# Supporting Information

## Coplanar *versus* Non-coplanar Carboxyl groups: The Influence of Sterically Enforced Non-Coplanarity on the 2D Mixing Behavior of Benzene Tricarboxylic Acids

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**Section 1:** Additional STM data

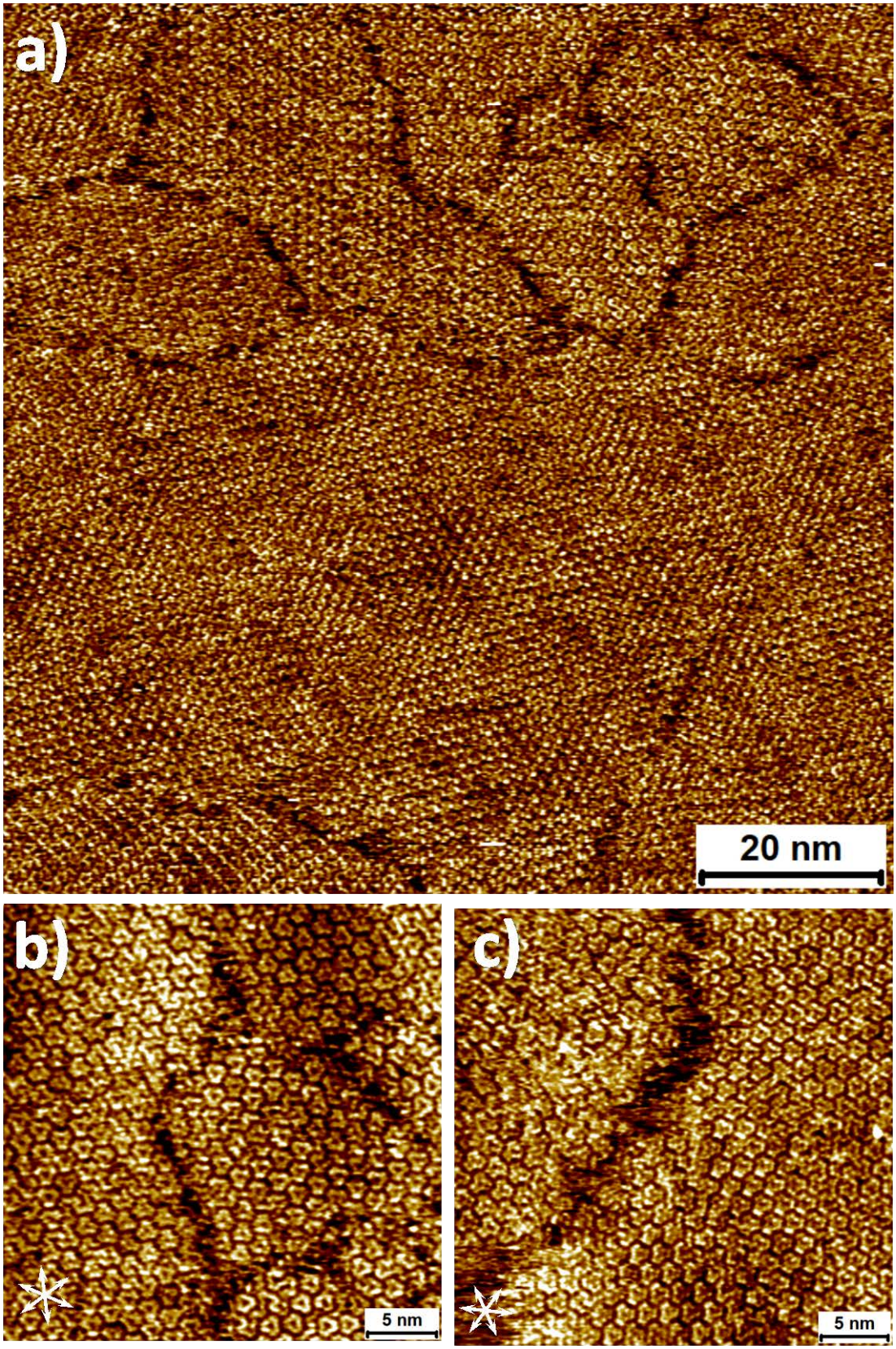



**Figure S1.** Additional STM image of the **I-TMA** network formed at the heptanoic acid/HOPG interface. Imaging parameters (a): $I_{set}$ = 280 pA, $V_{bias}$ = -430 mV, (b, c): $I_{set}$ = 70 pA, $V_{bias}$ = -1200 mV.

