Supporting Information

SI1. Selection of crystalline surfaces

Molecular dynamics simulations and Bravais-Friedel Donnay-Harker (BFDH) method were used to predict the crystal habit for α-RDX, β-HMX and ε-CL-20 (Fig. S1, Table S1). The final chosen crystalline directions were considered only only about total facet area, but also about the total anisotropy.

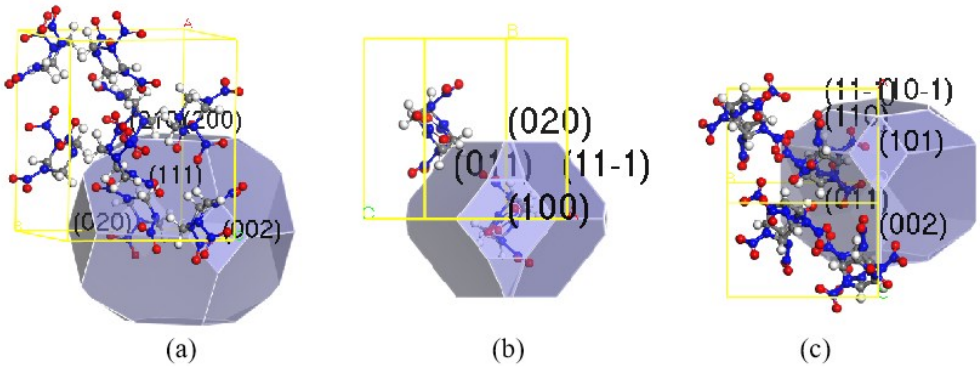

Fig. S1 Crystal structure and main growth faces for α-RDX (a), β-HMX (b) and ε-CL-20 (c)

Table S1 Crystal habits for α-RDX, β-HMX and ε-CL-20

hkl	Multiplicity	dhkl	Distance	Total facet area	% Total facet area
RDX (1 1 1)	8	6.7513	14.8120	2849.7870	74.08
RDX (2 0 0)	2	6.5910	15.1722	495.7448	12.89
RDX (0 2 0)	2	5.7870	17.2801	277.4410	7.21
RDX (2 1 0)	4	5.7274	17.4598	100.3021	2.61
RDX (0 0 2)	2	5.3545	18.6759	123.5935	3.21
HMX (0 1 1)	4	6.0248	16.5980	2076.4910	39.96
HMX (0 2 0)	2	5.5250	18.0995	686.8502	13.22
HMX (1 1 -1)	4	5.5230	18.1061	1620.2130	31.18
HMX (1 0 0)	2	5.4027	18.5093	563.2068	10.84
HMX (1 1 0)	4	4.8536	20.6032	196.2668	3.78
CL-20 (0 1 1)	4	8.9680	11.1507	1548.8370	56.41
CL-20 (1 0 -1)	2	8.2511	12.1196	510.7743	18.60
CL-20 (1 1 0)	4	7.0236	14.2377	428.9399	15.62
CL-20 (1 1 -1)	4	6.8955	14.5023	117.3673	4.27
CL-20 (0 0 2)	2	6.4067	15.6087	17.5760	0.64

