Electronic Supplementary Material (ESI) for CrystEngComm.


# Supporting Information

## Theoretical insight into the formation driving force and electric field assistant desolvation process of CL-20 based solvates

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**Table S1** Crystal morphology in vacuum of the CL-20/DMF cocrystal calculated by the AE Method.

| (*h k l*) | Multiplicity | $d_{hkl}$ | $E_{att}$ (kcal mol$^{-1}$) | Area (%) |
|---|---|---|---|---|
| (0 1 0) | 2 | 11.82 | -33.52 | 31.40 |
| (0 0 1) | 2 | 11.31 | -41.57 | 22.61 |
| (1 0 -1) | 2 | 7.40 | -52.05 | 17.72 |
| (0 1 -1) | 2 | 10.72 | -45.98 | 15.69 |
| (1 1 -1) | 2 | 6.59 | -53.01 | 8.83 |
| (1 0 0) | 2 | 7.45 | -68.56 | 3.75 |

**Table S2** Crystallographic information for different solvates of CL-20.

| | CL-20 | CL-20/DMF | CL-20/DO | CL-20/NMP ($H_2O$) |
|---|---|---|---|---|
| CCDC number | 117778 | 832144 | 832145 | 946608 |
| Stoichiometry | - | 1:2 | 1:3.5 | 1:2(:1) |
| Reference | 6 | 16 | 16 | 17 |

**Table S3** The comparison of relaxed lattice parameters of CL-20 and CL-20 based solvates with experimental values.[a]

| | CL-20 | | CL-20/DMF | | CL-20/DO | | CL-20/NMP | |
|---|---|---|---|---|---|---|---|---|
| | Exp | PBE+G06 | Exp | PBE+G06 | Exp | PBE+G06 | Exp | PBE+G06 |
| a | 13.231 | 13.327(0.72%) | 7.784 | 7.871(1.11%) | 10.306 | 10.299(-0.07%) | 11.904 | 11.785(-1.00%) |
| b | 8.170 | 8.325(1.90%) | 12.857 | 13.036(1.39%) | 10.769 | 10.501(-2.49%) | 15.824 | 15.781(-0.27%) |
| c | 14.876 | 14.964(0.59%) | 13.002 | 12.965(-0.28%) | 14.530 | 14.878(2.40%) | 14.504 | 14.358(-1.00%) |
| α | - | - | 113.730 | 112.972(-0.67%) | 73.897 | 72.815(-1.46%) | - | - |
| β | 109.170 | 109.044(-0.12%) | 106.340 | 106.020(-0.30%) | 89.527 | 89.620(0.10%) | 96.671 | 96.348(-0.33%) |
| γ | - | - | 92.430 | 92.577(0.16%) | 85.057 | 84.879(-0.21%) | - | - |
| V | 1518.89 | 1569.34(3.32%) | 1125.060 | 1159.610(3.07%) | 1543.380 | 1530.680(-0.82%) | 2713.600 | 2653.860(-2.20%) |

[a]The absolute values in parentheses correspond to the percentage differences relative to the experimental data.

**Table S4** Calculated and experimental bond lengths (Å) of the N-$NO_2$ bond for the CL-20 molecules in pure CL-20 and its cocrystals.[a]

| Bond | CL-20 | | CL-20/DMF | | CL-20/DO | | CL-20/NMP | |
|---|---|---|---|---|---|---|---|---|
| | Expt | DFT | Expt | DFT | Expt | DFT | Expt | DFT |
| N1-N2 | 1.405 | 1.442 (2.63%) | 1.392 | 1.442 (3.59%) | 1.343 | 1.425 (6.11%) | 1.405 | 1.450 (3.20%) |
| N3-N4 | 1.422 | 1.463 (2.88%) | 1.392 | 1.44 (3.45%) | 1.427 | 1.456 (2.03%) | 1.393 | 1.444 (3.66%) |
| N5-N6 | 1.416 | 1.464 (3.39%) | 1.391 | 1.442 (3.67%) | 1.415 | 1.454 (2.76%) | 1.412 | 1.463 (3.61%) |
| N7-N8 | 1.396 | 1.443 (3.37%) | 1.383 | 1.430 (3.40%) | 1.404 | 1.450 (3.28%) | 1.377 | 1.432 (3.99%) |
| N9-N10 | 1.440 | 1.484 (3.06%) | 1.373 | 1.426 (3.86%) | 1.423 | 1.454 (2.18%) | 1.427 | 1.471 (3.08%) |
| N11-N12 | 1.375 | 1.410 (2.55%) | 1.369 | 1.411 (3.07%) | 1.377 | 1.416 (2.83%) | 1.356 | 1.404 (3.54%) |
| Averg | 1.409 | 1.451 (2.98%) | 1.383 | 1.432 (3.51%) | 1.398 | 1.443 (3.20%) | 1.395 | 1.444 (3.52%) |

