Supporting Information

Crystal structure prediction of CL-20 polymorphs using a tailor-made polarizable force field

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1. Periodic DFT optimization and energy ranking of the low energy structures predicted by TMPFF.
Periodic DFT optimization of the low energy structures predicted by TMPFF was conducted using VASP program with the plane-wave basis and the projected augmented wave(PAW) method[1-2], GGA-PBE functional[3] was used and DFT-D3 correlation was applied to improve van der Waals description[4]. The kinetic cutoff energy was chosen to be 500 eV and the Brillouin zone was sampled with a gamma-center k-mesh which was generated with KP-resolved values of $2\pi \times 0.04$ Å^{-1}. For all the computations, the convergence thresholds were set as 10^{-6} eV in energy and 0.01 eV/ Å in force. No constrains of space groups are applied during optimization.
The energy ranking is shown in Figure S1, note that the energy of *β*-EA223 and *β*-EA153(conformation#3) converged after the optimization, and identified the same(PS_{ab}=0.033) using CrystalCMP program.

Table S1. Results of the periodic DFT optimizations of CL-20 experimental polymorphs and low energy structures predicted by TMPFF.

	ID	*a*(Å)	*b*(Å)	*c*(Å)	*α*(°)	*β*(°)	*γ*(°)	E(eV)
Conformation#1	*β*-CL-20 (PUBMUU01)	9.611	11.491	13.091	90.00	90.00	90.00	-950.204
	EA435	9.596	11.506	13.100	90.00	90.00	90.00	-950.203
	EA1155	8.063	12.126	15.055	90.00	90.00	90.00	-949.779
	EA1114	10.970	11.647	11.863	90.00	90.00	90.00	-949.998
Conformation#2	*γ*-CL-20 (PUBMUU)	8.169	13.195	14.811	90.00	109.29	90.00	-950.279
	EA2024	8.000	13.345	14.900	90.00	109.48	90.00	-950.228
	EA2103	7.878	13.170	15.751	90.00	113.72	90.00	-950.039
	EA2300	8.881	12.546	13.782	90.00	106.64	90.00	-949.714
Conformation#3	*ε*-CL-20 (PUBMUU02)	8.851	12.554	13.342	90.00	106.56	90.00	-950.376
	EA1497	8.884	12.499	13.341	90.00	106.61	90.00	-950.366
	EA223	8.835	12.513	13.080	90.00	90.00	90.00	-950.276
	EA153	8.823	12.497	13.111	90.00	90.00	90.00	-950.275

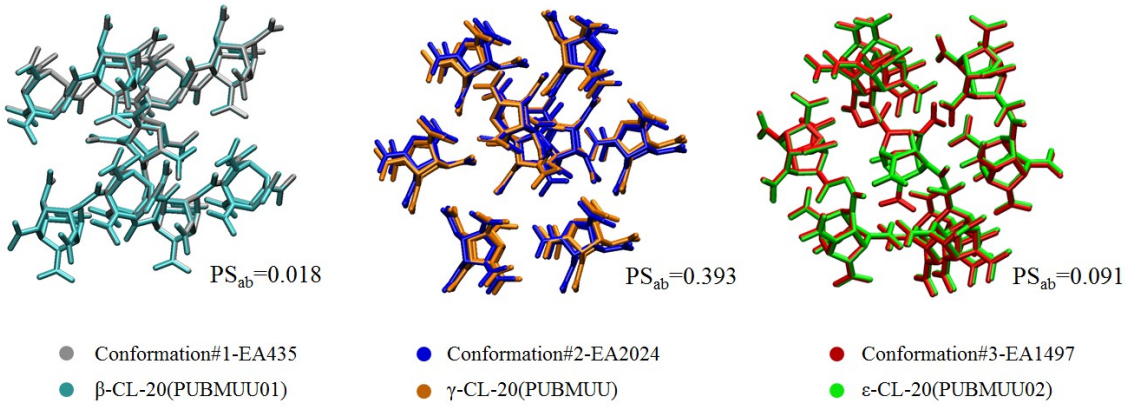

Figure S1 The comparison of predicted structures and experimental polymorphs of CL-20 after periodic DFT optimizations.

2. Multipole parameters calculated under B3LYP/6-311G(d,p) and BHandHLYP/6-311G(d,p) level of basis.
Multipoles of the atoms are calculated with Distributed Multipole Analysis of Gaussian wavefunctions (GDMA) program developed by Stones *et. al*[5], the Gaussian checkpoint file of QM optimization of *ε*-CL-20 molecule is input. Results are shown in Table S2.

