

Conflicting evidence for ferroelectricity

ARISING FROM S. A. Tayi *et al.* *Nature* **488**, 485–489 (2012); doi:10.1038/nature11395

Organic ferroelectric materials operating at room temperature are in demand in the emerging field of lightweight, flexible and environmentally friendly electronics. Tayi *et al.*¹ reported room-temperature ferroelectricity in organic mixed-stack charge-transfer crystals, produced using a supramolecular design concept—the lock-arm supramolecular ordering (LASO)—that synergistically combines intermolecular charge transfer and hydrogen bonds^{2,3}. Here we present an independent experimental investigation that found no evidence for ferroelectricity in one of the LASO compounds described in ref. 1 and, together with theoretical calculations, demonstrates that a possible ferroelectric behaviour is not of electronic origin as proposed in ref. 1. We therefore question the reproducibility of the room-temperature ferroelectricity claimed for LASO systems¹. There is a Reply to this Comment by Tayi, S. A. *et al.* *Nature* **547**, <http://dx.doi.org/10.1038/nature22802> (2017).

Room-temperature ferroelectricity has been claimed for three charge-transfer crystals formed by the same electron acceptor (A) and three different donors (D) using LASO¹. The ferroelectric behaviour was ascribed to a sizeable charge ρ transferred from D to A molecules arranged in non-centrosymmetric structures characterized by polar dimers [...($D^{+\rho}A^{-\rho}$)($D^{+\rho}A^{-\rho}$)...], as observed in other mixed-stack charge-transfer crystals, albeit at cryogenic temperatures^{4,5}. Tayi *et al.*¹ supported their finding with a combination of structural, vibrational and dielectric measurements that we replicate here for their system 1·2 (see Fig. 1a). We note that the X-ray diffraction data of the three LASO crystals have been recently re-examined by the same authors, assigning all of them to centro-symmetric space groups³, which is incompatible with ferroelectricity.

We synthesized compounds 1 and 2 and grew single crystals of compound 1·2 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 $P\bar{1}$ than for the $P1$ group initially proposed in ref. 1. 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 charge-transfer crystals⁶. Totally symmetric molecular vibrations offer an unambiguous probe of the dimerization of the lattice: these Raman-active modes show up in infrared spectra polarized along the stack axis only in dimerized phases, where they modulate the asymmetric flow of electronic charge, acquiring a much larger intensity than that of other vibrations. Being sensitive to local static or dynamic disorder, vibrational spectroscopy offers information complementary to X-ray diffraction data, which probes only long-range order. Our absorption infrared and Raman spectra in Fig. 1b do not present coincident peaks, firmly excluding stack dimerization, whether local or nonlocal, static or dynamic. The frequency coincidences in infrared and Raman spectra reported by Tayi *et al.*¹ are probably accidental, owing to the presence of many bands in their limited-quality infrared spectra. We assume their infrared spectra were obtained by applying the Kubelka–Munk transformation to the single-point reflectance spectra of single crystals, although this transformation is appropriate only for the diffuse reflectance spectra of powders⁷.

Infrared spectroscopy also allows us 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 sizeable charge transfer to the three LASO compounds ($\rho=0.67$ for 1·2, $\rho=0.89$ for 1·3 and $\rho=0.43$ for 1·4), based on the frequencies of the carbonyl stretching of 1, and 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 chemical intuition, experimental literature⁹, 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 any need of calculation or calibration, Fig. 1c compares the infrared 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 is also confirmed by Raman spectra (see Extended Data Fig. 1). This 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 our DFT results (see Extended Data Table 1) further support the conclusion, pointing to largely neutral states for all three systems.

