

## Supporting Information

### Isothermal Structural Evolution of CL-20/HMX Cocrystals Under Slow Roasting at 190 °C

Wentao Liang<sup>a\*</sup>, Xiaoyu Sun<sup>b\*</sup>, He Wang<sup>a</sup>, Junke Wang<sup>a</sup>, Zhilei Sui<sup>c</sup>, Haichao Ren<sup>d</sup>, Rucheng Dai<sup>b</sup>, Xianxu Zheng<sup>c</sup>, Zhongping Wang<sup>b†</sup>, Xiaohui Duan<sup>e†</sup>, and Zengming Zhang<sup>b†</sup>

<sup>a</sup> Department of Physics, School of Physics Science, University of Science and Technology of China, Hefei, Anhui, 230026, China

<sup>b</sup> The Center for Physical Experiments, School of Physics Science, University of Science and Technology of China, Hefei, Anhui, 230026, China

<sup>c</sup> Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, China

<sup>d</sup> Xi'an Modern Chemistry Research Institute, Xi'an, Shanxi 710065, China

<sup>e</sup> Key Laboratory of friendly Energy Materials, Southwest University of Science and Technology, Mianyang, 621010, China

\* Coauthors: liangwt@mail.ustc.edu.cn and xysun2015@ustc.edu.cn

† Corresponding authors: zpwang@ustc.edu.cn, duanxiaohui@swust.edu.cn and zzm@ustc.edu.cn

Author Contributions: W. L. and X. S. contributed equally.

