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SUPPORTING INFORMATION

The cooperative effect of the sorption of volatile molecules into metal-oxide frameworks as a function of the dielectric constant

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Experimental Section

Synthesis

The crystalline powders of three POMs ($Mo_{72}Fe_{30}$, Mo_{132} and Mo_{138}) were synthesized in accordance with previously reported methods.[3,14,15] All chemicals were analytical reagent grade. Structure verification of the obtained POMs was carried out by comparing the IR and Raman spectra with reference data from the literature. The spectra are presented in Supporting Information (**Figure S9-S11**). The IR spectra of the POMs' crystalline powders were measured at room temperature using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) in diffuse reflectance absorption (DRA) mode. The Raman spectra were measured with an Alpha 300 AR WiTec scanning confocal Raman microscope, equipped with a He—Ne gas laser at different laser wavelengths: 633 nm (for Mo_{132} and $Mo_{72}Fe_{30}$) and 488 nm (for Mo_{138}). The solvents in the sorption experiments had to be analytical grade.

Measuring A_{lim}

The limit sorption values of the organic compounds (including camphor) were obtained from a gaseous medium via the absorption of saturated vapors in a sorption chamber at room temperature and atmospheric pressure. ACCULAB ALC analytical balances (Sartorius Group) were used for qualitative measurements. Before the sorption experiments, samples of Keplerate Mo_{132} and toroidal Mo_{138} were exposed to a temperature of 100 ^{0}C in order to remove weakly bonded water and obtain a constant weight. Due to the structure's significant instability[11] (decomposition began at temperatures above 70 ^{0}C), a sample of $Mo_{72}Fe_{30}$ was used as prepared to avoid destruction.

Determining the free Gibbs energies

The free Gibbs energies of the sorption process were obtained with a gravimetric variant of interval static isothermal sorption,[44] which allowed us to simultaneously measure the amount of vapour adsorbed by a sample and the equilibrium pressure of this vapour. A quartz spiral balance with a sensitivity of ~0.3 × 103 m/kg in a setup with a V-630 microcathetometer (measurement accuracy 0.005 mm) was also used. Sorption experiments were conducted at 298 K and a residual air pressure of 10^{-3} Pa. The obtained data were in the form of sorption isotherms plotted along $x/m–P/P_s$ coordinates, where x is the amount of sorbate (g) adsorbed by 1 g of POM, m is the weight of the sorbent and P/P_s is the relative vapour pressure. The overall relative error of x/m determination did not exceed 3%, and the error of P/P_s determination was at most 0.5%. Knowing the amount of adsorbed substance in a specified range of relative vapour pressure, the weighed fractions of the sorbate (ω_1) and POM (ω_2) in the system were calculated using the following equations:

$$\omega_2 = \frac{m}{m+x} = \frac{1}{1+x/m};$$

$$\omega_1 = 1 - \omega_2$$

The obtained vapour sorption isotherms were then treated in the usual way.[44] The change in the chemical potential of the solvent upon sorption $\Delta\mu_1$ was determined according to the following equation:

$$\Delta\mu_1 = \frac{RT}{M_1} ln \frac{P}{P_S}$$

The change in the chemical potential of polymer $\Delta\mu_2$ was calculated by means of the Gibbs-Duhem equation:

$$\Delta\mu_2 = - \int_{-\infty}^{\Delta\mu_1} \frac{\omega_1}{\omega_2} d\Delta\mu_1$$

Using these values, the Gibbs energy of mixing Δg^m was determined with an average accuracy of about 5%:

$$\Delta g^m = \omega_1 \Delta \mu_1 + \omega_2 \Delta \mu_2$$

Measuring enthalpy

The thermal effects in our thermochemical studies were measured using a Kalve-type DAK-1-1 micro-calorimeter. The weighed samples of the polyoxometalate (0.050–0.065 g) were placed into sealed glass tubes. The calorimeter's working cell was filled with 6 mL of distilled water or an appropriate solvent. The tubes were thermostated in the device's working chamber at room temperature and broken using a special tool. The integral amount of heat exuded (consumed) was determined in each experiment.

