# Supramolecular ferroelectrics

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**Supramolecular chemistry uses non-covalent interactions to coax molecules into forming ordered assemblies. The construction of ordered materials with these reversible bonds has led to dramatic innovations in organic electronics, polymer science and biomaterials. Here, we review how supramolecular strategies can advance the burgeoning field of organic ferroelectricity. Ferroelectrics — materials with a spontaneous and electrically reversible polarization — are touted for use in non-volatile computer memories, sensors and optics. Historically, this physical phenomenon has been studied in inorganic materials, although some organic examples are known and strong interest exists to extend the search for ferroelectric molecular systems. Other undiscovered applications outside this regime could also emerge. We describe the key features necessary for molecular and supramolecular dipoles in organic ferroelectrics and their incorporation into ordered systems, such as porous frameworks and liquid crystals. The goal of this Review is to motivate the development of innovative supramolecular ferroelectrics that exceed the performance and usefulness of known systems.**

Computers that require less power, devices that harvest energy from an individual's movements, materials that produce electricity when heated or cooled — these are just some of the breakthroughs that could be realized following the development of organic ferroelectrics that are efficient, scalable and cheap to produce. This goal could be accomplished by synthetic organic and supramolecular chemists. Ferroelectric materials possess a spontaneous electrical polarization that can be macroscopically inverted by using an external electric field (Box 1). Since the discovery of ferroelectricity in Rochelle salts[1] almost one century ago, the field has been dominated by inorganic materials such as $BaTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$ (PZT)[2], and polymers such as polyvinylidene fluoride[3]. Structural requirements identified within inorganic systems also enabled the discovery of ferroelectricity in organic crystals, hybrid frameworks and liquid crystals, with some organics even performing comparably to inorganics[4,5]. Despite these advancements, the present challenge is to synthesize new organic ferroelectrics that manifest all of their numerous advantages (including low density, low cost and solution processibility) while also being easy to integrate with other devices, such as ferroelectric tunnel junctions[6] or ferroelectric field-effect transistors[7].

Supramolecular chemistry offers a strategy for designing new ferroelectric materials (Fig. 1). To generate ferroelectric systems, individual molecules must organize into ordered lattices that are dynamic under the influence of electric fields. The source of the bistable polarization in organic ferroelectrics is either an intrinsic molecular dipole or an induced dipole from supramolecular interactions between molecules. In all cases, this dipole must reside within a non-centrosymmetric ordered structure because dipoles within a symmetric lattice will sum to a zero net polarization. A lattice can assume a noncentrosymmetric phase through either a displacive phase transition or an order–disorder phase transition. In a displacive phase transition, the molecules displace relative to each other to form a polar, non-centrosymmetric lattice with a macroscopic polarization[2]. In an

order–disorder phase transition, the dipoles are randomly oriented but then spontaneously align, in a correlated manner, below a critical temperature. The process of polarization switching requires that atoms, molecules or electrons move in concert within a lattice — such dynamics are an important component of ferroelectricity. Achieving ferroelectricity involves engineering the interactions between molecules and controlling their correlated motion. The relative interactions between adjacent dipoles (inter-chain coupling) will also strongly influence the macroscopic polar order, and must be properly considered to avoid dipole–dipole cancellation (antiferroelectricity). This Review focuses on the important supramolecular interactions and designs used to form ferroelectrics through molecular self-assembly. We discuss the different types of organic ferroelectrics in terms of their supramolecular organization, dipole origin and dipole dynamics, and finally offer our perspective on the potential of this approach.

## Supramolecular dipoles

Polarization in a ferroelectric comes from dipoles in a non-centrosymmetric lattice; this section will cover organic ferroelectrics whose dipoles originate from supramolecular interactions. Non-covalent bonds are generally polar because an asymmetry in electron density arises when two or more molecules interact. For example, this type of dipole forms when ions crystallize into a solid-state structure or when an organic ligand, such as carboxylic acid, forms a coordination bond with a metal ion. These structures — molecular crystals of organic–inorganic salts[5,8] and metal-coordination systems[9] — have been shown to exhibit ferroelectricity and are thus an active area of research. Although they are interesting, we will focus on supramolecular interactions in organic compounds, such as hydrogen bonds and charge-transfer (CT) complexes, which can also produce electrical dipoles.

**Hydrogen displacement.** Hydrogen bonding creates a dipole between the hydrogen-donating molecule, which becomes partially negative, and the hydrogen-accepting molecule, which

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## Box 1 | Behaviour of ferroelectrics.

Ferroelectrics are characterized by how an external electric field modulates their polarization bistability; experimentally, this phenomenon is captured by the canonical polarization hysteresis curve (Fig. B1a). Hysteresis curves are produced by measuring the current across a ferroelectric capacitor when a triangular waveform in voltage is applied. Initially, the dipole moment within a structure can be oriented in the direction of a positive electric field, leading to a macroscopic saturated polarization (position 1 in Fig. B1a). At zero field, ferroelectric materials retain a remnant polarization $P_R$ (position 2); standard dielectrics, in contrast, cannot sustain a polarization without a voltage. At a critical negative electric field known as the coercive field ($E_C$), the net polarization is zero because an equal number of dipoles point in opposite directions and thus cancel out (position 3). A larger negative bias leads to the polarization of dipoles in the opposite orientation (position 4). As the electric field is swept towards the positive end, the hysteresis loop forms; the hysteresis itself represents the energy consumed by switching the dipoles. Although this measurement may seem trivial, one should be aware that dielectric leakage through a device can contribute to the measurement, produce erroneous hysteresis loops (for example, banana loops), and lead to incorrect conclusions about the ferroelectric properties of a material[123]. Additionally, antiferroelectricity can be observed by electrical measurements as well — this physical phenomenon manifests as a double hysteresis loop[2].

Ferroelectricity may not be observed at all temperatures: at higher temperatures, ferroelectrics may assume a centrosymmetric lattice or develop a disordered structure with randomly oriented dipoles. When cooled, the material may become ferroelectric, which occurs at the Curie temperature $T_C$. Phase transitions can be measured by electrical and optical techniques. For example, a ferroelectric phase transition is characterized by a discontinuity in the temperature-dependent dielectric constant (Fig. B1b); this discontinuity at $T_C$ is strongly dependent on temperature and other environmental parameters (for example, pressure) but is independent of the measurement frequency. Beyond electronic measurements, second-harmonic generation is also used to characterize the non-centrosymmetry of a medium, stability of the remnant polarization or existence of a phase transition. Second-harmonic generation, also known as frequency doubling, is an optical phenomenon that occurs in nonlinear (non-centrosymmetric) materials when photons of the same wavelength combine to form photons with half the wavelength. Finally, ferroelectrics are a subset of a class of polarized materials known as piezoelectrics — materials that generate an electric field under an applied mechanical stress. Given this relationship, ferroelectrics should exhibit piezoelectricity; piezoresponse force microscopy has emerged recently as an additional experimental protocol for measuring piezoelectricity at nanoscopic length scales[101] (Fig. B1c).
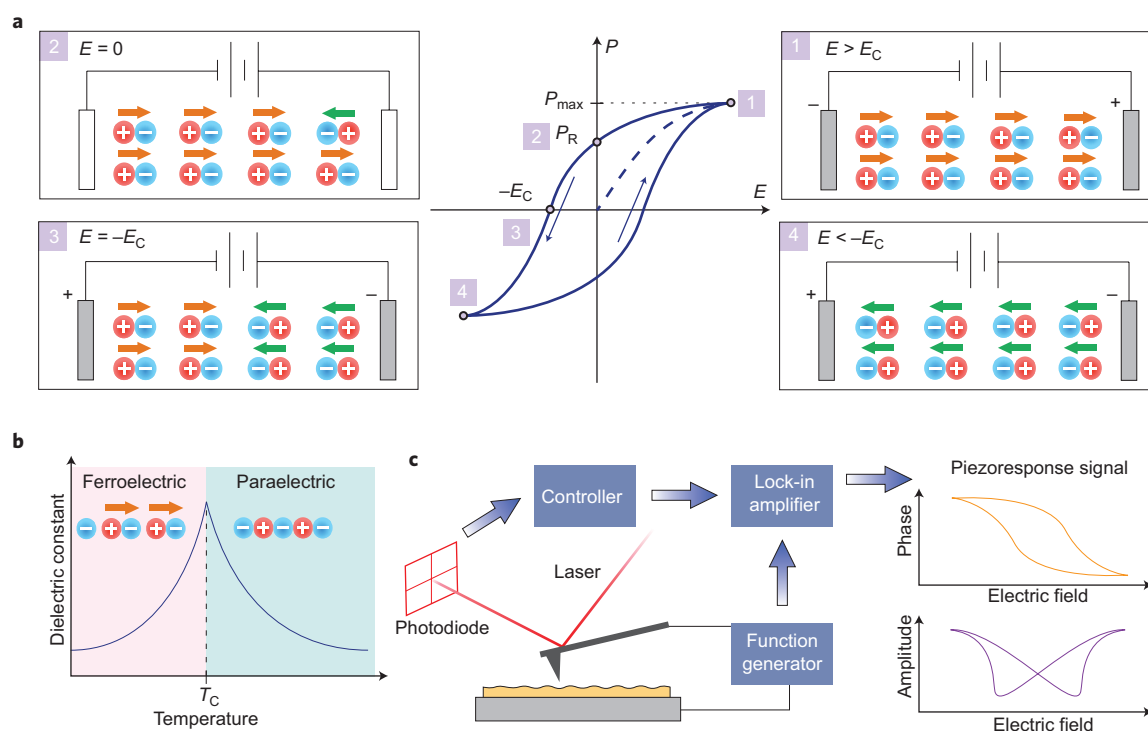


