Supporting Information

Solvatomorphism and Phase Transformation of CL-20: Probing Properties and Investigating Mechanisms

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Preparation of the powdered solvate samples

Samples of CL-20·DMC and CL-20·DES were prepared by adding a requisite amount of ε-CL-20 into the pure solvents and heating the mixtures to certain temperatures below their respective boiling points. Then the solvates were crystallized from the solutions by spontaneous cooling to 20 °C.

CL-20·EMC and CL-20·DEO was prepared by producing the saturated solution of ε-CL-20 in EMC and DEO respectively at 50 °C and subsequently evaporating the solution at 20 °C for a few hours to obtain the solvates.

CL-20·ACN, CL-20·DMA, CL-20·DMF and CL-20·γ-BL were prepared by anti-solvent crystallization method. Concentrated solutions of CL-20 in ACN, DMA, DMF and γ-BL were prepared at 20 °C. A certain amount of CTC was added into these solutions and kept stirring for 30 min, then we obtained corresponding solvates.

CL-20·PX was prepared by slurry method wherein excess ε-CL-20 was added to PX and allowed to equilibrated for more than 72 h at 60 °C. The mixture was cooled to 20 °C and CL-20·PX formed.

These precipitated solvates were stored in the mother liquor, filtered and dried before characterization.

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Table S1 Solvent classification and the crystal forms obtained during solvate screening.

Solvent	Group[a]	Classification[b]	Crystal form
n-Heptane	1	AAA	N/A[c]
Cyclohexane	1	AAA	N/A[c]
Ethyl formate	2	AP	Form ε
Ethyl acetate	2	AP	Form ε
Butyl acretate	2	AP	Form ε
Dimethyl carbonate	2	AP	CL-20·DMC solvate
Diethyl carbonate	2	AP	Form ε
Methanol	3	HBD	Form ε
Ethanol	3	HBD	Form ε
1-Propanol	3	HBD	Form ε
2-Propanol	3	HBD	Form ε
Toluene	4	AALP	N/A[c]
o-Xylene	4	AALP	Form ε
m-Xylene	4	AALP	Form ε
Acetone	5	AP	Form ε
Cyclohexanone	5	AP	Form ε
N,*N*-dimethylacetamide	6	AP	CL-20·DMA solvate
Dichloromethane	7	AP	Form ε
Chloroform	7	EPD/HBD/AP	N/A[c]
Nitromethane	8	AP	Form ε

[a] Groups are based on the following solvent parameters: hydrogen bonding capability, dielectric constant, polarity/dipolarity and dipole moment.

[b] Abbreviated instructions: AAA = aliphatic aprotic apolar, AP = aprotic polar, HBD = hydrogen bond donors, AALP = aromatic apolar or lightly polar, EPD = electron pair donors.

[c] No crystals were obtained due to too low solubility.

FTIR spectra

The FTIR spectra of CL-20 solvates and polymorphs are presented in Fig. S1. Some new peaks appeared due to the inclusion of different solvent molecules, which were marked in the spectra using asterisks. The noticeable differences can be observed in the carbonyl group (C=O) stretching region, since most of the solvent molecules are esters and amides. Compared with the FTIR spectra of pure solvents,

some red shifts can be observed in the C=O stretching vibration, appearing at 1742, 1737, and 1738 cm^{-1} for CL-20·DMC, CL-20·EMC, and CL-20·DEO, respectively.

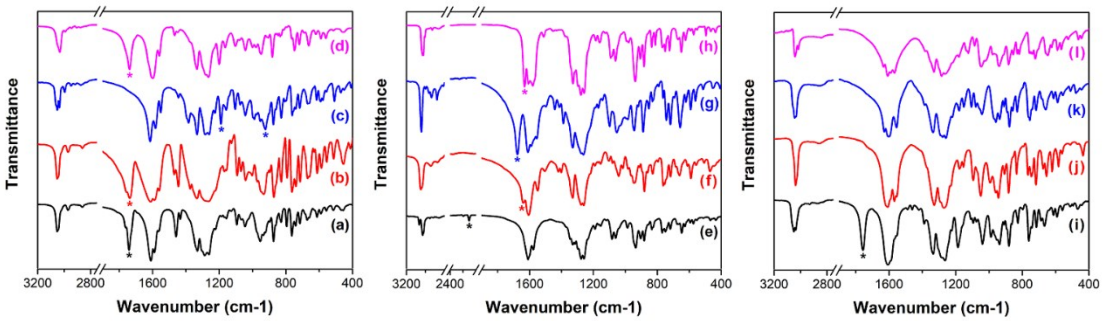


Fig. S1 The FTIR spectra of CL-20 solvates and polymorphs (a) CL-20·DMC, (b) CL-20·EMC, (c) CL-20·DES, (d) CL-20·DEO, (e) CL-20·ACN, (f) CL-20·DMA, (g) CL-20·DMF, (h) CL-20·PX, (i) CL-20·γ-BL, (j) form β, (k) form γ, and (l)form ε. The asterisks mark the bands due to the incorporation of solvent molecules.

Raman spectra

Raman measurements were also conducted to characterize CL-20 solvates owing to the convenient sample preparation method, which has no destructive effect on the crystal samples. The Raman spectra of the nine solvates are summarized and compared with the figures of three polymorphs in Fig. S2. The CL-20 solvates are readily distinguishable from the other three polymorphs, based on distinct differences in peak positions and relative intensities. The most easily noticeable difference in Raman spectra was in range from 200 cm^{-1} to 400 cm^{-1}. The peak at 301 cm^{-1} appears for CL-20·DMC and CL-20·EMC, whereas the peak for CL-20·DES moves slightly to 305 cm^{-1} with a tiny hump following it. CL-20·DEO shows peak at 288 cm^{-1} and CL-20·ACN shows a single peak at 273 cm^{-1}. CL-20·DMA and CL-20·DMF are characterized by the peak at 308 cm^{-1} and 314 cm^{-1}, respectively. CL-20·PX and CL-20·γ-BL exhibit characteristic peaks at 321 cm^{-1} and 310 cm^{-1}, respectively. Moreover, CL-20·DMC and CL-20·EMC show similar Raman spectra throughout the frequency

range owing to the structural similarities.