Ligand exchange

The treatment of Mo_{132} with three alcohols (n-butanol, isopropanol and methanol) was performed in the following way: the Mo_{132} powder was vigorously mixed in pure alcohol for 8 hours for methanol and for 2 days for the other alcohols; the suspensions were centrifuged at 10 000 rpm for 10 min and dried in a vacuum at 45 ^{0}C. It should be noted that we did not examine ligand exchange for the ethanol-Mo_{132} system, because ethanol always exists as a mixture with ~5% water in normal conditions. The presence of such a number of water molecules can very quickly reverse the exchange process, as has been shown for $Mo_{72}Fe_{30}$.[31] The Raman spectra of the treated Mo_{132} were measured with an Alpha 300 AR WiTec scanning confocal Raman microscope equipped with a He—Ne gas laser (λ = 633 nm).

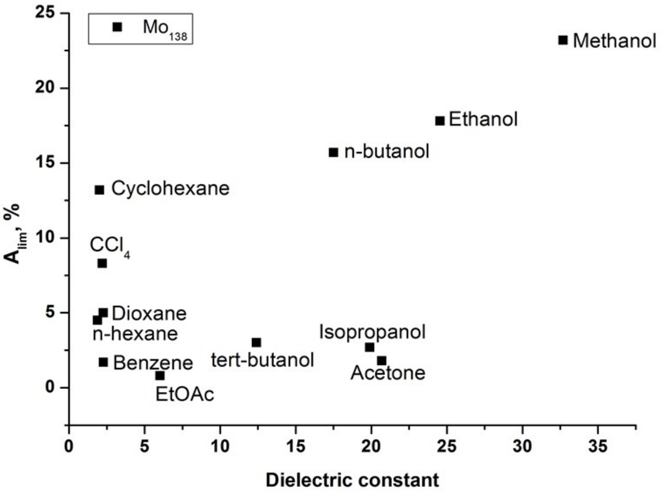

Figure S1. Dependency of limit adsorption (A_{lim}) as a percentage value per one gram of POM on the dielectric constant for Mo_{138}.

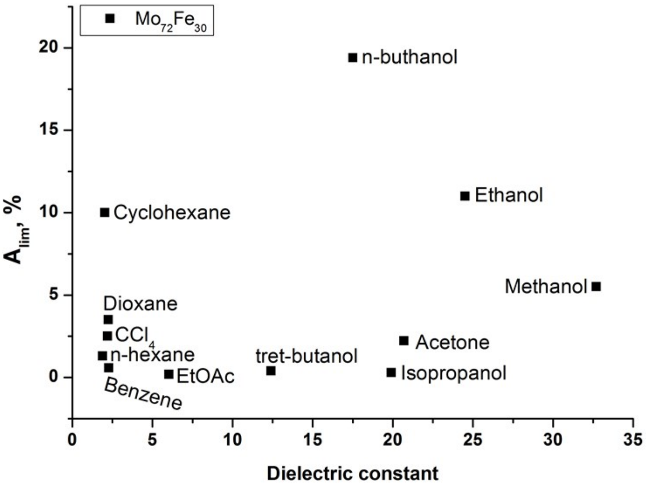

Figure S2. Dependency of limit adsorption (A_{lim}) as a percentage value per one gram of POM on the dielectric constant for $Mo_{72}Fe_{30}$.