**Figure B1 | Behaviour of ferroelectrics. a**, The canonical hysteresis loop of electric field (*E*) against polarization (*P*) is one type of evidence for ferroelectricity. This electronic behaviour occurs because of the lattice distortion that rearranges the orientation of dipoles within a material in the presence of an electric field. The polarization value in the absence of an electric field is known as the remnant polarization ($P_R$) and the electric field needed to reverse the polarization is called the coercive field ($E_C$). **b**, Ferroelectrics possess a Curie temperature ($T_C$), a critical temperature below which the material loses its ferroelectric qualities (for example, becomes paraelectric). This temperature can be measured experimentally as a discontinuity in the temperature-dependent dielectric constant, where the lattice is paraelectric above $T_C$ and ferroelectric below. **c**, Piezoresponse force microscopy, whereby a voltage applied at the surface of a ferroelectric film causes a mechanical displacement, is another method for measuring the ferroelectric properties of a thin film. Experimentally, this ferroelectric response produces a hysteresis loop of phase against electric field and a 'butterfly' loop that is characteristic of amplitude against electric field.
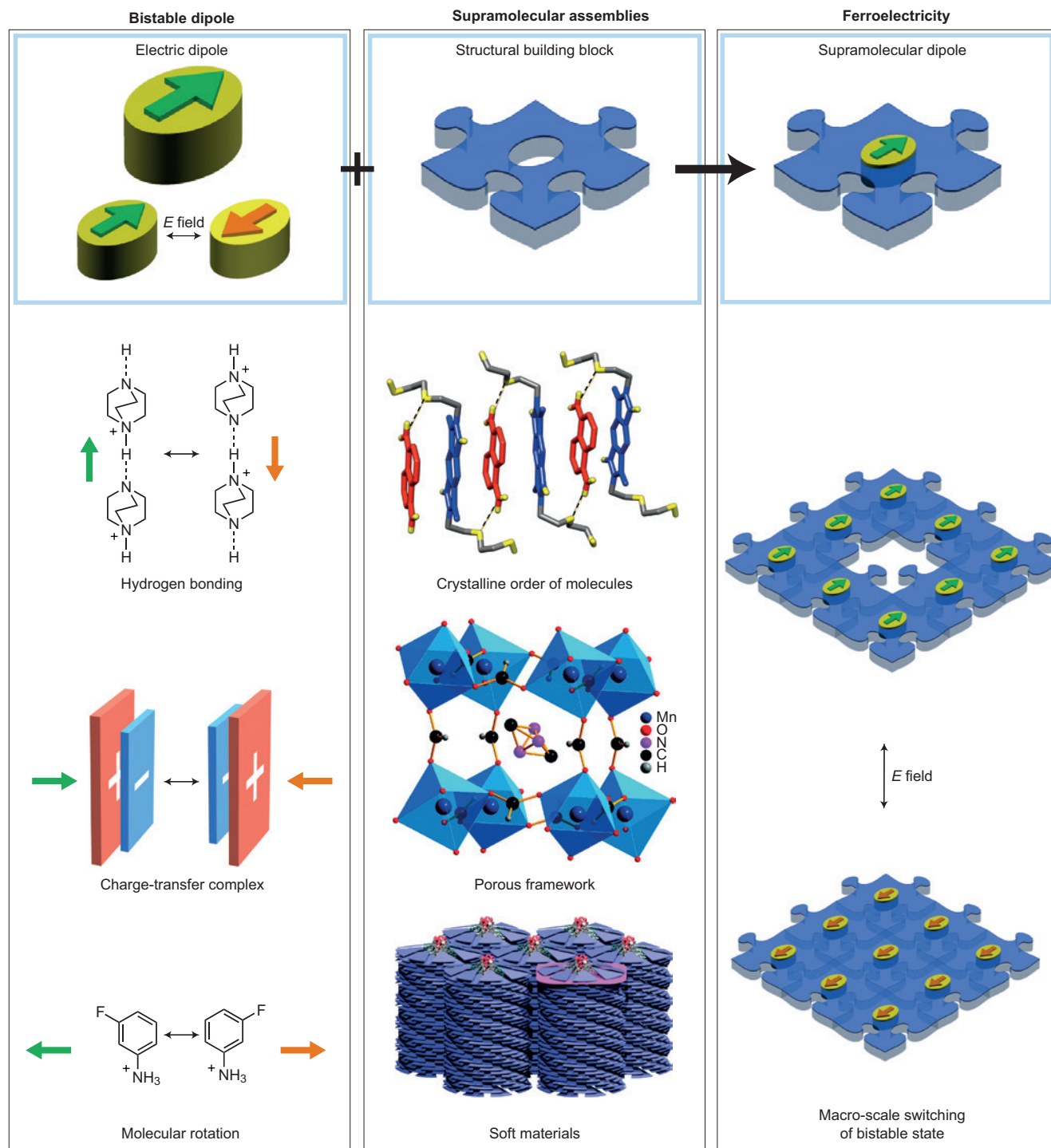
**Figure 1 | Supramolecular designs for ferroelectricity.** The two requirements for ferroelectrics are bistable electronic dipoles (represented by the green and orange arrows) and a non-centrosymmetric lattice. Intermolecular interactions play a critical role in organic ferroelectrics because molecules must be pre-programmed to form ordered lattices with sufficient dynamics to switch the polarization. The dipole originates within a molecule or between molecules (supramolecular interaction). The material can be ferroelectric if these dipoles are placed within a non-centrosymmetric, ordered assembly. Ferroelectricity, shown schematically in the right column, can thus emerge when bistable dipoles (left column) manifest within a non-centrosymmetric supramolecular assembly (middle column); this physical behaviour is observed in molecular machines, host–guest systems and liquid crystals, to name a few. This Review discusses the illustrated examples of dipoles (hydrogen-bonded dabco chains, charge-transfer complexes, molecular rotation) and supramolecular assemblies (organic crystalline lattices, porous materials such as metal–organic frameworks, soft materials such as columnar liquid crystals).