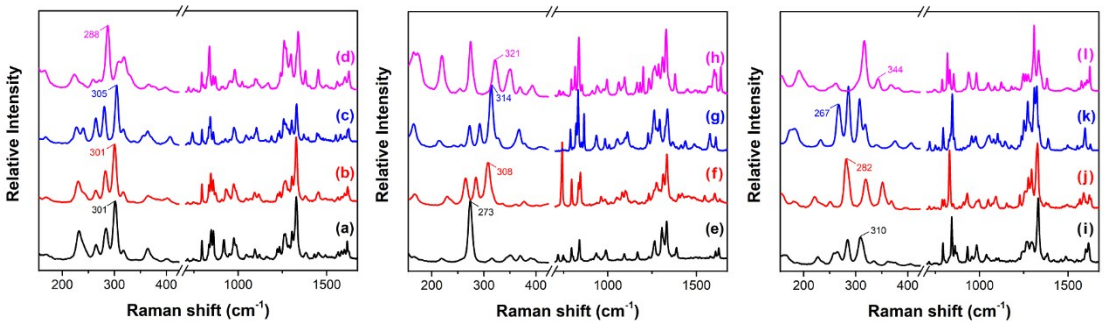


Fig. S2 The Raman spectra of CL-20 solvates and polymorphs (a) CL-20·DMC, (b) CL-20·EMC, (c) CL-20·DES, (d) CL-20·DEO, (e) CL-20·ACN, (f) CL-20·DMA, (g) CL-20·DMF, (h) CL-20·PX, (i) CL-20·γ-BL, (j) form β, (k) form γ, and (l)form ε.

Table S2 The torsion angles of CL-20 molecules in CL-20 polymorphs and solvates.

Crystal form	C(1)-C(2)-N(1)-N(2)[a]	C(2)-C(1)-N(5)-N(4)	C(4)-C(3)-N(5)-N(6)
Form β	-67.24	138.95	150.45
Form γ	-141.07	155.33	164.92
Form ε	-142.26	67.14	147.88
CL-20·DMC	-149.27	154.56	169.22
CL-20·EMC	-151.80	152.14	167.72
CL-20·DES	-146.18	152.13	167.47
CL-20·DEO	-136.80	141.56	158.14
CL-20·ACN	-70.66	152.02	143.42
CL-20·DMA	-140.73	153.43	162.15
CL-20·DMF	-139.95	126.86	143.22
CL-20·PX	-66.98	146.27	143.67
CL-20·γ-BL	-145.95	155.96	159.79

[a] The definition of atomic numberings is provided in Fig. 5a.

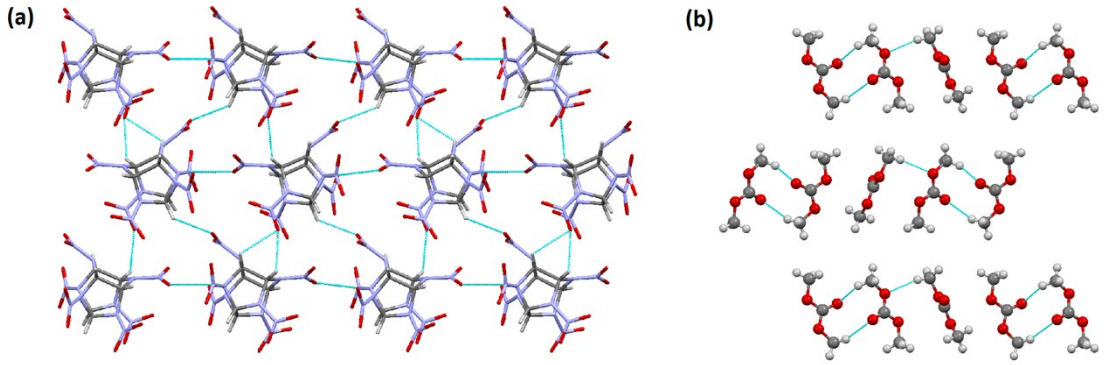


Fig. S3 Intermolecular interactions of (a) CL-20 molecular layer and (b) DMC molecular layer in CL-20·DMC (viewed along *c*-axis).

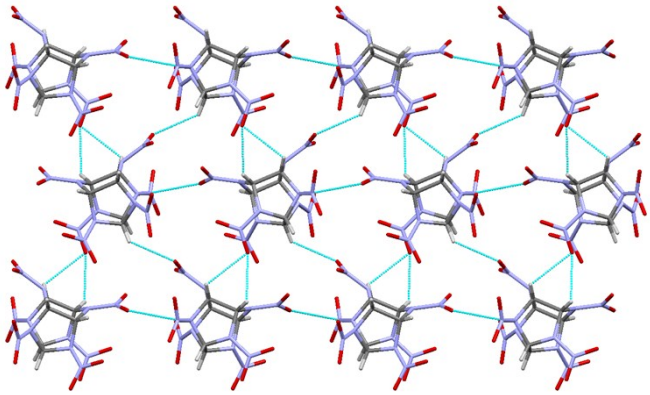


Fig. S4 Intermolecular interactions of CL-20 molecular layer in CL-20·EMC (viewed along *c*-axis).

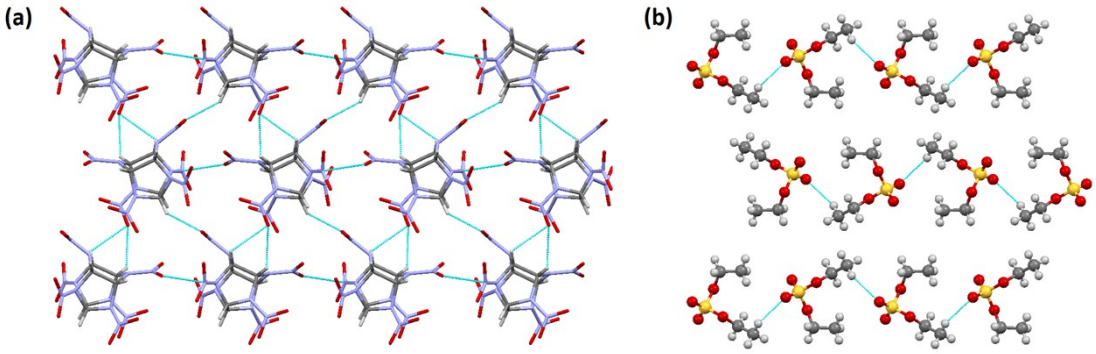


Fig. S5 Intermolecular interactions of (a) CL-20 molecular layer and (b) DES molecular layer in CL-20·DES (viewed along *c*-axis).

