

Organic ferroelectrics

Ferroelectricity results from one of the most representative phase transitions in solids, and is widely used for technical applications. However, observations of ferroelectricity in organic solids have until recently been limited to well-known polymer ferroelectrics and only a few low-molecular-mass compounds. Whereas the traditional use of dipolar molecules has hardly succeeded in producing ferroelectricity in general, here we review advances in the synthesis of new organic materials with promising ferroelectric properties near room temperature, using design principles in analogy to inorganic compounds. These materials are based on non-covalent molecules formed by two or more components, in which ferroelectricity arises either from molecular displacements or from the collective transfer of electrons or protons. The principle of using multi-component molecular compounds leads to a much broader design flexibility and may therefore facilitate the development of future functional organics.

SACHIO HORIUCHI¹ AND YOSHINORI TOKURA^{1,2,3}

¹Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8562, Japan

²ERATO Multiferroic Project, Japan Science and Technology Agency (JST), c/o AIST, Tsukuba, 305-8562, Japan

³Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8656, Japan

e-mail: s-horiuchi@aist.go.jp; tokura@ap.t.u-tokyo.ac.jp

Ferroelectricity, which enables the electric switching of electric polarization, has long been an important topic in condensed-matter science, and its application is important as a basic element of devices and memories¹. The connection between ferroelectricity and organic molecules started in 1920 with the discovery of the first ferroelectric crystal, Rochelle salt, containing organic tartrate ions². Nevertheless, examples of organic ferroelectrics have not been abundant. Their invention may not only pose a fresh challenge to materials chemistry but may also find many new applications of their lightness, flexibility and non-toxicity in the emerging field of organic electronics.

Ferroelectrics are polar substances of either solid (crystalline or polymeric) or liquid crystal, in which spontaneously generated electric polarization can be reversed by inverting the external electric field. The critical electric field for reversing the polarization is called a coercive field. The electric displacement (D) as a function of field strength (E) consequently draws a hysteretic curve (D - E loop) between opposite polarities, and this electric bistability can be used, for example, for non-volatile memory elements. In particular, ferroelectric random access memory (FeRAM) and ferroelectric field-effect transistors are current targets for practical applications³. The ferroelectric compounds usually have a Curie temperature T_c for a paraelectric-to-ferroelectric phase transition. As the temperature approaches T_c , the dielectric constant (κ), obeying the Curie–Weiss law, is amplified to large values, which can be exploited for a high- κ condenser and capacitor. The other important property is pyroelectricity, in which the temperature dependence of spontaneous polarization generates an electric current on heating or cooling when both ends of the polarized ferroelectrics are short-circuited. The pyroelectric effect is

especially large just below T_c , being useful as a thermal-imaging sensor and an infrared detector. Furthermore, ferroelectricity itself brings a key cross-correlation phenomenon between electric and mechanical properties; the stress generates electric polarization (charge), whereas the electric field creates strain in the material. The large electrostriction and piezoelectric effects are used in actuators, transducers, ultrasonic motors, piezoelectric elements, and microsensors, for example. In addition, the polar crystal structure yields second-order optical nonlinearity, causing second-harmonic generation activity and a linear electro-optic effect. The possible technological areas of application are diverse: electronics, electro-optics and electromechanics. Importantly, most of these operations under ambient conditions demand a T_c near or above room temperature. For instance, in the 1950s the glycine molecule was discovered to exhibit room-temperature ferroelectricity in its salts with inorganic counterions⁴, such as triglycine sulphate ($T_c \approx 50^\circ\text{C}$), as well as pyroelectricity in the representative pyroelectric materials. The potential for applications would certainly be true for purely organic materials. Indeed, the room-temperature ferroelectricity of a polymer⁵ saw the early commercial use of piezoelectricity in electroacoustic and electromechanical transducers such as headphones and loudspeakers⁶. As with the low-molecular-mass compounds, however, there had been very few examples^{7,8} in spite of their potential for use in organic electronics. However, this has changed recently, as new approaches for materials design of organic ferroelectrics have been developed. We begin our overview of recent progress with the general features of conventional materials.

CONVENTIONAL FERROELECTRICS

Schematic drawings of the inorganic (Fig. 1a) and organic (Fig. 1b) ferroelectric solids illustrate how conventional materials achieve ferroelectricity on a microscopic level. The most straightforward mechanism, as exemplified by sodium nitrite (NaNO_2) is that the permanent dipoles of the polar molecules or ions generate spontaneous polarization, and their reorientation generates the ferroelectricity. The dipole moments are ordered without cancelling each other out in the ferroelectric state, whereas the paraelectric state

