

Supplementary Information

High-precision imaging of an encapsulated Lindqvist Ion and correlation of its structure and symmetry with quantum chemical calculations

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I. Computational Methods (CASTEP and Vibrational Analysis)

The optimised structures and the total energies of the $[W_6O_{19}]^{2-}$ ion in the (12,6), (16,0) and (9,9) nanotubes have been calculated using density functional theory with the PW91 functional as implemented in the CASTEP program,^{S1} utilizing periodic boundary conditions. Ultra-soft pseudopotentials for the core electrons of the atoms were generated 'on-the-fly' using CASTEP. An energy cutoff of 320 eV was used, and due to the size of the unit cell the Brillouin zone was sampled with one k-point. The vibrations of the Lindqvist anion $[W_6O_{19}]^{2-}$ in the gas phase have been calculated using semiempirical quantum chemical PM6 method as implemented in the MOPAC 2009 package.^{S2}

The Lindqvist anion has nominal symmetry O_h giving a total of 69 vibrational modes. From the symmetry degeneracy of the modes, 28 frequencies are expected in the vibrational spectra as shown by the following analysis. Five modes are of A type: $3A_{1g}+1A_{2g}+1A_{2u}$, five modes are doubly degenerate: $4E_g+1E_u$ and 18 modes belong to T representations triply degenerate: $3T_{1g}+4T_{2g}+7T_{1u}+4T_{2u}$. Among them, there are 7 IR active modes T_{1u} , and 11 Raman active modes represented by $3A_{1g}+4E_g+4T_{2g}$. 17 IR and Raman active vibrations over the 18 theoretically predicted have been found in experimental spectra.^{S3} The PM6 computed frequencies are compared to the reported experimental Raman and Infrared frequencies in Table S1. We do not obtain the exact degenerate frequencies because of a slight distortion of the Lindqvist anion obtained during the PW91-DFT relaxation. Such distortions are known in polyoxometalates and have been studied recently by Yan et al^{S4} but no negative frequencies were observed. The PM6 semiempirical method performs well when compared to several previously published first principles calculations. The root-mean-square deviation (RMSD) as described in section III has been obtained in this work for the PM6 frequencies and its value is $RMSD = 39$. The RMSD for the GGA (PW91) DFT vibrational analysis has been previously reported in [S5] and for the LDA (VWN) DFT analysis in [S6]. The LDA DFT results^{S5} gives a better RMSD of 29. The deviations observed between experimental and calculated values are due to the underestimation of electron correlation effects in first principles and semiempirical methods, as well as due to the anharmonic nature of the interatomic potential.^{S7} However, no negative frequencies were found at the end of the present calculation indicating that the pseudo-octahedral $[W_6O_{19}]^{2-}$ ionic structure is at a minimum of the potential energy surface after DFT optimisation, thus confirming the anion is likely in the ground state.

II. Unit Cell assignments for DFT calculations

Figure S1 shows the (12,6), (16,0) and (9,9) SWNT unit cells, structure composites (with the $[W_6O_{19}]^{2-}$ ion dispositions indicated) and end-on views (single ion composite only) used in the DFT optimization described in Section 3.1.

III. RMSD Analysis

RMSD analysis of the resulting ion structures was performed using Kabsch algorithm^{S8} to align the structures in order to minimise the RMSD. The RMSD is given by equation S1 where N is the number of atoms, x corresponds to the cartesian coordinates of the gas-phase free ion, y corresponds to the cartesian coordinates (frequencies) of the structure that being compared, and the weights, w , are set equal to one. The RMSDs are computed as follows

$$RMSD(N; x, y) = \left[\frac{\sum_{i=1}^N w_i |x_i - y_i|^2}{N \sum_{i=1}^N w_i} \right]^{1/2} \quad (S1)$$

Equation (S1) has also been used to estimate the RMSD associated with vibrational analysis of the gas phase $[\text{W}_6\text{O}_{19}]^{2-}$ anion which is presented in Table S1.

Supplementary Information References

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Table S1 Experimentally determined Raman and Infrared (in bold) vibrational frequencies versus computed vibrational frequencies of the $[W_6O_{19}]^{2-}$ anion using the PM6 functional in MOPAC 2009 (VWM assignments are also shown for comparison). One of the T_{2g} Raman active modes is not experimentally observed. O_t , O_b , O_c are terminal, bridging and central oxygen atoms respectively. Deformations refer to vibrations different from stretching.

