Supplementary information

Design of solvent systems for ε-CL-20 crystals with high sphericity preparation assisted by molecular simulation

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1. Characterization of compound

The nuclear magnetic resonance (NMR) spectra of solvent and compound CL-20 were measured. The CL-20 was dissolved in solvent (Acetone-d6, 99.9%, Shanghai Yien Chemical Technology Co., Ltd., China) and analyzed using a NMR (AVANCE III HD 400 MHz, Bruker, Switzerland). The ^{1}H-NMR spectrum of solvent is shown in **Fig. S1**. There are the peaks with δ (chemical shift) = 0 ppm, δ = 0.6 ppm, δ = 2.1 ppm, and δ = 2.8 ppm. The ^{1}H-NMR spectrum of CL-20 raw material is shown in **Fig. S2**. Compared to **Fig. S1**, there are two additional peaks with δ = 8.22 ppm, δ = 8.37 ppm in the spectrum, and the ratio of peak area integrals is approximately 2:1. It can be determined that the peak with δ = 8.37 ppm originates from part A of CL-20 structure, and the peak with δ = 8.22 ppm originates from part B of CL-20 structure. The NMR spectrum of CL-20 measured by Bazaki et al.[S1] is shown in **Fig. S3**. The result indicates that the δ of two peaks are approximately 8.4 ppm and 8.2 ppm, respectively. The above NMR spectra are consistent, proving that the compound used in this work is CL-20. There are no other impurities in CL-20 raw material.

