Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

For

Taming CL-20 through hydrogen bond interaction with nitromethane

Contents

1 Preparation Of Cocrystal

Use a pipette to accurately pipette 2.0 mL of nitromethane solution into a 10 mL vial, accurately weigh 400.0 mg ε-CL-20 on an analytical balance and add it to the above solution, stir 2h at room temperature, and wait until all is dissolved , At 10 ℃, through the solvent slow volatilization method, the transparent block crystals are precipitated.

2 Powder X-ray Diffraction

PXRD patters were obtained by Bruker D2 Advance with a Cu Kα radiation at 40kv-45mA, The sample was scanned within the scan range of 2θ from 5° to 50° continuous san with a step size of 0.015° and a scan speed of 0.2 s per step

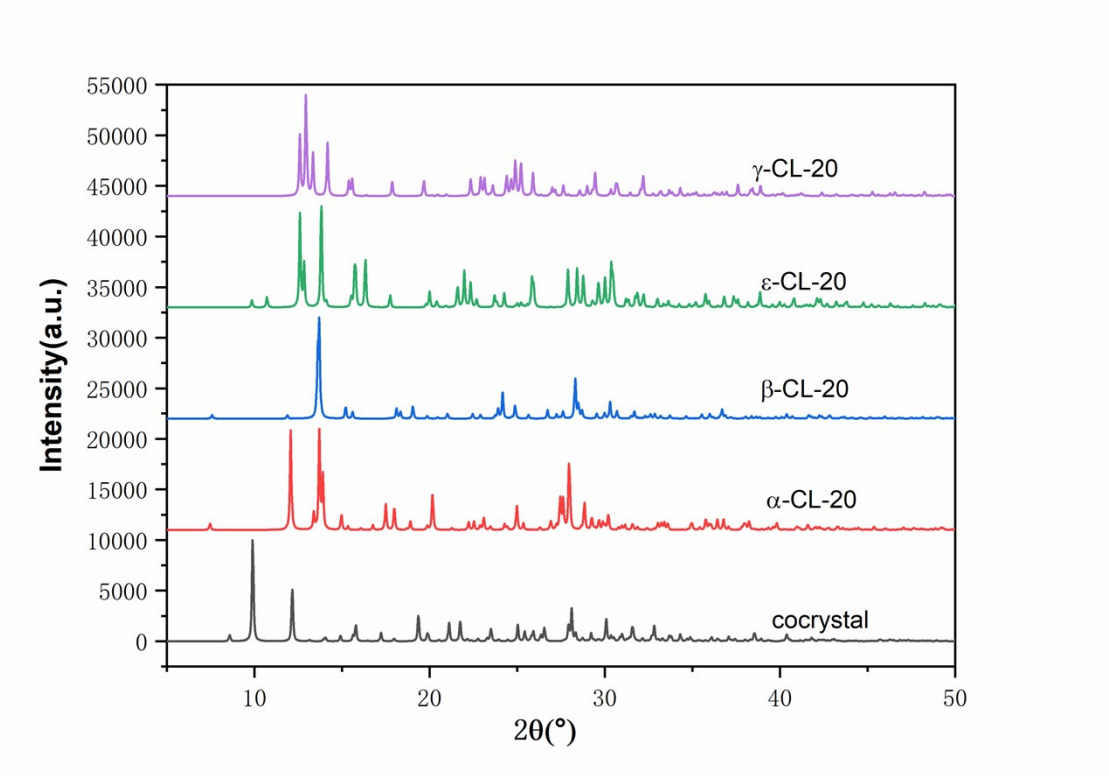


Fig S1 P-XRD patterns of cocrystal and ε-CL-20、β-CL-20 and γ-CL-20

3 Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data for cocrystal 1 and 2 were collected using a Rigaku AFC10K Saturn. Single crystal of suitable quality was chosen and purged with a cooled nitrogen gas stream at 170 K throughout the data collection. X-ray reflections were collected on a Xcalibur Eos CCD detector with graphite-monochromated Gu-Kα radiation (λ=1.34139 Å). Data were collected and processed using Olex-2 software. Structure was solved by direct methods and SHELX was used for structure solution and least-squares refinement. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model. The solvent-masking routine in Olex-2 [equivalent to SQUEEZE in PLATON] was used to remove the contributions of unspecified disordered components from the structure factor list in the CIF

Table 1 Crystallographic Data for cocrystal

	cocrystal
Empirical formula	$C_8H_{12}N_{14}O_{16}$
Formula weight	560.32
Temperature/K	153.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.9053(18)
b/Å	12.585(3)
c/Å	17.847(4)
α/°	90
β/°	90.73(3)
γ/°	90
Volume/Å^3	1999.9(7)
Z	4
ρ_{calc}g/cm^3	1.861
μ/mm^{-1}	0.179
F(000)	1144
Crystal size/mm^3	0.23 × 0.21 × 0.18
Radiation	MoKα (λ = 0.71073)

2θ range for data collection/°	3.96 to 54.974
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 16, -23 ≤ l ≤ 23
Reflections collected	13110
Independent reflections	4547 [R_{int} = 0.0303, R_{sigma} = 0.0285]
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1482
Final R indexes [all data]	R_1 = 0.0564, wR_2 = 0.1848

