Electronic Supporting Information

# Defects in Metal-Organic Frameworks: A compromise between adsorption and stability?

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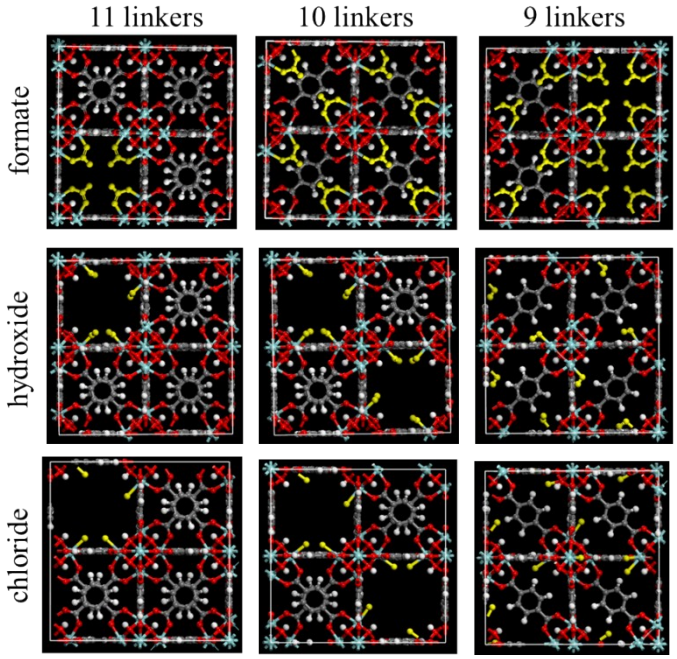


Figure S1: Schematic representation of defect UiO-66 unit cell with 11 linkers per cluster, 10 linkers per cluster and 9 linkers per cluster capped with formate (top), hydroxides (middle) and chlorine (bottom) group to compensate the charges.

Table S1: Calculated geometric and accessible surface area, framework density and free volume for defective UiO-66 structures.

| No of linkers per cluster | Type of defects | Accessible* (Geometric) Surface Area ($m^2/g$) | $\rho_f$ ($g/cm^3$) | $V_{free}$ ($cm^3/g$) based on helium |
|---|---|---|---|---|
| 11 linkers per | D1 | 1319 (954) | 1.156 | 0.492 |

| | | | | |
|---|---|---|---|---|
| cluster | D2 | 1319 (912) | 1.172 | 0.481 |
| | D3 | 1280 (863) | 1.215 | 0.473 |
| 10 linkers per cluster | D1 | 1501 (1169) | 1.127 | 0.524 |
| | D2 | 1404(1061) | 1.183 | 0.496 |
| | D3 | 1319 (951) | 1.182 | 0.482 |
| 9 linkers per cluster | D1 | 1612 (1411) | 1.082 | 0.557 |
| | D2 | 1450 (1272) | 1.112 | 0.533 |
| | D3 | 1360 (1111) | 1.156 | 0.503 |

*Accessible surface area calculated based on $N_2$ isotherms satisfying BET consistency criteria. The value in bracket refers to geometric surface area.

D1 – charge compensated by two hydroxide ions per missing linkers,

D2 – charge compensated by two chloride ions per missing linkers,

D3 – charge compensated by two formate ions per missing linkers

Table S2: DDEC calculated partial charges for formate capped defective UiO-66 with 11, 10 and 9 linkers per unit cell and the atom types are labelled as shown in Figure S2.

| Atom Type | Partial charge | | |
|---|---|---|---|
| | 11 linkers | 10 linkers | 9 linkers |
| Zr | 2.5356 | 2.5128 | 2.5379 |
| O1 | -0.6714 | -0.6662 | -0.6693 |
| O2 | -1.1878 | -1.1675 | -1.1893 |
| O3 | -1.2194 | -1.2165 | -1.2211 |
| C1 | 0.7329 | 0.7356 | 0.7398 |
| C2 | -0.0770 | -0.0776 | -0.0827 |
| C3 | -0.0869 | -0.0843 | -0.0840 |
| C4 | 0.6547 | 0.5770 | 0.6492 |
| HO | 0.4745 | 0.4773 | 0.4740 |
| H3 | 0.1205 | 0.1224 | 0.1206 |
| H4 | 0.0206 | 0.0217 | 0.0210 |

Table S3: DDEC calculated partial charges for hydroxide capped defective UiO - 66 with 11, 10 and 9 linkers per unit cell and the atom types are labelled as shown in Figure S3.