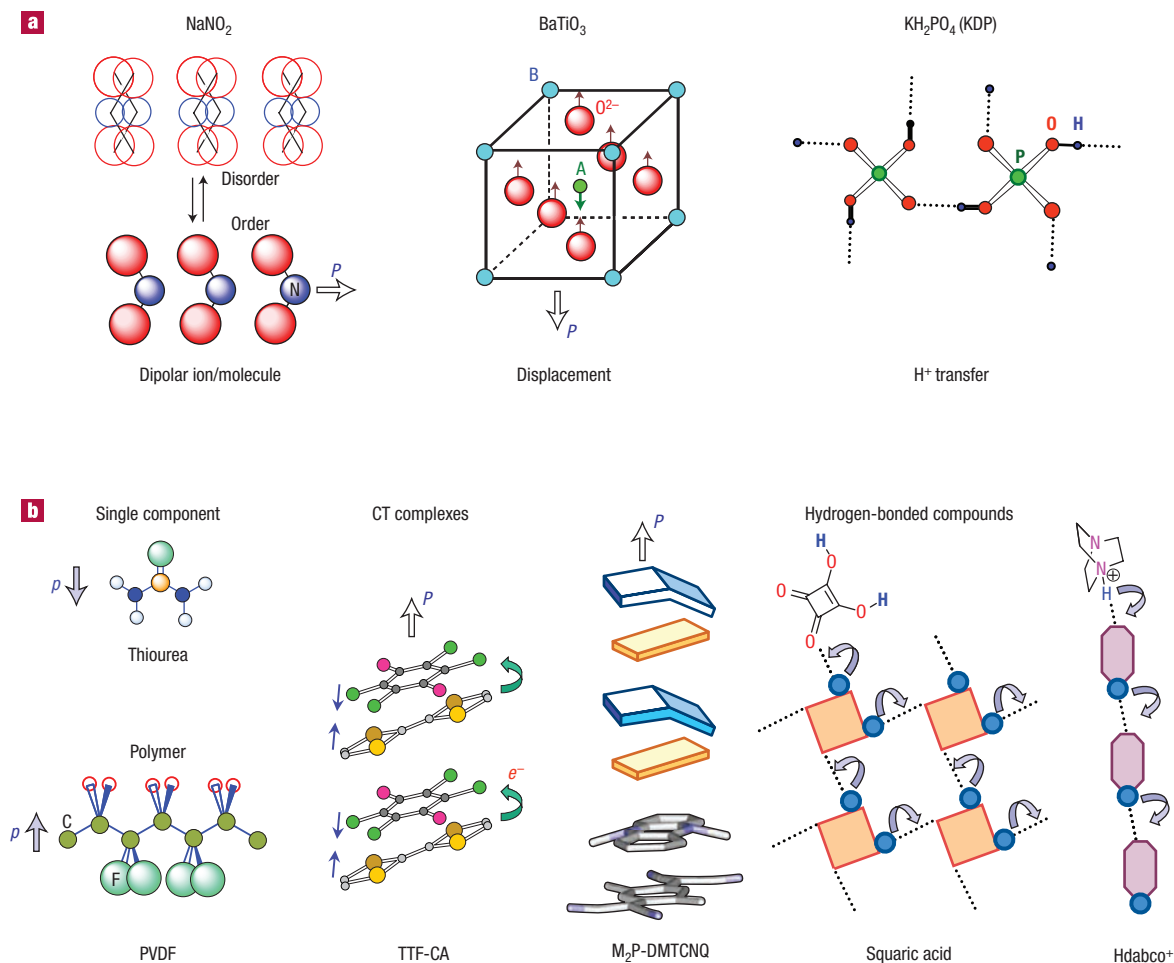


Figure 1 Conventional designs of ferroelectric materials and the origin of their dipole moment p or polarization P (open arrows). **a**, Typical examples of inorganic ferroelectric materials. **b**, Conventional organic ferroelectric or antiferroelectric substances. PVDF, poly(vinylidene difluoride).

corresponds to disorder in their orientations. These transformations are mostly classified by the order–disorder type phase transition. The corresponding type of organic solid includes most of the single-component low-molecular-mass compounds as well as the polymer ferroelectrics⁹ and a vinylidene fluoride oligomer in thin-film form¹⁰. Ferroelectric liquid crystals^{11,12}, which are beyond the scope of this review, apparently also belong to this class. Thiourea was the first example of a genuinely organic ferroelectric of low molecular mass^{13,14}; it has been extensively studied since the discovery of its ferroelectricity in 1956. The considerable interest in it arises from its complicated structural transformations, passing various phases of commensurate and incommensurate superstructures between the paraelectric and ferroelectric phases¹⁵. Later on, the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, also known as tanane) free radical, well known for its stability, was also found to be an organic ferroelectric of the polar molecular type near room temperature¹⁶. Another notable organic ferroelectric is 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne^{17–19}, a diacetylene monomer that can polymerize while maintaining its single-crystal form. The ferroelectric transition with low T_c (46 K) is found to vanish on polymerization¹⁷.

In comparison with inorganic compounds, organic substances have been synthesized in large numbers but ferroelectric properties have been found in them only rarely. The other feature is the tendency to form highly anisotropic structures with much lower lattice

symmetry. Despite their occasional crystallization to polar structures, their dielectric properties and possible ferroelectricity were not always examined. By inspecting the reported organic ferroelectrics, Choudhury and Chitra recently proposed²⁰ that transformation between the different degenerate orientations for ferroelectricity would demand a molecular symmetry higher than C_1 , which is still encountered in as many as 30% of pure organic structures. To seek undisclosed ferroelectric candidates, Zikmund *et al.*²¹ performed a symmetrical analysis on the polar crystal structures using the Cambridge Structure Database. The strategy was to discover the hidden ‘pseudosymmetry’, which would survive in the paraelectric structure. They suggested more than ten potential molecules for ferroelectricity and succeeded in finding a weak ferroelectric, the cyclohexane-1,1'-diacetic acid²². However, the investigation of polar molecules has not met with much success because ferroelectricity poses some difficult hurdles. The dipole–dipole interactions usually tend to cancel out neighbouring molecular dipoles in the crystals. Large numbers of non-centrosymmetric molecules have been synthesized, and they can occasionally crystallize to polar (and hence acentric) solids without cancelling out their dipoles. A further constraint on molecular packing is a low enough energy barrier for the molecular reorientations to overcome in the crystalline solid. For the existing polymer ferroelectrics, the steric difficulty in reorienting dipoles gives rise to an exceptionally large coercive field compared

with other ferroelectrics¹⁰. In low-molecular-mass compounds, this approach has yielded only a few ferroelectrics. The organic ferroelectrics and their dielectric properties are listed in Table 1 and compared with several selected inorganic and inorganic–organic hybrid ferroelectric compounds. Apart from thiourea¹⁴, these single-component organic compounds have a rather low dielectric constant κ and show spontaneous polarization. This is because their ferroelectricity is mostly a side-effect of an extrinsic origin such as a ferroelastic or structural instability other than dipole–dipole interactions. Such structural phase transformations are classified as improper ferroelectric and are distinguished from the usual proper ferroelectrics, where spontaneous polarization is an order parameter, describing well the phase-transition phenomena.

With the above features in mind, the search for alternative routes to new organic ferroelectrics would involve other ferroelectric mechanisms. A useful approach is to consider the analogy with many ferroelectric oxides such as BaTiO₃, which do not contain polar ions. In this class, the relative displacement of ions creates spontaneous polarization; this mechanism is therefore called displacive. Such ferroelectricity requires some structural instability that produces spontaneous lattice deformations into a polar state. This can happen when the electrostatic attractive force is originally in a delicate balance with the competing short-ranged repulsion force between the ions. The corresponding design of organic ferroelectrics should start with ‘multi-component’ molecular compounds with possible molecular displacements. Subsequent sections will describe applications of this principle.

Besides dipolar molecules and ion displacement, there is a case in which dynamic protons on hydrogen bonds trigger the ferroelectric ordering of the lattice. A typical example is the KH₂PO₄ (KDP) family, in which the collective site-to-site transfer of protons in the O–H...O bonds switches the spontaneous polarization (Fig. 1a). This class of ferroelectrics will hereafter be called KDP type or proton-transfer type. The actual ferroelectric crystals may show both order–disorder and displacive characteristics, which are not mutually exclusive. In the KDP family, the simultaneous displacive deformation of PO₄^{3–} ions contributes mainly to spontaneous polarization alongside protonic order–disorder phenomena²³. In comparison with dipolar molecules, one can imagine that moving protons only within the hydrogen bond would be generally advantageous in minimizing steric difficulties for ferroelectricity. In fact, the KDP has a small coercive field.

In the case of hydrogen-bonded organic systems, ferroelectricity has recently been found in tricyclohexylmethanol (TCHM)²⁴, which has a hydrogen-bonded dimer and shows a minute pyroelectric charge at low temperature. However, the origin of ferroelectricity is a dipole-reorientation process distinct from that of the KDP type: the two O–H...O bonds linking two TCHM molecules are simultaneously broken while two OH groups are reoriented around the C–O bonds^{25,26}. The correlated proton dynamics, similar to that of KDP, is found in some other hydrogen-bonded organic molecules. Squaric acid²⁷, shown in Fig. 1b, is a dipolar molecule with two protons, affording four-fold degenerate configurations. Its crystal forms a sheet-like polar network with the intermolecular O–H...O hydrogen bonds. When the polarity of the sheet is reversed

Table 1 Properties of purely organic ferroelectrics compared with those of selected typical ferroelectrics of polymeric, inorganic and inorganic–organic hybrid compounds

