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Multifunctional Supramolecular Organic Ferroelectrics

Indrė Urbanavičiūtė

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Complex Materials and Devices

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Cover image

Artistic impression of hexagonally packed self-assembled supramolecular structures of multifunctional organic ferroelectrics leading to electrostatic frustration of adjacent columnar macrodipoles.

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Abstract

Ferroelectric materials are known and valued for their multifunctionality arising from the possibility to perturb the remnant ferroelectric polarization by electric field, temperature and/or mechanical stimuli. While inorganic ferroelectrics dominate the current market, their organic counterparts may provide highly desired properties like eco-friendliness, easy-processability and flexibility, concomitantly opening unique opportunities to combine multiple functionalities into a single compound that facilitates unprecedented device concepts and designs. Supramolecular organic ferroelectrics of columnar discotic type, that are the topic of this thesis, offer additional advantages related to their strong hierarchical self-assembly and easy tunability by molecular structure modifications, allowing optimization of ferroelectric characteristics and their hybridization with, *e.g.*, semiconductivity. This not only leads to textbook ferroelectric materials that can be used as model systems to understand the general behaviour of ferroics, but also gives rise to previously unobserved effects stemming from the interplay of different functionalities.

The core-shell structure of the molecules under the scope enables multiple pathways for rational design by molecular structure modification. This was firstly pursued via peripheral tail engineering on an archetypal self-assembling ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA). We found that by shortening the alkyl chain length all the ferroelectric properties can be continuously tuned. In particular, changing the tail from $C_{18}H_{37}$ to C_6H_{13} causes an increase in depolarization activation energy (~ 0.8 eV to ~ 1.55 eV), coercive field (~ 25 V μm^{-1} to ~ 50 V μm^{-1}) and remnant polarization (~ 20 mC m^{-2} to ~ 60 mC m^{-2}). The combination of the mentioned characteristics resulted in a record polarization retention time of close to 3 months at room temperature for capacitor devices of the material having the shortest alkyl chain – BTA-C6, which at the time of writing was one of the best results for liquid-crystalline ferroelectrics.

Taking one step further, we experimentally demonstrated how introduction of branched-tail substituents results in materials with a wide operating temperature range and a data retention time of more than 10 years in thin-film solution-processed capacitor devices already at elevated temperatures with no measurable depolarization at room temperature. The observed differences between linear- and branched-tail compounds were analysed using density functional theory (DFT) and molecular dynamics (MD) simulations. We concluded that morphological factors like improved packing quality and reduced disorder, rather than electrostatic interactions or intra/inter-columnar steric hindrance, underlay the superior properties of the branched-tailed BTAs. Synergistic effects upon blending of compounds with branched and linear sidechains were shown to further improve the materials' characteristics.

Exploiting the excellent ferroelectric performance and the well-defined nanostructure of BTAs, we experimentally determined the Preisach (hysteron) distribution of BTA and confronted it to the one obtained for the semi-crystalline P(VDF:TrFE). This allowed to elucidate how the broadening of the Preisach distribution relates to the materials' morphology. We further connected the experimental Preisach distribution to the corresponding microscopic switching kinetics. We argue that the combination of the two underlays the macroscopic dispersive switching kinetics as commonly observed for practical ferroelectrics. These insights lead to

guidelines for further advancement of ferroelectric materials both for conventional and multi-bit data storage applications.

Although having strong differences in the Preisach distribution, BTA and P(VDF:TrFE) both demonstrate negative piezoelectricity – a rare anomalous phenomenon which is characteristic to two-phased materials and has never been observed in small-molecular ferroelectrics. We measured a pronounced negative piezoelectric effect in a whole family of BTAs and revealed its tunability by mesogenic tail substitution and structural disorder. While the large- and small-signal strain in highly ordered thin-film BTA capacitor devices are dominated by intrinsic contributions and originates from piezoestriction, rising disorder introduces additional extrinsic factors that boost the large-signal d_{33} up to -20 pm/V in short-tailed molecules. Interestingly, homologues with longer mesogenic tails show a large-signal electromechanical response that is dominated by the quadratic Maxwell strain with significant mechanical softening upon polarization switching, whereas the small-signal strain remains piezoelective. Molecular dynamics and DFT calculations both predict a positive d_{33} for defect-free BTA stacks. Hence, the measured negative macroscopic d_{33} is attributed to the presence of structural defects that enable the dimensional effect to dominate the piezoelectric response of BTA thin films.

The true multifunctionality of supramolecular discotics manifests when large semiconducting cores surrounded by field-switchable strongly polar moieties are introduced in the structure. We showed how the combination of switchable dipolar side groups and the semiconducting core of the newly synthesized C3-symmetric benzotrithiophene molecule (BTTTA) leads to an ordered columnar material showing continuous tunability from injection- to bulk-limited conductivity modulation. Both these resistive switching mechanisms may lead to the next-generation high-density non-volatile rewritable memory devices with high on/off ratios and non-destructive data readout – the element that has been desperately sought after to enable fully organic flexible electronics.

Populärvetenskaplig sammanfattning

Utbredd elektronisering och det högst aktuella fenomenet *sakernas internet* (Internet of Things) ställer höga krav på nästa generations elektroniska system. Produkterna ska vara lätta att framställa med miljövänliga metoder, låg kostnadsproduktion och skalbarhet (t. ex. tryckt elektronik), återvinningsbarhet eller biologisk nedbrytbarhet (gällande engångselektronik), mekanisk flexibilitet (formbara bärbara system), kemisk stabilitet, till och med biokompatibilitet (t. ex. implanterbara system) – dessa är bara några utmaningar som den kommande tekniken behöver övervinna. Organiska material kan åstadkomma alla dessa önskade egenskaper, samtidigt som man skapar unika möjligheter att kombinera flera funktionaliteter till en enda sammansättning som underlättar nydanande komponenter och design.

Ferroelektriska material kännetecknas av pyroelektriska, piezoelektriska och dielektriska egenskaper. Denna mångsidighet möjliggör icke-flyktiga minnesenheter, temperatur- och taktila sensorer, olika transduktorer och manöverdon, som alla baseras på förändringar av den ferroelektriska restpolarisationen genom fält-, temperatur- och / eller mekaniska stimuleringar. Diskformade supramolekylära organiska ferroelektriska ämnen ger ytterligare fördelar tack vare deras modifierbara molekylstrukturer och starka hierarkiska självorganisation som staplar diskarna i kolumner. På detta sätt kan lättbearbetningsbara organiska ferroelektriska material med hög restpolarisering och extrem datalagring konstrueras molekylärt. På grund av deras väldefinierade nanostrukturer kan sådana material användas som modellsystem för att förstå det allmänna beteendet hos polykristallina ferroelektriska material. De uppvisar också en sällsynt negativ piezoelektricitet som är atypisk för små molekulära material och härrör från deras komplexa nanostruktur.

Den verkliga multifunktionaliteten hos diskformade supramolekylära ämnen framträder när stora halvledande kärnor omgivna av starkt polära delar, som är växlingsbara via ett elektriskt fält, introduceras i strukturen. Oöverträffad resistiv omkoppling, inducerad av den asymmetriska laddningstransporten beroende på polarisationsriktningen med rekordhög datalagringstid, upptäcktes efter optimering av molekylstrukturen. Även en konceptuellt enklare resistiv omkopplingsmekanism bunden till en modulation av laddningsinjektionsbarriären genom gränssnittsdiplomerna observerades. Båda dessa fenomen kan bidra till nästa generations icke-flyktiga överskrivningsbara minnesenheter med hög densitet, stora på av-förhållanden, och icke-destruktiv dataavläsning – vilket är kritiskt för att möjliggöra helt organisk flexibel elektronik.

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Author's contributions to the papers

- [I] Prepared the samples, performed the ferroelectric characterization, analysed the data, wrote the manuscript draft and revised it together with the coauthors.
- [II] Prepared the samples, performed the ferroelectric characterization, analysed the ferroelectric and partially the simulations results, wrote the manuscript draft and revised it together with the coauthors.
- [III] Prepared the samples, developed and performed the polarization switching time measurements at certain Preisach coordinates, together with T.D.C and M.K. created a theoretical basis for analysis of the experimental Preisach distribution, together with T.D.C. wrote the manuscript draft and revised in together with the coauthors.
- [IV] Prepared the samples, performed the ferroelectric and piezoelectric characterization, analysed the ferroelectric, piezoelectric and partly simulations results, wrote the manuscript draft and revised it together with the coauthors.
- [V] Prepared the samples, performed the ferroelectric and electrical characterization, analysed the results, partly wrote the manuscript draft and revised it together with the coauthors.

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1 Introduction

1.1 Prospects of multifunctional supramolecular organic ferroelectrics

Facing the first reverberations of the climate crisis, lifestyle and technology orient towards renewable energy solutions and possibilities for sustainable development. The upcoming technological approaches will have to tackle two coherent problems – growth of demand and environmental challenges – which will lead to an unavoidable search for compromises. Considering the nascent trend of vast electrification and the emerging concept of the Internet of Things, electronic devices must conform to the contemporary movement and provide the required set of characteristics. Easy-processability using eco-friendly methods, low-cost production and scalability (*e.g.* printed electronics), recyclability or biodegradability (referring to disposable electronics), mechanical flexibility (conformable wearables), chemical stability, even biocompatibility (*e.g.* implantable devices) – these are just a few challenges that the next-generation electronic devices face. The answer to each of these requirements to a large extent hides under the keyword ‘organics’. Due to their carbon-based structure, organic materials are often of low environmental impact. The non-covalent interactions that are prevalent in organics provide mechanical flexibility while maintaining sufficient performance levels. All these advantageous properties have been exploited in photovoltaics, light emissive devices, field-effect transistors and various sensors that are all based on well-established organic (semi)conductors. Only recently it has been shown that the field of plastic electronics can be enriched with new exciting functionalities if ferroelectricity is introduced.

Ferroelectricity, carrying pyroelectricity and piezoelectricity under the umbrella, is a versatile phenomenon underlying the operation of non-volatile memory devices, temperature and tactile sensors, various transducers as well as actuators that all rely on perturbation of the remnant ferroelectric polarization by field, temperature and/or mechanical stimuli. While the current market is dominated by inorganics, these materials hardly meet the requirements for the 21st century electronics stated above. Ferroelectricity in organic matter can be induced using multiple strategies, many of which are discussed in this thesis. Some of the most robust designs include dipolar molecular switches – field-rotatable moieties comprising a permanent dipole moment. This technique has led to such examples as the successfully commercialized ferroelectric copolymer P(VDF-TrFE) or the leading star of this thesis – the supramolecular ferroelectric BTA.

