

Supplementary Information

Surface-Induced Enhanced Sensitivity of Energetic β -HMX Nanoparticles: A Density Functional Tight-Binding and Quantum Mechanical Study

Zhichao Liu, Weihua Zhu,^{*} Heming Xiao

Institute for Computation in Molecular and Materials Science and Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China

^{*} Corresponding author. E-mail: zhuwh@njust.edu.cn

Table S1 Number of molecules (M) , surface area (A), and calculated total energy of various HMX NPs at DFT and DFTB levels.

model	M	total energy		A ($\text{\AA}^2$)	
		DFTB ($\text{kcal}\cdot\text{mol}^{-1}$)	DFT (Ha.)	DFTB	DFT
uni ^a	1	-34780.38	-1195.87	-	-
NP _{1.4}	8	-278380.64	-9567.21	1125.17	1089.41
NP _{1.6}	13	-452407.76	-15546.77	1508.53	1465.12
NP _{1.8}	15	-522029.13	-17938.62	1664.24	1614.70
NP _{2.0}	20	-696085.46		1996.58	
NP _{2.2}	22	-765711.29		2132.00	
NP _{2.3}	24	-835286.77		2427.25	
NP _{2.4}	30	-1044175.09		2704.05	
NP _{2.5}	34	-1183420.95		2960.83	
NP _{2.6}	40	-1392318.48		3233.72	
NP _{2.8}	47	-1635949.69		3805.29	
NP _{2.9}	55	-1914493.93		4110.31	
NP _{3.0}	59	-2053768.96		4122.65	
NP _{3.2}	70	-2436695.53		4796.94	
NP _{3.4}	86	-2993670.80		5887.01	
bulk ^b		-69647.26	-2391.90	-	-

^auni represents an isolated HMX molecule.

^bbulk represents the ideal HMX bulk crystal.

Table S2 Lattice parameters and calculated total energy of relaxed β -HMX slab

models at DFT and DFTB levels.

facet	total energy (kcal·mol ⁻¹)	DFTB				total energy (Ha.)	DFT			
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>A</i> (Å ²)		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>A</i> (Å ²)
(120)	-1114022.4	17.36	30.98	38.02	1076.19	-9567.43	8.70	15.36	27.87	267.20
(10 $\bar{2}$)	-1114102.5	22.16	21.65	36.85	959.62	-9567.46	10.90	10.81	26.75	235.78
(100)	-1114086.2	22.16	17.37	43.64	769.88	-9567.47	10.90	8.700	33.67	189.7
(010)	-1114260.6	14.83	12.85	64.57	381.22	-4783.75	7.303	6.555	31.74	95.75
(001)	-1114229.9	12.85	22.16	51.45	569.63	-9567.52	6.555	10.90	40.99	142.94
(10 $\bar{1}$)	-1114142.7	22.16	14.83	48.01	657.51	-9567.49	10.90	7.303	38.39	159.25
(30 $\bar{4}$)	-1114018.3	22.16	24.47	37.96	1084.85	-9567.30	10.90	24.18	20.31	527.34
(011)	-1114226.6	26.67	12.85	44.11	685.43	-9567.52	13.12	6.55	33.77	172.04
(11 $\bar{1}$)	-1114139.3	14.83	25.62	42.24	760.03	-9567.49	7.303	12.72	32.44	185.82

