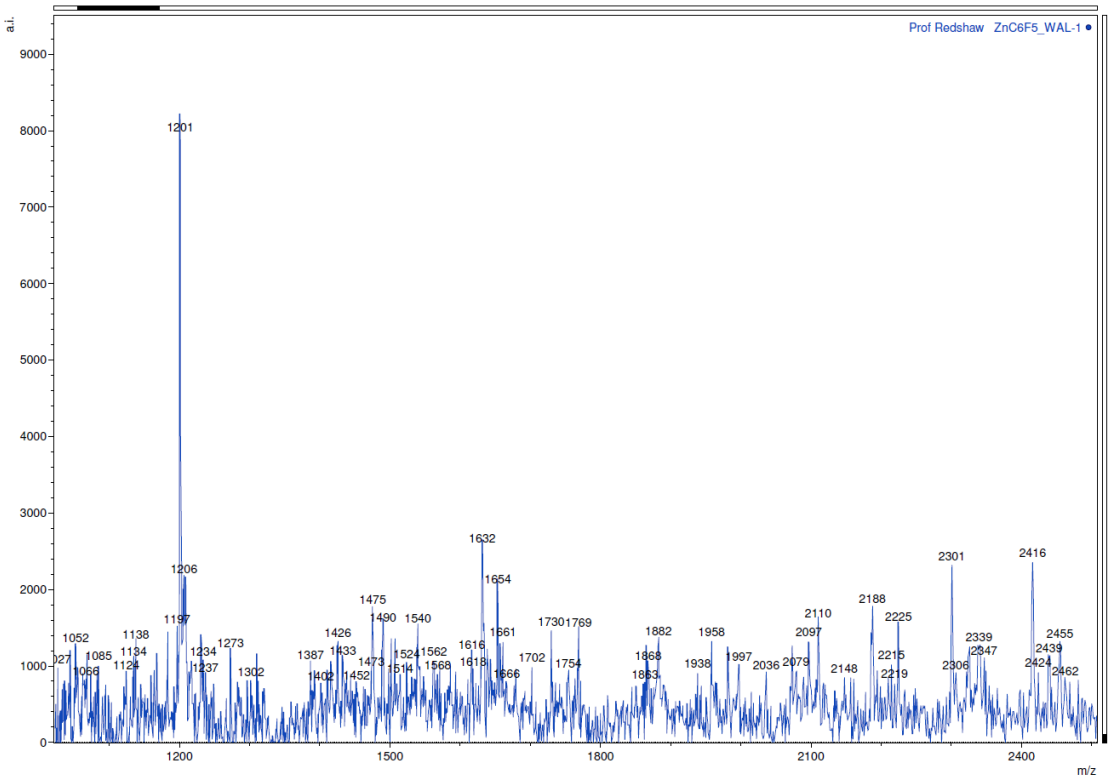
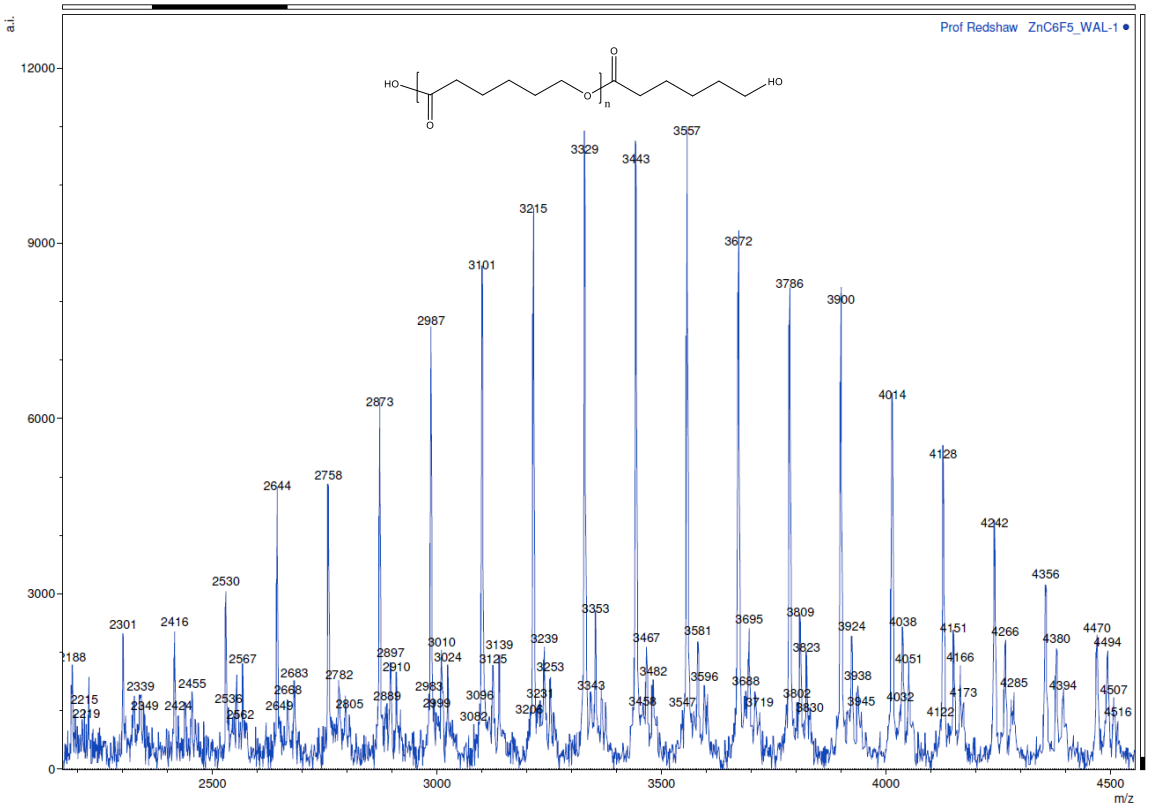


