Temperature-dependent decomposition of CL-20/MTNP cocrystal after phase separation

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Supporting Information

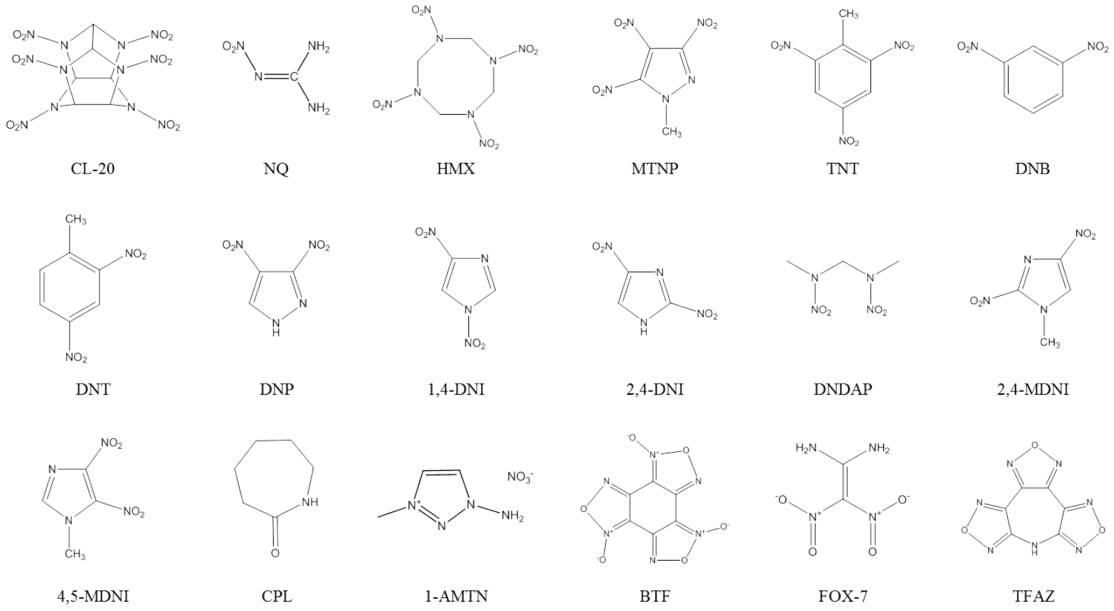

Fig. S1 The chemical formulae of the involved energetic compounds.

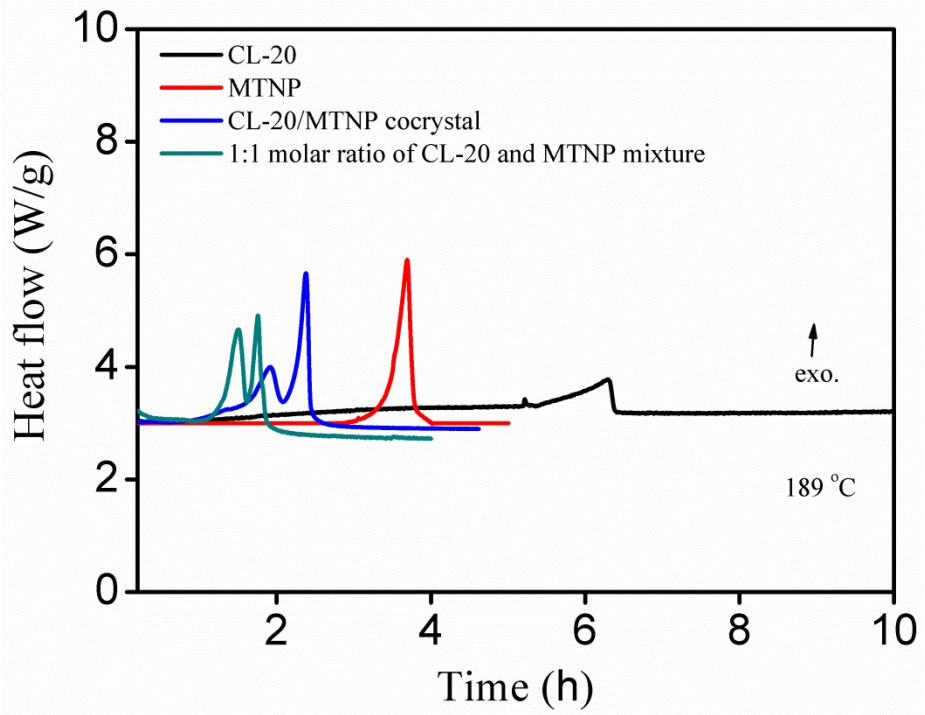

Fig. S2 Isothermal DSC curves of CL-20, MTNP, CL-20/MTNP cocrystal, and 1:1 molar ratio of CL-20 and MTNP mixture at 189 °C.

