

Supporting Information

Single-Molecule Imaging and Kinetic Analysis of Intermolecular Polyoxometalate Reactions

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Conversion Factor

To follow the overall progression of the reaction a conversion factor was used where 0% conversion is a SWNT with only filled with POM, and 100% conversion is a SWNT only filled with tungsten metal. The change in the length of SWNT that was filled with POM was calculated by:

$$\Delta l = \frac{l_0 - l_t}{l_0}$$

where l_0 is the length of SWNT that is filled with contrasting material at the beginning of the time series and l_t is the length of SWNT that is filled with contrasting material at time t . A maximum possible contraction in the length of filled nanotube was required in order to correctly quantify the conversion. Based on experimental data, a single $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ molecule occupied approximately 0.8 nm of the length of a SWNT with a 1.4 nm diameter. A single $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ molecule would yield 18 atoms of tungsten metal, which based on the density of metallic tungsten (19.3 g cm^{-3}) would occupy approximately 0.3 nm^3 , so for a SWNT with a diameter of 1.4 nm:

$$l = \frac{0.3}{\pi (0.7)^2}$$

$$l = 0.19 \text{ nm}$$

with the maximum observable contraction in the length of a $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ molecule over the course of the reaction is therefore:

$$\Delta l_M = \frac{0.8 - 0.19}{0.8} = 77 \%$$

Leading to the overall conversion:

$$\text{Conversion \%} = \frac{\Delta l}{0.77}$$

Multislice image simulation

Table S1 gives the atomic coordinates and partial charges calculated for the optimised geometry of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, as shown in Figure S7. These charges were used in the multislice image simulation in Figure 2 & S4. Table S2 shows the mean partial charges of five distinct atom classes within this structure, with O atoms bonded to P with the O-P bond aligned with the C_3 axis; O atoms bonded to P out of the C_3 axis;

and O atoms bonded to W comprising three separate classes. These average atomic charges were used in the multislice image simulations of the two extended structures shown in Figure 2 (main text).

The incorporation of partial atomic charges into the multislice image simulations was found to be essential to accurate reproduction of the experimentally observed image contrast. Figure S8 compares multislice image simulations of the $[P_2W_{18}O_{62}]^{6-}$, using: neutral atoms (no partial charges) in a neutral molecule (net charge = 0); the calculated partial charges of a neutral molecule; and the calculated partial charges of a molecule with -6 net charge; experimental electron doses. At the low electron dose per image used experimentally, it can be seen that the ionic nature of the bonding in the POM structure must be taken into account in order to reproduce the substantial image contrast, while accounting for the overall net charge on the molecule has a more limited effect on the resulting simulated image.

Reaction of oxygen with SWNT walls

DFT calculations were performed as described in the methods section to investigate the stability of epoxides forming on the interior wall of the SWNT. The SWNT has two inequivalent C-C bond environments; for the armchair SWNT used in the calculations these correspond to C-C bonds that are orthogonal to the SWNT axis (bond length 1.424 Å) and those that are not (bond length 1.406 Å). Epoxides were found to be stable minima when located on either of these C-C bonds, with the latter being lower in energy than the former by 0.36 eV.

When considering di-epoxide species with the two epoxide groups separated by a single central C-C bond, there are four possibilities: with the epoxides being located trans or cis with respect to one another and the central C-C bond being either of the two inequivalent bonds discussed above. The finite SWNT model used (Figure S10) introduces a fifth possibility due to positioning along the length of the SWNT.

Starting with the lowest energy identified di-epoxide configuration (iii) (Figure S9 and Table S3), geometry optimisations were performed for the corresponding di-carbonyl and resulting divacancy defect, as shown in Figure 5 in the main text. A peroxide species was also found to be stable, although under the e-beam would be more expected to result in the emission of O₂ rather than CO, leaving the SWNT wall intact.