Figure S1. XRD patterns of CL-20/HMX cocrystals at different temperatures

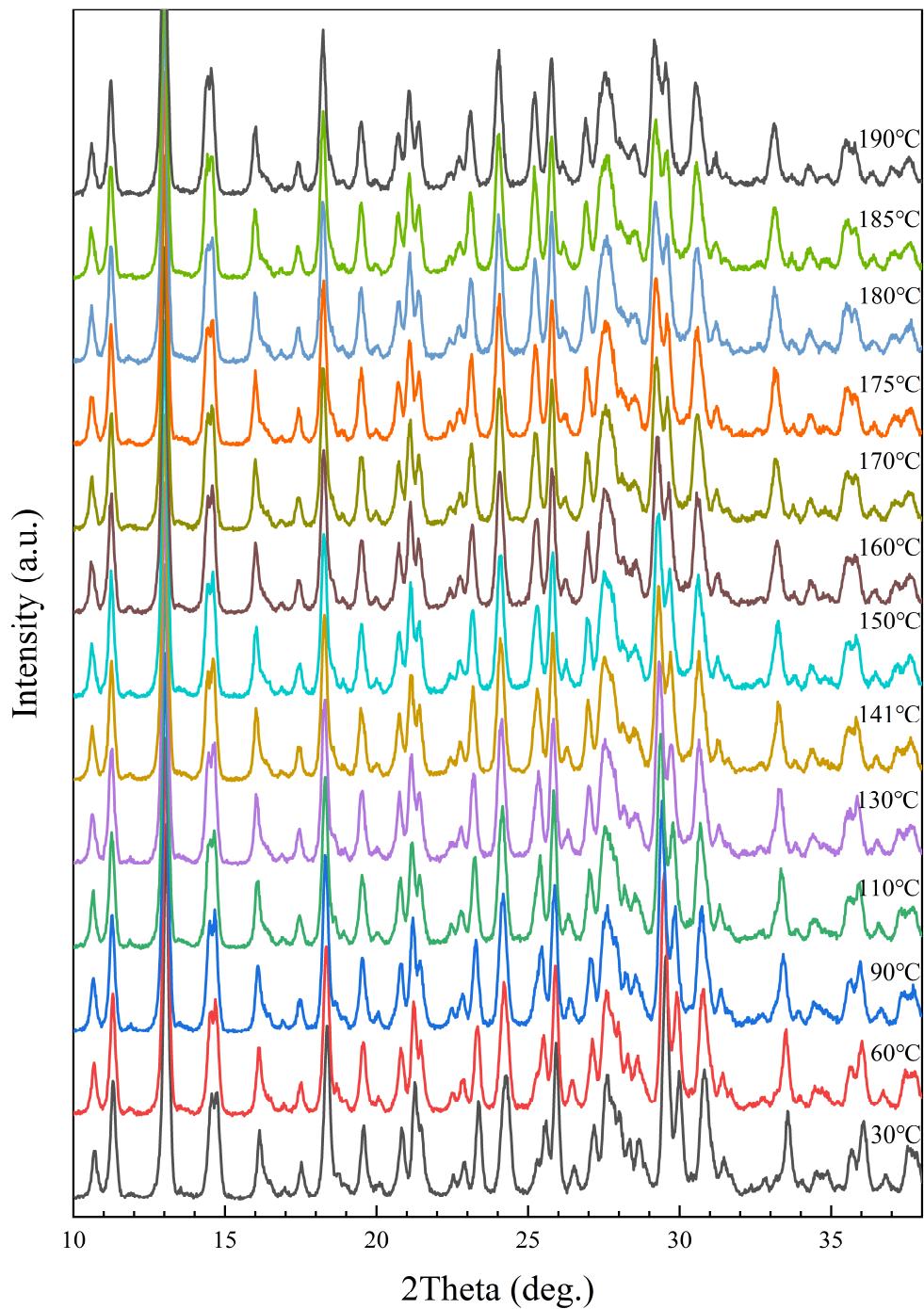
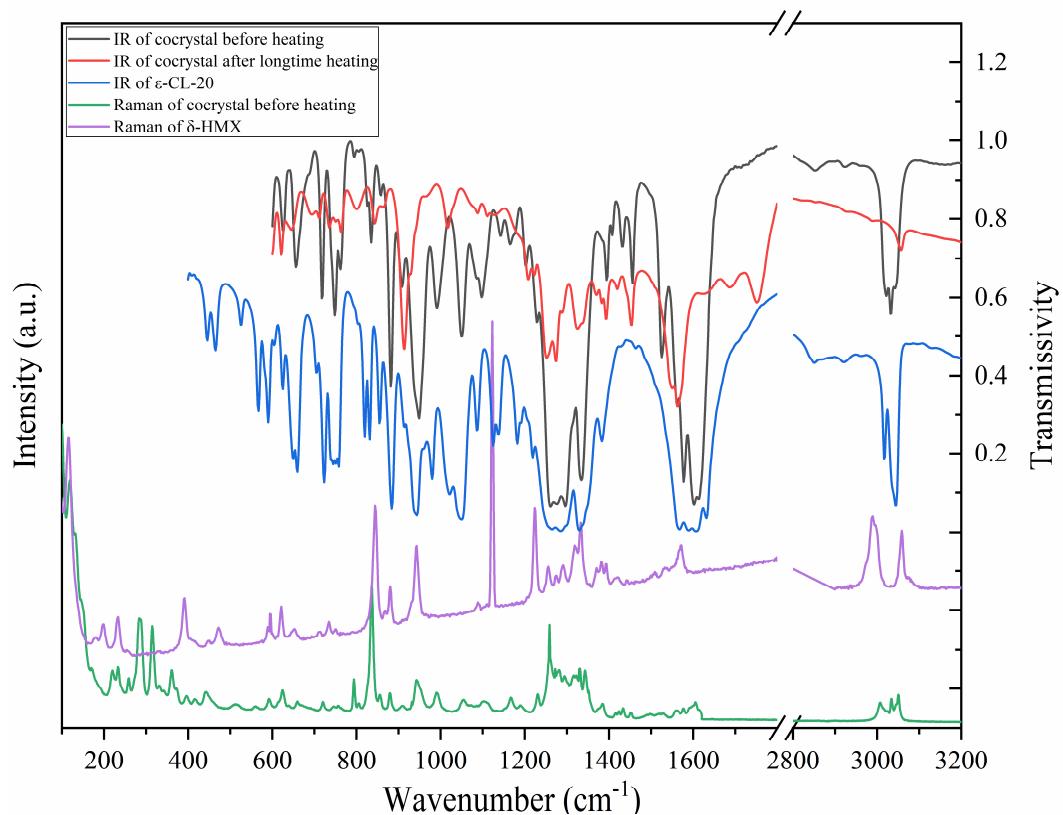


Figure S2. The Raman and IR spectra of CL-20/HMX cocrystals before and after long-term heating, pure CL-20 and  $\delta$ -HMX.



As seen in Fig. S2, Raman and IR spectra for CL-20/HMX cocrystals reveal that there are two sets of vibrational modes from CL-20 and HMX components. After holding at 190 °C for a long time, the vibrational modes of IR for the residual component are the same as those of Raman for  $\delta$ -HMX. This indicates that the CL-20 component completely decomposes and that all residual HMX molecules recrystallize into  $\delta$ -phase HMX.

