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Supplementary Materials for

2D-IR spectroscopy for oil paint conservation: Elucidating the water-sensitive structure of zinc carboxylate clusters in ionomers

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Supplementary Materials and Methods

X-ray absorption near-edge structure (XANES)

XANES spectra were collected at the DiffAbs beamline of synchrotron Soleil (Gif-sur-Yvette, France) using a micro-beam spot size of about 10×10 µm^2. The spectra were collected in transmission mode using an ion chamber detector. Zn foil was used to calibrate the XANES spectra. The spectra were normalized and baseline corrected. Samples were prepared by wrapping a stack of five pieces of thick LO/Zn film tightly in kapton tape (total thickness ~0.75 mm) that were either soaked in water or stored under high vacuum (~1 mbar) for two weeks prior to the measurement.

For XANES calculations, the same optimized structures of the oxo complex and terminated chain complex were used as for the calculation of IR frequencies. The XANES calculations were performed using the FEFF9 code (*40*) on the basis of self-consistent-field (SCF) real-space multiple-scattering (RSMS) theory. For the Zn K-edge calculation, a cluster of radius 5.0 Å around the central Zn atom was used to calculate the SCF muffin-tin atomic potentials within the Hedin-Lundqvist exchange potential, and a radius of 5.1 Å was used for the full multiple scattering (FMS) calculation.

Powder X-ray diffraction (pXRD)

pXRD traces were recorded on a Rigaku MiniFlex II desktop X-ray diffractometer using Cu Kα radiation. Powder samples were finely ground with mortar and pestle, and manually pressed into glass sample holders.
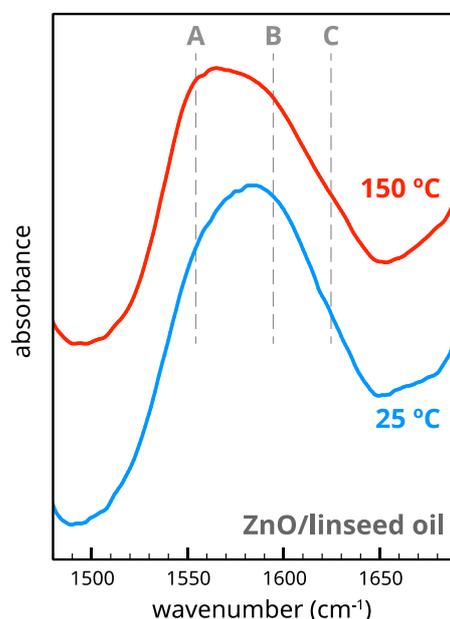

Fig. S1. The change in the carboxylate band envelope in a ZnO-LO mixture. Comparison of the asymmetric carboxylate stretch vibration band envelope under ambient and dry conditions in a pigmented paint film (1:1 w/w ZnO in linseed oil, spread on a glass slide to ~40 µm thickness, dried and aged for 16 months at 25 ºC and ~50%RH). While the difference is notably smaller than in Fig. 1C, it is clear that, upon drying, the relative intensity of bands A+C increases at the expense of band B, causing the overall band maximum to shift to lower wavenumbers.
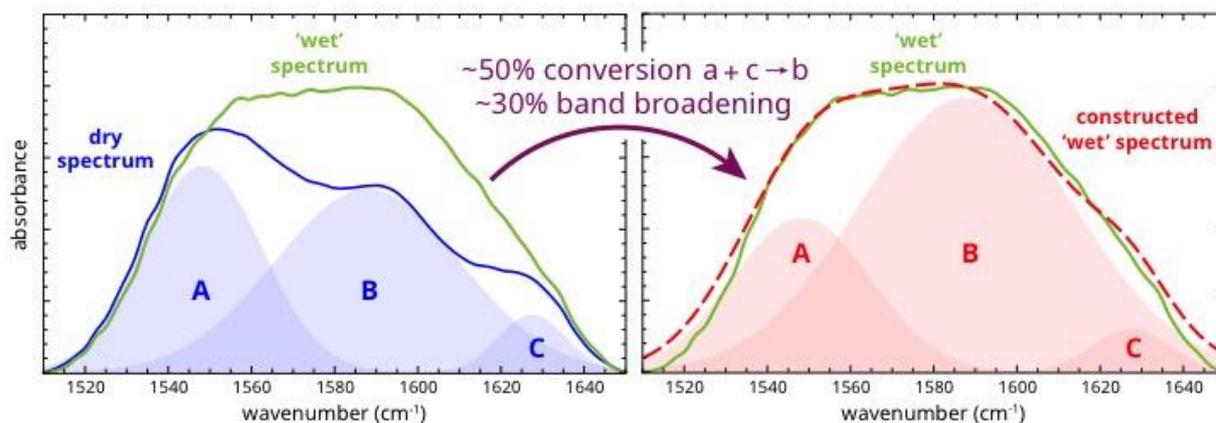
Fig. S2. Quantification of the change in the carboxylate band envelope upon drying.
Three Gaussian band shapes (labeled A, B and C) were fitted to the carboxylate band
envelope in spectrum of a dried LO/Zn, after linear baseline subtraction. To investigate the
differences between the 'wet' and 'dry' polymer, the center position of each Gaussian band
was fixed and the band intensities were coupled so any increase in the height of band B
causes a reduction of bands A and C while maintaining the intensity ratio of A and C. This
procedure with only a conversion factor and band width multiplication factor as adjustable
parameters allowed the reproduction of the 'wet' spectrum, with a conversion of species of
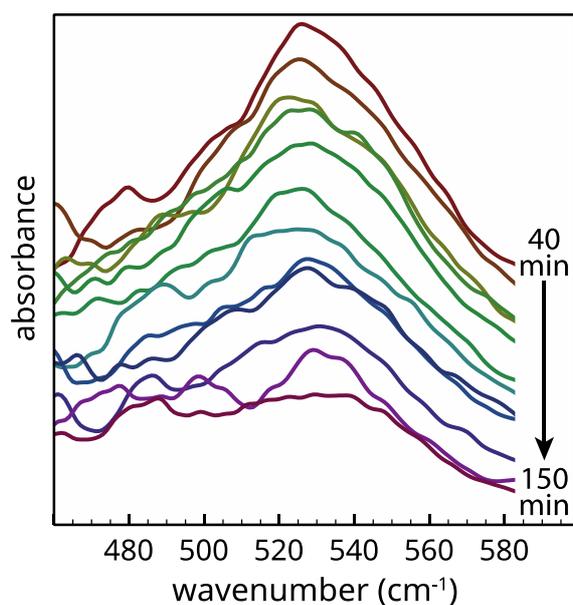approximately 50% and an increase in band width of 30%.