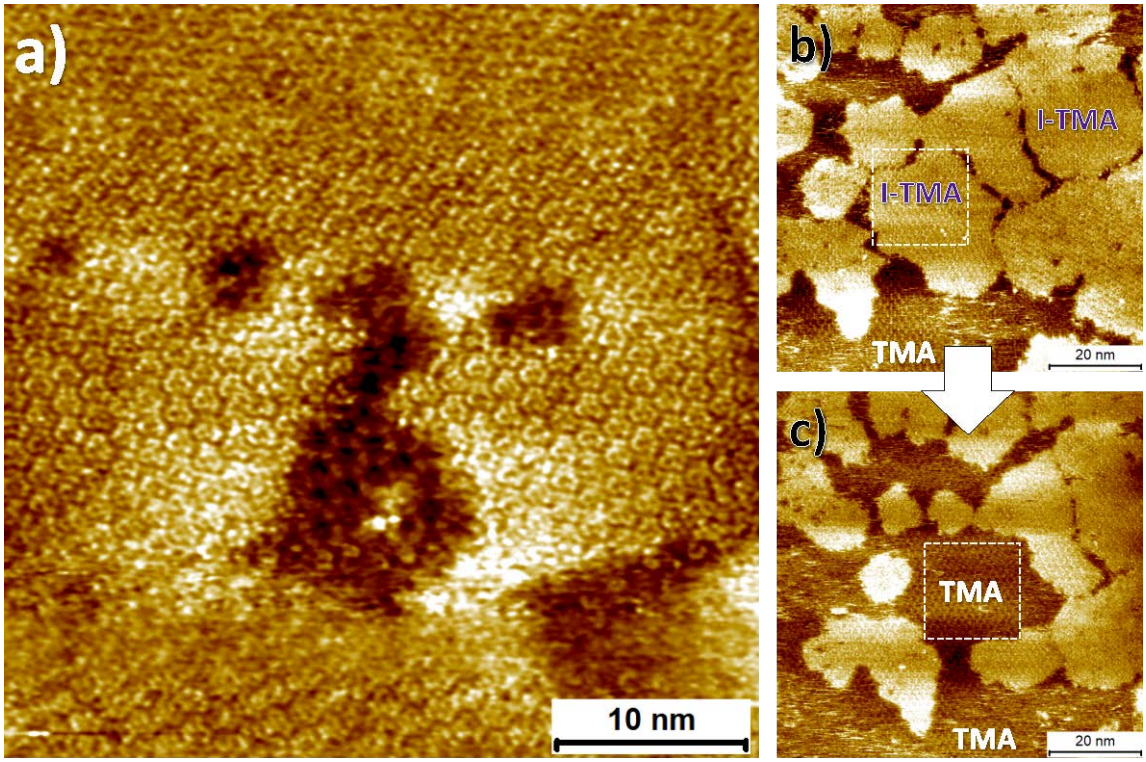



**Figure S2.** Additional STM data showing the **TMA/I-TMA** supramolecular heterostructure formed at the heptanoic acid/HOPG interface. (a) STM images showing **I-TMA** monolayer residing atop the **TMA** monolayer. The bottom **TMA** layer is visible *via* the defects in the top **I-TMA** monolayer. (b, c) A sequence of STM images showing the controlled removal of the **I-TMA** layer by STM nanolithography by scanning at higher tunnelling currents. The area highlighted by the white square was scanned at 1 mV/400 pA. The image presented in panel (c) was obtained by scanning under normal imaging parameters which reveals the bottom **TMA** layer. Imaging parameters (a) $I_{set}$ = 100 pA, $V_{bias}$ = -900 mV (b, c): $I_{set}$ = 130 pA, $V_{bias}$ = -280 mV.