Materials	References	Transition temperature (K)		Dielectric constant		$C(\times 10^3 \text{ K})$	$P_s (\mu\text{C cm}^{-2})$; temperature	$E_c (\text{kV cm}^{-1})$
		T_c	T_c^D	κ_{RT}	κ_{max}			
Single-component (polar) organic molecules								
Thiourea	14	169	185	30	10^4	3.7	3.2; 120 K	0.2
TEMPO	16	287	288	10	16	-	0.5	-
CDA	22	397			25	-	-	-
TCAA	76, 77	355		4.5	6.5	0.0076	0.2; RT	4
Benzil	78	84	88		2.7		3.6×10^{-3} ; 70 K*	-
DNP	18, 19	46		4.0	22	0.026	0.24; 10 K*	-
TCHM	24	104		9.6	100	2.7	6×10^{-3} ; 96 K*	-
VDF oligomer	10	-		6			13; RT	1,200
CT complexes								
TTF-CA	39, 44	81	84	40	500	5.7	-	-
TTF-BA	38	50			20	-	-	-
H-bonded supramolecules								
Phz-H ₂ ca	55, 61	253	304 †	110	3×10^3	5.0	1.8; 160 K*	0.8
Phz-H ₂ ba	55, 61	138	204 †	30	1.7×10^3	4.0	0.8; 105 K*	0.5
[H-55dmbp][Hia]	57	269	338 †	250	900	14	4.2*; 110 K*	2
Clathrate								
β-Quinol–methanol	79	63.7			220	-	6×10^{-3} ; 25 K*	-
Polymers								
VDF _{0.65} –TrFE _{0.35}	5	363		20	50	-	8; RT	500
Nylon-11	8	-			4	-	5; RT	600
Inorganic compounds								
NaNO ₂	8	437			4×10^3	4.7	10; 140 K	5
BaTiO ₃	8	381		5×10^3	10^4	150	26; RT	10
PbTiO ₃	8	763		210	9×10^3	410	75; RT	7
SbSI	8	293			6×10^4	233	20; 270 K	-
KH ₂ PO ₄ (KDP)	8	123	213	30	2×10^4	2.9	5.0	0.1
Organic–inorganic compounds								
HdabcoReO ₄	36	374		6	22	-	16; RT*	>30
TGS	4, 8	323	333	45	2×10^3	3.2	3.8; 220 K	0.9
TSCC	8	127		5	80	-	0.27; 80 K	3
Rochelle salt	8	297	308		4×10^3	2.24	0.25; 276 K	0.2

β -Quinol, hydroquinone; CDA, cyclohexan-1,1'-diacetic acid; dabco, diazabicyclo[2.2.2]octane; DNP, 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiene; TCAA, trichloroacetamide; TCHM, tricyclohexylmethanol; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy (tanane); TGS, triglycine sulphate; TSCC, Tris-sarcosine calcium chloride; VDF oligomer, CF₃(CH₂CF₂)₁₁I (thin film); VDF_{0.65}–TrFE_{0.35}, vinylidene fluoride–trifluoroethylene copolymer ((CH₂CF₂)_{0.65}(CHF–CF₂)_{0.35})_n; T_c^D , transition point for deuterated compound, κ_{RT} , dielectric constant at room temperature; κ_{max} , maximum dielectric constant at T_c ; C , paraelectric Curie constant; P_s , spontaneous polarization; E_c , coercive field; RT, room temperature.
*Pyroelectric charge measurements.
†Deuterated only in the hydrogen bond.

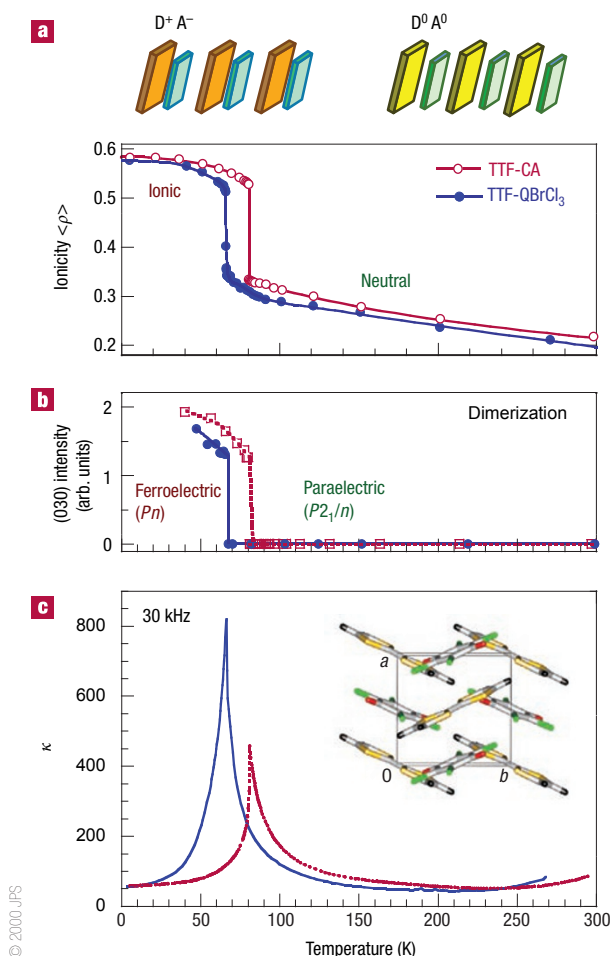


Figure 2 Neutral-ionic phase transitions for TTF-CA and TTF-QBrCl₃ crystals. Reprinted with permission from ref. 44. **a**, Molecular ionicity $\langle \rho \rangle$ obtained from frequency shift of the charge-sensitive intramolecular C=O stretch vibrational mode. **b**, Degree of symmetry-breaking dimerization for long-range ferroelectric order monitored by the X-ray (030) reflection intensity. **c**, Dielectric constant measured with the a.c. electric field E ($f = 30$ kHz) parallel to the DA stack. The schematic illustrations at the top of **a** represent the ionic dimerized (ferroelectric) and neutral undimerized (paraelectric) lattice forms. The inset to **c** shows the molecular stacking viewed along the crystallographic c direction.

by correlated proton transfer, the crystal has a very large in-plane dielectric constant κ (about 300) above the order-disorder transition temperature (373 K)²⁸. Although interlayer ordering cancels out the bulk polarization in an antiferroelectric manner, recent theoretical calculations suggest a huge in-plane polarization²⁹. Squaric acid contains β -diketone enol (enolone, HO-C=C-C=O) units with a strong coupling between the proton and the π -electron system, which can drive tautomerization³⁰ between the keto and enol forms: $\text{C}=\text{O}\cdots\text{HO}-\text{C}=\text{C} \leftrightarrow \text{C}=\text{C}-\text{OH}\cdots\text{O}=\text{C}$. Such a conjugated form is called resonance-assisted hydrogen bonding (RAHB) and is responsible for strong intramolecular or intermolecular interactions³¹. Similar tautomerization was therefore examined as a possible candidate for ‘organic KDP’ effects in the cyclic β -diketoalkanes³², hydroxyphenalenones^{33,34} and bisquaric acids³⁵. Many of these compounds did indeed demonstrate the expected tautomerization as well as quantum paraelectricity, a strong isotope effect and/or deuterium-substitution-induced phase transitions.

However, their ferroelectric ordering is only of antiferroelectric nature. No KDP-type ferroelectrics have therefore yet been found among organic single-component materials.