becomes partially positive. The first ferroelectrics to be discovered, such as Rochelle salt and $KH_2PO_4$, were based on hydrogen bonding and inspired researchers to study hydrogen-bonded organic crystals. Ditopic molecules subsequently emerged as the basic design for hydrogen-bonded ferroelectrics because they enable both reversibility and bistability. An early example[10] of single-component ferroelectric crystals was a perchlorate salt of 1,4-diazabicyclo[2.2.2]octane (dabcoHClO$_4$). In the solid state, hydrogen-bonded chains of dabco molecules crystallized into a non-centrosymmetric, orthorhombic space group in an antiparallel
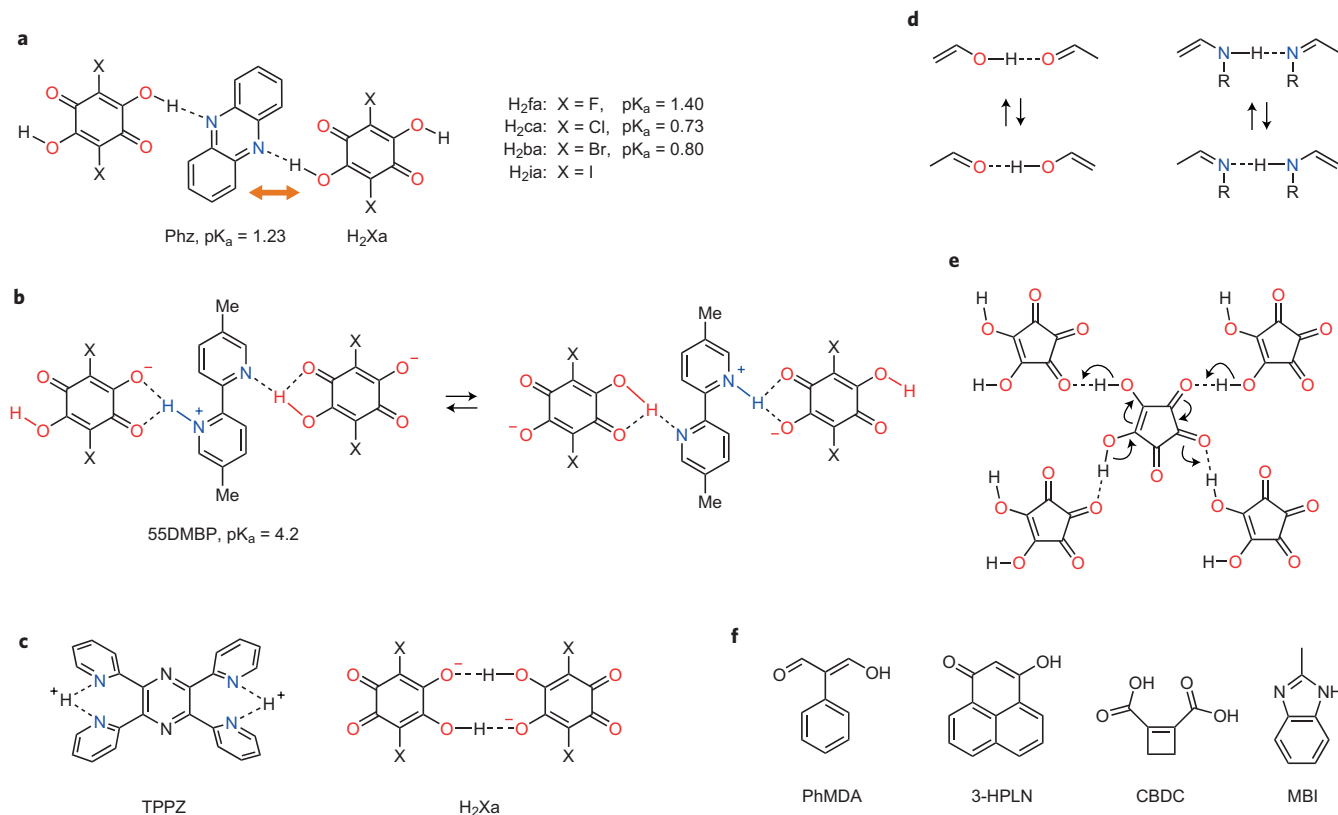
**Figure 2 | Mechanisms for ferroelectricity in hydrogen-bonded crystals. a**, A neutral acid–base co-crystal of hydrogen-bond donors, such as halogenated quinones (chloranilic acid), and hydrogen-bond acceptors (phenazine Phz) produces ferroelectricity when molecules shift within the lattice (orange arrow). **b**, In the ionic co-crystal of 55DMBP-H$_2$Xa, the correlated protonation of the ditopic acids and bases within the crystal allow for polarization reversal. **c**, A proton sponge (TPPZ) co-crystallized with H$_2$Xa will contain the proton within both bipyridyl substituents. Ferroelectricity in this system arises when the proton shuttles between the two pyridine units on one side of the TPPZ. **d**, Tautomery, such as imine–enamine and enol–ketone transitions, is a promising mechanism for ferroelectric switching. **e**, Croconic acid is the first single-component organic ferroelectric with above-room-temperature ferroelectricity. This molecular crystal employs tautomery within the single monolayer. **f**, The molecules shown self-assemble into single-component crystals with non-centrosymmetric lattices. In the solid state, these molecules form hydrogen-bonded chains that demonstrate ferroelectricity at room temperature and above. The compounds are 2-phenylmalondialdehyde (PhMDA), 3-hydroxyphenalenone (3-HPLN), cyclobutene-1,2-dicarboxylic acid (CBDC) and 2-methylbenzimidazole (MBI).

configuration. Polarization hysteresis was observed perpendicular to the hydrogen-bonding direction, which suggests that the protons deviated from the hydrogen bond. Indeed, polarization hysteresis measurements were obtained at room temperature and the Curie temperature ($T_C$) of the system was 377 K. Ferroelectricity parallel to the hydrogen-bonded axis was observed in further studies of dabco-based co-crystals with ReO$_4^-$ counterions, which demonstrates the importance of proton displacement in ferroelectricity (Fig. 1, left)[11].

The dabco-based system inspired a number of recent supramolecular approaches to hydrogen-bonded ferroelectrics, a prominent example being a two-component crystal based on chloranilic acid, H$_2$ca, (or bromanilic acid, H$_2$ba) and phenazine (Phz) (Fig. 2a)[12]. These ditopic compounds are structurally symmetric, yet crystals of this complex are composed of alternating hydrogen-bonded chains of H$_2$ca and Phz. This makes the pKa of the compounds important in these acid–base crystals: acids and bases with equivalent pKa (Phz: pK$_1$ = 1.20; H$_2$ca: pK$_1$ = 0.73; H$_2$ba: pK$_1$ = 0.80) will keep the system neutral, ensure that the hydrogen is shared, and reduce the energetic penalty for lattice switching. Below 253 K in H$_2$ca, the hydrogen-bonded molecules displaced collectively to produce a ferroelectric lattice. Unlike the dabco-based crystal, the dynamics of this two-component system involve the movement of the molecules themselves. The neutral state of the crystal was ascertained by neutron scattering, which is an important technique for visualizing the hydrogens in a crystal[13]. The thermal ellipsoid of the hydrogen

between the OH group on either acid and the nitrogen on the Phz was elongated, thus contributing to the polarization. Deuteration further raises $T_C$ to 304 K and enables room-temperature ferroelectricity in this system[14]. The strong isotope effect confirms that proton displacement is a key component of the ferroelectric mechanism.

In comparison, hydrogen bonding produces charged molecules when the difference in pKa is significant, as in the case of the two-component system of 5,5′-dimethyl-2,2′-bipyridine (55DMBP; pKa = 4.2) and iodanilic acid (H$_2$ia)[15]. Because 55DMBP is more basic than Phz, the base in the co-crystals is constantly protonated on one of its pyridyl units, thus leading to an ionic complex with the transfer of a single proton. Although salts with H$_2$ca and H$_2$ba are antiferroelectric[16], the salt with H$_2$ia is ferroelectric. The protonation equilibrium in this complex implies a correlated site-to-site transfer of protons that polarizes the system in one direction (Fig. 2b).

Another class of hydrogen-bonded ferroelectrics uses 'proton sponges', such as 2,3,5,6-tetra(2-pyridinyl)pyrazine (TPPZ)[17], to form high-temperature ferroelectrics (Fig. 2c). This base can capture protons from a co-crystal former (such as H$_2$Xa) between adjacent pyridinyl rings, producing intramolecular N–H···N bridges. Because this ditopic compound has two pairs of pyridinyl rings, it can sequester two protons per molecule. Unlike the previously discussed systems, TPPZ does not form an intermolecular hydrogen bond with the anilic acid. Instead, the dynamic shuttling of the proton between neutral and protonated pyridinyl rings is the source of the polarization.

In the aforementioned hydrogen-bonded systems, the supramolecular dipole switched when protons shuttled between acids and bases. Recently, tautomerism in single-component crystals has emerged as an example of hydrogen displacement derived from supramolecular interactions. Tautomerization is commonly facilitated by intramolecular proton migration and observed between ketone and enol groups, or imine and enamine groups (Fig. 2d). Interestingly, hydrogen bonding can exist between those complementary functional groups, thus enabling intermolecular hydrogen migration and the growth of one-dimensional supramolecular structures. Moreover, the presence of conjugated $\pi$-bonds between the two units ensures the correlated motion of the hydrogens and stabilizes the crystal through $\pi$–$\pi$ interactions. Recent studies by Tokura et al. have identified croconic acid as the first single-component ferroelectric with proton transfer[4]. In an electric field, the migration of a proton from the $\beta$ position to the enol leads to the ketone (Fig. 2e), inverts the symmetry between neighbouring molecules, and switches the polarization. Electronic studies of this compound showed an astonishingly high polarization (21 $\mu$C cm$^{-2}$) and a reasonable coercive field (14 kV cm$^{-1}$); these values are remarkably competitive with inorganic materials. This tautomery can serve as a guide for identifying existing hydrogen-bonded complexes that self-assemble into ferroelectric materials[18,19]. Horiuchi et al. cleverly found several ferroelectric compounds within the Cambridge Structural Database. The results included molecules that not only contained $\beta$-diketone enol moieties[20] or an imidazole motif[21], but also possessed pseudo-centricity, which allowed them to switch easily (Fig. 2f).

The aforementioned molecular design — described in part by asymmetric, telechelic conjugated molecules with hydrogen-bond acceptors on one side and hydrogen-bond donors on the other — could be a simple approach to ferroelectrics based on proton dynamics. This hydrogen-bonding motif is a flexible design for organic ferroelectrics because it aids the self-assembly process and aligns the polarization.

**Charge-transfer complexes.** A CT complex is a pair of electron-rich (donor) and electron-poor (acceptor) molecules that share an electron when complexed (Fig. 3a). These complexes can form one of two crystalline architectures: segregated stack or mixed stack. Segregated stacks may exhibit metallic conduction[22], whereas mixed stacks have the propensity for ferroelectricity. In both cases, an electron is partially transferred (quantified by the ionicity $\pm\rho$) from the HOMO of the donor molecule to the LUMO of the acceptor in the ground state. Mixed-stack crystals are one-dimensional CT co-crystals where the donors and acceptors assemble in a face-to-face stack in an alternating fashion. The CT process results in a supramolecular dipole and an attractive interaction between donors and acceptors that depends on the ionization potential of the donor and the electron affinity of the acceptor. Most mixed-stack crystals are centrosymmetric — the donors and acceptors are equally spaced apart — and are thus paraelectric. This stack can be distorted by a Peierls instability, in which the donors and acceptors move relative to one another along the axis of the stack; this breaks the symmetric periodicity into pairs of donors and acceptors (dimerization) (for example, DA.DA.DA.DA…) to produce macroscopic polarization (Fig. 3c). Therefore, an external field can cause the dynamic switching of partners within the stack (for example, D.AD.AD.AD.A) to reverse the polarization of the crystal.