| Atom Type | Partial charge | | |
|---|---|---|---|
| | 11 linkers | 10 linkers | 9 linkers |
| Zr1 | 2.5336 | 2.5278 | 2.5099 |

| | | | |
|---|---|---|---|
| Zr2 | 2.5480 | 2.5424 | 2.5395 |
| O1 | -0.6766 | -0.6808 | -0.6828 |
| O2 | -1.1942 | -1.1965 | -1.1980 |
| O3 | -1.2185 | -1.2099 | -1.2010 |
| O4 | -1.0125 | -1.0088 | -1.0166 |
| C1 | 0.7362 | 0.7386 | 0.7403 |
| C2 | -0.0798 | -0.0814 | -0.0811 |
| C3 | -0.0852 | -0.0847 | -0.0837 |
| HO | 0.4785 | 0.4813 | 0.4837 |
| H3 | 0.1205 | 0.1210 | 0.1217 |
| H4 | 0.4214 | 0.4238 | 0.4225 |

Table S4: DDEC calculated partial charges for chlorine capped defective UiO - 66 with 11, 10 and 9 linkers per unit cell and the atom types are labelled as shown in Figure S4.

| Atom Type | Partial charge | | |
|---|---|---|---|
| | 11 linkers | 10 linkers | 9 linkers |
| Zr1 | 2.5357 | 2.5314 | 2.5278 |
| Zr2 | 2.4562 | 2.4515 | 2.4329 |
| O1 | -0.6755 | -0.6784 | -0.6790 |
| O2 | -1.188 | -1.1837 | -1.1868 |
| O3 | -1.2195 | -1.2165 | -1.2082 |
| C1 | 0.7381 | 0.7416 | 0.7438 |
| C2 | -0.0799 | -0.0817 | -0.0837 |
| C3 | -0.0841 | -0.0827 | -0.0815 |
| Cl | -0.6167 | -0.6078 | -0.5984 |
| HO | 0.4779 | 0.4797 | 0.4799 |
| H3 | 0.1214 | 0.1227 | 0.1237 |

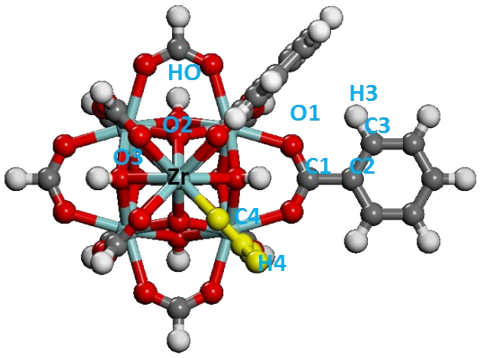


Figure S2: Atom types for formate capped defective UiO-66 structure. The yellow region represents the missing linker.

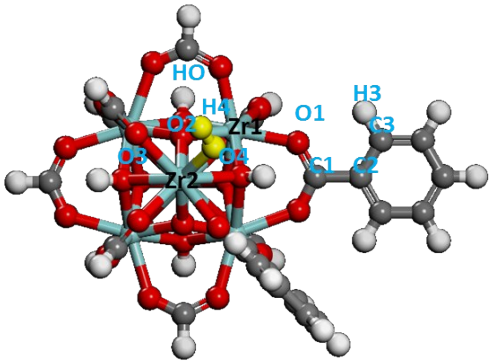


Figure S3: Atom types for hydroxide capped defective UiO-66 structure. The yellow region represents the missing linker.

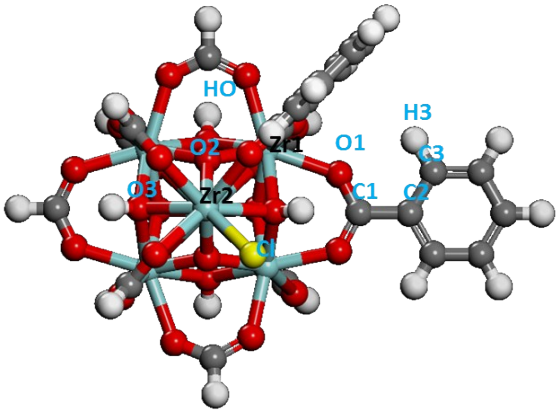


Figure S4: Atom types for chlorine capped defective UiO-66 structure. The yellow region represents the missing linker.