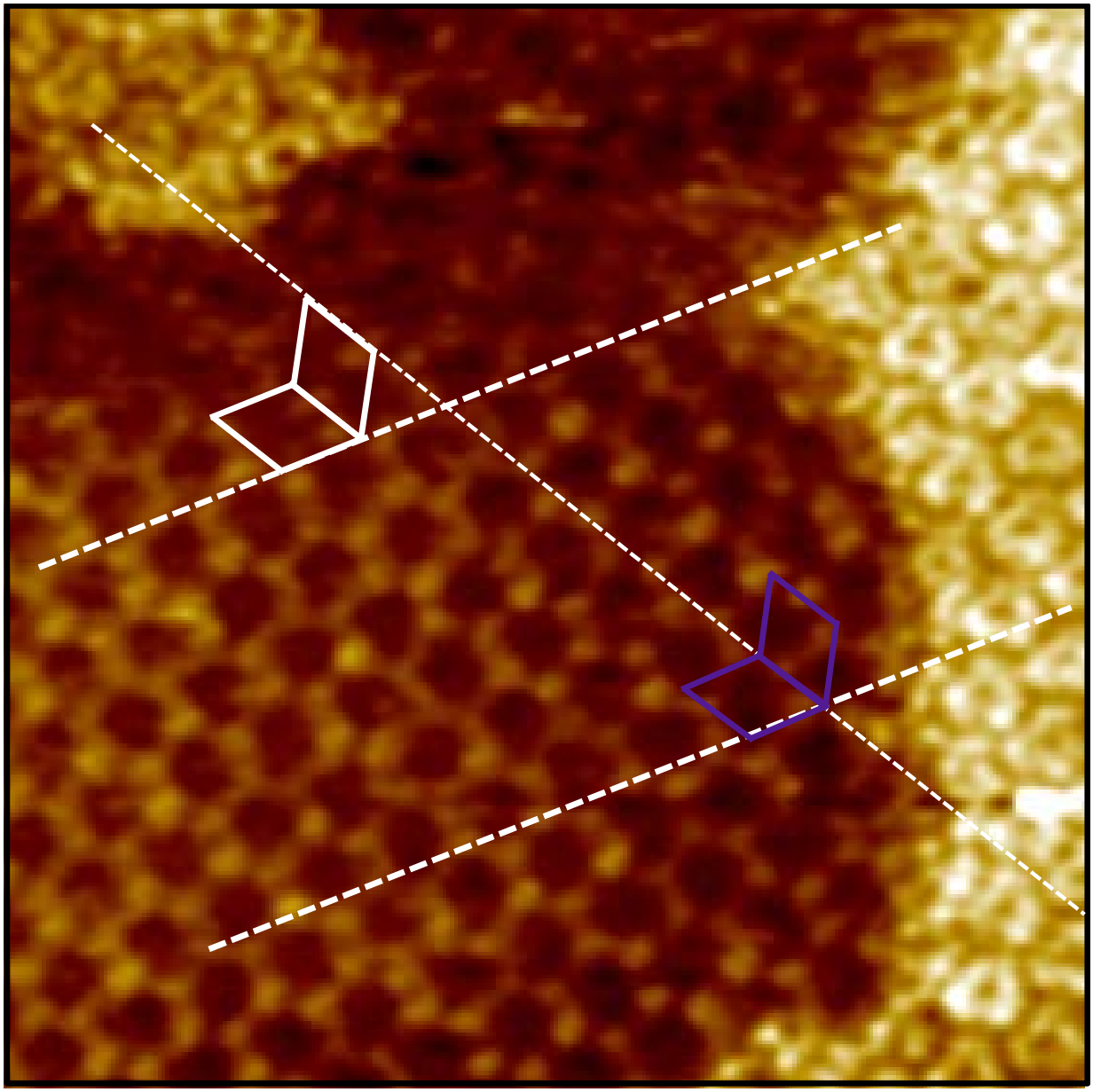


**Figure S3.** STM image of the **TMA/I-TMA** supramolecular heterostructure showing the coincidence of the unit cells of the two components. Imaging parameters: $I_{set}$ = 110 pA, $V_{bias}$ = -700 mV.