One of the most thoroughly studied electron donor–acceptor systems is based on neutral tetrathiafulvalene (TTF) and halogenated quinones, such as H$_2$ca or H$_2$ba (Fig. 3b,c). These compounds are produced by sublimation and have been investigated by crystallography[23] and vibrational spectroscopy[24–26]. At room temperature, the TTF–H$_2$ca co-crystal is centrosymmetric and has an ionicity of

approximately 0.2, which makes it paraelectric[23,27]. Cooling below $T_C$ — 81 K for TTF–H$_2$ca and 53 K for TTF–H$_2$ba — results in molecular-scale dynamics: a Peierls transition induces dimerization of donors and acceptors in the lattice (Fig. 3d). This paraelectric-to-ferroelectric phase transition can also be induced at higher pressures[24,28–30]. A challenge with these systems is dielectric leakage, which often prevents the measurement of a ferroelectric hysteresis loop. Moreover, the inability to obtain crystals of sufficient size and quality hindered the measurement of polarization hysteresis in these systems for several decades[31]. Despite extensive studies of this class of complexes, the first ferroelectric hysteresis measurements of TTF–H$_2$ba and co-variants were obtained in 2010 and 2012, respectively, by Tokura et al.[32,33].

Given the limitations of TTF–quinone-based systems, one must consider how to force the lattice into a non-centrosymmetric structure at room temperature. Recent work by Stupp et al.[34] has shown that supramolecular chemistry can be used to coax electron donors and acceptors into single-crystal, ferroelectric lattices at room temperature (Fig. 3e,f). Their approach was to combine orthogonal non-covalent interactions — hydrogen bonding and CT — to disrupt the traditional centrosymmetric packing of CT complexes. In this system, donors based on naphthalene, pyrene and tetrathiafulvalene, and an acceptor based on pyromellitic diimide, were functionalized with 'arms', such as diethylene glycol chains and amines, that could interact with each other to form supramolecular structures. These complexes crystallized easily and formed a three-dimensional hydrogen-bonded network in the solid state that was radically different in structure to the conventional TTF–quinone-based systems. The three supramolecular networks reported showed ferroelectric hysteresis at 300 K (Fig. 3g) and a $T_C$ of more than 400 K.

An advantage of this supramolecular design is its modularity: a myriad of donors and acceptors may be synthesized with a similar motif to form new CT ferroelectrics. Generally, subsequent CT ferroelectrics would benefit from incorporating other non-covalent interactions, such as hydrogen bonding, which may coax CT complexes into non-centrosymmetric structures. Creating a supramolecular scaffold such as a hydrogen-bonded network, within which CT pairs can be embedded[35,36], may also be promising. This approach could be modular and versatile — two key qualities required for rapid technological progress.

## Organization of molecular dipoles

The intrinsic dipole of a molecule has been used as the source of polarization in organic crystals. Thiourea is a classic example[37] of this phenomenon: the dynamics of molecules or subunits within the lattice switches the polarization between two stable states. Another example is the polymer polyvinylidene fluoride — a piezoelectric material used in acoustic transducers and microphones. This polymer can also be processed into a thin organic film for ferroelectric capacitors[38,39]. An external electric field rotates the polymer chain around the length of the polymer, thus switching its polarization. These polymeric dynamics can only occur in the ferroelectric $\beta$ phase, as the $\alpha$ phase is paraelectric[40]. However, such dramatic reorganization is often hampered by significant energy barriers, even in crystals comprised of small molecules. To promote the motion of molecules in densely packed crystals, two approaches have been studied simultaneously: molecular dipoles within porous lattices, and liquid crystals.

**Encapsulation of dipoles in three-dimensional lattices.** Porous frameworks, such as molecular sieves and zeolites, have been used over the past three decades to encapsulate a myriad of polar guests. These guests can self-organize within the lattice by interacting with themselves or the host to produce a non-centrosymmetric network. Resulting materials have demonstrated a second-harmonic generation response and, in some cases, a pyroelectric response[41,42]. One
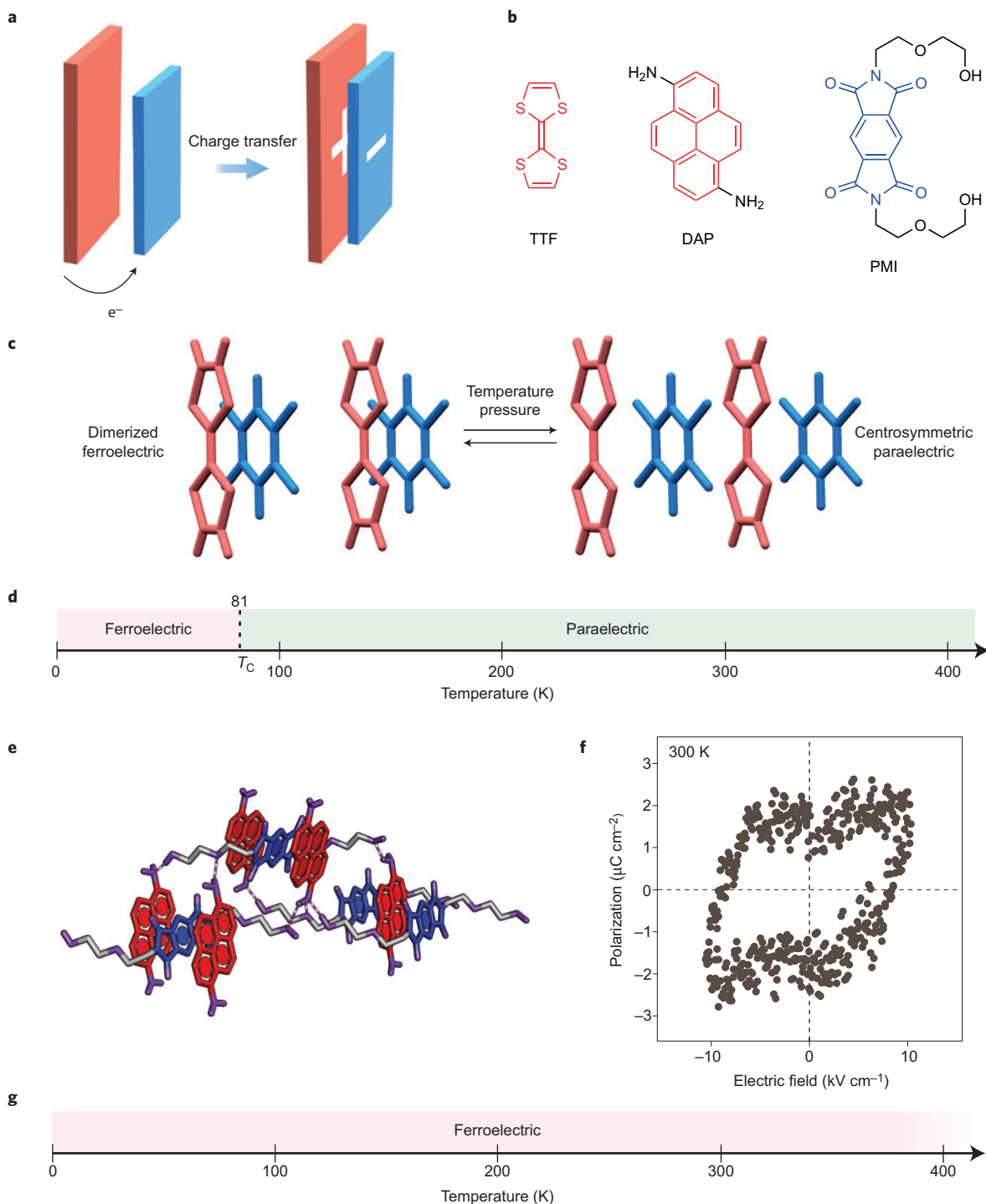
**Figure 3 | Ferroelectricity in CT crystals. a**, Charge-transfer is a non-covalent interaction in which an electron is donated from an electron-rich (donor) molecule to an electron-poor (acceptor) molecule (red and blue, respectively). **b**, Chemical structure of tetrathiafulvalene (TTF), 1,6-diaminopyrene (DAP) and a pyromellitic diimide derivative (PMI) used to form CT complexes. **c,d**, One of the canonical CT ferroelectrics is based on tetrathiafulvalene (TTF) and chloranilic acid. Although the crystals of alternated donor and acceptor molecules are centrosymmetric above $T_C$ — and are thus paraelectric — a neutral-to-ionic phase transition at low temperature decreases the symmetry of the lattice, thereby promoting its non-centrosymmetry and the polar nature of the stack, which becomes ferroelectric (**d**). **e**, In this co-crystal between DAP and PMI (structures shown in **b**), $\pi$–$\pi$ stacking and CT exist between donors and acceptors within a mixed stack; however, hydrogen bonding forms a three-dimensional network that locks individual stacks together. **f**, The hysteresis curve of polarization against electric field attests to the ferroelectricity of this material at room temperature[34]. **g**, No phase transitions are observed over a wide temperature range for the assembly of DAP and PMI.