SI2. Profiles of potential energies versus time

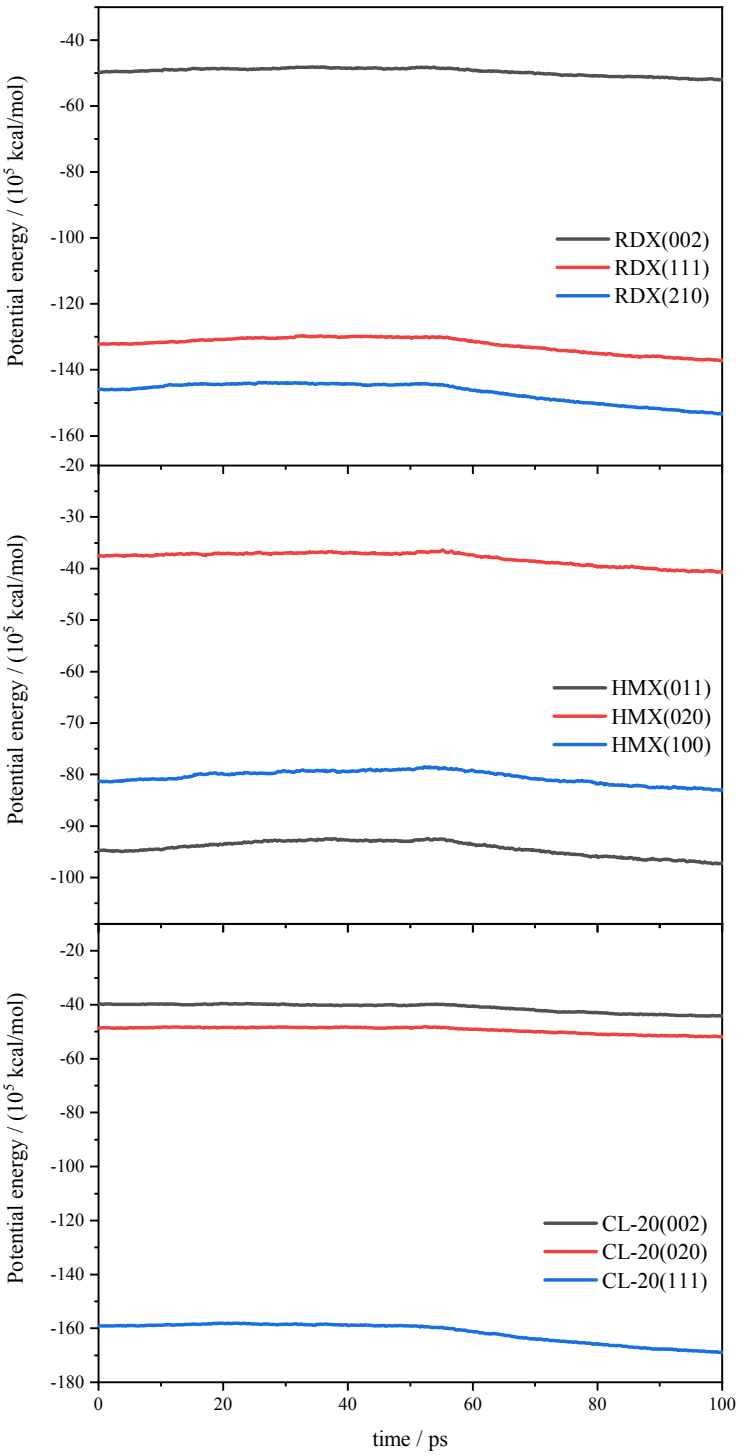

Fig. S2 Comparison of potential energy evolution for heated energetic composites, including F_{2311} on RDX, HMX and CL-20 surfaces.

SI3. Profiles of highest frequent primary reactions

Table S2 Highest frequent primary reactions for pure RDX and RDX interfaces

Systems	Frequencies: the first 10 primary reactions	
	RDX interfaces	Pure RDX
F_{2311}/RDX(0 0 2)	61 : CO + F → COF	185 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
	59 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$	140 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$
	41 : CN + F → CNF	110 : $C_3H_6O_2N_4 \rightarrow C_3H_6N_3 + NO_2$
	24 : 2F → F_2	31 : $HNO_2 \rightarrow OH + NO$
	23 : CNF + F → CNF_2	29 : $C_3H_6N_3 + NO_2 \rightarrow C_3H_5N_3 + HNO_2$
	21 : CHF_2 + F → CHF_3	26 : $C_3H_6O_4N_5 \rightarrow C_3H_6N_3 + 2NO_2$
	20 : H + OH → H_2O	26 : $H_2NO_2 \rightarrow H_2O + NO$
	19 : H + NO_2 → HO_2N	25 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_2N_4 + 2NO_2$
	18 : CH_2F + F → CH_2F_2	18 : HNO + NO_2 → HNO_2 + NO
	17 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$	16 : HNO_2 + ON → HN_2O_3
F_{2311}/RDX(1 1 1)	216 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$	542 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
	118 : CO + F → COF	371 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$
	76 : CN + F → CNF	272 : $C_3H_6O_2N_4 \rightarrow C_3H_6N_3 + NO_2$
	59 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$	126 : 2NO → N_2O_2
	51 : H + NO_2 → HNO_2	89 : $H_2NO_2 \rightarrow H_2O + NO$
	51 : CO_2 + F → CO_2F	73 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_2N_4 + 2NO_2$
	49 : $HNO_2 \rightarrow HO + NO$	73 : $C_3H_6O_4N_5 \rightarrow C_3H_6N_3 + 2NO_2$
	44 : $H_2NO_2 \rightarrow H_2O + NO$	67 : $C_3H_6N_3 + NO_2 \rightarrow C_3H_5N_3 + HO_2N$
	43 : H + HO → H_2O	63 : $HNO_2 \rightarrow OH + NO$
	43 : CHN + F → CHNF	52 : HNO + NO_2 → HNO_2 + NO
F_{2311}/RDX(2 1 0)	302 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$	609 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
	135 : CO + F → COF	405 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$
	103 : $C_3H_6O_4N_5 \rightarrow C_3H_6O_2N_4 + NO_2$	283 : $C_3H_6O_2N_4 \rightarrow C_3H_6N_3 + NO_2$
	103 : CN + F → CNF	102 : $C_3H_6O_4N_5 \rightarrow C_3H_6N_3 + 2NO_2$
	46 : $HNO_2 \rightarrow HO + NO$	94 : $C_3H_6O_6N_6 \rightarrow C_3H_6O_2N_4 + 2NO_2$
	45 : $C_3H_6O_2N_4 \rightarrow C_3H_6N_3 + NO_2$	86 : $C_3H_6N_3 + NO_2 \rightarrow C_3H_5N_3 + HNO_2$
	45 : CO_2 + F → CO_2F	86 : $H_2NO_2 \rightarrow H_2O + NO$
	41 : CHN + F → CHNF	84 : $HNO_2 \rightarrow OH + NO$
	39 : H + NO_2 → HNO_2	79 : HNO + NO_2 → HNO_2 + NO
	37 : $C_3H_6O_5N_6 \rightarrow C_3H_6O_3N_5 + NO_2$	51 : $H_2NO_2 + NO_2 \rightarrow 2HNO_2$

