

Electronic Supplementary Information

Computational discovery of weak-intermolecular-interaction-tuning ferroelectricity/ferroelasticity of pure organic rotator-stator-type assemblies designed through symmetry/structure-limited structure search

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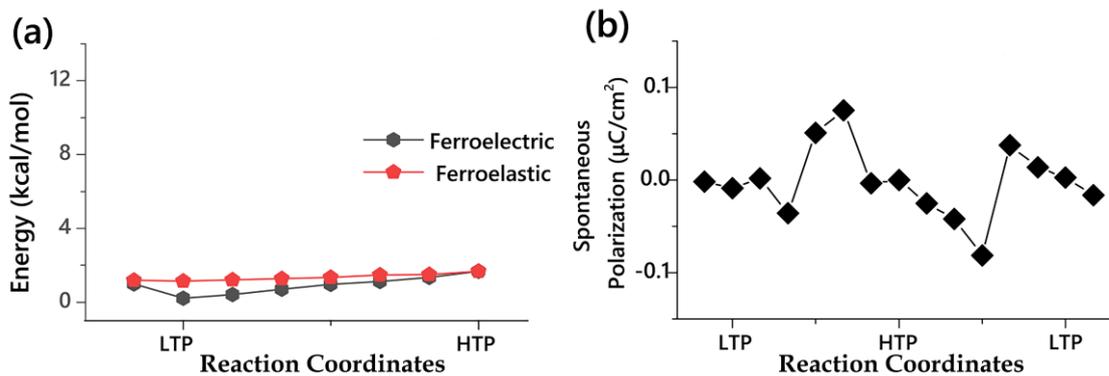


Figure S1. (a) Variation of energy and (b) variation of spontaneous polarization with reaction coordinates for ferroelectric (black solid line with hexagon) and ferroelastic (red line with pentagon) phase transitions of the model system H-DABCO-[Cu(H₂O)Cl₃] crystal.

The calculated energy barriers are 1.6 kcal/mol for ferroelectric phase transition and 0.5 kcal/mol for ferroelastic phase transition, respectively. An estimated value of spontaneous polarization is about 0.1 $\mu\text{C}/\text{cm}^2$, well agreeing with the reported value of 0.12 $\mu\text{C}/\text{cm}^2$.^{S1}

