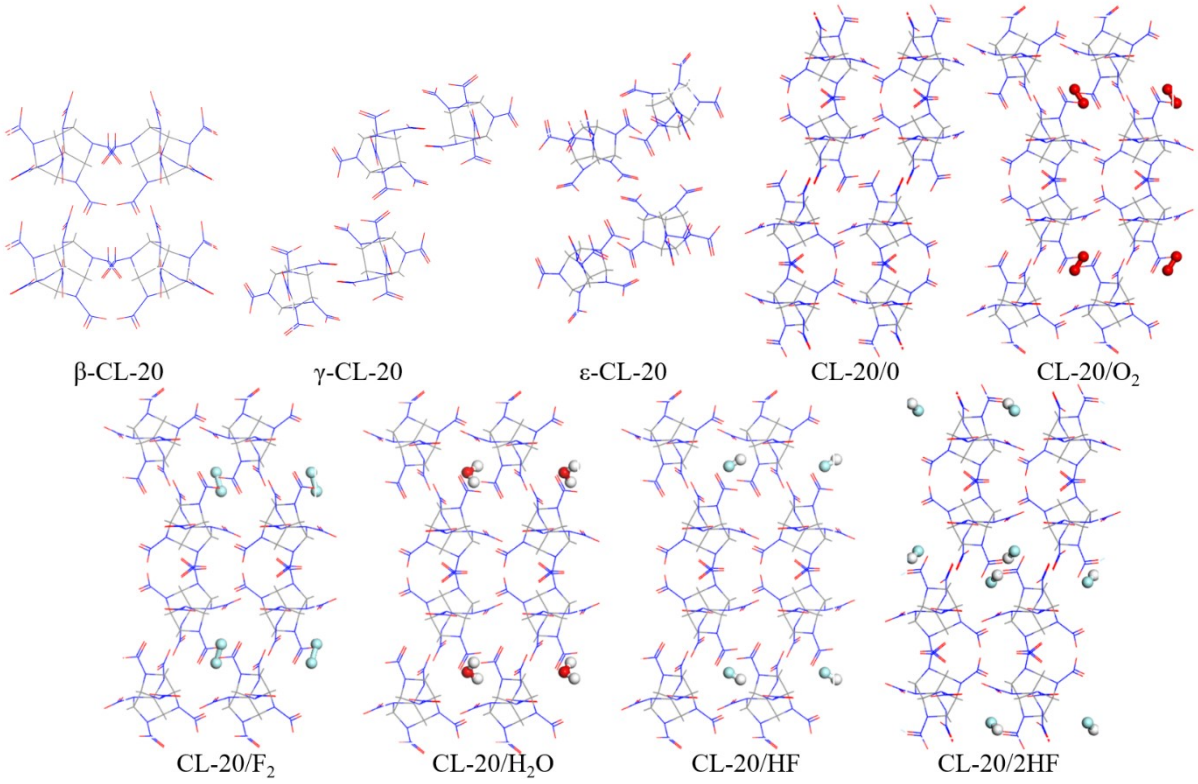


Fig S1 The structure of ε-CL-20 and a series of CL-20 host-guest systems optimized using DFT methods

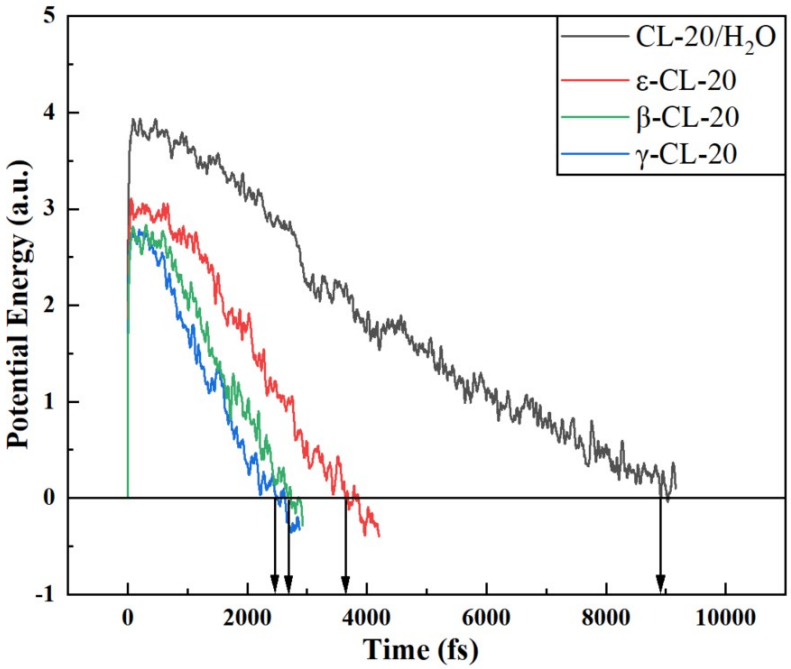


Fig S2 The potential energy evolution of four different polymorphs of CL-20 systems during the adiabatic decomposition process simulated by DFTB