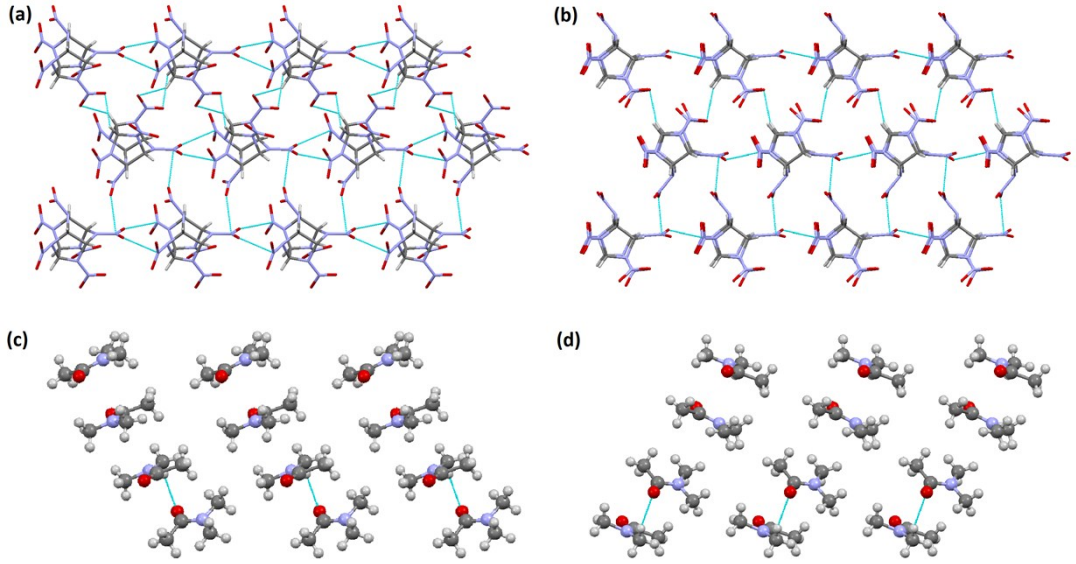


Fig. S6 Intermolecular interactions of (a)-(b) the two kinds of CL-20 molecular layers and (c)-(d) the two kinds of DMA molecular layers in CL-20·DMA (viewed along *c*-axis).

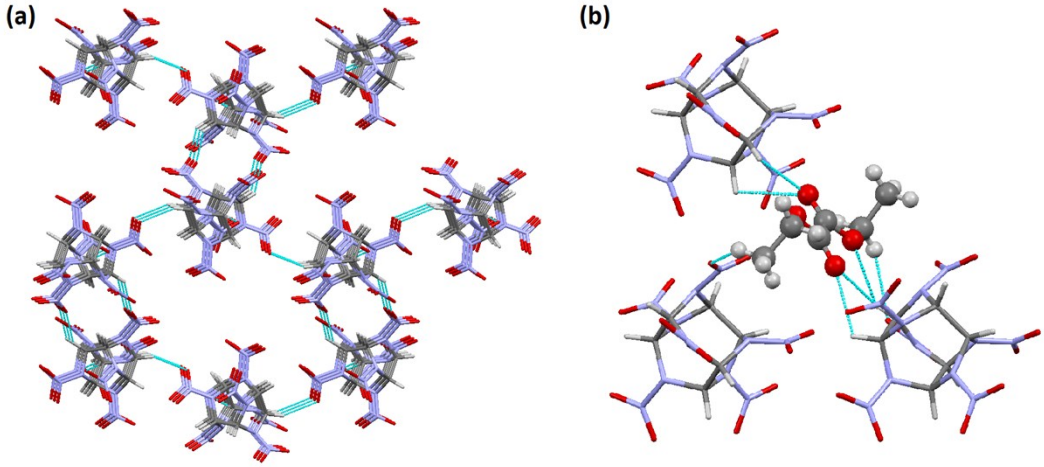


Fig. S7 (a) Intermolecular interactions between adjacent infinite CL-20 chains (viewed along *a*-axis); and (b) the host-guest intermolecular interactions (viewed along *b*-axis) in CL-20·DEO.

Structural information of CL-20·ACN (CCDC: 1569059)

CL-20·ACN belongs to the monoclinic system, space group *C*2/*c*, the molecular stoichiometry ratio of CL-20 to acetonitrile is 1:1. Compared with the published crystal structures of CL-20 polymorphs, the molecular conformation of CL-20 in acetonitrile solvate is close to form β. It can also be observed that the CL-20 acetonitrile solvate is a channel-type solvate, in which the acetonitrile molecules

occupy the channels along *b*-axis. CL-20 and ACN molecules interact depending on the C–H···O, C–H···N, and O···C intermolecular interactions.

Structural information of CL-20·DMF (CCDC: 832144)

CL-20·DMF is crystallized in the triclinic crystal system, space group $P\bar{1}$, and molecules are arranged in alternate layers of CL-20 and DMF. In DMF layer, two independent molecules form dimers over inversion centers. In CL-20 layers, the molecules adopt the molecular conformation of γ-polymorph, and the CL-20 molecules are lined by weak C–H···O interactions along two dimensions. In the third direction (perpendicular to the layers), the most significant intermolecular interaction occurs between the O atoms of DMF and the H atoms of CL-20 (C–H···O, 2.241 to 2.732 Å).