Table S2. Multipole parameters of ε-CL-20 calculated under B3LYP/6-311G(d,p) and BHandHLYP/6-311G(d,p) level of basis

ID	B3LYP/6-311G(d,p)				BHandHLYP/6-311G(d,p)			
	charge	0.21994			charge	0.2121		
	dipole	0.00548	0	0.32367	dipole	0.00374	0	0.33638
C1		0.48258				0.50555		
	quadrupole	0	-0.35752		quadrupole	0	-0.38159	
		0.01844	0	-0.12506		0.01705	0	-0.12396
	charge	0.17272			charge	0.18224		
	dipole	0.00129	0	-0.12665	dipole	0.00235	0	-0.13089
H1		-0.01526				-0.01548		
	quadrupole	0	-0.01547		quadrupole	0	-0.01572	
		0.00296	0	0.03073		0.00366	0	0.0312
	charge	-0.30537			charge	-0.30876		
	dipole	0.19929	0	-0.00819	dipole	0.21744	0	-0.01692
N1		0.05687				0.01172		
	quadrupole	0	-0.3995		quadrupole	0	-0.44082	
		-0.19672	0	0.34263		-0.24982	0	0.4291
	charge	1.05609			charge	1.07685		
	dipole	-0.01834	0	-0.06316	dipole	-0.02036	0	-0.04478
N2		0.25175				0.19612		
	quadrupole	0	-0.4823		quadrupole	0	-0.41151	
		0.01807	0	0.23055		0.01666	0	0.21539
	charge	-0.53563			charge	-0.55038		
	dipole	0.14908	0	-0.13232	dipole	0.13374	0	-0.12972
O1		-0.52588				-0.50812		
	quadrupole	0	0.24966		quadrupole	0	0.2035	
		0.1314	0	0.27622		0.11814	0	0.30462
	charge	-0.53563			charge	-0.55038		
	dipole	0.14908	0	-0.13232	dipole	0.13374	0	-0.12972
O2		-0.52588				-0.50812		
	quadrupole	0	0.24966		quadrupole	0	0.2035	
		0.1314	0	0.27622		0.11814	0	0.30462
	charge	0.08896			charge	0.09651		
	dipole	0.13635	0	0.31563	dipole	0.13816	0	0.35826
C2		0.37608				0.37933		
	quadrupole	0	-0.71246		quadrupole	0	-0.80139	
		0.04081	0	0.33638		0.04455	0	0.42206
	charge	0.16989			charge	0.18084		
	dipole	0.00021	0	-0.12423	dipole	0.00102	0	-0.12982
H2		-0.01628				-0.01573		
	quadrupole	0	-0.01484		quadrupole	0	-0.01476	
		0.00122	0	0.03112		0.00153	0	0.03049
	charge	-0.2073			charge	-0.21614		
	dipole	0.00018	0	-0.26747	dipole	-0.00938	0	-0.28186
N3		0.64169				0.63746		
	quadrupole	0	-1.31795		quadrupole	0	-1.39558	
		-0.01378	0	0.67626		0.0039	0	0.75812
	charge	1.14403			charge	1.16788		
	dipole	0.01407	0	-0.09968	dipole	0.01394	0	-0.08352
N4		0.32268				0.25859		
	quadrupole	0	-0.47522		quadrupole	0	-0.39969	
		-0.00615	0	0.15254		-0.00559	0	0.1411
	charge	-0.58349			charge	-0.59795		
	dipole	0.16947	0	-0.16235	dipole	0.15248	0	-0.1608
O3		-0.48364				-0.4632		
	quadrupole	0	0.24811		quadrupole	0	0.20151	
		0.16086	0	0.23553		0.14678	0	0.26169

