# Electronic Supplementary Information

## Dielectric and optical properties of an organic-inorganic hybrid phase transition material

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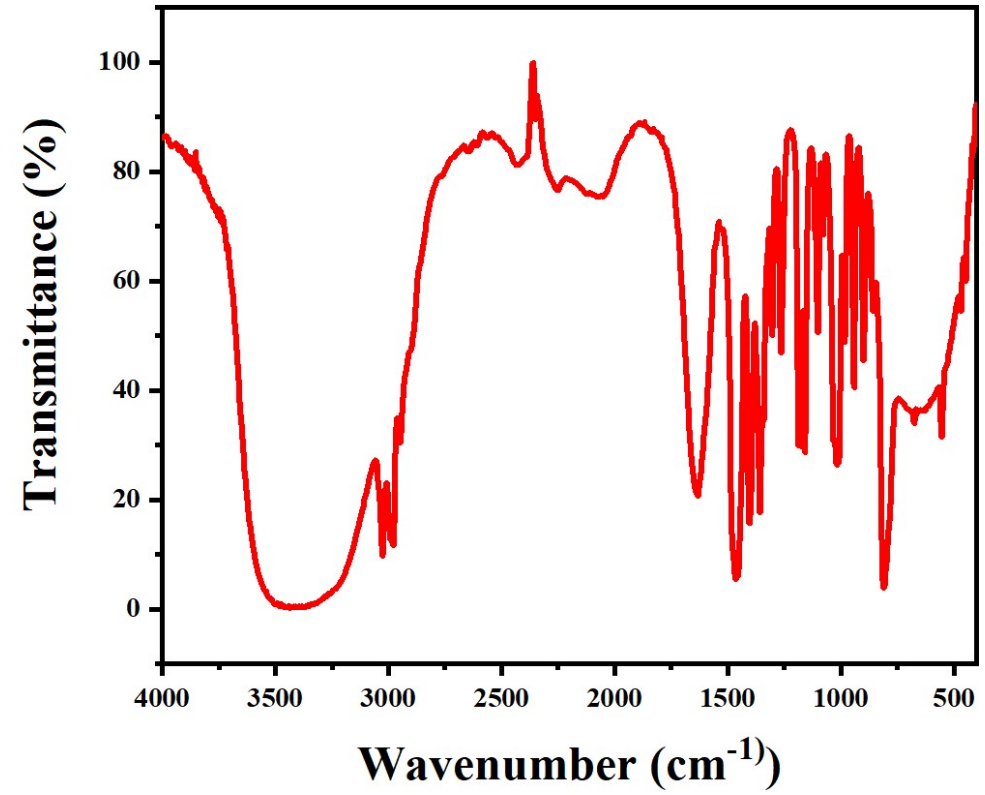