A genuine prototype has been found in diazabicyclo[2.2.2]octane (dabco) salts with inorganic tetrahedral anions³⁶. The monovalent Hdabco⁺ cations are linked linearly, with N-H⁺...N bonds between the basic nitrogen and its conjugate acid form. The resultant linear chain adopts bistable orientations, which can undergo reversal by a collective proton-transfer process (Fig. 1b). This polarity reversal can achieve ferroelectricity with a spontaneous polarization as large as 16 $\mu\text{C cm}^{-2}$. A similar structural motif has also been fabricated in monoprotonated pyrazinium salts, with a resultant anomalous dielectric response³⁷. From the above features we can identify two requirements for designing KDP-type ferroelectrics. First, the hydrogen-bond interactions forming a chain, a sheet or a three-dimensional network must be strong enough to relay protons from site to site. The above RHAB system and ionic hydrogen bonds of a homonuclear type such as O-H...O⁺ and N-H⁺...N would be useful for this purpose. Second, the bistable nature of ferroelectrics requires preservation of the chemical identities of molecules and also the number of attached protons during the proton transfer. Particularly for an intermolecular hydrogen-bonded system, this constraint implies a correlated motion of protons rather than independent hopping. For instance, KDP reserves two protons in total on each PO₄ unit. Such a constraint is observed typically in ice — the so-called ice rule — and is essential for polarization reversal.

In contrast with the above single-component molecules, the ‘displacive’ and ‘proton-transfer’ mechanisms in systems with two or more components have been successfully applied in the design of new organic ferroelectrics with improved ferroelectric properties. In what follows, we describe these contemporary designs of organic ferroelectrics and highlight two types of binary compound: charge-transfer complexes of electron donors and acceptors, and proton donor-acceptor compounds (supramolecules) with intermolecular hydrogen bonds.

ELECTRON DONOR-ACCEPTOR SYSTEM

One might expect that a multi-component molecular system would produce a typical displacive-type ferroelectric by displacing oppositely charged species. The charge-transfer (CT) complex composed of electron donor (D) and acceptor (A) molecules provides such a route to organic ferroelectrics. In the crystal, the molecules are more or less electrically charged as D^{+ ρ} and A^{- ρ} with a finite CT degree ρ ($0 < \rho < 1$) through their CT interactions. Here we focus on the conventional structural motif of a mixed stack (Fig. 2) forming a π - π stack with alternating D^{+ ρ} and A^{- ρ} molecules. The originally nonpolar DA DA... sequence with regular intermolecular separation can be symmetry-broken to a polar chain by forming dipolar DA dimers. The polarity reversal between the two degenerate DA DA... and AD AD... forms should be compatible with the displacive-type mechanism. The signatures of one-dimensional ferroelectricity were noticed first in dielectric measurements on a few CT complexes³⁸. The phase transition was clearly identified with a sharp peak anomaly in the dielectric constant for tetrathiafulvalene (TTF) complexes with *p*-bromanil (tetrabromo-*p*-benzoquinone; BA)³⁸ and *p*-chloranil (tetrachloro-*p*-benzoquinone; CA)³⁹. It should be noted that all these component molecules are planar and nonpolar. The later structural studies on their low-temperature phases confirmed symmetry breaking by molecular displacement into polar (ferroelectric) structures^{40,41}.

The most systematically studied is the TTF-CA crystal. This is because its ferroelectric ordering accompanies a novel valence transformation called a neutral-ionic (NI) phase transition^{42,43}, which involved switching between the two contrasting states of matter in a solid, namely van der Waals molecular assembly and ionic solid.

Figure 2a shows a jump in molecular ionicity ρ from 0.2–0.3 to 0.6 in TTF-CA and its mono-bromine-substituted analogue, TTF-QBrCl₃ (2-bromo-3,5,6-trichloro-*p*-benzoquinone)⁴⁴ through intermolecular collective electron transfer. This valence instability arises from a subtle energetic balance between the cost of ionizing constituent molecules and gains in the electrostatic (Madelung) energy of the ionized lattice^{42,43}. The ionized molecules form the DA dimers. Importantly, the dimerization changes the monoclinic lattice (space group $P2_1/n$) into a polar one (space group Pn)⁴⁰. The sudden appearance of (0*k*0) X-ray reflections (where *k* is odd) below the NI transition temperature (T_{NI}) unambiguously proves ferroelectric ordering with a loss of two-fold screw axis (Fig. 2b). The dielectric constant measured along the DA chain obeys the Curie–Weiss law in the paraelectric phase, and increases to 500 (Fig. 2c) before its discontinuous jump at T_{NI} , which is reminiscent of a first-order ferroelectric phase transition^{39,44}. Just above the transition point, the soft mode appears as a Drude-like high-reflectance band in the stack-axis polarized reflectivity of the far-infrared region⁴⁵. The appearance of a soft mode manifests a phase transition typical of the displacive type, which is also accompanied by an unusually enhanced fluctuation of molecular valence. The driving force of the molecular displacement shown above is considered to be an electronic origin called Peierls instability, which is inherent in the one-dimensional nature of the DA chain⁴⁶. Indeed, derivatives of dimethyl-substituted TTF (a series of DMTTF-CA) were also found to undergo the NI transition with similar dimeric distortion but with antiferroelectric ordering⁴⁷. Soos *et al.* reproduced their huge dielectric constant at the NI transition point by calculations with the one-dimensional Peierls–Hubbard model and the Berry phase theory for the polarization of dielectrics⁴⁸. In addition, the actual dielectric constant, especially in its low-frequency region, is affected by the dynamics of one-dimensional polar domains accompanied by soliton-like domain walls^{38,39}. This leads to a large deviation from the Curie–Weiss law in the ferroelectric phase, as observed for TTF-QBrCl₃ (Fig. 2c).

The NI transition system may be viewed as a unique correlated-electron organic system in which intermolecular electron transfer triggers the ferroelectricity simultaneously with rearrangement of the molecular-charge distribution. In this regard, we mention that ferroelectric-like behaviours akin to that of the NI transition have recently been observed in the dielectric constant of some organic conducting charge-transfer salts such as (TMTTF)₂X and (ET)₂RbZn(SCN)₄ (where TMTTF is tetramethyl-TTF, ET is bis(ethylenedithio)TTF, and X represents monovalent (inorganic) ions such as PF₆[−] and ReO₄[−])⁴⁹. The CT process in these salts occurs only on the self-aggregated one-dimensional chain or two-dimensional sheet of fractionally oxidized electron donors (D^{+p} ; $\rho = 0.5$). In contrast with a homogeneous ρ with a delocalized electron in the normally conducting (metallic) state, the ferroelectric-like charge-polarized state originates from the so-called charge ordering with a periodical disproportionation of ρ on D molecules. The phase transition is accompanied by a huge peak anomaly in the dielectric constant but still by quite a large conductance.