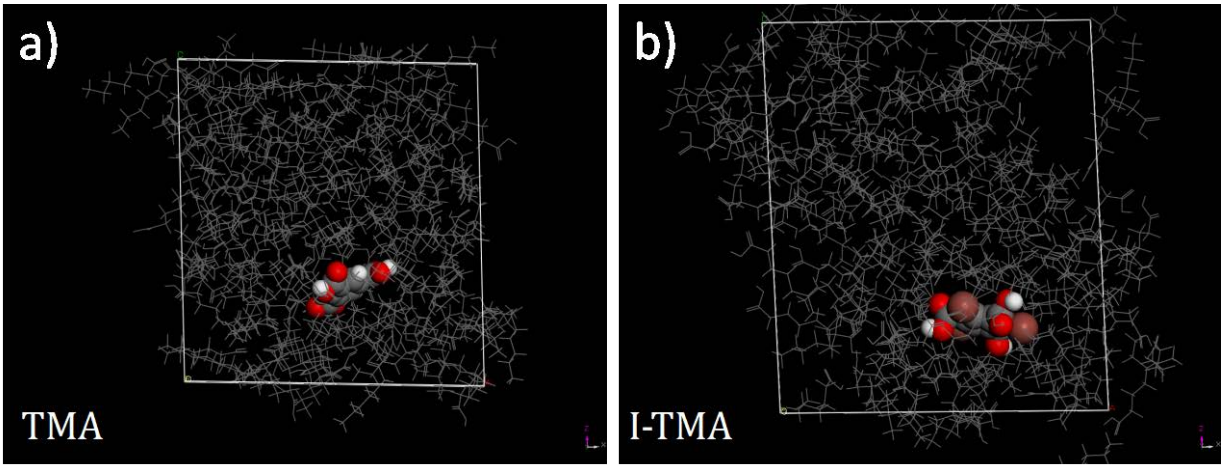



**Figure S4.** Model for a solvated single (a) **TMA** and (b) **I-TMA** molecule The simulation box is periodic, to avoid edge effects.

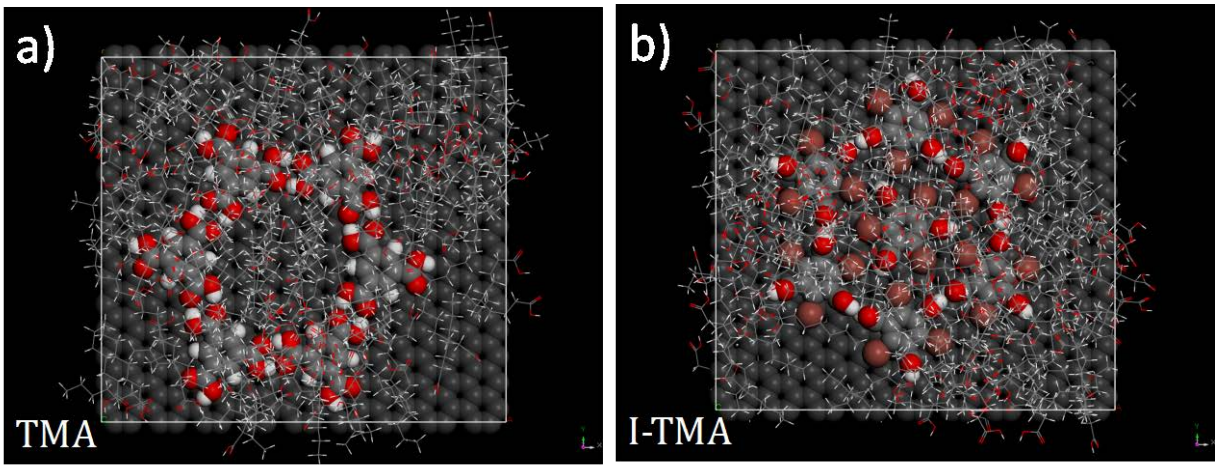
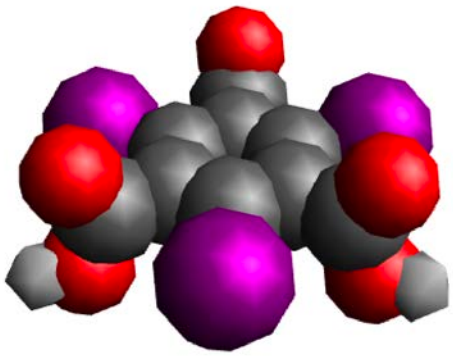
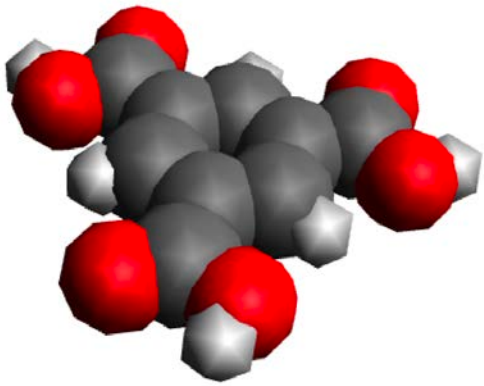