type of porous framework, metal–organic frameworks (MOFs), possess an intriguing supramolecular design and are easily synthesized[43,44]. MOFs are perfect hosts for new host–guest ferroelectrics because they self-assemble into nearly perfect three-dimensional

crystals with large voids that extend along multiple axes. Moreover, the synthesis process is modular because different ligands or metallic ions can be used. In one case, the encapsulation of ethanol molecules within the pores of the formate-based framework
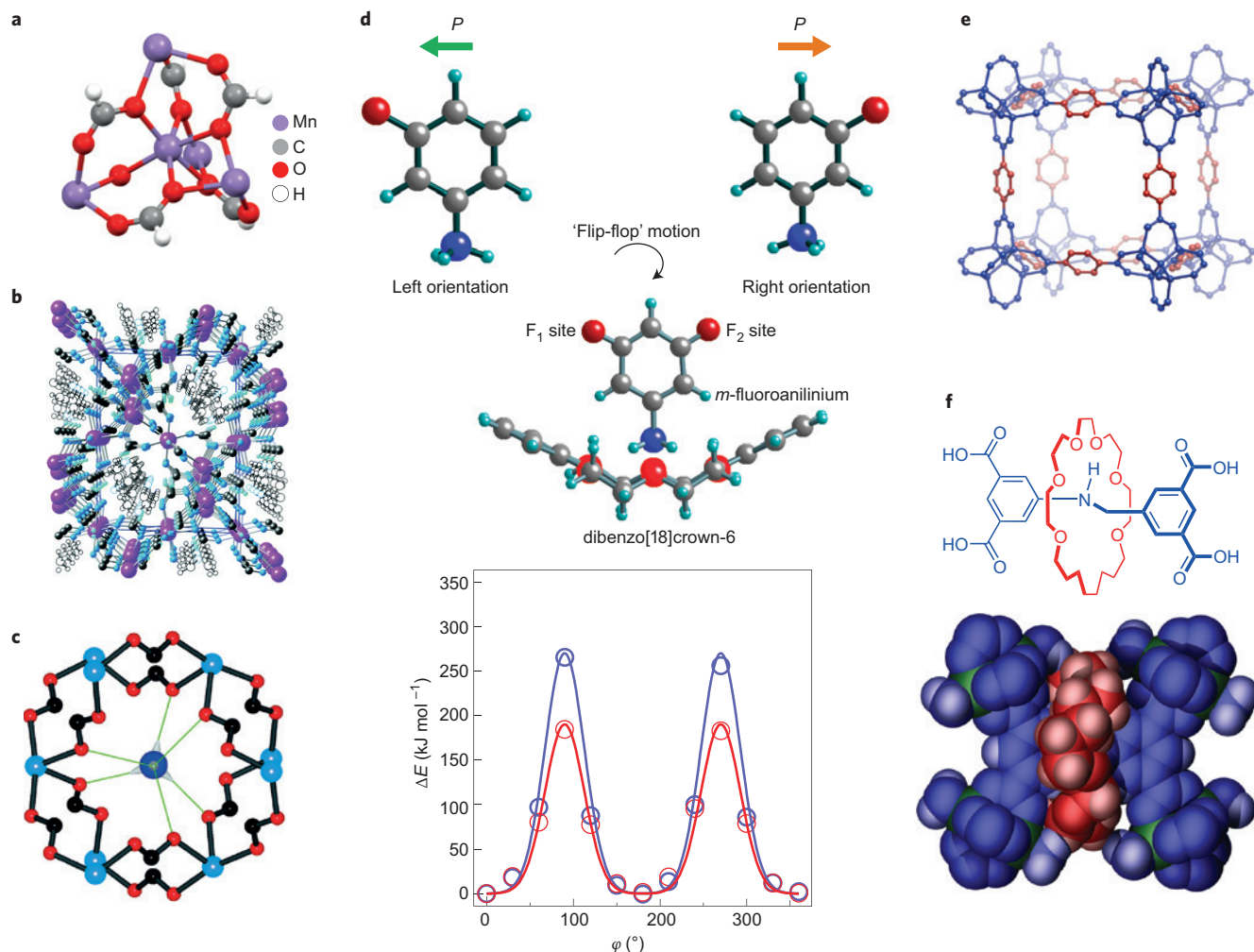
**Figure 4 | Metal–ligand systems and molecular rotators as ferroelectrics. a**, Metal–organic frameworks, such as the metal formate framework of [Mn(HCOO)$_6$], are centrosymmetric porous lattices that can encapsulate small guest molecules. **b**, Crystal structure of [Mn(HCOO)$_6$](C$_2$H$_5$OH), viewed along the *b* axis. Mn, purple; C, black; O, blue; H, pale blue. Open circles show the C and O atoms of guest ethanol molecules. The polar guest molecules are localized within the framework's channel in three possible positions; this organization yields a bistable, polar structure. **c**, In [NH$_4$][Zn(HCOO)$_3$], hydrogen bonds between the ammonium cations and the lattice stabilize the polar order. Zn, pale blue; C, black; O, red; N, blue. Green lines, N−H···O hydrogen bonds. **d**, Host–guest complexes of dibenzo[18]crown-6 with *m*-fluoroanilinium display a ferroelectric response. The anilinium guest can be oriented with an electric field by rotating around its central axis, thereby inducing its stabilization in two opposite polar states (green and orange arrows), according to the site occupancy of the fluorine atom. Also shown is the calculated potential energy curve function of the rotation angle ($\varphi$) of the phenyl ring in the *m*-fluoroanilium salt (blue) whose structure is shown and its non-fluorinated analogue (red). The presence of the fluorine group increases the potential energy barrier to the 'flip-flop' motion. **e**, New ferroelectric MOFs are envisaged: the phenyl rings (red) of 1,4-phenylenedicarboxylates ligands are free to rotate in the MOF lattice formed from ZnO$_4$ clusters. **f**, Top: interlocked rotaxane introduced in the ligand of a MOF based on copper-paddlewheel building units. Free rotation of the oligoethylene wheel (red) along the rigid strut (blue) could provide a ferroelectric response within an amphidynamic structure. Bottom: space-filling model of the MOF shown with the same colour code; red, wheel; blue, rigid strut; green, copper centres of the paddle-wheel structure (not shown above).

[Mn$_3$(HCOO)$_6$] leads to a host–guest system that demonstrates ferroelectricity at 160 K (Fig. 4a,b)[45]. The organization of guests within the gallery of the porous lattice is critical for realizing ferroelectric frameworks because smaller guests, such as water and methanol, do not form a stable polar order[46]. Complex phenomena can also be observed in these systems because the intrinsic properties of the components can contribute to the properties of the complex. Hence, this framework also happens to be multiferroic — a material with coexisting ferroelectricity and (anti)ferromagnetism.

The guest molecules inside a porous framework can organize into a polar structure through non-covalent interactions with the lattice. One system that demonstrates this behaviour is a charge-balanced MOF with dimethylammonium cations that hydrogen-bond to the formate-based framework [M$^{II}$(HCOO)][NR$_2$H$_2$]

(M = Zn, Fe, Co, Ni)[47,48]. These cations can assume three different positions within the unit cell, leading to antiferroelectric behaviour below a phase transition at around 160–185 K, depending on the type of metallic ion. Several types of cationic amines have been explored[49], with a clear demonstration of ferroelectricity in some cases, for example in [Zn(HCOO)][NH$_4$] (Fig. 4c)[50].

Amphidynamic behaviour — the rotation of molecules in a crystalline lattice — can also occur in media more dense than porous frameworks. One promising class of supramolecular systems is host–guest molecular rotators; these systems exhibit dramatic molecular motion of guests in crystals, and with proper energetic barriers can lead to ferroelectricity. Akutagawa *et al.* demonstrated this approach by utilizing a complex of dibenzo[18]crown-6 with 4-fluoroanilinium, which has a stator–rotator host–guest design (Fig. 4d)[51]. Here,

the asymmetric guest can rotate — known as 'flip-flop' motion — to assume one of two energetically equivalent orientations with an applied electric field. The rotation of the cation was stabilized by the steric hindrance of the counter anion. This fascinating report remains a rare demonstration of an organic, rotator-based ferroelectric. Xiong et al. subsequently demonstrated that pendulum-like motions of an anilinium derivative can also re-orient the molecular dipole in the crystal[52]. In conjunction with single-crystal analyses, they used solid-state NMR to demonstrate that the relation between different molecular motions and phase transitions leads to ordered structure and ferroelectricity[53,54]. Controlling the motion of molecules within a crystalline lattice is an ongoing challenge, which could lead to the development of new functional materials[55]. Amphidynamic behaviour could inspire new supramolecular ferroelectrics and has long been investigated by Garcia-Garibay and others[56]. Crystals of single molecules, MOFs[57,58] and porous organic frameworks[59] can exhibit free rotation of ligands around a static axis and could assume bistable orientations (Fig. 4e). Rotating polar ligands have been crystallized successfully[60,61], but stabilizing their orientation is still difficult owing to dipole–dipole interactions among neighbouring ligands. We believe the aforementioned MOF and amphidynamic systems are a promising source of novel ferroelectrics; they can be synthesized easily, are modular, and may have polarization hysteresis in three dimensions. For example, freely rotating crowns were recently incorporated into MOFs as struts[62] (Fig. 4f), and could be influenced by an electric field. Moreover, Zhang et al. described amphidynamic MOFs based on the motion of an unbound dimethylammonium. However, this system demonstrated weak cooperative motion among adjacent dipoles[63]. The key challenge is to introduce an energetic barrier and stabilize the polar rotator without entirely obstructing its motion. Several designs could be used to overcome this limitation, as steric groups or non-covalent interactions can constrain the motion of the dynamic polar units[64].

