Electronic Supplementary Information (ESI)

Predicted Detonation Properties at the Chapman-Jouguet State for Proposed Energetic Materials (MTO and MTO3N) from Combined ReaxFF and Quantum Mechanics Reactive Dynamics

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Table S1 Additional training sets used to re-optimize the three parameters in the ReaxFF-*lg* force field

Reactions	ReaxFF-*lg* (kcal/mol)	$ReaxFF_{MTO}$ (kcal/mol)	DFT(B3LYP/ 6-311G**++) (kcal/mol)
N2/ 1 +CO2/ 2 +CH4/ 2 -MTO/ 3	-29.51	-48.59	-65.81
N2/ 1 +CO2/ 2 +C2H6/ 4 +H2/ 4 -MTO/ 3	-31.29	-50.37	-60.47
N2/ 3 +CO2/ 6 +C6H6/ 36 +H2/ 4 -MTO/ 9	-11.28	-17.65	-16.78
N2/ 1 +CO/ 1 +H2/ 1 -MTO/ 3	4.92	-14.16	-24.25
N2/ 2 +CO2/ 2 +H2O/ 6 -MTO/ 18 -MTO3N/ 9	-48.82	-67.13	-75.26
N2/ 1 +CO2/ 1 +H2/ 2 -MTO/ 6 -MTO3N/ 6	-78.62	-110.87	-122.10
N2/ 1 +CO2/ 1 +O2/ 2 -MTO3N/ 3	-80.34	-125.75	-123.60
N2/ 1 +CO/ 1 +O2/ 1 -MTO3N/ 3	1.49	-43.93	-27.15
MTO_O/ 1 +H2O/ 1 -MTO/ 1 -H2/ 1	-37.91	-58.32	-76.98
MTO_O/ 1 +N2O/ 1 -MTO/ 1 -N2/ 1	18.58	4.02	4.00
MTO_O/ 1 +CO2/ 1 -MTO/ 1 -CO/ 1	-64.42	-84.83	-89.69
MTO_2O/ 2 +H2O/ 1 -MTO/ 2 -H2/ 1	-36.92	-54.16	-73.98
MTO_3O/ 3 +H2O/ 1 -MTO/ 3 -H2/ 1	-37.72	-56.38	-71.29
MTO3N_O/ 1 +H2O/ 1 -MTO3N/ 1 -H2/ 1	-59.82	-72.88	-88.83
MTO3N_O/ 1 +N2O/ 1 -MTO3N/ 1 -N2/ 1	-3.33	-10.55	-7.85
MTO3N_O/ 1 +CO2/ 1 -MTO3N/ 1 -CO/ 1	-86.33	-99.39	-101.50
MTO3N_2O/ 2 +H2O/ 1 -MTO3N/ 2 -H2/ 1	-60.10	-74.64	-86.42
MTO3N_3O/ 3 +H2O/ 1 -MTO3N/ 3 -H2/ 1	-51.48	-67.53	-84.51

Table S2 The comparison of Hugoniot values calculated from two simulation procedures

	$V/V_0 = 0.75$	
T (K)	H_g	H_g^*
2700	1160.388	1143.254
2500	512.014	519.268
2300	-114.987	-103.147

H_g is calculated by heating the system directly to the target temperatures; H_g^* is calculated by first heating the system to higher temperature and then cooling down to the target temperatures. The results from the two simulation procedures are very close to each other.

Table S3 Bond order cutoff values for various atom pairs used to identify molecular fragments