Besides the NI transition, the one-dimensional $S = 1/2$ spin system, as realized with the mixed stack of ionic D^+ and A^- radicals is often unstable to the similar (spin-)Peierls-type dimerization, giving rise to the non-magnetic (spin-singlet) state of a D^+A^- pair. Many ionic paramagnetic CT complexes such as TTF-BA are of this type⁵⁰. Such an electronic instability of a one-dimensional DA chain can therefore provide an effective route to a ferroelectric. Figure 1b also illustrates an additional modified scheme in which one of the component molecules is spontaneously bent so as to form a dipolar DA chain⁵¹. For example, the 5,10-dihydro-5,10-dimethylphenazine (M₂P) molecule is originally bent at the nitrogen atoms in the neutral form but becomes flat by extending π -conjugation on ionization. Its complex with 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane

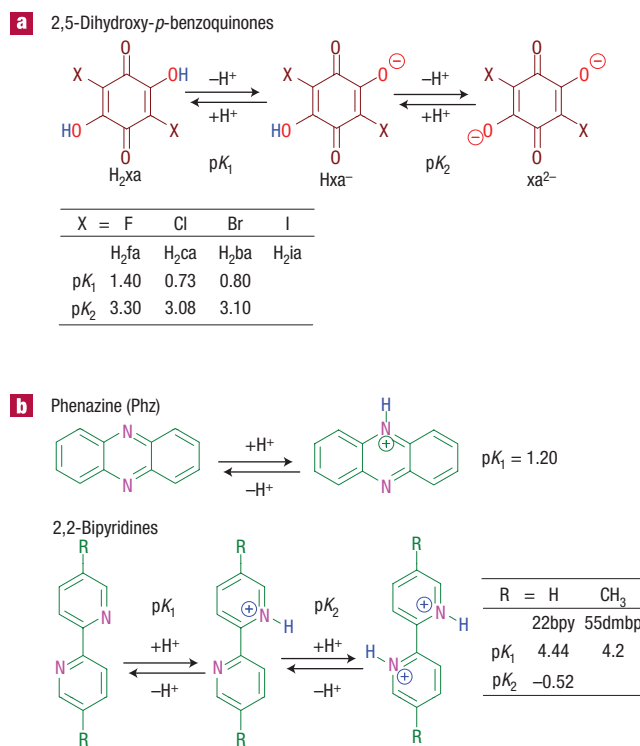


Figure 3 Deprotonation/protonation processes and acidic dissociation constants of acid/base molecules. **a**, Anilic acids with two proton-donating hydroxy groups. **b**, Base molecules with two proton-accepting nitrogen atoms.

(DMTCNQ) is incompletely charged ($\rho \approx 0.5$) and is therefore flexible between the flat and bent forms, permitting its deformation dynamics and ordering with large dielectric anomaly at the phase transition point (170 K). We again note here that multicomponent molecular assembly is the key feature of these design principles.

The CT complexes have displayed a large dielectric constant, varying from a few hundred up to about 2,000 (ref. 52). The exceptionally large κ has been realized by forming a relaxor with an impurity-doped TTF-CA crystal. Unfortunately, dielectric losses remain a drawback. These compounds, including the above-mentioned CT salts, are usually semiconductors or incomplete insulators, and in particular the NI transition itself requires a narrow charge gap as its driving mechanism⁴². The CT complexes also experience current-induced resistance switching to a low-resistance state⁵³, which would also prevent genuine ferroelectricity. Indeed, no data have yet been reported for polarization reversal, such as a D – E hysteresis loop. Such electric leakage would degrade spontaneous polarization, hampering various ferroelectric applications. This difficulty can be overcome by replacing CT interactions with hydrogen-bonding interactions, because ferroelectricity with minimal dielectric loss has been achieved in many hydrogen-bonded crystals. This motivated us to use supramolecular compounds, as we describe in detail in the next section.

HYDROGEN-BONDED BINARY COMPOUNDS

An acid–base combination is a straightforward alternative to binding binary or multi-component molecules through intermolecular hydrogen bonds. Indeed, organic crystals with a variety of supramolecular structures have recently been demonstrated that will be of interest in crystal engineering and may have roles in

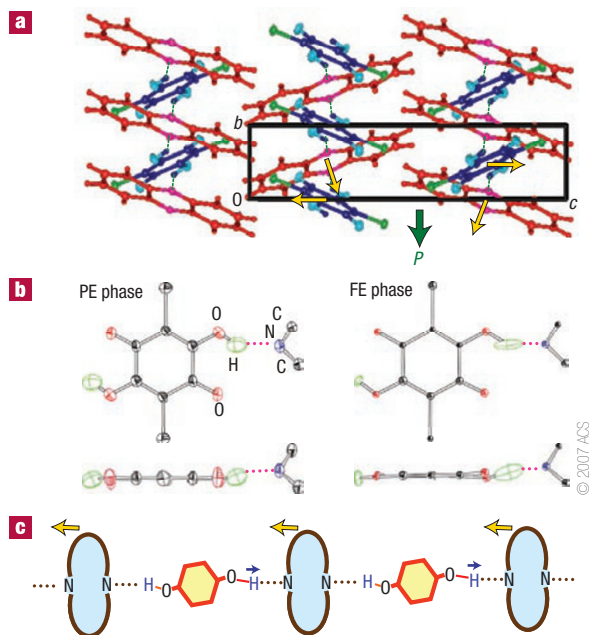


Figure 4 Crystal structure of Phz-H₂xa cocrystals. **a**, Molecular packing and displacement (yellow arrows) viewed along the *a* direction. **b**, Molecular structures of H₂ba in paraelectric (PE) and ferroelectric (FE) phases, as determined by single-crystal neutron diffraction measurements at 300 and 110 K, respectively. Reprinted with permission from ref. 66. **c**, Schematic drawing of the displacement of hydrogen atoms (blue arrows) and molecules (yellow arrows) in the FE phase.

biological functions⁵⁴. Nevertheless, their dielectric properties including ferroelectricity have mostly been overlooked until quite recently. In this section we describe the two prototypical cases of ferroelectricity realized by this chemical approach. The first case is the neutral supramolecular system of simply hydrogen-bonded nonpolar molecules⁵⁵, whereas in the second case a proton transfer reaction yields an ionic supramolecular system^{56,57}. Both classes of ferroelectrics consist of linear chains of alternating acid and base molecules and display novel dynamics of hydrogen-bonding protons with crucial but different roles in ferroelectricity.

The ferroelectric compounds presented below commonly include the 2,5-dihalo-3,6-dihydroxy-*p*-benzoquinones (or anilic acid, abbreviated as H₂xa hereafter; Fig. 3) as the acidic component (proton donor D), although the organic ferroelectrics of this kind would not be limited to these acids. The H₂xa molecules release two protons one at a time, as shown in Fig. 3. The low acidic dissociation constants pK_1 and pK_2 (Fig. 3a)⁵⁸ indicate their strong acidity, being comparable to those of typical carboxylic acids. The pK_1 values are smaller than those of typical bipyridine bases⁵⁹. Earlier studies showed that the H₂xa transfers one or two protons to various bipyridine bases to form ionic DA adducts with a variety of supramolecular structures⁶⁰. In contrast, chloranilic acid (H₂ca) and bromanilic acid (H₂ba) maintain two protons attached in the ferroelectric cocrystals, with the weaker base (A) phenazine (Phz) having the lower pK_1 value (Fig. 3)⁵⁹. These selected dibasic acid or base molecules locate two proton-donating O–H groups or proton-accepting nitrogen atoms symmetrically on both sides, and are therefore suitable for hydrogen-bond formation into an infinite DA alternating chain. The other important feature of the molecular geometries is that the neutral and divalent forms are symmetrical, whereas the monovalent species become asymmetric (Fig. 3a). This is also true for the 2,2′-bipyridines (22bpy and 5,5′-dimethyl-2,2′-bipyridine (55dmbp); Fig. 3b) in a planar *trans* form.