**Liquid crystalline order.** The issues of steric hindrance in crystalline structures can be overcome by using a more dynamic type of condensed matter, such as liquid crystals (Fig. 5). Ferroelectricity in liquid crystals arises from either the organization of chiral mesogens or the intrinsic dipole within achiral molecules. Liquid crystals are supramolecular systems that can organize molecular dipoles, provide the pseudo-rigidity needed to stabilize a remnant polarization, and allow the facile switching of molecular dipoles. In 1975, Meyer et al. demonstrated that chiral rod-like mesogens change the structure of the smectic C phase to one in which the tilted and layered molecules possess net polarization (Fig. 5c). Although this low-symmetry structure — known as the chiral smectic C phase (SmC*) — has latent polarization[65], the layers of mesogens in this liquid crystal form a helical superstructure, resulting in an apolar material. Clark and Lagerwall were able to unwind this helical structure into a ferroelectric assembly by constructing thin devices with treated substrates to orient the mesogen and fix the polar order using surface mechanical forces (Fig. 5a, left)[66]. Subsequent developments of these ferroelectric materials have been focused on optical applications[67,68].

Analogous to the chiral smectic C phase, discotic mesogens with pendent chiral side chains can form ferroelectric columnar mesophases (Fig. 5e). These mesogens are tilted within a column and also form helical arrangements that cancel the polarization. An electric field can be used to unwind the helical structure into a tilted column with a polarization perpendicular to the long axis (Fig. 5b, left)[69–71]. The mechanism for ferroelectric switching remains unclear, but it has been suggested that either the entire column rotates 180° around the columnar axis, or the molecules reorient independently[72]. In both cases, the rotating structure encounters resistance from neighbouring molecules or columns, which delays the switching process.

Achiral polar molecules, such as bent-core mesogens with low $C_{2v}$ symmetry, may exhibit ferroelectric ordering. The molecules

themselves self-assemble into chiral or achiral superstructures; both have the potential to be ferroelectric. In the liquid-crystalline state, the bent-core mesogens pack into a hierarchical, head-to-tail arrangement where the molecules assemble into layers with the same orientation. This structure leads to a macroscopic polarization of the domains (Fig. 5a, right). Takezoe et al.[73] were the first to report ferroelectric measurements of the bent-core liquid crystals designed by Matsunaga (Fig. 5d)[74]. Occasionally, adjacent layers will have antiparallel polarizations that suppress ferroelectricity. The orientation of polarizations in adjacent layers, combined with the tilt angle of the mesogens in each layer, will change the chirality of the supramolecular structure[75–77]. These structural characteristics are rooted in the spatial frustration between the flexible chains and the rigid bent core. In a previous report, replacing the alkyl chains with siloxane spacers eliminated the interdigitation of flexible tails, which in turn promoted dipole–dipole alignment and prevented a tilted molecular packing of mesogens[78]. This specific design yielded ferroelectric liquid crystals with high symmetry (Fig. 5f)[79].

In the use of the aforementioned liquid crystals, surface treatment of the substrate destabilizes the helical mesophase to produce a device with macroscopic polarization, yet clearly these materials are not intrinsically ferroelectric. These constraints limit the use of ferroelectric liquid crystals in functional devices. Many have considered hexagonal columnar liquid crystals, whose polarization is parallel to the columnar axis, as an appropriate supramolecular design for achieving intrinsic ferroelectricity. Interestingly, in hexagonally packed columnar phases, the triangular lattice of polar columns is asymmetric and has antiparallel packing, which ensures a stable, macroscopic polarization[80,81]. This polar order has been observed numerous times for bowl-shaped mesogens[82,83].

Macrocyclic cone-shaped mesogens can form columnar liquid crystals with polarized domains[82,84]. Unfortunately, these compounds are known to switch concavity and polarity spontaneously, even though they do so at rates slower than those in solution. Despite this spontaneous inversion, it is possible to use non-covalent interactions (for example, metal coordination to the calixarene, or hydrogen bonding with a guest molecule) to limit the motion, although doing so can prevent polarization reversal[85,86]. Once the core is fixed, the polarization can only be switched by rotating the mesogens or the entire assembly, which are both sterically unfavourable mechanisms[87,88]. Other systems, such as a tribenzocyclononene core with chiral side chains (Fig. 5g), have been shown to exhibit ferroelectric switching, but the exact mechanism could not be determined. In this case, it is believed to be a conformational inversion of the bowl-shaped core, rotation of the mesogens themselves, or an induced tilt angle within the supramolecular structure by the chiral mesogens[89].

In the aforementioned systems, the covalent bonds rigidify the complex, inhibit conformational dynamics and limit switching under an external electric field. Instead, a supramolecular assembly of bent-core molecules can organize into bowl-shaped structures that are stacked in head-to-tail columns (Fig. 5b, right). This organization is due to phase segregation between the aromatic core and the paraffinic side chains (Fig. 5h)[90]. Moreover, the conical mesogenic unit is obtained by non-centrosymmetric organization of dipoles oriented face-to-face such that the sum of the dipoles is not null. The polarization of the column could invert with an applied electric field, but nanoscopic fragmentation of the columns into antiparallel stacks cancels the macroscopic polarization. This structure is paraelectric; in order to form a ferroelectric structure, a more rigid core would be necessary.