BTA (trialkylbenzene-1,3,5-tricarboxamide) is an archetypal ferroelectric columnar discotic liquid-crystal. It is equipped with all the essential elements for successful self-assembly and ferroelectric switching – a planar π - π stacking conjugated core, strongly polar free-to-rotate hydrogen-bonding groups and solubilizing aliphatic sidechains that also act as spacers. This core-shell molecular architecture promotes multi-stage hierarchical ordering starting with axial 1D self-assemblies that further pack in tight, typically hexagonal lattices. By small modifications of the molecular structure (*e.g.* core or tail substitution) this packing can be tuned both geometrically, increasing the dipole density, and energetically leading to a more supramolecular polymer-like rather than liquid-crystalline behaviour, which results in substantial polarization stabilization. As discussed throughout the thesis, materials synthesized based on this template typically demonstrate textbook ferroelectricity with polarization switching proceeding via well-known nucleation-limited mechanisms typical to polycrystalline ferroelectrics. The underlying theoretical models are presented and explained in brief.

Due to its well-defined nanostructure, BTA becomes a perfect system to understand the general ferroelectric properties of polycrystalline materials, and the effect of structural/energetic disorder in particular. By contrasting the polycrystalline BTA with the semi-crystalline P(VDF:TrFE) new important insights related to the shape of the Preisach (or local electric fields) distribution and corresponding polarization switching kinetics can be obtained that have direct implications for multi-bit data storage via intermediate polarization states and associated materials designs. The behaviour strongly resembling that of hypothetical ideal ferroelectric particles – hystérons – is found to be due to the unique nanostructure and related nanoscopic switching mechanisms, which is hardly attainable in inorganics.

Turning to the concomitant piezoelectric response, BTAs have been shown to demonstrate a negative piezoelectric effect – a rare phenomenon which has been observed only in two-phased ferroelectric materials with the renowned example of the semi-crystalline P(VDF:TrFE). The piezoelectric constant d_{33} and other figures of merit of the best BTAs are found to be close to those of commercially available ferroelectric polymers which brightens the future of these materials to be used for piezoelectric applications. Longer substituted homologues with stronger expressed liquid-crystalline properties, though having Maxwell strain rather than piezoelectric dominated electromechanical response, reveal an unprecedented strain amplification around the coercive fields. This effect manifests in piezoelectric governed short-tailed BTAs as well and can be attributed to a considerable increase in mechanical compliance during polarization reversal.

In addition to tuning the ferro- and piezoelectric properties, rational molecular structure modifications can lead to entirely new functionalities. This is related to the hybridization of ferroelectric and semiconducting properties that coexist in a single discotic molecule if larger conjugated cores are introduced. Initially, semiconducting ferroics (or photo-ferroics) was an enthusiastically welcomed class of inorganic materials that has been argued to potentially provide high photovoltages originating from the anomalous bulk photovoltaic effect. Keeping the molecular segments responsible for ferroelectricity (=dipolar motifs) and semiconductivity (=conjugated cores) at close proximity but functionally independent (in contrast to perovskite-structure semiconducting ferroelectrics where both functions arise from the same elements), can have a positive impact on the resultant effects and especially their stabilization. An electrical equivalent of this bulk photovoltaic effect – asymmetric transport of injected charges depending on the polarization direction – has been recently demonstrated in several BTA analogues with larger, semiconducting cores. Devices based on these materials showed successful resistive switching induced by this mechanism with extreme data retention after molecular structural optimization. A conceptually simpler resistive switching mechanism related to a charge injection barrier modulation by interface dipoles was also observed. Both these phenomena may lead to the next generation of high-density non-volatile rewritable memory devices with high on/off ratios and non-destructive data readout – the element that has been desperately sought after to enable fully organic flexible electronics.

1.2 Note to the reader

This thesis consists of two major parts: an introductory piece including chapters 1, 2 and 3, which discusses the main concepts, phenomena and (developed) theoretical models put in context of the multifunctional supramolecular organic ferroelectrics; and material design-related chapters 4 and 5, presenting general guidelines for inducing ferroelectric behaviour in inorganics as well as organics with a further focus on the columnar discotic mesophases.

Each section starts with a short exordium and an overview of the following subsections. Related manuscripts are numbered and given in the end of the thesis. Table 1 in the Appendix provides comparison of ferroelectric characteristics of the materials discussed in Sections 4 and 5.

1.3 Para-, ferro-, pyro-, piezo- or dielectric?

All matter as we know it exists due to the interplay among atoms through their electron clouds. If left at rest, common materials will stay electrically neutral with all their intrinsic charges balancing each other at all scales in a highly symmetric fashion. There is however a class of materials that does not fully obey this rule. Consider a heteronuclear diatomic molecule with an asymmetric charge distribution – where the electron cloud favours one atom over the other (*i.e.* different electronegativity). This charge disbalance creates a *permanent electrical dipole*, μ . Naturally, larger molecular units (*e.g.* water, urea, amides) and crystalline unit cells can also have a permanent dipole moment if this electrostatic asymmetry persists. Such materials are referred to as *polar*. Molecular dipoles within polar materials will sense the external electric field, to which they will attempt to align to minimize their energy, very much like a compass needle would align to the Earth’s magnetic poles. Doing this, the dipoles will ‘consume’ the field, due to which its initial value will be effectively reduced (‘screened’) in the material by a certain fraction, namely, by the *relative permittivity* ϵ_r (*=dielectric constant*).

Induced or spontaneous directional arrangement of dipolar units and thus net charge separation creates *electrical polarization*, P . From a geometric perspective, polarization defines a volumetric density of dipole moments ($M = \sum \mu$) in the material, $P = M/V$. If we have a highly field-responsive collection of such permanent (or induced) molecular dipoles in a substance, this results in a very useful *dielectric* material, which has become essential in electronics. For dielectrics, polarization is linear to field $P = \chi_e \epsilon_0 E$ and will vanish immediately after the field is removed, see Fig. 1a left. Here $\chi_e = (\epsilon_r - 1)$ is the electric susceptibility and ϵ_0 is the vacuum electric permittivity. If we arrange these dipoles in an orderly fashion to form a *centrosymmetric* (*i.e.* having inversion symmetry) lattice, the material will acquire properties of a *paraelectric*¹ (see Fig. 1a middle), which finds its application in energy harvesters or electrocaloric cooling devices due to its ability to effectively release its stored energy, as no or very small zero-field polarization is maintained. Similarly, a *non-centrosymmetric* system comprising (reasonably) strongly interacting permanent dipoles will lead to a spontaneous and remnant polarization with a considerable energy barrier between the opposite polarization states, see Fig. 1a right. This so-called *ferroelectric* material, conveniently yet unsoundly (having no direct relation to *ferrum* = iron) named as an analogue to *ferromagnetism*, is considered one of the most perspective candidates for the next-generation memory devices and various energy harvesters with a potential to revolutionize the technology. Ferroelectric materials typically have a critical temperature point after which they lose the initial ferroelectric

ordering (thus, remnant polarization) and become paraelectric. This ferroelectric–paraelectric transition (or depolarization) temperature is often referred to as the *Curie temperature* (T_0) and determines the operation temperature range of the ferroelectric. It can be straightforwardly obtained from the temperature measurements of the dielectric susceptibility as a breakdown point of the formula $\chi = \frac{1}{a_0(T-T_0)}$, known as the *Curie-Weiss law* (Fig. 1b).

Figure 1. (a) Schematic electric displacement–field characteristics for an ideal dielectric (left), paraelectric (middle) and ferroelectric (right) material. (b) Curie-Weiss behaviour around the critical ferroelectric-paraelectric phase transition temperature T_0 .

Lack of inversion symmetry (*i.e.* non-centrosymmetry) is inherent to certain classes of crystalline lattices. Yet only a fraction of these demonstrate spontaneous ferroelectric polarization. Others have useful pyroelectric and/or piezoelectric properties. Arranged in a tight crystalline lattice, dipoles are naturally sensitive to lattice variations. This creates a possibility to influence the polarization by external factors such as temperature, known as *pyroelectric* response, or mechanical deformations, referred to as *piezoelectricity*, in addition to the ferroelectric behaviour responsive to the electric field. In fact, all three phenomena are inextricable and, as a rule, every ferroelectric material will have pyroelectric and piezoelectric properties, primarily being a dielectric (Figure 2). Curiously, ferroelectricity was one of the last to be discovered. Some sources claim that the first observations of pyroelectricity date 24 centuries back, to the Ancient Greece, when a heated gem, most likely tourmaline, was noticed to attract small pieces of wood.² A couple millennia later, in the last decades of the 19th century, based on the knowledge on pyroelectricity, piezoelectricity was demonstrated by the famous Curie brothers. And only then, around 1920, Rochelle salt, which was long known to be

piezoelectric and pyroelectric, was shown to also give a ferroelectric response.³ Nowadays, this versatility is one of the most attractive qualities of ferroelectrics.

Figure 2. Relation of ferroelectric, pyroelectric, piezoelectric and dielectric phenomena.

2 Pyroelectricity and piezoelectricity

Both pyroelectricity and piezoelectricity are differential polarization-coupled effects, induced by changes in temperature and mechanical deformation, respectively, with coefficients $p = \frac{\partial P(\text{polarization})}{\partial T(\text{temperature})}$ and $d = \frac{\partial P(\text{polarization})}{\partial X(\text{stress})}$ quantifying the direct effect. An example of the differentiating pyroelectric response of P(VDF:TrFE) to a periodically changing temperature is given in Fig. 3a. The opposite, inverse operation is thermodynamically allowed for both cases as well. A reversed pyroelectric process, the so-called *electrocaloric effect*, is the ‘youngest’ effect among the discussed, discovered around 1930.⁴ It arises from the field-induced change in entropy of the material near the ferroelectric-paraelectric phase transition boundary, which affects the system’s temperature. While direct pyroelectricity allows to produce different types of highly efficient thermal sensors⁵, electrocaloric devices based on the converse effect may provide solutions for the next-generation compact and environmentally friendly cooling technology⁶. Compared to the pyroelectric effects, piezoelectricity is a well-established, mature technology. The direct piezoelectric effect – generation of charges upon mechanical deformation – underlies operation of various mechanical energy harvesters, transducers, acoustic and tactile sensors.⁷ Whereas the converse effect, causing electric field-induced strain, drives different kinds of actuators or (ultra)sound generators.

Figure 3. (a) Pyroelectric current response (blue line) to a sinusoidal temperature variation (black line). (b) Longitudinal 33 and lateral 31 device operation modes. The stress axis is indicated in yellow.