	C	H	N	O
C	0.55	0.40	0.30	0.80
H		0.55	0.55	0.40
N			0.55	0.55
O				0.65

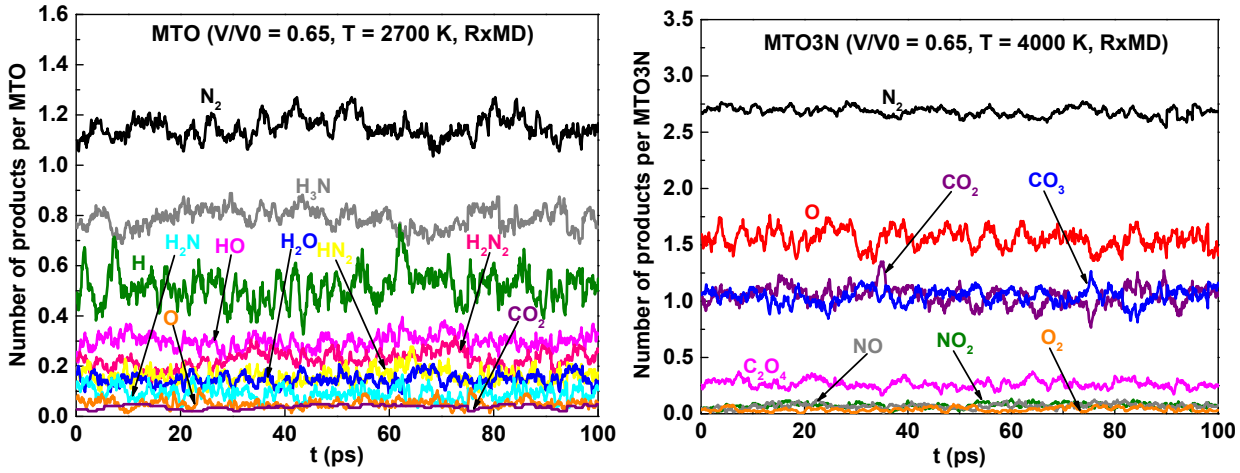


Fig. S1 Time evolution of final products over the last 100 ps of RxMD simulations for the large cells of MTO (V/V_0 = 0.65, T = 2700 K) and MTO3N (V/V_0 = 0.65, T = 4000 K). The products reach equilibrium within the timescale of the simulations.