As discussed previously, hydrogen bonds can be polarized and thus could be used to stabilize the structure of a columnar liquid crystal. Although head-to-tail assemblies of amide bonds and urea motifs, for example, are polarizable and have been reported to be ferroelectric[91,92], this phenomenon vanishes rapidly without an electric field[93]. A successful molecular design has been reported
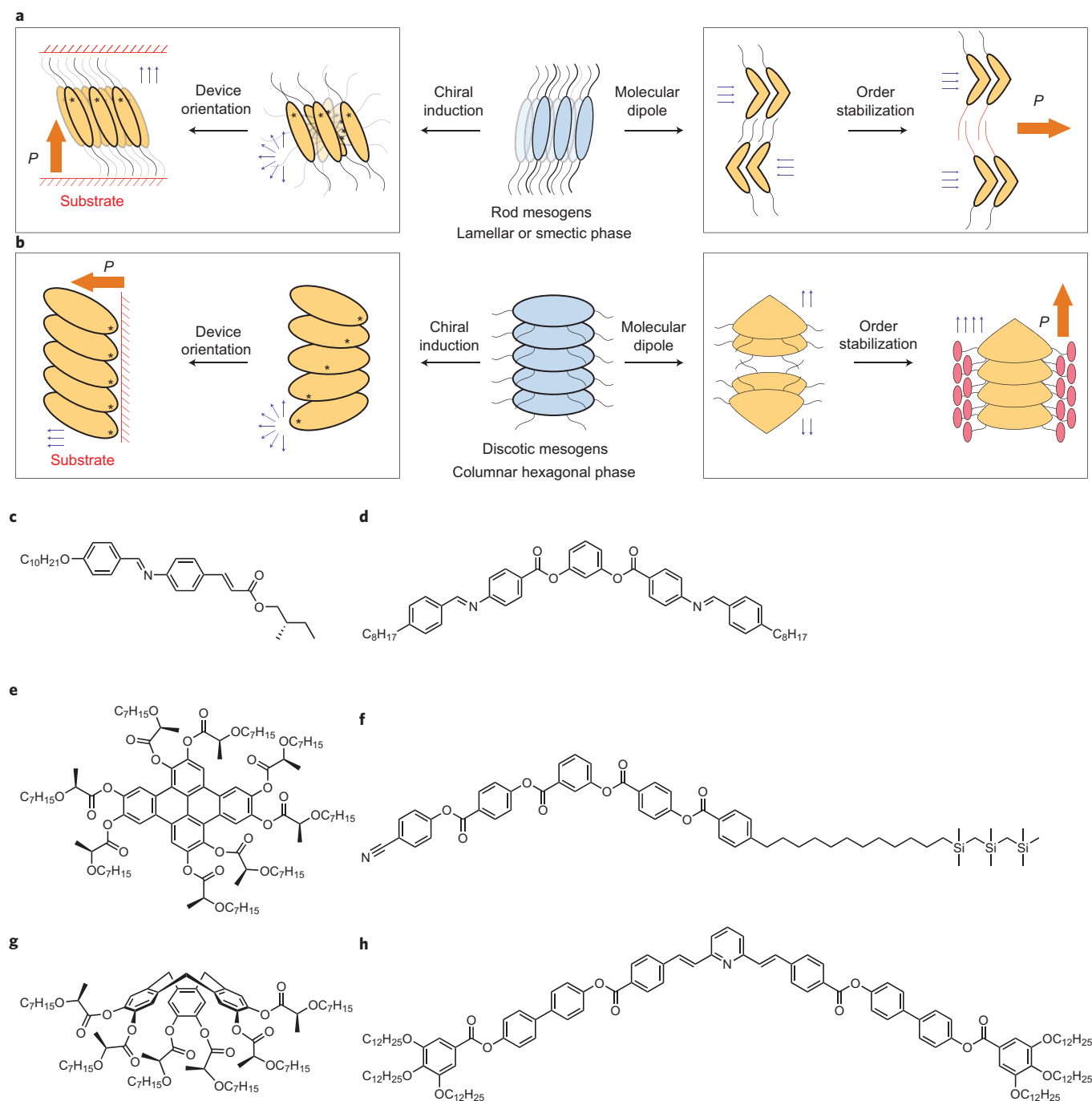
**Figure 5 | Ferroelectric liquid crystals. a,b**, Evolution of molecular designs for rod-shape (**a**) and discotic (**b**) mesogens that induce ferroelectric ordering in the liquid-crystalline state. The aromatic core is shown in blue or yellow when apolar or polar, respectively; the flexible side chains are shown in black. The first approach relies on the introduction of chiral centres (represented by an asterisk): these centres coerce the mesogens into a non-polarized helical superstructure with the lamellar or smectic phase (**a**, left) or the columnar hexagonal phase (**b**, left), in which the molecular dipole moments (blue arrows) are cancelled out. The helical structure can unwind at the interface with the substrate, thus yielding a polar phase (orange arrow labelled *P*). Polar mesogens can also form polar assemblies, but the antiparallel organization of molecular dipoles results in zero polarization of the liquid-crystal phase. The dipole between adjacent layers is cancelled by this local assembly (**a**, right) or by the coexistence of compensating polar orders within each column (**b**, right). Limited dipolar interaction between layers (**a**, right) or stabilization of column stacks using supplementary interactions (**b**, right) can be introduced by functional units (red) to yield ferroelectric phases. **c–h**, Chemical structures of chiral rod-shaped mesogen (**c**), chiral discotics (**e**), bent-core molecules (**d,f**), cone-shaped mesogen (**g**) and fan-shaped molecules (**h**). This last molecule self-assembles into hexagonal columnar phase.

that combines the paraelectric arrangement of hydrogen bonds to stabilize the bowl-shaped assembly of phthalonitrile derivatives (Fig. 6a) into supramolecular columns and to orient them homeotropically with an external electric field (Fig. 6b)[94]. The non-centrosymmetry was further characterized by second-harmonic generation measurements, for which polarization switching was clearly observed (Fig. 6c)[95]. This system is the first demonstration of intrinsic ferroelectricity in a liquid crystal without any treatment of the device surface or additional processing. Aida *et al.* determined that the phthalonitrile units — not the hydrogen bonds — were
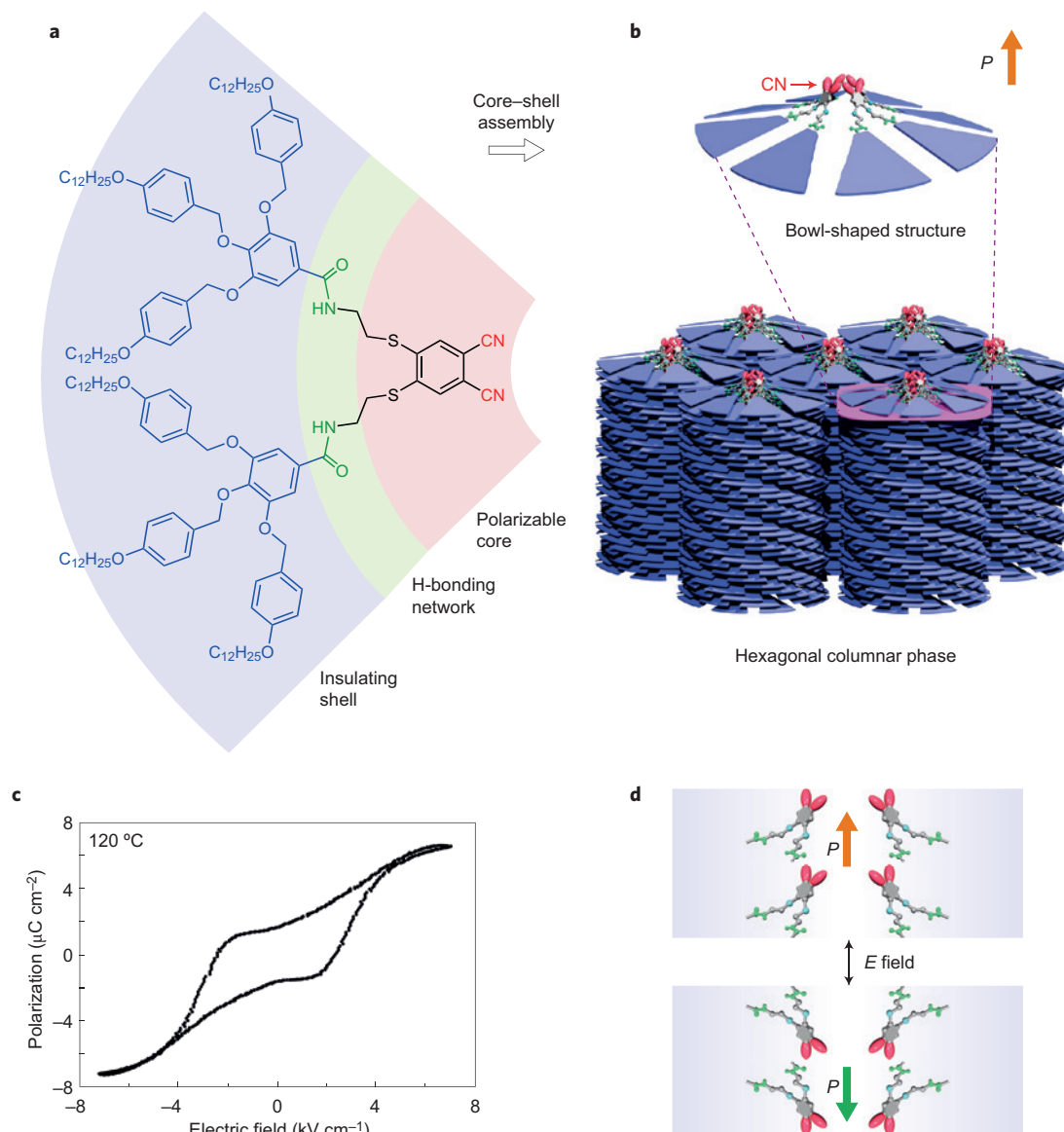
**Figure 6 | Ferroelectricity in columnar liquid crystals. a,b**, The chemical structure (**a**) of a mesogen that assembles into a hexagonal columnar phase (**b**). Assembly proceeds by the segregation of four mesogens into a core–shell structure, with polar phthalonitrile units inside and the aliphatic side chains outside. **c**, The intrinsic ferroelectric nature of the columnar liquid crystal is shown by the hysteresis of polarization against electric field. **d**, The cyano group in the core of the columns are either pointing up or down (according to the applied electric field) and yield a polar order parallel to the column axis (orange and green arrows for cyano groups pointing up and down, respectively).

responsible for the ferroelectricity (Fig. 6d). Although the polar amide units do not contribute to the ferroelectric effect, their bond polarization ensures and maintains the unidirectional columnar orientation. The ferroelectric properties of this system are sensitive to several details of the molecular design. The key parameters are the flexibility of the core, congestion of the shell structure, molecular packing within the core, and intracolumn hydrogen bonds. This columnar liquid crystal is intrinsically ferroelectric (for example, as a free-standing film or device) and illustrates the potential for easily processable ferroelectric materials[96].

## Perspective

The molecular and supramolecular design of soft matter that exhibits ferroelectricity is still a mostly unexplored field, and future progress could contribute to fundamental discoveries of great important in materials science and biology. However, the ways in which ferroelectric properties manifest in soft materials could be largely unrelated to the vision of large, non-volatile memories using hard materials. In this context, we offer our perspective on promising directions in the science of organic ferroelectricity.