First we describe ferroelectricity in the neutral compounds Phz-H₂xa⁵⁵. At room temperature, both component molecules are exactly symmetrical and electrically neutral without proton transfer to the base molecules. The crystal structure (Fig. 4a) is highly anisotropic and involves π -stacked columns parallel to the *b* axis and DA-alternating supramolecular chains with a short O–H...N bond (O...N distance 2.72 Å) along the crystallographic [110] and [110] directions. The ferroelectric polarization along the *b* direction is suggested first by the Curie–Weiss behaviour of the *b*-axis dielectric constant $\kappa = C/(T - \theta)$; κ exceeds 100 even at room temperature (Fig. 5a) and increases rapidly to 2,000–3,000 at the Curie temperature ($T_c = 253$ and 138 K for *D* = H₂ca and H₂ba, respectively). At temperatures below T_c , observations of both the pyroelectric charge (Fig. 5b; S.H., unpublished observations) with reversible polarity and a clear polarization hysteresis curve (Fig. 5c) validate the ferroelectric state. The crucial roles of acidic protons in ferroelectricity have been demonstrated by deuterium substitution, which increases T_c by more than 50 K (Fig. 5a, b) with an elongation of the hydrogen-bonding O...N distance by 0.15 Å (ref. 61). Meanwhile, there were no perceptible changes in T_c on full deuteration of the Phz molecule (S. H., unpublished). This significant isotope effect is related to fact that the O–D vibrational mode is much softer in nature than the O–H one. The important consequence is the room-temperature ferroelectricity ($T_c = 304$ K) achieved for the deuterated Phz-D₂ca crystal (Fig. 5c). Its spontaneous polarization is as large as 0.7–0.8 $\mu\text{C cm}^{-2}$ at room temperature and increases to about 2 $\mu\text{C cm}^{-2}$ at low temperature (Fig. 5b). A displacive-type mechanism was suggested by the magnitude of the polarization and also by the heat-capacity measurements, demonstrating small entropy changes at T_c compared with that expected for the configurational order–disorder mechanism⁶². The dielectric constant, spontaneous polarization, heat capacity, and X-ray diffraction results consistently find an additional two successive phase transitions at lower temperatures, as indicated by the arrows in Fig. 5b. These transitions preserve the ferroelectric state but induce the multiplication of the unit cell by means of a narrow intermediate phase with incommensurate lattice periodicity as detected unambiguously by the X-ray diffraction (R. Kumai, personal communication). Some reports on the same compound considered a fully proton-transferred ionic state^{63,64}, in contradiction of the observed lattice for this lowest-temperature phase; this will require further investigation.

The spontaneous polarization of Phz-H₂xa along the *b* axis arises from a change in crystal symmetry from space group $P2_1/n$ to the uniaxially polar space group $P2_1$. In spite of the significant H/D isotope effect seen in the hydrogen-bonded ferroelectrics, these compounds seem to be distinct in nature from KDP and its analogues. In particular, all the acidic protons retain the neutral O–H...N form in the low-temperature ferroelectric structures, in place of the site-to-site proton transfer between O and N atoms. Moreover, the observed increase in T_c with increasing hydrostatic pressure is opposite to the effect observed for KDP, in which the pressure reduces the potential barrier for collective transfer and thus tends to suppress ferroelectric ordering. The X-ray analysis of crystal structure showed the relative displacement (arrows in Fig. 4a) of the D and A molecules. Recent neutron diffraction measurements⁶⁵ have unambiguously disclosed the displacement of a hydrogen nucleus as the microscopic origin of the broken molecular symmetry (Fig. 4b). In the ferroelectric phase, one of the hydrogen atoms displaces toward the central position of the O–H...N bond by 0.2–0.3 Å from the position in the paraelectric phase. The elongated O–H site strengthens its hydrogen bond with decreasing the O...N distance. Such disproportionation of the hydrogen bonds is responsible for the molecular displacement, as drawn with arrows schematically in Fig. 4c. This sort of proton migration is an incipient phenomenon of the acid–base reaction to the proton-transferred monovalent form.

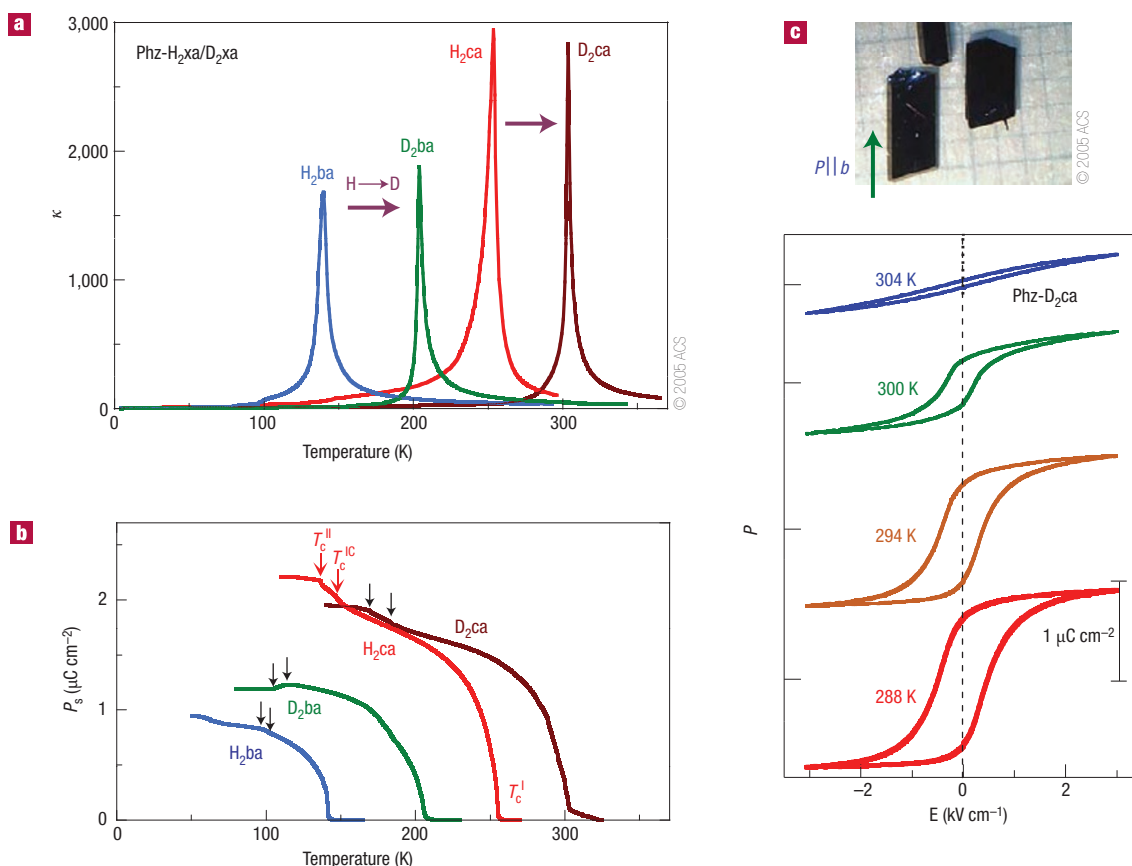


Figure 5 Temperature variation of dielectric properties of Phz- H_2xa cocrystals. **a**, Dielectric constant. **b**, Spontaneous polarization obtained by pyroelectric current measurements after cooling from above T_c with the application of a d.c. poling field E_{pol} of 0.3–0.4 kV cm⁻¹. In addition to the paraelectric-to-ferroelectric transition (T_c^I), there are ferroelectric-to-incommensurate (T_c^{II}) and incommensurate-to-second ferroelectric (T_c^{III}) transitions (arrows). **c**, P - E hysteresis curves. The electric field E was applied parallel to the crystal b axis and crystal long axis (see picture). Parts **a** and **c** reprinted with permission from ref. 62.