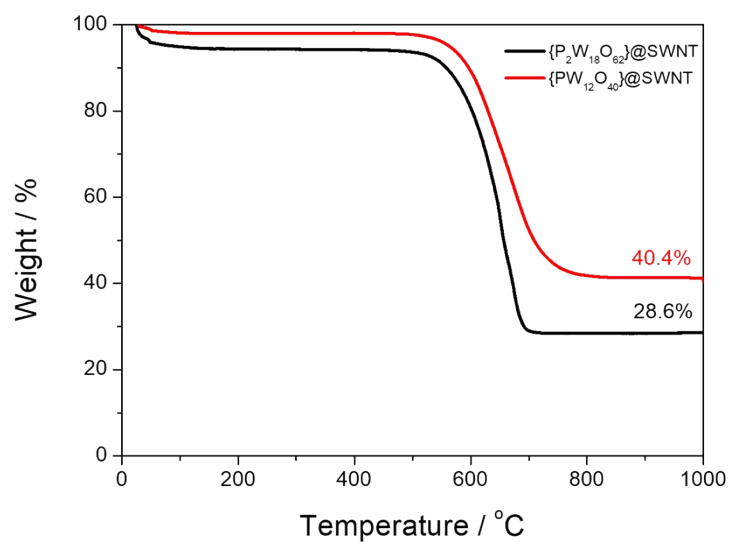


Figure S1. Thermal gravimetric analysis of both samples carried out in air.

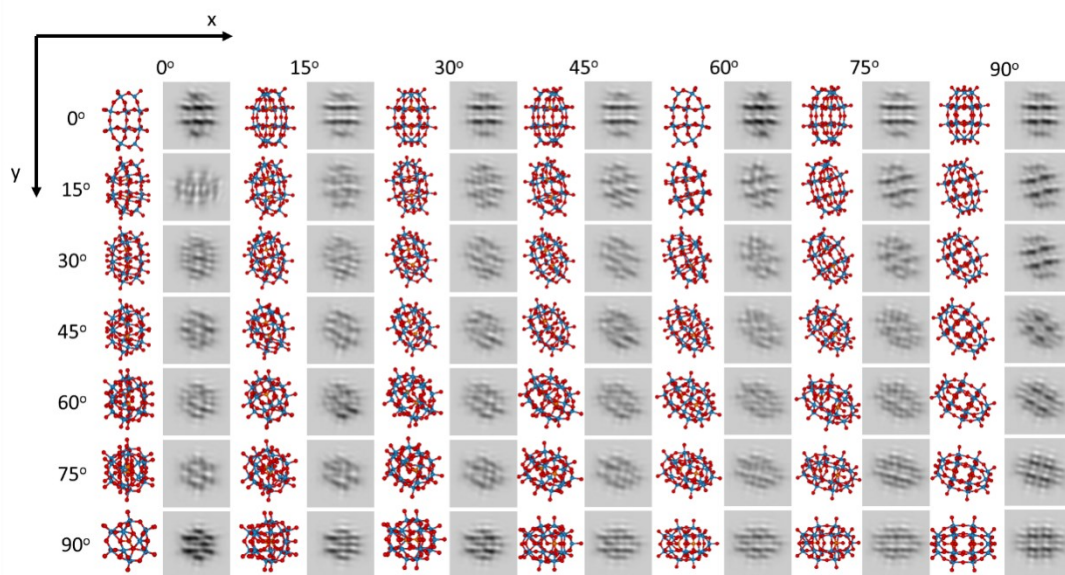


Figure S2. Multislice Image simulations of $[P_2W_{18}O_{62}]^{6-}$.

