

Electronic Supplementary Information (ESI)

Electron Microscopy of Polyoxometalate Ions on Graphene by Electrospray Ion Beam Deposition

N. Vats,^{a*} S. Rauschenbach,^{a,b} W. Sigle,^a S. Sen,^a S. Abb,^a A. Portz,^c M. Dürr,^c M. Burghard,^a P. A. van Aken,^a and K. Kern^{a,d}

^a *Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany*

^b *Department of Chemistry, University of Oxford, OX2, Oxford UK*

^c *Institut für Angewandte Physik, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany*

^d *Institut de Physique, École Polytechnique Fédérale de Lausanne,*

CH-1015 Lausanne, Switzerland

**E-Mail: N.Vats@fkf.mpg.de*

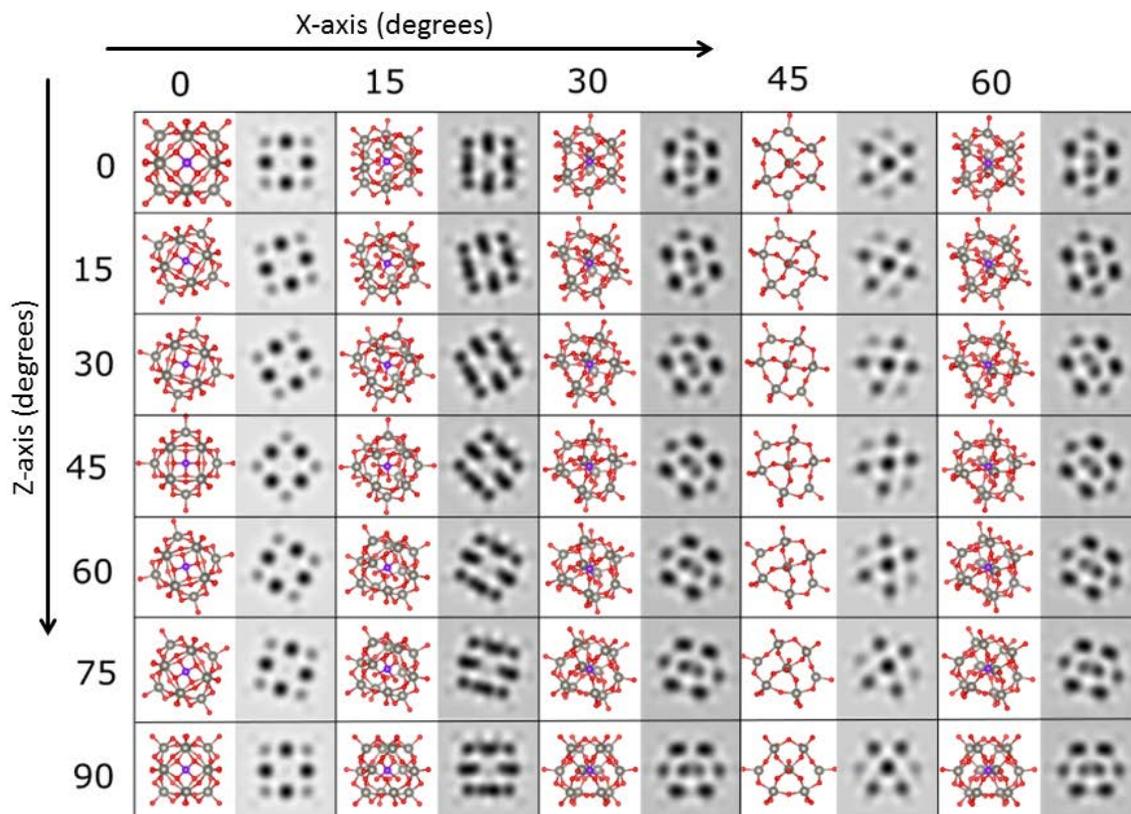


Figure S1. HRTEM image simulation tableau of PTA anion molecule $[\text{PW}_{12}\text{O}_{40}]^{3-}$ rotated at 15-degree steps around X- and then Z-axes. Ball-and-stick structure model of the PTA anion molecule is placed on the left side in each column and its corresponding image simulation on the right. Image simulations were carried out using the multi-slice QSTEM software package with an applied voltage of 80 kV, spherical aberration (C_s) = 1 μm , and defocus = -2.5 nm.