Structural information of CL-20·PX (CCDC: 1022276)

CL-20·PX belongs to the orthorhombic system, space group *Pbca*, and the molecular number ratio of CL-20 to *p*-xylene is 2:1. The γ-conformation of the CL-20 molecules can be observed in the crystal structure of CL-20·PX. Alternation of two CL-20 layers and one *p*-xylene layer can be found. In CL-20 layers, a network of weakly linked CL-20 molecules is established through C–H···O intermolecular interactions. The most important host-guest interactions exist between the methyl H atoms of *p*-xylene and the nitro O atoms of CL-20. Besides, the O···C and O···N stacking interactions between CL-20 and *p*-xylene also stabilize the structure of CL-20·PX.

Structural information of CL-20·γ-BL (CCDC: 832146)

CL-20·γ-BL is crystallized in the monoclinic system, space group *Cc*, and the molecular number ratio of CL-20 to γ-BL is 1:1. There are four CL-20 molecules and four γ-BL molecules in one asymmetric unit. The CL-20 molecules adapt the γ-

conformation and are linked by C–H···O (2.326(6) to 2.663(6) Å) to form chains running parallel to the *a*-axis. Moreover, the chains can be arranged in two layers, resulting in a zig-zag network of CL-20 molecules in the *ab*-plane. The γ-BL molecules form two chains running parallel to the *a*-axis, and no significant interactions are observed between γ-BL molecules themselves. The host and guest molecules are contacted by C–H···O interactions between the H atoms of CL-20 and the ring/carbonyl oxygen of γ-BL.

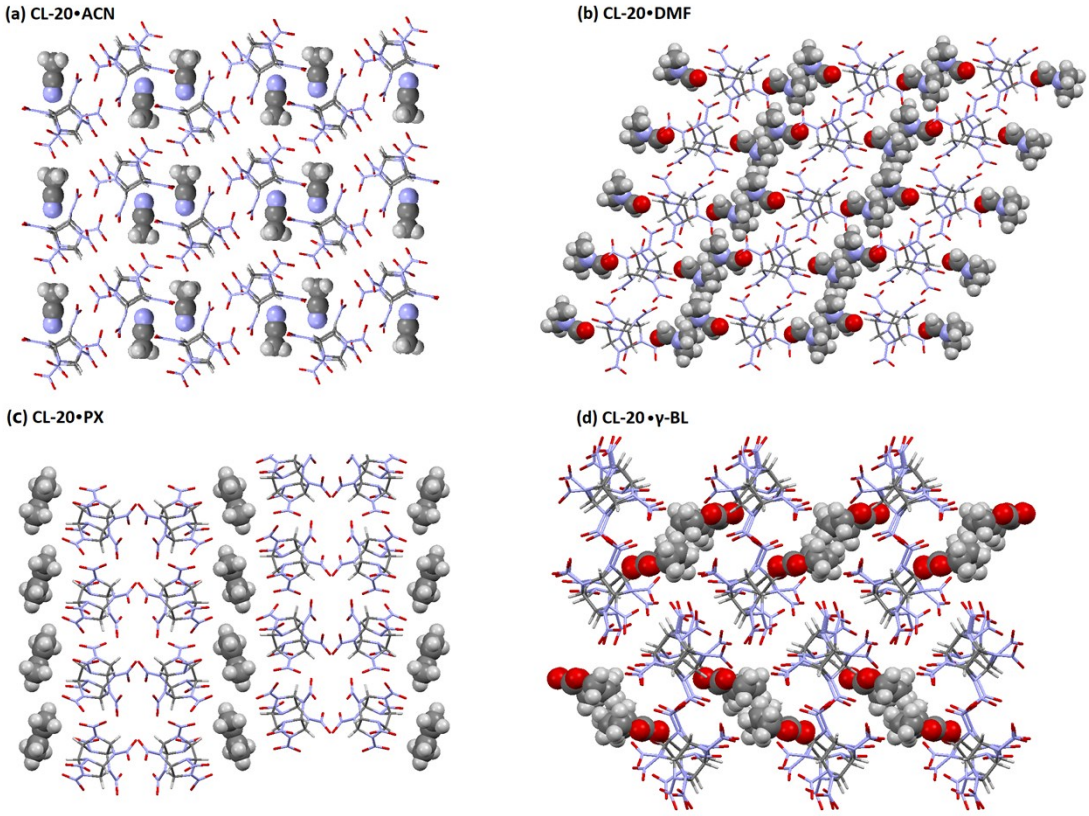


Fig. S8 The packing diagrams for the already published CL-20 solvates. Packing diagrams for (b), (c) and (d) are viewed along *a*-axis; packing diagrams for (a) is viewed along *b*-axis.

Table S3 Geometric parameters of intermolecular interactions in CL-20 polymorphs and solvates.[a]

D—H···A [b]	H···A/Å	D···A/Å	D—H···A/°	D—H···A	H···A/Å	D···A/Å	D—H···A/°
Form β				CL-20·DMA			
C7-H7···O4A	2.55	3.273(5)	135	C4-H4···O25	2.11	2.857(5)	130
C9-H9···O6A	2.58	3.233(4)	134	C7-H7···O26	2.13	2.795(5)	122

