

Interplaying the amphipathic polyoxometalate interactions in solution and at solid–liquid interfaces: A toolbox for the technical application

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1. General analytical methods and chemicals

All starting materials were commercial and used as received. Elemental analysis was performed using a Vario EL elemental analyzer. ^1H , ^{31}P and ^{51}V NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature using CD_3CN as solvent. Chemical shifts (δ) are given in ppm. IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer by using KBr pellets ($m_{\text{KBr}} \approx 250$ mg) in the $4000\text{--}400\text{ cm}^{-1}$ range. ESI mass spectra in positive and negative ion modes were recorded on a ThermoFisher Scientific LTQ-Orbitrap XL mass spectrometer system in acetonitrile.

2. Infrared (IR) spectra

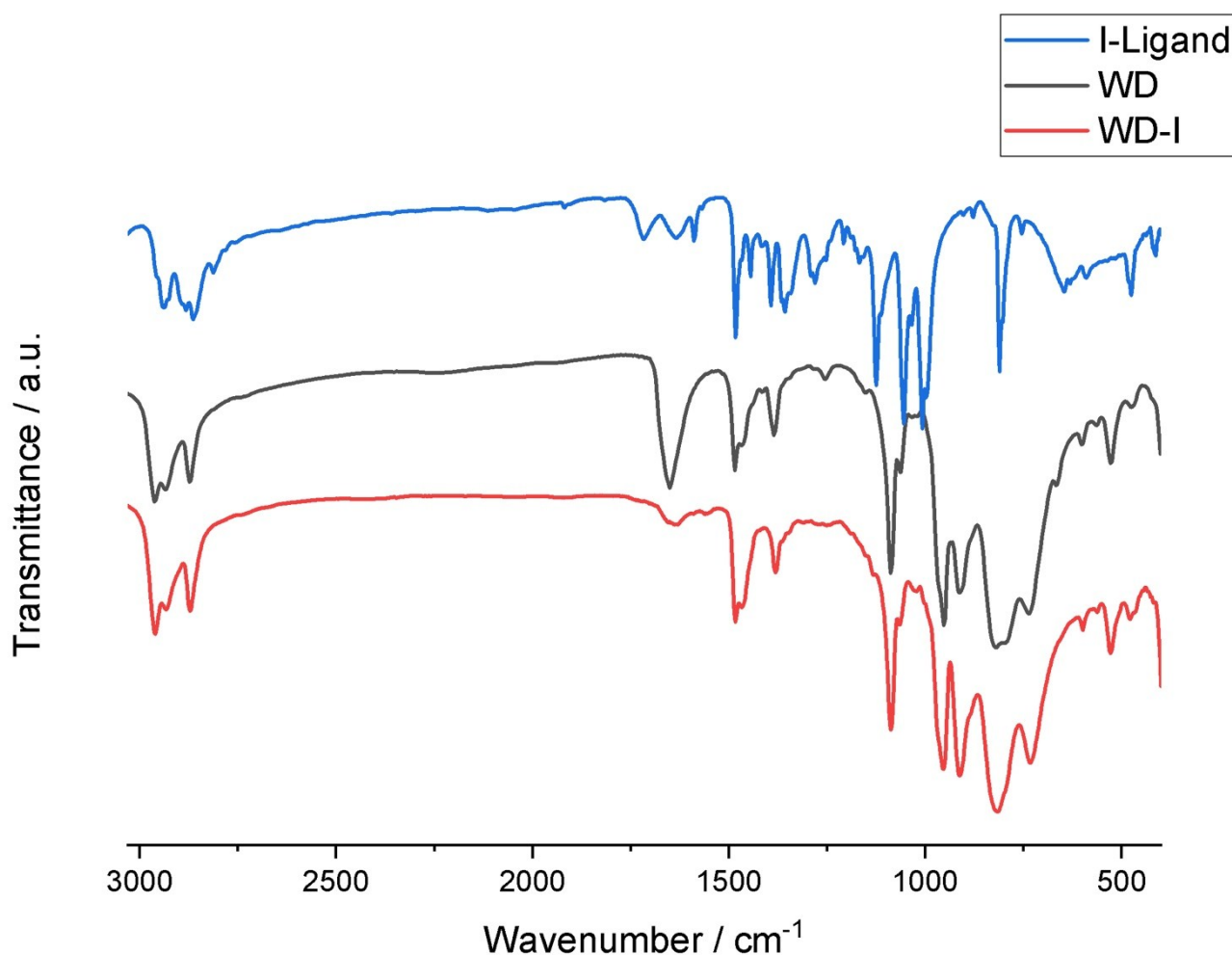


Fig. S1. Comparison between the IR spectra of the triol $(\text{HOCH}_2)_3\text{CCH}_2\text{OCH}_2\text{C}_6\text{H}_4\text{I}$ ligand (I-Ligand), unfunctionalized POM compound $(n\text{Bu}_4\text{N})_5[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ ($(n\text{Bu}_4\text{N})_5\text{WD}$) and the target $(n\text{Bu}_4\text{N})_5[\text{HP}_2\text{V}_3\text{W}_{15}\text{O}_{59}((\text{OCH}_2)_3\text{CCH}_2\text{OCH}_2\text{C}_6\text{H}_4\text{I})]$ compound ($(n\text{Bu}_4\text{N})_5\text{WDI}$).