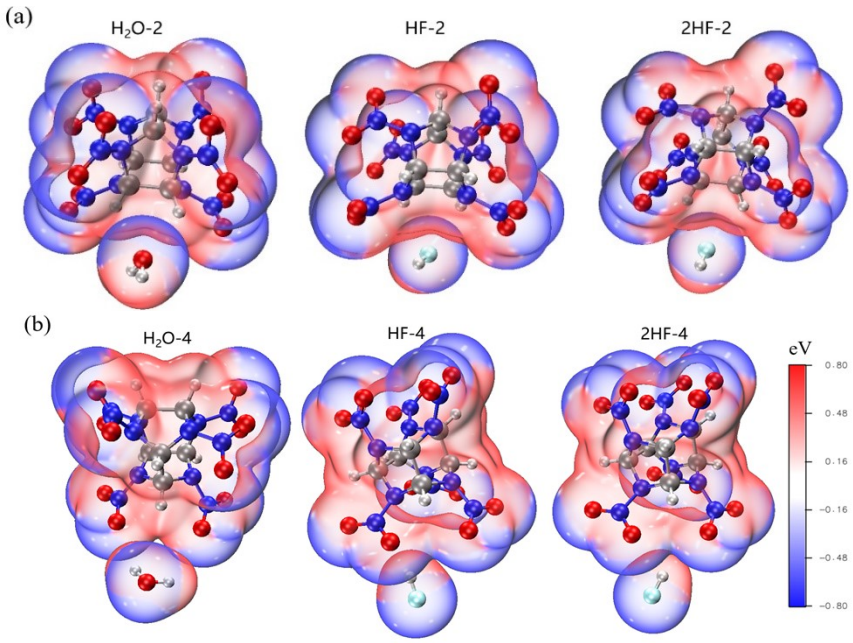


Fig S3 Electrostatic potential surface penetration diagrams of the cluster complexes $H_2O$-2, HF-2, 2HF-2, $H_2O$-4, HF-4, and 2HF-4