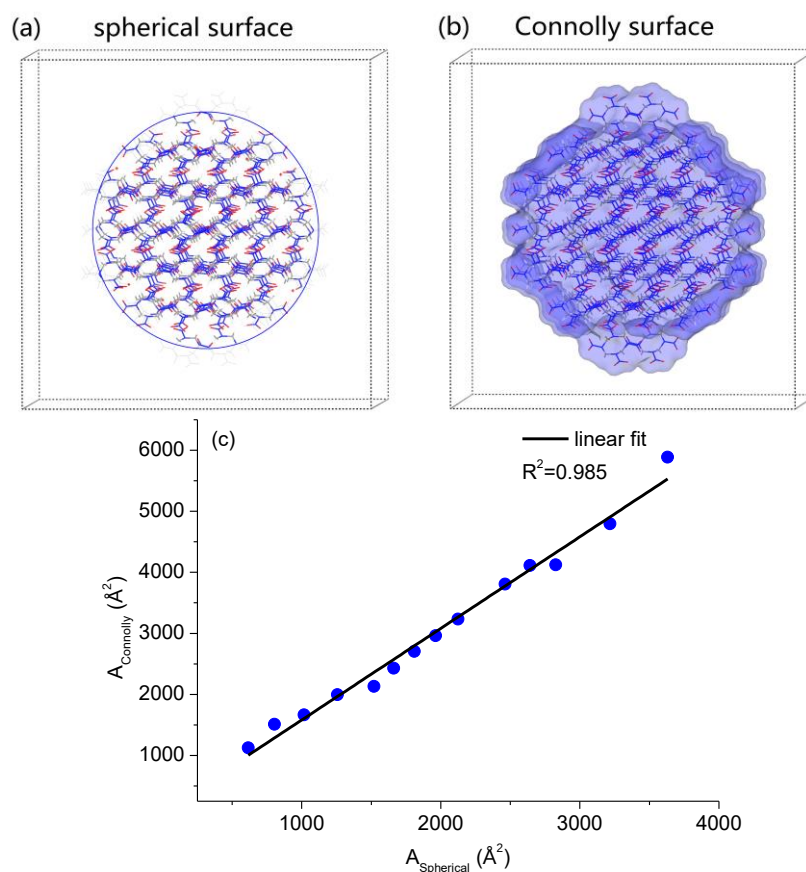


Fig. S1. An illustration of (a) the spherical surface and (b) the Connolly surface for evaluating the surface area of the HMX NPs. (c) The comparison of the calculated surface areas of the HMX NPs by the two methods. The Connolly surface is plotted with vDW scale factor of 1.0 and Connolly radius of 2.0 Å.

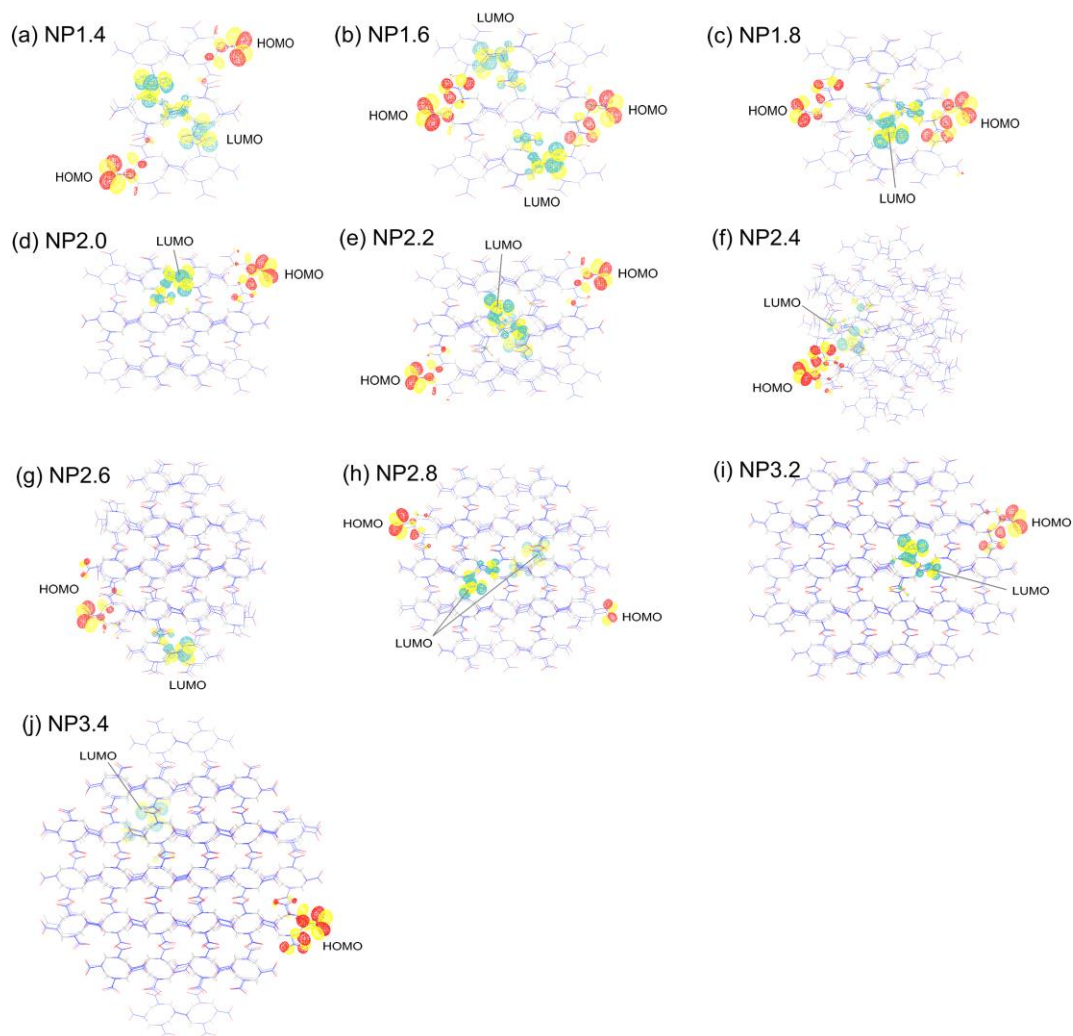


Fig. S2. Surface states in the spherical HMX NPs with sizes in the range 1.4-3.4 nm.

The isosurfaces are plotted with isovalue of 0.02.