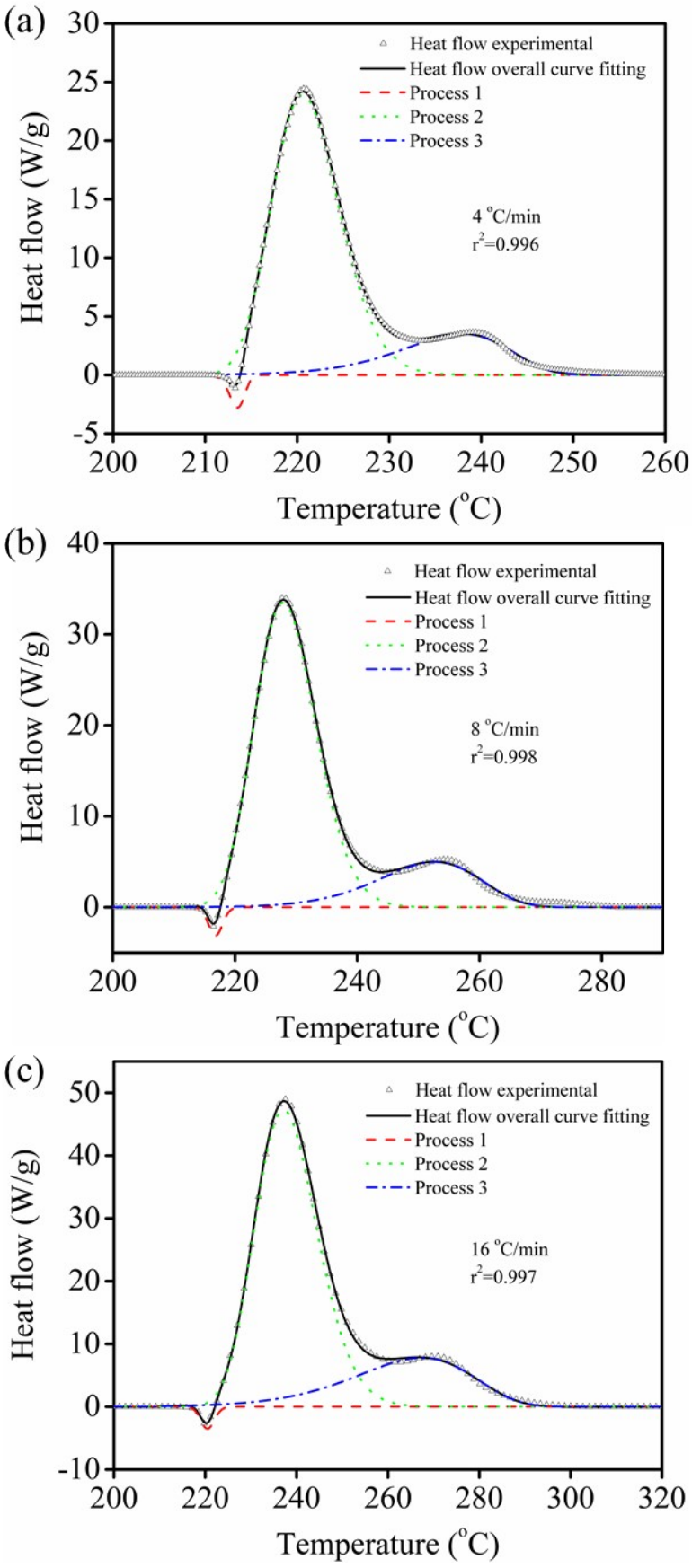
(a)
Heat flow experimental
Heat flow overall curve fitting
Process 1
Process 2
Process 3
4 °C/min
r²=0.996
Heat flow (W/g)
Temperature (°C)
(b)
Heat flow experimental
Heat flow overall curve fitting
Process 1
Process 2
Process 3
8 °C/min
r²=0.998
Heat flow (W/g)
Temperature (°C)
(c)
Heat flow experimental
Heat flow overall curve fitting
Process 1
Process 2
Process 3
16 °C/min
r²=0.997
Heat flow (W/g)
Temperature (°C)

Fig. S3 Experimental heat flow curves (symbols) at different heating rates and the fitting curves for each component process (dotted line) and overall process (solid line) simulated by the deconvolution procedure using Fraser-Suzuki function: (a) 4 °C/min; (b) 8 °C/min and (c) 16 °C/min. The correlation coefficients of the fitting are incorporated into the figures.