**Fig. S1** Infrared spectrum of compound **1** at room temperature.

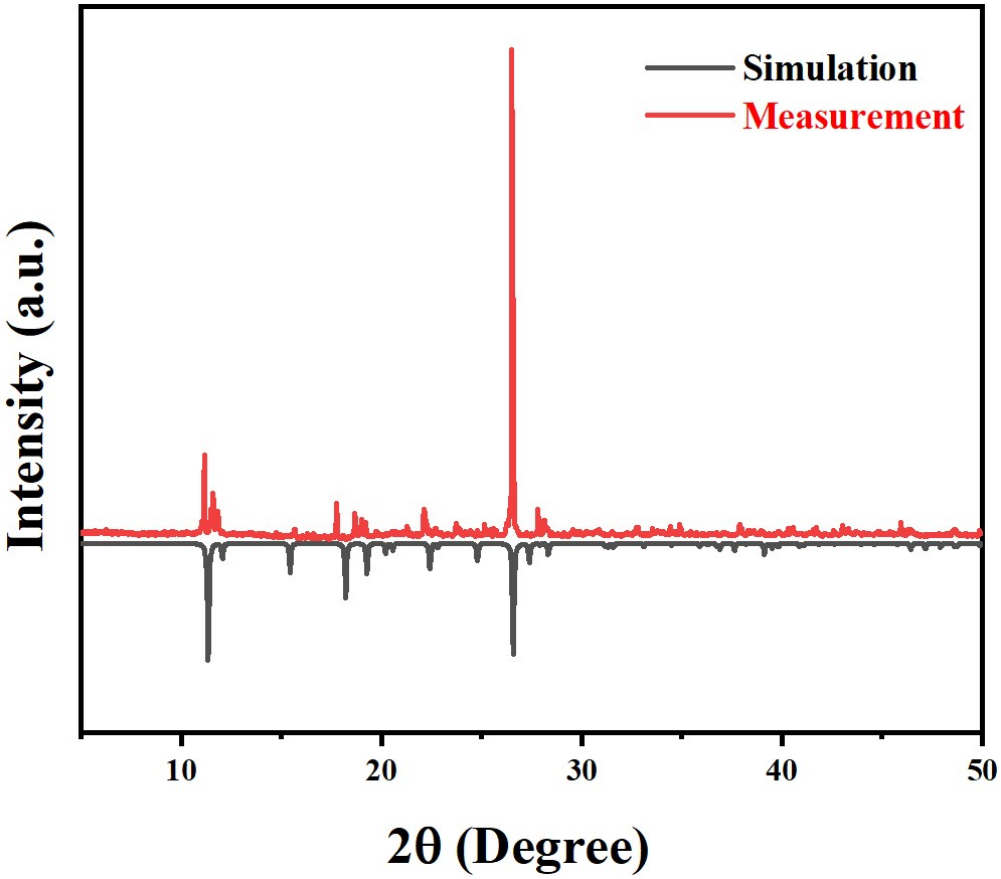


**Fig. S2** PXRD patterns (measurement and simulated) of compound **1**.

**Table S1** Basic crystal structure information of compound **1** at 150 K and 340 K.

| **Temperature** | **150K** | **340K** |
|---|---|---|
| Empirical formula | $C_{28}H_{68}Cl_{12}Mn_2N_4$ | $C_{14}H_{34}Cl_6MnN_2$ |
| Formula weight | 497.58 | 498.07 |
| Temperature/K | 150.0 | 340.00 |
| Crystal system | triclinic | tetragonal |
| Space group | $P\bar{1}$ (2) | $P4_2/nmc$(137) |
| a/Å | 12.9520(9) | 9.2031(9) |
| b/Å | 13.4792(10) | 9.2031(9) |
| c/Å | 15.8481(12) | 14.662(2) |
| α/° | 110.169(2) | 90 |
| β/° | 113.276(2) | 90 |
| γ/° | 90.899(3) | 90 |
| Volume / Å3 | 2348.4(3) | 1241.8(3) |
| Z | 4 | 2 |
| $\rho_{calc}$ g/cm3 | 1.407 | 1.332 |
| F(000) | 1034 | 518 |
| $R_{int}$ | 0.0641 | 0.0433 |
| Goof | 1.052 | 1.400 |
| $R_1$ [I>2 sigma(I)] | 0.0780 | 0.0898 |
| $wR_2$ [I>2 sigma(I)] | 0.1954 | 0.3186 |

**Table S2** Bond lengths (Å) for compound **1** at 150 K.

| **Atom-Atom** | **Length(Å)** | **Atom-Atom** | **Length(Å)** |
|---|---|---|---|
| Mn1–Cl3 | 2.3540(16) | C4–H4AA | 0.9900 |
| Mn1–Cl5 | 2.3654(16) | C4–H4AB | 0.9900 |
| Mn1–Cl6 | 2.3451(16) | C4–H4BC | 0.9900 |
| Mn1–Cl7 | 2.3651(17) | C4–H4BD | 0.9900 |
| Mn2–Cl4 | 2.3728(17) | C4–C30A | 1.505(13) |
| Mn2–Cl8 | 2.3862(18) | C20–H20A | 0.9800 |
| Mn2–Cl9 | 2.3706(18) | C20–H20B | 0.9800 |
| Mn2–Cl12 | 2.353(2) | C20–H20C | 0.9800 |
| Cl10–C7 | 1.761(6) | C18–H18A | 0.9800 |
| Cl11–C10 | 1.738(6) | C18–H18B | 0.9800 |
| Cl13–C14 | 1.733(7) | C18–H18C | 0.9800 |
| C29–H29A | 0.9800 | C7–H7A | 0.9900 |
| C29–H29B | 0.9800 | C7–H7B | 0.9900 |
| C29–H29C | 0.9800 | C1–H1A | 0.9900 |
| C29–C3 | 1.482(13) | C1–H1B | 0.9900 |
| Cl15–C4 | 1.738(8) | C1–C28 | 1.553(8) |
| N5–C6 | 1.512(7) | C19–H19A | 0.9800 |
| N5–C8 | 1.533(7) | C19–H19B | 0.9800 |
| N5–C5 | 1.527(7) | C19–H19C | 0.9800 |
| N5–C7 | 1.504(7) | C25–H25A | 0.9800 |