**Biological systems.** Since the discovery of piezo- and pyroelectricity in organic tissues more than half a century ago[97,98], there has been great interest in finding a functional role for ferroelectricity in biology. Some suggested the possible importance of ferroelectricity in cellular processes[99] or its influence on biomaterials and proteins[100]. It is believed that numerous biological systems possess the basic elements of ferroelectricity; that is, polarized states and coercive fields needed to reorient dipoles in space. Advances in the instrumentation and measurement of ferroelectricity in unconventional materials, such as piezoresponse force microscopy, have created new ways to measure ferroelectricity in nanoscale structures[101], crystals of γ-glycine[102], seashells[103] and, more surprisingly, in the extracellular matrix of mammalian aortic wall (Fig. 7a)[104]. It has recently been
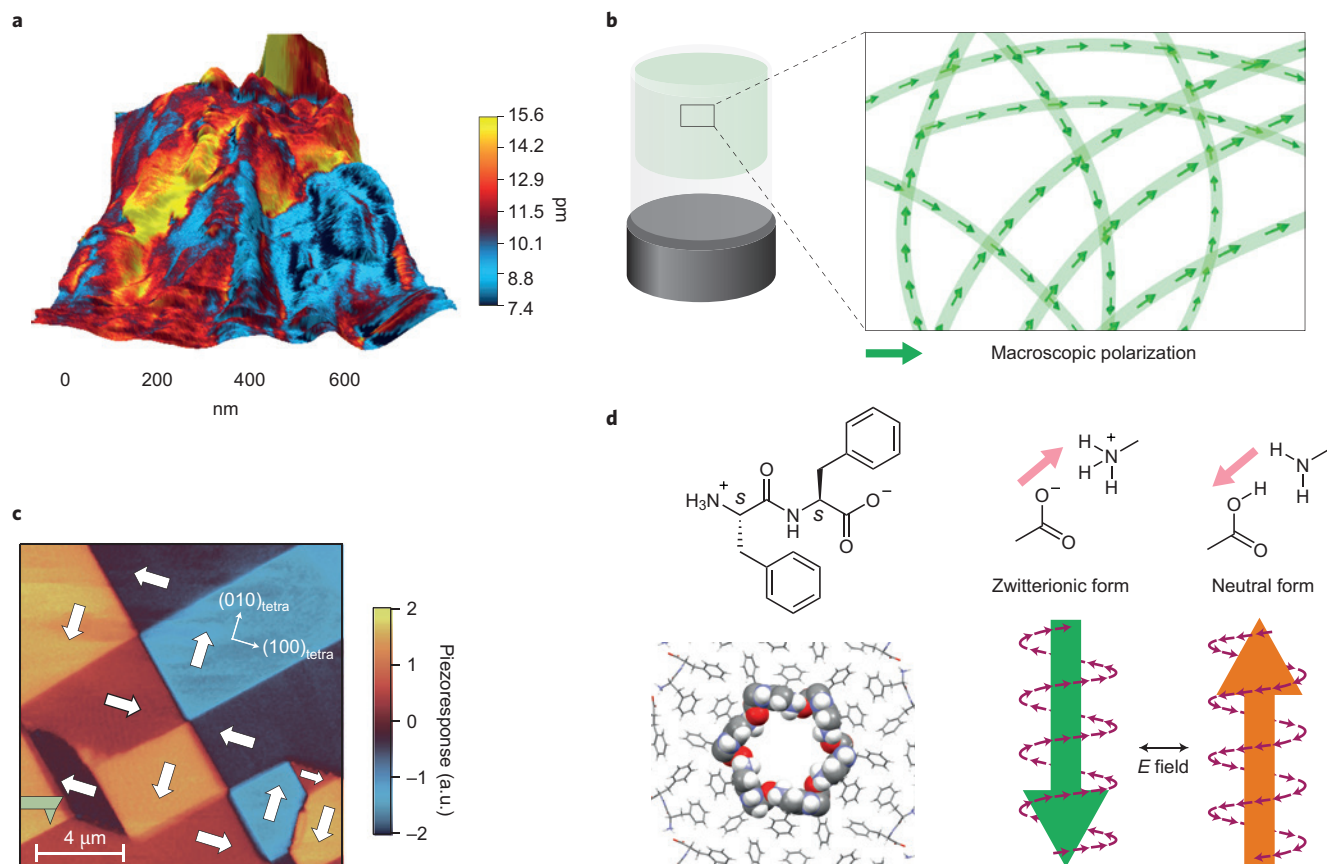
**Figure 7 | Perspective. a**, Recent improvements in piezoresponse force microscopy offer new ways to probe the ferroelectric response in soft biological tissues, such as the microscopic observation of the piezoresponse (amplitude) in the inner aortic wall of mammals. **b**, Ferroelectricity could be observed in the three-dimensional network of gels and supramolecular fibres by the bistable ordering of the polarized molecular units (green arrows). **c**, The amplitude of the piezoresponse provides a measure of the two-dimensional ferroelectric organization in crystals of 2-methylbenzimidazole, by mapping the polarization order (white arrows) of adjacent domains. **d**, Diphenylalanine (structure shown top left) can self-assemble into helical nanotubes (one nanotube is emphasized in a space-filling model, bottom left)[124]. According to the electrical state of the molecules (zwitterionic or neutral), their dipoles (pink arrows) yield a macroscopic polarization (green or orange arrows, bottom right) which is invertible in an electric field under irradiation.

demonstrated that the ferroelectric effect in blood vessels is rooted in the fibrillar structure of elastin[105], and that the ferroelectricity can be modulated by glycation of the polymer, through alteration of its structure[106].

In biological systems, the structure of water may form polarized hydration shells around proteins. It was recently suggested that a temporary memory effect can accompany the evolution of polarization in these systems[107]. This ferroelectric ordering may indeed be possible, given that some ferroelectric ice structures have already been reported[108–110], particularly in confined environments such as MOFs[111]. Despite the observation of ferroelectricity in blood vessels and hybrid materials, protein-based ferroelectrics have not yet been reported. This prospect is not far-fetched, as one could envision that oriented polar domains in a protein structure could switch with an external potential[112]. Moreover, some have posited that collections of hydrated biomolecules, such as lipids and proteins in a cell membrane, may also have properties reminiscent of ferroelectricity or flexoelectricity[113,114].

**Hierarchical structures.** Hierarchical self-assembly, which involves the creation of materials with order parameters spanning multiple length scales, is a largely unexplored field. This type of self-assembly could therefore be valuable in developing ferroelectric systems with novel structures. Multiple orthogonal supramolecular interactions could be used in tandem to produce a supramolecular dipole and an ordered structure. Integrating these interactions into one system

could generate the necessary assembly for organic ferroelectrics. One can also consider that hierarchical structures might generate ferroelectricity along multiple axes, which would be interesting from a functional standpoint. The independence of each axis could allow for several polarization states in one system, thereby offering new possibilities such as greater information storage density. Recent reports of two-dimensional ferroelectric ordering in organics[21,34] suggest that two perpendicular dipoles, or dipoles having more than two bistable states, could be possible (Fig. 7c).

**Dimensionality.** An interesting direction is to consider the dimensionality of a ferroelectric material, such as two-dimensional structures on surfaces or one-dimensional assemblies in supramolecular polymers. Intriguing applications of ferroelectrics, for example in catalysis, exploit the surface or interfacial properties of the system[115]. Therefore, assembling molecules on a surface could be a simpler approach for forming ferroelectric lattices. Lahav and Lubomirsky *et al.* reported the pyroelectric properties of centrosymmetric crystals of amino acids, which originate from the polar layer of water molecules adsorbed on the {010} surfaces[116]. The hydrogen-bonded structure of adsorbed molecules has been extensively studied on graphene and mica[117], and could be combined with ferroelectric mechanisms such as proton displacement. Self-assembled monolayers or inclusion complexes on porous surfaces are also interesting[118] but would require control of the dynamics (molecular switching and correlated motion) with an electric field.

Functional supramolecular polymers may stimulate the synthesis of new ferroelectrics because they can form self-organized scaffolds within which ferroelectric moieties can reside (Fig. 7b)[119]. This approach could yield higher-throughput fabrication, full alignment of ferroelectric domains and low manufacturing costs. In one example, the dipeptide diphenylalanine forms nanotubular assemblies that are both piezoelectric and ferroelectric (Fig. 7d)[120,121]. The possibility of crystallizing supramolecular polymers could also be useful in discovering new organic ferroelectrics[122].

## Conclusions

In this Review we have highlighted how supramolecular chemistry can be used to create organic ferroelectric phases. Non-covalent interactions can increase the ferroelectric figures of merit, yield processable materials and develop systems that can operate at room temperature, given the great structural diversity offered by self-assembly. Ferroelectricity and supramolecular chemistry are two highly synergistic areas of science. Here, order and dynamics are strongly intertwined; this relationship provides a platform from which emergent phenomena can be discovered while creating bio-inspired materials that change or adapt in response to external environments. Whereas the beginning of organic ferroelectricity focused on static crystals and rigid polymers, future work could broaden this field by exploring systems of low dimensionality or mechanical deformability that are reminiscent of biological systems in form and function.

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## Author contributions

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## Additional information

## Competing financial interests

The authors declare no competing financial interests.