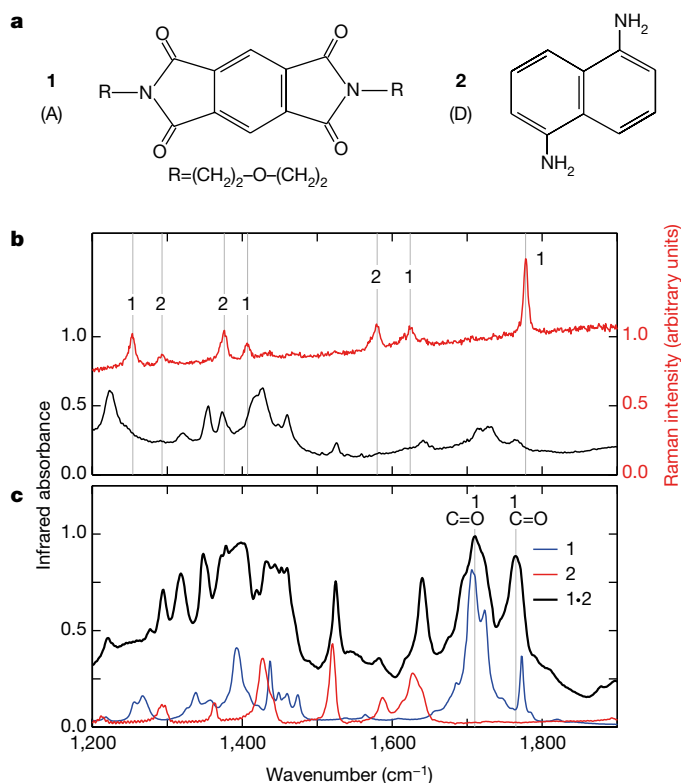


Figure 1 | Vibrational spectra of LASO compound 1·2. a, Structure of the electron acceptor (A, 1) and donor (D, 2) molecules forming the LASO complex. b, Room-temperature infrared (polarization along the stack axis) and Raman spectra for 1·2. Vertical lines mark the Raman modes of the two molecules, none of which appear in the infrared spectrum, indicating the presence of inversion symmetry. c, Infrared 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 charge transfer ($\rho\approx 0$).

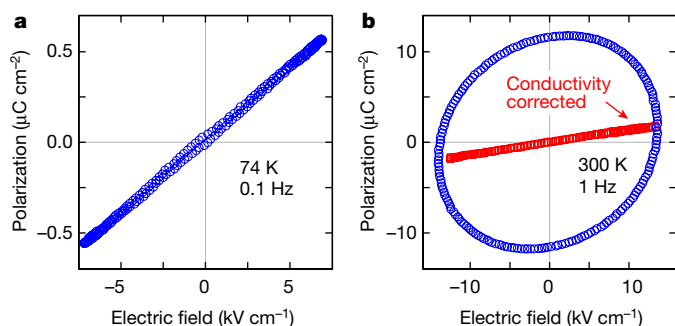


Figure 2 | Dielectric measurements for LASO compound 1-2. Electric-field-dependent polarization of **1-2** at 74 K (**a**) and 300 K (**b**). The red squares in **b** show the conductivity-corrected result at 300 K. A neat paraelectric response is obtained for temperatures in the range 7–400 K.

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 charge-transfer 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 for the difficulty of detecting it using X-rays or vibrational spectroscopy. To check for possible ferroelectric behaviour in the **1-2** complex, we performed electrical polarization hysteresis measurements at various temperatures between 7 K and 400 K, with different fields and frequencies. Figure 2a shows a typical $P(E)$ curve collected at 74 K, showing a nearly linear behaviour with only a slight hysteresis, typical for a linear, slightly lossy, dielectric. At 300 K (Fig. 2b), the significantly larger loss contribution from direct-current 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, $P(E)$ behaviour. 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 the possibility 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, for example, from stray capacitance. We performed additional positive-up, negative-down (see Extended Data Fig. 2)¹⁴ measurements at 300 K 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 charge-transfer 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 the conflicting evidence through a rigorous protocol of sample preparation and of ferroelectricity measurements, to establish reproducibility and to exclude all possible causes of experimental artefact¹⁵. In any case, our analysis rules out the possibility that the ferroelectricity of LASO systems, if present, is electronic in nature.

Methods

Compound **1** was synthesized from pyromellitic bis(anhydride) and characterized with different techniques. Compound **2** was acquired from Sigma-Aldrich. Vibrational spectra were recorded with a Renishaw 1000 (Raman, exciting line 647 nm) and a Bruker IFS infrared spectrometer, both coupled to a microscope. The spectral resolution was 2–3 cm^{-1} . Electrical measurements using a ferroelectric analyser (aixACCT TF2000) were performed on needle-like samples contacted at the tips opposite to the gold electrodes with a special graphite paste, whose solvent (diethylsuccinate) does not cause organic charge-transfer crystals to deteriorate¹⁴. All-electron DFT calculations were performed at the B3LYP/6-31G(d) level with the CRYSTAL09 code.

Data availability. All data are available from the corresponding author upon reasonable request.

