Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Dielectric Phase Transition Triggered by the order-disorder Transformation of Cyclopropylamine in a layered Organic-Inorganic Halide Perovskite

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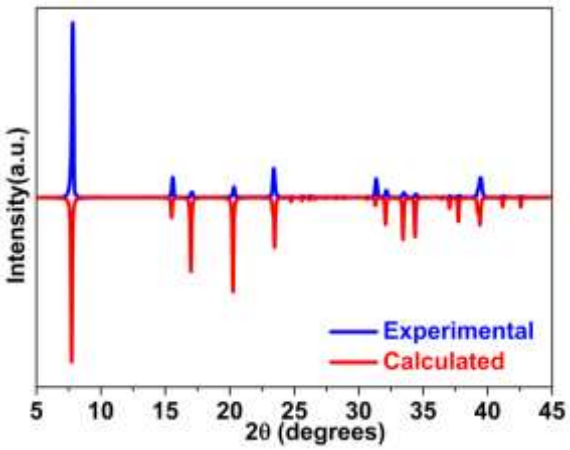



**Figure S1.** Experimental and calculated powder X-ray diffraction patterns of **CPA** at room temperature.

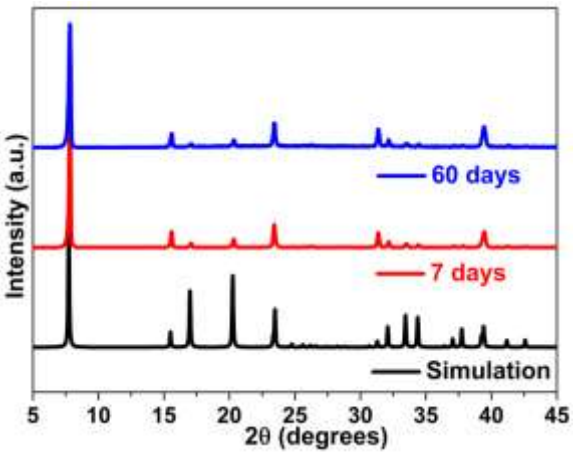



**Figure S2.** PXRD patterns of **CPA** recorded after 7/60 days at room temperature.

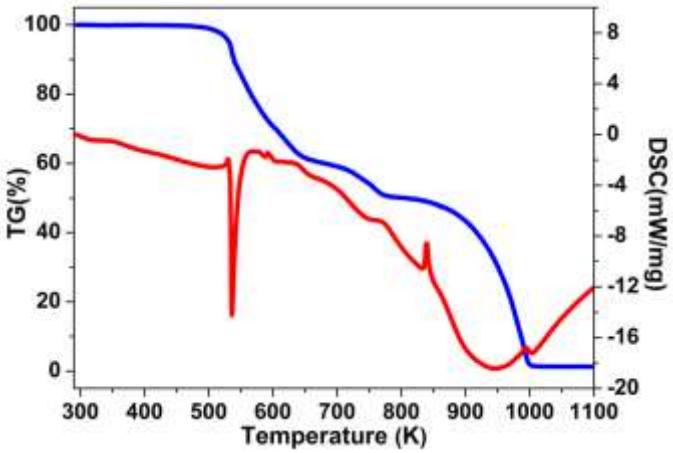



**Figure S3.** The TG curves of **CPA** with heating rate 10 K/min.

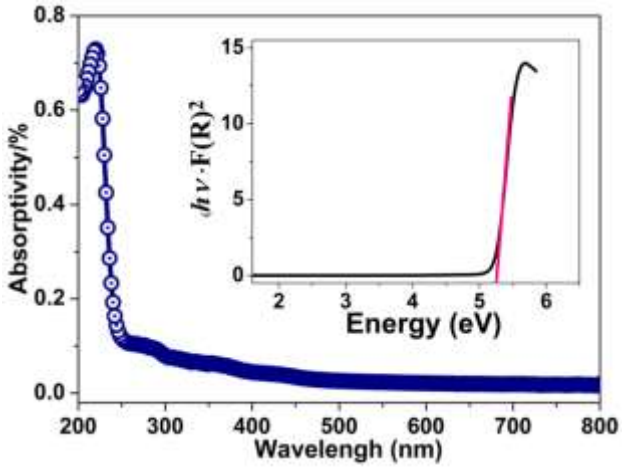
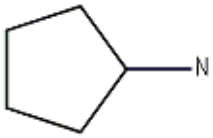
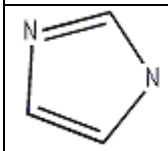
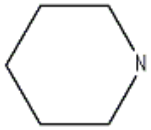
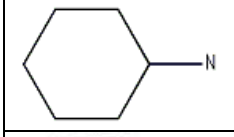
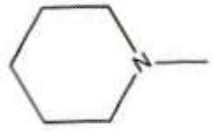
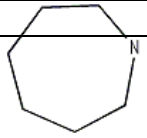
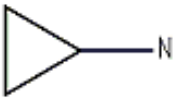


**Figure S4.** Ultraviolet-Vis diffuse reflectance spectrometry for **CPA**. Inset: Calculated band gap of **CPA**.

**Table S1. Organic-inorganic hybrid phase transition compounds based on various cyclic organic amines.**

| Cyclic amines | Organic cation | Compound formula | Transformation temperature | Ref. |
|---|---|---|---|---|
| Five-membered ring |  | $[C_5H_9NH_3][CdCl_3]$ | 290 K | [1] |
| |  | $[C_3N_2H_5]_5[Sb_2Br_{11}]$ | 125 K; 145 K; 353 K | [2] |
