Large electric-field-induced strain in centrosymmetric crystals of a dipolar ruthenium alkylnyl complex

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Dipolar molecular crystals present different physical properties than traditionally strongly correlated ionic solid-state inorganic crystals due to the weak intermolecular bonding. Herein, centrosymmetric dipolar molecular crystals of the organoruthenium complex $\text{trans-}[\text{Ru(C=C}_6\text{H}_4\text{-}4\text{-NO}_2\text{)(C=CPh)(dppe)}_2]$ [$\text{dppe} = 1,2\text{-bis(diphenylphosphino)ethane}$] display a large electric-field-induced strain behaving differently from conventional piezoelectric materials that must, structurally, be noncentrosymmetric. Further studies of related systematically varied crystalline organoruthenium complexes reveal that the strong electromechanical coupling effect is not from classical ferroelectricity, electrostriction, flexoelectricity or electrochemical strain. It is, instead, attributed to the disorder in the molecular packing, which facilitates reorientation of the molecular dipoles under the action of an applied electric field. This provides a fresh insight into the design and development of new functional materials and a promising source of electromechanical coupling in organometallic, and more generally dipolar molecular, crystals.

1. Introduction

Electromechanical coupling is a ubiquitous feature of inorganic, organic and biological materials that underpins diverse phenomena and devices ranging from cardiac activity, actuators, sensors and transducers as well as energy harvesting devices.\(^1\)\(^-\)\(^3\) Strong electromechanical coupling has conventionally been found in piezoelectric and ferroelectric materials that structurally must not possess an inversion centre, such as lead zirconate titanate (PZT),\(^4\)\(^-\)\(^5\) lead zinc niobate-lead titanate (PZN-PT)\(^6\) and lead indium niobate-lead magnesium niobate-lead titanate (PIN-PMN-PT).\(^7\)\(^-\)\(^9\) These piezoelectric and ferroelectric families have been extended to encompass organic systems such as polyvinylidene fluoride and its copolymers,\(^10\) charge-transfer complexes\(^11\) and supramolecular assemblies of nonpolar conjugated molecules.\(^12\) This is motivated, in part, by the different molecular bonding and packing inherent in organic systems that give rise to novel causes of ferroelectricity including rotation of the molecular chain,\(^13\) charge-transfer, proton-transfer and bond dimerization,\(^14\) rather than the displacement of cations or anions typically observed in classical inorganic ferroelectric materials.\(^15\)

The impact of molecular bonding and packing on the properties of organic crystals is not limited to ferroelectricity. Weak intermolecular bonding is responsible for the high compressibility, low resistance to shear deformation and large thermal expansion observed with molecular crystals.\(^16\) It is also responsible for accommodating the large strain induced by an external mechanical force in the organic co-crystal bis(8-hydroxyquinolinato)copper(II)-7,7,8,8-tetracyanoquinodimethane (CuQ\(_2\)-TCNQ).\(^17\) Additionally, molecular packing is known to affect charge-carrier transport, optical properties and polarization.\(^18\) All of these imply that the development of new functional materials based on organic crystals must take into consideration the impact of molecular bonding and packing on the resulting material properties.

In this work, we report a large electric-field-induced strain in centrosymmetric crystals of the dipolar organoruthenium complex $\text{trans-}[\text{Ru(C=C}_6\text{H}_4\text{-}4\text{-NO}_2\text{)(C=CPh)(dppe)}_2]$ (I) [$\text{dppe} = 1,2\text{-bis(diphenylphosphino)ethane}$], for which the electric-field-induced strain is comparable to that of $\text{Pb(In}_{1/2}\text{Nb}_{1/2})\text{O}_3$-$\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-$\text{PbTiO}_3$ (PIN-PMN-PT), one of the best piezoelectric materials.\(^7\)\(^-\)\(^9\) From a systematic structural and switching spectroscopy piezoresponse force microscopy analysis of I and systematically-varied crystalline organoruthenium compounds as well as theoretical calculations, we propose that the strong electromechanical coupling originates from disorder in the molecular packing allowing realignment of the molecular dipoles under the action of an applied electric field, and that it is unrelated to classical ferroelectricity, electrostriction, flexoelectricity or electrochemical strain.