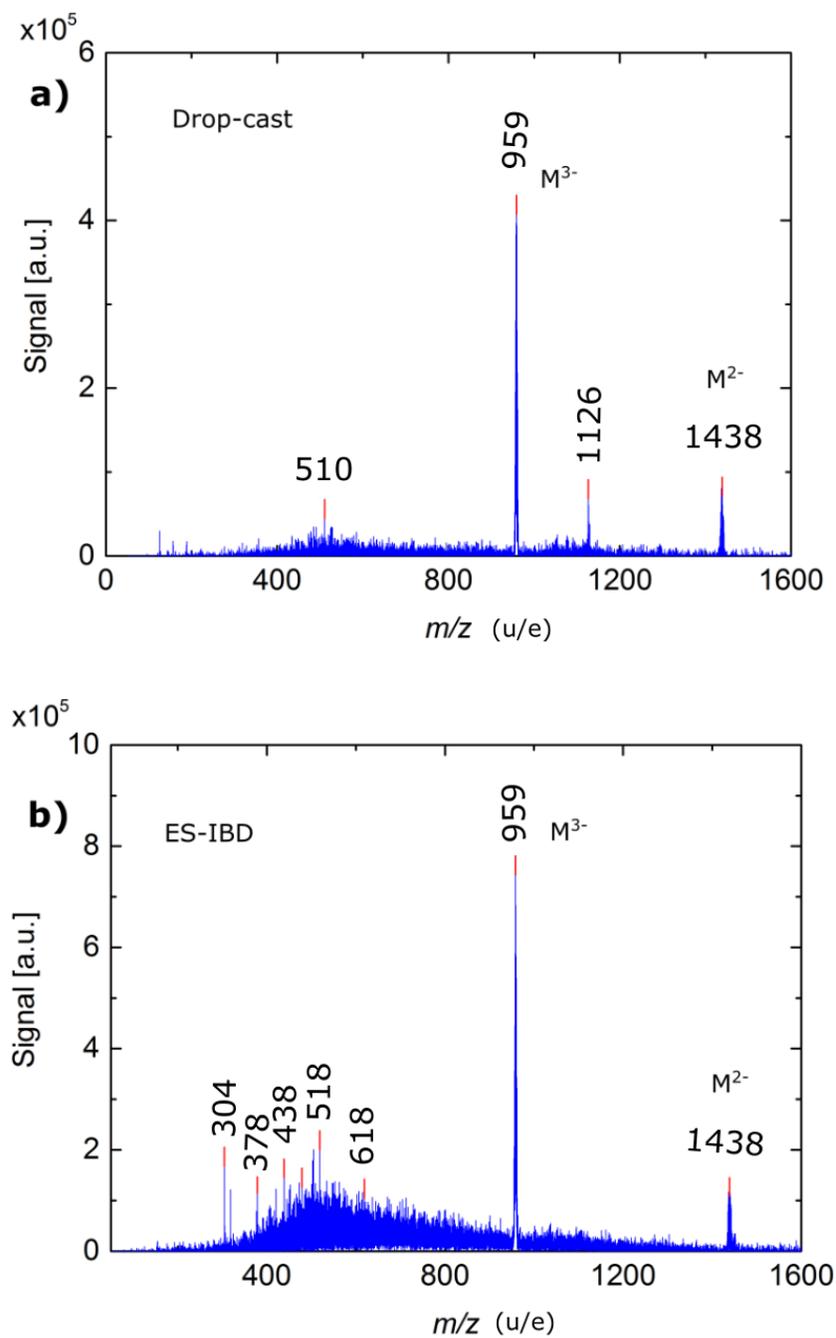