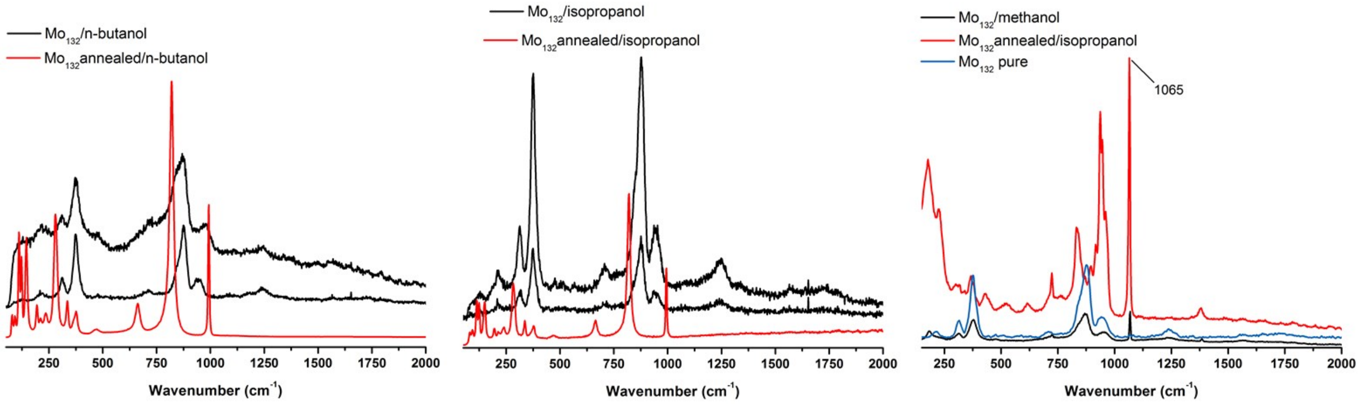

Figure S3. Raman spectra of Mo_{132} samples treated with n-butanol (left), isopropanol (center) and methanol (right). Black lines – Raman spectra of treated Mo_{132} at different laser powers; red lines – Raman spectra of treated Mo_{132} after thermal destruction in a laser beam; blue line – Raman spectrum of untreated Mo_{132}.

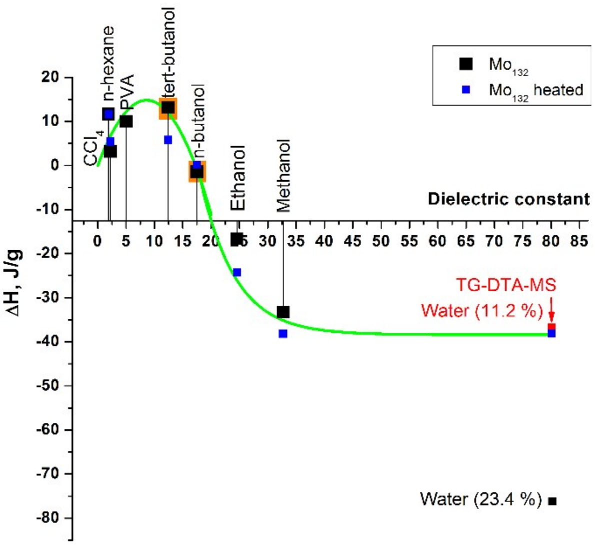

Figure S4. Dependency of adsorption enthalpy on the dielectric constant for preheated and non-heated (hydrated) Mo_{132} with an extrapolated point of the theoretical value of the enthalpy of sorption of all water molecules, including constitutional aqualigands.

