# Supplementary data

## Coordination and Catalysis of Zn²⁺ in Epoxy-Based Vitrimers

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## 1. Materials - Fatty acids

Pripol® 1040 was kindly provided by Croda. This material, usually referred as trimer acid is actually a complex mixture of polycarboxylic acids produced from coupling reactions of bio-based unsaturated fatty acids (mainly oleic and linoleic) and partially hydrogenated. According to the manufacturer's specifications, Pripol 1040 contains 77 wt% of tricarboxylic acid trimers and 23 wt% of dicarboxylic acid dimers (70 mol% and 30 mol% respectively). IR and NMR data are consistent with the cycloaliphatic structure generally accepted [1-3]. Isomers and acyclic dimers may be also present.[4-6] Feed ratios in epoxy-acid reactions were calculated on the basis of the acid value given by the manufacturer, which corresponds to an equivalent weight of 296 g per mole of COOH functions.

| $\delta$ (ppm) / TMS | attribution | integral found | expected |
|---|---|---|---|
| 0.89 (triplet) | $CH_3$ | | |
| expected: 0.80 to 1.25 | cyclic CH (axial) | | |
| expected: 1.13 to 1.18 | cycle—$C\underline{H}_2$—$(CH_2)_n$- | | |
| 1.26 | $CH_2$ (chain) | 76 | 74 to 82 * |
| 1.63 | $C\underline{H}_2$—$CH_2$—COOH | | |
| 1.5 to 1.8 | cyclic CH (equatorial) | | |
| 2.0 and 2.5 | allylic CH | | |
| expected 5.10 to 5.40 | -C$\underline{H}$=CH- | 0.8 | 0 to 8 * |
| 2.34 (triplet) | -C$\underline{H}_2$-COOH | 5.4 | 5.4 |
| 9.3 (very broad) | -COO$\underline{H}$ | 1.3 | 2.7 |

**Table S1.** ^{1}H NMR (CDCl$_3$) bands attribution, *depending on residual unsaturation

| wavelength (cm$^{-1}$) | attribution [4] | |
|---|---|---|
| 2250-3500 | $\nu_{O-H}$ | acid |
| 2953 (shoulder) | $\nu_a$ $CH_3$ | |
| 2922 | $\nu_a$ $CH_2$ | |
| 2870 (shoulder) | $\nu_s$ $CH_3$ | |
| 2853 | $\nu_s$ $CH_2$ | |
| 1707 | $\nu_{C=O}$ | acid |
| 1461 | $\delta$ $CH_2$ | scissoring |
| 1413 | $\nu_{C-O} + \delta_{OH}$ comb. | acid |
| 1375 | $\delta_s$ $CH_3$ | |
| 1285 and 1238 | $\nu_{C-O}$ | acid  (H-bond dimerized) |
| 1119 | $\nu_{C-O}$ | acid (not dimerized) |
| 933 | $\delta_{OH}$ | out-of-plane bending |
| 724 | $\delta$ $(CH_2)_n$ | rocking |

**Table S2**. ATR-IR bands attribution

## 2. Fatty acid-based zinc dicarboxylate (compound 1)
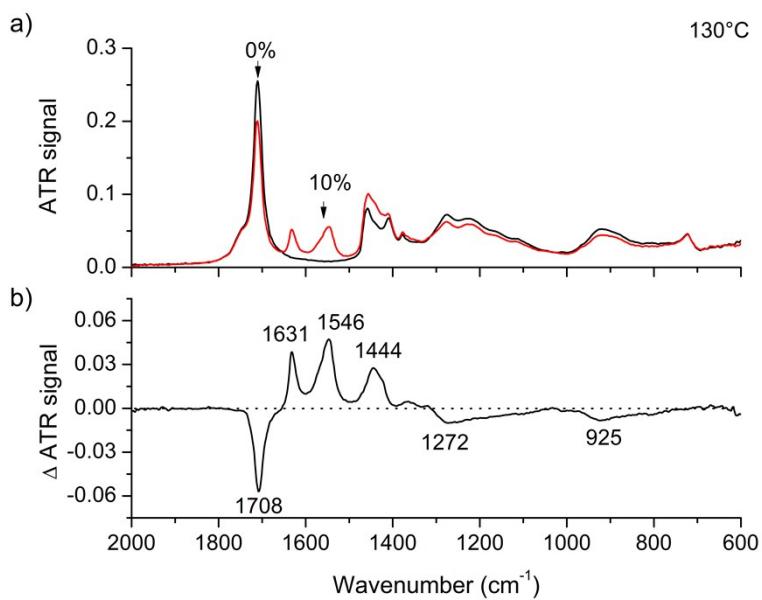


**Figure S1.** a) ATR-IR spectrum of starting fatty acid (black) and fatty acid-based zinc dicarboxylate 10 mol% (red), b) ATR signal difference.