	charge	-0.58349			charge	-0.59795		
	dipole	0.16947	0	-0.16235	dipole	0.15248	0	-0.1608
O4		-0.48364				-0.4632		
	quadrupole	0	0.24811		quadrupole	0	0.20151	
		0.16086	0	0.23553		0.14678	0	0.26169
	charge	0.05858			charge	0.06641		
	dipole	-0.00449	0	0.23281	dipole	-0.00368	0	0.25493
C3		0.64368				0.62741		
	quadrupole	0	-0.66398		quadrupole	0	-0.71165	
		-0.05541	0	0.0203		-0.05002	0	0.08424
	charge	0.172			charge	0.17534		
	dipole	0.00915	0	-0.11591	dipole	0.01068	0	-0.12539
H3		-0.01858				-0.01606		
	quadrupole	0	-0.01595		quadrupole	0	-0.01438	
		0.01255	0	0.03453		0.01301	0	0.03044
	charge	-0.26105			charge	-0.27811		
	dipole	0.05263	0	-0.11256	dipole	0.04008	0	-0.10497
N5		0.1783				0.18124		
	quadrupole	0	-0.81174		quadrupole	0	-0.89258	
		-0.10656	0	0.63344		-0.10914	0	0.71134
	charge	1.10753			charge	1.12935		
	dipole	-0.0011	0	-0.12777	dipole	0.00186	0	-0.11304
N6		0.24631				0.17665		
	quadrupole	0	-0.48563		quadrupole	0	-0.40166	
		-0.01106	0	0.23932		-0.01542	0	0.22501
	charge	-0.57991			charge	-0.59337		
	dipole	0.1768	0	-0.16137	dipole	0.16363	0	-0.15882
O5		-0.53804				-0.52564		
	quadrupole	0	0.27		quadrupole	0	0.22738	
		0.16973	0	0.26804		0.15695	0	0.29826
	charge	-0.57991			charge	-0.59337		
	dipole	0.1768	0	-0.16137	dipole	0.16363	0	-0.15882
O6		-0.53804				-0.52564		
	quadrupole	0	0.27		quadrupole	0	0.22738	
		0.16973	0	0.26804		0.15695	0	0.29826
	charge	0.1916			charge	0.20816		
	dipole	0.00983	0	0.24885	dipole	0.00591	0	0.26287
C4		0.38595				0.39949		
	quadrupole	0	-0.23155		quadrupole	0	-0.29165	
		0.0012	0	-0.1544		-0.00234	0	-0.10784
	charge	0.16784			charge	0.1719		
	dipole	0.00249	0	-0.11353	dipole	0.00244	0	-0.12045
H4		-0.01736				-0.01657		
	quadrupole	0	-0.01745		quadrupole	0	-0.01673	
		0.00319	0	0.03481		0.00296	0	0.0333
	charge	-0.31978			charge	-0.33239		
	dipole	0.11634	0	-0.03004	dipole	0.11766	0	-0.02639
N7		0.21392				0.23545		
	quadrupole	0	-0.84026		quadrupole	0	-0.9269	
		-0.1694	0	0.62634		-0.17854	0	0.69145
	charge	1.09489			charge	1.11717		
	dipole	-0.00035	0	-0.10917	dipole	0.00248	0	-0.096
N8		0.22405				0.15251		
	quadrupole	0	-0.45192		quadrupole	0	-0.3657	
		-0.01018	0	0.22787		-0.01503	0	0.21319
	charge	-0.5766			charge	-0.58971		
	dipole	0.17075	0	-0.15153	dipole	0.15738	0	-0.14906
O7		-0.52777				-0.51577		
	quadrupole	0	0.24991		quadrupole	0	0.20694	
		0.16088	0	0.27786		0.15055	0	0.30883