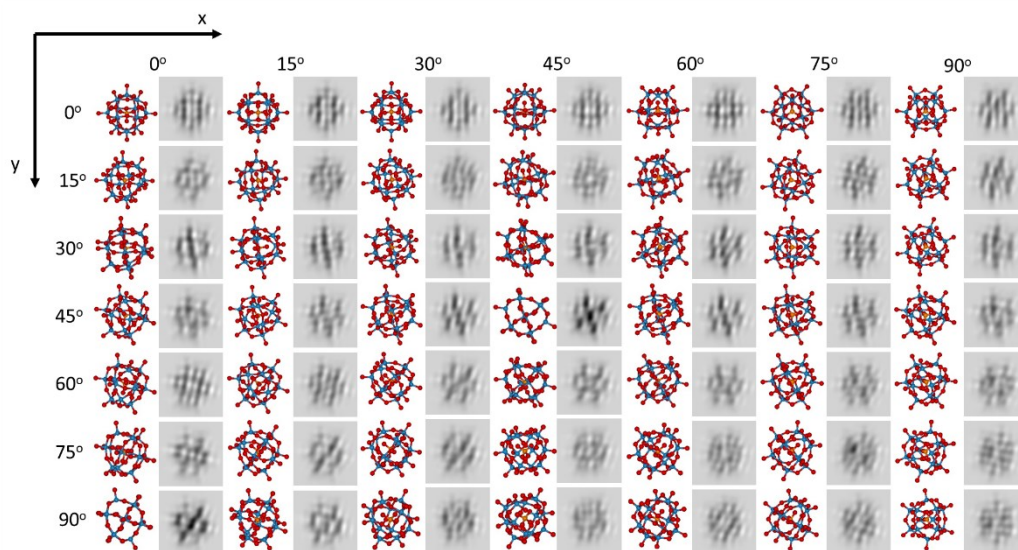


Figure S3. Multislice Image simulations of $[PW_{11}O_{40}]^{3-}$.

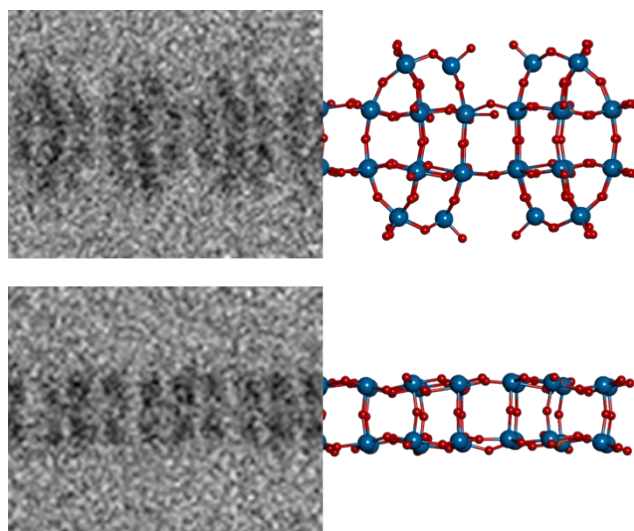


Figure S4. Top shows 4 $[P_2W_{18}O_{62}]^{6-}$ bonded together through bridging metal-oxo-metal bonds and bottom shows the nanowire seen in Figure 2 (main text). The nanowire was constructed by removing the top and bottom hemispheres of the structure seen above.