Table S1 Fitting parameters (a_0, a_1, a_2, and a_3) of Frasier-Suzuki function (eq. (4)) for deconvolution of the experimental DSC curves for the thermal behavior of CL-20/MTNP cocrystal using Peakfit software.

	a_0	a_1	a_2	a_3	r^2
Process 1					
4 °C/min	-2.77774	213.521	1.94097	-0.13405	0.996
8 °C/min	-3.15345	216.795	2.6504	0.0308782	0.998
10 °C/min	-3.19103	217.462	2.91214	0.023586	0.999
16 °C/min	-3.50293	220.489	3.55066	0.0376535	0.997
Process 2					
4 °C/min	23.8924	220.586	8.60427	0.146933	0.996
8 °C/min	33.4871	227.866	11.7911	0.120191	0.998
10 °C/min	36.9296	230.329	13.1059	0.132421	0.999
16 °C/min	47.2374	237.145	15.9316	0.143237	0.997
Process 3					
4 °C/min	3.50682	237.982	13.7578	-0.303037	0.996
8 °C/min	4.98173	252.678	19.6046	-0.235653	0.998
10 °C/min	5.83585	256.349	23.3638	-0.334144	0.999
16 °C/min	7.78418	267.38	30.5106	-0.292408	0.997

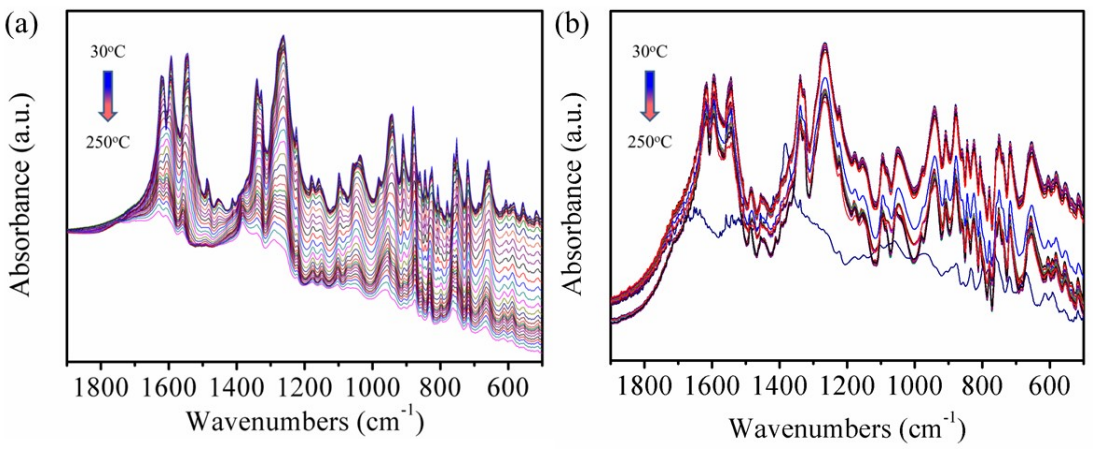

Fig. S4 Full *in situ* IR spectra of CL-20/MTNP cocrystal at heating rates of 1 °C/min (a) and 5 °C/min (b) (the temperature was raised gradually from the top to bottom).