2. Results and Discussion
Figure 1. (a) Cell-packing diagram from the single-crystal X-ray diffraction study of trans-[Ru(C≡C[4-H-4-NO\textsubscript{2}]C=CPh)(dppe)\textsubscript{2}] (I), viewed approximately down the \(b\) axis. Pink: Ru; dark green: P; red: O; light blue: N; black: C. Hydrogen atoms have been omitted for clarity. The nitro substituent is disordered over the two 4-phenylethynyl sites with half occupancy. (b) Molecular structure of I. (c) Amplitude-bias loop of PIN-PMN-PT. (d) Amplitude-bias and (e) phase-bias loops of two different samples of I. The same cantilever was used for SSPFM characterisation of PIN-PMN-PT and I. The AC driving voltage for c-e was 1 V.

Complex I crystallizes in the centrosymmetric triclinic space group \(P\overline{1}\), with molecules of I stacking in parallel planes (Figure 1a). Although molecules of I are polar (Figure 1b), the crystal structure is nonpolar due to the nitro substituent being disordered over the two 4-phenylethynyl substituent sites. The disorder of the nitro substituent has been corroborated by density functional theory (DFT), which shows negligible energy difference on swapping the orientation of individual molecules within the crystal. From symmetry considerations, I cannot be piezoelectric, and by extension ferroelectric, because it crystallizes in the centrosymmetric space group, \(P\overline{1}\).

Piezoresponse force microscopy (PFM) imaging of crystals of I shows a flat surface morphology without any contrast in the angle between the tip and crystal plane. In order to gain further understanding of the electric-field-induced strain in I, a systematic SSPFM analysis of I was carried out, with a particular focus on determining the impact of electrostriction and flexoelectricity on the electromechanical coupling of I, as these two phenomena typically cause electric-field-induced strains in centrosymmetric materials. The dependence of the amplitude-bias loop on the magnitude of the applied DC bias has been investigated (Figure 2a). The AC voltage was maintained at 1 V. Butterfly-like amplitude-bias loops are acquired at voltages greater than 20 V. At 10 V (Figure 2a inset) a linear hysteretic amplitude-bias is observed. At about 50 V, the amplitude saturates at nearly 8 pm. The saturation of the amplitude-bias loops suggests that the electromechanical coupling is not due solely to electrostrictive effects. This is supported by the lack of butterfly-like amplitude-bias loops at 10 V, indicative of a threshold voltage for electromechanical coupling. In addition, only remanent hysteresis loops are presented as this minimizes the impact of electrostriction. Although ferroelectricity has been ruled out due to symmetry considerations.

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The electromechanical response of I at two different AC voltages (1 V and 2.5 V) is presented in Figure 2b. Normalization of the amplitude-bias loops (Figure 2c) demonstrates that the electric-field-induced strain is proportional to the AC voltage, in agreement with SSPFM on ferroelectric materials and electrochemical scanning microscopy. To explore the impact of flexoelectricity on the electric-field-induced strain, the applied
force during SSPFM has been varied (Figure 2d). This is because the AFM tip can cause large local deformations, which results in mechanical strain gradients that have been shown to affect the polarization of ferroelectric materials. However, the amplitude-bias loops do not show any dependence on the applied force (Figure 2d), thereby excluding flexoelectricity as the cause of the electric-field-induced strain.23

![Graph showing amplitude-bias loop](image)

**Figure 3.** (a) Typical dynamic amplitude-bias loop of 1, consisting of 64 loops acquired at 4 ms intervals after 25 ms DC bias pulse. (b) Amplitude relaxation trend after a 60 V pulse, along with a Debye fit to the measured data.