3. Nuclear magnetic resonance (NMR) spectra

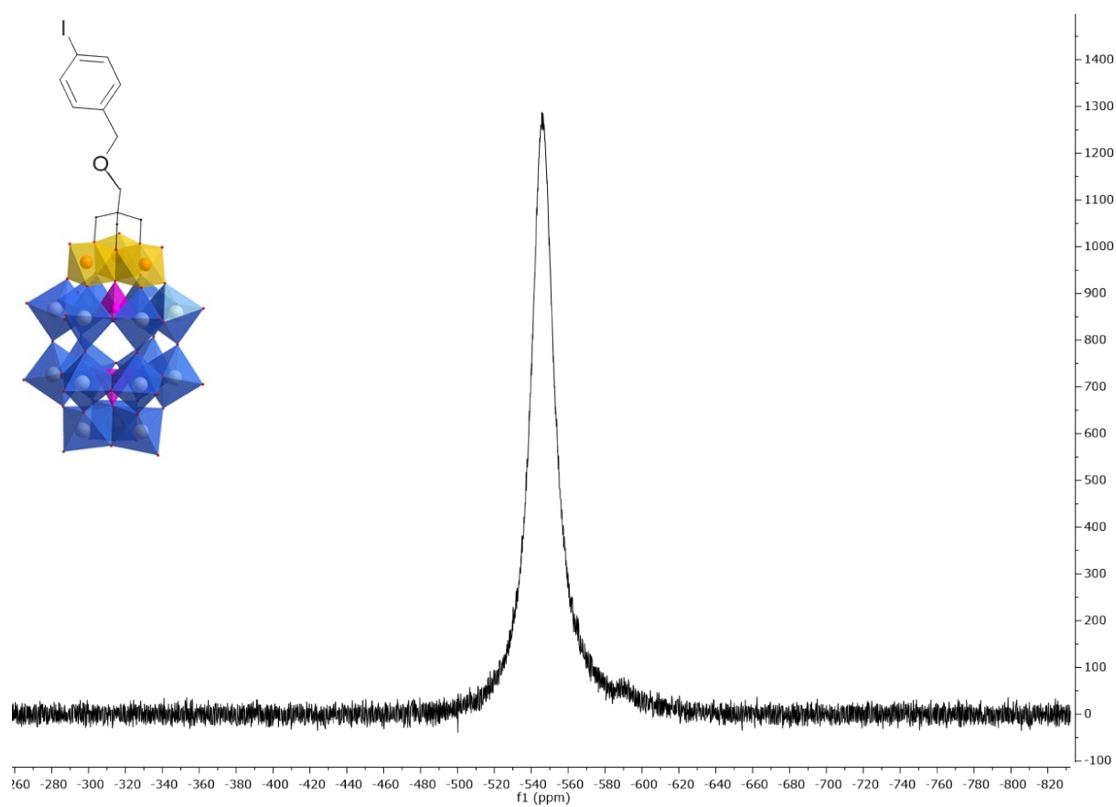


Fig. S2. ^{51}V NMR (105 MHz, CD_3CN) spectrum of WDI.

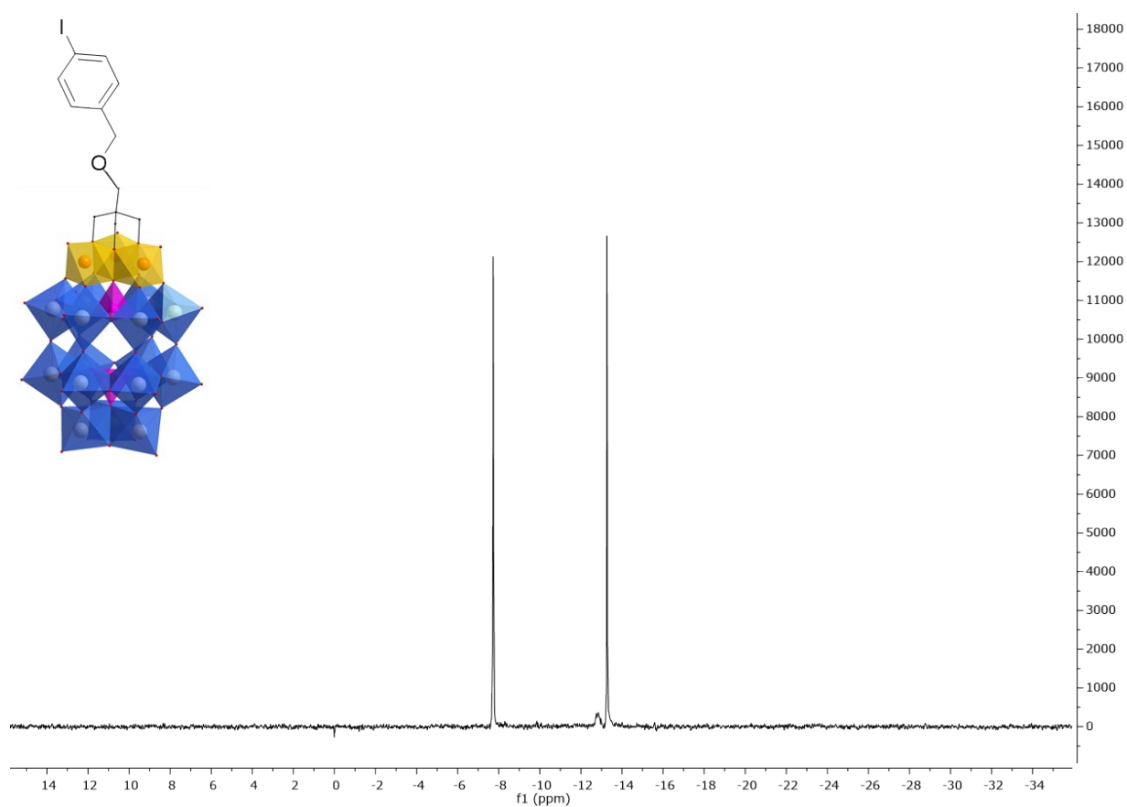


Fig. S3. ^{31}P NMR (162 MHz, CD_3CN) spectrum of WDI.