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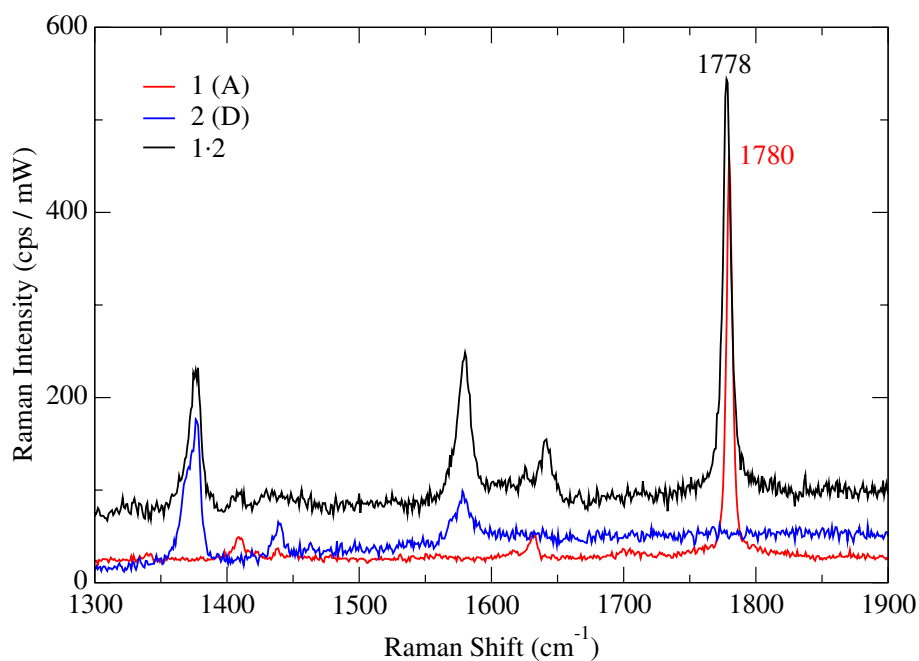
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Supplementary Information accompanies this Comment.

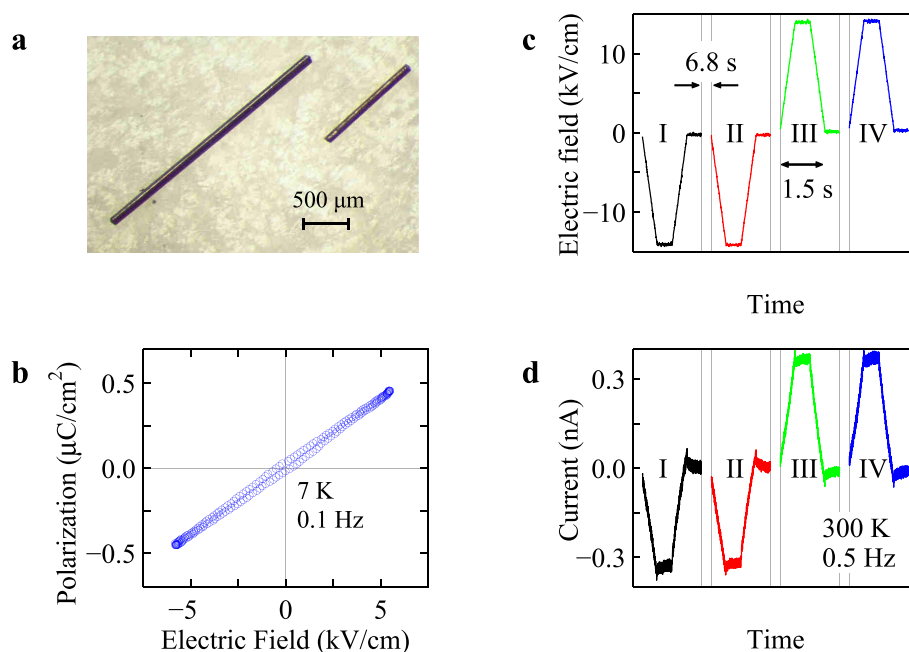
Author Contributions G.D. and A.G. designed the research and wrote the Comment with contributions from the other authors. Experimental work was performed by M.S. and I.R. (materials synthesis and crystallization), X.F. (X-ray diffraction), M.M. (vibrational spectra) and J.K.H.F. (dielectric measurements). 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 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 is also evident from the infrared spectra in Fig. 1c. Raman intensity is given in counts per second per mW of laser power.



Extended Data Figure 2 | Additional electric measurements for LASO compound 1·2. **a**, Picture of two of the single crystals of 1·2 after removal of the contacts. The measured crystals are of good quality, with smooth surfaces and no branching or splintering. **b**, Electric-field-dependent polarization of 1·2 at 7 K (circles). **c**, **d**, Room-temperature time-dependent

excitation field (**c**) and current response (**d**) of the positive-up, negative-down measurements. The responses of pulses I and II are identical, just as the responses of pulses III and IV are identical, indicating the absence of polar order.

Extended Data Table 1 | DFT calculations for the three LASO crystals of ref. 1

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

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 were used.