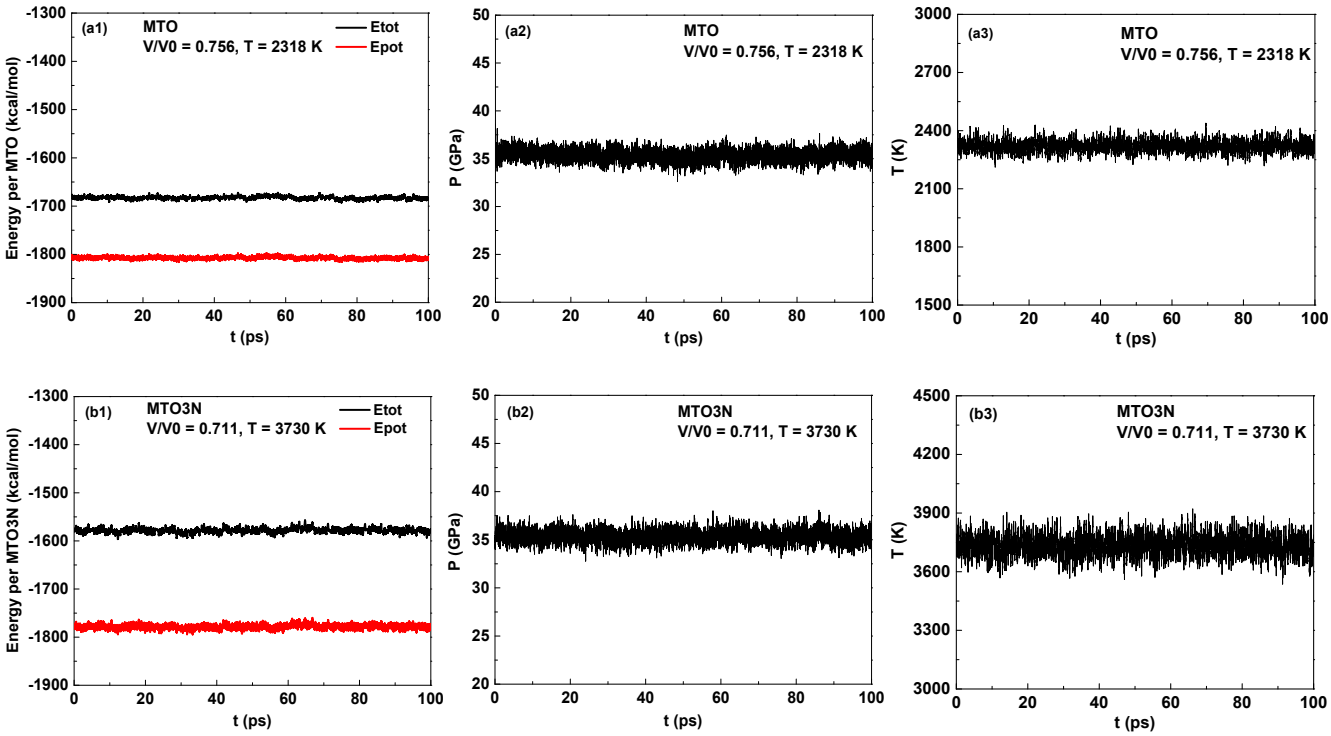


Fig. S2 Time evolution of energy, pressure, and temperature over the last 100 ps of RxMD simulations at the CJ state for the large cells of MTO (a1, a2, a3) and MTO3N (b1, b2, b3). The thermal properties have reached equilibrium within the timescale of the simulations.

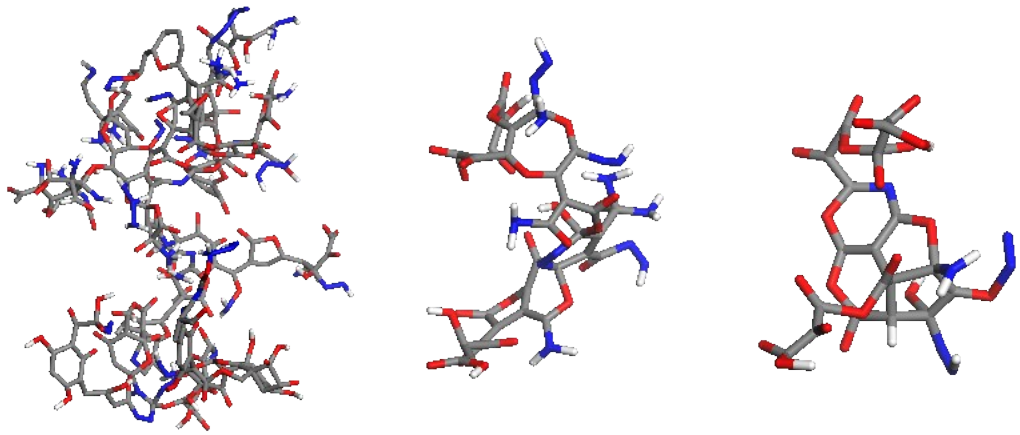


Fig. S3 The final structures of the three biggest carbon clusters ($C_{272}H_{94}N_{74}O_{187}$, $C_{30}H_{18}N_{13}O_{23}$, and $C_{20}H_7N_4O_{20}$) formed during the RxMD simulation at the CJ state for the large cell of MTO (T = 2318 K, V/V_0 = 0.756). The C, H, N, and O atoms are represented by gray, white, blue, and red colors, respectively.

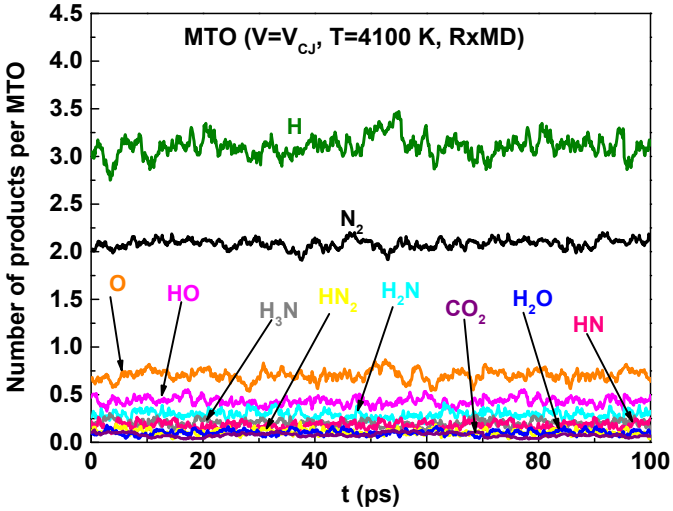
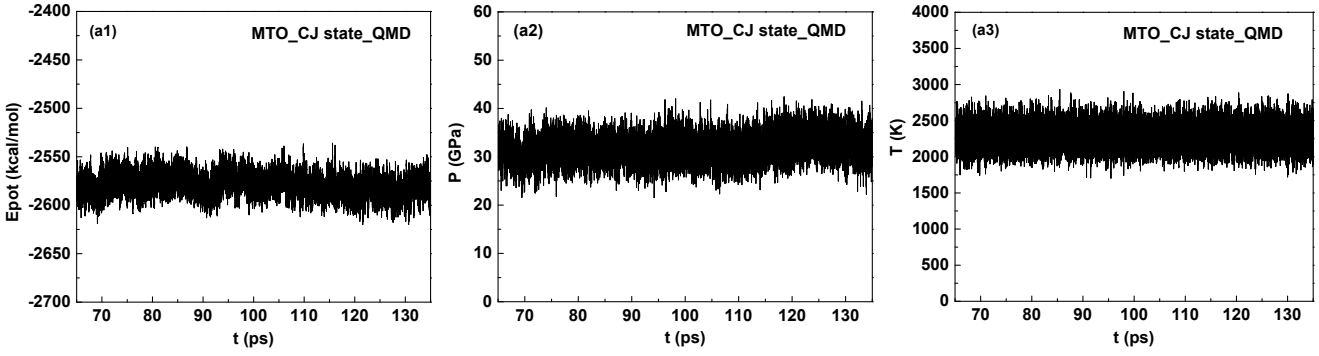