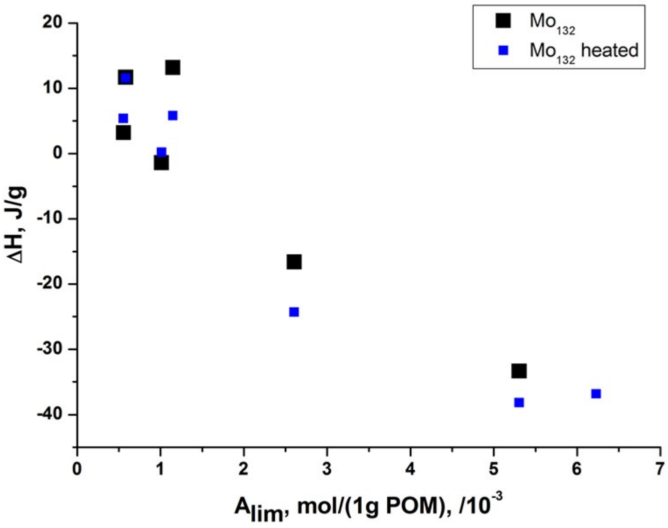

Figure S5. Dependency of the adsorption enthalpy on the limit sorption (A_{lim}) for heated and fully hydrated Mo_{132}.

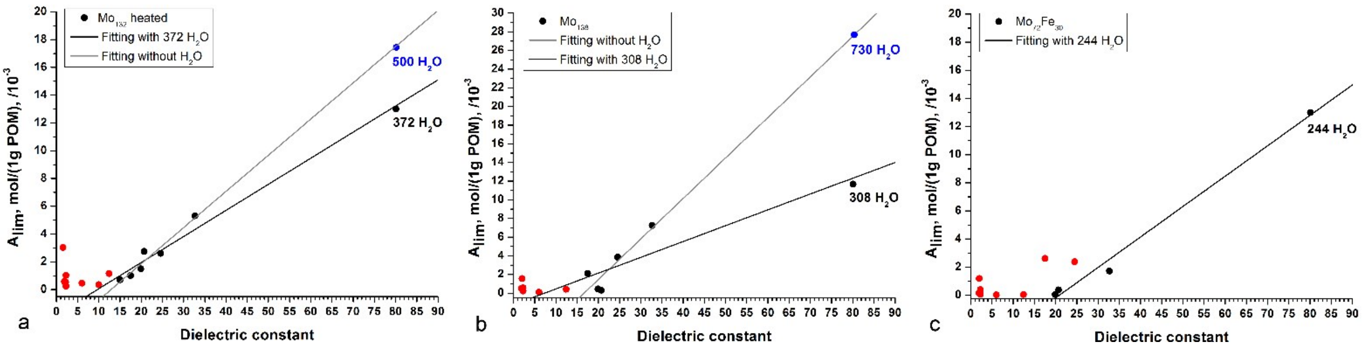

Figure S6. A comparison of amounts of cluster water for Mo_{132}, Mo_{138} and $Mo_{72}Fe_{30}$ (from left to right, respectively) obtained with different extrapolation modes: the amount of water is obtained through the extrapolation of common dependency (blue H_2O points); the real amount of water is included into the fitting data (black H_2O points). See explanation below.

If we apply the linearized dependencies of the limit adsorption from the dielectric constant for all the aforementioned POMs, we can determine theoretically how many water molecules were adsorbed. We compared the obtained theoretical (T) values with the real (R) number of water molecules taken from the composition of current POMs: 500 (T) and 372 (R) for Mo_{132}; 730 (T) and 308 (R) for Mo_{138} (**Figure S6**). For $Mo_{72}Fe_{30}$ (which contains 244 H_2O molecules), we cannot approximate the dependency of ε_r on water because there is no linear curve as in the cases of Mo_{132} and Mo_{138}. For the Keplerate Mo_{132}, the relationship between A_{lim} and the dielectric constant after the cyclohexanol point can be satisfactorily linearized either at 500 or 372 water molecules per nanocluster. This shows the strong correlation of the suggested approach to sorption analysis in a real situation. However, in the line $Mo_{132} \rightarrow Mo_{138} \rightarrow Mo_{72}Fe_{30}$, with a decreasing number of water molecules per POM, the positive correlation between the A_{lim} value and the dielectric constant diminishes and inverts (**Figure 4a**, See Manuscript).