Table S3 Highest frequent primary reactions for pure HMX and HMX interfaces

Systems	Frequencies: the first 10 primary reactions	
	HMX interfaces	Pure HMX
F_{2311}/HMX(0 1 1)	126 : CO + F → COF	284 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_6N_7 + NO_2$
	89 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_6N_7 + NO_2$	193 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_4N_6 + NO_2$
	71 : CN + F → CNF	132 : $C_4H_8O_4N_6 \rightarrow C_4H_8O_2N_5 + NO_2$
	33 : COF + F → COF_2	85 : $C_4H_8O_2N_5 \rightarrow C_4H_8N_4 + NO_2$
	30 : H + H_2O → H_3O	64 : HNO_2 → OH + NO
	27 : H + NO_2 → HNO_2	53 : HNO + NO_2 → HNO_2 + NO
	26 : CNF + F → CNF_2	52 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_2N_5 + 2NO_2$
	24 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_4N_6 + NO_2$	51 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_4N_6 + 2NO_2$
	22 : C_2 + F → C_2F	50 : H_2NO_2 → H_2O + NO
	22 : CO_2 + F → CO_2F	46 : $C_4H_8O_4N_6 \rightarrow C_4H_8N_4 + 2NO_2$
F_{2311}/HMX(0 2 0)	26 : CO + F → COF	96 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_6N_7 + NO_2$
	13 : 2F → F_2	66 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_4N_6 + NO_2$
	12 : CNF + F → CNF_2	52 : $C_4H_8O_4N_6 \rightarrow C_4H_8O_2N_5 + NO_2$
	12 : CF_2 + F → CF_3	38 : $C_4H_8O_2N_5 \rightarrow C_4H_8N_4 + NO_2$
	9 : CO_2 + F → CO_2F	28 : H_2NO_2 → H_2O + NO
	9 : COF + F → COF_2	24 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_2N_5 + 2NO_2$
	8 : $C_4H_9O_8N_8 \rightarrow C_4H_9O_6N_7 + NO_2$	21 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_4N_6 + 2NO_2$
	8 : CN + F → CNF	17 : $C_4H_8O_4N_6 \rightarrow C_4H_8N_4 + 2NO_2$
	8 : CHF_2 + F → CHF_3	17 : $C_4H_8N_4 + NO_2 \rightarrow C_4H_7N_4 + HNO_2$
	6 : C_3F_2 + F → C_3F_3	14 : NO_2 + NO → N_2O_3
F_{2311}/HMX(1 0 0)	71 : CO + F → COF	234 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_6N_7 + NO_2$
	44 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_6N_7 + NO_2$	161 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_4N_6 + NO_2$
	43 : CN + F → CNF	102 : $C_4H_8O_4N_6 \rightarrow C_4H_8O_2N_5 + NO_2$
	40 : COF + F → COF_2	47 : 2NO → N_2O_2
	30 : CO_2 + F → CO_2F	43 : $C_4H_8O_2N_5 \rightarrow C_4H_8N_4 + NO_2$
	25 : $C_4H_9O_8N_8 \rightarrow C_4H_8O_6N_7 + HO_2N$	41 : HNO + NO_2 → HNO_2 + NO
	23 : HNO_2 → HO + NO	39 : $C_4H_8O_6N_7 \rightarrow C_4H_8O_2N_5 + 2NO_2$
	22 : H + H_2O → H_3O	34 : HNO_2 → OH + NO
	22 : CNF + F → CNF_2	33 : $C_4H_8O_8N_8 \rightarrow C_4H_8O_4N_6 + 2NO_2$
	22 : 2F → F_2	33 : H_2NO_2 → H_2O + NO