Symmetry	Frequency number	Experimental ¹ cm ⁻¹	VWM ^{a,b,2} cm ⁻¹	PM6 (this work) ^c cm ⁻¹	Q-Chem GCA-ECP ^d cm ⁻¹	Assignment
T_{2g}	ν_{21}	122	173	121	133	elongation W...W
T_{1u}	ν_{20}	174	169	158	167	deformation W- O_b
E_g	ν_9	178	126	163	170	elongation W...W
T_{2g}	ν_{23}	215	176	209	221	deformation W- O_b
T_{1u}	ν_{19}	226	185	211	227	deformation W- O_b
A_{1g}	ν_3	230	233	214	229	deformation W- O_b
T_{1u}	ν_{18}	369	356	359	368	deformation W- O_c +stretching W'- O_c
T_{1u}	ν_{17}	444	448	364	457	deformation W'- O_c +stretching W- O_c
E_g	ν_8	501	512	534	499	deformation W- O_b
A_{1g}	ν_2	557	576	597	560	deformation +stretching W- O_b
T_{1u}	ν_{16}	586	596	611	562	deformation +stretching W- O_b
T_{2g}	ν_{21}	658	584	664	563	stretching W- O_b
T_{1u}	ν_{15}	812	848	796	797	stretching+small deformation W- O_b
E_g	ν_7	836	870	813	800	stretching +deformation W- O_b
E_g	ν_6	968	1029	902	928	stretching W- O_t
T_{1u}	ν_{14}	972	1029	904	929	stretching W- O_t +deformation W- O_b
A_{1g}	ν_1	992	1051	916	951	stretching of all bonds W- O_t

^aRMSD assignment 1 - 40

^bRMSD assignment 2 - 36

^cRMSD - 39

^dRMSD - 31

Figure Captions

Figure S1 – Structural depiction of the structure models used in the DFT optimisations of the $[\text{W}_6\text{O}_{19}]^{2-}$ anions in ‘inner’ helical (12,6), ‘zig-zag’ (16,0) and ‘armchair’ (9,9) conformation SWNTs. On the left of each structure, the unit cell for each nanotube is indicated. The three models in the middle indicate the positioning of the ions relative to each nanotube in terms of the repeating unit defined in the text (i.e. 2 unit cells in the case of the (12,6) SWNT, 4 unit cells in the case of the (16,0) SWNT and 8 unit cells in the case of the (9,9) SWNT). The repeating unit used in the calculation is doubled for each model in order to show the periodic displacement of the $[\text{W}_6\text{O}_{19}]^{2-}$ anions and their relative separation. The three models at right show end-on perspective view of each single repeating unit $[\text{W}_6\text{O}_{19}]^{2-}@\text{SWNT}$ composite.

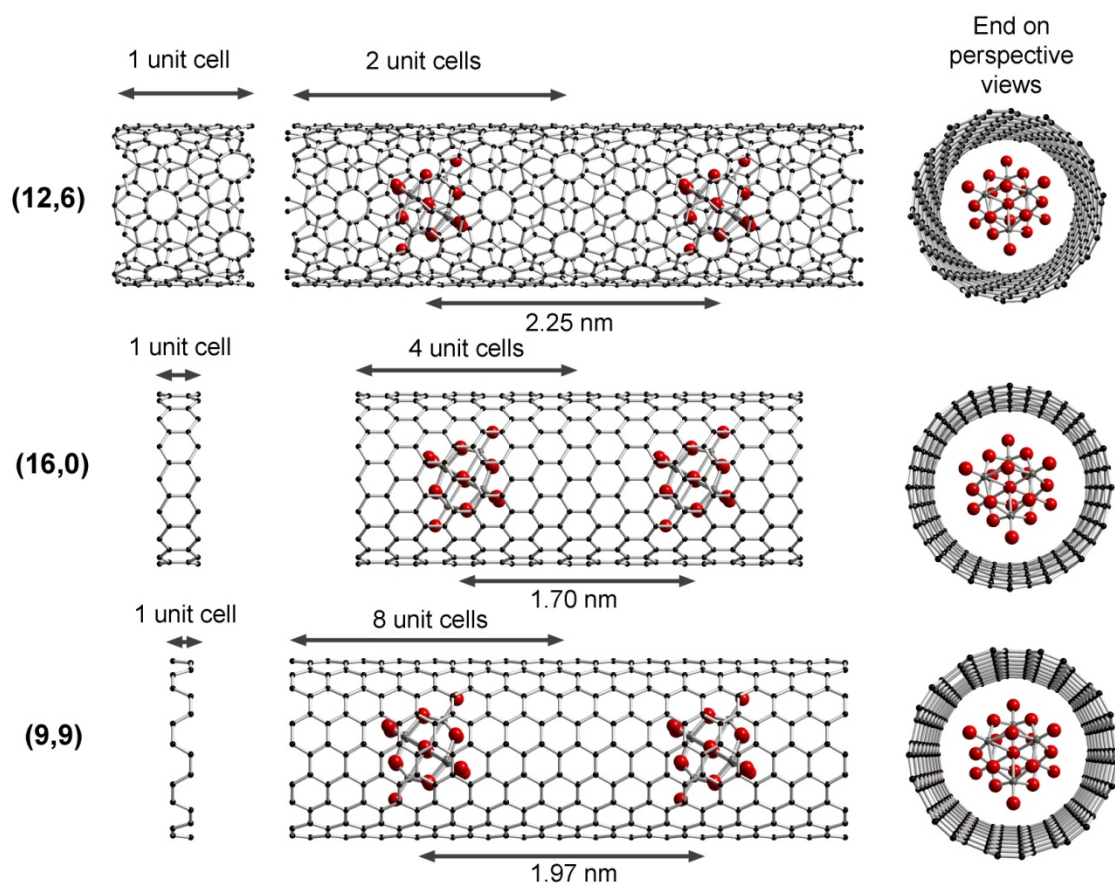


Figure S1