Figure S3. XRD pattern for CL-20/HMX cocrystals held at 190°C for 1500 minutes refined by the Rietveld method.

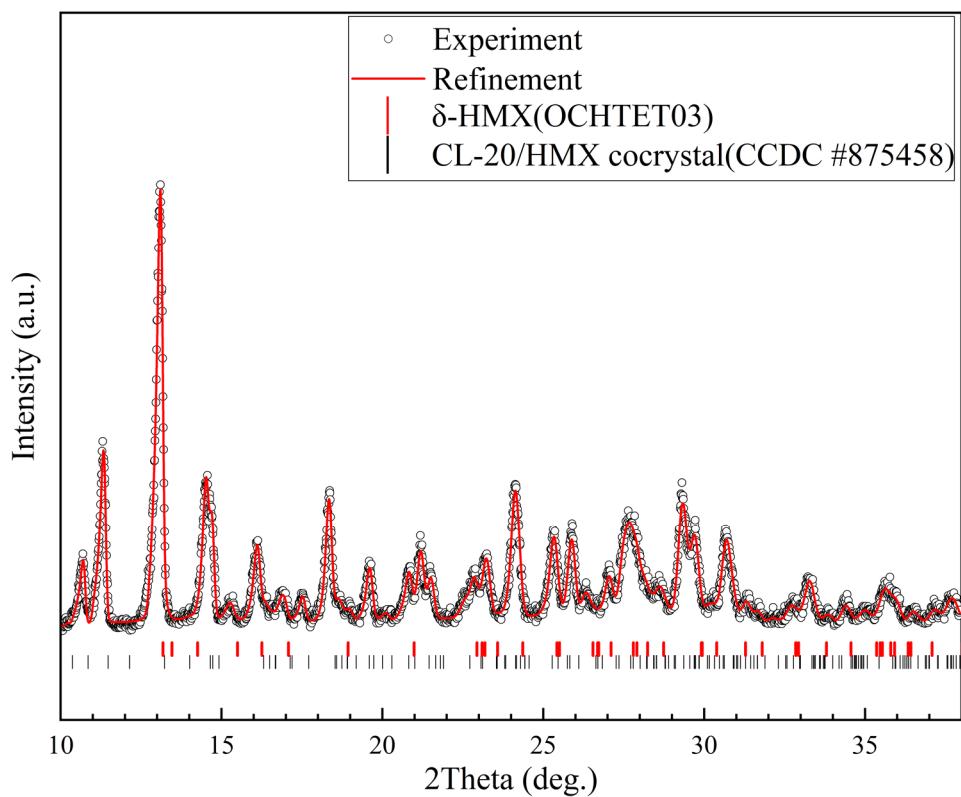


Figure S4. XRD pattern for the samples of CL-20/HMX cocrystals held at 190°C for 1800 minutes refined by the Rietveld method.