Figure S6. MALTI-TOF spectrum of PCL from **3** (entry 14, table 1). The main polymer are cyclic polymers [M = 22.99 (Na+) + n × 114.14 (CL)] (e.g. peak 1734= 15*114.14+23) and chain polymer (terminated by 2 OH) [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na+)] (e.g. peak 1752= 15*114.14+23+18).

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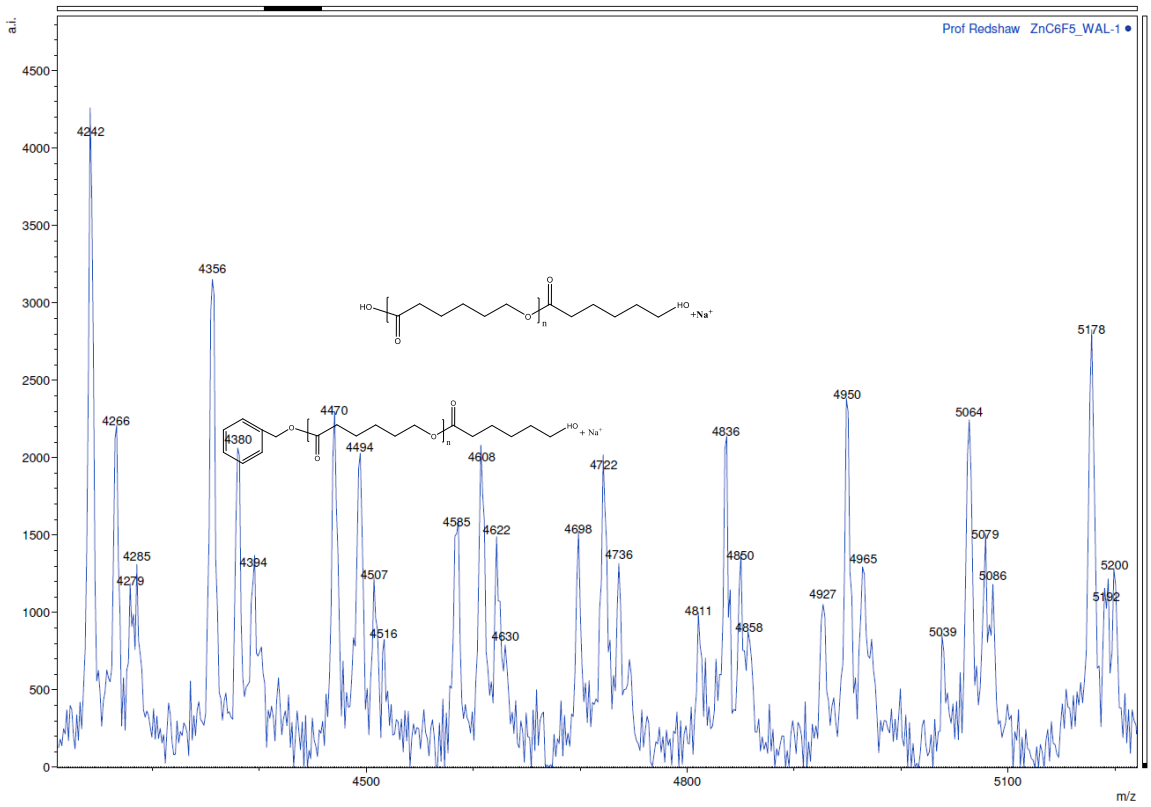
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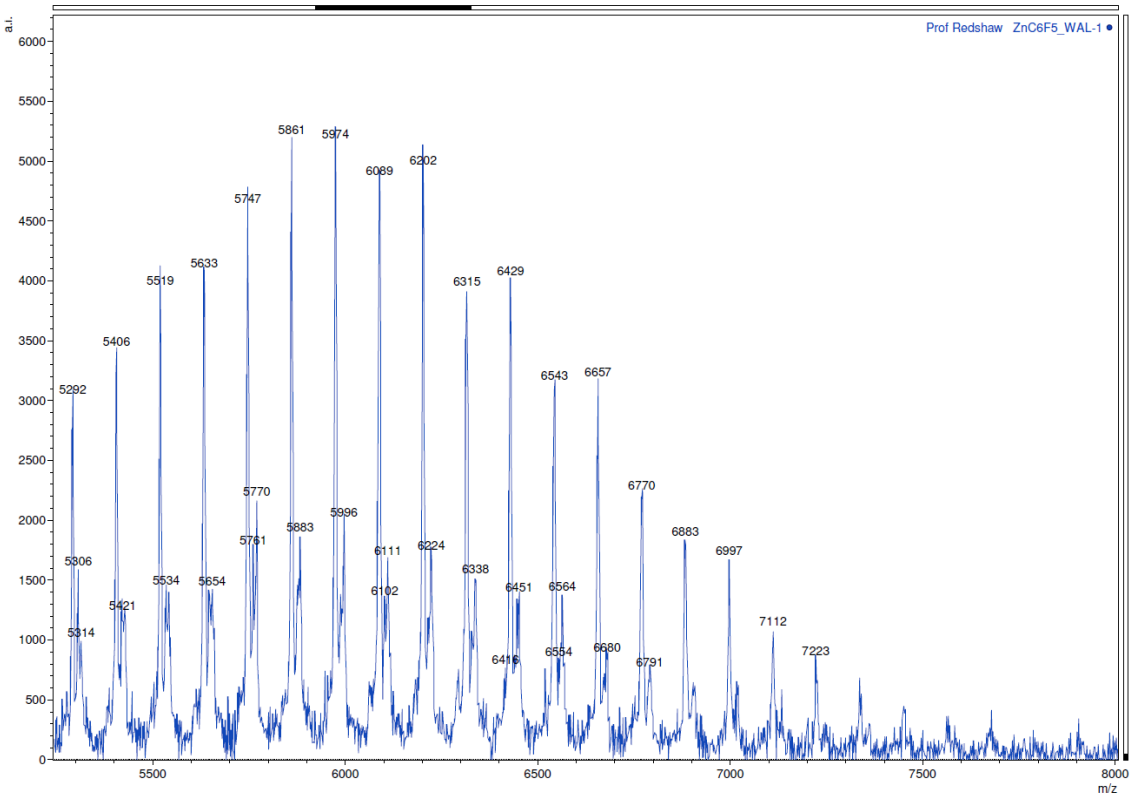