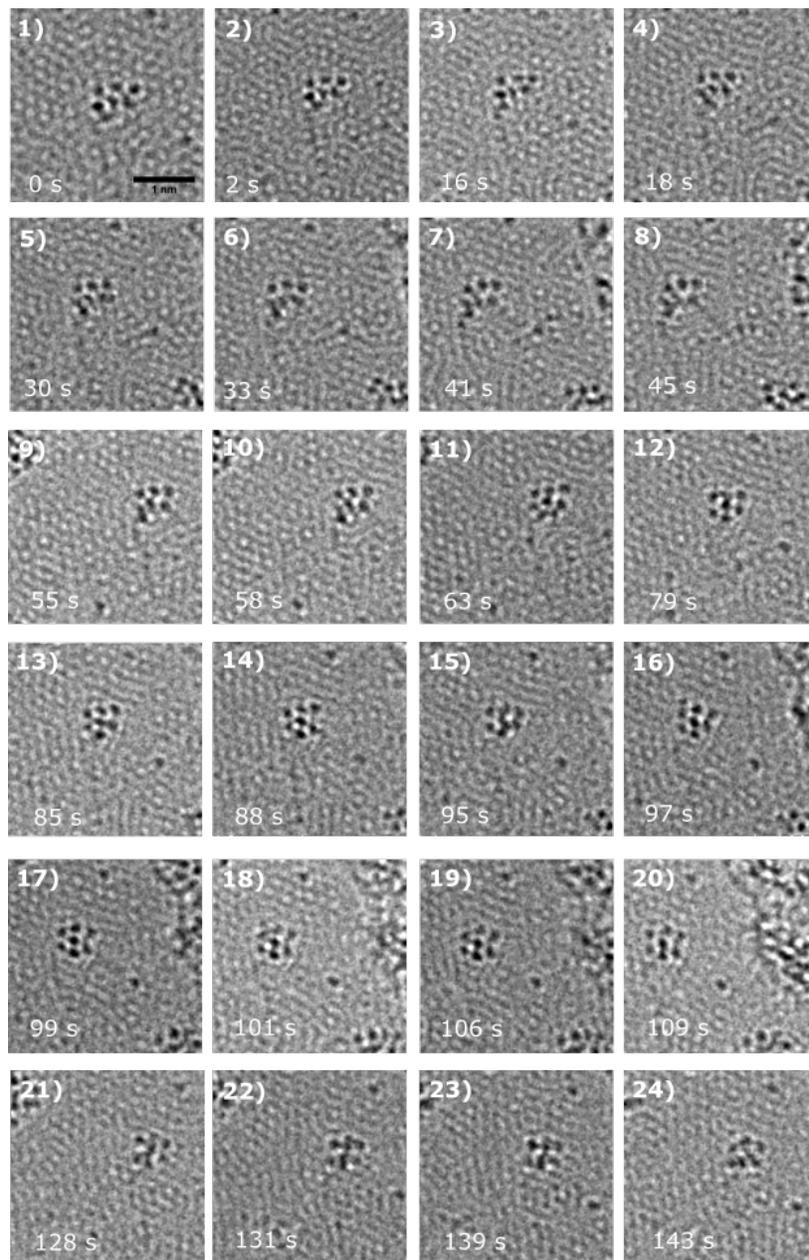


