Revealing the unusual rigid diamond net analogues in superhard titanium carbides
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Figure S1. The simulated power X-ray diffraction (\(\lambda = 0.5608\) Å and the diffraction data are obtained from powder diffraction and not single crystal) for experiment structures (a) cubic TiC and (c) cubic Ti\(_2\)C at ambient pressure, our predicted corresponding structures (b) TiC and (d) Ti\(_2\)C at ambient pressure.
Table S1. Lattices parameters and atomic coordinates of Ti$_2$C, Ti$_3$C$_2$, Ti$_6$C$_5$, TiC-TiC$_4$ at ambient pressure.

| Space Group | Lattice Parameters (Å,°) | Atoms | x     | y     | z       |
|-------------|-------------------------|-------|-------|-------|---------|
| Ti$_2$C     | Fd-3m                   | a=b=c=8.641 | Ti(32e) | -0.6312 | 0.1312  | 0.1312  |
|             |                         |       | C(16c) | -0.8750 | 0.3750  | 0.3750  |
| Ti$_3$C     | R-3m                    | a=b=3.087,c=14.471 | Ti(6c) | 0.3333  | 0.6667  | 0.4212  |
|             |                         |       | C(3b)  | 0.3333  | 0.6667  | 0.1667  |
| Ti$_3$C     | I4/m                    | a=b=5.551,c=4.555 | Ti(8h) | 0.6604  | 0.8258  | 0.5     |
|             |                         |       | C(4e)  | 0       | 0       | 0.3249  |
| Ti$_3$C     | I4/m                    | a=b=5.552,c=4.554 | Ti(8h) | 0.340   | 0.174   | 0       |
|             |                         |       | C(4e)  | 0       | 0       | 0.825   |
| Ti$_3$C$_2$ | C2/m                    |       |       |       |         |         |
|             |                         |       |       |       |         |         |
| Ti$_3$C$_2$ | P4/mmb                  | a=b=5.315,c=2.855 | Ti(2b) | 0       | 0       | 0.5     |
|             |                         |       | Ti(4g) | 0.1821  | 0.6821  | 0       |
|             |                         |       | C(4h)  | 0.1029  | 0.3972  | 0.5     |
| Ti$_3$C$_2$ | P4/mmb                  | a=b=5.940,c=3.076 | Ti(2a) | 0       | 0       | 0       |
|             |                         |       | Ti(4g) | 0.1579  | 0.6579  | 0.5     |
|             |                         |       | C(4h)  | 0.1520  | 0.3480  | 0       |
| Ti$_4$C$_5$ | C2/m                    | a=b=5.532,c=6.139 | Ti(8j) | -0.0065 | -0.1752 | 0.2544  |
|             |                         |       | Ti(4i) | 0.0260  | -0.5    | 0.2632  |
|             |                         |       | C(4h)  | 1.0     | 0       | 0.5     |
|             |                         |       | C(4g)  | 1.0     | -0.3335 | 0.5     |
|             |                         |       | C(4g)  | -0.5    | -0.1666 | 0       |
| Ti$_4$C$_5$ | C2/m                    | a=b=5.234,c=5.523 | Ti(8j) | 0.2410  | 0.1736  | 0.2462  |
|             |                         |       | Ti(4i) | 0.7603  | 0       | 0.2390  |
|             |                         |       | C(4h)  | 0       | 0.1665  | 0.5     |
|             |                         |       | C(4g)  | 0       | 0.3332  | 0       |
| TiC         | Fm-3m                   | a=b=c=4.336 | Ti(4a) | 0.5     | 0.5     | 0       |
|             |                         |       | C(4b)  | 0.5     | 0       | 0       |
| TiC         | Fm-3m                   | a=b=c=4.328 | Ti(4a) | 0       | 0       | 0       |
|             |                         |       | C(4b)  | 0.5     | 0.5     | 0.5     |
| TiC$_2$     | R-3m                    | a=b=2.649,c=11.959 | Ti(3b) | 0.3333  | 0.6667  | 0.1667  |
|             |                         |       | C(6c)  | 0       | 0       | 0.3137  |
| TiC$_3$     | R-3m                    | a=b=2.603,c=30.670 | Ti(6c) | 0       | 0       | 0.1013  |
|             |                         |       | C(6c)  | 0.6667  | 0.3333  | 0.3075  |
|             |                         |       | C(6c)  | 0.6667  | 0.3333  | 0.1594  |
|             |                         |       | C(6c)  | 0.3333  | 0.6667  | 0.0421  |
| TiC$_4$     | P-3m                    | a=b=2.588,c=12.299 | Ti(2d) | 0.3333  | 0.6667  | 0.1633  |
|             |                         |       | C(2d)  | 0.3333  | 0.6667  | 0.9818  |
|             |                         |       | C(2d)  | 0.3333  | 0.6667  | 0.4796  |
|             |                         |       | C(2c)  | 0       | 0       | 0.6893  |
Ref 1. C. Jiang and W. S. Jiang, Pressure–composition phase diagram of Ti–C from first principles, *Phys. Status Solidi B.*, 2014, **251**, 533–536.