Fig. S4 Time evolution of the products with relatively high concentration for the large cell of MTO during the last 100 ps RxMD simulation at $V = V_{CJ}$ and T = 4100 K



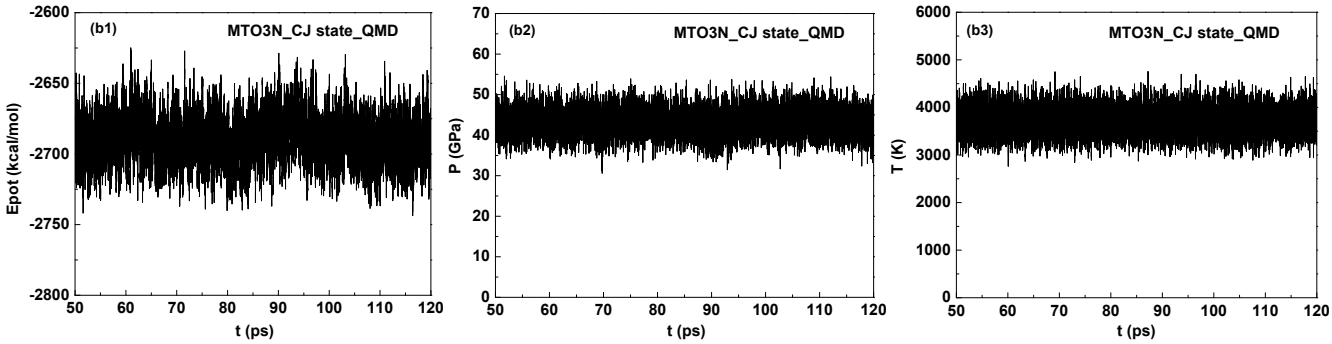


Fig S5 Time evolutions of potential energy, pressure, and temperature for the small cells of MTO at $V/V_0 = 0.756$ and $T = 2318$ K (a1, a2, a3) and for MTO3N at $V/V_0 = 0.711$ and $T = 3730$ K (b1, b2, b3) from the extended 70 ps QMD simulation

Table S4 The number of reaction products at various times for the small cell of MTO predicted from pure QMD and RxMD simulations