C11-H11···O10B	2.54	3.161(4)	127	C8-H8···O28	2.42	2.905(5)	109
Form γ				C9-H9···O28	2.49	2.933(5)	106
C1-H1···O6A	2.55	3.324(4)	137	C10-H10···O26	2.53	3.018(6)	110
C9-H9···O2A	2.47	3.326(3)	156	C15-H15C···O24	2.55	3.300(8)	133
Form ε				C16-H16B···O24	2.58	3.441(8)	147
C1-H1···O6B	2.44	3.177(3)	136	C20-H20B···O10	2.46	3.174(8)	129
C9-H9···O2A	2.52	3.360(3)	150	C23-H23C···O23	2.54	3.499(9)	165
C11-H11···O8B	2.54	3.052(3)	116	CL-20·DMF			
CL-20·DMC				C2-H21···O40	2.54	2.913(2)	102
C4-H4···O31	2.34	2.933(3)	117	C5-H51···O31	2.40	2.891(2)	110
C7-H7···O29	2.38	3.067(3)	126	C6-H61···O31	2.24	2.797(3)	115
C9-H9···O29	2.26	3.008(3)	131	C34-H342···O26	2.51	3.245(2)	134
C10-H10···O25	2.34	3.117(3)	134	CL-20·γ-BL			
C1-H1···O32	2.28	3.235(3)	159	C107-H1071···O138	2.40	2.900(10)	111
C15-H15A···O13	2.53	3.488(4)	165	C114-H1141···O138	2.45	2.916(10)	109
C20-H20C···O20	2.59	3.167(4)	118	C122-H1221···O6	2.47	3.417(10)	163
C20-H20C···O8	2.60	3.500(4)	153	C22-H221···O137	2.39	2.898(11)	112
CL-20·DES				C23-H231···O137	2.50	2.973(11)	109
C1-H1···O14	2.58	3.042(3)	108	C30-H301···O7	2.55	3.506(10)	166
C2-H2···O14	2.54	3.013(3)	109	C59-H591···O7	2.32	2.845(10)	114
C4-H4···O13	2.34	3.022(3)	125	C82-H821···O6	2.28	2.851(10)	116
C1-H1···O16	2.46	3.419(3)	161	C112-H1121···O1	2.29	3.122(10)	142
C7-H7A···O8	2.55	3.512(4)	163	C17-H171···O9	2.32	3.128(10)	140
C7-H7B···O5	2.58	3.424(4)	143	C57-H571···O133	2.35	3.149(10)	139
CL-20·DEO				C87-H871···O140	2.41	3.183(10)	135
C1-H1···O15	2.50	3.028(2)	112	C134-H1342···O117	2.46	3.067(10)	121
C2-H2···O15	2.57	3.072(2)	111	C134-H1341···O99	2.50	3.139(11)	124
C3-H3···O13	2.49	2.903(2)	104	C141-H1412···O26	2.44	3.257(11)	142
C4-H4···O13	2.59	2.961(2)	102	C141-H1411···O35	2.47	3.037(12)	116
C1-H1···O14	2.55	3.414(2)	145	C1-H11···O131	2.48	3.348(13)	146
C8-H8B···O1	2.59	3.371(2)	136	C1-H12···O27	2.54	3.356(13)	142
C12-H12A···O5	2.54	3.206(2)	125	C135-H1351···O42	2.39	3.132(13)	135
CL-20·ACN				C2-H21···O49	2.45	3.130(11)	126
C1-H1A···N13	2.41	3.205(3)	138	C2-H22···O67	2.42	3.054(12)	122
							120
C4-H4A···N13	2.36	3.180(3)	140	C10-H101···O20	2.59	3.189(10)	
C7-H7B···O9	2.57	3.348(5)	145	C10-H101···O80	2.40	3.056(10)	125
CL-20·DMA				C10-H102···O105	2.45	3.245(11)	138
C2-H2···O27	2.52	2.945(5)	105	C13-H132···O129	2.45	3.052(12)	120
C3-H3···O27	2.44	2.900(5)	108				

[a] Definition of the atomic numberings can be obtained in CIF files.

[b] D = Donor, A = Acceptor.

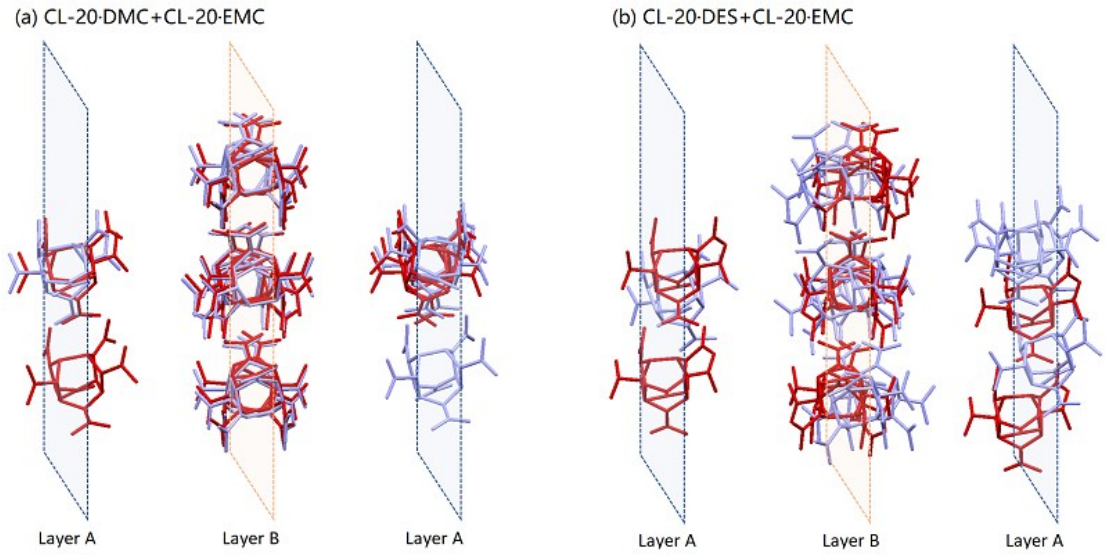


Fig. S9. Overlay of the packing motifs of CL-20 molecules in (a) CL-20·DMC + CL-20·EMC, (b) CL-20·DES + CL-20·EMC.

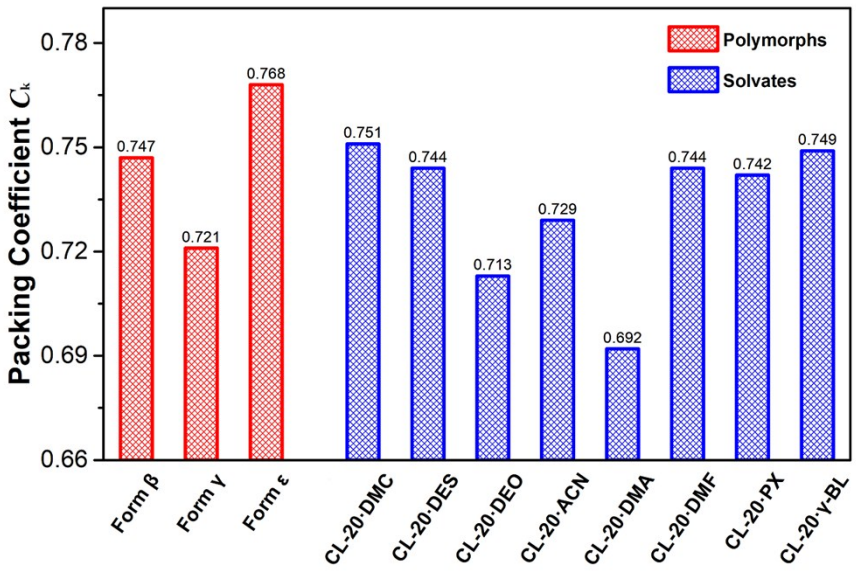


Fig. S10 The packing coefficients of CL-20 polymorphs and solvates.