2.1 Piezoestriction

Piezoelectricity is not the only effect inducing electromechanical response in materials. So does, for example, the negative Maxwell stress (see section 2.1.3.1) that is broadly applied in elastomer actuator technology⁸, or the ion migration in artificial muscles based on ionic electroactive polymers.⁹ Typically, these effects are characteristic to ‘soft’ matter and are overshadowed by polarization-induced strain in ferro/piezoelectric materials that are typically ‘hard’.¹⁰ Generally, mechanical strain S in a ferroelectric material is expressed through a product of the electrical displacement squared D^2 and a material-related factor Q – the electrostriction coefficient¹¹:

$$S_{33} = Q_{33}D^2 = Q_{33}(\epsilon_r\epsilon_0 E + P_r)^2 = Q_{33}(\epsilon_r\epsilon_0 E)^2 + Q_{33}P_r^2 + 2Q_{33}\epsilon_r\epsilon_0 P_r E. \quad (2.1.1)$$

This electrostriction formula can be decomposed to reveal different contributions to the total strain. The electrostriction due to the applied field has a quadratic field dependence $S_d = Q_{33}(\epsilon_r\epsilon_0 E)^2$ and is characteristic to all dielectrics. In organic ferroelectrics like BTA or P(VDF:TrFE) the effect is very weak, resulting in $<0.005\%$ strain. The ferroelectric polarization-induced electrostriction, or piezoestriction, $S_p = (2Q_{33}\epsilon_r\epsilon_0 P_r)E = d_{33}E$ underlies the common linear piezoelectric effect in otherwise spontaneously strained $S_r = Q_{33}P_r^2$ ferroelectric layers. The electrostriction coefficient Q_{33} is inversely proportional to the elastic stiffness constant Y_{33} (Young’s modulus) through $Q_{33} = \gamma_{33}/Y_{33}$, where γ_{33} is the electrostrictive coupling parameter. All the properties of ferro/pyro/piezoelectrics are highly anisotropic, therefore all the descriptive coefficients are tensors, with the longitudinal 33 and lateral 31 modes (see Fig. 3b) being the most relevant for applications. The longitudinal and lateral piezoelectric constants are related via the Poisson’s ratio $\nu = -\frac{d_{31}}{d_{33}}$, which, being positive for common materials, determines opposite signs of these constants.

d_{ij} , the so-called piezoelectric charge constant, is one of four coefficients describing the polarization-field-strain-stress relations (tensor notation is omitted for simplicity)^{12,13}:

$$d = \left(\frac{\partial D}{\partial X}\right)_E = \left(\frac{\partial S}{\partial E}\right)_X = 2\epsilon_r\epsilon_0 Q P_r = \epsilon_r\epsilon_0 g, \quad (2.1.2)$$

$$g = -\left(\frac{\partial E}{\partial X}\right)_D = \left(\frac{\partial S}{\partial D}\right)_X = 2Q P_r, \quad (2.1.3)$$

$$e = \left(\frac{\partial D}{\partial S}\right)_E = -\left(\frac{\partial X}{\partial E}\right)_S = 2\epsilon_r\epsilon_0 \gamma P_r = \epsilon_r\epsilon_0 h = d \cdot Y, \quad (2.1.4)$$

$$h = -\left(\frac{\partial E}{\partial S}\right)_D = -\left(\frac{\partial X}{\partial D}\right)_S = 2\gamma P_r = g \cdot Y. \quad (2.1.5)$$

The first and second terms in brackets correspond to the direct and converse piezoelectric effect, respectively. Further terms show relationships between these coefficients, including the Young's modulus Y that quantifies stress-to-strain ratio in a material. Here, D is electric displacement, E – electric field, $\epsilon_r \epsilon_0$ – dielectric permittivity of a piezoelectric, γ – electrostrictive coupling coefficient, P_r – remnant polarization, Q – electrostriction coefficient, S – strain, X – stress and Y – Young's modulus.

2.1.1 Large-signal and small-signal response

The magnitude of these piezoelectric coefficients may vary between small-signal and large-signal conditions.^{10,14} This is due to reversible and irreversible mechanisms dominating polarization switching, respectively. Reversible processes include dielectric response and polarization fluctuations of small amplitude around local energy minima and thus are governed by intrinsic microscopic effects. Irreversible contributions arise from switching between global polarization minima and are related to domain-wall movement, which occurs largely at the macroscopic scale (Fig. 4). Typically, these domain motion-related macroscopic irreversible contributions at large-signal conditions yield larger piezoelectric constants, compared to the ones measured at the small-signal regime.^{10,14}

Figure 4. Potential energy landscape of a defect-containing ferroelectric and related reversible (inside local energy minima) and irreversible (between local energy minima) domain wall motion.

2.1.2 The sign of d_{33}

Interestingly, the sign of the piezoelectric coefficients can vary as well, depending on the (nano)structure of the material. For conventional organic and inorganic ferroelectrics (see section 4 for examples) the longitudinal piezoelectric constant d_{33} is positive. This is due to the direct coupling between the applied stress/field and the crystalline lattice parameters, along with a lack of structural inhomogeneities in the nanoscale as well as macroscopically, see Fig. 6 left. This way, positive/negative stress will compress/stretch the lattice and thus reduce/increase the dipole moment. Correspondingly, an electric field applied along/opposite to the polarization direction will lead to expansion/compression of the layer, see Fig. 5. The operation mechanism of the positive piezoelectricity is highly intuitive and is based on straightforward electrostatic interactions. It is therefore not surprising that the choice of materials with the anomalous – negative – piezoelectric effect is narrow, and, until very recently, the only examples with $d_{33} < 0$ were considered to be the ferroelectric copolymers P(VDF:TrFE).¹¹ Now, the negative ferroelectricity has been found in a few more van der Waals ferroelectrics, namely, the two-dimensional layered CuInP_2S_6 ,^{15,16} and the leading star of this thesis – the self-assembling BTA.¹⁰

Figure 5. Direct (stress, $X \rightarrow$ electric displacement, D) and converse (electric field, $E \rightarrow$ strain, S) modes in case of positive and negative piezoelectricity. The stress-induced lattice deformations, leading to changes in the dipole moment μ for direct positive piezoelectricity, and the dimensional effect causing direct negative piezoelectricity are illustrated in the top panels. Bottom panels depict idealized strain–field butterfly loops for each case in the converse regime.

2.1.3 Negative piezoelectricity

Though not impossible to be found in single-phased systems,¹⁷ negative piezoelectricity is experimentally observed only in materials combining two phases, in the broadest sense. This can be explained by the underlying mechanism, which is based on the dimensional effect. Consider a multilayer sandwich of magnetic discs spaced by a soft, easily anisotropically deformable (Poisson's ratio much less than 0.5) material, such as sponge. Once under uniaxial stress, mostly the sponge will be compressed, while rigid magnets will remain intact. The result will be an increased volumetric density of the magnetic dipoles (=magnetization) in the system. A similar effect causes negative piezoelectricity in two-phased ferroelectric materials when the electric dipole density is largely controlled by the soft (amorphous or van der Waals interactions-governed) part and not the comparatively stiff dipolar units. A good example of such a system is the semi-crystalline ferroelectric polymer P(VDF:TrFE). See section 4.2.3.1 for more details. A properly conditioned P(VDF:TrFE) layer comprises rigid crystalline lamellae that are surrounded by disordered amorphous material of higher mechanical compliance. At a smaller scale, within these crystallites pseudo-hexagonally packed polymer chains are held together by van der Waals interactions. Both conditions favour the requirements of the dimensional model. It has been shown experimentally¹¹ and by molecular dynamics simulations¹⁸ that the negative piezoelectricity arises both from within crystallites and from the interplay between crystalline and amorphous matter in the bulk. In fact, single polymer chains add their contribution as well, due to complex dipole interactions at the quantum level that lead to elongation of the molecular backbone (and axial compression) under the action of an applied electric field.¹⁹ This places P(VDF:TrFE) on the right side of the diagram in Fig. 6, together with 2D layered van der Waals ferroelectrics like CIPS.¹⁵

There is however a class of materials – the self-assembling amide-based ferroelectrics – that carries properties of both positive and negative piezoelectricity, see Article IV. We have recently found that short-tailed trialkylbenzene-1,3,5-tricarboxamides, or BTAs, demonstrate textbook-like negative piezoelectricity in solution-processed thin-film devices in the converse regime.¹⁰ Yet, differently to the P(VDF:TrFE) case, molecular dynamics simulations and computations based on density functional theory suggest positive piezoelectric constants of BTA at the nanoscale (see Fig. 9), which does not agree with the experimentally observed behaviour¹⁰. The final morphology of the BTA layers is determined by several, hierarchical levels of self-assembly. First, individual discotic molecules stack in a head-to-tail manner to form columns that are stabilized by hydrogen-bonding of the dipolar amides and π - π stacking

of the conjugated cores. These columns further pack in a tight hexagonal lattice. For details on the molecular structure of BTAs, see section 5. At this stage of aggregation, the material would demonstrate positive piezoelectricity, as under pressure the molecular stacks compress, consequently reducing the dihedral angle of the dipolar moieties and thus the net dipole moment. It is the last step of film-forming that determines the negative sign of the macroscopic piezoelectric constants. The described ideality of aggregation is hardly achievable in real devices, where ordered segments will be interrupted by areas of higher disorder, see Fig. 6, middle bottom panel. We estimated that ~5% of this higher compliance disordered matter is sufficient to cause the dimensional effect to dominate. The considered scenario is also confirmed by the observed positive correlation between the macroscopic piezoelectric constants and increasing structural disorder in the BTA layers.¹⁰ Hence, in the BTA case, the positive piezoelectricity at the nanoscale is conquered by the bulk-governed negative piezoelectricity arising from the dimensional effect. While this explains the negative slope of the strain-field loops, the linear dependence itself originates from previously introduced piezostriktion.

Figure 6. Examples of materials demonstrating positive and negative piezoelectricity with characteristic nanoscopic (top row) and macroscopic (bottom row) structure: examples of PZT, BTA and P(VDF:TrFE).

Application-wise, the sign of the piezoelectric constants is not of any importance. It is the other qualities of the materials with negative piezoelectricity that makes them appealing. First, due to the dominating non-covalent interactions, materials with negative piezoelectricity are lightweight, flexible and soft. This allows fabrication of bendable, conformable devices, for which brittle ceramics, single-crystals or epitaxial films are unsuited. Low density also improves their chances to be used for implantable devices⁷, as their acoustic impedance $\rho \cdot v_{\text{sound}}$ of $4.2 \cdot 10^6 \text{ kg/m}^2/\text{s}$ for P(VDF:TrFE)²⁰ and predicted $1.3 \cdot 10^6 \text{ kg/m}^2/\text{s}$ for BTA is significantly closer to that of the soft body tissues $\sim 1.5 \cdot 10^6 \text{ kg/m}^2/\text{s}$, compared to, for example, $\sim 40 \cdot 10^6 \text{ kg/m}^2/\text{s}$ of PZT.²⁰ P(VDF:TrFE), being a close relative of the famously chemically inert Teflon, and BTAs also demonstrate very good chemical resistance, which is advantageous for *in vivo* applications in harsh biological environments. The organic nature of these materials improves their bio/cytocompatibility in comparison to the often lead-based and thus toxic inorganic piezoelectrics. Despite the named advantages, some of the ferro/piezoelectric parameters of P(VDF:TrFE), CIPS and BTA still lag behind in magnitude when put in context of the current progress in inorganics, although they outperform a number of hybrid materials²¹ and organic crystals²². For comparison of the key properties, see Appendix I, Table 1.