		MTO (small system)											
		t = 20 ps		t = 30 ps		t = 35 ps		t = 45 ps		t = 55 ps		t = 65 ps	
		QM	Reax	QM	Reax	QM	Reax	QM	Reax	QM	Reax	QM	Reax
Products /8 MTO	N2	6	5	7	13	7	10	7	12	8	13	7	12
	H2O	4	4	4	3	5	4	4	3	3	3	2	4
	NH3	1	2	0	4	2	5	1	7	0	6	1	6
	CO2	0	2	0	1	0	2	0	2	1	2	1	2
	HO	0	2	0	4	0	1	0	1	1	1	0	1
	H	6	0	9	0	1	0	0	0	2	0	0	0
	H2	0	1	0	3	0	1	0	0	0	0	0	1
	NH2	0	0	1	1	0	0	0	0	0	0	0	0
	N2H	0	2	0	1	0	0	0	0	0	0	0	0
	N2H2	0	1	0	2	0	4	0	2	0	3	0	3
	NH4	0	0	0	0	0	1	0	0	0	0	0	0
	CO	1	0	0	0	0	0	0	0	0	0	0	0
	C2O3	0	0	0	0	0	1	0	0	0	0	0	0
	C2O4	0	0	0	0	0	0	0	0	0	0	0	1
	CHO2	0	0	0	1	0	0	0	0	0	0	0	0
	C2H2O4	0	0	0	0	0	0	0	1	0	0	0	0
	C2HO	0	0	0	1	0	0	0	0	0	0	0	0
	CNO	0	0	0	1	0	0	0	0	0	0	0	0
	CH3NO2	0	0	0	0	0	0	0	0	0	0	1	0
	CHNO	0	0	1	0	0	0	0	0	0	0	0	0
	CHN2O	0	1	0	0	0	0	0	0	0	0	0	0
	CH2N3	0	1	0	0	0	0	0	0	0	0	0	0
	CHN3O	0	1	0	0	0	0	0	0	0	0	0	0
	N2O	0	0	1	0	0	0	0	0	0	0	0	0
	CHO	0	0	1	0	0	0	0	0	0	0	0	0
	CH2N2	1	0	0	0	0	0	0	0	0	0	0	0
	CHN3	0	0	1	0	0	0	0	0	0	0	0	0

	CH2NO	1	0	0	0	0	0	0	0	0	0	0	0
	CH2NO2	0	0	1	0	0	0	0	0	0	0	0	0
	CN2O2	1	0	0	0	0	0	0	0	0	0	0	0
	CHNO2	1	0	0	0	0	0	0	0	0	0	0	0
	CH3N2O3	1	0	0	0	0	0	0	0	0	0	0	0
	CH4N2O	0	0	1	0	0	0	0	0	0	0	0	0
	C2HN2O	0	1	0	0	0	0	0	0	0	0	0	0
	C2H5N6O	0	0	1	0	0	0	0	0	0	0	0	0
	C2H3N3O	0	1	0	0	0	0	0	0	0	0	0	0
	C2H3N2O2	0	0	1	0	0	0	0	0	0	0	0	0
Clusters (%)[a]	C	75.00	62.50	62.50	79.17	100.0	83.33	100.0	83.33	95.83	91.67	91.67	83.33
	H	47.92	37.50	25.00	22.92	64.58	20.83	77.08	22.92	81.25	35.42	64.58	27.08
	N	56.25	35.42	33.33	20.83	66.67	29.17	68.75	27.08	66.67	20.83	66.67	25.00
	O	45.83	20.83	45.83	45.83	79.17	50.00	83.33	50.00	75.00	66.67	79.17	45.83

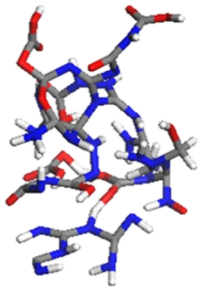
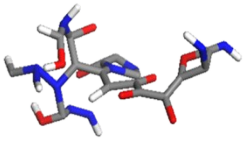
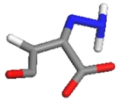
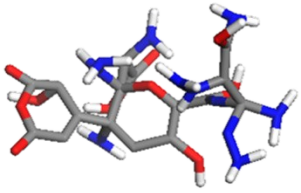
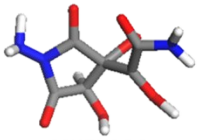
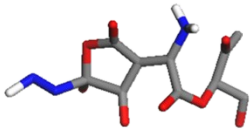
a Number of atoms (% of system total) in carbonaceous clusters. For example, there are 75 % × 24 = 18 carbon atoms in clusters.