| | | | |
|---|---|---|---|
| N2–C9 | 1.530(7) | C25–H25B | 0.9800 |
| N2–C10 | 1.512(7) | C25–H25C | 0.9800 |
| N2–C11 | 1.527(7) | C25–C15 | 1.560(9) |
| N2–C12 | 1.516(7) | C28–H28A | 0.9800 |
| N1–C4 | 1.521(7) | C28–H28B | 0.9800 |
| N1–C1 | 1.517(7) | C28–H28C | 0.9800 |
| N1–C2 | 1.516(7) | C24–H24A | 0.9800 |
| N1–C3 | 1.517(8) | C24–H24B | 0.9800 |
| N3–C15 | 1.520(8) | C24–H24C | 0.9800 |
| N3–C14 | 1.555(9) | C24–C16 | 1.589(9) |
| N3–C16 | 1.496(8) | C23–H23A | 0.9800 |
| N3–C13 | 1.495(8) | C23–H23B | 0.9800 |
| C9–H9A | 0.9900 | C23–H23C | 0.9800 |
| C9–H9B | 0.9900 | C23–C13 | 1.603(10) |
| C9–C22 | 1.540(8) | C12–H12A | 0.9900 |
| C21–H21A | 0.9800 | C12–H12B | 0.9900 |
| C21–H21B | 0.9800 | C2–H2A | 0.9900 |
| C21–H21C | 0.9800 | C2–H2B | 0.9900 |
| C21–C12 | 1.628(8) | C2–C26 | 1.502(9) |
| C17–H17A | 0.9800 | C15–H15A | 0.9900 |
| C17–H17B | 0.9800 | C15–H15B | 0.9900 |
| C17–H17C | 0.9800 | C26–H26A | 0.9800 |
| C17–C8 | 1.521(8) | C26–H26B | 0.9800 |
| C10–H10A | 0.9900 | C26–H26C | 0.9800 |
| C10–H10B | 0.9900 | C3–H3BC | 0.9900 |
| C6–H6A | 0.9900 | C3–H3BD | 0.9900 |
| C6–H6B | 0.9900 | C3–H3AA | 0.9900 |
| C6–C18 | 1.516(9) | C3–H3AB | 0.9900 |
| C11–H11A | 0.9900 | C3–Cl14 | 1.777(8) |
| C11–H11B | 0.9900 | C14–H14A | 0.9900 |
| C11–C20 | 1.588(8) | C14–H14B | 0.9900 |
| C8–H8A | 0.9900 | C16–H16A | 0.9900 |
| C8–H8B | 0.9900 | C16–H16B | 0.9900 |
| C5–H5A | 0.9900 | C13–H13A | 0.9900 |
| C5–H5B | 0.9900 | C13–H13B | 0.9900 |
| C5–C19 | 1.540(9) | C30A–H30A | 0.9800 |
| C22–H22A | 0.9800 | C30A–H30B | 0.9800 |
| C22–H22B | 0.9800 | C30A–H30C | 0.9800 |
| C22–H22C | 0.9800 | | |

**Table S3** Selected angles [°] for compound **1** at 150 K.

| **Atom1-to-Atom2-to Atom3** | **Angle[°]** | **Atom1-to-Atom2-to Atom3** | **Angle[°]** |
|---|---|---|---|
| Cl3–Mn1–Cl5 | 111.47(8) | H20A–C20–H20B | 109.5 |