In very strong hydrogen bonds, the length of the covalent bond increases until, in the extreme case, the proton is centred like a symmetrical O–H–O bond⁶⁶. The height of the potential barrier for protons can be greatly diminished or removed in the symmetrical wall. Similarly, proton migration is obtained even for the asymmetric bonds in the present heteronuclear type by the well-matched proton affinities of the nitrogen and oxygen atoms⁶⁷. Nearly the same pK_1 values for Phz and H_2xa are thus responsible for this unusual hydrogen displacement. The nature of strong hydrogen bonding in general has been regarded as quasi-covalent⁶⁶. The contemporary theory of electric polarization based on the Berry-phase picture⁶⁸ has demonstrated a crucial role of covalency between ions in many displacive-type ferroelectrics⁶⁹. A state-of-the-art first-principles calculation of the electronic structure was performed on Phz- H_2ca to deduce the polarization value²⁹. In fact, the covalent character of the O–H...N bond was also suggested for the present compound; the magnitude of spontaneous polarization is enhanced about threefold in a hydrogen-bonded crystal form in comparison with the isolated molecular model. These observations tell us that the formation of a strong hydrogen bond between molecules with well-matched proton affinities should be one useful strategy in designing molecular ferroelectrics.

Another type of ferroelectricity was discovered in a monovalent ionic compound using 55dmbp as the base^{56,57}. The supramolecular structure given in Fig. 6a stands for the proton-ordered form observed below the phase-transition temperature T_c . All the protons are in

long-range order, so that the O–H and N–H⁺ bonds are all aligned in the same direction and the alternating O–H...N and N–H⁺...O⁻ bonds constitute a polar chain (Fig. 6b). As all the protons are transferred simultaneously, the chain is reversed in polarity without losing its chemical identity. This collective proton transfer process under an external electric field is nothing other than ferroelectricity. This is illustrated schematically in Fig. 6c, emphasizing the contrast with displacive-type ferroelectricity in Fig. 4c. At temperatures above T_c , the hydrogen-bonded chains in 55dmbp salts change to a nonpolar state, reviving the inversion symmetry. The molecules were found to maintain a nominally monovalent state but their protons are disordered in the O–H...N and N–H⁺...O⁻ forms. Importantly, the π -electron geometry is closely coupled with the protonation state for both molecules, as demonstrated by the changes in the C–O bond length in H_2xa and the C=N–C angle at the pyridine nitrogen⁵⁷; these are 1.32–1.33 Å and 116–117° for O–H...N, and 1.25–1.26 Å and 121–123° for N–H⁺...O⁻. For the high-temperature (paraelectric) phase, all the π -bond geometries converge on these intermediates, indicating an averaged state (disordered state) between the two tautomeric forms.

The above order-disorder dynamics of protons in 55dmbp salts was corroborated by the large dielectric response that was observed only along the hydrogen-bonded directions. For [H-55dmbp][Hca], the phase transition appears above room temperature ($T_c = 318$ K)⁵⁶. The high dielectric constant ($\kappa \approx 140$) and its rounded maximum instead of a divergent peak are similar to those of squaric acid.

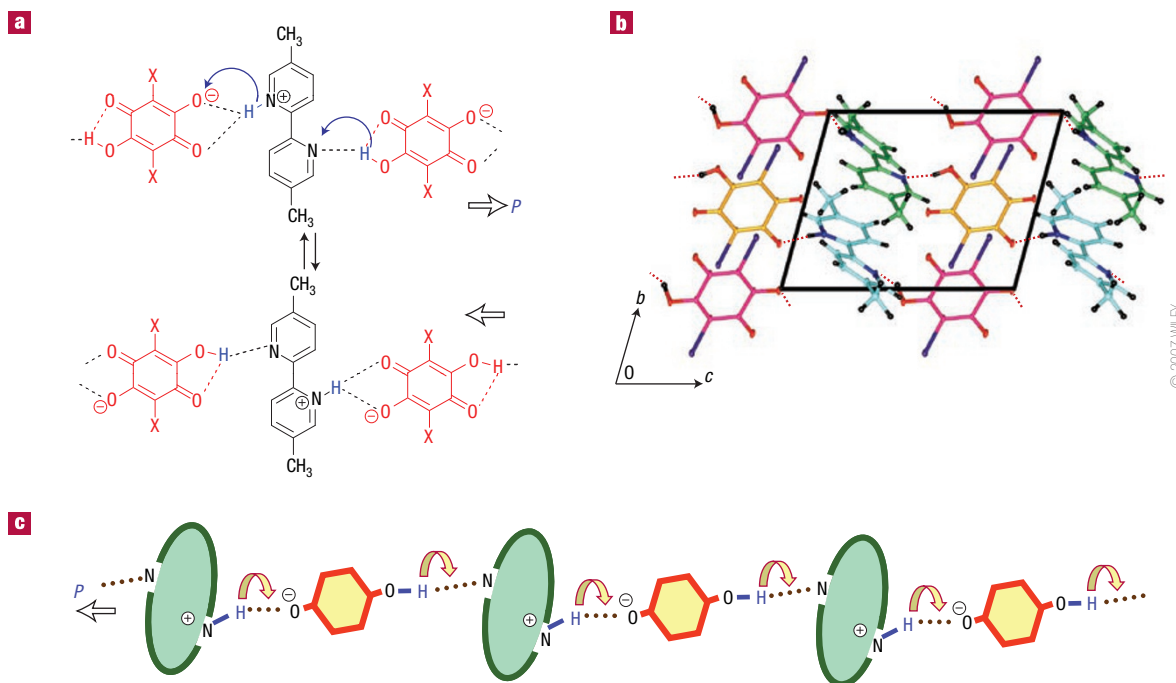


Figure 6 Structure of [H-55dmbp][Hia] cocrystal in the ferroelectric phase. **a**, Molecular structures and hydrogen bonds (broken lines) for the two opposite polarizations P (open arrows), which can be reversed by proton transfer (curved arrows). **b**, Crystal structure at 50 K viewed along the a axis. Reprinted with permission from ref. 57. **c**, Schematic drawing of a proton-ordered ferroelectric chain and collective proton transfer processes (curved arrows) during the polarization reversal.

Actually, its antiferroelectric nature was shown by the doubling of the unit cell into an antiparallel arrangement of the polar chains. In contrast, ferroelectricity was discovered for [H-55dmbp][Hia] by the appearance of divergent-like behaviour of κ (Fig. 7a), polarization hysteresis (Fig. 7b) and pyroelectric charge (Fig. 7b)⁵⁷. The ferroelectric or antiferroelectric nature discriminating the two compounds originates from the parallel chain polarities in the Hia salt. In comparison with Phz-H₂xa, spontaneous polarization is greatly amplified ($P_s = 3\text{--}4\text{ }\mu\text{C cm}^{-2}$) and the transition point (269 K) is higher, approaching room temperature. Application of hydrostatic pressure suppresses the ferroelectric phase transition (Fig. 7a) as occurs in KDP and other displacive-type ferroelectrics, and the ferroelectric phase suddenly disappears at a pressure of only 0.8 GPa. Such sensitivity to pressure could be explained by compression of the hydrogen bond, which should flatten the potential well and favour the disordered state for protons. As in Phz-H₂xa, T_c is also significantly elevated by deuteration of the hydrogen bond, which is therefore a crucial influence on the phase transition. The [D-55dmbp][Dia] salt is a room-temperature ferroelectric ($T_c = 338\text{ K}$). It can show significant pyroelectricity (the red broken line in Fig. 7b) at about room temperature and is comparable to the typical pyroelectric material triglycine sulphate, with a large pyroelectric coefficient ($-dP/dT \approx 400\text{ }\mu\text{C m}^{-2}\text{ K}^{-1}$), which is the important parameter for applications as pyroelectric sensors⁷⁰.