The dynamic behaviour of the amplitude-bias loop of 1 has been studied with dynamic switching spectroscopy piezoresponse force microscopy (D-SSPFM). A similar bias pulse to SSPFM was used; however, the cantilever response was monitored as a function of delay time after the pulse, specifically, the response was acquired for 256 ms in 4 ms intervals,26-28 the measurements being performed using the band-excitation method.28-30 The D-SSPFM shows rapid relaxation of the electric-field-induced strain. (Figure 3a) For each DC bias, the time dependence of the amplitude is found to fit the Kohlrausch-Williams-Watts (KWW) model

\[
\text{Amplitude}(t) = A_0 + A_1 \times \exp\left(-\frac{t}{\tau}\right)^eta
\]

where \(A_0\) denotes the non-relaxing component, \(A_1\) the relaxing component, and \(\beta\) and \(\tau\) are fitting parameters.27, 31 Figure 3b shows an example fit for a 60 V DC bias. The appropriateness of the KWW model is addressed later.

Since 1 contains redox-active ruthenium atoms and nitro substituents,32 it is possible that the electromechanical coupling is due to electrochemical processes at either site leading to a change in molar volume,33, 34 thereby causing the observed electric-field-induced strain in 1. The strain is expected to be reversible, based on cyclic voltammetry and UV-VIS-NIR spectroelectrochemistry.32 Typically, the amplitude-bias loop for electrochemical strain caused by a redox process results in a single hysteresis loop, but it is possible that the two redox-active sites in 1 with different redox potentials may cause a butterfly-like amplitude-bias hysteresis. In order to explore the impact of electrochemical strain, two related crystalline organoruthenium complexes, trans-[Ru(C≡CC6H4-4-NO2)Cl(dppe)2] (2) and trans-[Ru(C≡CPh)2(dppe)2] (3), have been selected based on the similarities of their redox potentials in solution. The oxidation potential of the ruthenium-centred process in 1, 2 and 3 is 0.08, 0.16 and -0.03 V, respectively, with respect to the ferrocene/ferrocenium couple.35 The reduction processes centred at the nitro substituents are irreversible, so no further comment is made here. 1 and 2 are very similar because (as we have noted previously) the phenylacetylide ligands are (electronic- and geometrically) pseudo-halides in these types of complexes.36 Their redox potentials in solution are therefore quite similar, and there is no significant difference in electrochemical response between the three complexes. Both 2 and 3 crystallize in the centrosymmetric triclinic space group P-1. The cell-packing diagram from the single-crystal X-ray structural study of 2, viewed approximately down the b axis. Pink: Ru; light green: Cl; dark green: P; red: O; light blue: N; black: C. Hydrogen atoms have been omitted for clarity. (b) Molecular structure of 2. Typical single-point (c) amplitude-bias and (d) phase-bias loops of 2. (e) Cell-packing diagram from the single-crystal X-ray diffraction study of trans-[Ru(C≡CC6H4-4-NO2)Cl(dppe)2] (2), viewed approximately down the b axis. Pink: Ru; light green: Cl; dark green: P; red: O; light blue: N; black: C. Hydrogen atoms have been omitted for clarity. (f) Molecular structure of 3. Typical single-point (g) amplitude-bias and (h) phase-bias loops of 3.

![Cell-packing diagram](image)

**Figure 4.** (a) Cell-packing diagram from the single-crystal X-ray diffraction study of trans-[Ru(C≡CC6H4-4-NO2)Cl(dppe)2] (2), viewed approximately down the b axis. Pink: Ru; light green: Cl; dark green: P; red: O; light blue: N; black: C. Hydrogen atoms have been omitted for clarity. (b) Molecular structure of 2. Typical single-point (c) amplitude-bias and (d) phase-bias loops of 2. (e) Cell-packing diagram from the single-crystal X-ray diffraction study of trans-[Ru(C≡CC6H4-4-NO2)Cl(dppe)2] (3), viewed approximately down the b axis. Pink: Ru; dark green: P; black: C. Hydrogen atoms have been omitted for clarity. (f) Molecular structure of 3. Typical single-point (g) amplitude-bias and (h) phase-bias loops of 3.