Tayi *et al.* replyREPLYING TO G. D'Avino *et al.* *Nature* **547**, <http://dx.doi.org/10.1038/nature22801> (2017)

Charge-transfer molecular complexes are an important class of well studied ferroelectric organic systems. First postulated¹ in 1981, tetrathiafulvalene-*p*-chloranil is among the first charge-transfer compounds to demonstrate ferroelectric hysteresis curves, three decades after the discovery of such compounds². The lock-arm supramolecular ordering (LASO) complexes we designed³ are similar materials, incorporating hydrogen bonds in a three-dimensional network that exhibits ferroelectricity at room temperature. In the accompanying Comment⁴, D'Avino *et al.* attempt to reproduce our ferroelectric measurements. However, we draw attention to two serious concerns with their crystal quality and device measurement protocols, which we addressed in our work³. D'Avino *et al.*⁴ present room-temperature measurements for only one crystal; the crystal exhibits considerable leakage current and the low-temperature measurements reveal linear capacitive behaviour as opposed to ferroelectricity.

Using the resistivities from our original paper³, we modelled the resistive contribution to our original polarization measurements; the resistive contribution in our measurements is an order of magnitude smaller than that reported by D'Avino *et al.*⁴. We believe that this discrepancy is likely to be related to poor crystal quality, as indicated by splintering of the crystal (as observed in figure S4 of their supplementary information of ref. 4), which is an indication of crystal defects. In addition, the authors use conductive adhesives that differ from those we recommended in ref. 3. In our experience, such adhesives contain solvents that may have deleterious effects on supramolecular co-crystals.

In the short time since the submission of the accompanying Comment⁴, we have requested members of our laboratories who did not collect data for the original paper³ to reproduce (Fig. 1a) the room-temperature ferroelectric measurements of LASO complexes for co-crystal 1·3. The hysteresis loops we measured are not the

canonical lossy dielectric, or 'banana', loops⁵. Furthermore, devices made with splintered or faceted crystals from our laboratory do not show (Fig. 1b) ferroelectric hysteresis. We believe it is these defects that preclude the observation of ferroelectric behaviour.

Since the publication of ref. 6, we have learned more about these materials. We agree with the community that truly centrosymmetric crystals cannot be ferroelectric. Traditional methods of identifying non-centrosymmetry (such as X-rays) may be insufficient for such crystals⁷. Furthermore, supramolecular interactions (for example, hydrogen bonding) and redistribution of charge (charge transfer) within the crystal could create non-centrosymmetries that are not detectable by X-ray crystallography. Hydrogen atoms, for example, which are directly involved in the construction and behaviour of LASO complexes, are at times difficult to locate directly and accurately using X-rays. We have recently observed⁸ ferroelectricity and second harmonic generation (evidence of non-centrosymmetry) in additional co-crystals that exploit the same supramolecular design but that differ in their chemistry and crystal morphology; these co-crystals add to the number of known ferroelectric LASO compounds.

We are confident of our electronic measurements, and our future work will elucidate the mechanistic details behind ferroelectricity in these charge-transfer complexes. We recognize that the theoretical calculations carried out by some of the authors of the accompanying Comment⁴ do not support the connection between charge transfer and ferroelectricity, but we believe experimental work proves otherwise. We offer to share our materials and devices, and to host the authors of the accompanying Comment⁴ at Northwestern University in an effort to clarify all discrepancies in reproducibility. (We thank A. Narayanan for contributing to reproducing the measurements.)

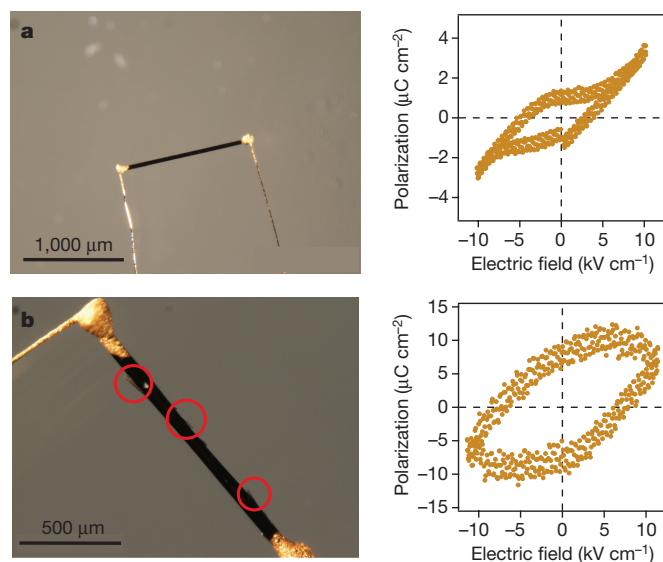


Figure 1 | Images of the devices made with co-crystal 1·3 and splintered co-crystal 1·3 and their room-temperature (300 K) hysteresis curves.

a. The co-crystal 1·3 device (left) and the corresponding reproduction of room-temperature ferroelectric hysteresis (right). **b.** The splintered co-crystal 1·3 device (left; the locations of the splintered edges are identified with red circles) and its corresponding lossy dielectric hysteresis (right).

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BRIEF COMMUNICATIONS ARISING

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