Conflicting evidence for ferroelectricity

Gabriele D'Avino^{1,2,3}, Manuel Souto⁴, Matteo Masino⁵, Jonas K. H. Fischer⁶, Imma Ratera⁷, Xavier Fontrodona⁸, Gianluca Giovannetti⁹, Matthieu J. Verstraete¹, Anna Painelli⁵, Peter Lunkenheimer⁶, Jaume Veciana⁴, Alberto Girlando⁵

¹Université de Liège, Institut de Physique, and European Theoretical Spectroscopy Facility, Allée du 6 Août 19, Sart-Tilman, 4000 Liège, Belgium

²Laboratory for the Chemistry of Novel Materials, University of Mons, 7000 Mons, Belgium

³CNRS, Institut Néel, 25 Rue des Martyrs, F-38042 Grenoble (France)

⁴Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus de Bellaterra, E-08193 Cerdanyola del Vallès, Spain

⁵Dipartimento di Chimica, Parma University and INSTM-UdR Parma, 43124 Parma, Italy

⁶Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany

⁷Serveis Científico-Tècnics, Campus de Montilivi, University of Girona, E-17071 Girona, Spain

⁸CNR-IOM-Democritos National Simulation Centre and International School for Advanced Studies (SISSA), Via Bonomea 265, I-34136 Trieste, Italy

Email: gabriele.davino@neel.cnrs.fr

The rising field of flexible and bio/eco-friendly electronics is knocking on the door of material scientists demanding for organic ferroelectric active elements operating at room temperature. Tayi *et al.*¹ reported room temperature ferroelectricity in organic mixed-stack charge transfer (CT) crystals, resulting from a novel supramolecular design concept, the Lock-Arm Supramolecular Ordering (LASO) that synergistically combines intermolecular CT and hydrogen bonds^{2,3}. Here we present an independent experimental investigation that found no evidence for ferroelectricity in one of the LASO crystals and, together with theoretical calculations, demonstrates that a possible ferroelectric behaviour is not of electronic origin as originally proposed. This study raises fundamental questions on the elusiveness and reproducibility of the claimed room temperature ferroelectricity in LASO systems¹.

Room temperature ferroelectricity has been claimed for three CT crystals formed by the same electron acceptor (A) and three different donors (D)¹. The ferroelectric behavior has been ascribed to a sizeable charge ρ transferred from D to A molecules arranged in non-centrosymmetric structures characterized by polar dimers [...($D^{+p}A^{-p}$) ($D^{+p}A^{-p}$)...], as observed in other mixed-stack CT crystals, albeit at cryogenic temperatures^{4,5}. Tayi *et al.*¹ supported their finding by a combination of structural, vibrational and dielectric measurements that we replicate here for their system **1·2** (see Figure 1a). We note that the X-ray diffraction data of the three LASO crystals has been recently re-examined by the same authors, assigning all of them to centro-symmetric space groups³, clearly incompatible with ferroelectricity.

Compounds **1** and **2** have been synthesized and single crystals of compound **1·2** have been grown in different solvent mixtures under strictly anhydrous conditions. Our independent X-ray structural determination confirms the growth of the same polymorph reported in Ref. 1. We also find, as in Ref. 3, that a better structural refinement is obtained for the non-polar space group P-1, than for the P1 group initially proposed. Density functional theory (DFT) calculations consistently indicate that the non-polar phases are the most stable for the three LASO compounds.

Vibrational spectroscopy provides information on both electronic and structural properties of mixed-stack CT crystals⁶. Totally symmetric molecular vibrations offer an unambiguous probe of the dimerization of the lattice: these Raman-active modes show up in infrared (IR) spectra polarized along the stack axis only in dimerized phases, where they modulate the asymmetric flow of electronic charge, acquiring a much larger intensity compared to other vibrations. Being sensitive to local static or dynamic disorder, vibrational spectroscopy offers complementary information to X-ray diffraction data, which only probes long-range order. Our absorption IR and Raman spectra in Figure 1b do not present coincident peaks, firmly excluding stack dimerization, whether local or nonlocal, static or dynamic. The frequency coincidences reported in the spectra by Tayi *et al.*¹ are probably accidental, due to the presence of many bands in their limited quality IR spectra. We presume their IR spectra have been obtained by applying the Kubelka-Munk transformation to “single point reflectance” spectra of single crystals, whereas this transformation is only appropriate for the diffuse reflectance spectra of powders⁷.

