## Supporting Information

# Unlocking ferroelectricity in a metal-free adamantane derivative via

# targeted symmetry reduction

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### **Experimental section**

#### Synthesis and thin-film fabrication

All chemicals were commercially available and were used without further purification. In a 10 mL aqueous solution containing 2-adamantanamine hydrochloride (1.87 g, 10 mmol), fine powder of Ag<sub>2</sub>CO<sub>3</sub> (1.375 g, 5 mmol) was added. The mixture was stirred at room temperature for 1 hour, followed by filtration. Subsequently, 40% hydrobromic acid (1.36 mL, 10 mmol) was added to the filtrate, and the resulting solution was stirred for another hour before filtration. Rod-like colorless crystals of 2-ADAB were obtained by slow evaporation of the filtrate (Fig. S1). The synthesis of 1-ADAB followed a similar procedure, with the substitution of 2-adamantanamine hydrochloride with amantadine hydrochloride.

The 2-ADAB thin films were prepared by drop-coating approach. A solution of 2-ADAB with a concentration of 0.1 g/ml was prepared, and 50  $\mu$ L of the solution was dropped on 1×1 cm<sup>2</sup> Platinum (Pt) coated glass. Large area transparent films can be obtained after the solution has evaporated at 70 °C.

#### X-ray Crystallographic Analysis

The *in-situ* variable-temperature single-crystal diffraction intensities data were collected on a Rigaku Oxford diffractometer equipped with Mo K $\alpha$  sealed tube ( $\lambda = 0.71073$  Å). The CrysAlisPro software suite was used for data collection, cell refinement and data reduction. Using the Olex<sup>2</sup> program, the structures were solved by using Intrinsic Phasing with the SHELXT structure solution program and using full-matrix least-squares method with the SHELXL refinement program.<sup>[1-2]</sup> Non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically. The crystal data and structure refinement results for 1-ADAB and 2-ADAB are listed in Table S1. Selected hydrogen bonds are listed in Table S2-S3. Powder X-ray diffraction (PXRD) patterns (Cu- $K_a$ ,  $\lambda = 1.54184$  Å) were collected on Panalytical Empyrean with Cu-K $\alpha$  X-ray radiation (40 kV, 45 mA). Phase purity was confirmed by PXRD (Fig. S2).

#### **Thermal Analysis**

Thermogravimetric analysis (TGA) was carried out on a Hitachi NEXTA STA300 with a heating rate of 10 K min<sup>-1</sup> from 295 to 673 K under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a NETZSCH DSC 204F1 Phoenix instrument under a dinitrogen atmosphere in aluminum crucibles with heating and cooling rates of 10 K min<sup>-1</sup>.

#### Ferroelectric and dielectric measurements

The dielectric measurement was conducted using a Hewlett-Packard 4284A LCR meter at varied frequencies, applying a voltage of 1.0 V, and employing a temperature sweeping rate of 5 K min<sup>-1</sup> under a programmable cryogenic cooling system. The powder sample of 2-ADAB was ground and pressed into tablets. The capacitors were made by painting the two faces of tablet sample with silver conducting paste and using copper wires as the electrodes. Polarization–electric field (*P*-*E*) hysteresis loops measurements of 2-ADAB were done on ~2.0 x 1.3 x 2.1 mm<sup>3</sup> sized single crystal sample with silver paste electrodes by using a TF analyzer (TFA-2000).

#### **PFM Measurement**

Piezoelectric Force Microscopy (PFM) measurements were conducted using the NTEGRA Aura scanning probe microscope (NT-MDT, Russia), equipped with a custom signal preamplifier and an external HF2LI lock-in Amplifier (Zurich Instruments, Switzerland). Budget Sensors Tap190E-G cantilevers with a spring constant of 48 N/m, resonance frequency of approximately 190 kHz, and conductive Cr/Pt coating were used. Out-of-plane and in-plane PFM imaging was performed at 21 kHz, significantly distant from the first flexural contact resonance frequency of

 $\sim$ 700 kHz, applying 8 V AC-voltage. Calibration of the probe displacements was conducted based on quasi-static measurements of force–distance curves. <sup>[3-4]</sup>