Table S5 The number of reaction products at various times for the small cell of MTO3N predicted from pure QMD and RxMD simulations

Products /8 MTO3N	MTO3N (small system)							
	t = 20 ps		*t* = 30 ps		*t* = 40 ps		*t* = 50 ps	
	QM	Reax	QM	Reax	QM	Reax	QM	Reax
N2	13	5	18	12	12	18	15	15
CO2	14	4	20	5	20	6	20	9
CO3	0	0	1	3	2	9	2	4
NO2	4	4	1	4	3	3	5	1
NO	10	0	10	1	6	0	9	1
N2O	3	0	0	0	3	0	2	1
O	1	0	0	0	1	0	0	2
O2	0	4	3	1	0	1	0	0
N2O2	0	0	0	1	0	1	0	0
C2O4	2	0	0	0	0	1	0	1
C2O5	0	0	0	0	0	0	1	1
C2O6	0	0	0	0	0	1	0	0
C3O6	0	0	0	1	0	0	0	0
CO4	1	0	1	1	0	0	0	1
CNO3	0	3	0	0	0	0	0	0
CNO4	0	1	0	1	0	1	0	0
CN2O2	0	0	0	1	0	0	0	0
C2N2O3	1	0	0	0	0	0	0	0
C3O7	1	0	0	0	0	0	0	1
C2NO7	0	0	1	0	0	0	0	0
C2N3O7	0	0	0	0	1	0	0	0
N3O2	0	0	0	1	1	0	0	1
N3O	0	1	0	0	1	0	0	0

NO3	0	1	0	0	0	0	0	0
CNO	0	2	0	0	0	0	0	0
C2NO4	0	1	0	0	0	0	0	0
C3N10O9	0	1	0	0	0	0	0	0
C2N5O4	0	1	0	0	0	0	0	0
C3N3O5	0	1	0	0	0	0	0	0
C4N5O7	0	1	0	0	0	0	0	0
CN2O	0	0	0	1	0	0	0	0
C3N4O7	0	0	0	1	0	0	0	0
C4N2O9	0	0	0	1	0	0	0	0
C2N3O5	0	0	0	1	0	0	0	0
CN2O5	0	0	0	0	0	1	0	0
C3N4O4	0	0	0	0	0	1	0	0
N4O2	0	0	0	0	0	0	0	1
C2N2O6	0	0	0	0	0	0	0	1
CN5O6	0	0	0	0	0	0	0	1

Table S6 The structures of carbon clusters formed at the end of pure QMD, RxMD, and RxMD(cQM) simulations for the small cell of MTO

<table>
<tr><td colspan="4">MTO (small system)</td></tr>
<tr><td colspan="2">t = 65 ps</td><td>t = 10 ps
(following RxMD)</td><td>t = 250 ps</td></tr>
<tr><td>pure-QMD</td><td>RxMD</td><td>RxMD(cQM)</td><td>RxMD</td></tr>
<tr><td> 
C22H38N32O18</td><td> 
C16H10N10O8
 