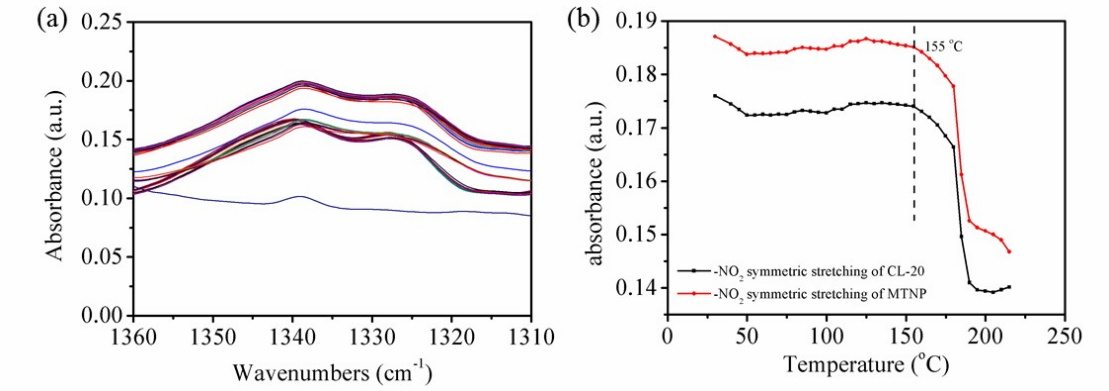

Fig. S5 Temperature-dependent IR spectra of (a) $-NO_2$ groups of CL-20 and MTNP in CL-20/MTNP cocrystal; (b) the corresponding absorbance verses temperature curves (the heating rate was 5 °C/min).

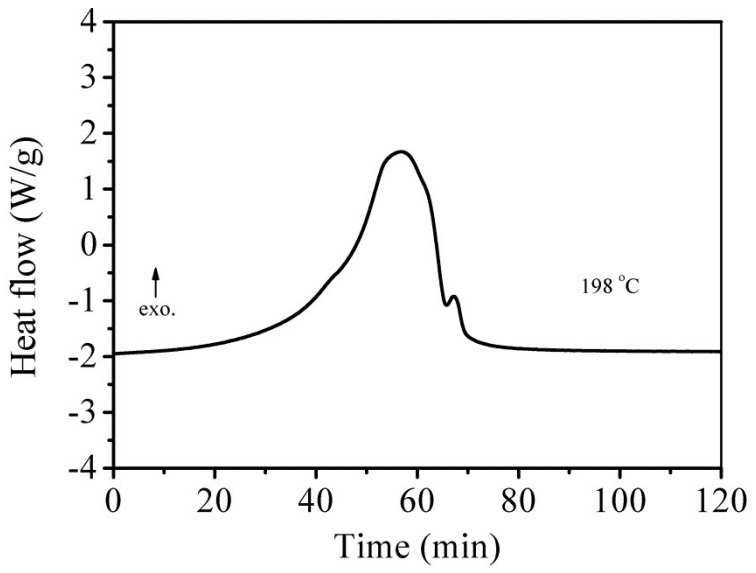

Fig. S6 Isothermal DSC curve of CL-20/MTNP cocrystal at 198 °C.

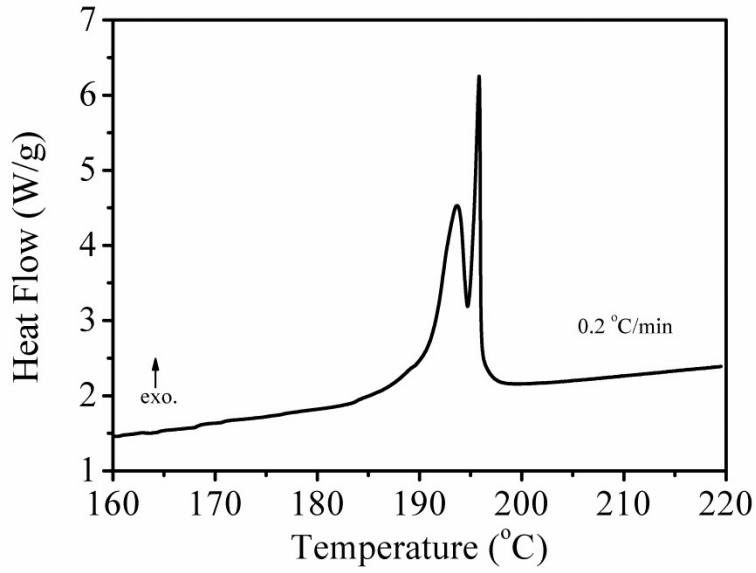

Fig. S7 DSC curve of the CL-20/MTNP cocrystal at heating rate of 0.2 °C/min.