| | | | |
|---|---|---|---|
| Cl3–Mn1–Cl7 | 108.22(8) | H20A–C20–H20C | 109.5 |
| Cl5–Mn1–Cl7 | 111.72(8) | H20B–C20–H20C | 109.5 |
| Cl6–Mn1–Cl3 | 106.36(8) | C6–C18–H18A | 109.5 |
| Cl6–Mn1–Cl5 | 109.81(8) | C6–C18–H18B | 109.5 |
| Cl6–Mn1–Cl7 | 109.09(8) | C6–C18–H18C | 109.5 |
| Cl4–Mn2–Cl8 | 102.65(8) | H18A–C18–H18B | 109.5 |
| Cl9–Mn2–Cl4 | 114.57(8) | H18A–C18–H18C | 109.5 |
| Cl9–Mn2–Cl8 | 109.10(8) | H18B–C18–H18C | 109.5 |
| Cl12–Mn2–Cl4 | 107.73(9) | Cl10–C7–H7A | 108.9 |
| Cl12–Mn2–Cl8 | 115.03(10) | Cl10–C7–H7B | 108.9 |
| Cl12–Mn2–Cl9 | 107.90(10) | N5–C7–Cl10 | 113.2(5) |
| H29A–C29–H29B | 109.5 | N5–C7–H7A | 108.9 |
| H29A–C29–H29C | 109.5 | N5–C7–H7B | 108.9 |
| H29B–C29–H29C | 109.5 | H7A–C7–H7B | 107.7 |
| C3–C29–H29A | 109.5 | N1–C1–H1A | 108.0 |
| C3–C29–H29B | 109.5 | N1–C1–H1B | 108.0 |
| C3–C29–H29C | 109.5 | N1–C1–C28 | 117.3(7) |
| C6–N5–C8 | 112.7(6) | H1A–C1–H1B | 107.2 |
| C6–N5–C5 | 109.2(6) | C28–C1–H1A | 108.0 |
| C8–N5–C5 | 108.4(6) | C28–C1–H1B | 108.0 |
| C7–N5–C6 | 108.7(6) | C5–C19–H19A | 109.5 |
| C7–N5–C8 | 106.3(5) | C5–C19–H19B | 109.5 |
| C7–N5–C5 | 111.6(6) | C5–C19–H19C | 109.5 |
| C9–N2–C11 | 109.2(6) | H19A–C19–H19B | 109.5 |
| C10–N2–C9 | 112.4(6) | H19A–C19–H19C | 109.5 |
| C10–N2–C11 | 107.5(6) | H19B–C19–H19C | 109.5 |
| C10–N2–C12 | 107.2(6) | H25A–C25–H25B | 109.5 |
| C12–N2–C9 | 108.6(6) | H25A–C25–H25C | 109.5 |
| C12–N2–C11 | 111.9(6) | H25B–C25–H25C | 109.5 |
| C4–N1–C3 | 108.7(6) | C15–C25–H25A | 109.5 |
| C1–N1–C4 | 112.4(6) | C15–C25–H25B | 109.5 |
| C1–N1–C2 | 109.1(6) | C15–C25–H25C | 109.5 |
| C1–N1–C3 | 108.1(6) | C1–C28–H28A | 109.5 |
| C2–N1–C4 | 107.7(6) | C1–C28–H28B | 109.5 |
| C2–N1–C3 | 110.9(6) | C1–C28–H28C | 109.5 |
| C15–N3–C14 | 103.7(6) | H28A–C28–H28B | 109.5 |
| C16–N3–C15 | 110.8(7) | H28A–C28–H28C | 109.5 |
| C16–N3–C14 | 110.3(6) | H28B–C28–H28C | 109.5 |
| C16–N3–C13 | 110.5(7) | H24A–C24–H24B | 109.5 |
| C13–N3–C15 | 112.6(6) | H24A–C24–H24C | 109.5 |
| C13–N3–C14 | 108.8(6) | H24B–C24–H24C | 109.5 |
| N2–C9–H9A | 108.3 | C16–C24–H24A | 109.5 |
| N2–C9–H9B | 108.3 | C16–C24–H24B | 109.5 |
| N2–C9–C22 | 115.8(6) | C16–C24–H24C | 109.5 |

| | | | |
|---|---|---|---|
| C11–C20–H20C | 109.5 | H30B–C30A–H30C | 109.5 |

**Table S4** Bond lengths (Å) for compound **1** at 340 K.

| Atom-Atom | Length(Å) | Atom-Atom | Length(Å) |
|---|---|---|---|
| Mn1–Cl1$^{\#1}$ | 2.328(2) | C2–H2A | 0.9600 |
| Mn1–Cl1$^{\#2}$ | 2.328(2) | C2–H2B | 0.9600 |
| Mn1–Cl1$^{\#3}$ | 2.328(2) | C2–H2C | 0.9600 |
| Mn1–Cl1 | 2.328(2) | C3–H3A | 0.9700 |
| N1–C1 | 1.475(10) | C3–H3B | 0.9700 |
| N1–C3 | 1.476(12) | C7–H7A | 0.9700 |
| N1–C7 | 1.457(11) | C7–H7B | 0.9700 |
| N1–C5 | 1.471(12) | C7–Cl2 | 1.715(16) |
| C1–H1A | 0.9700 | C5–H5A | 0.9700 |
| C1–H1B | 0.9700 | C5–H5B | 0.9700 |
| C1–C2 | 1.556(10) | C5–C6 | 1.543(10) |
| C4–H4A | 0.9600 | C6–H6A | 0.9600 |
| C4–H4B | 0.9600 | C6–H6B | 0.9600 |
| C4–H4C | 0.9600 | C6–H6C | 0.9600 |
| C4–C3 | 1.559(10) | | |