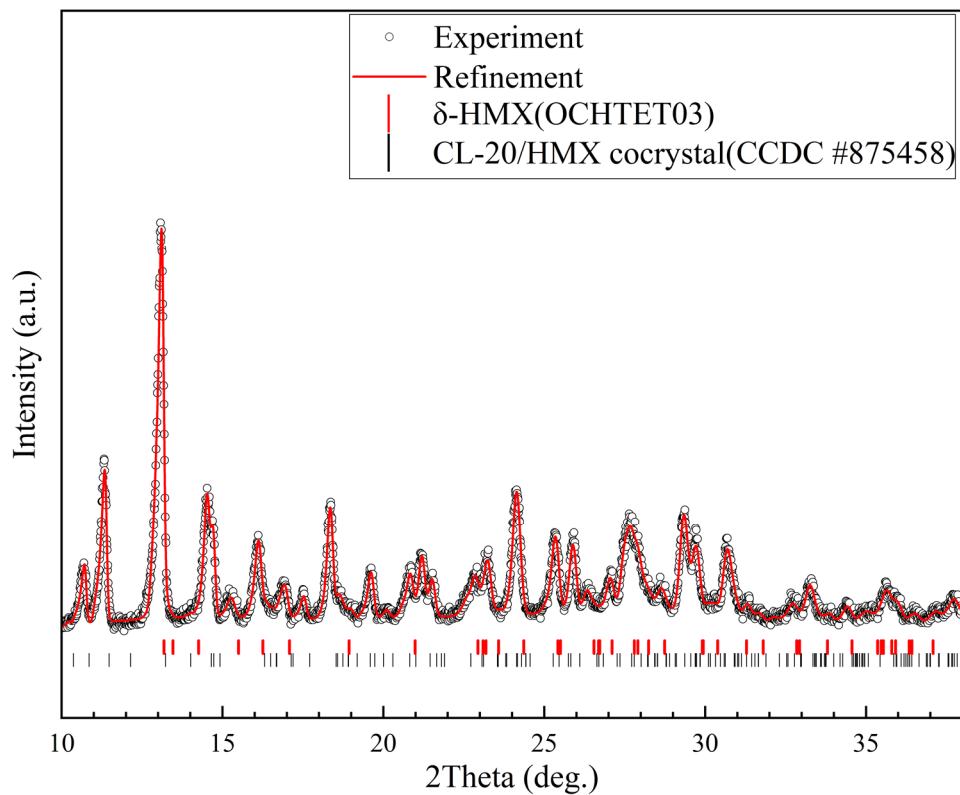


Figure S5. XRD pattern for the samples of CL-20/HMX cocrystals held at 190°C for 2100 minutes refined by the Rietveld method.

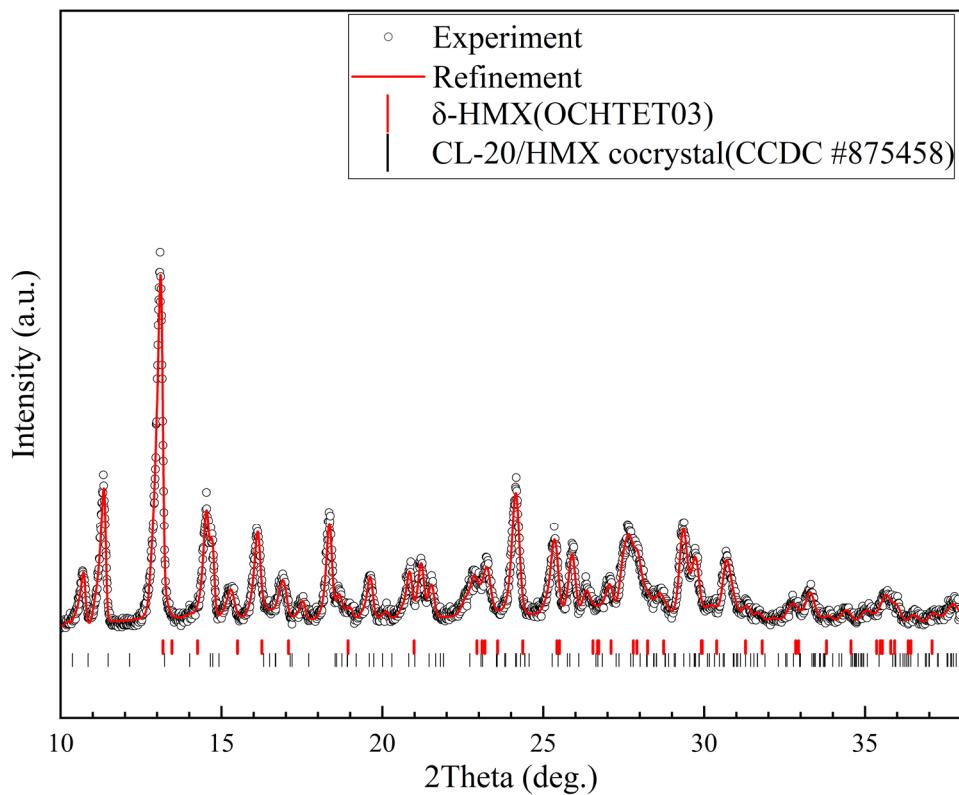


Figure S6. XRD patterns of CL-20/HMX cocrystals held at 190°C for different times