Figure S7. MALTI-TOF spectrum of PCL from **6**/BnOH (entry 19, Table 1). The main polymer are polymers with BnO end groups [M = n × 114.12 (CL) + 17 (OH) + 1(H)] (e.g. peak 3443 = 114.14*30 +18). The middle series ($^{m}/_{z}$ 4380, 4494, 4608, 4722 etc.) is likely HO-/-H end groups and the third series ($^{m}/_{z}$ 4356, 4470, 4585, 4698 etc.) is likely CH_3O-/-H end groups.

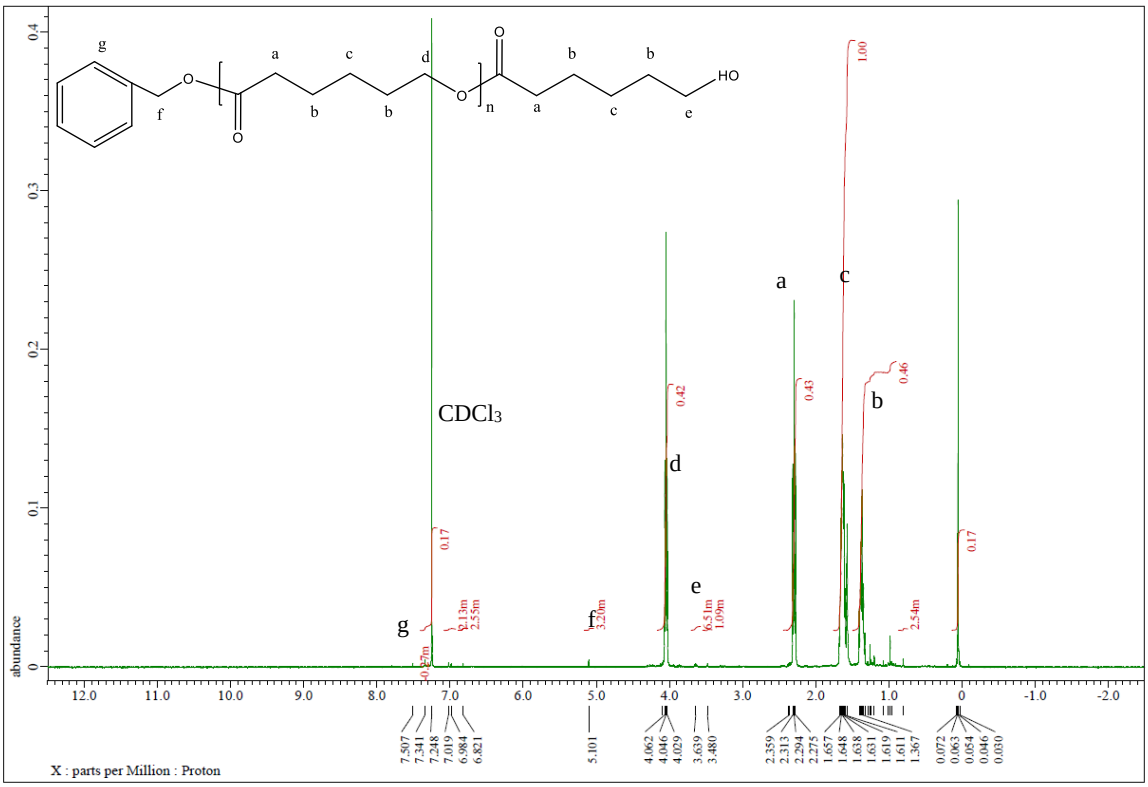