	charge	-0.5766			charge	-0.58971		
	dipole	0.17075	0	-0.15153	dipole	0.15738	0	-0.14906
O8		-0.52777				-0.51577		
	quadrupole	0	0.24991		quadrupole	0	0.20694	
		0.16088	0	0.27786		0.15055	0	0.30883
	charge	0.18232			charge	0.19031		
	dipole	0.02224	0	0.24849	dipole	0.03035	0	0.26334
C5		0.70524				0.70609		
	quadrupole	0	-0.60163		quadrupole	0	-0.64421	
		-0.00289	0	-0.10361		-0.00174	0	-0.06188
	charge	0.15981			charge	0.16323		
	dipole	0.00429	0	-0.1246	dipole	0.00364	0	-0.13379
H5		-0.01089				-0.00948		
	quadrupole	0	-0.01557		quadrupole	0	-0.01362	
		0.002	0	0.02646		0.00175	0	0.0231
	charge	-0.24043			charge	-0.24184		
	dipole	0.01565	0	-0.17724	dipole	0.01785	0	-0.20848
N9		0.41283				0.38603		
	quadrupole	0	-1.11056		quadrupole	0	-1.2315	
		0.04231	0	0.69773		0.03644	0	0.84547
	charge	1.08741			charge	1.11023		
	dipole	-0.026	0	-0.08274	dipole	-0.02503	0	-0.06493
N10		0.2728				0.21188		
	quadrupole	0	-0.46989		quadrupole	0	-0.39935	
		0.03902	0	0.19709		0.03399	0	0.18747
	charge	-0.54602			charge	-0.56178		
	dipole	0.15365	0	-0.13747	dipole	0.1381	0	-0.13651
O9		-0.50734				-0.48906		
	quadrupole	0	0.25059		quadrupole	0	0.20576	
		0.14582	0	0.25675		0.13157	0	0.2833
	charge	-0.54602			charge	-0.56178		
	dipole	0.15365	0	-0.13747	dipole	0.1381	0	-0.13651
O10		-0.50734				-0.48906		
	quadrupole	0	0.25059		quadrupole	0	0.20576	
		0.14582	0	0.25675		0.13157	0	0.2833
	charge	0.08299			charge	0.09082		
	dipole	-0.10063	0	0.35841	dipole	-0.10093	0	0.38763
C6		0.45046				0.46666		
	quadrupole	0	-0.72292		quadrupole	0	-0.80307	
		0.01505	0	0.27246		0.00626	0	0.33641
	charge	0.16582			charge	0.1743		
	dipole	0.00713	0	-0.12504	dipole	0.00707	0	-0.13036
H6		-0.01457				-0.01433		
	quadrupole	0	-0.01581		quadrupole	0	-0.01561	
		0.00714	0	0.03038		0.0067	0	0.02994
	charge	-0.3324			charge	-0.32849		
	dipole	0.17909	0	0.01683	dipole	0.19113	0	-0.00213
N11		0.07142				0.02798		
	quadrupole	0	-0.37455		quadrupole	0	-0.42827	
		-0.22765	0	0.30313		-0.2714	0	0.40029
	charge	1.06709			charge	1.08743		
	dipole	-0.00165	0	-0.07722	dipole	-0.00199	0	-0.05813
N12		0.25589				0.19624		
	quadrupole	0	-0.48419		quadrupole	0	-0.41241	
		-0.01409	0	0.2283		-0.01406	0	0.21617
	charge	-0.53994			charge	-0.55448		
	dipole	0.14728	0	-0.13817	dipole	0.13154	0	-0.13578
O11		-0.50557				-0.48736		
	quadrupole	0	0.2401		quadrupole	0	0.19398	
		0.14135	0	0.26547		0.12716	0	0.29338

	charge	-0.53994			charge	-0.55448		
	dipole	0.14728	0	-0.13817	dipole	0.13154	0	-0.13578
O12		-0.50557				-0.48736		
	quadrupole	0	0.2401		quadrupole	0	0.19398	
		0.14135	0	0.26547		0.12716	0	0.29338

Table S3. Atom-by-atom comparison of polarizability parameters of ε-CL-20 molecule fitted by AMOEBA and TMPFF.

atom index	α_{AMOEBA} (Å^3)	α_{TMPFF} (Å^3)	atom index	α_{AMOEBA} (Å^3)	α_{TMPFF} (Å^3)
1-C	1.334	1.59	19-C	1.334	1.07
2-H	0.496	0.45	20-H	0.496	0.27
3-N	1.073	1.52	21-N	1.073	1.67
4-N	1.073	0.90	22-N	1.073	1.13
5-O	0.837	0.57	23-O	0.837	0.72
6-O	0.837	0.75	24-O	0.837	0.76
7-C	1.334	2.37	25-C	1.334	1.77
8-H	0.496	1.14	26-H	0.496	0.70
9-N	1.073	1.64	27-N	1.073	1.82
10-N	1.073	0.84	28-N	1.073	0.82
11-O	0.837	0.83	29-O	0.837	0.74
12-O	0.837	0.61	30-O	0.837	1.01
13-C	1.334	0.93	31-C	1.334	0.69
14-H	0.496	0.32	32-H	0.496	0.20
15-N	1.073	1.64	33-N	1.073	1.15
16-N	1.073	1.16	34-N	1.073	0.81
17-O	0.837	0.74	35-O	0.837	0.74
18-O	0.837	0.75	36-O	0.837	0.88

As shown in Table S3, the polarizabilities of C, H, N, and O atoms in AMOEBA are uniformly set as 1.334, 0.496, 1.073, and 0.837, respectively. On the other hand, the polarizability estimated by the QTAIM method differs, reflecting the different chemical environments of each atom. For example, 3-N is located in the bone structure of the cage of ε-CL-20, and 4-N is located in the $–NO_2$ group, the lone pair electrons on the sp3 hybridized 3-N atom can be easier affected by an external electric field than the delocalized electrons on the sp2 hybridized 4-N atom, thus the polarizabilities are 1.52 and 0.90, respectively. The AMOEBA parameters overestimate the polarizabilities of C, H, and O atoms, and underestimate the polarizability of N atoms. Same results for the β- and γ-CL-20.