SUMMARY AND OUTLOOK

The exploration and design of organic ferroelectrics should be of continuing importance not only in an academic sense but also for technological developments such as flexible and low-temperature processable ferroelectric components. In comparison with single-component polar-molecular crystals, the use of multicomponent molecular compounds may increase complexity, but should lead

to much more variety in the design and synthesis of ferroelectrics from numerous organic resources. The latter approach also permits the use of more deliberate strategies with a consideration of intermolecular interactions rather than solely those of individual molecules. For CT complexes, the valence and/or (spin-)Peierls instabilities or the flexibility of the molecular moiety is crucial for driving the one-dimensional ferroelectric displacement. In contrast, the intermolecular strong hydrogen bonds can give rise to ferroelectricity with the correlated proton dynamics of orientational, displacive and/or proton-transfer-type mechanisms in the intermolecular space. The design principles described above are the matching of proton affinities in acid–base combinations and the coupling of the ice rule with π -molecular topological features. In particular, ferroelectricity derived from the alternation of base and acid molecules represents a successful design of supramolecular functions. Future advances in crystal engineering may also find opportunities in biological systems such as hydrogen-bonded base pairs. Supramolecular systems show a high transition temperature and a sizable κ , pyroelectricity, and spontaneous polarization with a small coercive field, in contrast with single-component molecular ferroelectrics (summarized in Table 1). As expected from the generally soft nature of organic crystals, all these compounds showed a quite high sensitivity of T_c to applied hydrostatic pressure, which would also be of interest for their potential for high piezoelectricity. Thus, these physical features imply a potential for organic ferroelectrics in future applications. For ferroelectric CT complexes, their inferior dielectric loss is unfavourable for such ferroelectric devices. Nevertheless, present interests^{71–73} arise from their unique correlated electron dynamics, which may attain an ultrafast photo-response in phase transformation and may then find other kinds of application such as ultrafast photo-switching devices.

Another challenge is the fabrication of organic ferroelectrics into various forms of devices. For instance, several investigations

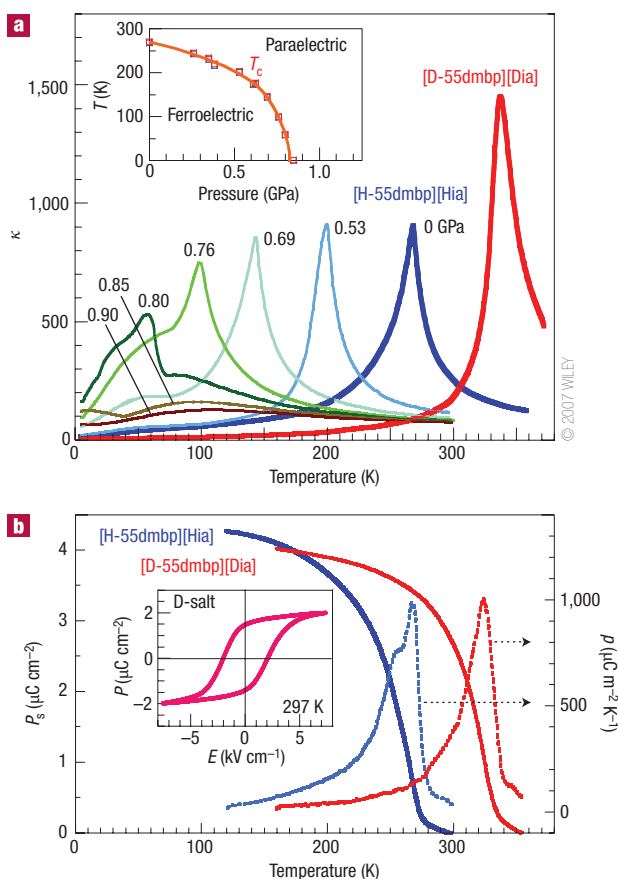


Figure 7 Dielectric properties of the [H-55dmbp][Hia] cocrystal. **a**, The temperature variation of dielectric constant of pressurized crystal and deuterated [D-55dmbp][Dia] crystal. Inset: temperature–pressure phase diagram. Reprinted with permission from ref. 57. **b**, The temperature variation of spontaneous polarization P_s (solid curves) and pyroelectric coefficient $p = -dP_s/dT$ (broken curves), which were obtained by measurements of pyroelectric current. The d.c. poling field E_{pol} of 2–3 kV cm⁻¹ was applied before cooling from above T_c . Inset: P – E hysteresis curve at room temperature for the deuterated salts. The electric field E was applied along the crystal c axis.

on field-effect transistors have recently started to use organic ferroelectrics to fabricate ‘entirely organic’ non-volatile memory because organic semiconductors can be now used for the active layer. High-performance memory has been demonstrated with a polymer ferroelectric⁷⁴. In contrast, one of the merits of low-molecular-mass organic compounds is applicability with solution and/or dry processes such as spin-coating, spray-on, inkjet printing and vapour-phase deposition techniques. This would be also advantageous in the fabrication of flexible, lightweight, large-area, low-cost organic devices. As is often true of organic compounds, the electron (or proton) donor (or acceptor) component molecules are more or less soluble in common organic solvents, and occasionally even in water for the acid and the base. In addition, many of these components and even some of their molecular compounds can be thermally sublimed *in vacuo*. A typical example is the vapour-phase deposition of a ferroelectric thin film of vinylidene fluoride oligomer¹⁰, as demonstrated recently, in place of the non-volatile polymers. Meanwhile, complex formation of molecular compounds from two or more components often results in insoluble and/or non-volatile compounds. This problem can be solved by *in situ* complex-formation techniques such as double-shot inkjet

printing, which has been applied to CT complexes such as patterned organic conducting electrodes⁷⁵. In using organic substances, poorer thermal or mechanical stability than that of inorganic ferroelectrics is a typically encountered problem that needs to be overcome for future device applications through the vigorous development and improvement of materials. Nevertheless, whereas conventional ferroelectrics and relaxors such as lead zirconate titanate and lead magnesium niobate used in many applications contain undesirably toxic lead as the key elements for ferroelectricity, the lead-free organic ferroelectrics would also have the advantage of being environmentally benign. With these features in mind, we hope that this article will stimulate both academic and technological interests in organic ferroelectrics and innovative advances in the ever-growing field of organic electronics.

doi:10.1038/nmat2137

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Acknowledgements

We thank R. Kumai, Y. Tokunaga, F. Ishii, N. Nagaosa, Y. Okimoto, T. Hasegawa, T. Arima and Y. Noda for discussions and collaborations in experiments. S.H. is grateful for support by a Grant-in-Aid for Scientific Research (no. 18750133) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.