Figure S2. Negative ion DINEC mass-spectra of PTA molecules (a) deposited by means of drop-casting. Below $m/z = 800$, impurities are present in the drop-cast solution prepared with PTA anion salt. Similarly, many small-intensity peaks are observed in the ES-IBD sample (b) which represents contamination tentatively attributed to the sample transfer through ambient.

Time-series of the PTA Molecule under Electron-beam Irradiation



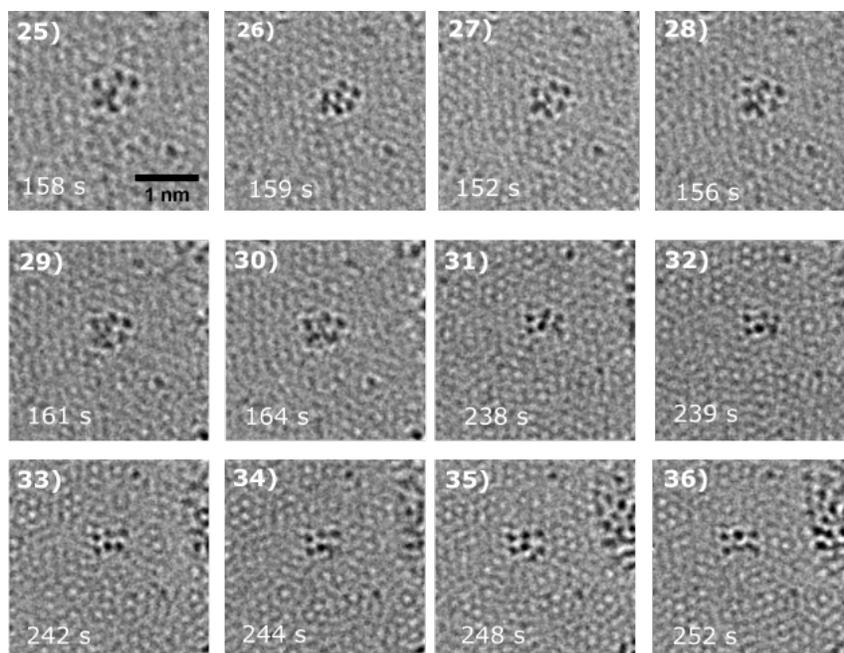


Figure S3. Time-series HRTEM images of PTA anion molecule acquired for 252 s. Image frames 15 and 17 correspond to Figure 4c and 4b.