4. Electrospray ionisation (ESI) mass spectrometry data

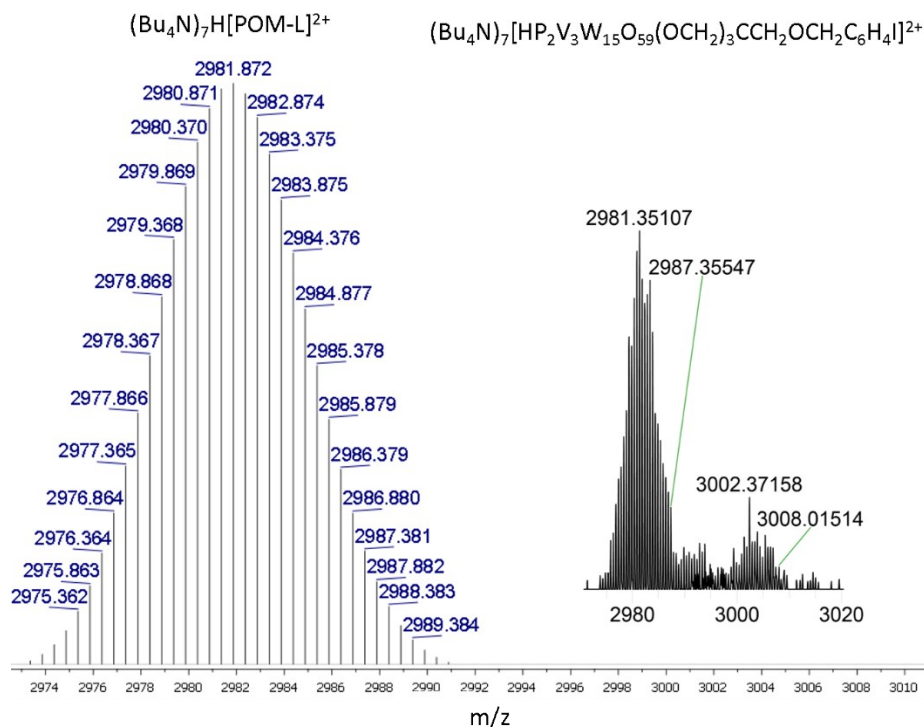


Fig. S4. Comparison of the calculated (left) and the measured (right) isotopic pattern of $(n\text{Bu}_4\text{N})_7\text{H}[\text{POM-L}]^{2+}$.

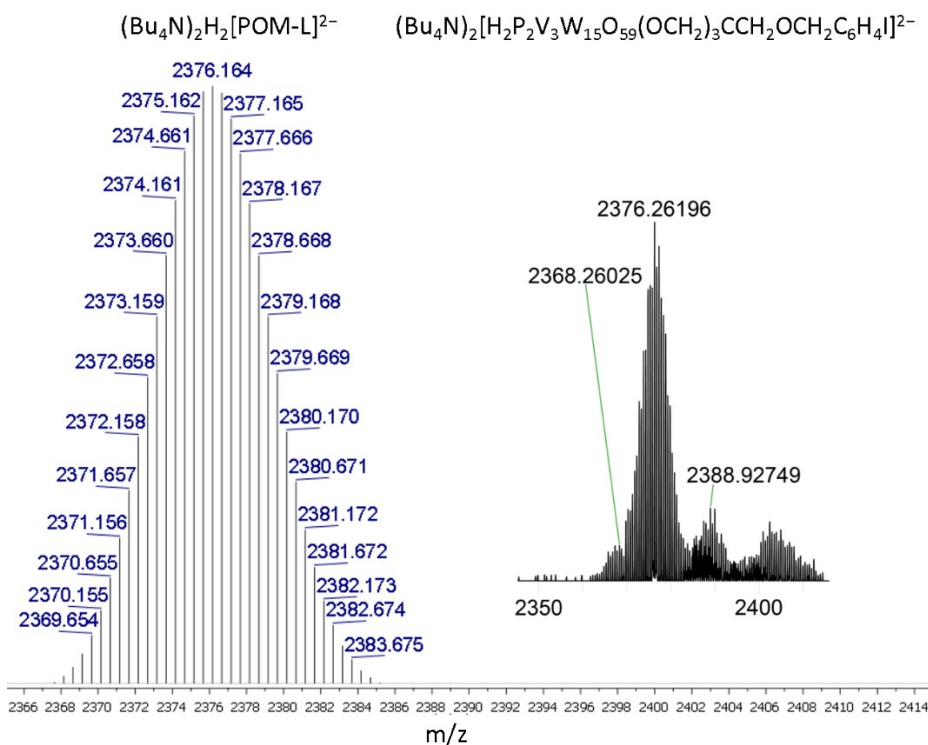


Fig. S5. Comparison of the calculated (left) and the measured (right) isotopic pattern of $(n\text{Bu}_4\text{N})_2\text{H}_2[\text{POM-L}]^{2-}$.