## 3. Vitrimer synthesis (compound 2)
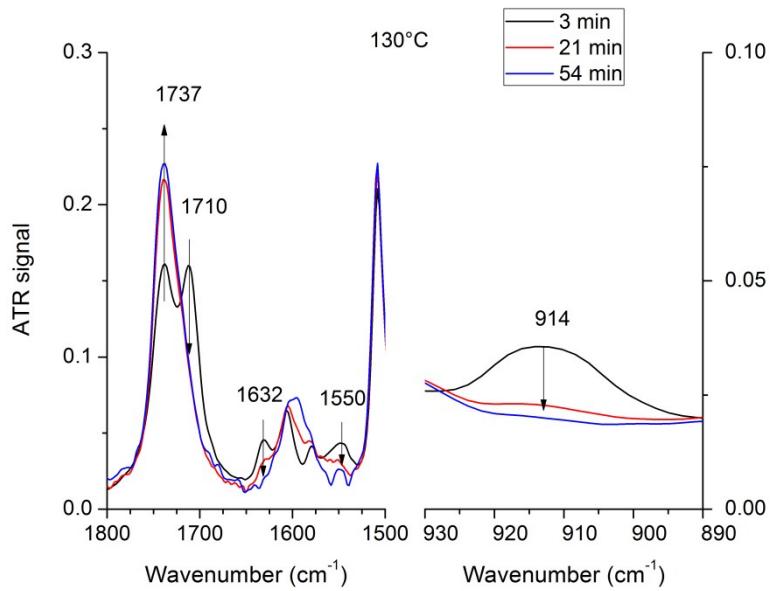


**Figure S2.** Carbonyl (1800-1500 cm$^{-1}$) and epoxy (930-890 cm$^{-1}$) regions of FTIR spectra during the curing of epoxy-acid networks at 130°C. Spectra were taken every 3 min.
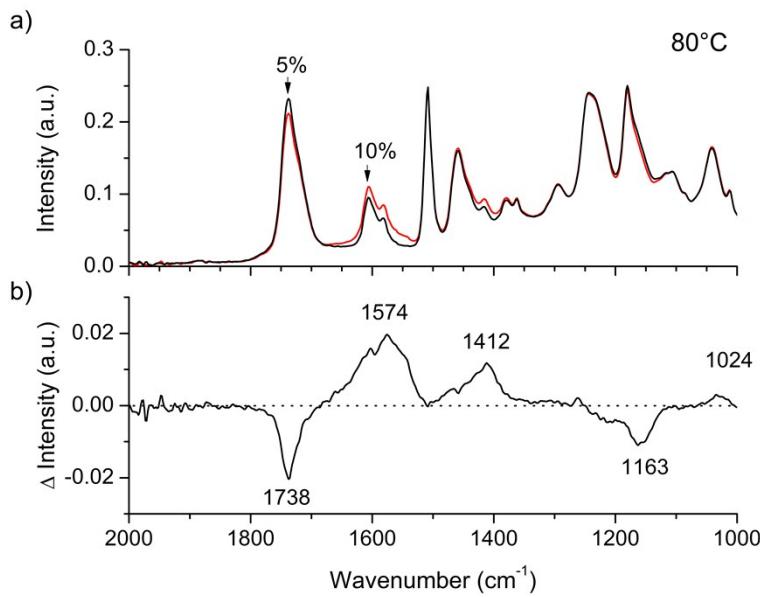
**Figure S3.** a) ATR-IR spectra of 5 mol% Zn-catalyzed epoxy vitrimer (black) and 10 mol% Zn-catalyzed vitrimer (red). b) ATR-IR spectrum difference A(10 %) - A(5 %).