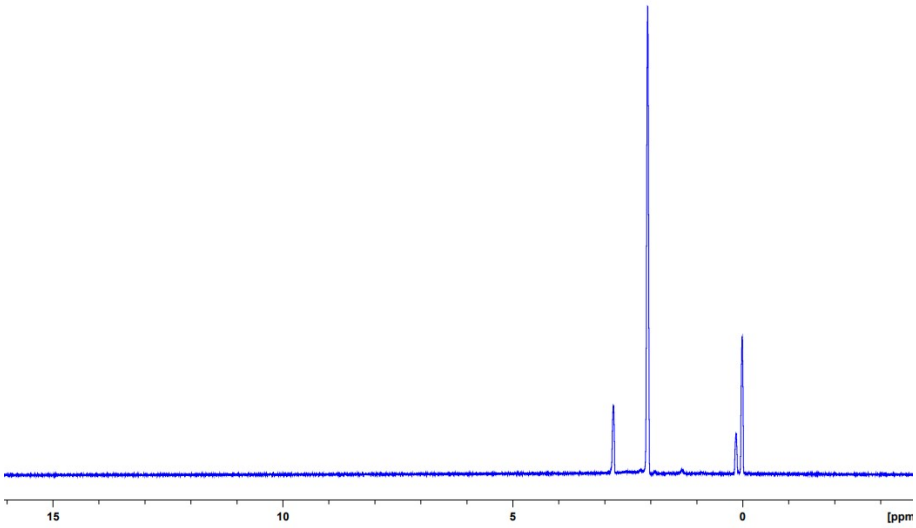

Fig. S1 ^{1}H-NMR spectrum of solvent

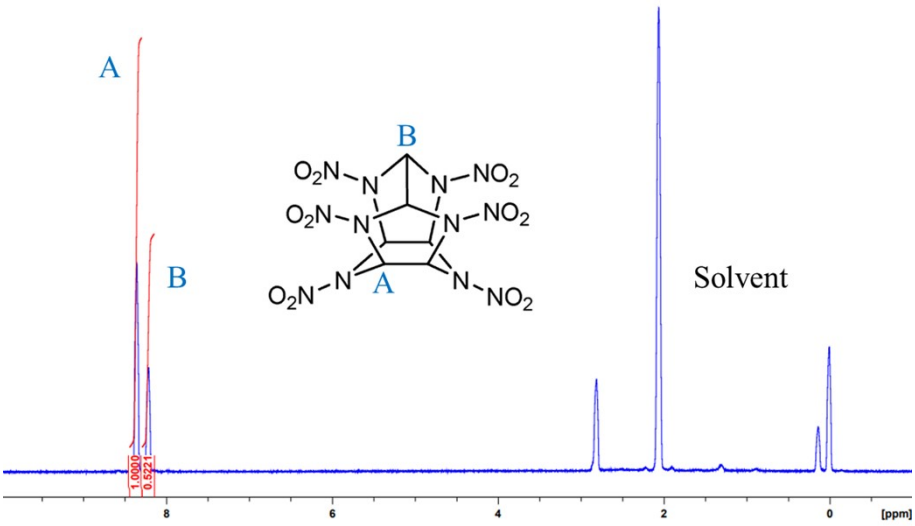

Fig. S2 ^{1}H-NMR spectrum of CL-20

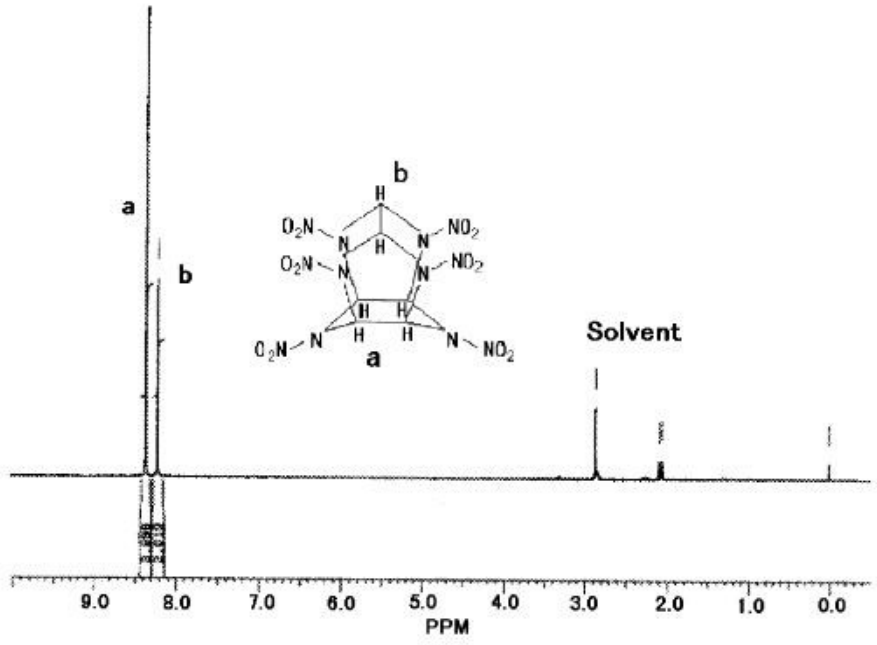

Fig. S3 NMR spectrum of CL-20 measured by H. Bazaki et al.[S1]

In order to make this work more accurate and complete, the CL-20 raw material was analyzed using a High-performance liquid chromatograph (HPLC, 1260 Infinity II, agilent, America). The results indicate that the mass percentage of raw material provided by Beijing Institute of Technology exceeds 99.5%, as shown in **Fig. S4**.

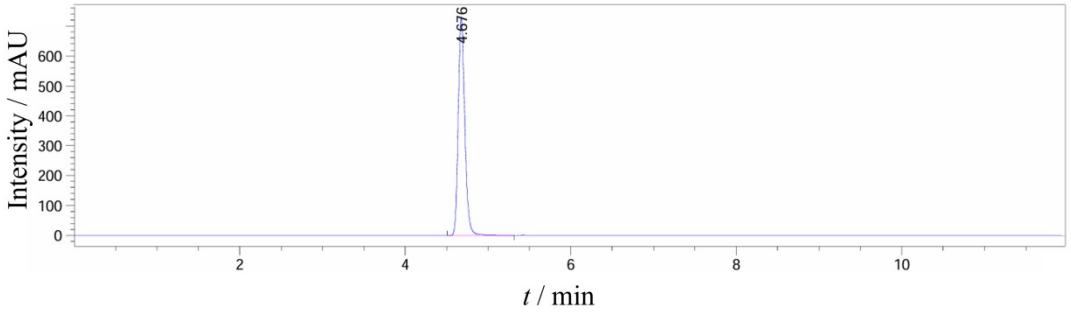

Fig. S4 HPLC of CL-20 raw material.

2. Crystal plane energies and area ratios of ε-CL-20

Table S1 Crystal plane energies and area ratios of ε-CL-20 in binary solvents at different temperatures

T/K		(1 1 0)	(0 0 1)	(1 1 -1)	(0 1 1)	(2 0 0)	(2 0 -1)
Ethyl acetate + Chlorobenzene							
303.15	E_{int}/kcal·mol^{-1}	-330.72	-476.30	-415.23	-485.43	-325.62	-490.95
	E_{att}^{m}/kcal·mol^{-1}	-12.89	16.11	-25.26	14.14	-57.92	-24.10
	Total facet area/%	47.03	18.36	0.00	30.42	0.00	4.19
313.15	E_{int}/kcal·mol^{-1}	-336.54	-463.23	-425.57	-478.87	-340.77	-525.29
	E_{att}^{m}/kcal·mol^{-1}	-11.59	13.20	-23.57	12.62	-56.20	-17.93
	Total facet area/%	55.35	9.49	0.00	29.08	0.00	6.10
323.15	E_{int}/kcal·mol^{-1}	-342.07	-441.69	-434.62	-463.64	-350.38	-537.43
	E_{att}^{m}/kcal·mol^{-1}	-10.35	8.42	-22.10	9.10	-55.11	-15.75
	Total facet area/%	57.66	3.93	0.00	35.91	0.00	2.49
Ethyl acetate + Dibromomethane							
303.15	E_{int}/kcal·mol^{-1}	-340.35	-515.25	-480.73	-531.54	-332.52	-453.39
	E_{att}^{m}/kcal·mol^{-1}	-10.74	24.77	-14.57	24.79	-57.14	-30.85
	Total facet	63.40	2.96	33.64	0.00	0.00	0.00