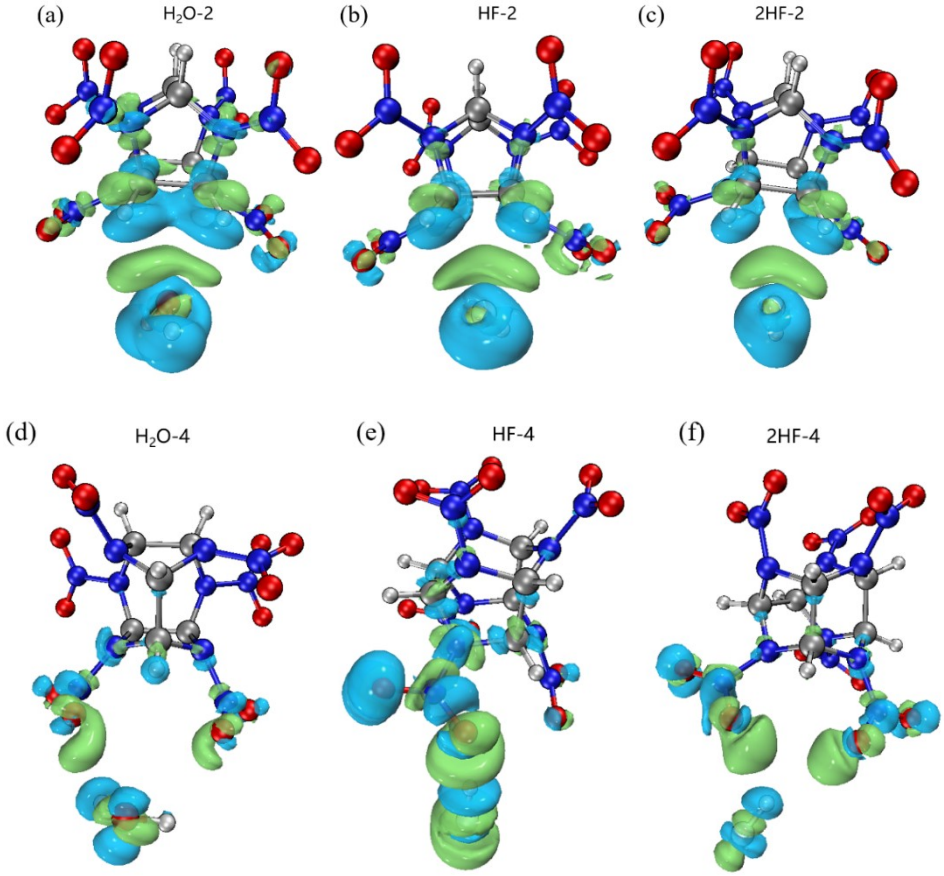


Fig S4 Electron density difference maps of the cluster complexes $H_2O$-2, HF-2, 2HF-2, $H_2O$-4, HF-4, and 2HF-4, where blue indicates a decrease in electron density, green indicates an increase, and the isosurface is set at 0.0005.

Table S1 Comparison of the optimized cell parameters of CL-20/$H_2O$ in this article with experimental values and other computational results

| Lattice parameter | CL-20/$H_2O$ | | | |
|---|---|---|---|---|
| | Expt[13] | GGA/PBE | GGA/PBE[18] | GGA/PBE[20] |
| a(Å) | 9.478 | 9.686(2.19%) | 9.247(-2.44%) | 9.643(1.74%) |
| b(Å) | 13.206 | 13.398(1.45%) | 12.842(-2.76%) | 13.478(2.06%) |
| c(Å) | 23.561 | 23.616(0.23%) | 22.842(-3.05%) | 23.669(0.46%) |
| Total error rate | / | 3.87% | 8.25% | 4.25% |

The values in parentheses represent the percentage difference between the computed and experimental values, while the total error rate refers to the sum of the absolute percentage differences of each cell parameter.

Table S2 The cell parameters of optimized ε-CL-20 and a series of CL-20 host-guest systems

| | Space group | a/Å | b/Å | c/Å | V/Å$^3$ | ρ/(g·cm$^{-3}$) |
|---|---|---|---|---|---|---|
| β-CL-20 | PB21A | 9.806 | 13.248 | 11.730 | 1485.14 | 1.910 |
| γ-CL-20 | P21/N | 13.400 | 8.300 | 15.085 | 1499.57 | 1.835 |
| ε-CL-20 | P21/N | 8.967 | 12.759 | 13.531 | 1482.14 | 1.964 |
| CL-20/0 | PBCA | 9.616 | 13.369 | 23.728 | 3050.49 | 1.908 |
| CL-20/$O_2$ | PB21A | 9.703 | 13.401 | 23.716 | 3083.81 | 1.957 |
| CL-20/$F_2$ | PB21A | 9.649 | 13.368 | 23.853 | 3076.68 | 1.974 |
| CL-20/$H_2O$ | PB21A | 9.686 | 13.398 | 23.616 | 3064.79 | 1.938 |
| CL-20/HF | PB21A | 9.678 | 13.533 | 23.679 | 3101.28 | 1.920 |
| CL-20/2HF | PBCA | 9.730 | 15.518 | 23.624 | 3107.61 | 1.959 |

Table S3 the average bond length ($L_{ave}$), the maximum length ($L_{MAX}$), the average intramolecular hyperconjugation effect ($E_{ave}$), average bond energy (BE), total electron density (ρ(r)), and total potential energy density (V(r)) of N-$NO_2$ in different CL-20 host-guest systems

| | CL-20/0 | CL-20/$F_2$ | CL-20/$O_2$ | CL-20/HF | CL-20/$H_2O$ | CL-20/2HF |
|---|---|---|---|---|---|---|
| $L_{MAX}$/Å | 1.4865 | 1.4866 | 1.4875 | 1.4878 | 1.4875 | 1.4744 |
| $L_{ave}$/Å | 1.4485 | 1.4476 | 1.4473 | 1.4465 | 1.4457 | 1.4456 |
| $E_{ave}$/(kcal·mol$^{-1}$) | 28.11 | 28.10 | 28.06 | 27.98 | 27.90 | 27.78 |
| BE/(kJ·mol$^{-1}$) | 411.11 | 411.25 | 411.51 | 411.68 | 411.89 | 412.53 |
| ρ(r) | 1.823 | 1.824 | 1.827 | 1.830 | 1.834 | 1.835 |
| V(r) | -2.550 | -2.551 | -2.555 | -2.558 | -2.570 | -2.573 |