**Figure S5.** Model for a solvated single (a) **TMA** and (b) **I-TMA** aggregate on the surface of graphite. The simulation box is periodic, to avoid edge effects.

## Section 2: Frequency Analysis For I-TMA and TMA isolated molecules





| TI-TMA | | TMA | |
|---|---|---|---|
| Frequencies | Intensities | Frequencies | Intensities |
| 36.3743 | 0.0180716 | 102.762 | 0.00331831 |
| 36.4781 | 0.0180236 | 129.951 | 0.122811 |
| 50.0607 | 0.00347038 | 130.687 | 0.175348 |
| 62.8564 | 0.54597 | 192.86 | 0.000774834 |
| 63.0157 | 0.537286 | 193.936 | 0.000134754 |
| 63.8957 | 0.010747 | 271.391 | 0.406973 |
| 97.0862 | 0.0185354 | 325.513 | 0.295313 |
| 97.0997 | 0.0184874 | 350.241 | 0.0810207 |
| 97.7929 | 0.29575 | 359.998 | 0.245538 |
| 132.359 | 0 | 449.852 | 0.0805154 |
| 133.13 | 0.00183914 | 450.901 | 0.0551817 |
| 133.156 | 0.00190311 | 492.071 | 5.52725 |
| 162.943 | 7.99628e-05 | 504.735 | 2.14036 |
| 191.25 | 0.223432 | 577.526 | 41.7247 |
| 191.327 | 0.223656 | 590.494 | 2.23748 |
| 207.772 | 0.101521 | 610.071 | 0.0158841 |
| 207.78 | 0.101505 | 616.871 | 0.0333347 |
| 302.636 | 0.495929 | 638.875 | 14.4662 |
| 410.747 | 0 | 642.874 | 17.1186 |
| 420.929 | 0.0219098 | 677.528 | 5.94345 |
| 420.985 | 0.0216859 | 688.498 | 1.78438 |
| 424.857 | 0.294951 | 755.898 | 27.2275 |
| 474.531 | 2.73941 | 794.651 | 0.00859055 |
| 474.601 | 2.74427 | 795.264 | 0.0264623 |
| 604.434 | 28.7281 | 890.857 | 1.14473 |
| 604.552 | 28.7343 | 901.217 | 0.00171811 |
| 628.367 | 0.000239888 | 962.913 | 1.90397 |
| 653.112 | 0.0217659 | 984.34 | 0.214595 |
| 653.116 | 0.0207423 | 995.746 | 0.0704594 |
| 679.501 | 5.46414 | 1015.85 | 0.0679664 |
| 692.754 | 0.055862 | 1119.57 | 2.63287 |
| 692.826 | 0.0576692 | 1127.6 | 7.06094 |
| 743.2 | 3.13948 | 1146.19 | 17.9491 |
| 743.274 | 3.13181 | 1173.01 | 100 |
| 791.565 | 1.52919 | 1175.91 | 50.5329 |
| 821.633 | 0 | 1236.85 | 7.13511 |
| 898.97 | 6.75599 | | |

| | |
|---|---|
| 899.005 6.77998<br>1030.56 1.76417<br>1143.89 54.306<br>1171.72 37.7091<br>1171.82 37.637<br>1247.23 14.8994<br>1277.52 0<br>1316.11 15.6651<br>1316.15 15.6746<br>1391.65 0.00588526<br>1391.74 0.00625309<br>1402.46 16.0758<br>1567.14 17.9903<br>1567.17 17.9724<br>1821.54 15.1001<br>1821.63 15.0418<br>1827.17 100<br>3737.99 22.8165<br>3738.05 22.7994<br>3738.41 3.17206 | 1292.22 1.89489<br>1351.43 14.7613<br>1357.48 42.5284<br>1376.12 5.82342<br>1407.81 8.82241<br>1470.52 1.5238<br>1483.73 0.729136<br>1641.3 0.768265<br>1645.58 6.47209<br>1793.51 32.487<br>1798.97 65.7275<br>1806.82 86.5133<br>3234.06 1.19902<br>3241.37 0.89394<br>3250.2 0.581681<br>3765.8 33.8057<br>3765.96 16.864<br>3766.43 5.82628 |