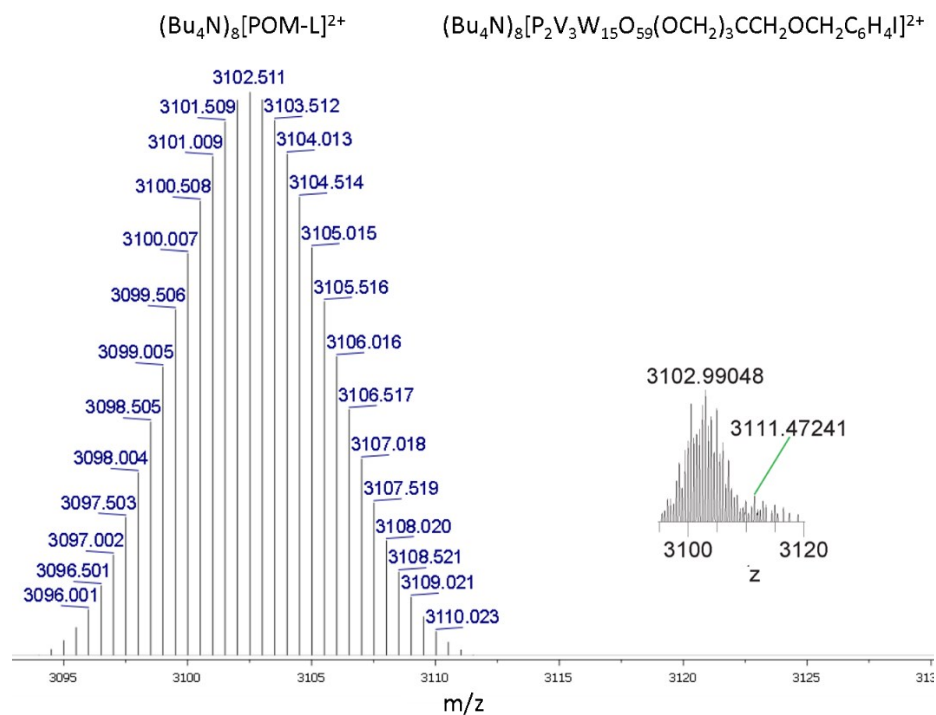


Fig. S6. Comparison of the calculated (left) and the measured (right) isotopic pattern of $(n\text{Bu}_4\text{N})_8[\text{POM-L}]^{2+}$.

Table S1. Selected ESI mass spectrometry data of $(n\text{Bu}_4\text{N})_5\text{WDI}$ measured in acetonitrile. L = ligand.

Composition	Sum formula	Calculated	Measured
$[(n\text{Bu}_4\text{N})_7\text{HPOM-L}]^{2+}$	$\text{C}_{124}\text{H}_{267}\text{N}_7\text{IO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{2+}$	2981.86	2981.35
$[(n\text{Bu}_4\text{N})_8\text{POM-L}]^{2+}$	$\text{C}_{140}\text{H}_{302}\text{N}_8\text{IO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{2+}$	3103.01	3102.99
$[(n\text{Bu}_4\text{N})\text{H}_2\text{POM-L}]^{3-}$	$\text{C}_{28}\text{H}_{52}\text{NIO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{3-}$	1503.01	1502.73
$[(n\text{Bu}_4\text{N})_2\text{HPOM-L}]^{3-}$	$\text{C}_{44}\text{H}_{87}\text{N}_2\text{IO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{4-}$	1584.11	1584.16
$[(n\text{Bu}_4\text{N})_2\text{H}_2\text{POM-L}]^{2-}$	$\text{C}_{44}\text{H}_{88}\text{N}_2\text{IO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{2-}$	2376.16	2376.26
$[(n\text{Bu}_4\text{N})_3\text{HPOM-L}]^{2-}$	$\text{C}_{60}\text{H}_{124}\text{N}_3\text{IO}_{63}\text{P}_2\text{V}_3\text{W}_{15}^{2-}$	2497.31	2497.40

5. Small-angle X-ray scattering (SAXS) evaluation and model description

The scattering of a system, composed of spherical units diluted in a medium is given by the product of the particle form factor $P(q)$ and the structure factor $S(q)$, which represents the scattering from a specific spatial organization of the composing spheres. The intensity distribution as a function of the scattering vector q is written as

$$I(q) = \phi \Delta\rho^2 V P(q) S(q)$$

where ϕ is the volume fraction of the spheres, $\Delta\rho^2$ the contrast factor, given as the squared difference between the particular electron densities for the sphere and the medium multiplied by the radius of the electron, and V is the volume of the scattering particle. If compositional information about the sphere is known, these parameters can be calculated a priori. $S(q)$ is 1 in the dilute, non-interacting state.