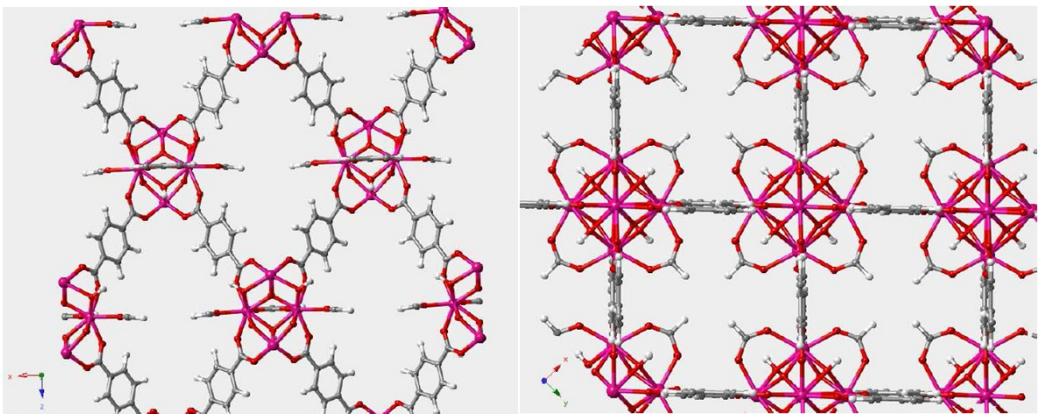

Figure S5: Two formate-substituted structures: the $z = 10$ case, represented in the $xz$ plane, and the $z = 8$ case in the $xy$ plane. Cartesian axes $x$, $y$, $z$ are shown in red, green and blue respectively.

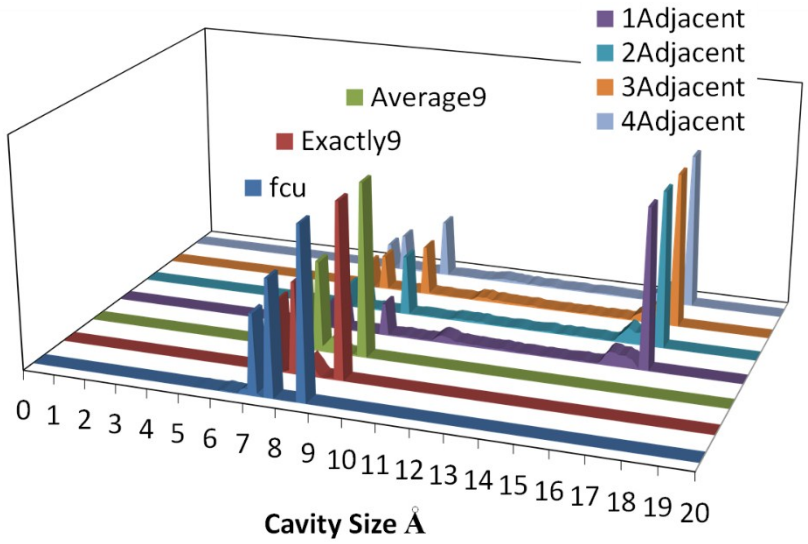


Figure S6: Cavity size (diameter) distributions of defect scenarios described in Figure 3 of main manuscript. Calculated with Zeo++.