For some applications the above defined piezoelectric constants are insufficient to describe the usefulness of materials. There are therefore several other figures of merit that are more suited for different types of applications²³. The electromechanical coupling factor $k = d\sqrt{Y}/\sqrt{\epsilon_r \epsilon_0}$ reflects an electrical-to-mechanical energy conversion efficiency. Typical inorganic piezoelectric materials are characterized by k ranging 0.3–0.7.²³ Compared to this, P(VDF:TrFE) with 0.2 and BTA with 0.1, which is mostly caused by their low Young's moduli sitting in the numerator, appear to be of lower usefulness. Yet, experience shows that these comparatively low electromechanical coupling factors do not limit the applicability of these and similar materials for energy harvesting. Deutz *et al.* argue that for energy harvesters and sensors, especially working away from the resonance²³, the $d \cdot g$ coefficient is more relevant.²¹ The dg coefficient is proportional to the energy density in the device under stress and is thus a more representative figure of merit when it comes to searching for potential candidates for energy harvesting applications. This brightens the future of soft piezoelectrics, as with dg of $\sim 8 \text{ pm}^3/\text{J}$ and $\sim 2 \text{ pm}^3/\text{J}$, P(VDF:TrFE) and BTA sit among the best inorganic and composite materials.^{21,23}

2.1.3.1 Non-piezoelectrostrictive electromechanical response

Maxwell stress is a well-known effect, present in parallel-plate capacitors due to attractive electrostatic forces acting on the oppositely charged electrode surfaces. This causes negative strain on dielectric spacers, which is directly proportional to the mechanical compliance ($s = 1/Y$) of the material. For small deformations (where $\frac{F}{A} = YS$ holds) the stress-strain relation is approximately $S = -\frac{\epsilon_r \epsilon_0}{2Y} E^2$, with Maxwell stress $\frac{F}{A} = \frac{1}{2} \epsilon_r \epsilon_0 E^2$, where F is the compressive force, Y is the Young's modulus, E is the applied field, $\epsilon_r \epsilon_0$ is the dielectric permittivity of the material, and A is the contact area. This effect has been extensively studied and successfully applied in the field of elastomer actuators⁸.

The linear negative piezoelectrostriction and the quadratic Maxwell strain are both present in ferroelectric films and are in principle competing mechanisms. The balance between these mechanisms is determined by the ferroelectric polarization and Young's modulus. Given $S_{33,Maxwell} = -\frac{\epsilon_r \epsilon_0}{2Y} E^2$ and $S_{33,Piezoelectrostrictive} = (2Q_{33} \epsilon_r \epsilon_0 P_r) E$, the ratio of the two is $S_{33,Maxwell}/S_{33,Piezoelectrostrictive} = \frac{1}{4Y_{33} Q_{33} P_r} E$, which leads to piezoelectrostriction (Maxwell strain) being dominant at fields lower (higher) than $4Y_{33} Q_{33} P_r$. The higher the $Y_{33} Q_{33} P_r$ coefficient, the less likely it is for the device to enter the Maxwell-strain dominated field-range in normal operation conditions (close to the coercive fields). This trend was clearly observed in BTAs¹⁰ when for shorter-substituted BTA homologues a linear piezoelectrostrictive response was recorded due to this critical field being far above the coercive field. For longer-tailed BTAs with lower P_r and Y_{33} these mechanisms become strongly competing, with an extreme example of BTA-C18 where the critical field was actually smaller than the coercive field, thus, its electromechanical response was dominated by the Maxwell strain, see Article IV.

2.1.3.2 Strain amplification

The unique nanostructure and the ferroelectric switching ability of BTAs provoke another anomalous previously unobserved behaviour – strain amplification upon polarization switching¹⁰. See Article IV for details. Due to mechanical softening during polarization reversal, an overshoot in strain is observed both in piezoelectrostriction (BTA-C6 example, Fig. 7 left) and in Maxwell strain (BTA-C12 example, Fig. 7 right) dominated regimes. Based on an analysis of the BTA-C12 case, a Gaussian distribution of the elastic modulus over field was obtained with a minimum at the coercive fields, which clearly corresponds to the polarization switching kinetics. DFT/MD simulations of a single self-assembled BTA molecular stack in

presence of an electric field (after polarization switching, $E \uparrow P \uparrow$) revealed a pronounced stiffening of the structure with increasing fields¹⁰. Yet, looking from the more macroscopic perspective, the minimum in elastic modulus would be a consequence of a high density of small domains and domain walls at the zero net polarization (=coercive field) point that leads to a significant weakening of the hydrogen-bonded supramolecular backbone. In contrast, the fully polarized state consists of large, well-developed axial domains, which accounts for the mechanical hardening and a maximal Young's modulus. From a practical perspective, this field-induced strain amplification enhances the electromechanical response within the particular range of fields, which boosts the effective piezoelectric coefficients.

Figure 7. Strain amplification (shaded in blue) due to modulation of the elastic constant during polarization switching for piezoestriction (BTA-C6, left) and Maxwell strain (BTA-C12, right) dominated cases. Black lines represent trends without this strain overshoot, grey dashed lines indicate the coercive field.

3 Ferroelectricity

Ferroelectricity embraces all the phenomena introduced above – dielectricity, piezoelectricity and pyroelectricity. The key to the multifunctionality of ferroelectric materials lies in their ability to hold electric polarization in thermal equilibrium. In other words, ferroelectric charges separate spontaneously, without external intervention. However, macroscopic spontaneous polarization is more of a theoretical idealistic aspiration, applicable to ideal ferroelectric single-crystals and epitaxial films. Spontaneous polarization in practical (polycrystalline) ferroelectrics is typically observed at the nanoscale. The polycrystalline nature of most real-life ferroelectric ceramics and thin films puts limits to the observable net bulk spontaneous polarization in electrically untreated samples due to structural fragmentation (*i.e.* grains and small domains)²⁴, see Fig. 8. A so-called poling procedure – typically prolonged application of a (cycled) electric field along the desired polarization axis – leads to forced orientation of the initially randomized domain polarization direction along the applied field, which brings the system closer to the idealized single-domain state. In the case of the self-assembling (liquid-crystalline) ferroelectrics that are the focus of this thesis, a similar treatment procedure is required, yet, using the polycrystalline materials terminology, it leads to reorientation of “grains” themselves. See section 5 for further details and discussion.

Figure 8. Spontaneous polarization in ideal ferroelectric single crystal (left), unpoled (middle) and poled (right) polycrystalline ferroelectric.

3.1 How much, how fast, how long?

Once properly conditioned, ferroelectric materials will be able to switch between the two polarization states – “up” and “down” – with the help of an applied electric field and ideally will store an electrical charge density referred to as the *remnant polarization*, P_r . These positive and negative remnant polarization points sit at the global minima of the free energy landscape when the material is in the ferroelectric phase (see Fig. 9), which assures thermodynamic stability of the set polarization, $\pm P_r$. The energy barrier between these states W_b must be overtaken by external factors like the applied electric field and (to some degree) temperature, which defines the critical field value for switching – the *coercive field*, E_c . This bistable non-volatile charge storage functionality underlies the potential of ferroelectric materials to be used for memory applications in binary systems (e.g. FeRAM). Intermediate polarization states by definition are thermodynamically unstable in ideal ferroelectrics. However, for certain classes of ferroelectrics like P(VDF:TrFE) this rule does not hold, which allows for multibit data storage in these intermediate states via partial poling.^{25,26} Regardless of the application, there are several points of interest and concern, related to the ferro/pyro/piezoelectric functionality. These are amongst others the:

- 1) intensity of the response that is largely determined by the remnant polarization (*i.e.* dipole density), dielectric constant, etc.;
- 2) the critical field required for changing the polarization state (*i.e.* coercive field);
- 3) operational temperature range (with the Curie temperature setting the upper limit);
- 4) speed of the response that corresponds to the polarization switching time (*i.e.* switching kinetics);
- 5) symmetry of the response affected by defects, impurities and other pinning sites (*i.e.* imprint issues);
- 6) resistance to prolonged operation, typically measured as the number of operation cycles before breakdown (*i.e.* fatigue);
- 7) depolarization rate that depends on the quality of the material and device structure (*i.e.* polarization retention);
- 8) mechanical properties (brittleness, density, etc.), environmental concerns, chemical resistance, toxicity, abundance of materials, ease of fabrication, cost efficiency, etc.

All these aspects must be considered and optimized for successful ferro/pyro/piezoelectric operation and sustainable development of the technology.

3.2 Thermodynamic description of ferroelectrics

The equilibrated thermodynamic state of an ideal macroscopic ferroelectric can be described using the expression of the free energy density for systems close to an order-disorder phase transition proposed by Landau and adapted to ferroelectrics by Devonshire²⁷:

$$G = G_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 - EP. \quad (3.2.1)$$

This truncated power series of the order parameter – for the case of ferroelectrics, polarization – gives a double-well free energy landscape for continuous (second-order) phase transitions, one of which is the ferroelectric-to-paraelectric phase transition. See Fig. 9a for typical zero-field $E = 0$ curves in the ferroelectric and paraelectric phases. Density functional theory (DFT) simulations on self-assembled BTA stacks reveal a similar energy landscape seen in panel (b) illustrating BTA's switchable bistable thus ferroelectric nature¹⁰.

Here, G_0 is the energy density of the unpoled paraelectric state (typically considered zero) and $\alpha = a_0(T - T_c)$ with a positive coefficient a_0 and Curie temperature T_c , leading to $\alpha < 0$ for $T < T_c$. As α is reciprocal to the dielectric susceptibility χ , for temperatures above T_c this relation gives the Curie-Weiss law introduced in section 1.3. The sign of β reflects the type of the phase transition and is positive for the continuous case. From these parameters the resulting remnant polarisation can be estimated $P = \pm(-\alpha/\beta)^{1/2}$ as well as the ferroelectric contribution to the dielectric constant $1/\epsilon\epsilon_0 = -2\alpha$. The barrier between the positive and negative polarization $w_b = -\alpha^2/4\beta$ is typically much larger than $k_B T$ and translates to coercive field values $E_c = 2\beta(-\alpha/3\beta)^{3/2}$ that are several orders of magnitude too high compared to the experimentally obtained ones^{28,29}, see section 3.4.1. This can be explained by presence of domains and domain walls as well as active nucleation taking place in real ferroelectrics, which requires revision of the theory, as discussed in sections 3.4–3.6.

Figure 9. (a) Zero-field free energy landscape in the ferroelectric phase (solid line) and in the paraelectric phase (dashed line), as described by the Landau-Devonshire theory²⁷. w_b is the energy barrier between the $\pm P_r$ states. (b) Energy profile of macrodipole switching (blue datapoints, right axis) determined at B3LYP-D3/cc-pVDZ level of theory^{10,30} for a BTA-C1 dimer. A corresponding interdisc distance relation to the dihedral angle is given as black datapoints, left axis. This growing trend indicates positive longitudinal piezoelectric constants at the nanoscale.

3.3 Saturated and remnant polarization

The whole polarization reversal process can be tracked in polarization–field hysteresis curves, as the one in Fig. 10a, that carry important experimental information – the available polarization P_r and the coercive field, E_c . The ferroelectric hysteresis loop is also a powerful tool to determine the quality of a ferroelectric. The form of a hysteresis curve close to the one shown in the rightmost panel of Fig. 1a is expected for ideal ferroelectrics. In reality the loops are slanted and rounded which gives clues about the level of structural disorder in the layer, which can be further used to describe both static and dynamic polarization switching processes in a ferroelectric,³¹ as discussed in section 3.7.