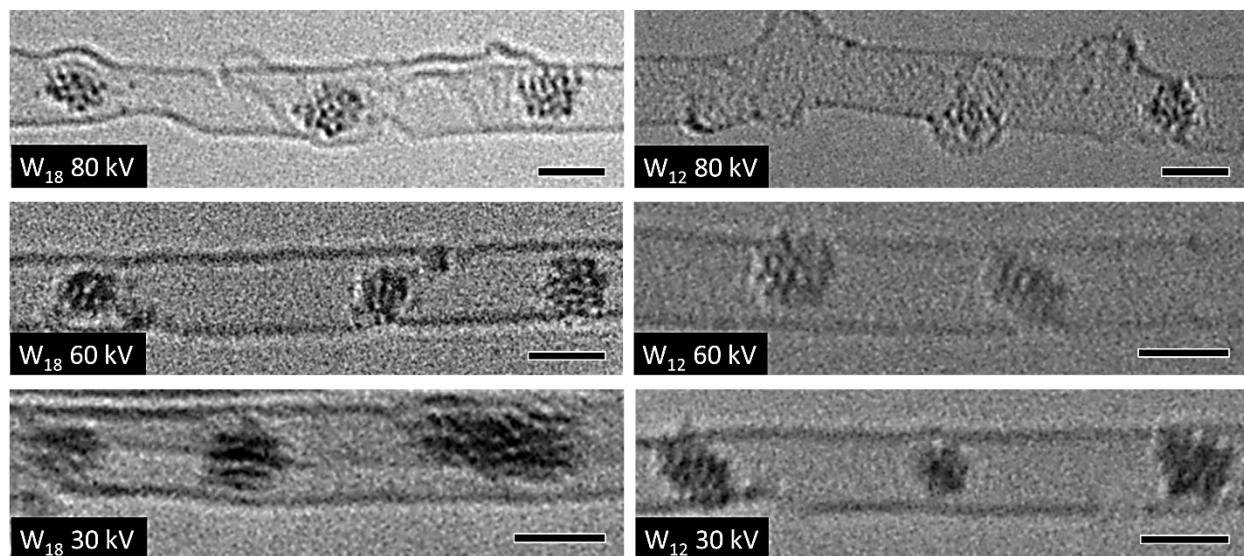


Figure S5. AC-TEM images of both {POM}@SWNT materials acquired at varying accelerating voltages at fluxes of approximately $1\text{--}2 \times 10^6 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$.

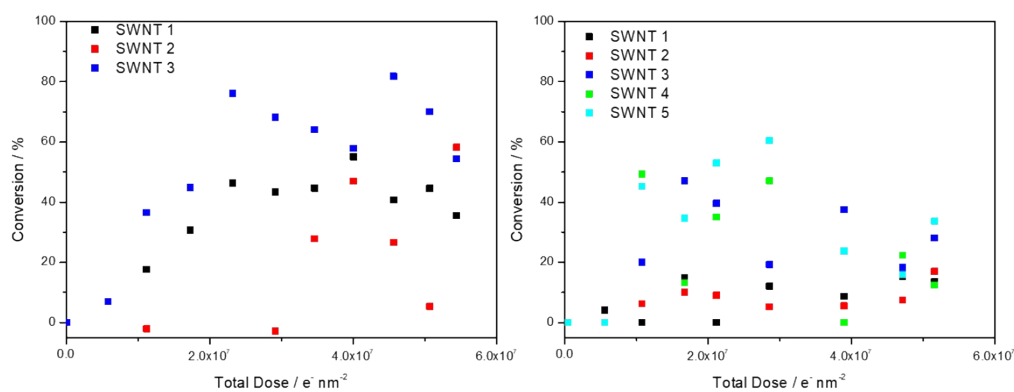


Figure S6. Conversion versus total dose for {PW₁₂O₄₀}@SWNT for fluxes of 8.87×10^4 and $7.42 \times 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$ respectively.

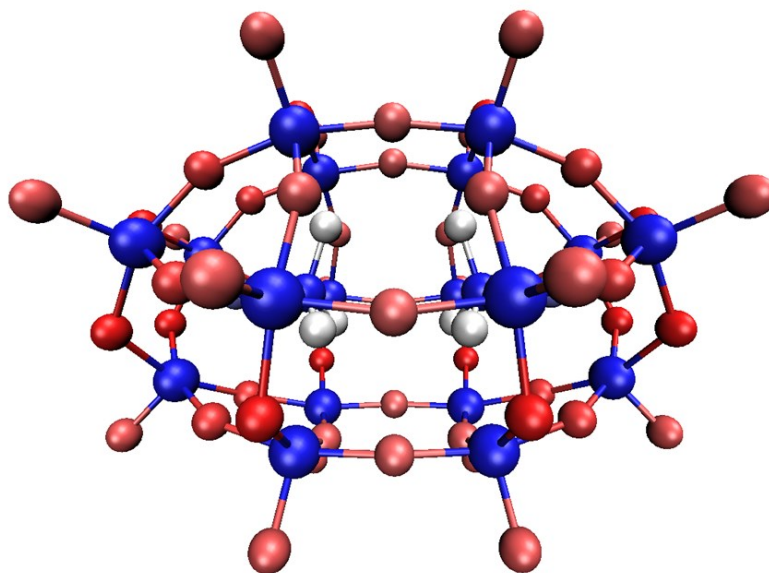


Figure S7. The optimised geometry of $[P_2W_{18}O_{62}]^{6-}$, with atom colours indicating the atomic partial charges given in Table S1 from -1.52 (red) to +2.84 (blue).