## 4. 3-phenoxy-1,2-propanediol (compound 3)
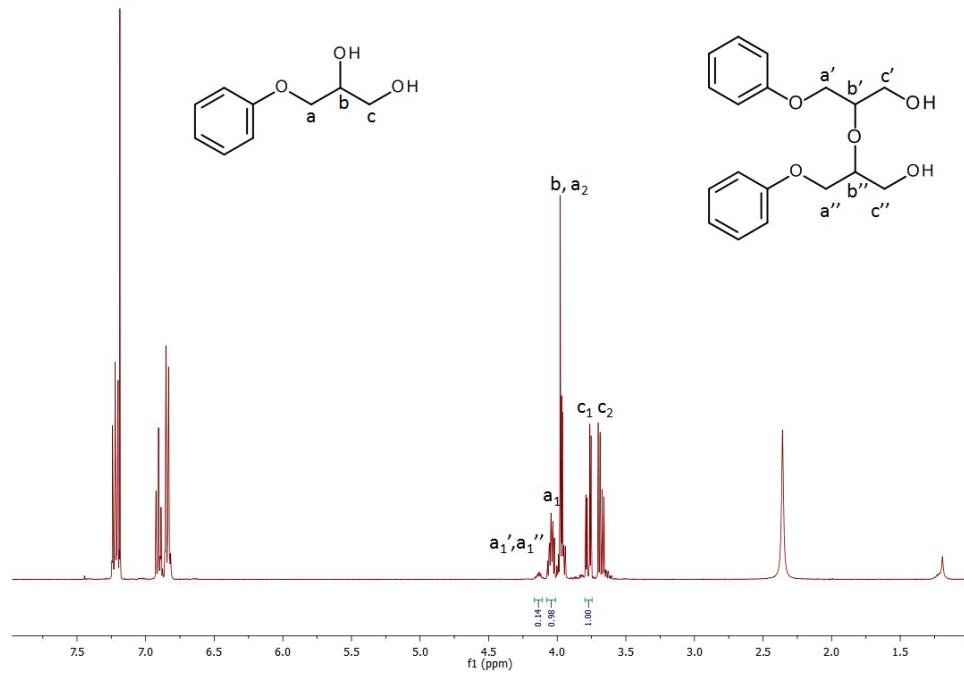


**Figure S4.** NMR of compound 3 in CDCl$_3$

## 5. 3-phenoxypropylene diacetate (compound 4)
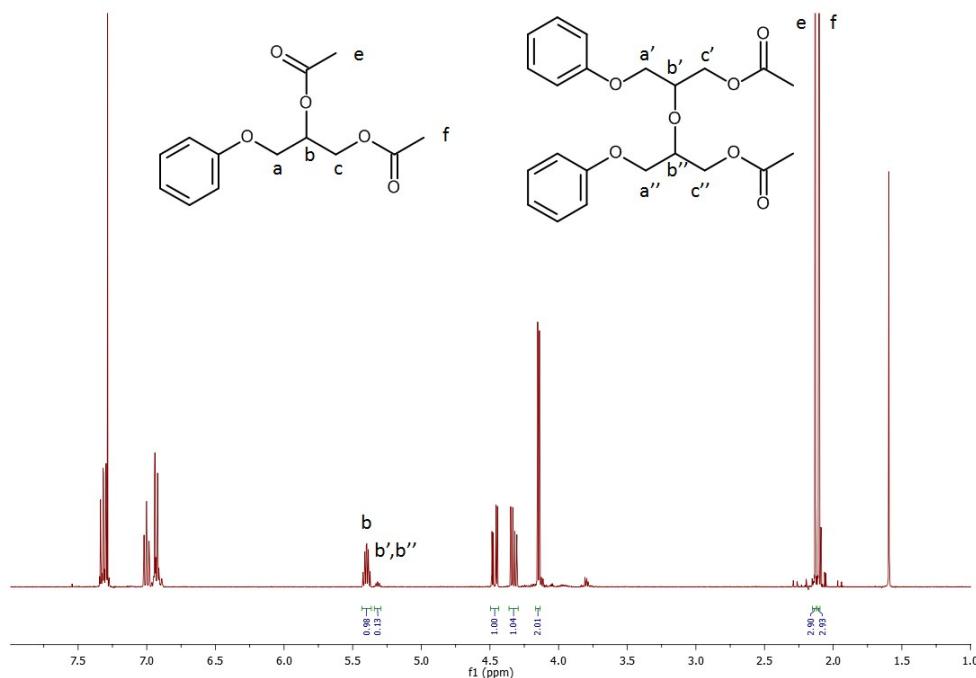


**Figure S5.** NMR of compound 4 in CDCl$_3$

## 6. Catalysis
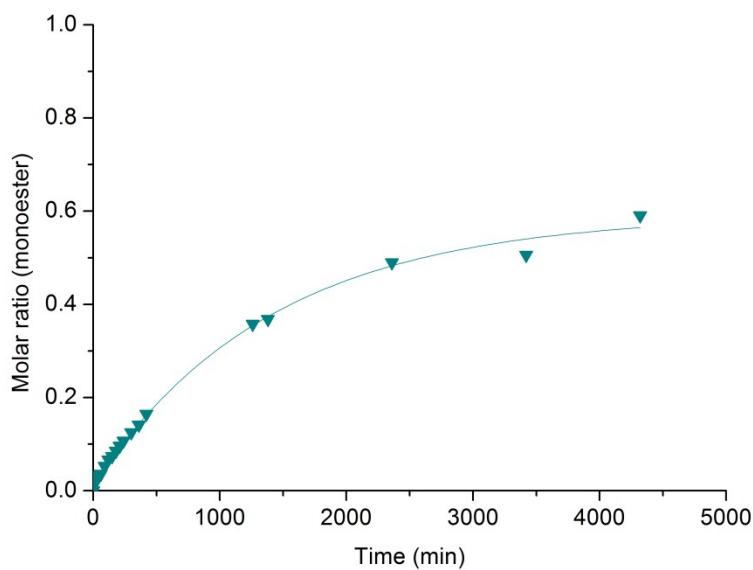


**Figure S6.** Transesterification kinetics results at 150°C for the di-ester and di-hydroxy mix model molecules without metal catalyst added.