Closed hysteretic D – E loops, reminiscent of those of ferroelectrics, can be obtained for conductors (resistors) or lossy dielectrics (Fig. 10b), yet these elongated banana-shaped curves (not to be confused with banana-shaped liquid crystals that are just fine, see section 4.2.3.2) must not be mistaken for being of ferroelectric origin.³² Some possible tests to confirm true ferroelectricity are given in section 3.3.1.

Polarization–field characteristics can be straightforwardly obtained by measuring the transient current during polarization switching as a response to a triangular voltage signal, which includes displacement currents and other possible secondary effects like ohmic leakage: $j = \frac{dD}{dt} + j_{\text{other}} = \frac{dP}{dt} + \left(\epsilon_r \epsilon_0 \frac{dE}{dt} + j_{\text{other}} \right) = j_{\text{sw.}} + j_{\text{nonsw.}}$. The final D – E hysteresis loop is derived by integration of the full signal over time. This way of measuring the hysteresis loops is preferred over the capacitive Sawyer-Tower circuit approach as it allows to characterize the device in real conditions with possible leakage and other artefacts of non-ferroelectric nature. These secondary non-switching contributions can be subsequently (separately) measured using the double-wave method (DWM) and then subtracted from the hysteresis loops to obtain a pure ferroelectric P – E curve. Yet, many sources present P – E characteristics including all (also non-ferroelectric) contributions, which leads to overestimation of the remnant³³ or saturated (maximum available) polarization³⁴.

Figure 10. (a) Typical ferroelectric displacement–field hysteresis loop with characteristic remnant polarization P_r and coercive field E_c values. A corresponding energy landscape for positive and negative poling is given as insets. (b) Possible artefacts of non-ferroelectric nature that influence the form of the measured electric displacement vs. field characteristics.

(c) Saturating polarization-field and (d) capacitance-field characteristics typical for ferroelectrics. Panels (a), (c) and (d) are examples of BTA-based devices.

3.3.1 Proofs of ferroelectricity

Closed hysteretic P - E loops or belonging to a characteristic non-centrosymmetric crystallographic point group³⁵ cannot be considered a sufficient proof of true ferroelectricity in materials. There are several other tests that must be run to confirm the hypothesis. First, as there is a limited number of available dipoles in a material, polarization should eventually reach saturation with increasing field, see the example of BTA in Fig. 10c. This saturated polarization value consequently should correspond to the geometrically available dipole density, depending on the structure of the material (*i.e.* packing properties, lattice parameters). If the accumulated charge density is much larger, other effects like electrochemical reactions^{36,37} or simple Ohmic contributions are at play; smaller accumulated charge densities may indicate partial switching or insufficient poling levels. Ferroelectrics also demonstrate variation in small-signal capacitance with field, which can be measured independently and gives characteristic butterfly loops similar to the one given in Fig. 10d for BTA. The Curie-Weiss behaviour (Fig. 1b), introduced earlier in the text, is a further proof for existence of a truly ferroelectric phase. And once again, a true ferroelectric should also demonstrate the concomitant pyroelectric and piezoelectric properties.

Focusing on the ferroelectric characterization, there are several theoretical models that describe ferroelectric switching processes and their dependences on the operation conditions, *vide infra*, the validity of which could be used as an argument for a true ferroelectric nature of the material. Finally, as the definition of ferroelectrics denotes, the set polarization state should be maintained with time, in absence of any supporting electric field. However, while holding for ideal (theoretical) ferroelectric structures, this condition is hardly attainable in real ferroelectric devices due to multitude of effects causing depolarization. For further details on the depolarization problem see section 3.5.

3.4 Coercive field

When characterizing ferroelectric materials, together with typical attainable polarization levels a critical electric field for polarization switching is typically provided. Though giving a ballpark value for the characteristic switching field of the material, the exact coercive field of devices based on this material will depend on operation conditions (alternating field frequency, poling duration, temperature) as well as on the device geometry and the material morphology. Due to so many influences playing a role in determining the final experimental coercive field value of ferroelectrics, the question has stimulated researchers' curiosity since the discovery of the phenomenon.

3.4.1 Intrinsic coercive field

Intuitively, a ferroelectric of any form should possess a definite minimum electric field which should be surpassed to start the polarization reversal. All fields below it would by definition be of insufficient strength. Here, we come to the concept of an *intrinsic coercive field* that originates from the thermodynamic description of ferroelectrics given above (the Landau-Devonshire theory). Its value is defined using intrinsic thermodynamic parameters like the Curie temperature and the spontaneous polarization of the system and excludes any domain-related factors³⁸. The coercive field in this case is $E_c \approx \frac{1}{2} \frac{P_s}{\epsilon_r \epsilon_0}$ if taken as a half of the depolarization field (section 3.5.1), and $E_c \approx \frac{1}{3\sqrt{3}} \frac{P_s}{\epsilon_r \epsilon_0}$ based on the Landau-Devonshire theory (section 3.2).²⁹ This high coercive field (*e.g.* experimental 0.2 V/ μm vs. intrinsic 100 V/ μm for inorganic barium titanate²⁹) would only be attainable in systems with no domain activity – that is a single-domain case, where polarization reversal proceeds via continuous homogeneous dipole reorientation (see Fig. 11, bottom). Though multiple attempts to enter this regime have been reported,^{29,38–40} the complexity of the required experimental conditions for suppressed domain formation (typically moving towards 2D state in ultrathin layers) still leaves the achievability of true intrinsic switching with a question mark. Very high coercive fields found in devices based on branched-tailed BTAs resemble the intrinsic polarization switching behaviour (see Paper II), yet more experimental work must be done to thoroughly investigate the issue.

In everyday ferroelectrics, polarization reversal progresses via formation of small oppositely oriented domains and their subsequent growth that is seen as domain wall propagation (a domino effect) and that leads to full polarization inversion (Fig. 11, top). Extensive theoretical

work has been done to describe and explain this external switching process, some examples of which will be briefly discussed in the following sections.

Figure 11. Intrinsic continuous (bottom) and extrinsic, proceeding via domain nucleation-and-growth, (top) switching mechanisms. Grey and blue shades indicate opposite polarization directions.

3.4.2 Ishibashi-Orihara model

The intrinsic coercive field introduced above only carries limited information related to the materials' thermodynamic state and omits any factors related to the real layer structure and actual operation conditions. Ishibashi and Orihara developed an empirical model relating the true experimental external coercive field of a ferroelectric to the applied field frequency. The underlying assumption is that the coercive field is probed in a continuous, cyclic fashion as is typically the case⁴¹. As in real devices ferroelectric domains have defined switching speeds, at higher applied field frequencies domains start to lag behind the driving field, which causes an increase in the effective critical switching (=coercive) field, see Fig. 13a. In other words, larger fields are required to achieve faster polarization switching. A power-law frequency dependence was derived with the geometrical dimensionality factor $d = 1, 2, 3$ and an empirical constant α that is dependent on the waveform of the applied field signal and equals ~ 6 for triangular and sinusoidal waves:

$$E_c \propto f^{d/\alpha}. \quad (3.4.2.1)$$

This model nicely complements the classical Kolmogorov-Avrami-Ishibashi (KAI) theory introduced in section 3.6.1, which describes the switched polarization kinetics at a constant

applied electric field but does not grasp other kinetic properties and dependences. Yet, the Ishibashi-Orihara formalism, similarly to the KAI model, is mostly valid for ‘ideal’ bulk ferroelectrics as it considers domain-growth-limited (thus governed by domain wall movement) switching which is rarely observed in practical ferroelectrics.

3.4.3 Du-Chen model

Du and Chen developed an alternative thermally activated nucleation-limited-switching $E_c \sim f$ model⁴² with a more physical expression including domain wall energy γ , binding energy between structural defects and the wall γ_b , the change in polarization due to passing of the domain wall ΔP and a limiting domain switching frequency f_0 :

$$E_c = B' / \sqrt{k_B T \cdot \ln(f_0/f)}, B' = 2\sqrt{\pi} \gamma_b \sqrt{\gamma} / \Delta P. \quad (3.4.3.1)$$

Here k_B is the Boltzmann constant and T the absolute temperature. The parameter B' is typically used as a fitting parameter. This model has been shown to give much better fits of coercive field versus frequency trends for thin-film polycrystalline ferroelectrics^{43,44}, see also Fig. 13a.

3.4.4 Thermally activated nucleation-limited switching (TA-NLS) model

The Landau-Devonshire framework presented in section 3.2 defines the bistable nature of bulk ferroelectrics giving a free-energy profile with two global energy minima at $\pm$ remnant polarization, separated by an energy barrier of a defined height. However, this theory fails to explain experimental coercive fields because no domain-related and nucleation-governed mechanisms are considered, leading to overestimation of the values by several orders of magnitude. Vopsariou *et al.* adapted the formalism to real systems by considering extensive nucleation as a pathway for polarization reversal and by adding a thermal activation factor arising from the probabilistic nature of the polarization switching^{28,45,46}. According to this concept, the rate-determining step for polarization switching is the formation of a critical nucleus with a defined activation energy density w_b and a critical volume V^* that initiates a chain-reaction of domain propagation by a domino effect (Fig. 12). Nuclei that are of insufficient volume will cease to exist and will be consumed by the adjacent expanding domains. Consequently, all kinetic properties including the coercive field value and the switching time (see sections 3.6.4 and 3.6.5) become directly related to this nucleation process. The coercive field for this thermally activated nucleation-limited switching can be expressed using the same activation parameters:

$$E_c \cong \frac{w_b}{P_r} - \frac{k_B T \cdot \ln(v_0 t \cdot (\ln(2))^{-1})}{P_r V^*}. \quad (3.4.4.1)$$

Here, P_r is remnant polarization, v_0 is an attempt frequency (typically phonon frequency) and t is the duration of the experiment or the reciprocal probing frequency $1/f$. Within this framework the coercive field is linearly proportional to w_b , the energy barrier per unit volume between the two polarization states, and the temperature T . A temperature-dependent trend is clearly visible in Fig. 13b, where ferroelectric hysteresis curves measured upon cooling on a BTA-C8 device are given. This coercive field expression represents an extrinsic threshold value and is far lower than the theoretical intrinsic coercive field, coming from the pure Landau-Devonshire theory for an ideal crystal³⁸, which allows it to correctly describe various ferroelectric systems with different degrees of disorder. For BTAs specifically, the theory gives a solid basis to interpret the increasing coercive field trend and the extreme polarization retention in branched-tailed homologues⁴⁷, that have been repeatedly reported by unrelated sources to have larger characteristic self-assembled stack sizes⁴⁸. See Article II for details.

Figure 12. Illustration of the domino effect during polarization switching progression caused by nuclei of smaller and larger volume than the critical volume. A corresponding Gibbs free energy landscape is given above.