Agglomerating single spheres lead to a fully different scattering pattern. Due to the agglomeration the length scales of single and agglomerated particles may differ enormously. The empirical unified approach by Beaucage et al.,^{1,2} which assumes that each level of scattering units can be represented as a sum of a Guinier function at low q and a power law at high q , is simplified in the present case to

$$I(q) = \phi \Delta\rho^2 \left(V \exp\left(-\frac{(qR_{gp})^2}{3}\right) + ZV \exp\left(-\frac{(qR_{gcl})^2}{3}\right) + B_{cl} \exp\left(-\frac{(qR_{gp})^2}{3}\right) \left[\frac{\left(\operatorname{erf}\left(\frac{qR_{gcl}}{\sqrt{6}}\right)\right)^3}{q} \right]^D \right)$$

where B is a crossover parameter that connects both length scales and different scattering contributions. For special morphologies sometimes an analytical form for B exists. Since the primary particle is small, compared to the accessed length scales in the SAXS experiment, only the Guinier expression, i.e. the first term in the summation, remains of it.

The exponent D describes the high q decay of the intensity and is called the Porod exponent of the agglomerated species, which allows an interpretation of the local surface in terms of a fractal model. The agglomeration number Z and the size R_{gcl} are discussed in the main text.

The contribution of the water clusters, which possibly exist in mixtures of water and acetonitrile were approximated by their Guinier form factor, weighted by the contrast between the two solvents and fitting the radius of a water cluster R_w . This contribution³ was added incoherently.

Finally, also correlations between the components were included. Instead of a hard-sphere interaction a considerably softer but nevertheless effective description was used.⁴ We assumed the structure factor to follow a first-order correction similar to a virial analysis and claim that

$$S(q) = 1/(1 + FX(q))$$

with

$$X(q) = 3(\sin(q\zeta) - (q\zeta)\cos(q\zeta))/(q\zeta)^3$$

Here, ζ is the effective interaction radius and F the number of geometrical neighbors.

Summarized, the presented data are thus fitted to the sum of the single contributions i.e. coherent and incoherent scattering as

$$I(q) = \frac{\phi \Delta \rho^2 \left(V \exp\left(-\frac{(qR_{gp})^2}{3}\right) + ZV \exp\left(-\frac{(qR_{gcl})^2}{3}\right) + B_{cl} \exp\left(-\frac{(qR_{gp})^2}{3}\right) \left[\frac{\left(\operatorname{erf}\left(\frac{qR_{gcl}}{\sqrt{6}}\right) \right)^3}{q} \right]^D \right)}{\left(1 + F * \frac{3(\sin(q\zeta) - (q\zeta)\cos(q\zeta))}{(q\zeta)^3} \right)} + (1 - \phi) < I_{solvent} > + (1 - \phi) \phi_{H2O} \Delta \rho_{solvent}^2 \left(\frac{4\pi}{3} \right)^2 R_w^3 \exp\left(-\frac{(qR_w)^2}{5}\right)$$

The q -independent incoherent background of the solvent is given by $<I_{solvent}>$. It depends on the water content and was not subtracted beforehand. A decomposition of the 10 % water mixture scattering into the single contributions and joined according to the former expression is shown below. From top to bottom: $S(q)$, total intensity, the model for agglomerated particles, the primary particle scattering, the mixed solvent incoherent background scattering and water cluster scattering.