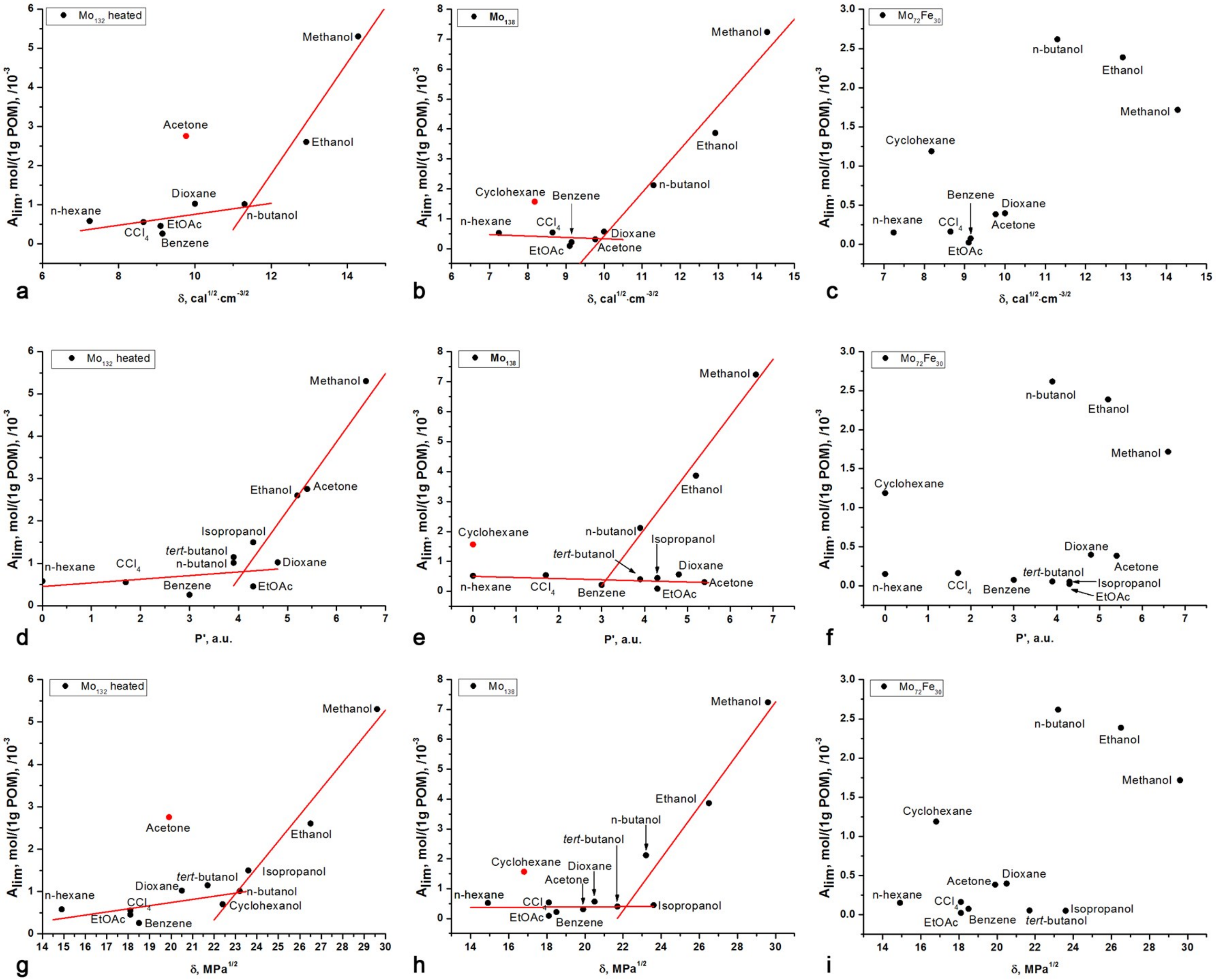

Figure S7. The dependencies of the limit sorption (A_{lim}) of POMs (Mo$_{132}$ – left column; Mo$_{138}$ – central column; Mo$_{72}$Fe$_{30}$ – right column) on the Hildebrand solubility parameter (a, b, c), the Snyder polarity index (d, e, f) and the Hansen solubility parameter (g, h, i).