For regular ferroelectrics, the TA-NLS model successfully grasps the probabilistic nature of field-induced thermally activated polarization switching, especially in polycrystalline materials; however, introduction of disorder would bring us one step closer to a full description

of real ferroelectric devices. Based on this, we formulated an extended theoretical formalism including the characteristic structural and energetic disorder, which was able to explain many additional ferroelectric switching properties, as described in Article III. See section 3.7 for more details.

Figure 13. (a) Coercive field dependence on the triangular voltage signal frequency at different temperatures. (b) P - E characteristics with increasing temperature (from red 130°C to blue 23°C), BTA-C8 example. The coercive field increases linearly upon cooling while the remnant polarization remains constant in the measured temperature range.

3.5 Depolarization (spontaneous polarization relaxation)

The ability of a ferroelectric to remain electrically polarized after the polarizing electric field is removed is called *polarization retention*. Infinite polarization retention is a natural aspiration for non-volatile memory applications (e.g. FeRAM), yet it is equally important for successful operation of all ferro/pyro/piezoelectric devices, including the ones based on electret behaviour like microphones. Temporal polarization stability was often taken for granted in ferroelectrics, possibly due to historical reasons when mostly large ferroelectric (single)crystals were investigated. With the relatively recent pursuit of thin-film technology, depolarization issues became of higher interest⁴⁹, however they remain largely overlooked in the scientific literature despite remaining one of the main obstacles limiting integration of ferroelectrics in actual electronic devices⁵⁰.

3.5.1 Depolarization fields

Polarization reversal is a field-activated thermally assisted process (see section 3.4.4 for details), which leads to switching between two (ideally) equipotent ground states of $\pm P_r$ with a finite energy barrier w_b between them, as illustrated in Fig. 9a. This barrier can be overcome in two ways – by external and internal electric fields. An external applied field greater than the coercive field is used to electrically polarize the film. However, an opposing internal field is consequently induced in a polarized ferroelectric, which is referred to as the *depolarization field*, see Fig. 14a. It arises from the bound charges at the surface ($\rho_{\text{surf.}} = -\nabla \cdot \vec{P}$) and is directly related to the remnant polarization and the dielectric permittivity of the material: $E_{\text{dep}} = -\frac{P_r}{\epsilon_0 \epsilon_{\text{ferro}}}$. Nature provided a means to alleviate this high depolarization field by forming smaller ferroelectric domains instead of a single continuous one. Still, the effective depolarization field can be close to or even higher^{30,51} than the measured coercive field, which unavoidably leads to rapid depolarization and may overshadow the ferroelectric nature of the material. It is the external screening of this depolarization field that makes a ferroelectric ferroelectric, i.e. enables stabilized net macroscopic polarization.

Real ferroelectrics are hardly isolated from other charged entities – this can be surrounding air molecules or deposited electrodes – which allows for (partial) compensation of the bound polarization charges at the interfaces and thus diminishing the depolarization field. In real-device context, perfect polarization screening is practically unattainable, typically due to electrode interface imperfections (passive, non-ferroelectric ‘dead’ layers) or non-ideal metal

electrodes (finite electron screening length), which results in a fraction (coefficient $|\beta| \leq 1$) of the depolarization field remaining uncompensated: $E_d(t) = \beta \frac{P_r(t)}{\epsilon_0 \epsilon_{\text{ferro.}}}$. The magnitude of this effective depolarization field decreases with decreasing polarization over time t and depends on the layer thickness and the (di)electric properties of the interface layer⁵² and the electrode⁵³:

$$E_d^{\text{int}}(t) = -\frac{P_r(t)d_{\text{int}}}{\epsilon_0 \epsilon_{\text{int}} d_f}, \quad (3.5.1.1)$$

$$E_d^{\text{metal}}(t) = -\frac{P_r(t)}{\epsilon_0 \epsilon_f} \left(\frac{\frac{2\epsilon_f}{d_f}}{\frac{2\epsilon_f}{d_f} + \frac{\epsilon_e}{\lambda}} \right). \quad (3.5.1.2)$$

Here, d_f and d_{int} are the thickness of the ferroelectric and interface layers, ϵ_0 , ϵ_{int} , ϵ_f , ϵ_e are the vacuum permittivity, dielectric constant of the interface layer, the ferroelectric and the electrode, respectively. P_r is the remnant polarization and λ the electron screening length in the metal.

Typical examples of organic ferroelectrics like P(VDF:TrFE) or BTA have high depolarization fields of ~ 900 V/ μm before screening due to a large $P_r/\epsilon_r \epsilon_0$ ratio, compared to, *e.g.* PZT, with an order of magnitude lower values (~ 70 V/ μm). However, in real devices it is inorganics that suffer from up to tenfold higher effective uncompensated depolarization fields because of the high remnant polarization. This makes inorganics more sensitive to the quality of the metal electrodes with $E_d^{\text{metal}} \approx 5\text{--}10$ V/ μm and $\approx 0.5\text{--}1.5$ V/ μm for organics with typical parameters[†], based on Eq. 3.5.1.2. Uncompensated depolarization fields due to possible ‘dead’ interface[‡] layers (Eq. 3.5.1.1) are more significant for both cases yet are more similar for organics and inorganics, ranging 15–25 V/ μm . The advantage of organics like BTA and P(VDF:TrFE) lies in the fact that these values are still far from their typical coercive field $\sim 50\text{--}100$ V/ μm , while for inorganics with $E_c \approx 0.1\text{--}10$ V/ μm the issue is critical⁵⁴. Additional factors like contact potential differences, gradients in polarization or injected charges may accelerate polarization relaxation as well, yet uncompensated depolarization fields remain the dominant problem. We showed with an example of BTAs that if this depolarization field is counteracted by a small opposing external electric field, polarization decay can be slowed down or suppressed completely⁵⁵, see Fig. 15 for an example of BTA-C12. This holds for inorganic ferroelectrics as well.⁵¹

[†] $d_f = 100$ nm; $\lambda = 0.5$ Å; $\epsilon_e = 7$; BTA $P_r = 55$ mC/m², $\epsilon_r = 7$; P(VDF:TrFE) $P_r = 80$ mC/m², $\epsilon_r = 10$; PZT $P_r = 600$ mC/m², $\epsilon_r = 1000$.

[‡] $d_f = 100$ nm; $d_{\text{int}} = 1$ nm; organics $\epsilon_{\text{int}} = 3.5$; inorganics $\epsilon_{\text{int}} = 40$.

Figure 14. Origins of the depolarization field and different cases of its compensation: (a) standalone polarized ferroelectric, no screening of the bound polarization charges, maximum depolarization field E_{dep} , (b) during polarization of a ferroelectric device with electrodes by application of an external electric field E_{app} , (c) partly uncompensated and (d) fully compensated depolarization field (idealized case) when the external field is removed and the device is left grounded (short-circuited).

3.5.2 Depolarization kinetics

Different empirical functions – power-law⁵¹, linear-log, exponential and stretched exponential⁵⁶ – have been shown to successfully fit the temporal polarization decay in different types of ferroelectrics, which indicates the absence of a unified theory and highlights the complexity of the problem.⁵² A stretched exponential function

$$P(t) = P_0 \cdot \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad (3.5.2.1)$$

with a depolarization time constant τ and a stretching exponent $\beta < 1$ successfully describes depolarization kinetics in polycrystalline, disordered thin-film ferroelectrics like PZT⁵⁶ with $\beta \approx 0.2$ or BTA with $\beta \approx 0.5$.^{47,57} See Fig. 15 bottom datapoints for typical kinetics. Though reminiscent of it, the model differs from the classical KAI theory describing field-induced polarization switching (Eq. 3.6.1.1) where β is the geometric dimensionality parameter of the nuclei growth and equals 1, 2 or 3, see section 3.6.1. The stretched exponential function is typically related to decay processes characterized by a distribution of energy barriers (=random walk processes)⁵⁶ and is widely used for relaxation analysis in disordered systems that have a distribution of relaxation times. A ferroelectric is considered to have fully depolarized when complete dipole and/or domain orientation randomization is reached (*i.e.* $N_{P\uparrow} = N_{P\downarrow}$, $P_{\text{net}} = 0$, $P_{\text{lost/remaining}} = \frac{1}{2}P_0$). Depolarization is accelerated exponentially at elevated temperatures T following the Arrhenius law

$$\tau = \tau_0 \cdot \exp\left(\frac{E_a}{k_B T}\right), \quad (3.5.2.2)$$

where $\tau_0 = 1/\nu_0$ is a characteristic switching time reciprocal to the attempt-to-flip frequency ν_0 , k_B is the Boltzmann constant and E_a is the depolarization activation energy. For BTAs E_a values range between 0.8–1.8 eV, depending on the tail substituent;^{47,58} the attempt frequency is typically found to be in the terahertz range. A strict stretched-exponential polarization decay and a clear Arrhenius-type depolarization activation in BTA devices allows to extrapolate the depolarization time constants to unmeasurable timescales and predict the behaviour at a wide temperature range, see Fig. 31 and Articles I, II, V for examples.

The polarization retention problem exacerbates in ultrathin ferroelectric films⁵¹, asymmetric devices and hybrid ferroelectric-semiconductor systems⁵⁹. In addition to these device design issues, nanoscopic morphological properties of the material influence the polarization stability. Kinetic Monte Carlo simulations of molecular ferroelectrics⁶⁰ revealed that spontaneous

polarization reversal (thermal depolarization) is initiated by defects in the bulk, in contrast to the field-driven polarization flipping which proceeds from the electrode interface. Therefore, polarization stability becomes critically sensitive to the structural (dis)order of the layer. We have recently shown with the example of BTAs that by reducing the number of structural defects in the material layers, which was a consequence of improved molecular packing properties (see section 5.1), polarization decay was (partly) suppressed. This way, polarization retention increased from minutes to more than ten years for the optimized structure materials^{47,57,58}. This vindicates soft organic and especially liquid-crystalline ferroelectrics that previously had notoriously poor polarization retention^{61,62}.

Figure 15. Effect of increasing supporting bias on depolarization kinetics attributed to compensation of the depolarization field (full polarization stabilization at around +6 V in this case). The experiment was performed on BTA-C12 at 60°C by applying a constant voltage during the waiting time between the poling (1) and probing (2) signals, as shown in the inset. Solid lines are guides to the eye. The bottom zero-bias (measured at short circuit conditions) datapoints obey the stretched exponential function with stretching exponent β of 0.5.

3.6 Switching time (field-assisted polarization reversal)

Another relevant kinetic parameter is the duration of a full polarization switching event when an electric field is applied, which determines the response speed of a ferroelectric device and is crucial for memory applications. Displacement-type ferroelectrics like PZT typically switch faster, in a sub-microsecond range, compared to the order-disorder ferroelectrics such as P(VDF:TrFE) or BTAs with sub-millisecond characteristic switching times. This is due to the more sophisticated microscopic switching mechanisms and higher energy barriers for dipole inversion in these systems. Naturally, the switching speed is strongly influenced by the morphology and domain structure of ferroelectric as well, and while polarization evolution in ideal ferroelectric single-crystals and epitaxial films can be described by simple generalized analytical models, the presence of grain boundaries, multidomain structures and other inhomogeneities in polycrystalline materials leads to dispersive and hampered switching. This aggravates the analysis and constrains our understanding of the polarization switching dynamics in disordered – real – ferroelectrics. Hereinafter, several classical and more recent theoretical approaches to comprehend and describe static and kinetic properties of ferroelectrics will be discussed.

