Supplementary information: Elucidation of dipolar dynamics and nature of structural phases in [(CH₃)₂NH₂][Zn(HCOO)₃] hybrid perovskite framework

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XRD data



Figure S1: Experimental and simulated powder XRD pattern of DMAZn powder. Measurements performed at room temperature using an X'Pert PRO X-ray diffraction system equipped with a PIXcel ultra-fast line detector and Soller slits for Cu K- α radiation ($\lambda = 1.54056$ Å).

Molecular dynamics simulation

MD simulations of DMAZn framework were performed using GROMACS 2018.2 software suite¹ on a desktop workstation equipped with 16 core AMD Ryzen 1950 Threadripper central processing unit accelerated by NVIDIA GeForce GTX1070 graphics processor for certain routines. The classical particle interactions were described by the generic Generalized Amber Force Field (GAFF).² The force field parameters were generated using the standard GAFF protocol as implemented in the Antechamber package,³ and Gaussian 09 D.01⁴ was utilized for all quantum chemical calculations necessary to obtain the electrostatic potential derived partial atomic charges via the Merz-Kollman scheme.

A supercell comprising 300 DMAZn formula units with dimensions of $43.04 \times 41.62 \times 38.18$ Å³ was constructed from the experimentally available crystallographic data.⁵ The GAFF optimized structure is identical to the experimental one with lattice parameters being ~5% smaller than the

experimental ones, and the obtained density of 2.122 g/cm³ about \sim 12% higher than the experimental 1.897 g/cm³. We believe that the generic GAFF force field performs reasonably well in describing the structure of this system and can be used for extracting more complex dynamic properties such as reorientation of DMA⁺ cations.

The molecular dynamics trajectories were generated in the NPT ensemble using the stochastic velocity re-scaling thermostat⁶ and Berendsen thermostat⁷ both with 1 ps time constant. All bonds involving hydrogen atoms were constrained using the LINCS algorithm⁸ allowing the use of a 2 fs velocity Verlet integration time step. Long-range electrostatic interactions were treated using the fourth order particle mesh Ewald method⁹ with a cutoff distance of 1.2 nm. Lennard-Jones interactions were only treated in the real space using a 1.2 nm cutoff distance.

A set of 10 ns independent trajectories were simulated at 1 bar pressure and different temperatures: 175 K (5 independent trajectories), 200 K (5 independent trajectories), 225 K (5 independent trajectories), 250 K (5 independent trajectories), 300 K (3 independent trajectories), 350 K (3 independent trajectories) and 400 K (3 independent trajectories). The first 500 ps were used for system to reach the equilibrium and were discarded from the subsequent analysis. The starting ordered configuration of the system is shown in Figure S2b, and the final high-temperature disordered phase is presented in Figure S2a.



Figure S2: Snapshots of the disordered (left) and ordered (right) phases of DMAZn obtained by the MD simulations. Zn atoms are indicated by cyan spheres and DMA⁺ cations by blue (N) and grey (C) tubes; all H atoms and formate units are not shown for clarity.

The reorientation dynamics of DMA⁺ units was analyzed by calculating the orientation selfcorrelation functions of the form:

$$C_n(t) = \left\langle P_n \frac{\mathbf{u}_{CNC}(0) \cdot \mathbf{u}_{CNC}(t)}{\mathbf{u}_{CNC}^2(0)} \right\rangle,\tag{1}$$

where P_n is the *n*-th order Legendre polynomial, $\mathbf{u}_{CNC}(t)$ denotes a normal vector to the plane spanned by the C-N-C atoms in DMA⁺ cation, and < ... > refers to the ensemble average. The resulting time dependence of the first order self-correlation function $C_1(t)$ at different temperature is depicted in Figure S3 revealing a complete orientational disorder of DMA⁺ cations above 300 K, as $C_1(t)$ approaches zero in less than 10 ns. The results also clearly indicate an increasingly slowing down of the orientational dynamics bellow 250 K with dynamics bellow 225 K being very slow and without marked reorientation even in a 100 ns long simulation.



Figure S3: Time dependence of the first order orientation self-correlation function of DMA⁺ cations in DMAZn simulated at different temperature.

The time dependence of $C_1(t)$ at different temperature was approximated using a triexponential decay of the following form:

$$C_1(t) = a_0 + a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right) + a_3 \exp\left(-\frac{t}{\tau_3}\right),\tag{2}$$

where a_i are constants constrained to $a_0 + a_1 + a_2 + a_3 = 1$, and τ_i denotes the characteristic relaxation time for various molecular processes. The first two time constants τ_1 and τ_2 are in the sub-picosecond and picosecond scale, respectively, and describe various local processes such as molecular vibrations and librations. Our further analysis concentrates on time constant τ_3 , which corresponds to the slowest time scale and is related to the reorientational dynamics of the DMA⁺ cations.

Additional dielectric spectroscopy data



Figure S4: (a) Frequency dependence of the imaginary part of the complex dielectric permittivity in the LT phase of DMAZn. The relaxation due to the DMA⁺ cation hopping at 172 K is presented for comparison. The solid curves indicate fits of the Cole-Cole model. (b) Inverse temperature dependences of the mean relaxation times for both processes with corresponding Arrhenius fits.

References

- Berendsen, H.; van der Spoel, D.; van Drunen, R. GROMACS: A Message-Passing Parallel Molecular Dynamics Implementation. *Comput. Phys. Commun.* 1995, *91*, 43–56.
- (2) Wang, J.; Wolf, R.; Caldwell, J.; Kollman, P.; Case, D. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* 2004, 25, 1157–1174.
- (3) Wang, J.; Wang, W.; Kollman, P. A.; Case, D. A. Automatic Atom Type and Bond Type Perception in Molecular Mechanical Calculations. *J. Mol. Graph.* 2006, 25, 247–260.
- (4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. Gaussian 09 Revision D.01.
- (5) Sánchez-Andújar, M.; Presedo, S.; Yánez-Vilar, S.; Castro-García, S.; Shamir, J.; Senarís-Rodríguez, M. A. Characterization of the Order-Disorder Dielectric Transition in the Hybrid Organic-Inorganic Perovskite-Like Formate Mn(HCOO)₃[(CH₃)₂NH₂]. *Inorg. Chem.* **2010**, *49*, 1510–1516.
- (6) Bussi, G.; Donadio, D.; Parrinello, M. Canonical Sampling through Velocity Rescaling. J. Chem. Phys. 2007, 126, 014101.
- (7) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. Molecular Dynamics with Coupling to an External Bath. J. Chem. Phys. 1984, 81, 3684–3690.
- (8) Hess, B.; Bekker, H.; Berendsen, H.; Fraaije, J. LINCS: A Linear Constraint Solver for Molecular Simulations. J. Comput. Chem. 1997, 18, 1463–1472.
- (9) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. A Smooth Particle Mesh Ewald Method. J. Chem. Phys. 1995, 103, 8577–8593.