| | | $[C_3N_2H_5]_3[Sb_2I_9]$ | 292 K; 325 K | [3] |
| | | $[C_3N_2H_5]_3[Bi_2I_9]$ | 275 K; 325 K | |
| | | $[C_3N_2H_5]_5[Bi_2Br_{11}]$ | 155 K; 355 K | [4] |
| Six-membered ring |  | $[C_5H_{10}NH_2]_2[SbCl_5]$ | 338 K | [5] |
| | | $[C_5H_{10}NH_2]_2[SbBr_5]$ | 365 K | [6] |
| | | $[C_5H_{10}NH_2]_2[BiCl_5]$ | 342 K | |
| | | $[C_5H_{10}NH_2]_2[BiBr_5]$ | 362 K | |
| |  | $[C_6H_{11}NH_3]_2PbBr_4]$ | 360 K | [7] |
| |  | $[C_6H_{13}NH]_2[ZnBr_4]$ | 345 K | [8] |
| | | $[C_6H_{14}N][FeBr_4]$ | 340 K | [9] |
| | | $[C_6H_{14}N](18\text{-crown-6})][ClO_4]$ | 250 K | [10] |
| Seven-membered |  | $[C_6H_{11}NH_3]_2[PbBr_3]$ | 338 K | [11] |

| | | | | |
|---|---|---|---|---|
| ring | | $[C_6H_{11}NH_3]_2[SbCl_5]$ | 335 K | [12] |
| Three-membered ring |  | $[C_3H_5NH_3]_2[CdCl_4]$ | 273 K | **CPA** |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[2] A. Piecha, A. Pietraszko, G. Bator and R. Jakubas, *J. Solid. State Chem*, 2008, **181**, 1155.

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[7] Z. H. Sun, X. T. Liu, T. Khan, C. M. Ji, M. A. Asghar, S. G. Zhao, L. N. Li, M. C. Hong and J. H. Luo, *Angew. Chem. Int. Ed*. 2016, **55**, 6545.

[8] T. Khan, M. A. Asghar, Z. H. Sun, A. Zeb, L. N. li, S. J. Liu, S. G. Zhao, C. M. Ji and J. H. Luo, *Chem. Asian J*. 2016, **11**, 2876.

[9] S. G. Han, J. Zhang, B. Teng, C. M. Ji, W. C. Zhang, Z. H. Sun and J. H. Luo, *J. Mater. Chem. C*, 2017, **5**, 8509.