Ferroelectric domain evolution during the field-induced polarization switching strongly resembles the nucleation-and-growth processes (Fig. 17b) of material crystallization that were studied and described by Kolmogorov and Avrami⁶³. This analogy was noticed by Ishibashi and Tagaki⁶⁴ which led to a unified Kolmogorov-Avrami-Ishibashi (KAI) theory for domain switching in ferroelectrics. However, while being able to successfully reproduce polarization switching kinetics in ideal ferroelectric crystals and epitaxial films, the model would overestimate the switching speed in higher-disorder polycrystalline ferroelectrics⁶⁵. See Fig. 16 for a (rather unextreme) example of BTA. The problem was especially evident at lower applied fields and larger timescales⁶⁶. Thus, an extension to the KAI theory was proposed by Tagantsev *et al.*, which includes a distribution in nucleation, or polarization initiation times due to structural defects and inhomogeneities causing variation in local fields⁶⁵. This approach considers the first – nucleation – step (Fig. 17b), rather than the last – domain coalescence, as assumed by the KAI theory – to be the rate-limiting one. Based on this, the model is named the nucleation-limited switching (NLS) model. As a consequence, much better fits of polarization switching kinetics are achieved for different types of ferroelectrics at all time scales^{31,44,66}. In most cases, a predetermined analytical (not experimental) switching time distribution is taken for fits, that varies from mesa-like or exponentially broad to more statistical log-Lorentzian⁶⁶ or

log-normal.^{44,67} For the case of BTA, the latter gives the best fitting results^{31,44}, see Fig. 16. Though different speculations for the origin of these distributions were given, their relation to the actual layer morphology and the characteristic domain structure of the system was essentially unknown.

One of the first attempts to relate the switching time distribution to specific features of the sample was reported by Zhukov *et al.*, who experimentally obtained a distribution of local fields that directly influences the switching time distribution. Based on these findings, the authors built a theoretical basis referred to as the inhomogeneous field mechanism (IFM)^{67,68}. We took one step further and acquired the whole experimental switching time distribution from the measured Preisach (local fields) distribution and the corresponding directly measured switching times at different local field (Preisach) coordinates.²⁶ This allowed for a full microscopic and macroscopic description of the ferroelectric switching without any initial theoretical presumptions, see section 3.7. In the following subsections the various models highlighted above will be presented in more detail.

Figure 16. Polarization switching kinetics of BTA after application of a constant electric field (grey line) fitted using the KAI model (blue dashed line), and the NLS model with a log-normal (blue solid line) and a log-Lorentzian (blue dotted line) switching time distribution.

3.6.1 Kolmogorov-Avrami-Ishibashi (KAI) model

The classical KAI model gives the temporal polarization evolution during switching from the opposite polarization state when a constant electric field E_{app} is applied (see Fig. 16, blue dashed line):

$$\Delta P(t) = 2P_r \left(1 - \exp \left(- \left(\frac{t}{t_{\text{sw}}} \right)^n \right) \right). \quad (3.6.1.1)$$

This polarization transient saturates at the double remnant polarization $2P_r$ and is cantered at the characteristic t_{sw} time. The steepness of the trend depends on the domain growth dimensionality, which influences the parameter n . Two cases of the model can be distinguished, based on the timing of the nucleation event. If nucleation is instantaneous and only takes place at $t = 0$, then n equals the geometrical dimensionality of the domain growth, where $n = 1, 2, 3$ indicates one-, two- and three-dimensional domain propagation, see Fig. 17a. Alternatively, if the nucleation proceeds continually at a constant rate, the dimensionality will equal $(n - 1)$. There is however no straightforward, non-arbitrary way to choose between the discussed cases. 1D or 2D domains are typically found. This also holds for BTAs with (quasi) one-dimensional domains which agrees with its self-assembled columnar structure. The KAI model assumes a gradual and unrestricted domain growth via four principal steps (Fig. 17b) in an infinite single-crystal, which limits its applicability to real ferroelectrics of higher disorder.

Figure 17. (a) One-, two- and three-dimensional domain growth indicated by arrows. (b) Presumptive sequence of polarization switching including (1) formation of nuclei, (2) forward and (3) sideways growth of domains finalized by (4) coalescence of adjacent domains. Blue and grey shaded areas represent opposite polarization directions.

3.6.2 Merz law

The KAI model only describes polarization switching kinetics as a response to a constant (usually a step signal) applied electric field. All other dependencies (field, temperature, etc.) hide in the fitting parameter t_{sw} , which is often taken as the switching time of the system, and which shortens with increasing field and temperature, as seen in Fig. 18 a, b. During the 1950s, Walter J. Merz proposed an empirical law for the relation between the switching time and the applied field which considers an activation field E_0 for nucleation of domains with opposite polarization, which was a new way of seeing the switching process, and includes a characteristic minimum response time t_0 at this field:

$$t_{sw} = t_0 \cdot \exp\left(\frac{E_0}{E}\right). \quad (3.6.2.1)$$

This nucleation activation field is unequal to and typically much higher than the experimental coercive field. The temperature and frequency dependences are not covered by this equation. Despite being able to describe the switching time versus applied field dependence in the high-field regime even in disordered ferroelectrics, the law was noticed to deviate from the experimental data at lower fields and in more complex systems. Thus, an upgraded hybrid version of the model was proposed.

3.6.3 Hybrid Merz model

Fatuzzo proposed an extended version⁶⁹ of the classical Merz law

$$t_{sw} = A \cdot E^{-n} \cdot \exp\left(\frac{E_0}{E}\right) \quad (3.6.3.1)$$

which included an additional field-dependent factor to correctly describe the rate of reversal of the ferroelectric polarization. Here $n = 2$ and A is typically used as a fitting parameter.⁷⁰ This hybrid model successfully describes t_{sw} vs. E dependence in many nucleation-limited systems including BTAs,⁴⁴ see Fig. 18b (solid lines).

3.6.4 Nucleation-limited switching (NLS) model

With growing interest in thin-film ferroelectrics for use in integrated electronics, easier-producible polycrystalline technology flourished. Theoretical models had to be adapted to these higher disorder systems, as the simple KAI and Merz laws failed to predict the polarization switching behaviour. Tagantsev *et al.*⁶⁵ suggested a solution to this problem by adding a

distribution in the local switching times $F(t_{\text{sw}})$, instead of the constant value used in KAI theory Eq. 3.6.1.1, and integrating the switching kinetics over these times:

$$\Delta P(t) = 2P_r \int_{-\infty}^{+\infty} \left[1 - \exp\left(-\left(\frac{t}{t_{\text{sw}}}\right)^d\right) \right] F(t_{\text{sw}}) dt_{\text{sw}}. \quad (3.6.4.1)$$

The authors attributed these local switching times to independent switching sites, or nuclei, with different switching dynamics. A broad mesa-like statistical distribution of the t_{sw} was used to reproduce the experimental data. However, further literature considers, likely more physical, Lorentzian^{66,67} and Gaussian distributions of the time logarithms^{31,44}

$$F(t_{\text{sw}}) = \frac{1}{w\sqrt{2\pi}} \exp\left(-\frac{(\log(t_{\text{sw}}) - \log(\tau))^2}{2w^2}\right). \quad (3.6.4.2)$$

Here w is the width and τ is the central value of the distribution. It gives nearly perfect fits to the experimental switching data of polycrystalline disordered ferroelectrics, as shown with an example of BTA in Fig. 16. In fact, using the well-defined nanostructure and a transparent polarization switching mechanism of BTAs, we showed (in Article III) that this log-normal switching time distribution originates from a Gaussian distribution of local internal fields (=Preisach distribution) and a quasi-exponential dependence of the local switching times on these fields that were all measured experimentally.³¹ This elucidates the previously debated relation between local field variations in the material and the dispersive polarization switching⁶⁶.

Figure 18. (a) Polarization switching kinetics for increasing applied field (solid lines) and a corresponding transient polarization switching current (dashed line). (b) Polarization switching time versus the reciprocal applied field at different temperatures. Theoretical models used for fitting are indicated in the legend.

3.6.5 TA-NLS model

The KAI and the NLS models reproduce polarization reversal kinetics for ideal and real ferroelectrics, while the Merz law and its extended version define the switching time relation with the applied field. A temperature dependence of all the parameters was left undiscussed and required an additional, Arrhenius-like model. When considering imperfect polycrystalline ferroelectric thin-films, it is now becoming generally accepted that the ferroelectric switching is nucleation-limited with a wide distribution of switching times^{65,66,71,72}.

Stemming from the description discussed in section 3.4.4, the polarization reversal time t_{sw} can be approximated using equations constructed by Vopsaroiu *et al.*^{28,45} for high applied fields E_{app}

$$t_{sw} \cong \frac{1}{\nu_0} \cdot \exp\left(\frac{(w_b - P_r E_{app})V^*}{k_B T}\right). \quad (3.6.5.1)$$

For the zero-field case when only thermal impact is expected, a prefactor of $\frac{1}{2}$ must be added to correctly reflect the probabilistic nature of the polarization switching:

$$t_{sw} \cong \frac{1}{2\nu_0} \cdot \exp\left(\frac{w_b V^*}{k_B T}\right). \quad (3.6.5.2)$$

Here P_r is the remnant polarization, E_{app} is the applied field, k_B is the Boltzmann constant, T is the temperature and ν_0 is an attempt frequency (*e.g.* a typical frequency of optical phonons or a molecular vibration in BTAs).

This thermally activated nucleation-limited switching (TA-NLS) theory has been successfully applied to analyse the switching processes in inorganic as well as organic ferroelectrics^{55,58,73,74}. Importantly, it is compatible with the idea of energetic disorder and can be modified by introducing a distribution in energies and random local fields.