[a]The absolute values in parentheses correspond to the percentage differences relative to the experimental data.

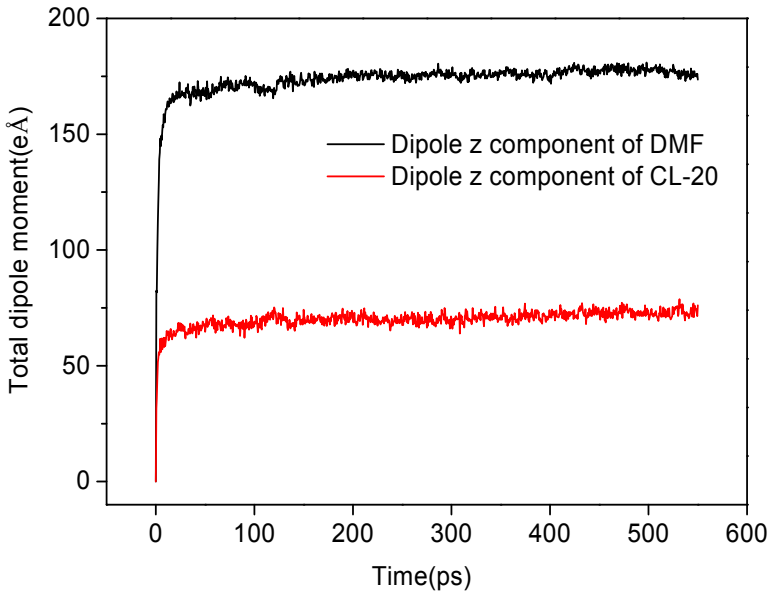


**Fig. S1** Time evolution of the z-component of total dipole moment for DMF and CL-20 molecules in Ez0.5.

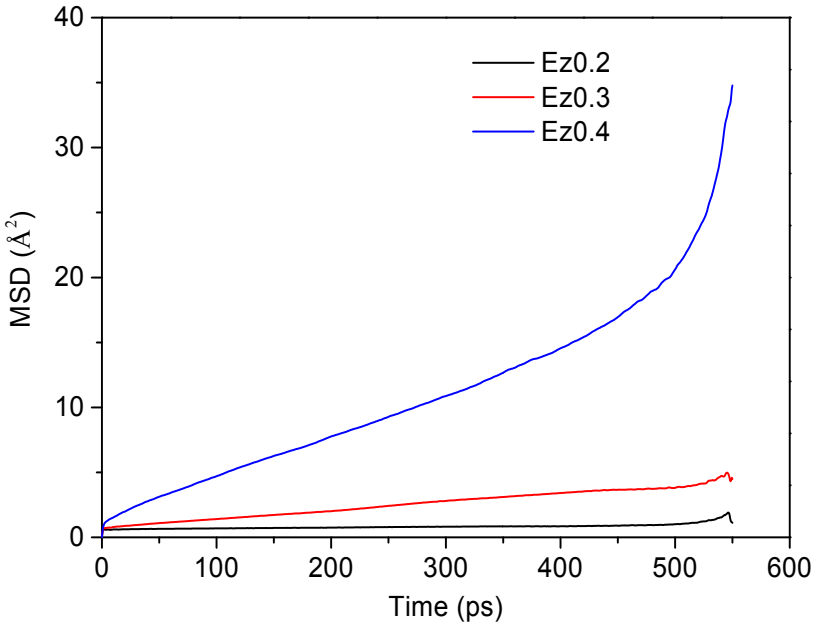


**Fig. S2** Mean square displacements (MSD) of the CL-20 molecules under different electric fields.