[10] T. Khan, M. A. Asghar, Z. H. Sun, A. Zeb, C. M. Ji and J. H. Luo, *J. Mater. Chem. C*, 2017, **5**, 2865.

[11] J. Zhang, X. T. Liu, X. F. Li, S. G. Han, K. W. Tao, Y. Y. Wang, C. M. Ji, Z. H. Sun and J. H. Luo, *Chem. Asian J*. 2018, **13**, 982.

[12] J. Zhang, S. G. Han, X. T. Liu, Z. Y. Wu, C. M. Ji, Z. H. Sun and J. H. Luo, *Chem. Commun,* 2018, **54**, 5614.


**Table S2. Crystal data and structure refinement for compound CPA.**

| | | |
|---|---|---|
| Empirical formula | $C_6H_{16}N_2CdCl_4$ | $C_6H_{16}N_2CdCl_4$ |
| Temperature | 100 K | 280 K |
| Formula weight | 370.41 | 370.41 |
| Crystallographic system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | *Cmca* |
| | $a$ = 11.9475(7) | $a$ = 7.5746(7) |

| | | |
|---|---|---|
| | $b$ = 7.2805(4) | $b$ = 22.852(2) |
| | $c$ = 7.6597(5) | $c$ = 7.5728(6) |
| | $\beta$= 108.539(2) | $\alpha = \beta = \gamma$ = 90.00 |
| Unit cell dimensions | $V$ = 631.69(7) | $V$ = 1310.8(2) |
| Z, Calculated density | 2, 1.9471 g/cm$^3$ | 4, 1.877 g/cm$^3$ |
| $F$(000) | 364.0 | 728.0 |
| Theta range for data collection | 5.596-55.19º | 6.454-55.072º |
| | -15 ≤ h ≤ 14 | -9 ≤ h ≤ 9 |
| Limiting indices | -9 ≤ k ≤ 9 | -29 ≤ k ≤ 27 |
| | -9 ≤ l ≤ 9 | -9 ≤ l ≤ 9 |
| Reflections collected / unique | 7996/1446 [$R_{int}$ = 0.0457] | 3665/808 [$R_{int}$ = 0.0366] |
| Completeness | 98.9% | 99.2% |
| Data / restraints / parameters | 1446/0/63 | 808/36/45 |
| Goodness-of-fit | 1.137 | 1.099 |
| Final $R$ indices [$I$>2sigma($I$)] | $R_1$ = 0.0370 | $R_1$ = 0.0635 |

**Table S3. N-H···Cl Hydrogen bonds of CPA at LTP.**

| D-H···A | d(D-H) | d(H···A) | < DHA | d(D..A) |
|---|---|---|---|---|
| N1-H1A···Cl2$^{\#1}$ | 0.910 | 2.309 | 168.68 | 3.207 |
| N1-H1B···Cl1$^{\#2}$ | 0.910 | 2.462 | 146.05 | 3.256 |
| N1-H1B···Cl2$^{\#3}$ | 0.910 | 2.757 | 125.15 | 3.365 |
| N1-H1C···Cl1 | 0.910 | 2.292 | 176.73 | 3.201 |

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -X+1, Y+1/2, -Z+3/2 $^{\#2}$ X, -Y+1/2, Z-1/2 $^{\#3}$ -X+1, -Y+1, -Z+1

**Table S4. N-H···Cl Hydrogen bonds of CPA at HTP.**

| D-H···A | d(D-H) | d(H···A) | < DHA | d(D..A) |
|---|---|---|---|---|
| N1-H1A···Cl1$^{\#1}$ | 0.890 | 2.470 | 171.31 | 3.353 |
| N1-H1B···Cl1$^{\#2}$ | 0.890 | 2.874 | 128.17 | 3.495 |
| N1-H1C···Cl1$^{\#3}$ | 0.890 | 2.877 | 127.89 | 3.495 |
| N1-H1C···Cl2$^{\#4}$ | 0.890 | 2.568 | 140.49 | 3.303 |