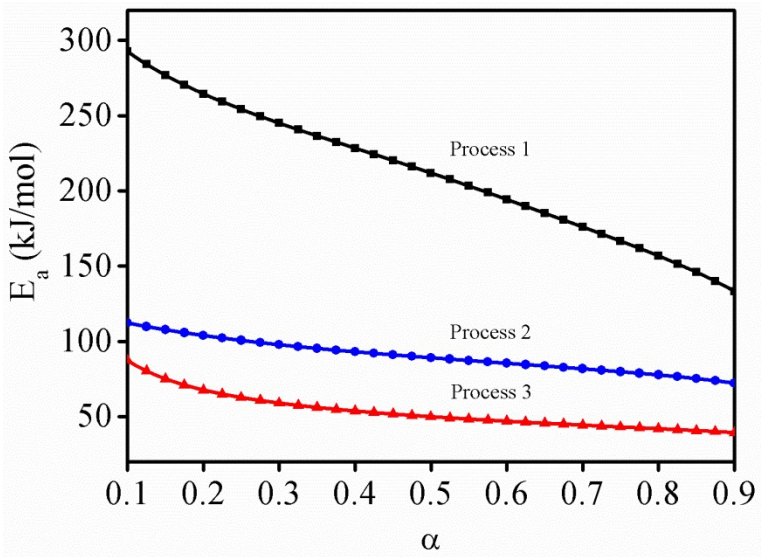

Fig. S8 Apparent activation energies at different reacted fraction values for each of the three processes contributing to thermal decomposition of CL-20/MTNP cocrystal, as determined by the Friedman isoconversional method.

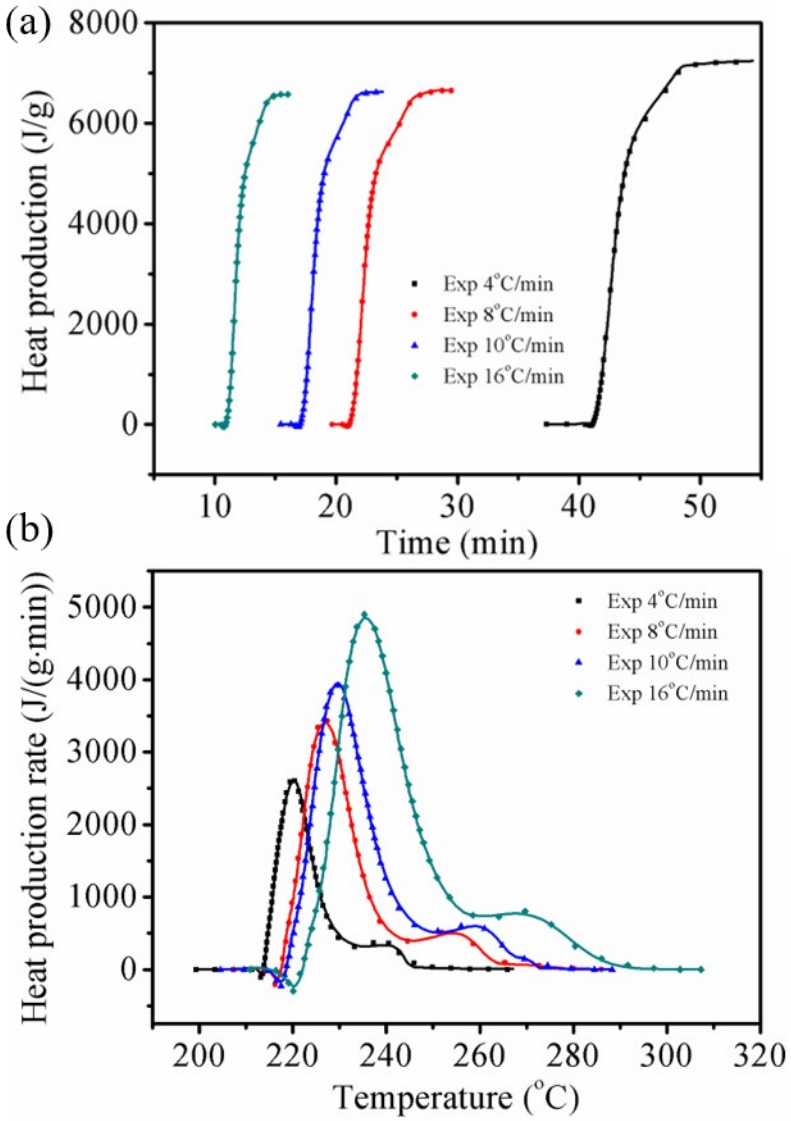

Fig. S9 Experimental heat production-*t* curves (symbols) (a) and heat production rate-*T* curves (symbols) (b) recorded for the thermal decomposition of CL-20/MTNP cocrystal at linear heating rates of 4, 8, 10 and 16 °C/min together with simulated curves (solid lines) constructed using the kinetic parameters determined for the thermal decomposition of CL-20/MTNP cocrystal (Table 3).