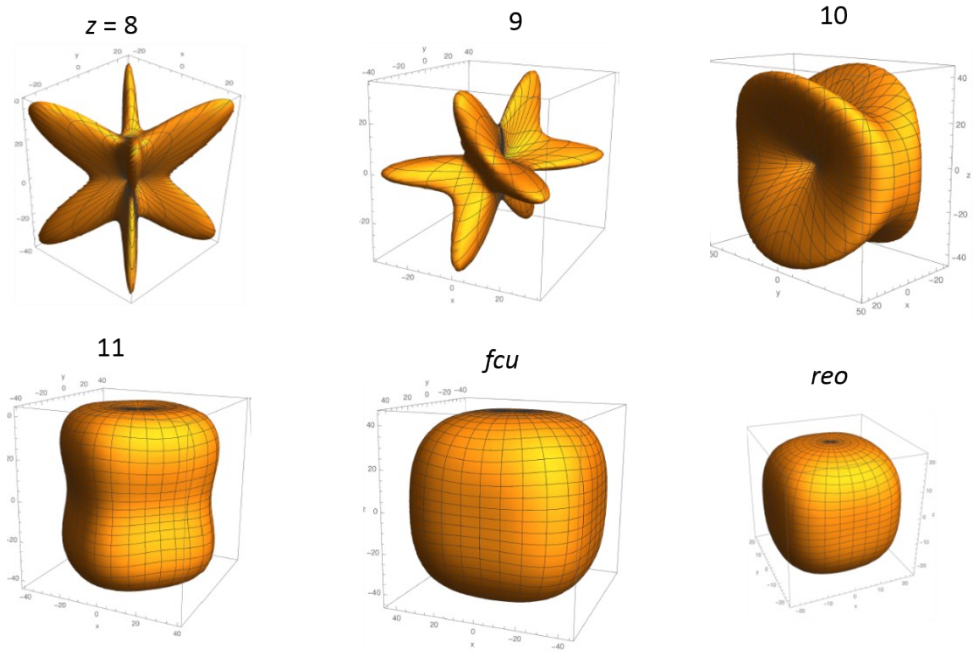


Figure S7: Young's modulus for UiO-66 with formate-based defects for different coordination number *z* and *reo* type.

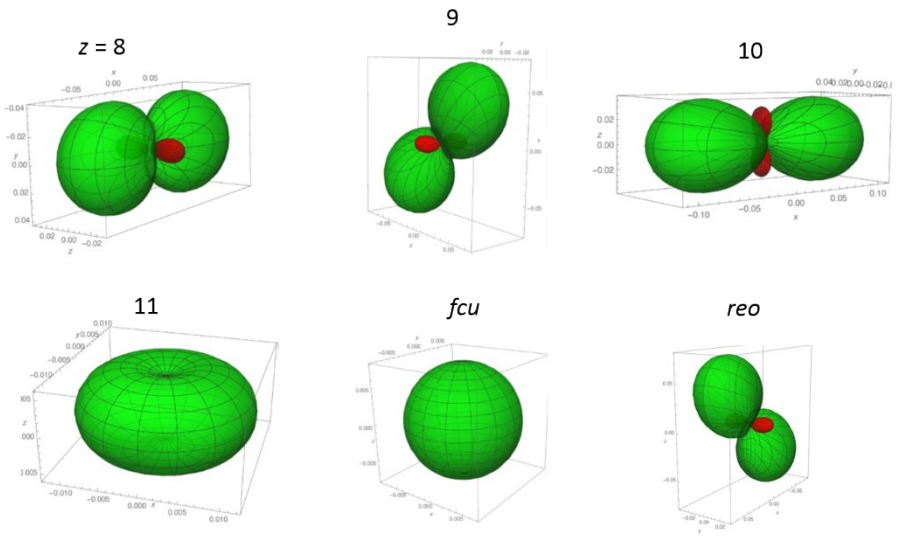


Figure S8: Linear compressibility for UiO-66 with formate-based defects for different coordination number *z* and *reo* type.

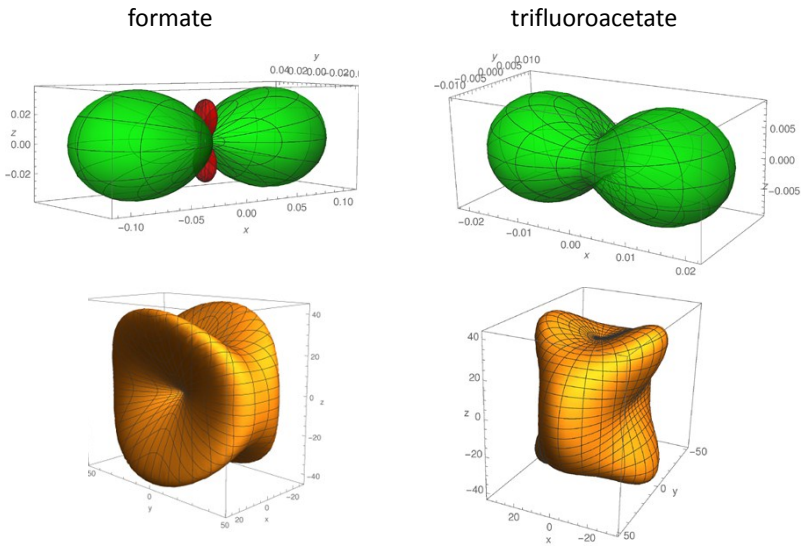


Figure S9: Linear compressibility (top) and Young's modulus (bottom) for UiO-66 with formate and trilfluoroacetate-based defects for $z = 10$.