## 7. X-ray powder diffraction

X-ray powder diffraction (XRD) was performed using a Philips X'Pert diffractometer. Co Kα radiation (1.79Å) was used at 40 kV and 40 mA. A counting time of 25 s per 0.05 ° step was used for the 2θ range 15−90 °.
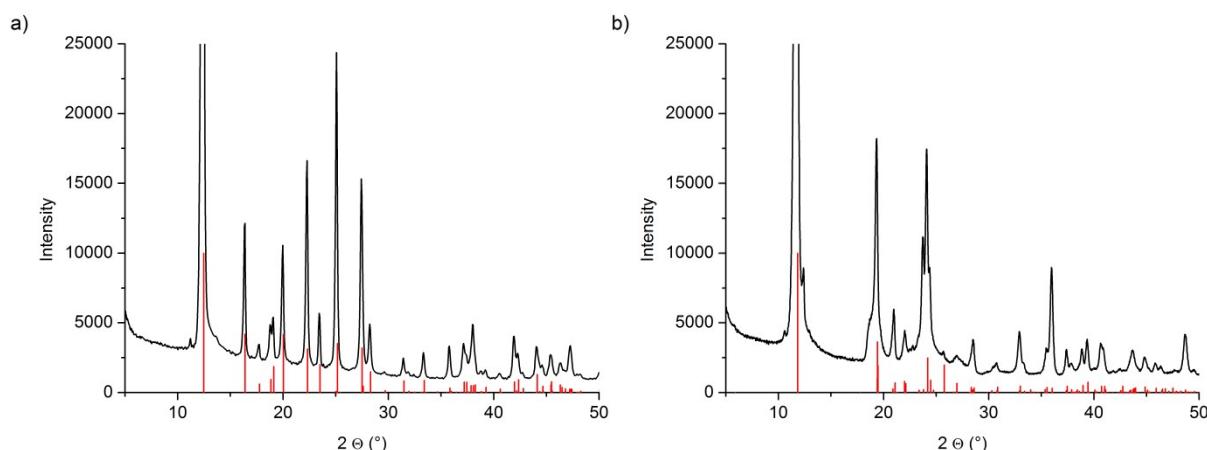


**Figure S7.** a) X-ray powder diffraction pattern of zinc acetate dihydrate and simulated (bottom, red) based on the crystal structure proposed by Ishioka[7] b) X-ray powder diffraction pattern of anhydrous zinc acetate and simulated (bottom, red) based on the crystal structure proposed by Clegg[8]