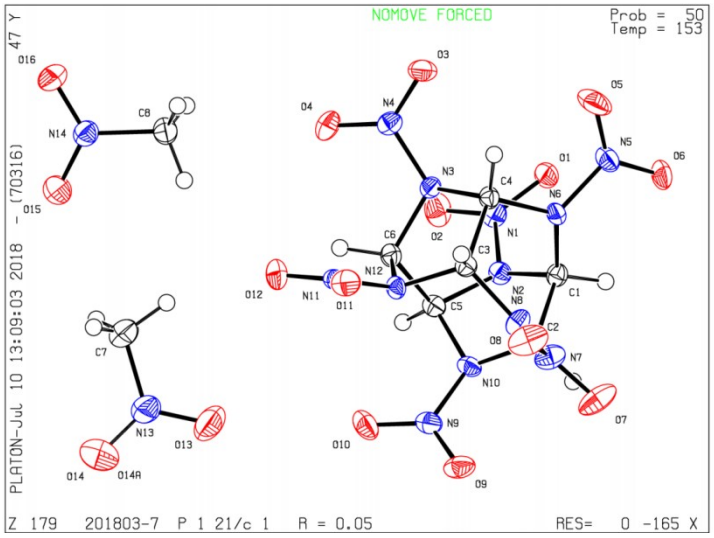


Fig S2 OPTEP diagram for cocrystal 1 with 50% probability ellipsoids(153K)

Table 2 Non-bonding force of cocrystal

D-H…A	Bond length	D-H…A	Bond length
C1-H1…O15	2.442	C2-H2…O15	2.774

C8-H8C…O4	2.49	C2-H2…N14	2.859
C7-H7A…O12	2.635	C8-H8C…N4	2.901
C8-H8C…O4	2.677	C5-H5…O6	2.904
C7-H7C…O6	2.693	C8-H8C…O3	2.936

4 Differential Scanning Calorimetry

Thermal analyses of all samples were performed on a TA Q100 differential scanning calorimetry. Test samples were placed into aluminum pans and scanned at a heating rate of 10 °C min^{-1} with a stream of flowing nitrogen at 50 mL min^{-1}

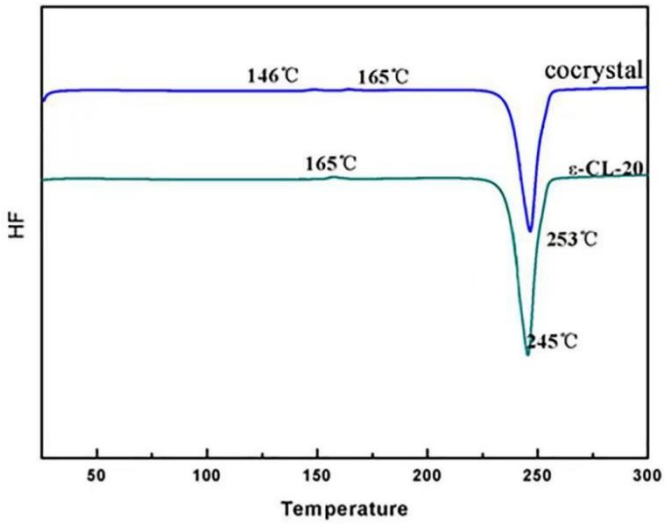


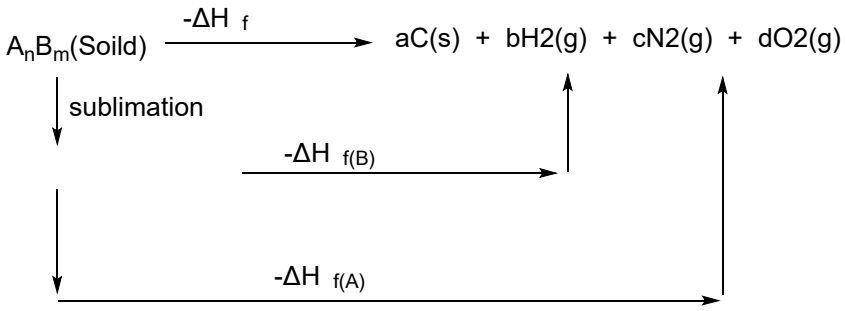
Fig S3 DSC traces of cocrystal 1 and ε-CL-20

5 Calculation Methods

Packing coefficients (PC) was calculated by using the equation (1), where Vm and Vc are the molecular and crystal volumes, respectively. A volume enclosed through a surface with an assigned electronic density was considered as Vm. In this work, the electronic density was calculated at the theory level of B3LYP/6-311+G(d,p), and the density of 0.003 au was adopted for Vm calculations.

$$PC=\Sigma V_{mol}V_{cell}^{-1} \quad (1)$$

The detonation properties including detonation velocities and detonation pressures for the cocrystal 1 and their respective components were calculated by using EXPLO5 (v6.01). The calculations were carried out using Gaussian 09 (Revision D.01) suite of programs. The gaseous enthalpies of formation of the cocrystals were calculated on the basis of a Born-Haber energy cycle



The number is simplified by equation 3:

$$\Delta H_f(\text{cocrystal},298K) = \Delta H_f(A,298K) + \Delta H_f(B,298K) - \Delta H_{sub}$$

The sublimation enthalpy of the cocrystal was obtained by the lattice energy of the cocrystal. The lattice energy of the cocrystal was calculated at the PBE/DNP level with Grimme dispersion correction in Dmol3.

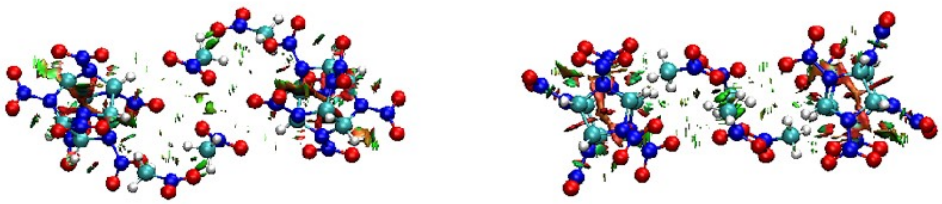


Fig S4 Noncovalent interaction of cocrystal