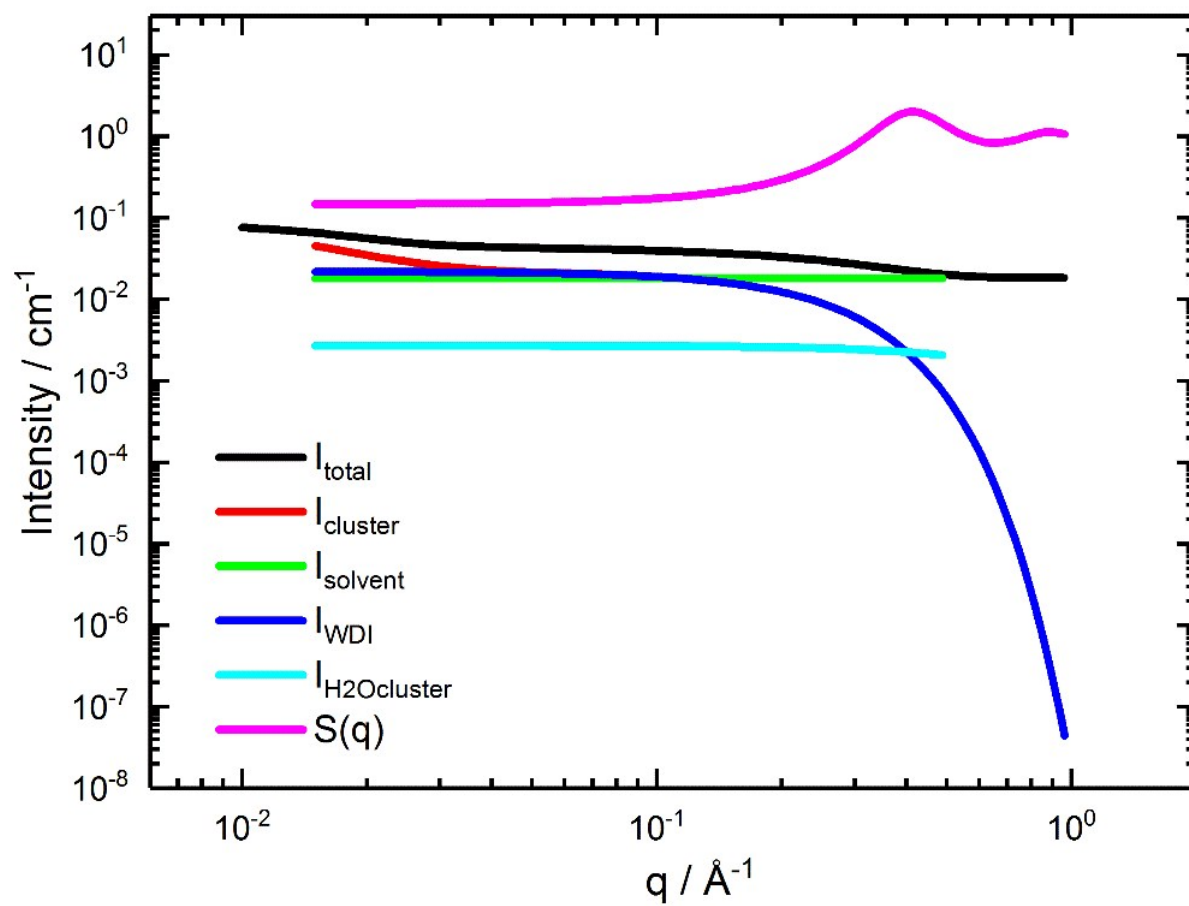


Fig. S7. Scattering contributions of a 10 % water-containing acetonitrile solution of **WDI**.

6. SAXS data

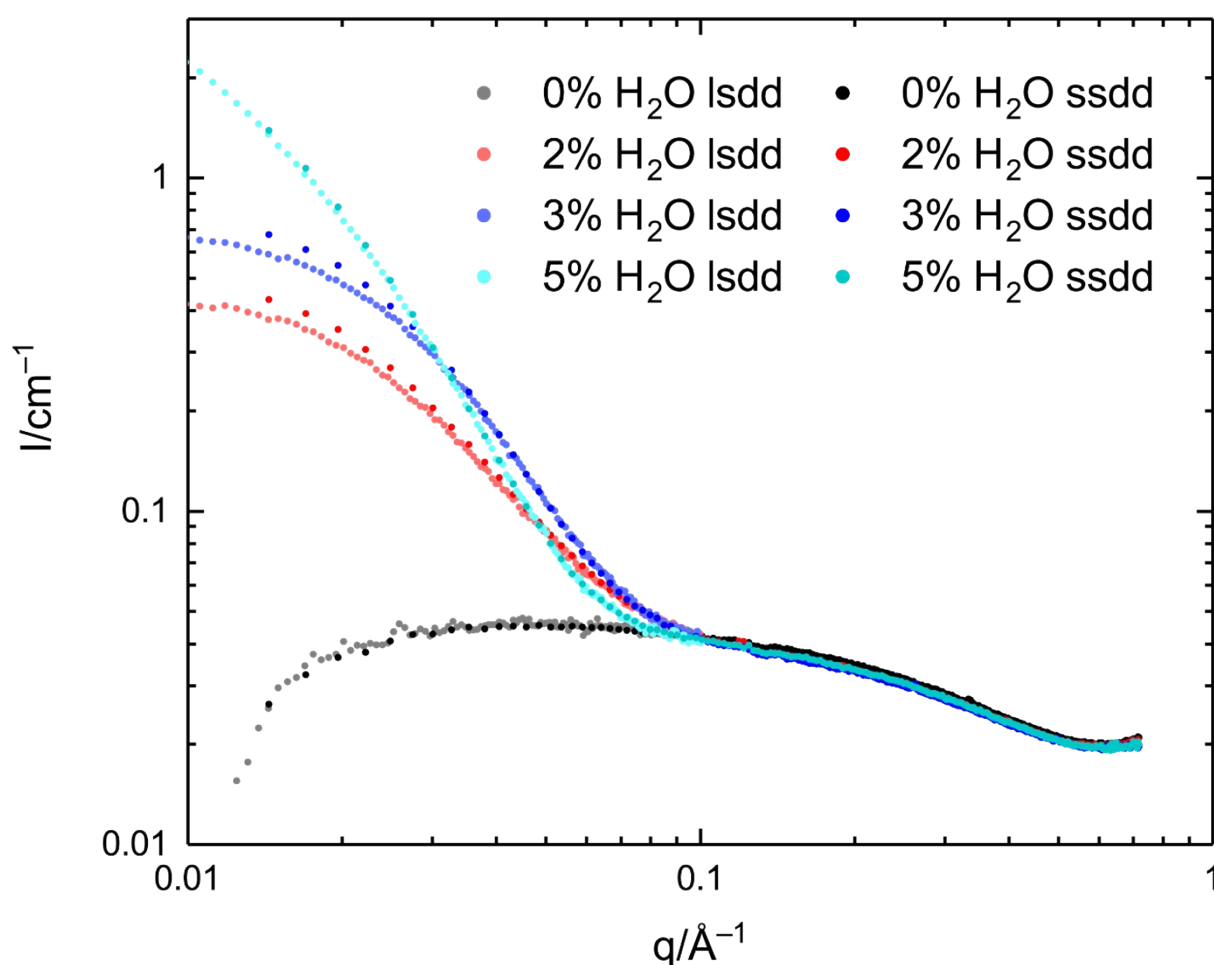


Fig. S8. SAXS intensities of the **WDI**-containing MeCN solutions with 0, 2, 3 and 5 % of water at lower temperatures.

Additional SAXS measurements of a highly concentrated **WDI** solution (180 μM) performed at lower temperatures (approx. 15°C) showed a clear precipitation effect in the water containing samples. Between the short detector distance (ssdd) and long detector distance (lsdd) measurements (time interval approx. one day) the spectra intensity was significantly decreased, which can only be explained by a partly precipitation of **WDI** under these conditions. The waterless sample remained unaffected.