Table S4 Energy decomposition of the interactions between CL-20 and nonpolar molecules under sSAPT0/jun-cc-pVDZ conditions

| Cluster | $E_{ele}$ | $E_{exc}$ | $E_{ind}$ | $E_{dis}$ | $E_{tot}$ | Unit | Contact |
|---|---|---|---|---|---|---|---|
| $O_2$-1 | -0.741 | 1.901 | -0.112 | -1.396 | -0.349 | kcal/mol | O-O |
| $O_2$-2 | -0.343 | 0.411 | -0.287 | -1.143 | -1.362 | kcal/mol | H-O |
| $O_2$-3 | -0.712 | 1.886 | -0.111 | -1.394 | -0.331 | kcal/mol | O-O |
| $O_2$-4 | -0.275 | 0.233 | -0.209 | -0.898 | -1.150 | kcal/mol | H-O |
| $F_2$-1 | -0.448 | 1.478 | -0.073 | -1.008 | -0.051 | kcal/mol | F-O |
| $F_2$-2 | -0.057 | 0.245 | -0.177 | -0.795 | -0.784 | kcal/mol | H-F |
| $F_2$-3 | -0.406 | 1.379 | -0.070 | -0.972 | -0.069 | kcal/mol | F-O |
| $F_2$-4 | -0.009 | 0.143 | -0.136 | -0.635 | -0.638 | kcal/mol | H-F |

Table S5 Energy decomposition of the interactions between CL-20 and polar molecules under sSAPT0/jun-cc-pVDZ conditions

| Cluster | $E_{ele}$ | $E_{exc}$ | $E_{ind}$ | $E_{dis}$ | $E_{tot}$ | Unit | Contact |
|---|---|---|---|---|---|---|---|
| $H_2O$-1 | -2.426 | 3.709 | -0.916 | -1.847 | -1.480 | kcal/mol | O-H···O |
| $H_2O$-2 | -9.195 | 6.317 | -1.683 | -3.225 | -7.786 | kcal/mol | C-H···O |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2O$-3 | 0.397 | 1.469 | -0.258 | -1.019 | 0.589 | kcal/mol | O-H···O |
| $H_2O$-4 | -2.907 | 2.726 | -0.539 | -1.595 | -2.315 | kcal/mol | O-H···O |
| HF-1 | -1.403 | 0.582 | -0.132 | -0.474 | -1.427 | kcal/mol | F-H···O |
| HF-2 | -4.294 | 3.906 | -0.870 | -2.139 | -3.397 | kcal/mol | C-H···F |
| HF-3 | -0.585 | 0.361 | -0.156 | -0.503 | -0.883 | kcal/mol | F-H···O |
| HF-4 | -5.365 | 9.522 | -4.700 | -2.446 | -2.988 | kcal/mol | F-H···O |
| 2HF-1 | -1.304 | 0.154 | -0.107 | -0.301 | -1.558 | kcal/mol | F-H···O |
| 2HF-2 | -5.289 | 2.822 | -0.772 | -1.746 | -4.985 | kcal/mol | C-H···F |
| 2HF-3 | -1.459 | 1.580 | -0.408 | -0.954 | -1.241 | kcal/mol | F-H···O |
| 2HF-4 | -2.043 | 2.440 | -0.873 | -1.157 | -1.633 | kcal/mol | F-H···O |

Table S6 Hydrogen bond lengths (Å) and angles (°) of the host-guest complexes

| Guest molecules | X-H···Y | d(X-H)/Å | d(H···Y)/Å | d(X-Y)/Å | angle (X-H···Y)/deg |
|---|---|---|---|---|---|
| $H_2O$ | C25-H25···O97 | 1.094 | 2.422 | 2.993 | 110.9 |
| | C37-H37···O97 | 1.093 | 2.419 | 2.999 | 111.6 |
| | O97-H49···O13 | 0.966 | 2.561 | 2.945 | 103.8 |
| | O97-H49···O49 | 0.966 | 2.287 | 3.001 | 130.1 |
| | O97-H53···O61 | 0.969 | 2.757 | 3.581 | 143.3 |
| | O97-H53···O73 | 0.969 | 2.751 | 3.358 | 121.3 |
| | O97-H53···O85 | 0.969 | 2.101 | 2.857 | 133.7 |
| HF | C25-H25···F1 | 1.093 | 2.494 | 2.993 | 106.5 |
| | C37-H37···F1 | 1.092 | 2.458 | 2.977 | 107.4 |
| | F1-H49···O1 | 0.955 | 3.029 | 3.158 | 88.9 |
| | F1-H49···O61 | 0.955 | 3.040 | 3.530 | 113.4 |
| | F1-H49···O73 | 0.955 | 2.985 | 3.384 | 116.6 |
| | F1-H49···O85 | 0.955 | 1.722 | 2.665 | 168.2 |
| 2HF | C1-H1···F38 | 1.094 | 2.600 | 3.118 | 108.0 |
| | C4-H4···F38 | 1.092 | 2.399 | 3.009 | 113.7 |