Hirshfeld surface analysis

For CL-20 solvates, the middle part between the spikes refer to H···H and O···O contacts. CL-20·DES, CL-20·ACN, CL-20·DMA, CL-20·DMF and CL-20·γ-BL exhibit obvious H···H contacts. The wings regions are more complicated and represent the H···H, O···H, N···H and C···H contacts. The wings regions of CL-20·DMC correspond to the C···H contact. The wings regions of CL-20·DES and CL-

20·DEO represent the H···H, O···H and N···H contacts (see Fig. S11a-b). For CL-20·ACN, the C···H contact exists on the two sides of the plot, and the two small wings represent the H···H, O···H, N···H, and C···H contacts (see Fig. S11c). The wings regions of CL-20·DMA depict the H···H, O···H, N···H and C···H contacts (see Fig. S11d). The C···H contact also exists on the two sides of the plot of CL-20·DMF. The wings regions of CL-20·γ-BL represent the O···H and N···H contacts (see Fig. S11e). In addition, the C···O and C···N contacts are also observed in the plots of the solvates.

For CL-20 polymorphs, the middle part between the two sharp spikes is the O···O contact between the O atoms of nitro groups. Besides, there also exist O···N, H···H, N···H and N···N contacts.

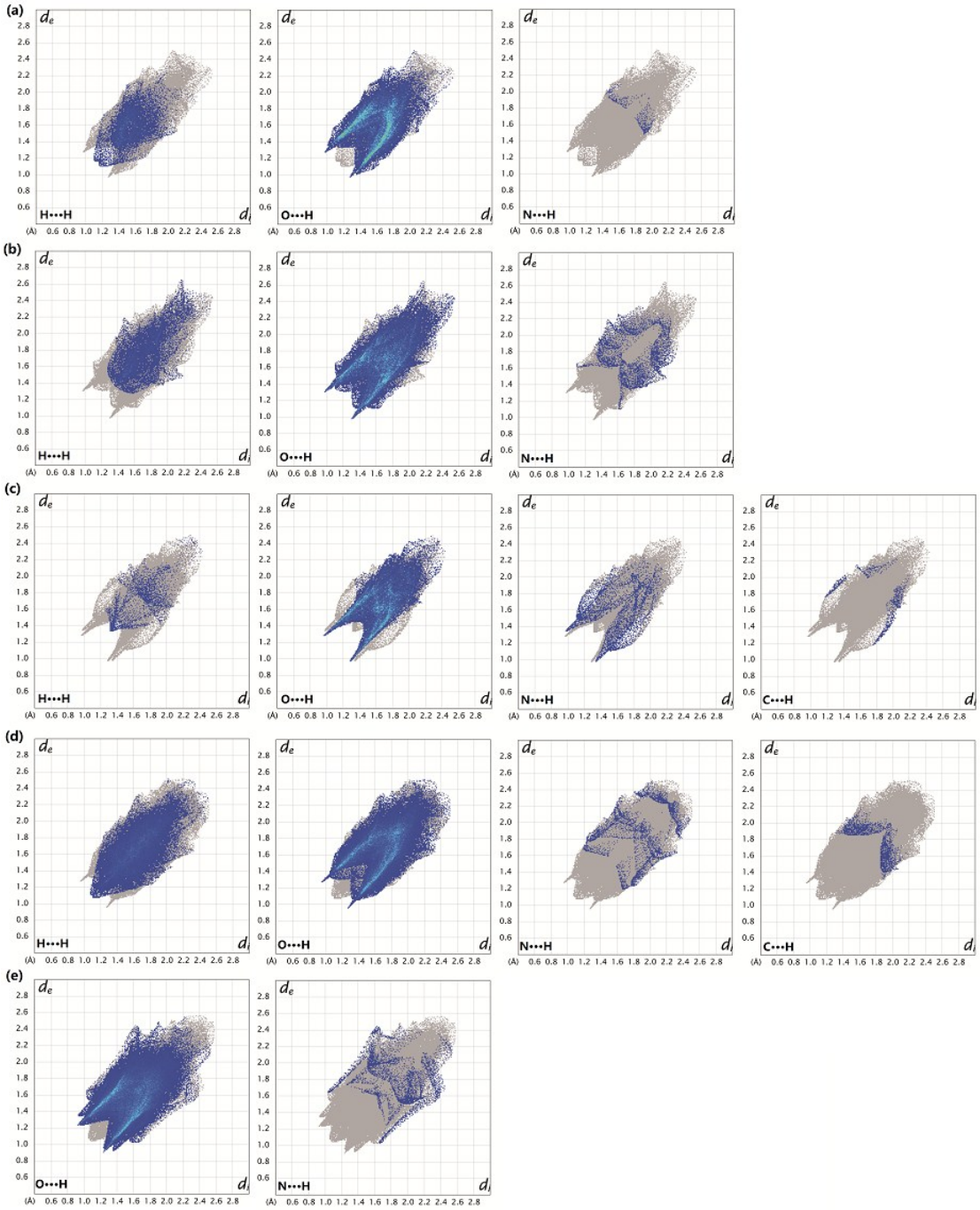


Fig. S11 The 2D fingerprint plots delineated into H···H, O···H, N···H and C···H contacts for (a) CL-20·DES, (b) CL-20·DEO, (c) CL-20·ACN, (d) CL-20·DMA, and (e) CL-20·γ-BL.