The surface topography of 2 and 3 reveals flat terraces; ferroelectric domains were not detected. Typical amplitude- and phase-bias loops for 2 (Figure 4c and 4d) and 3 (Figure 4g and 4h) show no electric-field-induced strain; the amplitude is invariant on sweeping the applied bias, and no phase shift is observed. If the electromechanical coupling is due to oxidation at the ruthenium, then electric-field-induced strain would be expected for all complexes, especially 3, since the oxidation
potential of ruthenium in 3 is the lowest; however, there is no electric-field-induced strain observed in 3. 2 should behave similarly to 1, but there is no induced strain observed in 2. All these experimental results and the reported electrochemical data\textsuperscript{36,39} suggest that the large-electric-field-induced strain observed in 1 (at least) is not dominated by the electrochemical response.

While ferroelectricity, electrostriction, flexoelectricity and electrochemical strain have been discounted as the cause of electromechanical coupling in 1, the question of the origin of the electromechanical coupling remains unanswered. We propose that the electromechanical coupling is due to disorder in the molecular packing allowing realignment of the molecular dipoles under the action of an applied electric field. This is motivated by the difference in the permanent and induced dipole moments of the crystallites studied. Table 1 lists the calculated permanent dipole moment, average polarizability and polarizability anisotropy of the studied crystals. The permanent dipole moment of 1 is the largest. While the average polarizability (which is related to the induced dipole moment) of 1, 2 and 3 are comparable due to their similar chemical framework, it is largest for 1. The higher polarizability anisotropy of 1 implies that the induced dipole moment can be much higher (or lower), depending on the direction of the applied electric field. The large permanent dipole moment and induced dipole moment of 1 cause the observed large electric-field-induced strain when the molecular dipoles realign under the action of an applied electric field. The lack of electric-field-induced strain in 3 is unsurprising since it is nonpolar. While the permanent dipole moment and average polarizability of 2 is lower than 1 it is still substantial, and yet no electric-field-induced strain is observed. It is proposed that the difference in electromechanical coupling between 1 and 2 is due to the disorder of the molecular packing. When an electric field is applied to 2, the ordered antiparallel stacking of molecules causes adjacent molecules to rotate in opposite directions, leading to large steric hindrance thus limiting the amount of electric-field-induced strain. In comparison, the disorder associated with the nitro substituent in 1 permits local regions with molecules stacked parallel to one another that can more readily realign under the action of an applied electric field due to the lower steric hindrance. The presence of different sizes of local regions with molecules stacked in parallel leads to a distribution of relaxation times, thereby justifying the appropriateness of the KWW model for fitting the amplitude relaxation (Figure 3b) (the model is appropriate for fitting such relaxation because it describes relaxation in disordered systems with a spread of relaxation times).

Table 1. Permanent dipole moment, average polarizability and polarizability anisotropy of 1, 2 and 3.

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<tr>
<th>Crystal</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>Permanent dipole moment (D)</td>
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<tr>
<td>Average polarizability (a.u.)</td>
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<td>1579</td>
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<tr>
<td>Polarizability anisotropy (a.u.)</td>
<td>309000</td>
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<td>71000</td>
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3. Conclusion

A large electric-field-induced strain was observed in centrosymmetric crystals of the dipolar organoruthenium complex 1. The maximum amplitude difference is comparable to that of one of the best piezoelectric materials, PIN-PMN-PT. The amplitude-bias and phase-bias of 1 are similar to those of ferroelectric materials, but the space group of 1 precludes ferroelectricity. Through a systematic structural and switching spectroscopy piezoresponse force microscopy analysis, we have demonstrated that ferroelectricity, electrostriction, flexoelectricity and electrochemical strain are not the cause of electromechanical coupling in 1. Instead, it is proposed that the electric-field-induced strain is a result of the disorder in the molecular packing allowing realignment of the molecular dipoles under the action of an applied electric field.

The large electric-field-induced strain in 1 is promising because 70% of achiral molecules crystallize in centrosymmetric space groups, and the majority of these compounds are polar in nature, suggesting that the hitherto-unobserved electric-field-induced strain in organometallics identified in the present study should be a common feature. The facile structural variation possible with organometallic complexes suggests that, with optimization of performance following appropriate molecular modification, such species may be of significant applications interest.

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Notes and references

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