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of PCL from **5**/BnOH (entry 17, table 1).

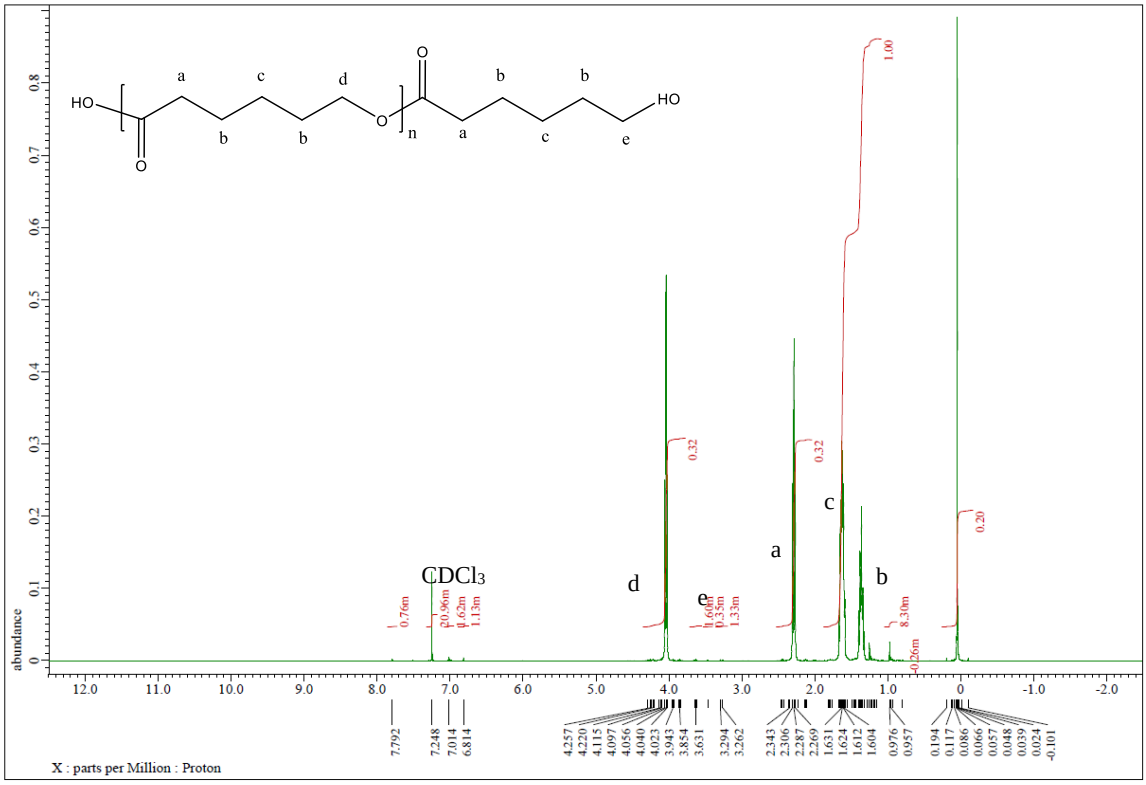

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL synthesized with **5** in the absence of BnOH (entry 18, Table 1).

References

[S1] C. Redshaw, M. R. J. Elsegood, J. A. Wright, H. Baillie-Johnson, T. Yamato, S. De Giovanni and A. Mueller, *Chem. Commun*. 2012, **48**, 1129-1131.