Single Molecule Imaging

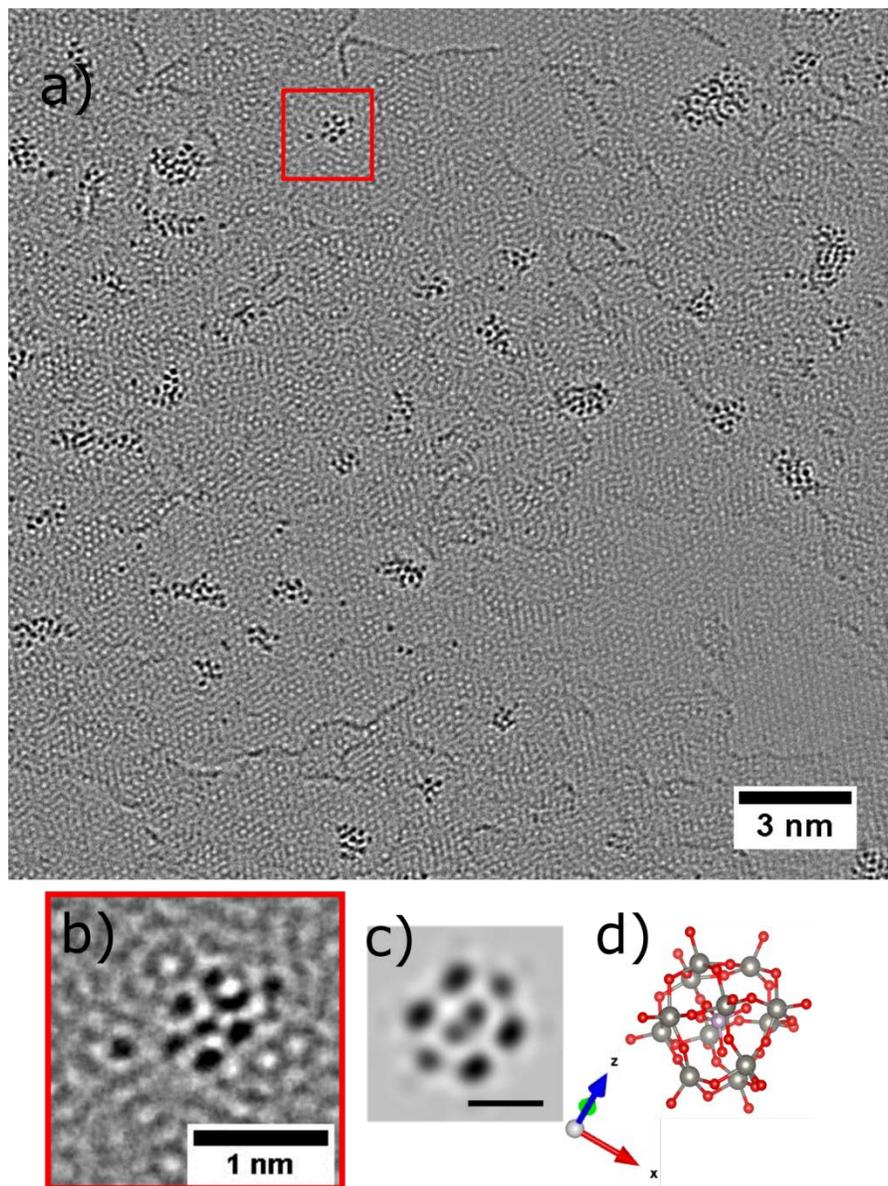


Figure S4. (a) Observation of individual single molecule on graphene substrate. (b) Enlarged image of the PTA molecule enclosed by red box in (a). (c) HRTEM image simulation at 80 kV, spherical aberration $C_s=0.001$ mm, and defocus = -2.5 nm of the corresponding structural model shown in (d). Scale bar in (c) corresponds to 0.5 nm.

Molecular Aggregate

A random molecular aggregate is constructed by assembly of eight PTA molecules using the Avogadro molecule building software and shown in (Figure S6d). In the next step HRTEM image simulation of the constructed molecular aggregate is performed using QSTEM as shown in Figure S6c and compared with a molecular aggregate selected in an experimental HRTEM image (Figure S6 a-b). The main purpose of molecular aggregate construction was to compare the atomic contrast originating from experimental and simulated PTA molecular aggregate as well as to differentiate the morphology of individual tungsten atom aggregates from PTA molecular aggregates. Though the molecular aggregate was prepared using a simple software tool without considering the interaction of underlying graphene substrate as well as the more accurate force field method, it provides a qualitative understanding of the general morphology of PTA molecular aggregates present on graphene.