## 8. EXAFS Spectroscopy
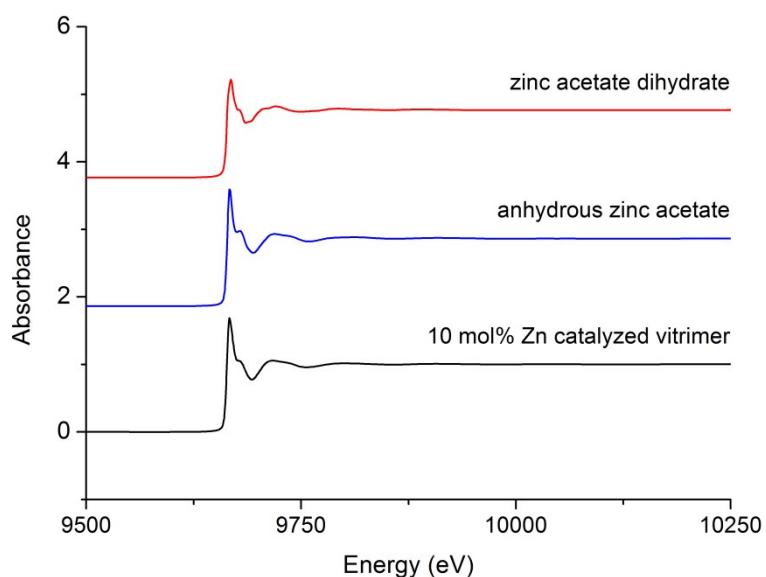


**Figure S8.** X-Ray absorption spectra (μ(E) plots) of anhydrous zinc acetate (top, red), zinc acetate dihydrate (middle, blue) and the 10 mol% Zn-catalyzed epoxy-acid vitrimer system (bottom, black).
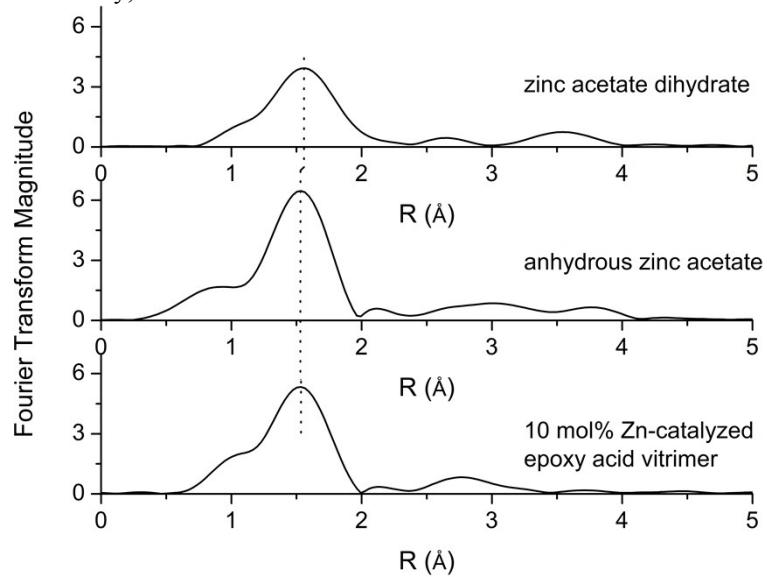
**Figure S9.** Radial structure functions of anhydrous zinc acetate (top), zinc acetate dihydrate (middle) and the 10 mol% Zn-catalyzed epoxy-acid vitrimer system (bottom).

## 8. Shift in carbonyl vibration by coordination with Zn2+

In order to estimate the IR peak shift by zinc coordination, four complexes with $Zn^{2+}$ and two molecules without $Zn^{2+}$ were calculated (Figure S10, Table S3). The calculated shifts for Zn...O=C coordination, with or without chelation are consistent with experimental data.
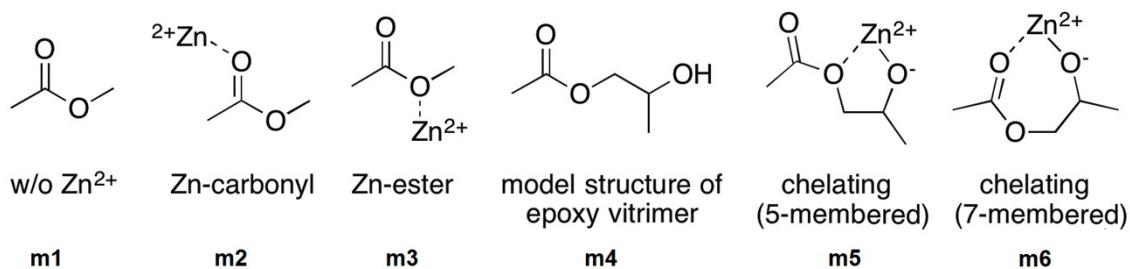


**Figure S10.** Possible complexation models of an ester with a zinc cation.

| | model complex | $\omega$ | shift | O-Zn distance [Å] |
|---|---|---|---|---|
| m1 | w/o $Zn^{2+}$ | 1750 | – | NA |
| m2 | Zn-carbonyl *(Structure I)* | 1373 1589 | 161 | 1.818 |
| m3 | Zn-ester | 1760 | −10 | 2.800 |
| m4 | model structure of epoxy vitrimer | 1743 | – | NA |
| m5 | chelating (5-membered) | 1853 | −103 | 1.826 (alcoxy) 2.018 (ester) |
| m6 | chelating (7-membered) | 1581 | 169 | 1.812 (alcoxy) 1.921 (carbonyl) |