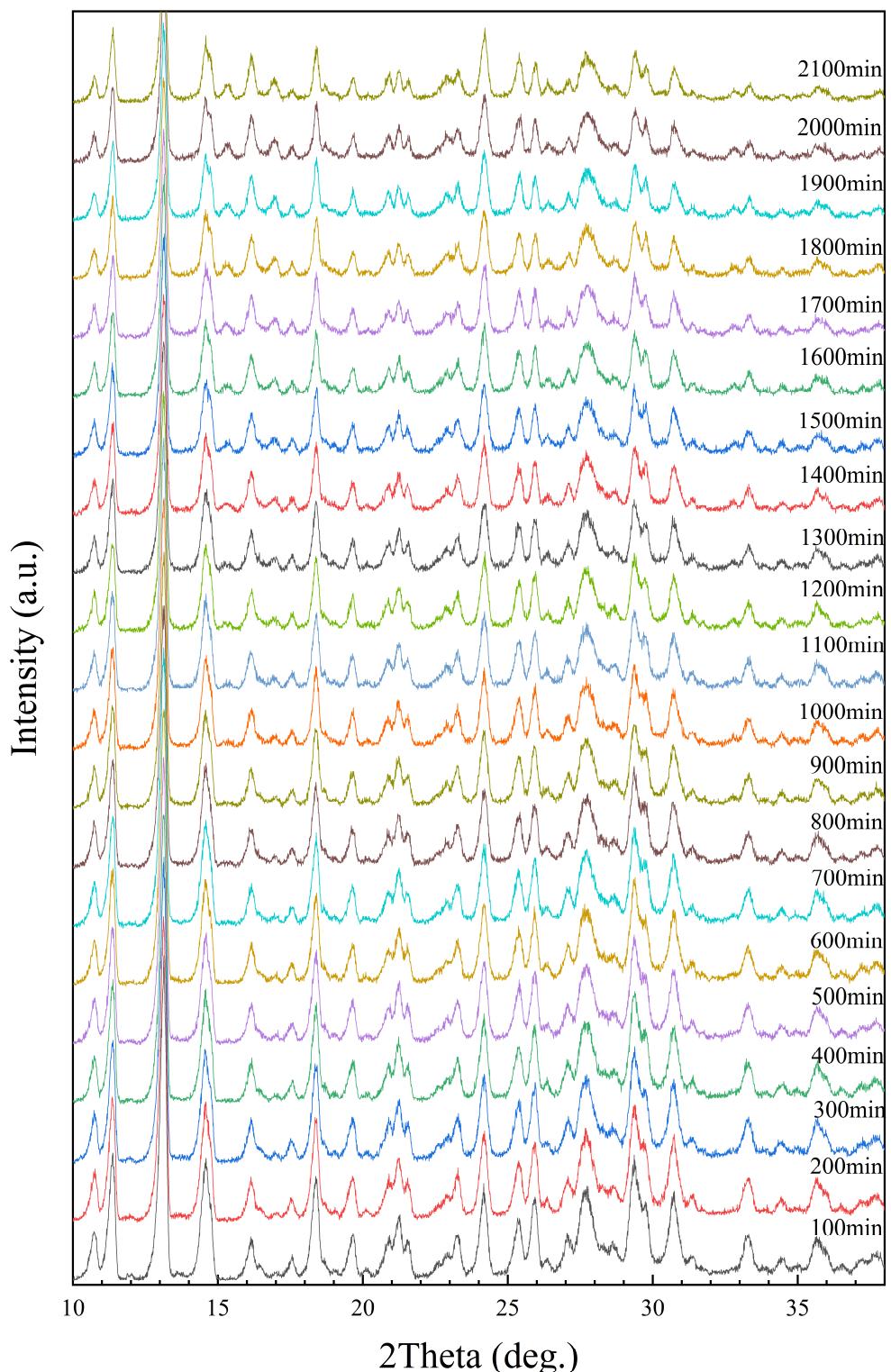


Table S1. The Rietveld refinement results of the XRD patterns for CL-20/HMX cocrystals at different temperatures