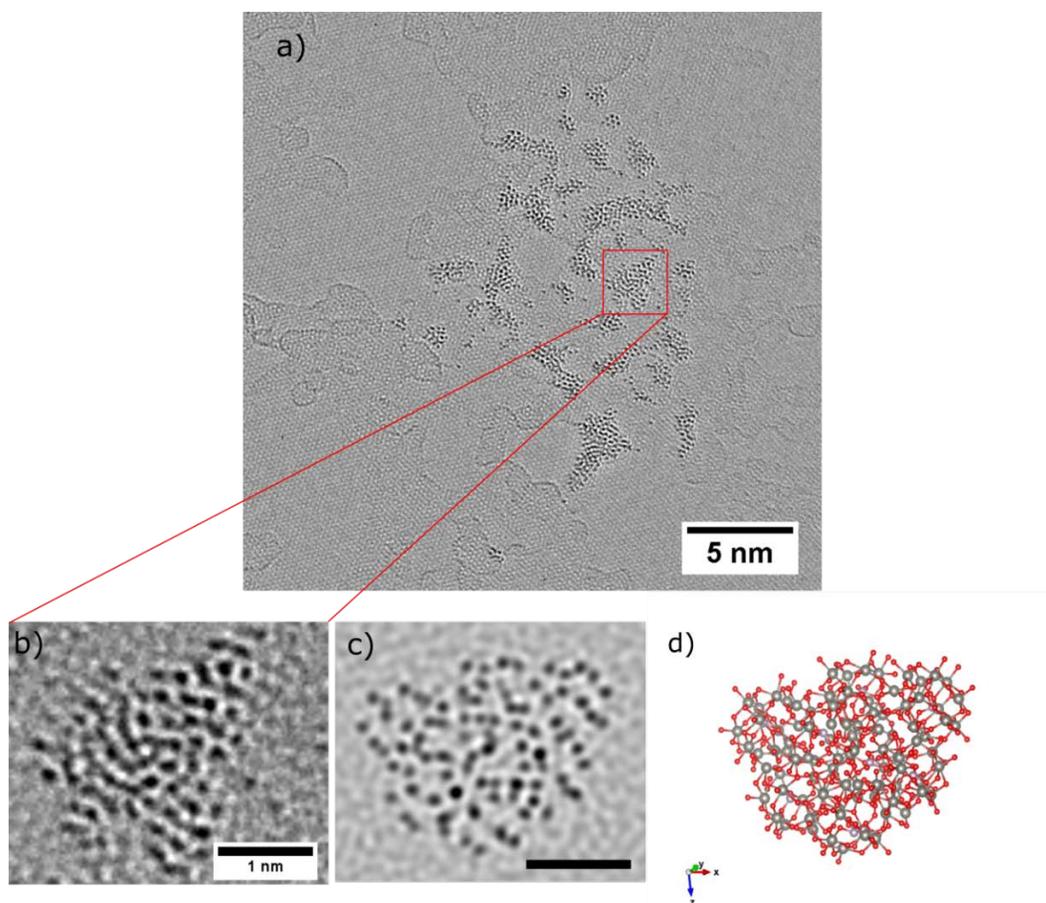


Figure S5. Comparing morphologies of a PTA molecular aggregate observed by HRTEM with image simulation. (a) HRTEM image of PTA molecular aggregate on graphene, (b) enlarged image of selected aggregate enclosed by the red box in (a). (c) Simulated HRTEM image of the structural model shown in (d). The scale bar corresponds to 1 nm. The structural model of the molecular aggregate in (d) contains 8 individual PTA molecules. The aggregate model with 8 individual PTA molecules was constructed using

the Avogadro molecule building software¹. After constructing the assembly of PTA molecules, the assembly was optimized using the default force field available in the program called universal force field (UFF) and the algorithm used was a default setting which uses steepest descent. Image simulations were carried out using the multi-slice QSTEM² software package with an applied voltage of 80 kV, spherical aberration (C_s) = 1 μm , and defocus = -2.5 nm (Scherzer defocus).

Size of Molecular Aggregate and Charge of Deposition

The size of PTA molecular aggregates in (nm^2) were measured for samples prepared with 50, 500, and 200 pAh charge of deposition. Four areas in each sample, in total 400 PTA molecular aggregates were analyzed for measurements of size distribution. Calculated maximum, minimum, and average values are shown in Tables 1, 2 and 3. Average sizes of molecular aggregates with respect to three different charges of deposition are plotted for quick comparison in the graph shown in S7d.

For 50 pAh

Area	A	B	C	D
Max	3.75	3.52	5.63	5.63
Min	0.68	0.68	0.68	0.68
Average	1.78	1.56	1.71	1.55

S6a. Table 1: Measured maximum, minimum, and average area in (nm^2) of PTA molecular aggregates at 50 pAh charge of deposition for four different selected areas namely A, B, C and D.

For 500 pAh

Area	A	B	C	D
Max	7.51	9.39	15.02	14.08
Min	0.93	0.93	0.93	0.93
Average	2.64	3.00	3.39	2.71

S6b. Table 2: Measured maximum, minimum, and average area in (nm^2) of PTA molecular aggregates at 500 pAh charge of deposition for four different selected areas namely A, B, C and D.

For 2000 pAh

Area	A	B	C	D
Max	28.17	30.98	28.17	28.17
Min	2.81	1.878	1.87	1.87
Average	9.83	9.19	11.74	8.62

S6c. Table 3: Measured maximum, minimum, and average area in (nm^2) of PTA molecular aggregates at 2000 pAh charge of deposition for four different selected areas namely A, B, C and D.