IR spectroscopy also allows to estimate the ionicity ρ , through the frequency shift of properly chosen “charge sensitive” vibrational modes, as is well established for the carbonyl (C=O) stretching of chloranil complexes^{8,9}. Tayi *et al.*¹ attributed a sizeable CT to the three LASO compounds ($\rho=0.67, 0.89, 0.43$ for **1·2**, **1·3** and **1·4**, respectively) based on the frequencies of the carbonyl stretching of **1**, using a calibration procedure employing tetracyanoquinodimethane complexes that is not clear to us. The inconsistencies of this approach have been pointed out in Ref. 10. Here we remark that, according to intuition, experimental literature, and DFT calculations⁸, the frequency of carbonyl modes is expected to decrease strongly upon negatively charging **1**, and not to increase slightly, as proposed in Ref. 1. Without need of calculation or calibration, Figure 1c compares IR spectra of **1** and **2** with those of the **1·2** crystal, polarized perpendicularly to the stack axis, where the C=O stretching bands appear. The spectrum of **1·2** is very similar to the superposition of the spectra of its components in the whole spectral range and specifically in the C=O

stretching region, as also confirmed by Raman spectra (see Extended Data Figure 1). This definitely proves that the **1·2** complex is essentially neutral ($\rho \approx 0$). A similar conclusion can be drawn for the LASO compounds **1·3** and **1·4**, based on the marginal shifts of the carbonyl stretching¹, Hubbard model calculations¹⁰, and original DFT results (see Extended Data Table 1) further support the conclusion, pointing to largely neutral states for all three systems.

The data presented so far exclude any indirect signature of ferroelectricity, at least according to the known mechanism of dimerization transitions in conventional mixed-stack CT crystals^{5,11,12}. Collective proton transfer phenomena are another known source of ferroelectricity in molecular systems characterized by the presence of hydrogen bonds^{4,13}. This mechanism could provide an explanation for the ferroelectricity of LASO systems and its elusiveness to X-rays or vibrational spectroscopy. To check for possible ferroelectric behavior in the **1·2** complex, we performed electrical polarization hysteresis measurements at various temperatures between 7 and 400 K, with different fields and frequencies. Figure 2a shows a typical $P(E)$ curve collected at 74 K, showing a nearly linear behavior with only a slight hysteresis, typical for a linear, slightly lossy, dielectric. At 300 K (Figure 2b), the significantly larger loss contribution from dc charge transport leads to an elliptical $P(E)$ curve. Subtracting a horizontal ellipse from the measured curve corrects for this contribution, and reveals purely linear, non-hysteretic, $P(E)$ behavior. The absolute values of the polarization detected in our experiments are significantly lower than in Ref. 1, for applied fields of similar magnitude. This excludes that the ferroelectric hysteresis curves reported by Tayi *et al.*¹ are drowned out by a dominating linear $P(E)$ contribution in our experiments, arising, e.g., from stray capacitance. Additional positive-up-negative-down (PUND, see Extended Data Figure 2)¹⁴ measurements were performed at 300 and 400 K with different fields and frequencies, without finding any indication for ferroelectricity.

In conclusion, our findings call into question the claim of room-temperature electronic ferroelectricity in LASO systems. Our measurements on the crystal **1·2** reveal a neat paraelectric response, instead of the hysteresis loops reported by Tayi *et al.*¹. Additional work is needed to reconcile these conflicting evidences through a rigorous definition of the experimental conditions required to observe ferroelectricity, excluding the possibility of artifacts in the measurements¹⁵. Finally, our analysis rules out that the ferroelectricity of LASO systems, if present, is of electronic nature as it was initially proposed.