C4H3N2O3</td><td> 
C16H21N11O10
 
C6H7N3O6</td><td> 
C12O7
 
C10H3N3O8</td></tr>
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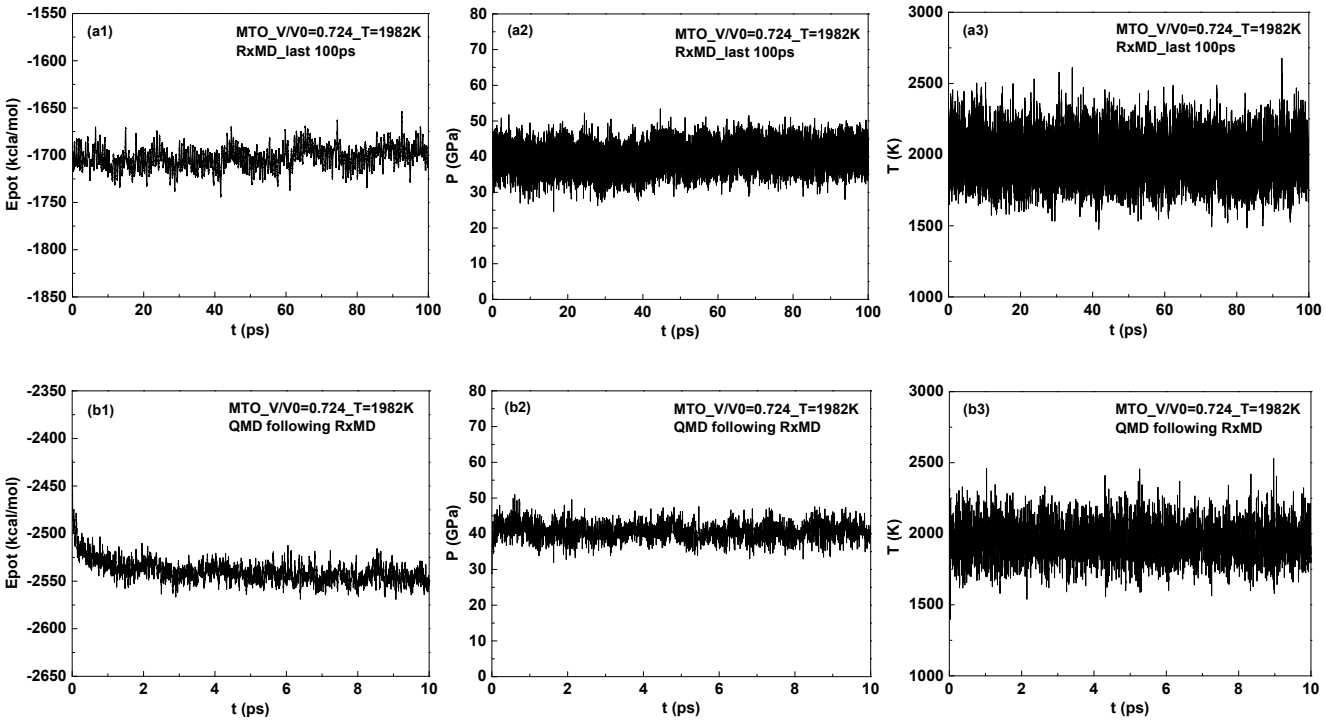


Fig. S6 Time evolutions of potential energy, pressure, and temperature for the small cell of MTO at V/V_0 = 0.724 and T = 1982 K from the last 100 RxMD simulation (a1, a2, and a3) and the following 10 ps QMD simulation (b1, b2, and b3)

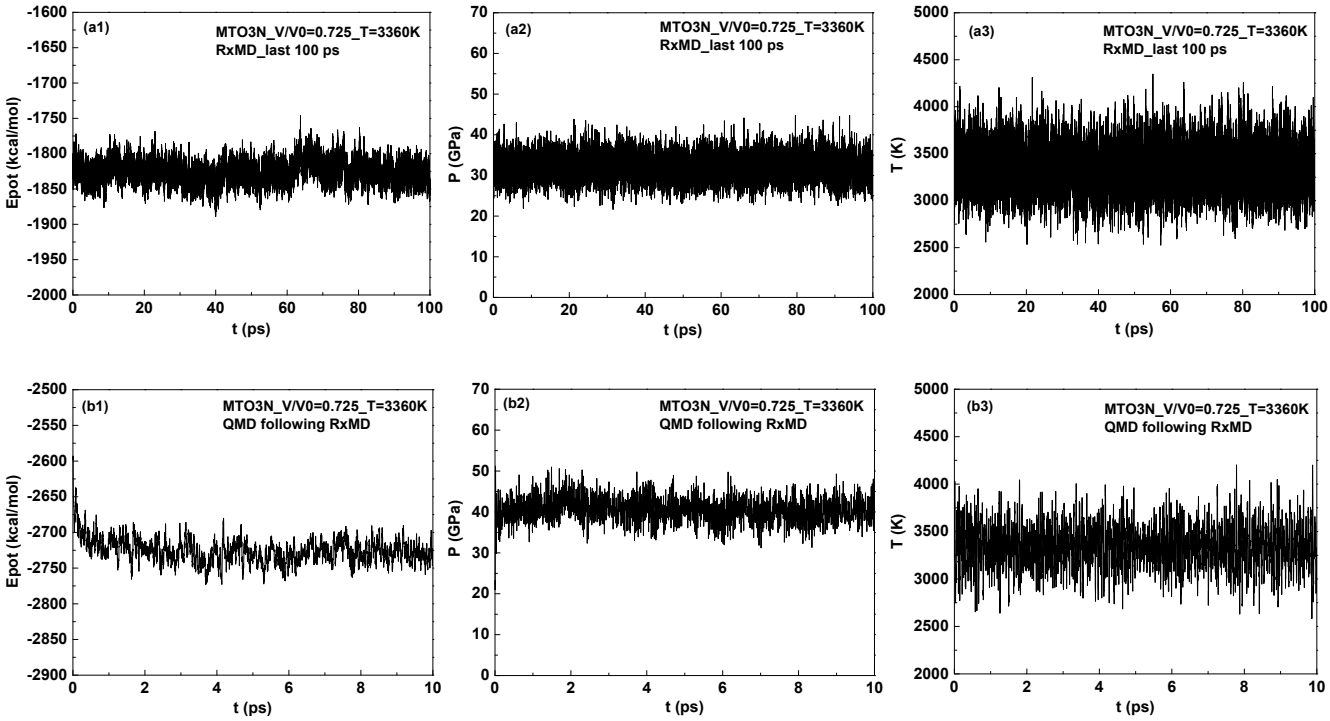
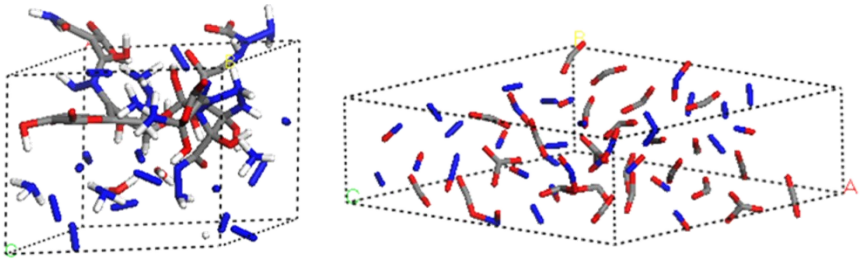