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ X+1/2, Y, -Z+3/2 $^{\#2}$-X+3/2, -Y+1, Z-1/2 $^{\#3}$-X+2, -Y+1, -Z+1 $^{\#4}$ X+1/2, Y, -Z+1/2

**Table S5. Cl-Cd-Cl Bond angles of compound CPA at LTP and HTP.**

| LTP | | | |
|---|---|---|---|
| **Bond Angle** | **(˚)** | **Bond Angle** | **(˚)** |
| Cl(11)-Cd(1)-Cl(1) | 180.0 | Cl(11)-Cd(1)Cl(2) | 92.15 |
| Cl(1)-Cd(1)-Cl(22) | 86.98 | Cl(22)-Cd(1)-Cl(21) | 91.63 |
| Cl(1)-Cd(1)-Cl(21) | 92.15 | Cl(23)-Cd(1)-Cl(21) | 88.37 |
| Cl(11)-Cd(1)-Cl(23) | 86.98 | Cl(22)-Cd(1)-Cl(2) | 88.37 |
| Cl(11)-Cd(1)-Cl(21) | 87.85 | Cl(23)-Cd(1)-Cl(22) | 180.0 |
| Cl(1)-Cd(1)-Cl(23) | 93.02 | Cl(23)-Cd(1)-Cl(2) | 91.63 |
| Cl(1)-Cd(1)-Cl(2) | 87.85 | Cl(21)-Cd(1)-Cl(2) | 180.0 |
| Cl(11)-Cd(1)-Cl(22) | 93.02 | | |
| **HTP** | | | |
| **Bond Angle** | **(˚)** | **Bond Angle** | **(˚)** |
| Cl(11)-Cd(1)-Cl(12) | 90.50 | Cl(21)-Cd(1)-Cl(12) | 89.85 |
| Cl(13)-Cd(1)-Cl(1) | 90.50 | Cl(21)-Cd(1)-Cl(13) | 90.15 |
| Cl(12)-Cd(1)-Cl(1) | 89.50 | Cl(2)-Cd(1)-Cl(12) | 90.15 |
| Cl(12)-Cd(1)-Cl(13) | 180.0 | Cl(2)-Cd(1)-Cl(11) | 89.85 |
| Cl(11)-Cd(1)-Cl(1) | 180.0 | Cl(2)-Cd(1)-Cl(1) | 90.15 |
| Cl(11)-Cd(1)-Cl(13) | 89.50 | Cl(21)-Cd(1)-Cl(1) | 89.85 |
| Cl(2)-Cd(1)-Cl(13) | 89.85 | Cl(2)-Cd(1)-Cl(21) | 180.0 |
| Cl(21)-Cd(1)-Cl(11) | 90.15 | | |

**Table S6. Cd-Cl Bond lengths of compound CPA at LTP and HTP.**

| LTP | | | |
|---|---|---|---|
| **Bond** | **(Å)** | **Bond** | **(Å)** |
| Cd(1)-Cl(11) | 2.5429(14) | Cd(1)-Cl(22) | 2.6878(14) |
| Cd(1)-Cl(1) | 2.5429(14) | Cd(1)-Cl(23) | 2.6878(14) |
| Cd(1)-Cl(2) | 2.7036(14) | Cl(2)-Cd(14) | 2.6878(14) |
| Cd(1)-Cl(21) | 2.7036(14) | | |
| **HTP** | | | |
| **Bond** | **(Å)** | **Bond** | **(Å)** |
| Cd(1)-Cl(1) | 2.6899(4) | Cd(1)-Cl(2) | 2.491(4) |
| Cd(1)-Cl(11) | 2.6899(4) | Cd(1)-Cl(23) | 2.491(4) |
| Cd(1)-Cl(12) | 2.6899(4) | Cl(1)-Cd(14) | 2.6899(4) |
| Cd(1)-Cl(13) | 2.6899(4) | | |