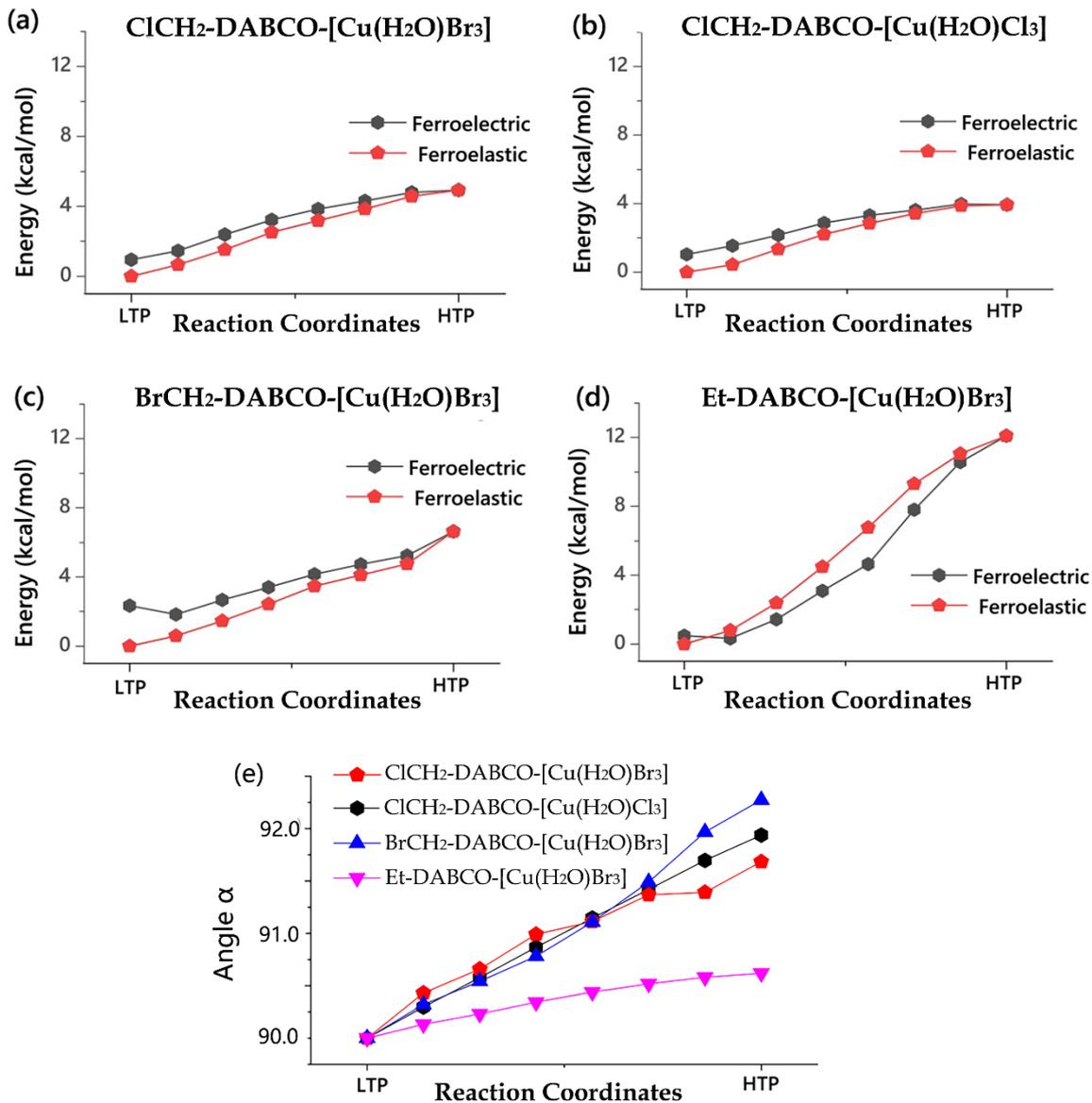


Figure S2. Variation of energy with reaction coordinates for both ferroelectric (black solid line with hexagon) and ferroelastic (red line with pentagon) phase transitions of (a) ClCH₂-DABCO-[Cu(H₂O)Br₃], (b) ClCH₂-DABCO-[Cu(H₂O)Cl₃], (c) BrCH₂-DABCO-[Cu(H₂O)Br₃] and (d) Et-DABCO-[Cu(H₂O)Br₃], respectively; (e) lattice parameter α change of these R-DABCO-[Cu(H₂O)X₃] crystals.

The calculated energy barriers in Fig. S2a are about 3.98 kcal/mol for ferroelectric phase transition and about 4.91 kcal/mol for ferroelastic phase transition, respectively. The calculated energy barriers in Fig. S2b are about 2.90 kcal/mol and about 3.92 kcal/mol for ferroelectric

and ferroelastic phase transitions, respectively. The calculated energy barriers in Fig. S2c are about 4.80 kcal/mol and about 6.63 kcal/mol for ferroelectric and ferroelastic phase transitions, respectively. The calculated energy barriers in Fig. S2d are about 11.6 kcal/mol and about 12.0 kcal/mol for ferroelectric and ferroelastic phase transitions, respectively. All these crystals are ferroelastics,^{S2-S5} supporting our assertion in the main text that the larger energy barriers after comparing between the ferroelectric phase transition and the ferroelastic phase transition indicate more preferred phase transition for each studied molecular crystal. Although we do not calculate the ferroelasticity-related physical parameter here, we can employ the lattice parameter change in Fig. S2e to indirectly evaluate the ferroelasticity. This similar indirect treatment has been also used before to experimentally describe the elastic behavior of a metal-organic framework (MOF) crystal under compression^{S6} and theoretically evaluate the piezoelectricity of hybrid organic-inorganic perovskites.^{S7}

Table S1. Computational relative energies (unit: kcal/mol) of different phases of Me-DABCO-[M(H₂O)Cl₃] (M = Cu and Ni) and their predicted properties.

Metal Ion	HTP ($P2_1/m$) ^a	LTP		Property
		Ferroelectric Phase ($P2_1$) ^a	Ferroelastic Phase ($P-1$) ^a	
Cu ²⁺	0.00	-0.05	-0.10	Ferroelastics
Ni ²⁺	0.00	0.52	0.57	Non-Phase Transitable

^aThe symbols in the parenthesis stand for the space groups of different phases.