Temperature /°C	a/Å	b/Å	c/Å	β/deg	O14-H6/Å	O7-H7A/Å	O9-H7A/Å	a*·sinβ/Å	σ	Rwp/%	Rb/%
30	16.5801	10.0511	12.2947	99.9729	2.5927	2.3279	2.3386	16.3295	2.1820	11.7805	8.1458
60	16.6116	10.0604	12.3106	100.0656	2.5962	2.3331	2.3409	16.3559	2.1698	11.6947	8.1152
90	16.6453	10.0735	12.3299	100.1744	2.6006	2.3388	2.3441	16.3835	2.1855	11.7646	8.0131
110	16.6710	10.0807	12.3472	100.2261	2.6035	2.3429	2.3459	16.4062	2.1451	11.5187	7.8425
130	16.6982	10.0903	12.3653	100.2841	2.6068	2.3473	2.3483	16.4300	1.9053	10.3761	7.2030
140	16.7112	10.0930	12.3731	100.3050	2.6081	2.3493	2.3490	16.4416	2.1087	11.2999	7.6942
150	16.7222	10.0970	12.3817	100.3301	2.6095	2.3511	2.3500	16.4512	2.1050	11.2789	7.8223
160	16.7383	10.1025	12.3888	100.3911	2.6114	2.3539	2.3514	16.4638	2.0602	11.0188	7.5627
170	16.7524	10.1071	12.3979	100.4409	2.6132	2.3564	2.3525	16.4750	2.0621	11.0278	7.5943
175	16.7596	10.1102	12.4036	100.4723	2.6144	2.3577	2.3533	16.4805	2.0801	11.1026	7.7292
180	16.7661	10.1117	12.4067	100.4836	2.6149	2.3587	2.3537	16.4862	2.0348	10.8872	7.4499
185	16.7737	10.1143	12.4104	100.5029	2.6158	2.3599	2.3543	16.4927	2.0021	10.7301	7.4680
190	16.7827	10.1172	12.4147	100.5139	2.6168	2.3612	2.3550	16.5010	1.9675	10.5612	7.2000

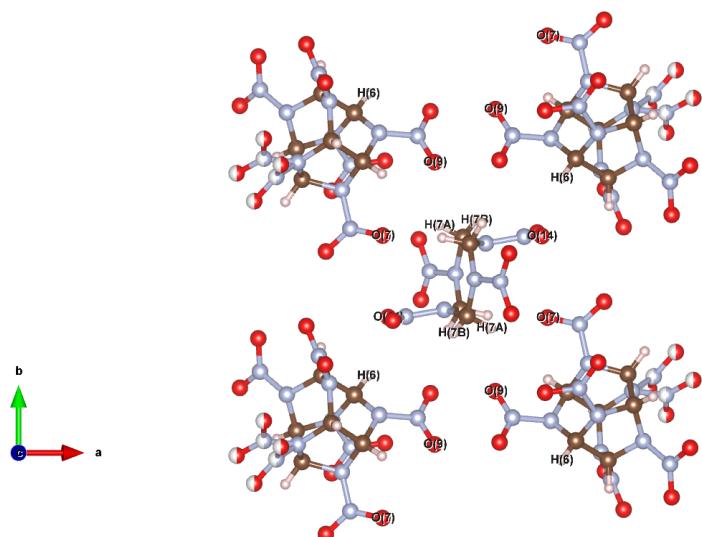


Table S2. The Rietveld refinement results of the XRD patterns for CL-20/HMX cocrystals held at 190°C for different durations

Time (min)	cocrystal weight (%)	δ-HMX weight (%)	δ-HMX: Total HMX (%)	Residual CL-20:Total CL-20 (%)	σ	Rwp(%)	Rb(%)
300	99.630	0.370	1.449	98.551	1.264	9.902	7.122
600	98.680	1.320	5.030	94.970	1.314	10.132	7.403
900	97.020	2.980	10.842	89.158	1.179	9.789	7.048
1200	94.990	5.010	17.274	82.726	1.202	10.312	7.676
1500	92.050	7.950	25.481	74.519	1.149	9.788	7.307
1800	89.480	10.520	31.763	68.237	1.158	10.010	8.398
2100	86.050	13.950	39.093	60.907	1.073	10.147	7.793

The cocrystal weight and δ-HMX weight are directly obtained from the refinement results.

δ-HMX: Total HMX is obtained from the following formula of  $m_{\delta}$ .

$$m_{\delta} = \frac{W_{HMX}}{W_{HMX} + W_{Cocrystal} \bullet \frac{M_{HMX}}{M_{Cocrystal}}} \quad S1$$

$W_{HMX}$  is the δ-HMX weight.  $W_{Cocrystal}$  is the cocrystal weight.  $M_{HMX}$  is the relative molecular mass of HMX, which is 296.155.  $M_{Cocrystal}$  is the relative molecular mass of the cocrystal, which is 1172.525.

Residual CL-20: Total CL-20 is obtained from the following formula of  $m_{CL-20}$ .

$$m_{CL-20} = \frac{W_{Cocrystal} \bullet \frac{M_{CL-20}}{M_{Cocrystal}}}{W_{HMX} \bullet \frac{2 \bullet M_{CL-20}}{M_{HMX}} + W_{Cocrystal} \bullet \frac{M_{CL-20}}{M_{Cocrystal}}} \quad S2$$

$M_{CL-20}$  is the relative molecular mass of CL-20, which is 438.185.