Ref 2. P. A. Korzhavyi, L. V. Pourovskii, H. W. Hugosson, A. V. Ruban, and B. Johansson, Ab initio study of phase equilibria in TiC(x), *Phys. Rev. Lett.*, 2002, **88**, 015505.

Ref 3. G. Amirthan, K. Nakao, M. Balasubramanian, H. Tsuda and S. Mori, Influence of N and Fe on α-Ti precipitation in the in situ TiC–titanium alloy composites, *J. Mater. Sci.*, 2011, **46**, 1103-1109.

Figure S2. The curves of phonon dispersion for TiC$_n$ (n>1) compounds. TiC$_2$ (a) at 0 GPa, (b) at 100 GPa; TiC$_3$ (c) at 0 GPa, (d) at 100 GPa; TiC$_4$ (e) at 0 GPa, (f) at 100 GPa, respectively.
Figure S3. The calculated three-dimensional representations of linear compressibility, Poisson’s ratio, shear ratio and Young’s modulus for the TiC structure.

Figure S4. The calculated three-dimensional representations of linear compressibility, Poisson’s ratio, shear ratio and Young’s modulus for the TiC₃ structure.

Figure S5. The calculated three-dimensional representations of linear compressibility, Poisson’s ratio, shear ratio and Young’s modulus for the TiC₄ structure.

Table S2. The calculated formation enthalpies ΔH of TMC₄ (TM= V, Zr, Nb, Hf and Ta).

|        | VC₄  | ZrC₄  | NbC₄  | HfC₄  | TaC₄  |
|--------|------|-------|-------|-------|-------|
| ΔH (eV/atom) | -0.46234 | -0.39428 | -0.17959 | -0.71717 | -0.14002 |
Table S3. Calculated elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young's modulus $Y$ (GPa), $B/G$ and Poisson's ratio $\nu$ of TMC$_4$ (TM= V, Zr, Nb, Hf and Ta).

|       | $C_{11}$ | $C_{33}$ | $C_{44}$ | $C_{56}$ | $C_{12}$ | $C_{13}$ | $B$   | $G$   | $Y$   | $B/G$ | $\nu$ |
|-------|----------|----------|----------|----------|----------|----------|-------|-------|-------|-------|-------|
| VC$_4$ | 881      | 687      | 315      | 357      | 166      | 126      | 362   | 332   | 762   | 0.92  | 0.15  |
| ZrC$_4$ | 720      | 623      | 269      | 298      | 125      | 102      | 301   | 282   | 645   | 1.07  | 0.14  |
| NbC$_4$ | 727      | 567      | 264      | 265      | 197      | 172      | 342   | 256   | 615   | 0.75  | 0.20  |
| HfC$_4$ | 739      | 632      | 272      | 304      | 131      | 96       | 305   | 288   | 656   | 1.06  | 0.14  |
| TaC$_4$ | 736      | 576      | 255      | 273      | 190      | 174      | 345   | 257   | 617   | 0.74  | 0.20  |