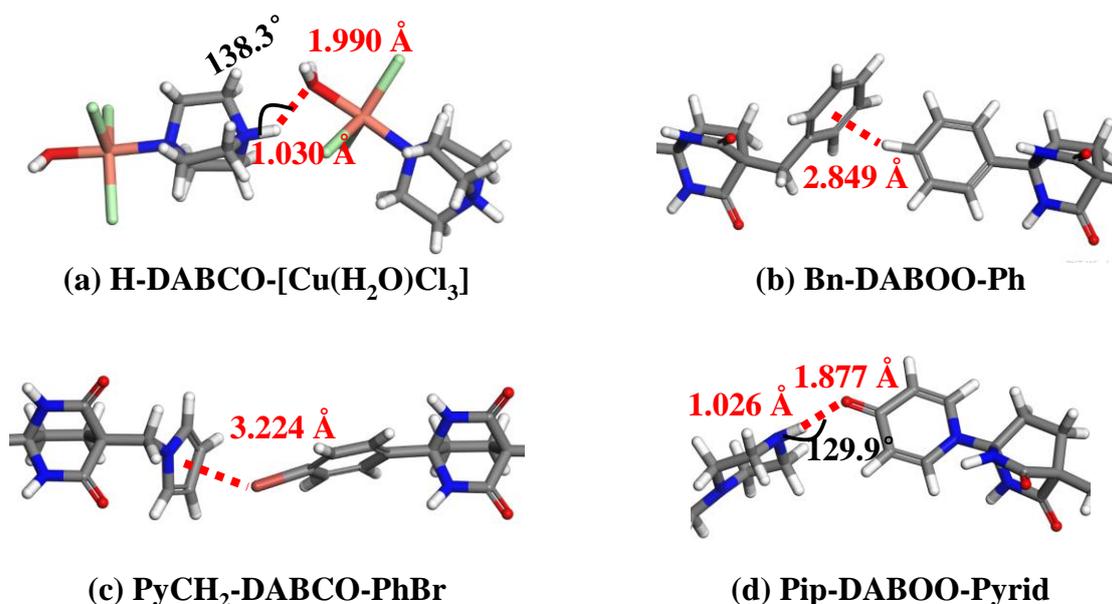
For Me-DABCO-[Ni(H₂O)Cl₃] with a $P2_1/m$ space group in r.t.p, we may expect that this material can realize the ferroelastic state in a lower temperature, since there are no extra weak intermolecular interactions between -Me and coordinated water. However, Me-DABCO-[Ni(H₂O)Cl₃] is non-phase transitable according to our computational results in Table S1, because the relative energies of symmetry-allowed ferroelectric or ferroelastic low-temperature phases are even higher than that of its high-temperature phase. It is not energy favorable to obtain low-temperature phases of Me-DABCO-[Ni(H₂O)Cl₃] crystal. That is surely the reason why the possible low-temperature phases cannot be found in experiment.^{S8}

Nonetheless, if we do not change the original structure and symmetry of Me-DABCO-[Ni(H₂O)Cl₃] crystal and but only replace Ni by Cu, we can obtain a new ferroelastics, Me-DABCO-[Cu(H₂O)Cl₃], with high-temperature space group of $P2_1/m$, because its corresponding ferroelastic phase would have a lower energy compared to its ferroelectric phase.

Though the low-temperature phases of Me-DABCO-[Ni(H₂O)Cl₃] crystal are not observed experimentally and the Me-DABCO-[Cu(H₂O)Cl₃] crystal are not reported experimentally, the predicted ferroelectric or ferroelastic space groups of Me-DABCO-[M(H₂O)Cl₃] crystals according to the symmetry analysis can also be accepted because of the rationality of our above calculations. Therefore, $P2_1$ and $P-1$ can be regarded as space groups of the ferroelectric phase and ferroelastic phase of Me-DABCO-[M(H₂O)Cl₃] crystals respectively for further discussion in the main text. These results discussed above also exhibit that the structure-property

relationship of the R-DABCO-[M(H₂O)X₃] model systems would be surely chemical-composition-dependent, even for divalent metal ions.

Table S2. Comparison of relative energies of different weak intermolecular interactions used to tune ferroelectricity in the main text calculated at the computational level of M06-2X/6-31+G(d) with the basis set superposition error (BSSE) correction. The computational models (a-d) (dimers taken from the low-temperature phases of studied crystals as examples) are also present here with relevant geometry parameters highlighted in insets.



Formula	Intermolecular Interaction		Type
	Energy (kcal/mol)		
	LTP ^a	HTP ^a	
R-DABCO-[Cu(H ₂ O)Cl ₃]	-28.50	-29.78	Hydrogen Bonding
Bn-DABOO-Ph	-2.89	-2.91	H- π
PyCH ₂ -DABOO-PhBr	-1.94	-2.35	X- π
Pip-DABOO-4O-Pyrid	-3.31	-3.36	Hydrogen Bonding

^aLTP and HTP indicate that the dimers used in the weak-intermolecular-interaction calculations are directly taken from our optimized low-temperature phases or high-temperature phases of each crystal.

Supplementary references

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