**Table S3.** Shift in calculated IR frequencies ($\omega$, cm$^{-1}$) of carbonyls by Zn coordination.

Calculations were performed with a Gaussian 09 program package.[9]  The density functional theory (DFT) method was employed using M06.[10]  Structures were optimized with a basis set consisting of the LANL2DZ basis set including a double-zeta valence basis set with the Hay and Wadt effective core potential (ECP).[11] Each stationary point was adequately characterized by normal coordinate analysis (no imaginary frequencies for an equilibrium structure).

## 9. Coordination of Zn2+ by the β-hydroxy-alkoxide anion

In the particular case of β–diol strucures, produced by transesterification, the coordination of Zn+ is examined (Figure 5). The calculation technique is the same as above. Chelation is favored.
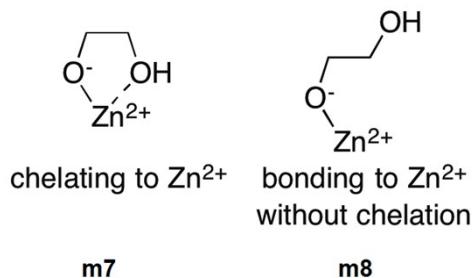


**Figure S11.** Complexation models of an ethylene glycol molecule and its anion with a zinc cation.

| model complex | | $\omega$ | O-Zn distance [Å] | C-O distance [Å] |
|---|---|---|---|---|
| **m7** | chelating to Zn$^{2+}$ | 819 (C-OH) **1053 (C-O⁻)** | 1.984 (alcohol) 1.828 (alcoxy) | 1.509 (C-OH) 1.453 (C-O⁻) |
| **m8** | bonding to Zn$^{2+}$ without chelation (unstable structure) | **1014 (C-O⁻)** 1143 (C-OH) | 1.823 (alcoxy) | 1.394 (C-OH) 1.428 (C-O⁻) |

**Table S4.** Calculated IR frequencies ($\omega$, cm$^{-1}$) of C-O bond by Zn coordination.

## 10. Calculated Coordinates

SCF Done:  E(RM06) = -268.183809469    A.U. after   13 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates X | (Angstroms) Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.789544 | -2.554025 | -0.403 |
| 2 | 1 | 0 | -0.278229 | -3.368703 | -0.923377 |
| 3 | 1 | 0 | -0.428667 | -1.614529 | -0.831401 |
| 4 | 1 | 0 | -1.86703 | -2.637595 | -0.544683 |
| 5 | 6 | 0 | -0.466303 | -2.601462 | 1.061594 |
| 6 | 8 | 0 | -1.271996 | -2.69337 | 1.992786 |
| 7 | 8 | 0 | 0.891216 | -2.525049 | 1.260654 |
| 8 | 6 | 0 | 1.352463 | -2.554218 | 2.642793 |
| 9 | 1 | 0 | 1.072274 | -3.499468 | 3.116623 |
| 10 | 1 | 0 | 2.435333 | -2.452662 | 2.588273 |
| 11 | 1 | 0 | 0.90937 | -1.729736 | 3.208777 |

**Table S5.** Compound **m1** (w/o Zn$^{2+}$)

SCF Done:  E(RM06) =  -332.908344000    A.U. after   14 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates X | (Angstroms) Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.738877 | -2.774 | -0.526454 |
| 2 | 1 | 0 | -0.425153 | -3.791724 | -0.776527 |
| 3 | 1 | 0 | -0.209473 | -2.117549 | -1.231176 |
| 4 | 1 | 0 | -1.81377 | -2.671579 | -0.685117 |
| 5 | 6 | 0 | -0.324853 | -2.443451 | 0.857039 |
| 6 | 8 | 0 | 0.815877 | -2.860577 | 1.25606 |
| 7 | 6 | 0 | 1.484503 | -2.639685 | 2.586644 |
| 8 | 1 | 0 | 0.885255 | -3.134842 | 3.352075 |
| 9 | 1 | 0 | 2.454143 | -3.115747 | 2.464633 |
| 10 | 1 | 0 | 1.578424 | -1.565294 | 2.750954 |
| 11 | 8 | 0 | -1.055922 | -1.726047 | 1.700936 |
| 12 | 30 | 0 | -2.600284 | -0.815375 | 1.999253 |