Fig. S3. The evolution of the Zn_4O band at 530 cm^{-1} during curing of LO/Zn. Time
series of ATR-FTIR spectra recorded during heating of a ~5 µm thick layer of LO/Zn at 190
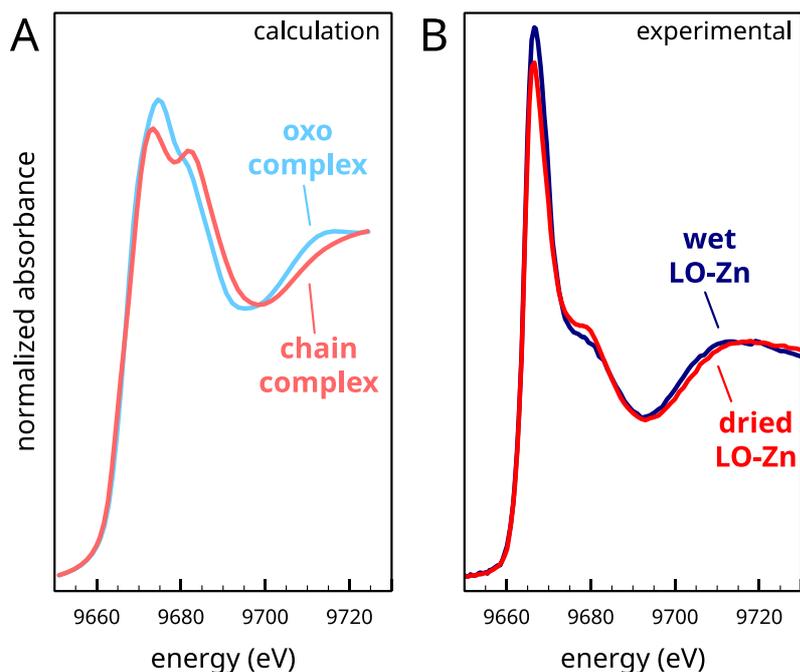°C in air on top of the ATR crystal, showing gradual weakening of the band at 530 cm^{-1}.