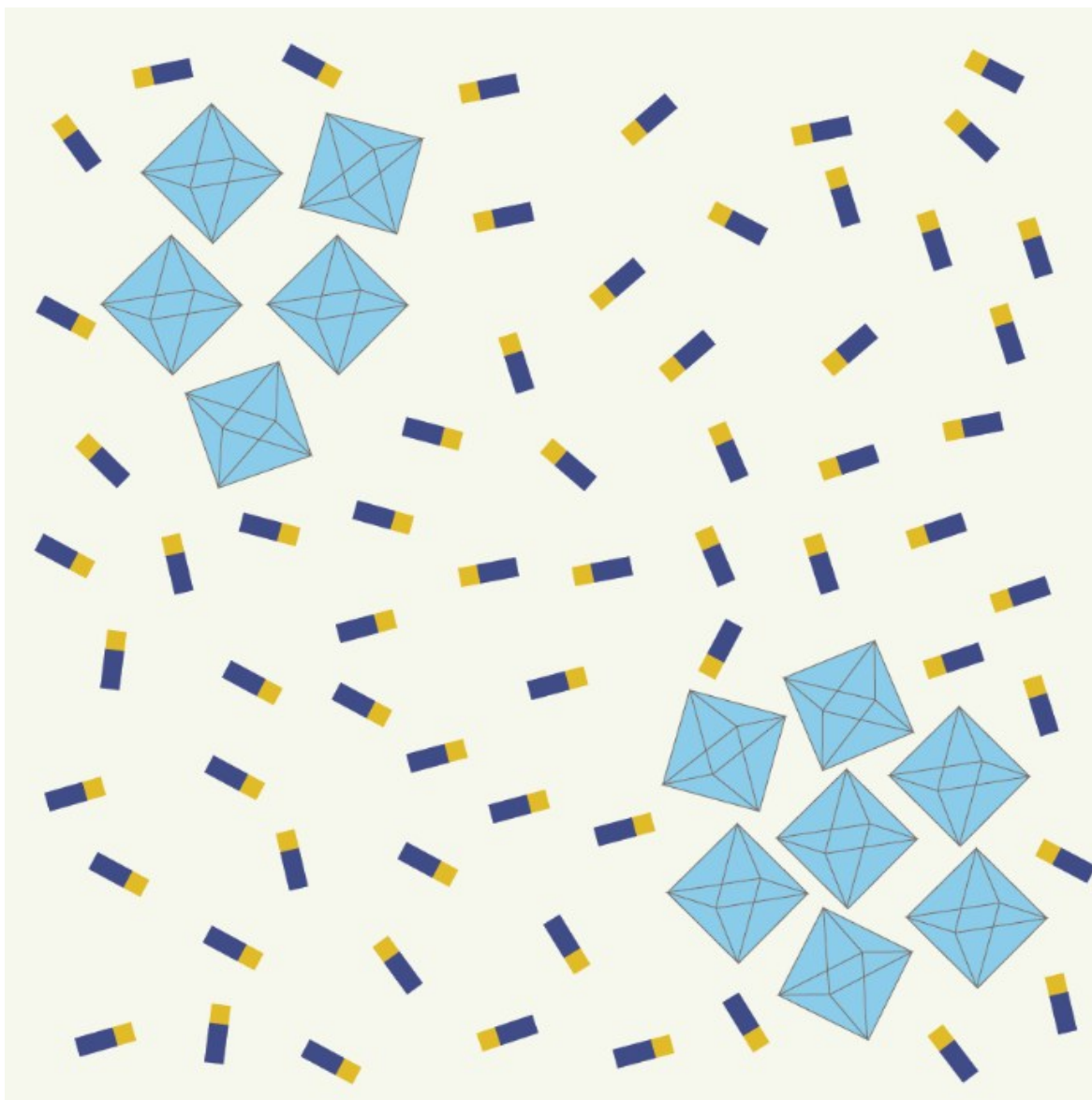


Fig. S9. Zoom-out on the schematic drawing of regime IV (cf. Fig. 3). The blue octahedrons represent densely packed **WDI** particles. Water molecules and $n\text{Bu}_4\text{N}^+$ counteranions are not shown for clarity.

To illustrate the special situation in regime IV a zoom-out of Figure 3 (IV) is shown in Figure S9. The geometry factor $P = 6$ indicates the formation of agglomerates consisting of densely packed **WDI** molecules. However, the rather low measured particle radius of gyration $R_g(p) = 9.40 \text{ \AA}$ can only be obtained if still a lot of isolated single **WDI** molecules are present under these conditions.