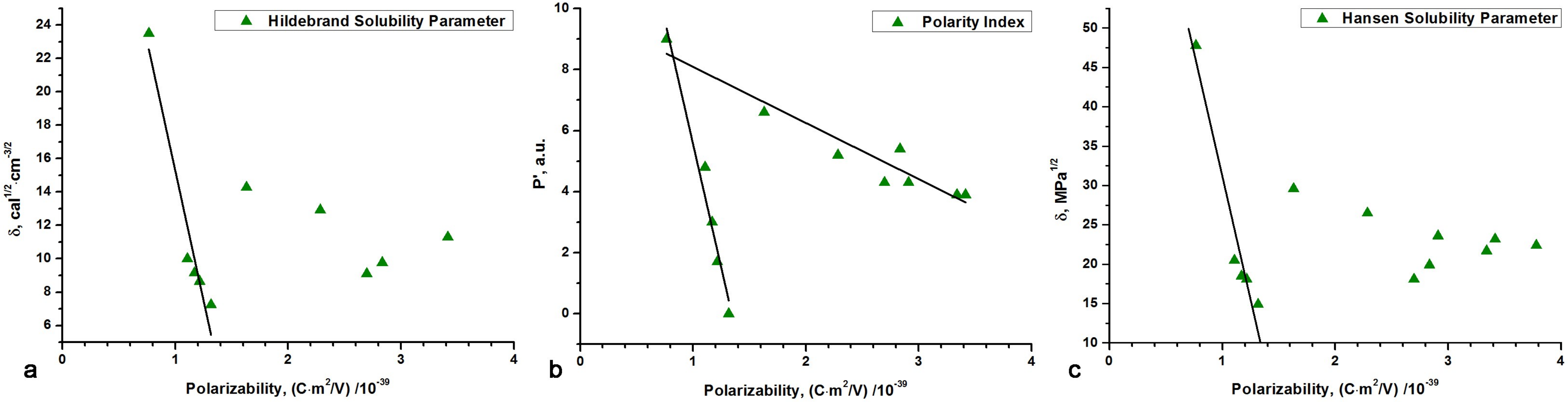

Figure S8. The dependencies of the Hildebrand solubility parameter (a), the Snyder polarity index (b) and the Hansen solubility parameter (c) on the dielectric constant of the solvent.

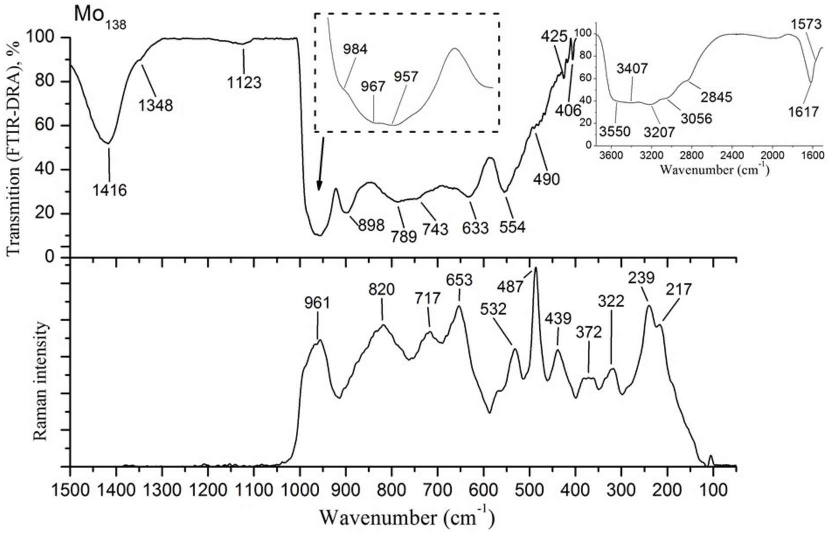

Figure S9. IR spectrum in DRA mode from the powder (top) and Raman spectra of a single crystal of the toroidal POM nanocluster Mo_{138} with a 488-nm laser (bottom). Insert in the dotted frame demonstrates the magnified fragment of the compound band near 1000 cm^{-1}.