Figure 1 | Vibrational spectra of LASO compound **1·2.** (a) Structure of the electron acceptor (A, **1**) and donor (D, **2**) molecules forming the LASO complex. (b) Room temperature IR (polarization along the stack axis) and Raman spectra of **1·2**. Vertical lines mark the Raman modes of the two molecules, none of which appear in the IR spectrum, proving the presence of inversion symmetry. (c) IR spectra (polarization perpendicular to stack axis) of **1**, **2** and **1·2**: the carbonyl stretching of **1** does not shift substantially upon complexation, indicating negligible CT ($\rho \approx 0$).

Figure 2 | Dielectric measurements for LASO compound **1·2.** Electric-field dependent polarization of **1·2** at 74 (a) and 300 K (b). The squares in (b) show the conductivity-corrected result at 300 K. A neat paraelectric response is obtained for temperatures in the 7 to 400 K range.

Methods

Compound **1** has been synthesized from pyromellitic bis(anhydride) and characterized with different techniques. Compound **2** has been acquired from Sigma-Aldrich. Vibrational spectra have been recorded with a Renishaw 1000 (Raman, exciting line: 647 nm) and a Bruker IFS spectrometer (IR), both coupled to a microscope. Spectral resolution: 2 to 3 cm⁻¹. Electrical measurements employing a ferroelectric analyser (aixACCT TF2000) have been performed on needle-like samples contacted at opposite tips to gold electrodes with a special graphite paste, whose solvent (diethylsuccinate) does not deteriorate organic CT crystals. All-electron DFT calculations have been performed at the B3LYP/6-31G(d) level with the CRYSTAL09 code.

Author Contribution

G.D. and A.G. designed the research and wrote the Communication with contributions from the other authors. Experimental work has been performed by M.S., I.R. (materials synthesis and crystallization), X.F. (X-ray diffraction), M.M. (vibrational spectra), J.K.H.F. (dielectric measurements). G.D. and G.G. performed DFT calculations. All authors discussed the results and contributed to data analysis.

Competing Financial Interests

Declared none.

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Extended Data

Extended Data Figure 1 | Raman spectra of compounds 1, 2 and 1·2. The negligible frequency variation of the C=O mode between **1** and **1·2** further confirms the very small charge transfer ($\rho \approx 0$) in the co-crystal, as also evinced from IR spectra in the main text.

Extended Data Figure 2 | Additional electric measurements for LASO compound 1·2. (a) Picture of two of the single crystal of **1·2** measured taken under optical microscope. Measured crystals are of good quality, with smooth surfaces and do not present evidence for branching or splintering. (b) Electric-field dependent polarization of **1·2** at 7 K (circles). (c) Time-dependent excitation field and (d) current response of the PUND measurements. The identical response to pulses I and II and to pulses III and IV indicate the absence of polar order.

Extended Data Table 1| Density Functional Theory (DFT) calculations on the three LASO crystals reported by Tayi *et al.*. Analysis of the relative stability of non-polar and polar structures of LASO complexes. In all cases the non-polar structures ($P\bar{1}$ for **1·2** and **1·4**, $P2_1/n$ for **1·3**) are found to be more stable than the polar ones ($P1$ for **1·2** and **1·4**, Pn for **1·3**): $\Delta E = E_{non-polar} - E_{polar} < 0$. The last column reports the degree of intermolecular charge transfer ρ computed from Mulliken atomic charges, which is found to be negligible. This confirms that the three LASO crystals are essentially neutral in accordance with vibrational measurements. DFT calculations were performed with the CRYSTAL09 code, employing the hybrid B3LYP functional and the 6-31G(d) basis set. Our calculations explicitly considered valence and core electrons and periodic boundary conditions in three dimensions with a $2 \times 2 \times 2$ sampling of the Brillouin zone. Empirical dispersion corrections have been used.

Crystal	$E_{non-polar}$ (Ha)	E_{polar} (Ha)	ΔE (eV)	ρ
1·2	-3809.1025	-3809.0753	-0.740	-0.03
1·3	-4268.5279	-4268.3446	-4.988	-0.04
1·4	-6921.1020	-6921.0818	-0.549	-0.09