Switching spectroscopy was performed with dual AC resonance tracking (DFRT) of the first flexural contact resonance utilizing the inherent capabilities of the HF2LI lock-in. Electromechanical signals were recorded using the NI-6361 data acquisition board (National Instruments) via a custom LabView program. The acquired responses at resonance were divided by the quality factor Q and adjusted by the resonance mode shape factor. <sup>[4]</sup>

#### **Theoretical Calculation**

Quantum-chemical calculations have been performed in the HyperChem 8.06 package using semi-empirical PM3 method including the restricted Hartree–Fock approximation. Convergence limit was set 10<sup>-8</sup>, iteration limit was 32767. The dipole moment was calculated for the asymmetric unit cell of 2-ADAB (Figure 9a) and its 2×2×2 supercell (Figure S9b). The atomic positions were derived from single crystals X-ray diffraction experiments, the unit cells were first generated using CCDC Mercury software [5] and then transferred to HyperChem for calculations. No additional geometry optimization was done.

The unit cell polarization, P (C/m<sup>2</sup>), was determined using the equation:  $P = 3.33556255 \times D/V$ , where D is the total dipole moment in Debye, and V is the unit cell volume in Å<sup>3</sup> determined from the X-ray analysis (Table S1). The numerical coefficient represents the combination of conversion factors to SI units. The obtained dipole moments and polarizations are presented in Table S4.

The molecular structure of the polar surface (010) (Figure S9c) was reconstructed based on the lattice energy calculations <sup>[5]</sup> and the morphology of 2-ADAB crystal was predicted by the Bravais-Friedel-Donnay-Harker method. <sup>[6]</sup> Both methods are implemented in CCDC Mercury software.<sup>[7]</sup>



Figure S1. Photograph of the bulk crystal of 2-ADAB.



**Figure S2.** Powder X-ray diffraction confirms the phase purity of the as-synthesized 2-ADAB sample at room temperature.



Figure S3. (a) asymmetric unit of 1-ADAB at 298 K. (b) Crystal structure of 1-ADAB.



Figure S4. Structural unit of 2-ADAB at 393 K.



Figure S5. Thermogravimetry trace of 2-ADAB.



**Figure S6.** Temperature-dependent (a) real part ( $\varepsilon$ ') and (b) imaginary part (*tan*  $\delta$ ) of the complex dielectric constant measured on the polycrystalline pellet of 2-ADAB at various frequencies in the cooling process.



**Figure S7.** Temperature-dependent real part ( $\varepsilon$ ') of the complex dielectric constant measured on the polycrystalline pellet of 2-ADAB at 1 MHz in the heating-cooling process.



**Figure S8.** The experimental powder X-ray diffraction pattern of the 2-ADAB thin film matching with the simulated pattern at 298 K, revealing the preferred crystal plane is (001).



Figure S9. Calculated polar properties of 2-ADAB crystal. (a) The dipole moment orientation of asymmetric unit.
(b) 2-ADAB 2×2×2 supercell and the direction of the polarization. (c) Molecular structure of the polar surface
(010) and the morphology of 2-ADAB crystal. Dotted cyan lines denote hydrogen bonds. Blue spots on the surface indicate the location of hydrogen bonds donors.



**Figure S10.** PFM imaging of 2-ADAB. (a) Topography. Out-of-plane PFM (b) phase and (c) amplitude. In-plane PFM (d) phase and (e) amplitude.