Table S5: Structural properties of the defective UiO-66 structures, as relaxed by Density Functional Theory using CRYSTAL14 and VASP. V (unit cell volume) is in Å$^3$ and lattice parameters $a$, $b$ and $c$ are in Å; $\alpha$, $\beta$ and $\gamma$ in degrees. "-" means that the value equals either to $a$ (for $b$ or $c$) or to 90° (for any angle). All quantities refer to a conventional (non primitive) cell of UiO-66, i.e. containing 4 clusters.

| Structure | V | *a* | *b* | *c* | *α* | *β* | *γ* |
|---|---|---|---|---|---|---|---|
| *CRYSTAL14* | | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| z12 | 8902.6 | 20.726 | - | - | - | - | - |
| formate_z11 | 8901.6 | 20.726 | - | 20.723 | - | - | - |
| formate_z10 | 8897.7 | 20.722 | - | 20.721 | - | - | 89.96 |
| formate_z9 | 8895.4 | 20.723 | 20.716 | 20.721 | - | 89.98 | - |
| formate_z8 | 8895.2 | 20.725 | - | 20.711 | - | - | 90.89 |
| formate_reo | 8895.1 | 20.720 | - | - | - | - | - |
| acetate_z8 | 9095.5 | 20.413 | 21.108 | 21.110 | 90.09 | 90.02 | 90.03 |
| ClH2O_z8 | 8755.2 | 20.545 | 20.534 | 20.753 | 89.84 | 90.01 | 89.85 |
| OHH2O_z8 | 8877.8 | 20.550 | 20.549 | 21.024 | 90.11 | 89.99 | 89.77 |
| acetate_z10 | 9036.6 | 20.996 | 20.996 | 20.508 | - | 90.00 | 91.72 |
| TFA_z10 | 9135.3 | 21.282 | 21.282 | 20.207 | - | 90.00 | 93.47 |
| | | | *VASP* | | | | |
| z12 | 9170.0 | 20.931 | - | - | - | - | - |
| formate_z11 | 9179.7 | 20.933 | - | 20.949 | - | - | - |
| formate_z10 | 9112.4 | 20.817 | - | 21.030 | - | - | 90.85 |
| formate_z9 | 9104.2 | 20.813 | - | 21.017 | - | - | - |
| formate_z8 | 9135.8 | 20.871 | - | 20.973 | - | - | - |

Table S6: Elastic tensors ($C_{ij}$) computed within Crystal14 for structures of UiO-66 (in units of GPa).

Elastic tensor for non-defective UiO-66:

| | | | | | |
|---|---|---|---|---|---|
| 64.937 | 30.741 | 30.741 | 0 | 0 | 0 |
| 30.741 | 64.937 | 30.741 | 0 | 0 | 0 |
| 30.741 | 30.741 | 64.937 | 0 | 0 | 0 |
| 0 | 0 | 0 | 21.27 | 0 | 0 |
| 0 | 0 | 0 | 0 | 21.27 | 0 |
| 0 | 0 | 0 | 0 | 0 | 21.27 |

Elastic tensor for defective structure, formate-capped with $z$ = 11:

| | | | | | |
|---|---|---|---|---|---|
| 52.085 | 20.203 | 29.196 | 0 | 0 | 0 |
| 20.203 | 52.085 | 29.196 | 0 | 0 | 0 |
| 29.196 | 29.196 | 64.874 | 0 | 0 | 0 |
| 0 | 0 | 0 | 21.286 | 0 | 0 |
| 0 | 0 | 0 | 0 | 21.286 | 0 |
| 0 | 0 | 0 | 0 | 0 | 12.939 |

Elastic tensor for defective structure, formate-capped with z = 10:

| | | | | | |
|---|---|---|---|---|---|
| 16.489 | 17.752 | 26.803 | 0 | 0 | 0 |
| 17.752 | 67.831 | 30.245 | 0 | 0 | 0 |
| 26.803 | 30.245 | 64.779 | 0 | 0 | 0 |
| 0.000 | 0 | 0 | 21.406 | 0 | 0 |
| 0.000 | 0 | 0 | 0 | 21.275 | 0 |
| 0.000 | 0 | 0 | 0 | 0 | 14.15 |

Elastic tensor for defective structure, formate-capped with z = 9:

| | | | | | |
|---|---|---|---|---|---|
| 30.666 | 26.736 | 2.459 | 0 | -0.437 | 0 |
| 26.736 | 64.621 | 26.736 | 0 | -0.004 | 0 |
| 2.459 | 26.736 | 31.071 | 0 | -0.686 | 0 |
| 0 | 0 | 0 | 21.351 | 0 | -0.016 |
| -0.437 | -0.004 | -0.686 | 0 | 0.82 | 0 |
| 0 | 0 | 0 | -0.016 | 0 | 21.364 |