Fig. S4. Calculated and experimental XANES spectra of LO/Zn. (**A**) Calculated XANES spectra of pure oxo and chain complexes. (**B**) Experimental XANES spectra showing the difference between water-saturated LO/Zn and dried LO/Zn. Though the differences are small, the observed reduction in edge peak intensity, increase in post-edge peak intensity and the shift in the third peak upon drying are all consistent with an increased relative concentration of chain complex in the polymer sample.
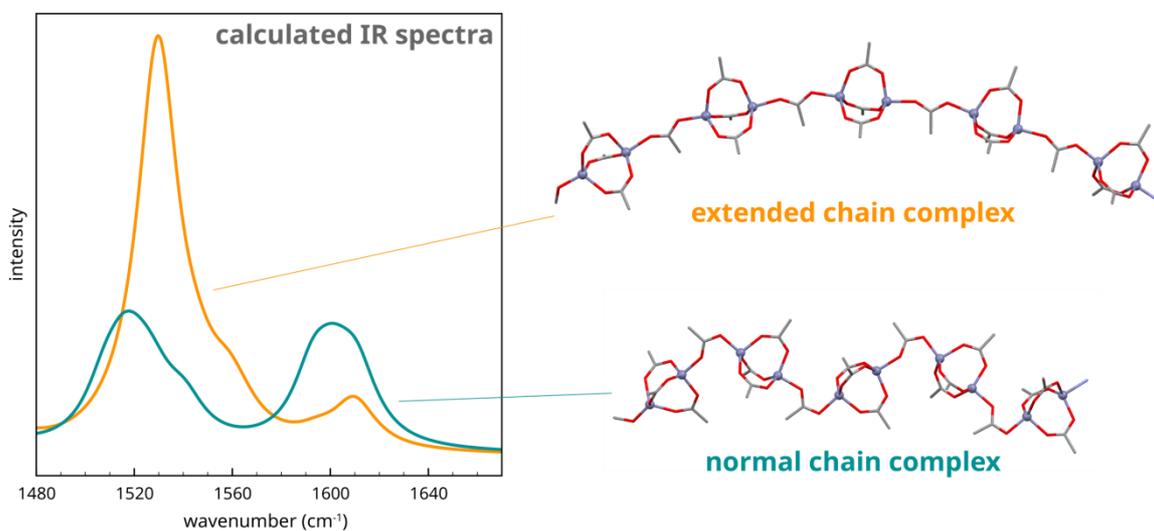

Fig. S5. Calculated IR spectra of a distorted chain complex. Calculated IR spectra showing the effect of rotating the $Zn_2(RCOO)_3$ clusters, leading to an extension of the chain complex. In the extended chain complex, the IR spectrum is dominated by a vibrational mode in which all carboxylate groups along the chain vibrate in phase, at a position similar to band A. Close to the position of band C, there is a weak band that is caused by out-of-phase vibrations of the cluster and linking carboxylate groups along the chain.
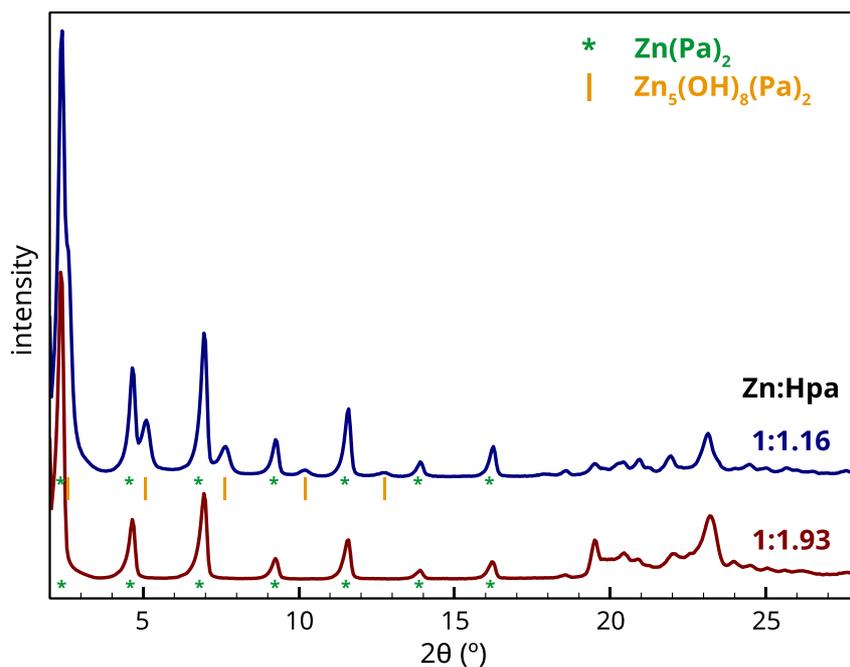
Fig. S6. Powder XRD traces of two types of ZnPa samples. With a Zn:HPa ratio in the reaction mixture close to the 1:2 stoichiometry of zinc palmitate, a pure product of ZnPa was obtained (bottom trace). When an excess of Zn^{2+} ions was present in the alkaline reaction mixture, a second crystalline phase precipitated, that was identified as $Zn_5(OH)_8(Pa)_2$ (*35*).