Figure S6. The curves of phonon dispersion for TMC$_4$ (TM= V, Zr, Nb, Hf and Ta) at ambient pressure. (a) VC$_4$, (b) ZrC$_4$, (c) NbC$_4$, (d) HfC$_4$ and (e) TaC$_4$. 
Table S4. The optimized lattices parameters and atomic coordinates of TMC₄ (TM= V, Zr, Nb, Hf and Ta) at ambient pressure.

| Space Group | Lattice Parameters (Å) | Atoms | x     | y     | z     |
|-------------|------------------------|-------|-------|-------|-------|
| VC₄         | P-3m1 a=b=2.5600, c=12.0099 |       | 0.66667 | 0.33333 | 0.52106 |
|             |                        |       | 0.66667 | 0.33333 | 0.01867 |
|             |                        |       | 0.33333 | 0.66667 | 0.34908 |
|             |                        | C (2c) | 0.33333 | 0.66667 | 0.35865 |
|             |                        | V (2d) | 0.66667 | 0.33333 | 0.84012 |
| ZrC₄       | P-3m1 a=b=2.6833, c=13.0102 |       | 0.66667 | 0.33333 | 0.51939 |
|             |                        |       | 0.66667 | 0.33333 | 0.01657 |
|             |                        |       | 0.66667 | 0.33333 | 0.36162 |
|             |                        | C (2c) | 0.66667 | 0.33333 | 0.67810 |
|             |                        | Zr (2d) | 0.66667 | 0.33333 | 0.83111 |
| NbC₄       | P-3m1 a=b=2.6529, c=12.7689 |       | 0.66667 | 0.33333 | 0.51979 |
|             |                        |       | 0.66667 | 0.33333 | 0.01824 |
|             |                        |       | 0.33333 | 0.66667 | 0.35865 |
|             |                        | C (2c) | 0.33333 | 0.66667 | 0.68201 |
|             |                        | Nb (2d) | 0.66667 | 0.33333 | 0.83333 |
| HfC₄       | P-3m1 a=b=2.6740, c=12.8550 |       | 0.66667 | 0.33333 | 0.51966 |
|             |                        |       | 0.66667 | 0.33333 | 0.01780 |
|             |                        |       | 0.33333 | 0.66667 | 0.36005 |
|             |                        | C (2c) | 0.33333 | 0.66667 | 0.68065 |
|             |                        | Hf (2d) | 0.66667 | 0.33333 | 0.83245 |
| TaC₄       | P-3m1 a=b=2.6577, c=12.7097 |       | 0.66667 | 0.33333 | 0.51992 |
|             |                        |       | 0.66667 | 0.33333 | 0.01958 |
|             |                        |       | 0.66667 | 0.33333 | 0.35818 |
Table S5. Calculated bond parameters and Vicker hardness of TMC$_4$(TM= V, Zr, Nb, Hf and Ta) structures.