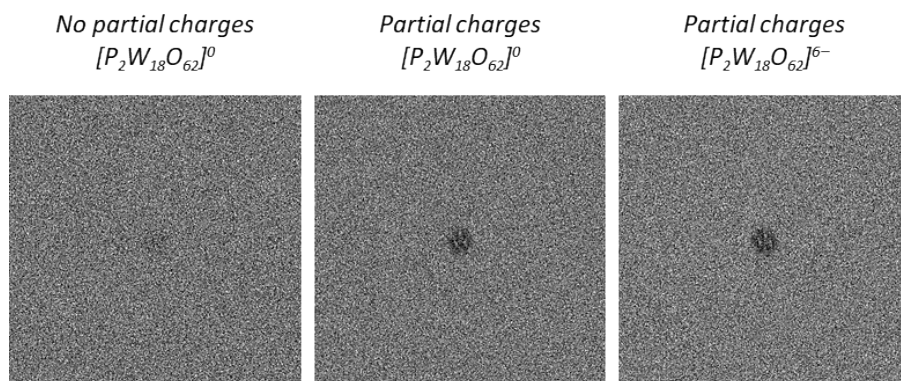


Figure S8. Comparison of image simulations using different atomic partial charges and overall molecular charges.

Table S1. Atomic coordinates (angstroms) and partial charges (e) calculated for the optimized geometry of $[P_2W_{18}O_{62}]^{6-}$.