Fig. S7 Time evolutions of potential energy, pressure, and temperature for the small cell of MTO3N at V/V_0 = 0.725 and T = 3360 K from the last 100 RxMD simulation (a1, a2, and a3) and the following 10 ps QMD simulation (b1, b2, and b3)



(a) MTO (b) MTO3N

Fig. S8 The final structures with detonation products for the small cells of MTO and MTO3N at the QM corrected CJ state from RxMD(cQM) simulations

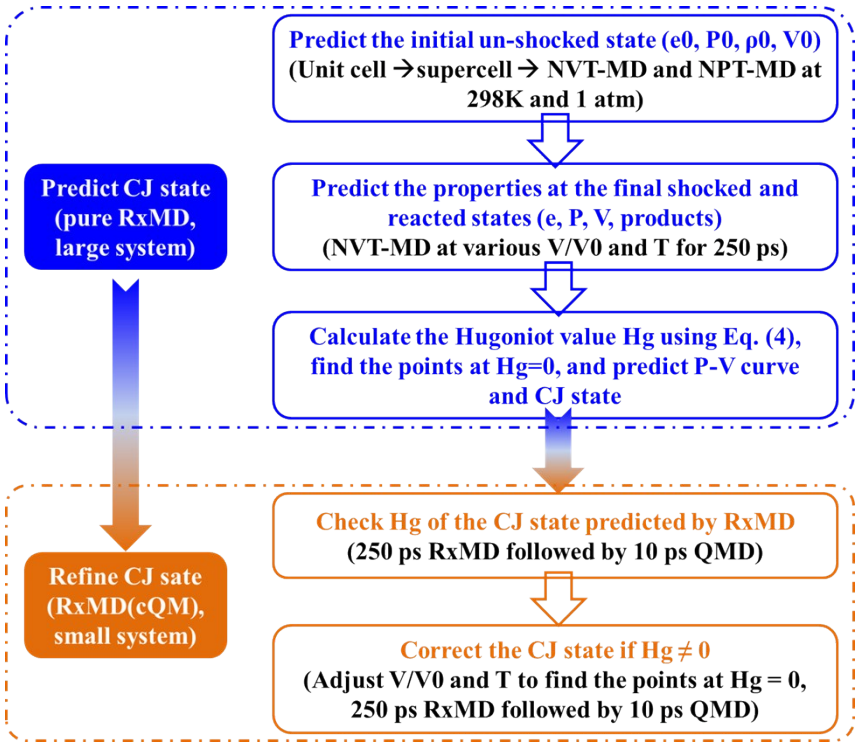


Fig. S9 A flowchart describing the entire simulation procedure