**Table S6.** Compound **m2** (Zn-carbonyl)

SCF Done:  E(RM06) =  -333.651594550    A.U. after   12 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates X | (Angstroms) Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.882763 | -2.484442 | -0.345629 |
| 2 | 1 | 0 | -0.15232 | -2.973969 | -0.997222 |
| 3 | 1 | 0 | -0.844357 | -1.411019 | -0.558405 |
| 4 | 1 | 0 | -1.882901 | -2.865106 | -0.553076 |
| 5 | 6 | 0 | -0.537253 | -2.732278 | 1.092824 |
| 6 | 8 | 0 | -1.262638 | -3.23206 | 1.95426 |
| 7 | 6 | 0 | 1.228454 | -2.483245 | 2.732807 |
| 8 | 1 | 0 | 1.207158 | -3.539696 | 3.012507 |
| 9 | 1 | 0 | 2.250673 | -2.10122 | 2.728742 |
| 10 | 1 | 0 | 0.600921 | -1.91484 | 3.424374 |
| 11 | 30 | 0 | 2.57625 | -0.976522 | -0.283361 |
| 12 | 8 | 0 | 0.749924 | -2.314002 | 1.364549 |

**Table S7.** Compound **m3** (Zn-ester)

SCF Done: E(RM06) = -727.908719412    A.U. after   15 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates | (Angstroms) | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | -1.975689 | -0.622175 | 0.219614 |
| 2 | 1 | 0 | -2.4587 | -1.610018 | 0.125438 |
| 3 | 1 | 0 | -1.988434 | -0.310267 | 1.27461 |
| 4 | 6 | 0 | -3.973811 | 0.654819 | -0.30693 |
| 5 | 6 | 0 | -4.706027 | 0.070506 | 0.738377 |
| 6 | 6 | 0 | -4.561953 | 1.623644 | -1.135866 |
| 7 | 6 | 0 | -6.036526 | 0.467755 | 0.945797 |
| 8 | 1 | 0 | -4.262476 | -0.677533 | 1.388601 |
| 9 | 6 | 0 | -5.886194 | 2.007376 | -0.917718 |
| 10 | 1 | 0 | -3.961161 | 2.05564 | -1.92975 |
| 11 | 6 | 0 | -6.632905 | 1.431286 | 0.125225 |
| 12 | 1 | 0 | -6.604167 | 0.01754 | 1.755182 |
| 13 | 1 | 0 | -6.337996 | 2.758355 | -1.558952 |
| 14 | 1 | 0 | -7.661885 | 1.732851 | 0.293239 |
| 15 | 8 | 0 | -2.657809 | 0.336263 | -0.607959 |
| 16 | 6 | 0 | -0.536743 | -0.671003 | -0.251869 |
| 17 | 1 | 0 | -0.511503 | -0.518508 | -1.340935 |
| 18 | 6 | 0 | 0.104599 | -2.014743 | 0.07453 |
| 19 | 1 | 0 | -0.395362 | -2.834684 | -0.458773 |
| 20 | 1 | 0 | 0.07117 | -2.193129 | 1.159114 |
| 21 | 8 | 0 | 0.166659 | 0.378717 | 0.435315 |
| 22 | 8 | 0 | 1.480183 | -1.877512 | -0.375867 |
| 23 | 6 | 0 | 2.442563 | -2.850313 | -0.15369 |
| 24 | 8 | 0 | 3.580124 | -2.647642 | -0.563328 |
| 25 | 6 | 0 | 2.006206 | -4.090987 | 0.590419 |
| 26 | 1 | 0 | 1.692775 | -3.843829 | 1.610438 |
| 27 | 1 | 0 | 1.167609 | -4.585796 | 0.089744 |
| 28 | 1 | 0 | 2.852413 | -4.776013 | 0.635478 |
| 29 | 1 | 0 | 1.085831 | 0.433489 | 0.104912 |