| Element | x | y | z | q | Element | x | y | z | q |
|---------|----------|----------|----------|-----------|---------|----------|----------|----------|-----------|
| W | 4.992951 | -1.94374 | -0.39614 | 2.522686 | O | 2.250683 | -5.05928 | 1.492408 | -0.969899 |
| W | 4.993737 | 0.63523 | 1.882255 | 2.504234 | O | -0.00102 | -3.4243 | 1.466404 | -1.388608 |
| W | 4.993285 | 1.319772 | -1.49107 | 2.488134 | O | 2.152158 | -2.67504 | 3.001378 | -1.514065 |
| W | 1.900805 | 0.637768 | -3.53151 | 2.982919 | O | 1.54758 | -1.00021 | 1.127704 | 0.697271 |
| W | 1.914068 | -2.61733 | -2.45434 | 2.955330 | O | 2.262551 | -0.90302 | 5.194054 | -0.967675 |
| W | 1.905088 | -3.37789 | 1.214357 | 2.980052 | O | 0.003261 | -1.06184 | 3.569971 | -1.385525 |
| W | 1.916427 | -0.81532 | 3.491934 | 2.968677 | O | 1.59838 | 1.064875 | 3.21353 | -1.259979 |
| W | 1.899777 | 2.740933 | 2.317551 | 2.977639 | O | 2.253562 | 3.819642 | 3.63489 | -0.969873 |
| W | 1.909927 | 3.433455 | -1.03794 | 2.964220 | O | 2.15359 | 3.939992 | 0.81633 | -1.511490 |
| W | -1.90493 | 3.433327 | -1.03948 | 2.966419 | O | -0.00303 | 2.984637 | 2.230153 | -1.393261 |
| W | -1.91394 | 0.635961 | -3.52933 | 2.973911 | O | 1.5414 | 1.474249 | 0.303177 | 0.682480 |
| W | -1.90013 | -2.6199 | -2.4545 | 2.965234 | O | 2.258785 | 4.946187 | -1.82161 | -0.968281 |
| W | -1.91159 | -3.37697 | 1.216326 | 2.977115 | O | 0.00077 | 3.629038 | -0.8604 | -1.401536 |
| W | -1.90063 | -0.81499 | 3.494287 | 2.972958 | O | -2.25575 | 4.945108 | -1.8241 | -0.968969 |
| W | -1.91473 | 2.739815 | 2.315947 | 2.974235 | O | -3.72253 | 2.704977 | -1.07886 | -1.459594 |
| W | -4.99326 | 0.616758 | 1.888467 | 2.506559 | O | -2.15489 | 3.940361 | 0.81482 | -1.510497 |
| W | -4.99703 | 1.325346 | -1.47993 | 2.491137 | O | -1.59406 | 2.246355 | -2.52225 | -1.239807 |
| W | -4.98965 | -1.94584 | -0.40869 | 2.519124 | O | -1.54273 | 1.474069 | 0.302945 | 0.688078 |
| P | 2.002184 | 0.000153 | -0.00026 | 2.844562 | O | -2.26186 | 1.234909 | -5.12459 | -0.968664 |
| P | -2.00198 | -0.00067 | 0.00021 | 2.844417 | O | -2.15345 | -1.26396 | -3.81638 | -1.509085 |
| O | 6.205192 | -3.17339 | -0.65443 | -0.964793 | O | -3.72492 | 0.762461 | -2.81092 | -1.466240 |
| O | 3.723539 | -2.28556 | -1.80161 | -1.463706 | O | -1.54065 | -0.47708 | -1.42746 | 0.708795 |
| O | 5.728212 | -0.48485 | -1.47022 | -1.476926 | O | -2.25425 | -4.05361 | -3.37242 | -0.970462 |
| O | 5.727899 | -1.02893 | 1.159224 | -1.475805 | O | -3.72027 | -2.28787 | -1.80315 | -1.464320 |
| O | 3.725547 | -2.82646 | 0.745772 | -1.477834 | O | -1.59644 | -3.30451 | -0.68326 | -1.236195 |
| O | 3.623651 | 0.002435 | -0.00112 | 1.122166 | O | -2.25425 | -5.05876 | 1.495619 | -0.969165 |
| O | 6.202027 | 1.034866 | 3.077542 | -0.965102 | O | -3.72687 | -2.82685 | 0.74609 | -1.480164 |
| O | 3.724154 | -0.41396 | 2.883165 | -1.472370 | O | -2.15076 | -2.67386 | 3.002956 | -1.515029 |
| O | 5.73314 | 1.51522 | 0.310063 | -1.479662 | O | -1.54605 | -1.00012 | 1.128501 | 0.691892 |
| O | 3.72165 | 2.056108 | 2.062352 | -1.456960 | O | -2.25234 | -0.9013 | 5.195326 | -0.968533 |
| O | 6.203779 | 2.158648 | -2.4291 | -0.965930 | O | -3.71984 | -0.41577 | 2.884987 | -1.469775 |
| O | 3.721656 | 0.763184 | -2.81462 | -1.467880 | O | -1.59825 | 1.066233 | 3.213894 | -1.261305 |
| O | 3.723081 | 2.704511 | -1.07924 | -1.459945 | O | -2.26328 | 3.820445 | 3.633117 | -0.969090 |
| O | 2.252269 | 1.237787 | -5.12557 | -0.969668 | O | -3.7251 | 2.053374 | 2.062242 | -1.459401 |
| O | -0.00273 | 0.438131 | -3.69911 | -1.397874 | O | -6.20162 | 1.016061 | 3.083799 | -0.965214 |
| O | 2.152881 | -1.26172 | -3.81758 | -1.509034 | O | -5.73265 | 1.512103 | 0.315708 | -1.478939 |
| O | 1.593235 | 2.247735 | -2.52193 | -1.237395 | O | -5.72776 | -1.03464 | 1.156567 | -1.475996 |
| O | 1.541182 | -0.47608 | -1.4281 | 0.710136 | O | -3.62338 | -0.00011 | -0.00029 | 1.120273 |
| O | 2.264022 | -4.05088 | -3.37413 | -0.969409 | O | -6.20738 | 2.164402 | -2.41792 | -0.965530 |
| O | 1.596677 | -3.3042 | -0.68504 | -1.241095 | O | -5.72874 | -0.48353 | -1.47017 | -1.477403 |
| O | 0.002755 | -2.56478 | -2.71535 | -1.404417 | O | -6.20196 | -3.17539 | -0.6674 | -0.965280 |