| Crystals | bond type | $d$(Å) | $v_b$(Å$^3$) | $P$ | $f_m$ | $H_{Vicker}$(GPa) |
|----------|-----------|--------|-------------|-----|-------|-------------------|
| VC$_4$   | C-C       | 1.544  | 1.296       | 0.90|       | 50.3              |
|          | C-C       | 1.560  | 1.337       | 0.79|       |                   |
|          | C-C       | 1.562  | 1.342       | 0.87|       |                   |
|          | C-C       | 1.568  | 1.357       | 0.88|       |                   |
|          | V-C       | 2.250  | 4.011       | 0.08| 1.157×10^{-3}|                   |
|          | V-C       | 2.290  | 4.228       | 0.08| 1.157×10^{-3}|                   |
| ZrC$_4$  | C-C       | 1.548  | 1.202       | 0.80|       | 41.9              |
|          | C-C       | 1.609  | 1.350       | 0.85|       |                   |
|          | C-C       | 1.630  | 1.404       | 0.83|       |                   |
|          | C-C       | 1.634  | 1.414       | 0.83|       |                   |
|          | Zr-C      | 2.514  | 5.149       | 0.08| 1.848×10^{-4}|                   |
|          | Zr-C      | 2.519  | 5.180       | 0.08| 1.848×10^{-4}|                   |
| NbC$_4$  | C-C       | 1.554  | 1.249       | 0.80|       | 43.9              |
|          | C-C       | 1.605  | 1.376       | 0.84|       |                   |
|          | C-C       | 1.613  | 1.397       | 0.84|       |                   |
|          | C-C       | 1.618  | 1.410       | 0.85|       |                   |
|          | Nb-C      | 2.431  | 4.783       | 0.09| 1.054×10^{-3}|                   |
|          | Nb-C      | 2.463  | 4.974       | 0.08| 1.054×10^{-3}|                   |
| HfC$_4$  | C-C       | 1.527  | 1.616       | 0.79|       | 49.3              |
|          | C-C       | 1.608  | 1.356       | 0.86|       |                   |
|          | C-C       | 1.622  | 1.391       | 0.83|       |                   |
|          | C-C       | 1.627  | 1.404       | 0.84|       |                   |
|          | Hf-C      | 2.484  | 5.688       | 0.12| 3.907×10^{-4}|                   |
Table S6. The different bond length $d$ (Å) within the Ti-C and C-C bonds and their corresponding integrated crystal orbital Hamiltonian population values ($\Delta$ICOHP, eV per bond).

| Bond     | $d$ (Å) | ICOHP (eV) |
|----------|---------|------------|
| **TiC**  |         |            |
| Ti-C1    | 2.168   | 2.99       |
| **TiC$_2$** |       |            |
| Ti-C1    | 2.228   | 1.42       |
| Ti-C1    | 2.331   | 1.55       |
| C1-C1    | 1.600   | 8.65       |
| **TiC$_3$** |       |            |
| Ti-C2    | 2.228   | 1.42       |
| Ti-C1    | 2.315   | 0.97       |
| Ti-C2    | 2.329   | 1.50       |
| Ti-C3    | 2.357   | 1.54       |
| C1-C1    | 1.586   | 8.39       |
| C2-C2    | 1.568   | 9.12       |
| C1-C3    | 1.584   | 9.06       |
| **TiC$_4$** |       |            |
| Ti-C1    | 2.232   | 1.40       |
| Ti-C1    | 2.328   | 1.49       |
| Ti-C3    | 2.330   | 0.90       |
| Ti-C4    | 2.350   | 1.58       |
| C1-C1    | 1.559   | 9.26       |
| C2-C2    | 1.576   | 9.22       |
| C3-C4    | 1.560   | 9.11       |
Table S7. Bader charge analysis using supercell calculations 2×2×2 of TiC, 2×2×2 of TiC$_2$, 2×2×1 of TiC$_3$ and 2×2×2 of TiC$_4$ at ambient pressure.

| Structure | Atom (Number) | Charge value (e) | $\delta$(e) |
|-----------|---------------|------------------|-------------|
| TiC       | Ti (32)       | 8.34             | 1.66        |
|           | C (32)        | 5.66             | -1.66       |
| TiC$_2$   | Ti (24)       | 8.99             | 1.01        |
|           | C (24)        | 4.50             | -0.50       |
|           | C (24)        | 4.51             | -0.51       |
| TiC$_3$   | Ti (24)       | 9.01             | 0.99        |
|           | C (12)        | 4.02             | -0.02       |
|           | C (12)        | 4.06             | -0.06       |
|           | C (24)        | 4.46             | -0.46       |
|           | C(9)          | 4.48             | -0.48       |
|           | C (15)        | 4.49             | -0.49       |
| TiC$_4$   | Ti (16)       | 9.01             | 0.99        |
|           | C(8)          | 3.99             | 0.01        |
|           | C (8)         | 4.49             | -0.49       |
|           | C (8)         | 4.00             | 0           |
|           | C(16)         | 4.03             | -0.03       |
|           | C (24)        | 4.48             | -0.48       |