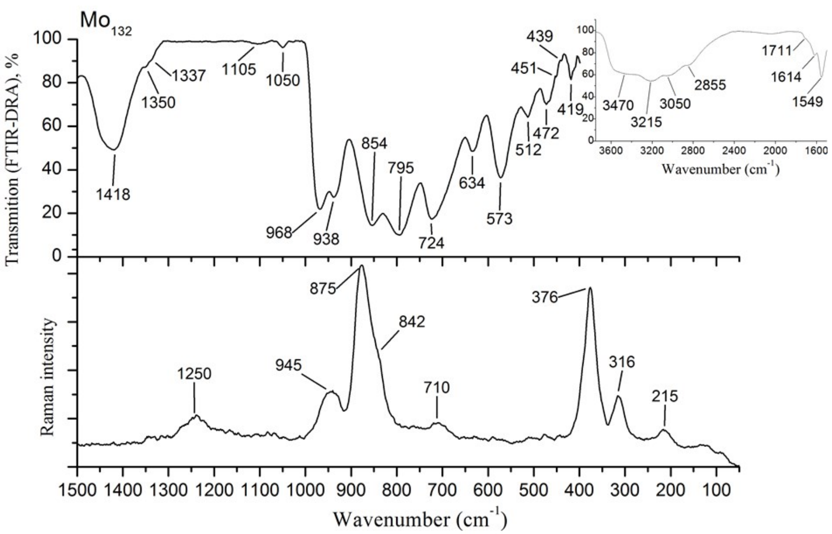

Figure S10. IR spectrum in DRA mode from the powder (top) and the Raman spectra of a single crystal of the Keplerate POM nanocluster Mo$_{132}$ with a 633-nm laser (bottom).

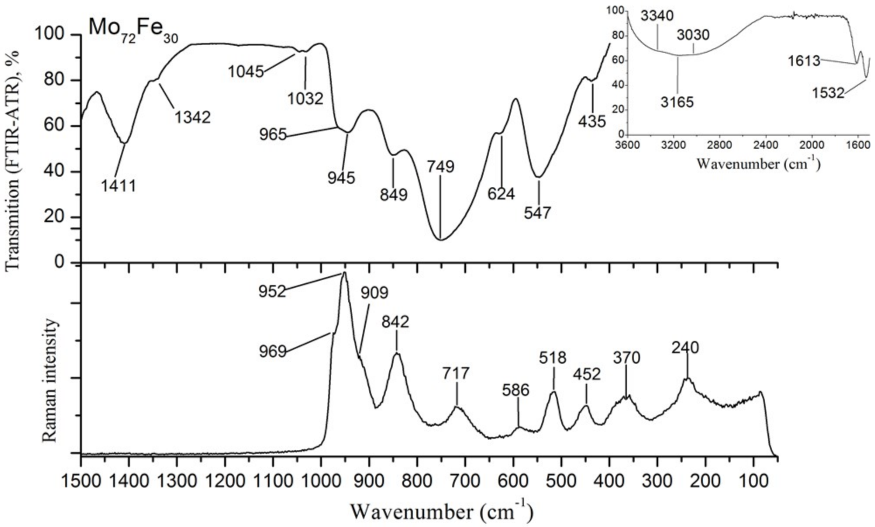

Figure S11. IR spectrum in DRA mode from the powder (top) and Raman spectra of a single crystal of the Keplerate POM nanocluster Mo$_{72}$Fe$_{30}$ with a 633-nm laser (bottom).