Table S4. Polarizability parameters calculated with and without D3 of ε-CL-20

ID	No D3 correction	With D3 correction	ID	No D3 correction	With D3 correction	ID	No D3 correction	With D3 correction
C1	1.59	1.59	C3	0.93	0.93	C5	1.77	1.77
H1	0.45	0.45	H3	0.32	0.32	H5	0.7	0.7
N1	1.52	1.52	N5	1.64	1.64	N9	1.82	1.82
N2	0.9	0.9	N6	1.16	1.16	N10	0.82	0.82
O1	0.57	0.57	O5	0.74	0.74	O9	0.74	0.74
O2	0.75	0.75	O6	0.75	0.75	O10	1.01	1.01
C2	2.37	2.37	C4	1.07	1.07	C6	0.69	0.69
H2	1.14	1.14	H4	0.27	0.27	H6	0.2	0.2
N3	1.64	1.64	N7	1.67	1.67	N11	1.15	1.15
N4	0.84	0.84	N8	1.13	1.13	N12	0.81	0.81
O3	0.83	0.83	O7	0.72	0.72	O11	0.74	0.74
O4	0.61	0.61	O8	0.76	0.76	O12	0.88	0.88

Table S5. Parameters of top 3 predicted crystal structures of conforamtion#1 with lowest energies, in comparison with β-CL-20 (PUBMUU01) in CCDC database.

ID	Space group	ρ (g/cm^3)	Energy (kcal/mol)	a(Å)	b(Å)	c(Å)	α(º)	β(º)	γ(º)
EA435	$Pca2_1$	1.980	-224.765	9.598	11.768	13.014	90.00	90.00	90.00
EA1155	$P2_12_12_1$	2.012	-224.688	7.893	12.269	14.762	90.00	90.00	90.00
EA1114	$Pca2_1$	1.918	-224.568	11.153	11.534	11.793	90.00	90.00	90.00
PUBMUU01	$Pca2_1$	1.985	/	9.676	11.649	13.006	90.00	90.00	90.00

Table S6. Parameters of top 3 predicted crystal structures of conforamtion#2 with lowest energies, in comparison with γ-CL-20 (PUBMUU) in CCDC database.

ID	Space group	ρ (g/cm^3)	Energy (kcal/mol)	a(Å)	b(Å)	c(Å)	α(º)	β(º)	γ(º)
EA2024	$P2_1/c$	1.910	-226.441	13.851	7.714	15.301	90.00	111.25	90.00
EA2103	$P2_1$	1.922	-226.357	13.129	7.747	15.973	90.00	111.23	90.00
EA2300	$P2_1/c$	1.953	-226.053	12.487	8.896	14.113	90.00	108.11	90.00
PUBMUU	$P2_1/c$	1.916	/	13.231	8.170	14.876	90.00	109.17	90.00

Table S7. Parameters of top 3 predicted crystal structures of conforamtion#3 with lowest energies, in comparison with ε-CL-20 (PUBMUU02) in CCDC database.

ID	Space group	ρ (g/cm^3)	Energy (kcal/mol)	a(Å)	b(Å)	c(Å)	α(º)	β(º)	γ(º)
EA1497	$P2_1/c$	2.021	-228.381	9.007	12.329	13.604	90.00	107.61	90.00
EA223	$P2_12_12_1$	1.989	-227.370	9.108	12.227	13.134	90.00	90.00	90.00
EA153	$P2_12_12_1$	1.986	-226.994	9.107	12.215	13.171	90.00	90.00	90.00
PUBMUU02	$P2_1/c$	2.044	/	8.852	12.556	13.386	90.00	106.82	90.00

1. Kresse, G.; Hafner, J., Ab Initio Molecular Dynamics for Liquid Metals. Physical Review B 1993, 47, 558-561.
2. Kresse, G.; Furthmüller, J., Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Computational Materials Science 1996, 6, 15-50.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865-3868.
4. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H-Pu. The Journal of Chemical Physics 2010, 132, 154104.
5. Stone, A. J. and Alderton, M. Distributed multipole analysis: methods and applications. Molecular Physics 1985, 56, 1047-1064.