| | | | | |
|---|---|---|---|---|
| F38-H37···O1 | 0.945 | 3.093 | 3.550 | 111.5 |
| F38-H37···O7 | 0.945 | 2.551 | 3.081 | 115.7 |
| F38-H37···O10 | 0.945 | 2.247 | 2.820 | 118.2 |

Table S7 Specific data on the electronic density ρ(r) and potential energy density V(r) of each N-$NO_2$ in CL-20, as well as changes in the average intramolecular hyperconjugation E{n(O)→σ*(N-N)} by rHBs and bHBs

| | CL-20/0 | CL-20/$H_2O$ | CL-20/HF | CL-20/2HF |
|---|---|---|---|---|
| E{n(O)→σ*(N-N)} /(kcal·mol$^{-1}$) | | | | |
| 1 | 26.67/26.56 | 25.50/26.20 | 27.05/26.94 | 26.59/26.52 |
| 2 | 26.70/28.62 | 27.19/27.97 | 27.77/29.00 | 27.12/28.55 |
| 3 | 29.95/29.65 | 29.97/29.83 | 30.10/29.65 | 30.02/29.92 |
| 4 | 31.60/31.09 | 30.71/30.77 | 31.04/30.95 | 30.35/30.68 |
| 5 | 29.98/28.92 | 29.87/27.72 | 29.20/24.47 | 29.96/27.96 |
| 6 | 24.16/23.45 | 23.90/23.49 | 23.83/23.51 | 24.02/23.45 |
| 7 | 26.67/26.56 | 26.93/26.76 | 26.66/26.30 | 26.59/26.52 |
| 8 | 26.70/28.62 | 26.25/28.06 | 26.36/29.14 | 27.12/28.55 |
| 9 | 29.95/29.65 | 30.15/29.60 | 30.3/29.87 | 30.02/29.92 |
| 10 | 31.60/31.09 | 31.53/31.07 | 31.36/31.11 | 30.35/30.68 |
| 11 | 29.98/28.92 | 29.73/28.52 | 29.93/28.97 | 29.96/27.96 |
| 12 | 24.16/23.45 | 24.2/23.64 | 24.21/23.68 | 24.02/23.45 |
| ρ(r) | | | | |
| 1 | 0.314 | 0.321 | 0.313 | 0.315 |
| 2 | 0.307 | 0.309 | 0.304 | 0.307 |
| 3 | 0.299 | 0.298 | 0.297 | 0.299 |
| 4 | 0.279 | 0.284 | 0.282 | 0.285 |
| 5 | 0.293 | 0.298 | 0.311 | 0.297 |
| 6 | 0.331 | 0.332 | 0.332 | 0.332 |
| 7 | 0.314 | 0.312 | 0.315 | 0.315 |
| 8 | 0.307 | 0.312 | 0.307 | 0.307 |
| 9 | 0.299 | 0.298 | 0.296 | 0.299 |
| 10 | 0.279 | 0.279 | 0.279 | 0.285 |
| 11 | 0.293 | 0.295 | 0.293 | 0.297 |
| 12 | 0.331 | 0.33 | 0.33 | 0.332 |
| V(r) | | | | |
| 1 | -0.448 | -0.461 | -0.445 | -0.450 |
| 2 | -0.431 | -0.434 | -0.424 | -0.430 |
| 3 | -0.413 | -0.411 | -0.408 | -0.413 |
| 4 | -0.374 | -0.384 | -0.379 | -0.386 |

| | | | | |
|---|---|---|---|---|
| 5 | -0.402 | -0.413 | -0.439 | -0.410 |
| 6 | -0.482 | -0.483 | -0.483 | -0.484 |
| 7 | -0.448 | -0.443 | -0.449 | -0.450 |
| 8 | -0.431 | -0.442 | -0.431 | -0.430 |
| 9 | -0.413 | -0.411 | -0.406 | -0.413 |
| 10 | -0.374 | -0.374 | -0.373 | -0.386 |
| 11 | -0.402 | -0.406 | -0.401 | -0.410 |
| 12 | -0.482 | -0.479 | -0.478 | -0.484 |