Erofeev and topochemical kinetics models

The Erofeev reaction can be described as (S1):

$$r = Ae^{-\frac{E}{RT}}(1-\alpha)[ln(1-\alpha)]^n \quad \text{(S1)}$$

where r is the reaction rate, A is the pre-exponential factor, E is the activation energy, n is the reaction order, R is the gas constant, T represents the temperature, and α is the conversion of samples.

Then, the two parallel Erofeev reactions can be described as

$$r = \sum r_i \quad \text{(S2)}$$

$$r_i = Ae^{-\frac{E}{RT}}(1-\alpha_i)[ln(1-\alpha_i)]^n \quad \text{(S3)}$$

$$\frac{d\alpha}{dt} = \sum r_i \quad \text{(S4)}$$

$$\frac{dQ}{dt} = \sum Q_i r_i \quad \text{(S5)}$$

where r_i, α_i, and Q_i represent the reaction rate, conversion, and heat production, respectively; i = 1 and 2, and t is the time.

The topochemical reaction can be described as (S6):

$$r = Ae^{-\frac{E}{RT}}(1-\alpha)^{n_1}[-ln(1-\alpha)]^{n_2} \quad \text{(S6)}$$

Similarly, the two parallel topochemical reactions can be described as

$$r = \sum r_i$$

(S7)

$$r_i = Ae^{-\frac{E}{RT}}(1-\alpha_i)^{n_1}[-ln(1-\alpha_i)]^{n_2}$$

(S8)

$$\frac{d\alpha}{dt} = \sum r_i$$

(S9)

$$\frac{dQ}{dt} = \sum Q_i r_i$$

(S10)

Adiabatic time to maximum rate *(TMR*$_{ad}$*)* and Self-accelerating decomposition temperature (SADT)

The specific heat capacity (c_p) of CL-20/MTNP cocrystal was determined using a C80 type Calvet microcalorimeter (SETARAM, France), which has a high sensitivity and was equipped with two 10-mL vessels. The precision of enthalpy measurement was better than 0.5 % after calibration. The obtained c_p of CL-20/MTNP cocrystal was 1.06 J/g/K.

TMR$_{ad}$ is the required time for a chemical reaching the maximum temperature rise rate at any temperature in an adiabatic environment, and it also called adiabatic explosion time. Generally, the adiabatic temperature rise rate can be written as (S11):

$$\frac{dT}{dt} = \frac{1}{\varphi}\frac{(-\Delta H_r)}{c_p}\frac{d\alpha}{dt}(\varphi \cong 1)$$

(S11)

where *dT/dt* means adiabatic temperature rise rate, φ is thermal inertial factor, ΔH_r is heat of reaction, c_p is specific heat capacity. Accordingly, TMR_{ad} was determined by numerical calculation based on kinetic model.

SADT is an important parameter to assessing the thermal hazard of chemicals in the process of storage and transportation. It is defined as the lowest temperature at which an overheating in the center of specific packaging exceeds 6 °C after the period of 7 days or less, which was measured from the time when the packing center temperature reaches 2 °C below the ambient temperature. Here, the thermal explosion parameter of CL-20/MTNP cocrystal was simulated and calculated. The specific calculation process is shown below.

For solid reagent thermal safety simulation, we ignore the influence of thermal convection and combine the thermal conductivity equation (S12), kinetic equation (S13), with heat power equation (S14):

$$\rho c_p \frac{\partial T}{\partial t} = div(\lambda \Delta T) + W \quad \text{(S12)}$$

$$r_i = \frac{\partial \alpha_i}{\partial t}$$

(S13)

$$W = \sum Q_i^{\infty} \cdot r_i$$

(S14)

Where ρ is the density, c_p is the specific heat capacity, T is the temperature, t is the time, λ is the heat conductivity, α is the degree of conversion of a component, r_i is the reaction rate, Q_i is the reaction calorific effect, and W is the heat power. Not only heat transfer equations but boundary conditions are of great importance to safety assessment. The boundary conditions can be defined by Newton's heat transfer law (S15):

$$-\lambda \frac{\partial T}{\partial n}|_s = U(T_{wall} - T_e) \quad \text{(S15)}$$

Here, *wall* and *e* relate to the parameters in environment and on the boundary, respectively, n is the unit outer normal on the boundary, and U is heat transfer coefficient of radiation surface. Accordingly, the SADT value for 50 kg CL-20/MTNP cocrystal was calculated.