Table S2. Mean partial charges (e) of the five distinct atomic environments in $[P_2W_{18}O_{62}]^{6-}$.

| Atom | P | W | O (-P, along C ₃ axis) | O (-P, out of C ₃ axis) | O(-W) |
|---------------------|------|------|-----------------------------------|------------------------------------|-------|
| Avg. Partial Charge | 2.84 | 2.82 | 0.7 | 1.12 | -1.27 |

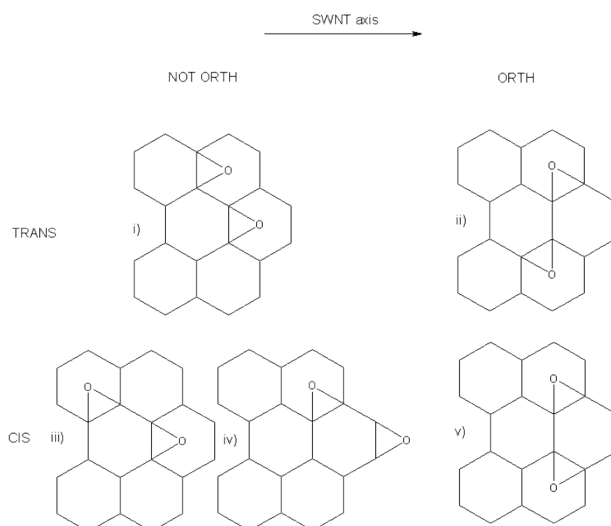


Figure S9. A schematic indicating the five inequivalent diepoxide configurations.

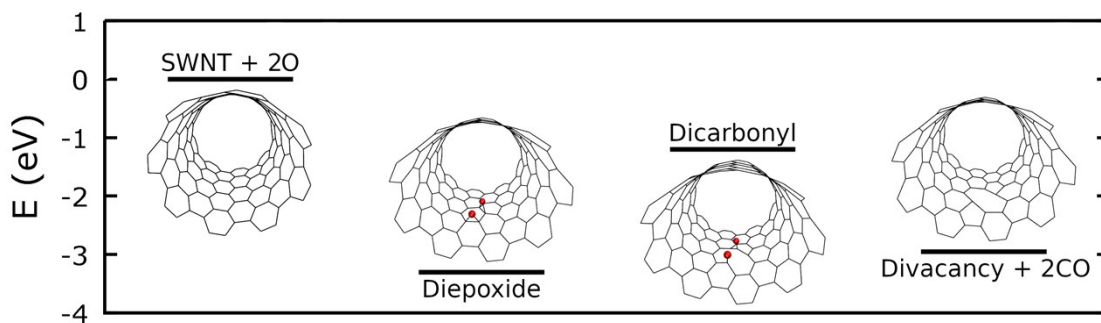


Figure S10. Full structures used to calculate the relative energies shown in figure 5.

Table S3. Corresponding energies of the inequivalent di-epoxide configurations shown in Figure S9.

| | Epoxide positions | Central C-C bond | Energy (eV) |
|------------|-------------------|-----------------------|--------------|
| i | Trans | Not orthogonal | -2.90 |
| ii | Trans | Orthogonal | -2.39 |
| iii | Cis | Not orthogonal | -3.31 |
| iv | Cis | Not orthogonal | -2.97 |
| v | Cis | Orthogonal | -2.51 |

| Species | SWNT + 2O | Di-epoxide | Di-carbonyl | V ₂ @SWNT + 2CO | Peroxide | SWNT + O ₂ |
|-------------|-----------|------------|-------------|----------------------------|----------|-----------------------|
| Energy (eV) | 0 | -3.31 | -1.22 | -2.95 | -2.21 | -5.43 |

Table S4. *The calculated energies of various 2O@SWNT species, relative to a zero energy of SWNT + 2O.*