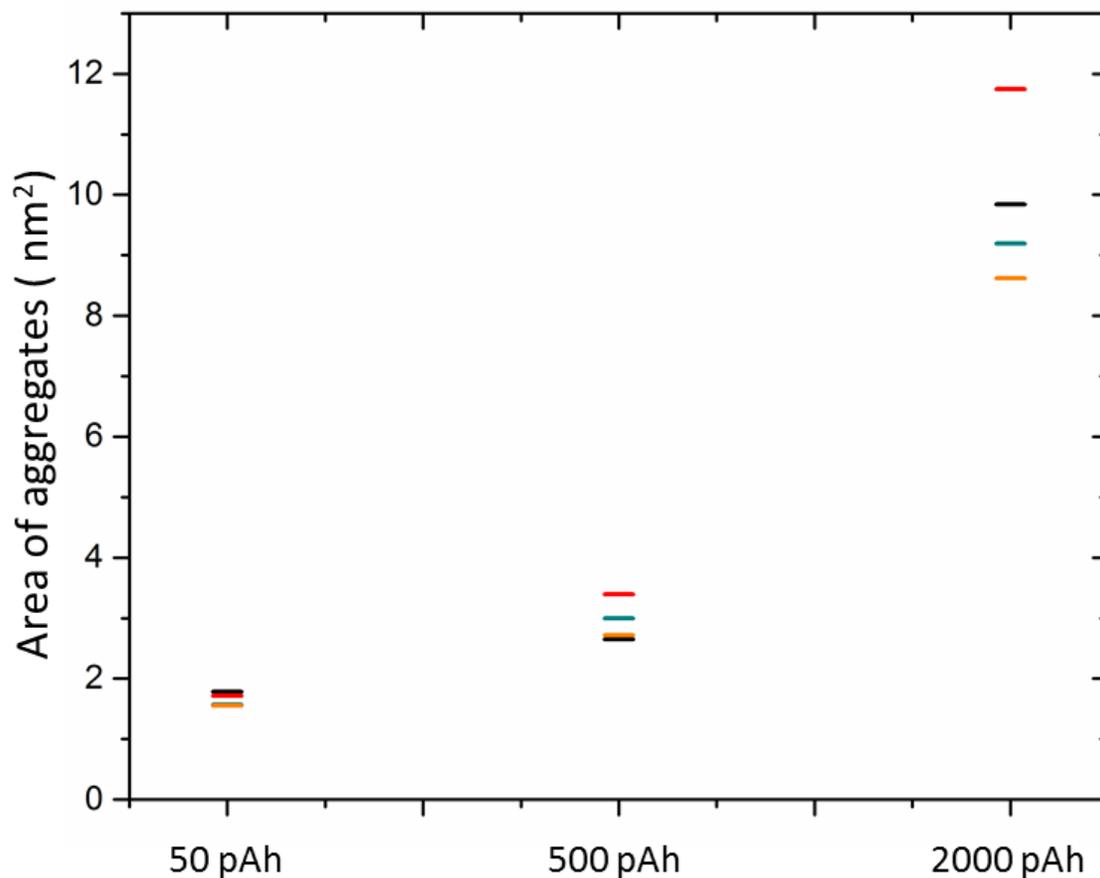


Figure S6d. Average values of molecular aggregate areas at 50, 500, and 2000 pAh charge deposition, represented by horizontal bars (black, red, green and orange color) with respect to the data shown in Table 1, 2, and 3. Four different colors of horizontal bars represent average value for four different areas that were selected for measurement.

Size of Molecular Aggregate and Landing Energy

For four different areas, PTA molecular aggregate sizes in (nm²) were measured for three different landing energies i.e. 150 eV, 300 eV, and 750 eV per molecule at constant charge of deposition 50 pAh. The measured values are tabulated in Tables 4, 5, and 6. Average size of aggregates at different landing energies are plotted for quick comparison in the graph shown in S8d.

For 150 eV

Area	A	B	C	D
Max	3.75	3.52	5.63	5.63
Min	0.68	0.68	0.68	0.68
Average	1.78	1.56	1.71	1.55

S7a. Table 4: Measured maximum, minimum, and average areas in (nm²) of PTA molecular aggregates at 150 eV landing energy for four different selected areas namely A, B, C, and D.

For 300 eV

Area	A	B	C	D
Max	3.25	2.56	2.18	2.56
Min	0.30	0.68	0.68	0.68
Average	1.34	1.53	1.54	1.51

S7b. Table 5: Measured maximum, minimum, and average area in (nm²) of PTA molecular aggregates at 300 eV landing energy for four different selected areas namely A, B, C, and D.

For 750 eV

Area	A	B	C	D
Max	1.53	1.91	1.53	0.68
Min	0.30	0.30	0.30	0.68
Average	0.47	0.41	0.4	0.689

S7c. Table 6: Measured maximum, minimum, and average areas in (nm²) of PTA molecular aggregates at 750 eV landing energy for four different selected areas namely A, B, C, and D.

