## Supporting information for

## Polymer-directed Crystallization of HMX to Construct Nano-/Microstructured Aggregates with Tunable Polymorph and Microstructure

Xin Zhou<sup>a</sup>, Yan Ren<sup>b</sup>, Hongzhen Li<sup>a\*</sup>, Xiaoqing Zhou<sup>a</sup>, Shilong Hao<sup>a</sup>,

Rong Xu<sup>a</sup>, Qi Zhang<sup>a</sup>

<sup>*a</sup>Institute of Chemical Materials, CAEP, Mianyang, Sichuan, 621999, China* <sup>*b*</sup>Mianyang City College, Mianyang, Sichuan, 621000, China</sup>

Sample	Conformation	Space group	Z	$\rho_{meas.} \left(g/cm^3\right)$
δ-ΗΜΧ	boat-boat	<i>P6</i> <sub>1</sub>	6	1.80 <sup>a</sup>
γ-HMX	boat-boat	Pc	4	1.76 <sup><i>a</i></sup>

Table S1 Crystal structure information of the HMX polymorphs

Note: <sup>*a*</sup> data collected from reference (*Miller, G. R et al, Review of the Crystal Structures of Common Explosives. Part 1: RDX, HMX, TNT, PETN, and Tetryl*)



Figure S1 TG-curves of the sphere aggregates

Sample	PVP (wt.%)	HMX (wt.%)
Flower sphere	6.8	93.2
Spiky spherulite	6.6	93.4
Spiky spherulite	8.1	91.9

Table S2 HPLC results of the aggregates

The critical drop height with 50% explosion probability ( $H_{50}$ ) was determined according to GJB-772A-97 standard method 601.2. Specifically, the sample (30 mg for each test) was tested 25 times to obtain  $H_{50}$ , which represents the height from which dropping a 2.5 kg weight will result in a 50% explosive event of the trials. We found that the spiky spherulite'  $H_{50}$  was 90.0 cm. The impact energy was then calculated as 22 J based on equation

## E=mgH<sub>50</sub>

where m is the hammer weight, g is the gravity constant. Then we compared this data with needle  $\gamma$ -HMX in a previous report (*Xiaolan Song et al, Journal of Hazardous Materials 2008, 159, 222-229*) and the results are listed in Table 1.

Sample	Impact energy with 50%	IS	FS
	explosion probability		
Needle γ-HMX	8.4 J	82%	100%
Spiky spherulite	22.1 J	20%	60%

Table S3 Comparison of the mechanical sensitivity

Clearly, spherulitic structuring of the  $\gamma$ -HMX significantly increases the impact energy by almost 3-fold, which demonstrates the excellent desensitizing capability of our strategy.