Elastic tensor for defective structure, formate-capped with z = 8:

| | | | | | |
|---|---|---|---|---|---|
| 15.824 | 15.967 | 26.126 | 0 | 0 | 0 |
| 15.967 | 17.154 | 27.423 | 0 | 0 | 0 |
| 26.126 | 27.423 | 64.461 | 0 | 0 | 0 |
| 0 | 0 | 0 | 21.813 | 0 | 0 |
| 0 | 0 | 0 | 0 | 20.915 | 0 |
| 0 | 0 | 0 | 0 | 0 | 13.893 |

Elastic tensor for defective structure, formate-capped with *reo* type defects:

| | | | | | |
|---|---|---|---|---|---|
| 31.146 | 13.947 | 13.947 | 0 | 0 | 0 |
| 13.947 | 31.146 | 13.947 | 0 | 0 | 0 |
| 13.947 | 13.947 | 31.146 | 0 | 0 | 0 |
| 0 | 0 | 0 | 10.478 | 0 | 0 |
| 0 | 0 | 0 | 0 | 10.478 | 0 |
| 0 | 0 | 0 | 0 | 0 | 10.478 |

Elastic tensor for defective structure, acetate-capped with z = 8:

| | | | | | |
|---|---|---|---|---|---|
| 47.275 | 18.773 | 19.306 | 0.136 | -0.298 | 0.115 |
| 18.773 | 28.224 | 1.305 | -0.177 | -0.468 | -0.342 |
| 19.306 | 1.305 | 29.137 | -0.217 | -0.427 | -0.213 |
| 0.136 | -0.177 | -0.217 | 2.748 | -0.357 | 0.146 |
| -0.298 | -0.468 | -0.427 | -0.357 | 20.279 | -0.028 |
| 0.115 | -0.342 | -0.213 | 0.146 | -0.028 | 20.344 |

Elastic tensor for defective structure, ClH20 with z = 8:

| | | | | | |
|---|---|---|---|---|---|
| 29.264 | 0.935 | 24.295 | -0.116 | -0.281 | -0.299 |
| 0.935 | 29.329 | 24.197 | -0.526 | 0.001 | 0.561 |

| | | | | | |
|---|---|---|---|---|---|
| 24.295 | 24.197 | 57.987 | -0.811 | -0.125 | 0.271 |
| -0.116 | -0.526 | -0.811 | 20.303 | 0.074 | 0.003 |
| -0.281 | 0.001 | -0.125 | 0.074 | 20.637 | 0.04 |
| -0.299 | 0.561 | 0.271 | 0.003 | 0.04 | 0.217 |

Elastic tensor for defective structure, OHH20 with z = 8:

| | | | | | |
|---|---|---|---|---|---|
| 29.264 | 0.935 | 24.295 | -0.116 | -0.281 | -0.299 |
| 0.935 | 29.329 | 24.197 | -0.526 | 0.001 | 0.561 |
| 24.295 | 24.197 | 57.987 | -0.811 | -0.125 | 0.271 |
| -0.116 | -0.526 | -0.811 | 20.303 | 0.074 | 0.003 |
| -0.281 | 0.001 | -0.125 | 0.074 | 20.637 | 0.04 |
| -0.299 | 0.561 | 0.271 | 0.003 | 0.04 | 0.217 |

Elastic tensor for defective structure, acetate-capped with z = 10:

| | | | | | |
|---|---|---|---|---|---|
| 27.632 | 19.656 | 28.244 | 0 | 0.003 | 0 |
| 19.656 | 66.266 | 28.411 | 0 | -0.002 | 0 |
| 28.244 | 28.411 | 60.713 | 0 | 0.004 | 0 |
| 0 | 0 | 0 | 19.998 | 0 | -0.002 |
| 0.003 | -0.002 | 0.004 | 0 | 21.532 | 0 |
| 0 | 0 | 0 | -0.002 | 0 | 13.339 |

Elastic tensor for defective structure, TFA-capped with z = 10:

| | | | | | |
|---|---|---|---|---|---|
| 35.294 | 20.892 | 29.301 | 0 | 0.025 | 0 |
| 20.892 | 66.158 | 26.756 | 0 | -0.001 | 0 |
| 29.301 | 26.756 | 57.855 | 0 | 0.009 | 0 |
| 0 | 0 | 0 | 18.808 | 0 | 0 |
| 0.025 | -0.001 | 0.009 | 0 | 22.141 | 0 |
| 0 | 0 | 0 | 0 | 0 | 10.85 |