**Table S5** Selected angles [°] for compound **1** at 340 K.

| Atom1-to-Atom2-to Atom3 | Angle[°] | Atom1-to-Atom2-to Atom3 | Angle[°] |
|---|---|---|---|
| Cl1–Mn1–Cl1 | 109.04(8) | H2A–C2–H2B | 109.5 |
| Cl1–Mn1–Cl1 | 109.04(8) | H2A–C2–H2C | 109.5 |
| Cl1–Mn1–Cl1 | 110.34(16) | H2B–C2–H2C | 109.5 |
| Cl1–Mn1–Cl1 | 110.34(16) | N1–C3–C4 | 126.1(19) |
| Cl1–Mn1–Cl1 | 109.04(8) | N1–C3–H3A | 105.8 |
| Cl1–Mn1–Cl1 | 109.04(8) | N1–C3–H3B | 105.8 |
| C1–N1–C3 | 107.4(13) | C4–C3–H3A | 105.8 |
| C7–N1–C1 | 111.6(16) | C4–C3–H3B | 105.8 |
| C7–N1–C3 | 109.4(15) | H3A–C3–H3B | 106.2 |
| C7–N1–C5 | 117.4(15) | N1–C7–H7A | 107.9 |
| C5–N1–C1 | 112.1(14) | N1–C7–H7B | 107.9 |
| C5–N1–C3 | 97.6(15) | N1–C7–Cl2 | 117.7(15) |
| N1–C1–H1A | 108.5 | H7A–C7–H7B | 107.2 |
| N1–C1–H1B | 108.5 | Cl2–C7–H7A | 107.9 |
| N1–C1–C2 | 114.9(18) | Cl2–C7–H7B | 107.9 |
| H1A–C1–H1B | 107.5 | N1–C5–H5A | 104.0 |
| C2–C1–H1A | 108.5 | N1–C5–H5B | 104.1 |
| C2–C1–H1B | 108.5 | N1–C5–C6 | 132.7(17) |
| H4A–C4–H4B | 109.5 | H5A–C5–H5B | 105.5 |
| H4A–C4–H4C | 109.5 | C6–C5–H5A | 104.1 |
| H4B–C4–H4C | 109.5 | C6–C5–H5B | 104.0 |

| | | | |
|---|---|---|---|
| C3–C4–H4A | 109.5 | C5–C6–H6A | 109.5 |
| C3–C4–H4B | 109.5 | C5–C6–H6B | 109.5 |
| C3–C4–H4C | 109.5 | C5–C6–H6C | 109.5 |
| C1–C2–H2A | 109.5 | H6A–C6–H6B | 109.5 |
| C1–C2–H2B | 109.5 | H6A–C6–H6C | 109.5 |
| C1–C2–H2C | 109.5 | H6B–C6–H6C | 109.5 |

**Table S6** Some dielectric abrupt with step-type and λ-type were collected.

| **Material** | **$T_c$** | **$\varepsilon$'(LP)** | **$\varepsilon$'(HP)** | **Type** | **Reference** |
|---|---|---|---|---|---|
| $(DPA)_5Pb_2Br_9$ | 300.6 K | 10.5 | 13 | step-type | 36 |
| $(DPA)_4AgBiBr_8$ | 375 K | 10.6 | 11.7 | step-type | 36 |
| (TEACCl)PbBr3 | 390 K | 11.2 | 15.3 | step-type | 29 |
| $NH_3(CH_2)_5NH_3MnCl_4$ | 298 K | 5.5 | 10.25 | step-type | 31 |
| $[N(CH_2CH_3)_3(CH_2Cl)][ClO_4]$ | 401.2 K, 455.2K | 6.5 | 10.1 | step-type | 4 |
| $(MTBA)_3Bi_2Br_9$ | 188 K, 425 K | 4.6 7.5 | 4.8 11 | step-type | 18 |
| $[(CH_3)_2(F\text{-}CH_2CH_2)NH]_3(CdCl_3)(CdCl_4)$ | 333 K | 10 | 80 | λ-type | 16 |
| $[Methylhydrazinium]_2PbBr_4$ | 370 K | Nearly 90 | 750 | λ-type | 23 |