**Figure S11.** Piezoresponse  $(R_{Cos\theta})$  local hysteresis loops.

Compound	1-ADAB	2-AI	DAB
Formula		C <sub>10</sub> H <sub>18</sub> Br N	
Formula weight (g/mol)		232.15	
Phase	/	Paraelectric	Ferroelectric
Temperature (K)	298(2)	393(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No.14)	<i>P</i> 2 <sub>1</sub> / <i>m</i> (No. 11)	<i>P</i> 2 <sub>1</sub> (No.4)
a/Å	11.3591(5)	7.8338(4)	7.7656(3)
b/Å	6.3615(2)	6.4470(4)	6.4026(2)
c/Å	14.7799(6)	10.1896(6)	10.1581(4)
<i>β</i> /°	103.823(4)	102.173(6)	102.526(4)
V/Å <sup>3</sup>	1037.08(7)	503.05(5)	493.04(3)
Ζ	4	2	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.487	1.533	1.564
$\mu/\mathrm{mm}^{-1}$	3.913	4.034	4.116
<i>F</i> (000)	480.0	240.0	240.0
$R_{1^{a}}\left[I > 2\sigma(I)\right]$	0.0579	0.0439	0.0346
$wR_{2^{b}}[I > 2\sigma(I)]$	0.0820	0.0967	0.0689
$R_1$ (all data)	0.1036	0.0716	0.0438
$wR_2$ (all data)	0.0936	0.1049	0.0712
GOF	1.075	1.068	1.054
Flack	/	/	0.18(2)
CCDC number	2345092	2345093	2345094

**Table S1.** Crystal data and structure refinement parameters for 1-ADAB and 2-ADAB.

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, {}^{b}wR_{2} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})^{2}]^{2}\}^{1/2}$ 

Table S2. The geometry (Å, °) of hydrogen-bonds in 1-ADAB at 298 K.

D–H…A	D-H (Å)	H…A (Å)	D…A (Å)	∠D–H…A (°)
N5–H5B…N3	0.89	2.18	3.068(9)	172.7
N6–H6C…N1 <sup>#1</sup>	0.89	1.92	2.816(2)	175.0
N6–H6D…Br <sup>#2</sup>	0.89	1.92	2.816(2)	175.0

 $^{\#1}(+x,1+y,+z);$   $^{\#2}(+x,1/2-y,+z)$ 

Table S3. The geometry (Å, °) of hydrogen-bonds in 2-ADAB at 298 and 393 K.

Temperature	D–H…A	D-H (Å)	H…A (Å)	D…A (Å)	$\angle D$ –H···A (°)
298 K	N1–H1A···Br1 <sup>#1</sup>	0.89	2.51	3.309(2)	149.9
	N1–H1B…Br1	0.89	2.62	3.491(6)	166.2
	N1–H1C···Br1 <sup>#2</sup>	0.89	2.61	3.456(6)	158.7
393 K	N1–H1A…Br1	0.89	2.73	3.495(1)	144.3
	N1–H1B···Br1 <sup>#3</sup>	0.89	2.61	3.495(1)	171.9
	N1–H1C…Br1 <sup>#4</sup>	0.89	2.56	3.331(3)	145.7

 $^{\#1}(1-x,1/2+y,-z);$   $^{\#2}(+x,1+y,+z);$   $^{\#3}(+x,1+y,+z);$   $^{\#4}(1-x,1/2-y,-z)$ 

**Table S4.** The calculated values of the dipole moments of adamantane, 1-ADAB, 2-ADAB molecules, and the total polarization of the unit cell at 298 K.

Molecule/compound	Dipole moments (D)	Polarization (µC/cm <sup>2</sup> )
adamantane	0	/
1-adamantylammonium	1.62	/
1-adamantylammonium bromide (1-ADAB)	15.57	0
2-adamantylammonium	1.31	/
2-adamantylammonium bromide (2-ADAB)	14.97	0.23

Compound	$T_{\rm c}\left({\rm K} ight)$	$P_{\rm r}$ ( $\mu$ C/cm <sup>2</sup> )	$E_{\rm c}$ (kV/cm)
2-ADBA (This work)	383	0.21	2.2
(N-methyl-N'-diazabicyclo[2.2.2]octonium)NH4I3 <sup>8</sup>	448	22	12
(N-methyl-N'-diazabicyclo[2.2.2]octonium)NH4(PF6)39	311	5.7	110
(N-chloromethyl-N'-diazabicyclo[2.2.2]octonium)NH4(ClO4)3 <sup>10</sup>	450	2.74	22
quinuclidinium perrhenate <sup>11</sup>	367	3.5	5
(hexamethylenetetramine)Cl <sup>12</sup>	390	8.1	1.0
(hexamethylenetetramine)Br <sup>12</sup>	435	8.3	1.0

Table S5. Comparison of ferroelectric performance parameters for representative metal-free ferroelectrics.

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