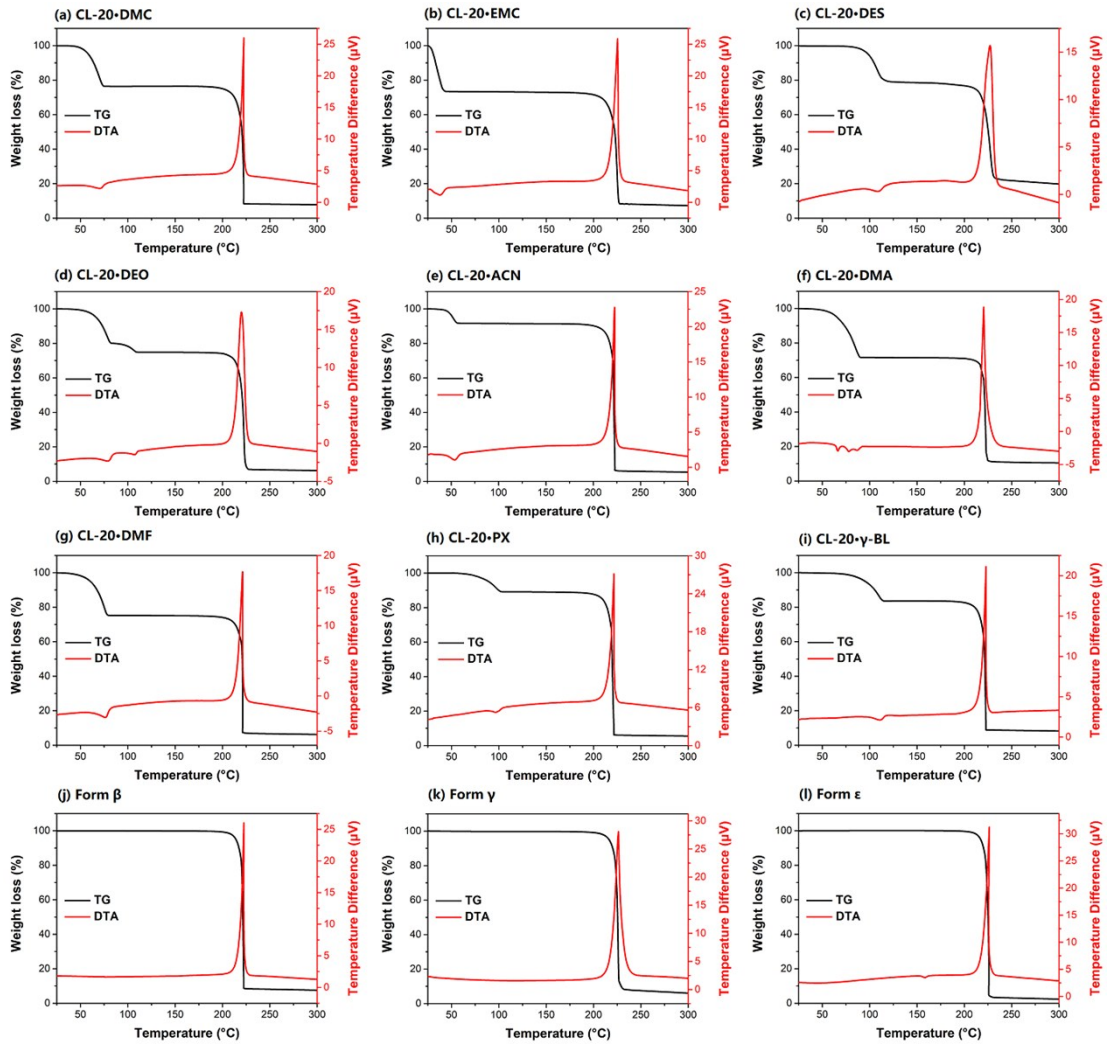
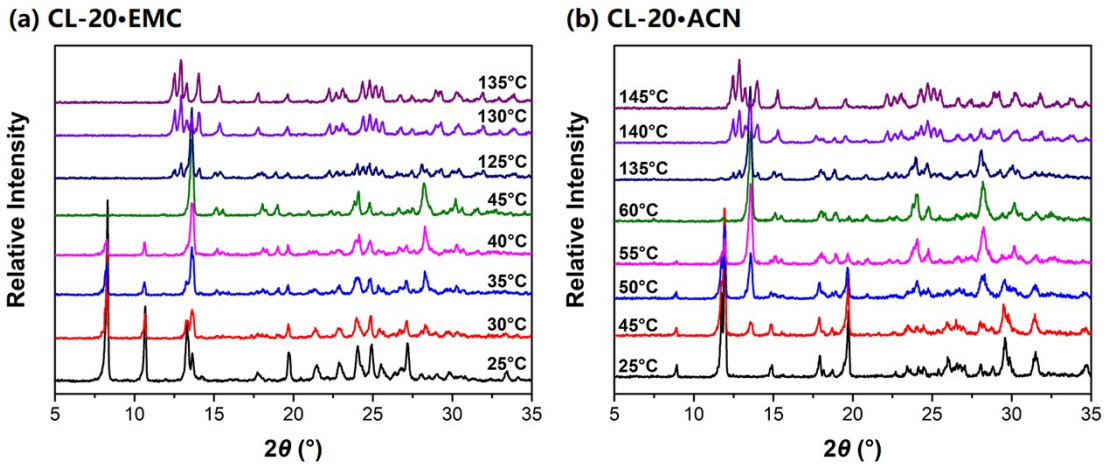


Fig. S12 The TG-DTA curves of (a)-(i) CL-20 solvates and (j)-(l) CL-20 polymorphs.