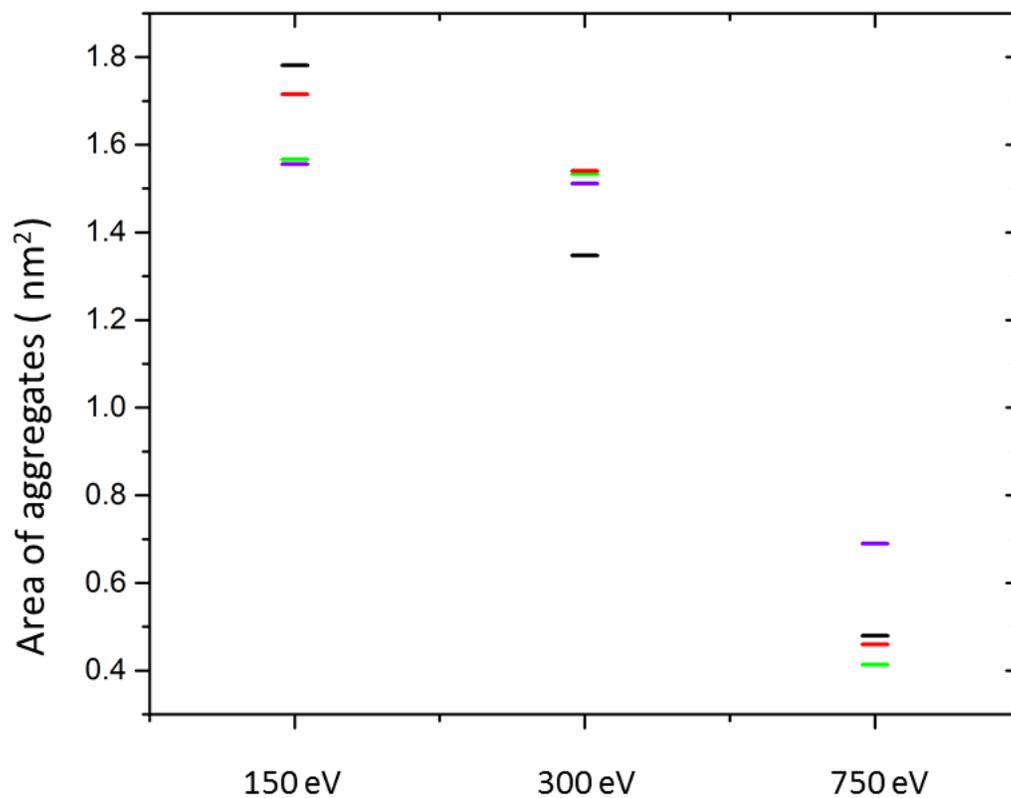


Figure S7d. Average values of molecular aggregate areas at 150, 300 and 750 eV energy per molecule, represented by horizontal bars (black, red, green, and violet color) with respect to the data shown in Tables 4, 5 and 6. Four different colors of horizontal bars represent average values for four different areas that were selected for the measurement.

Calculation of the Maximum Energy Transferred to the Tungsten (W) Atom in PTA Molecule from the Electron Beam

The maximum energy transferred to an atom by elastic collision of an electron can be calculated using relativistic kinematic equation,^{3,4}

$$E_{\max} = \frac{E_0(E_0 + 2m_0c^2)}{(m_0 + M)^2c^2 + 2ME_0}$$

Where, M is the nuclear mass of the target atom, E_0 is the energy of the incident electron beam; m_0 is the electron rest mass. As $m_0 \ll M$ and $E_0 \ll Mc^2$ this can be simplified to

$$E_{\max} = \frac{2E_0}{Mc^2}(E_0 + 2m_0c^2)$$

Substituting values,

$E_0 = 80$ keV, which is 1.2817×10^{-14} Joules ($\text{kgm}^2\text{s}^{-2}$)

$M = 183.84$ u which is 3.053×10^{-25} kg (for tungsten)

Rest mass of electron (m_0) = 9.11×10^{-31} kg

$c = 3 \times 10^8$ m/s

results in $E_{\max} = 1.026$ eV.

References

1. M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *Journal of Cheminformatics*, 2012, **4**, 17.
2. C. T. Koch, *Determination of core structure periodicity and point defect density along dislocations*, 2002.
3. B. Florian, *Reports on Progress in Physics*, 1999, **62**, 1181.
4. R. F. Egerton, R. McLeod, F. Wang and M. Malac, *Ultramicroscopy*, 2010, **110**, 991-997.