**Table S8.** Compound **m4** (model structure of epoxy vitrimer)

SCF Done: E(RM06) = -447.217644252    A.U. after   16 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates | (Angstroms) | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | 2.330919 | -0.787785 | -0.099781 |
| 2 | 1 | 0 | 2.239776 | -0.86781 | -1.189884 |
| 3 | 1 | 0 | 3.060772 | -1.526204 | 0.246877 |
| 4 | 6 | 0 | 0.989136 | -1.087134 | 0.578949 |
| 5 | 1 | 0 | 0.474468 | -1.945325 | 0.142771 |
| 6 | 1 | 0 | 1.083596 | -1.204571 | 1.661504 |
| 7 | 8 | 0 | 0.098805 | 0.124538 | 0.377851 |
| 8 | 8 | 0 | 2.841355 | 0.52649 | 0.263654 |
| 9 | 6 | 0 | -1.331423 | -0.087756 | 0.243546 |
| 10 | 6 | 0 | -2.039967 | 1.219919 | 0.098126 |
| 11 | 1 | 0 | -1.694469 | 1.755902 | -0.793255 |
| 12 | 1 | 0 | -3.109665 | 1.040281 | -0.009531 |
| 13 | 1 | 0 | -1.889356 | 1.845404 | 0.985459 |
| 14 | 8 | 0 | -1.763021 | -1.216413 | 0.261971 |
| 15 | 30 | 0 | 1.412756 | 1.655647 | 0.40541 |

**Table S9.** Compound **m5** (chelating (5-membered))

SCF Done:  E(RM06) =  -447.253363393    A.U. after   14 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | 2.222016 | -0.487288 | -0.234159 |
| 2 | 1 | 0 | 1.812909 | -1.491399 | -0.412733 |
| 3 | 1 | 0 | 3.262117 | -0.606796 | 0.092356 |
| 4 | 6 | 0 | 1.474801 | 0.177605 | 0.923925 |
| 5 | 1 | 0 | 1.821444 | -0.204677 | 1.883809 |
| 6 | 1 | 0 | 1.583838 | 1.27029 | 0.905108 |
| 7 | 8 | 0 | 0.004173 | -0.137976 | 1.006674 |
| 8 | 8 | 0 | 2.280554 | 0.285716 | -1.449199 |
| 9 | 6 | 0 | -0.957513 | 0.359442 | 0.253526 |
| 10 | 6 | 0 | -2.33807 | 0.099277 | 0.73409 |
| 11 | 1 | 0 | -2.669899 | 0.957855 | 1.330802 |
| 12 | 1 | 0 | -3.022373 | -0.000268 | -0.109211 |
| 13 | 1 | 0 | -2.363451 | -0.783344 | 1.37352 |
| 14 | 8 | 0 | -0.743562 | 1.033947 | -0.81484 |
| 15 | 30 | 0 | 0.780498 | 1.150423 | -1.978931 |

**Table S10.** Compound **m6** (chelating (7-membered))

SCF Done:  E(RM06) =  -294.689929342    A.U. after   9 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | -2.711038 | 1.403331 | -0.697969 |
| 2 | 1 | 0 | -2.427223 | 1.15017 | -1.727231 |
| 3 | 1 | 0 | -3.745499 | 1.75983 | -0.698063 |
| 4 | 6 | 0 | -2.626059 | 0.159722 | 0.202231 |
| 5 | 1 | 0 | -3.00472 | -0.731408 | -0.301573 |
| 6 | 1 | 0 | -3.121988 | 0.31199 | 1.164203 |
| 7 | 8 | 0 | -1.877034 | 2.481614 | -0.196394 |
| 8 | 8 | 0 | -1.165186 | -0.065469 | 0.505587 |
| 9 | 30 | 0 | -0.346848 | 1.741782 | 0.475489 |
| 10 | 1 | 0 | -0.938626 | -0.979714 | 0.749294 |

**Table S11.** Compound **m7**  (chelating to $Zn^{2+}$)

SCF Done:  E(RM06) =  -294.630638439    A.U. after   8 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | -0.996648 | 1.03303 | 0.130176 |
| 2 | 1 | 0 | -1.409441 | 1.764071 | -0.579046 |
| 3 | 1 | 0 | -1.331985 | 1.266743 | 1.145424 |
| 4 | 6 | 0 | -1.515688 | -0.373807 | -0.254648 |
| 5 | 1 | 0 | -0.725838 | -1.089555 | 0.187194 |
| 6 | 1 | 0 | -1.504195 | -0.536256 | -1.341239 |
| 7 | 8 | 0 | 0.422744 | 1.122495 | 0.002692 |
| 8 | 8 | 0 | -2.746071 | -0.609618 | 0.356314 |
| 9 | 30 | 0 | 1.353207 | -0.403365 | 0.36262 |
| 10 | 1 | 0 | -3.412164 | -1.070015 | -0.189133 |

**Table S12.** Compound **m8**  (bonding to $Zn^{2+}$ without chelation)

## 11. References

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