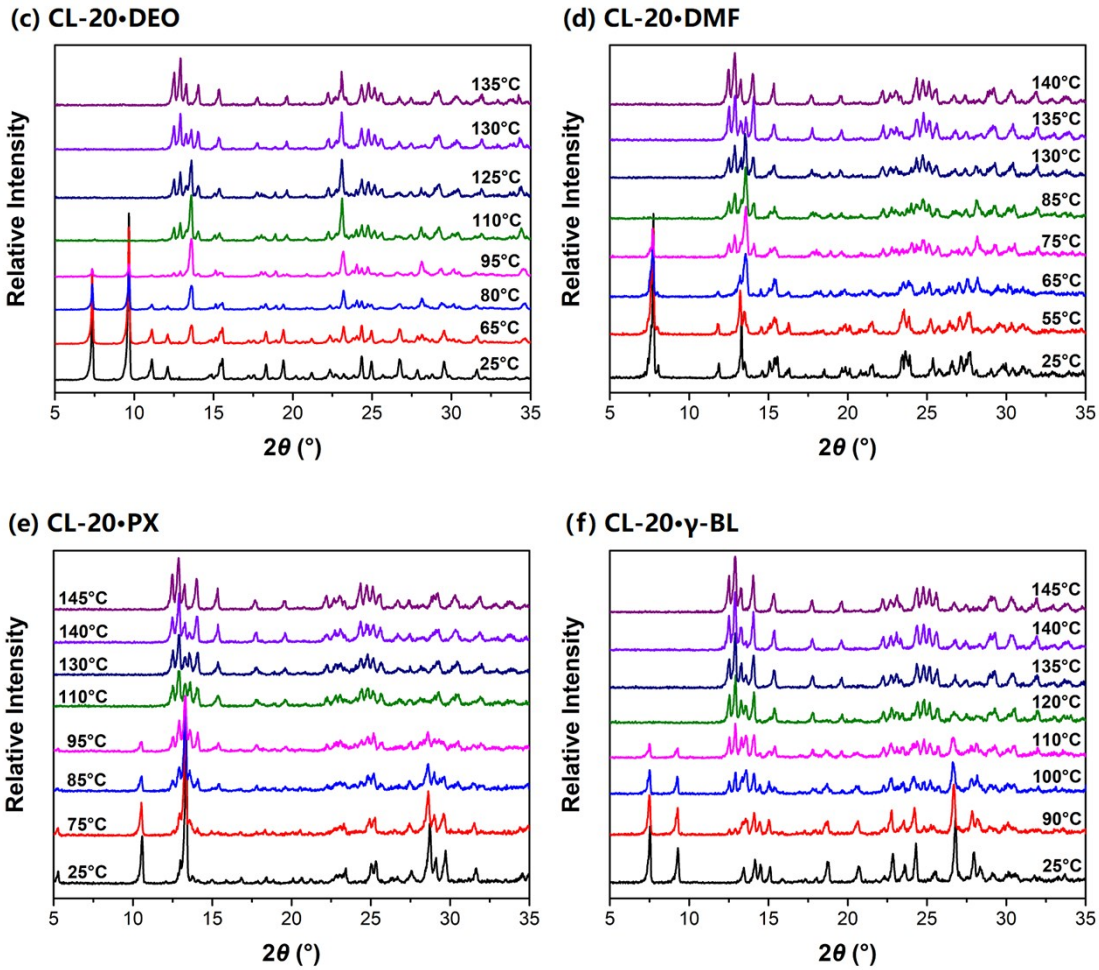


Fig. S13 The VT-PXRD patterns of CL-20 solvates.

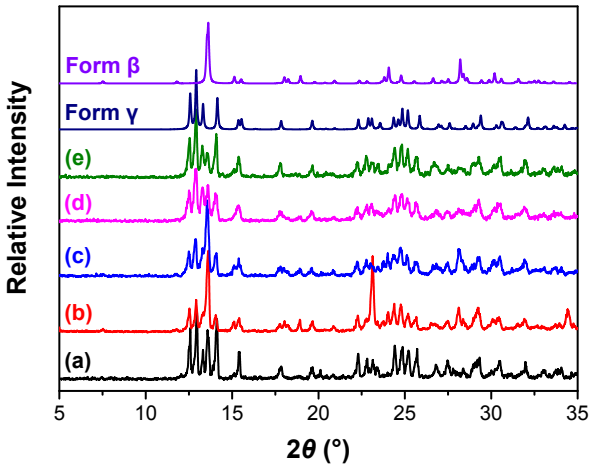


Fig. S14 The PXRD patterns of desolvation products of (a) CL-20·DES, (b) CL-20·DEO, (c) CL-20·DMF, (d) CL-20·PX, and (e) CL-20·γ-BL.

Table S4 Comparison of the desolvation and phase transformation temperatures observed in

DSC and VT-PXRD measurements, respectively.

Solvates or polymorphs	Desolvation onset temperature in DSC T_{desol} (°C)	Observed start temperature of desolvation in VT-PXRD (°C)	Peak temperature of phase transformation T_P (°C)	Observed start temperature of phase transformation in VT-PXRD (°C)
CL-20·DMC	58.1	60	128.5	125
CL-20·EMC	26.2	30	127.6	125
CL-20·DES	98.0	100	---	---
CL-20·DEO	70.6	65	128.1	125
CL-20·ACN	45.7	45	137.7	135
CL-20·DMA	63.7	65	---	---
CL-20·DMF	66.2	65	131.2	135
CL-20·PX	87.0	85	---	---
CL-20·γ-BL	95.4	90	---	---
Form β	---	---	141.83	140
From ε	---	---	159.47	155

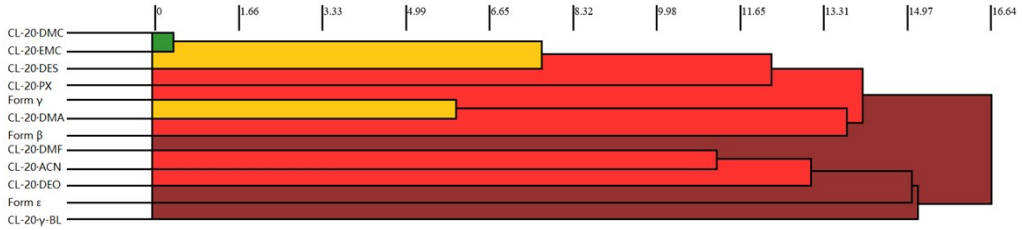


Fig. S15 Packing similarity tree diagram of CL-20 polymorphs and solvates.