	area/%						
313.15	E_{int}/kcal·mol^{-1}	-345.90	-495.28	-492.70	-532.11	-341.91	-468.56
	E_{att}^{m}/kcal·mol^{-1}	-9.50	20.33	-12.61	24.92	-56.07	-28.13
	Total facet area/%	64.94	0.92	34.14	0.00	0.00	0.00
323.15	E_{int}/kcal·mol^{-1}	-347.63	-480.25	-497.54	-567.47	-350.8	-489.23
	E_{att}^{m}/kcal·mol^{-1}	-9.18	16.99	-11.79	33.13	-55.06	-24.41
	Total facet area/%	65.76	0.3	33.94	0	0	0
Ethyl acetate + 1,1,2,2-Tetrachloroethylene							
303.15	E_{int}/kcal·mol^{-1}	-340.57	-546.33	-443.65	-577.15	-331.91	-492.70
	E_{att}^{m}/kcal·mol^{-1}	-10.69	31.68	-20.62	35.33	-57.21	-23.79
	Total facet area/%	70.89	0.75	28.13	0.00	0.00	0.23
313.15	E_{int}/kcal·mol^{-1}	-346.58	-520.61	-466.83	-584.29	-334.31	-507.84
	E_{att}^{m}/kcal·mol^{-1}	-9.35	25.96	-16.84	36.97	-56.94	-21.07
	Total facet area/%	73.71	0.36	25.80	0.00	0.00	0.12
323.15	E_{int}/kcal·mol^{-1}	-350.65	-498.08	-486.15	-586.70	-347.85	-528.24
	E_{att}^{m}/kcal·mol^{-1}	-8.44	20.95	-13.68	37.53	-55.39	-17.40
	Total facet area/%	75.22	0.24	23.78	0.00	0.00	0.75

Table S2 Crystal planes energies and area ratios of ε-CL-20 in ternary solvents at different temperatures

T/K		(1 1 0)	(0 0 1)	(1 1 -1)	(0 1 1)	(2 0 0)	(2 0 -1)
Ethyl acetate + Chlorobenzene + Dibromomethane							
303.15	E_{int}/kcal·mol^{-1}	-327.26	-510.09	-410.67	-502.68	-330.64	-470.59
	E_{att}^{m} /kcal·mol^{-1}	-13.66	23.63	-26.01	18.12	-57.35	-27.76

	Total facet area/%	58.36	0.00	0.00	35.17	0.00	6.47
313.15	E_{int}/kcal·mol^{-1}	-330.53	-498.88	-425.50	-491.35	-345.99	-501.80
	E_{att}^{m}/kcal·mol^{-1}	-12.93	21.13	-23.59	15.57	-55.61	-22.15
	Total facet area/%	59.29	0.00	0.00	35.73	0.00	4.98
323.15	E_{int}/kcal·mol^{-1}	-337.83	-486.00	-430.39	-483.06	-352.86	-524.03
	E_{att}^{m}/kcal·mol^{-1}	-11.30	18.27	-22.74	13.59	-54.82	-18.12
	Total facet area/%	64.03	0.00	0.00	33.47	0.00	2.50
Ethyl acetate + Dibromomethane + 1,1,2,2-Tetrachloroethylene							
303.15	E_{int}/kcal·mol^{-1}	-340.32	-514.13	-488.91	-556.38	-332.56	-493.61
	E_{att}^{m}/kcal·mol^{-1}	-10.75	24.50	-13.27	30.53	-57.13	-23.62
	Total facet area/%	66.71	0.39	32.90	0.00	0.00	0.00
313.15	E_{int}/kcal·mol^{-1}	-349.09	-492.29	-500.54	-574.52	-337.92	-510.79
	E_{att}^{m}/kcal·mol^{-1}	-8.79	19.67	-11.33	34.72	-56.52	-20.54
	Total facet area/%	64.14	0.29	35.57	0.00	0.00	0.00
323.15	E_{int}/kcal·mol^{-1}	-353.86	-484.79	-503.86	-587.80	-350.83	-520.21
	E_{att}^{m}/kcal·mol^{-1}	-7.72	18.00	-10.81	37.79	-55.05	-18.84
	Total facet area/%	62.74	0.05	37.22	0.00	0.00	0.00

References

[S1] H. Bazaki, S. Kawabe, H. Miya, T. Kodama, Synthesis and Sensitivity of Hexanitrohexaaza-isowurtzitane (HNIW), Propellants, Explos., Pyrotech. 23 (1998) 333-336.