**TMA Atomic Coordinates and Energy**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.833667 | -3.393141 | 0.287812 |
| 2 | 6 | 0 | 2.230095 | -3.480667 | 0.325647 |
| 3 | 6 | 0 | 3.008374 | -2.322042 | 0.234968 |
| 4 | 6 | 0 | 2.391136 | -1.070649 | 0.106460 |
| 5 | 6 | 0 | 0.994217 | -0.984161 | 0.068564 |
| 6 | 6 | 0 | 0.215354 | -2.144617 | 0.158906 |
| 7 | 6 | 0 | 0.048210 | -4.657507 | 0.389183 |
| 8 | 8 | 0 | -1.290385 | -4.451393 | 0.341623 |
| 9 | 8 | 0 | 0.535333 | -5.764421 | 0.502901 |
| 10 | 6 | 0 | 0.287902 | 0.321819 | -0.066396 |
| 11 | 8 | 0 | -0.919568 | 0.452712 | -0.105278 |
| 12 | 8 | 0 | 1.136228 | 1.376802 | -0.143551 |
| 13 | 6 | 0 | 4.491990 | -2.467530 | 0.279712 |
| 14 | 8 | 0 | 5.079473 | -3.524958 | 0.388228 |
| 15 | 8 | 0 | 5.141754 | -1.280531 | 0.185554 |
| 16 | 1 | 0 | 2.709302 | -4.448137 | 0.425703 |
| 17 | 1 | 0 | 2.992689 | -0.173300 | 0.036493 |
| 18 | 1 | 0 | -0.864331 | -2.059304 | 0.127838 |
| 19 | 1 | 0 | -1.714694 | -5.322629 | 0.414324 |
| 20 | 1 | 0 | 0.588169 | 2.174753 | -0.228759 |
| 21 | 1 | 0 | 6.093052 | -1.475489 | 0.223187 |

**TMA Atomic Coordinates and Energy**

| Center | Atomic | Atomic | Coordinates (Angstroms) |
|---|---|---|---|

| Number | Number | Type | X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.824438 | -3.287515 | 0.104156 |
| 2 | 6 | 0 | 2.204247 | -3.388150 | 0.319719 |
| 3 | 6 | 0 | 2.995132 | -2.241234 | 0.461453 |
| 4 | 6 | 0 | 2.388550 | -0.981607 | 0.384072 |
| 5 | 6 | 0 | 1.008960 | -0.859534 | 0.176933 |
| 6 | 6 | 0 | 0.236025 | -2.018710 | 0.036555 |
| 7 | 6 | 0 | -0.012597 | -4.530679 | -0.086239 |
| 8 | 8 | 0 | -0.500899 | -4.983517 | 1.085245 |
| 9 | 8 | 0 | -0.217912 | -5.054791 | -1.156340 |
| 10 | 6 | 0 | 0.358527 | 0.503708 | 0.136948 |
| 11 | 8 | 0 | -0.077881 | 1.077747 | 1.107252 |
| 12 | 8 | 0 | 0.325045 | 1.000717 | -1.115599 |
| 13 | 6 | 0 | 4.477938 | -2.363025 | 0.724059 |
| 14 | 8 | 0 | 4.969345 | -2.440562 | 1.825903 |
| 15 | 8 | 0 | 5.185351 | -2.376403 | -0.423246 |
| 16 | 53 | 0 | 3.112476 | -5.312179 | 0.432039 |
| 17 | 53 | 0 | 3.578980 | 0.773370 | 0.592100 |
| 18 | 53 | 0 | -1.863461 | -1.850478 | -0.287210 |
| 19 | 1 | 0 | -1.028661 | -5.779702 | 0.896673 |
| 20 | 1 | 0 | -0.102230 | 1.874606 | -1.073933 |
| 21 | 1 | 0 | 6.126597 | -2.456452 | -0.187419 |