7. Scanning tunneling microscopy (STM) data

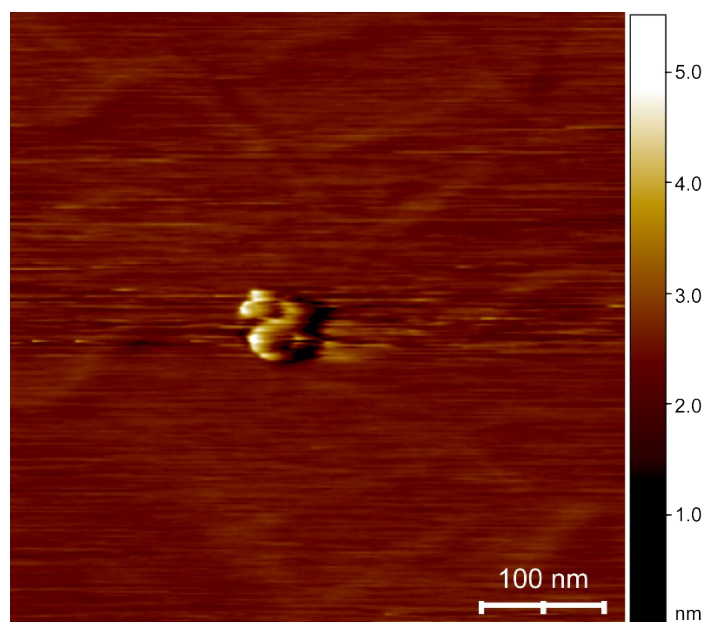


Fig. S10. STM image from an 80 μM concentrated acetonitrile solution of WDI (5 % of water) deposited on HOPG ($U_B = 1.0\text{ V}$; $I_T = 100\text{ pA}$; 500 nm x 500 nm).

Figure S10 depicts another POM agglomerate found on the HOPG surface after deposition of a slightly water containing acetonitrile solution of **WDI**. Within a scan range of 500 nm x 500 nm only single agglomerates were detected.

We also report a curious observation made during the STM measurements with a highly POM-covered HOPG surface (prepared with an 800 μM solution of **WDI**), which might easily lead to a wrong conclusion.

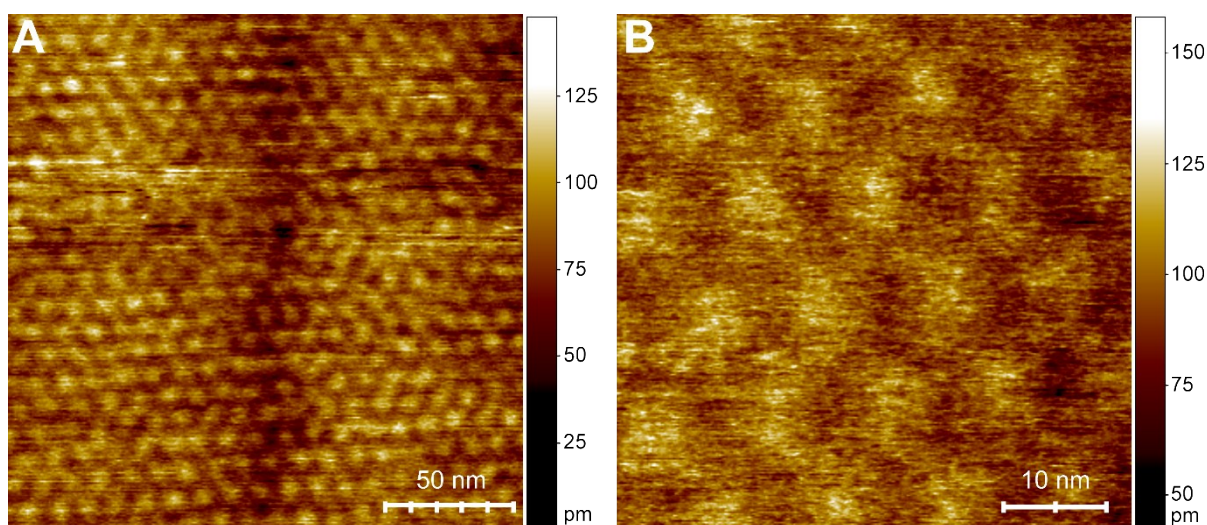


Fig. S11. Fourier filtered STM images of a highly concentrated WDI solution (800 μM) on HOPG. (A) The hexagonal superstructure covers large area ($U_B = 1.5\text{ V}$; $I_T = 100\text{ pA}$; 200 nm x 200 nm). (B) 50 nm x 50 nm ($U_B = 1.5\text{ V}$; $I_T = 100\text{ pA}$).

In a single measurement a well-ordered hexagonal super periodic structure with a periodicity of 11 nm was observed, which covered the whole range of the scanning area (up to 500 nm²). The apparent height of *ca.* 10 pm indicated an electronic origin of the structure. A bias voltage dependence was not observed. However, the superstructure could not be reproduced and the subsequent measurements with other surface-sensitive techniques such as low energy electron diffraction were not successful, so that an adsorbate related origin can be excluded. As shows the literature survey, similar observations on HOPG were already reported several times. These were explained by a Moiré pattern as a result of a misalignment of the topmost graphite layer.^{5,6} Song et al. described a similar structure on bare HOPG with a STM tip, which was modified by picking up a single Keggin-type H₃PW₁₂O₄₀ POM.⁷ We assume a similar tip modification by an accidentally picked up **WDI** molecule. This could give rise to the superstructure observed herein. The periodicity (D) of this Moiré pattern is a function of the rotation angle (β) at a given lattice constant (d).⁸

$$D = \frac{d}{2 \cdot \sin \frac{\beta}{2}} \quad [1]$$

Taking a lattice constant of 0.246 nm for graphite and inserting a periodicity of 11 nm results in a calculated misalignment angle of 1.3°. However, it is important to note that the observed Moiré pattern was obviously not caused by a long range order of **WDI** molecules on the surface but has been the result of a tip modification. This demonstrates impressively the practical difficulties of STM measurements of charged particles.

8. References

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