3.7 Disorder

The aspiration to create ideal structures and devices in any field of materials science unavoidably collides with the materials' tendency towards disorder. The field of ferroelectrics is no exception. Despite intensive experimental work on epitaxially deposited layers and carefully grown single crystals, ideal – immediate and fully defined – ferroelectric switching is hardly attainable^{75,76}. Any deviation from the idealized case of non-dispersive polarization switching and determinate coercive fields can be blamed on the effect of various crystal defects, vacancies, ionic impurities, external and internal contaminations, morphology issues (grain size, porosity, etc.) and other inhomogeneities. The named factors (typically negatively) influence the main characteristics of the ferroelectrics, including switching speed, coercive field, remnant polarization and its stability. To find ways to control the role of disorder, it must be comprehended. The work of Franz Preisach⁷⁷ around 1935 suggested a simple theoretical model describing disorder in magnetism, which created a ripple effect so profound that now the model has been shown to apply to almost any hysteretic system, including ferroelectrics^{31,78,79}. Though being largely mathematical, when merged with more physical formalisms, the Preisach model can be used to fully define the static and dynamic characteristics of disordered ferroelectrics and relate these to specific material morphologies. We recently demonstrated this mutuality investigating two ferroelectric materials of entirely different structure.³¹

Despite its typically ill-controlled nature, disorder can be harnessed to introduce new functionality in ferroelectric materials. The secret lies in a possibility to electrically address different parts of ferroelectrics by partial poling – the intermediate polarization states. While for some systems the stability of these intermediate states is questionable, based on the thermodynamic description of ferroelectrics, others, like P(VDF:TrFE), allow lasting partial poling with sufficient retention.²⁵ Thus, multi-bit ferroelectric memory devices^{31,80} can be created in this way that could potentially revolutionize memory technology. Quite ironically, the higher the disorder in the layer (*i.e.* the broader the distribution of characteristics), the more intermediate states are available for a multibit memory. Extensive discussion on that can be found in Article III.

3.7.1 Preisach theory

The essence of the Preisach theory lies in the concept of hysterons. A hysteron is a conceptual entity describing an independent microscopic polarization (initially, magnetization) unit, the sum of which over the whole ferroelectric equals the macroscopic polarization. To describe the electrostatic environment of these hysterons, each is characterized by a discrete up-switching and down-switching field (here, $E_{c\uparrow} = U$, $E_{c\downarrow} = V$), which results in a microscopic, hysteron-specific rectangular hysteresis loop with a polarization of unity, see Fig. 19 grey boxes on the left. Due to varying electrostatic environments in a real ferroelectric material, there is a whole spectrum of these hysterons, to which particular $(U;V)$ coordinates can be assigned. The number of hysterons with these exact coordinates depends on the material, as does the range of the coordinates. Typically, the hysteron (or Preisach) distribution $N(U;V)$ has a statistical double-Gaussian form and, as discussed further in the text, is well-centred with respect to the diagonal E_c axis, see the middle panel of Fig. 19. However, in reality due to various artefacts like imprint and other internal biases this does not always hold⁸¹. Despite that, the peak of the distribution will in most cases sit at the macroscopic coercive field value. The polarization switching current response measured upon field sweeping is in fact an experimental measurement of a $(U;V)$ projection (yellow bell curves of the middle panel in Fig. 19) of the Preisach distribution (PD). Although this can give a sense of the broadness of the PD, it will conceal its possible asymmetry.

Figure 19. Emergence of the Preisach distribution (PD) from structural and energetic disorder in ferroelectric layers (left). Critical domain size (=hysteron) distribution and differences in interaction between these domains influence the form of the PD (middle). The sum of all ideal square-looped hysterons leads to the final macroscopic polarization hysteresis curve (right).

A more physical picture of the Preisach distribution can be obtained when instead of the actual up- and down-switching coercive fields ($U;V$), the average value $E_c = \frac{U+V}{\sqrt{2}}$ and the ‘asymmetrisation’ (off-centre) field $E_i = \frac{U-V}{\sqrt{2}}$ are considered. Mind that typically $U > 0$, $V < 0$, yet the distribution spreading over other quadrants is theoretically possible and is often observed in magnetics⁸². The resultant 3D Gaussian distribution

$$N(E_i, E_c) = \frac{1}{4\pi\sigma_i\sigma_c} \exp\left(-\frac{(E_i-m_i)^2}{4\sigma_i^2}\right) \exp\left(-\frac{(E_c-m_c)^2}{4\sigma_c^2}\right) \quad (3.7.1.1)$$

is a powerful tool to quantify the energetic disorder in ferroelectrics. The change of ($U;V$) variables to ($E_c;E_i$) leads to an apparent 45° rotation of the PD axis, as depicted in Fig. 19 middle panel. The (m_i, m_c) consequently become the central coordinates of the distribution while $\sigma_{i/c}$ define its width. It is worth noting that the commonly used coercive field value which is displayed in regular P - E hysteresis curves is the coercivity U or V of the measured PD projection which is not necessarily equal to the global E_c from Eq. 3.7.1.1. The whole PD distribution can be measured directly using an adapted electric signal sequence, as we have shown in our recent publication, Ref. 31 that is Article III. We also explain how these experimentally obtained parameters, using the TA-NLS theory (sections 3.4.4 and 3.6.5) as a basis, can be interpreted for any ferroelectric domain morphology. In particular, variation in the critical field E_c originates from a distribution in the critical domain volume, while the width of the intrinsic interaction field E_i distribution is determined by the strength of inter-domain coupling. Due to a strong distance dependence of the electrostatic interactions, the more closely packed the adjacent domains (or hysterons) are, the wider the distribution in the E_i -direction of the system. These roundish PDs (Fig. 20 left) are typical for polycrystalline ferroelectrics with little structural inhomogeneities. Conversely, if domains are rather independent (*e.g.* spatially separated or otherwise electrostatically isolated), the Preisach distribution will become cigar shaped (Fig. 20 middle). Until now, the only experimentally confirmed example of an elongated PD is P(VDF:TrFE) due to its semi-crystalline morphology with crystalline lamellae surrounded by amorphous matter. Based on these guidelines, the Preisach distribution can in principle be engineered according to the needs. For most ferroelectric applications, a delta-like PD would be sought after, as having a clearly defined coercive field value would solve many practical device operation problems. For this, highly monodisperse weakly interacting structural units would be required, as sketched in Fig. 20 right.

Figure 20. The form of the Preisach distribution for different cases of domain size distributions and strength of inter-domain interactions. While conventional ferroelectric devices would profit from morphologies depicted in the right-most example, the wide hysteron distributions of left and middle cases would satisfy the requirements for multibit memory devices.

Independent of the form of the PD, the existence of a distribution in local coercive fields leads to dispersive polarization switching. Many authors have speculated that the distribution of characteristic switching times, which must be incorporated in the classical switching dynamics models to correctly describe the polarization reversal in most polycrystalline materials, may originate from a distribution in local fields. However, this was never pursued experimentally. Having measured the experimental Preisach (=local coercive fields) distribution, we attempted to obtain a characteristic polarization switching time for certain Preisach coordinates using a specially adapted measurement technique. Due to the strong nucleation limitation the measurement was successful and a 3D map of switching times on a 2D Preisach plane was assembled (Fig. 21 middle). This information was sufficient for the final macroscopic switching time distribution (Fig. 21 right) to be derived by convolution of both the graphs on the left. Though demonstrated on BTA and P(VDF:TrFE), the method is applicable to any kind of ferroelectric. More details on the method can be found in Article III.

Figure 21. Experimental pathway to obtain the global switching time distribution (right) by convolution of the directly measured dynamic Preisach distribution (left) and the experimentally obtained characteristic switching time at certain Preisach coordinates (middle).

3.8 Ferroelectric devices

Ferroelectric materials are known and valued for their multifunctionality, as it was discussed in previous sections. Yet, even without the concomitant phenomena – the pyro-, piezo- and dielectricity, ferroelectric materials can provide important new functionalities to electronics. One of the key applications, enabled by the bistable nature of ferroelectrics, remains the non-volatile memory devices. While inorganic FeRAM, though remaining a niche technology, slowly strengthens its position in the memory device market, easy-processable, conveniently scalable and flexible non-volatile data-storage solutions appear to be falling behind⁸³. Being an essential element of all but the simplest electronic devices, cheap, efficient and mechanically robust bendable non-volatile memories would give a boost to the plastic electronics field. One of the best candidates for such devices are organic ferroelectricity-based memories. Being non-volatile by nature, this technology is desired due to its fast response, great endurance and low energy consumption. Destructive data readout, necessitating extra post-read steps for data restoring, is the main drawback of conventional ferroelectric memories.

The solution to this limitation is separation of writing and reading functionalities in the device. This has been successfully implemented in binary ferroelectric and semiconducting materials systems, both in ferroelectric-semiconductor polymer blends⁸⁴ and in single core-shell structure molecules^{85,86}. Here, the bistable ferroelectric polarization serves as an on-off switch, while the semiconducting functionality allows for the given logical state to be probed as a high or low conductivity. Since this type of resistive switches is also rectifying, it satisfies fundamental requirements for data storage in high-density low-cost crossbar arrays⁸⁷. As compared to conventional ferroelectric memory technology, much lower ferroelectric polarization levels are sufficient, which facilitates the use of alternative ferroelectrics like flexible organics.

Figure 22. A prospective ultrahigh density single-bit memory device enabled by organic supramolecular discotics that form ferroelectrically switchable self-assembled stacks.

Due to technological difficulties and geometrical limitations of memory devices based on phase-segregated ferroelectric-semiconductor blends, combining both functionalities in a single material is highly desired. Amide-based supramolecular ferroelectrics are a relatively new and rapidly growing class of ferroelectric materials, see section 5. The symmetry-breaking in amide-based ferroelectrics (including polymers, such as nylons) is realized through introduction of rotatable dipolar moieties – amides (carrying a dipole moment of ~ 4 D each), and high-order molecular self-assembly due to non-covalent bonds, *viz.* $\text{C}=\text{O}\cdots\text{H}-\text{N}$ hydrogen bonding between these amides and π - π stacking of the conjugated cores. It is the combination of these two factors that leads to switchable remnant polarization and true ferroelectricity^{88,89}. These molecules tend to self-assemble in an orderly fashion, *e.g.* in hexagonally packed columns, which has led to speculations about an ultrahigh-density memory device (Fig. 22), if each column could be addressed individually and sufficient stability of the ferroelectric phase could be achieved³⁴.

A good example of such a material is the trialkylbenzene-1,3,5-tricarboxamide, or BTA. BTA has a small (insulating) benzene core and demonstrates textbook-like ferroelectric properties with clear Curie-Weiss behavior⁴⁴, saturating polarization with excellent retention exceeding the 10-year requirement for memory devices³⁰, low electrical fatigue, and a broad operational temperature range from above 140°C to room temperature^{30,90} – all that is needed for a good memory device. One of the main advantages of this type of materials is their excellent tunability via molecular structure modification, see section 5 for details. While mesogenic tail engineering allowed to achieve ferroelectric parameters approaching and even exceeding those of the popular organic polymer ferroelectric P(VDF:TrFE), variation of the conjugated core opened a new field of organic electronics – organic semiconducting-ferroelectrics^{86,91}. Over the last few years such amide-based ferroelectrics with a semiconducting conjugated core have demonstrated unprecedented hybrid functionality due to coexisting and interacting ferroelectricity and semiconductivity. Molecules synthesized following this template showed resistive switching based on different mechanisms, including a previously unobserved modulation of the bulk conductivity.

Figure 23. Schematics of j - E characteristics typical for different resistive switching mechanisms. (a) Bulk conductivity switching (BCS) with space-charge limited current (SCLC) both at the ‘on’ and ‘off’ states. (b) Injection barrier modulation (IBM) with SCLC at the ‘on’ state and injection-limited current at the ‘off’ state. In both cases, the on/off switching event occurs at the coercive field E_c of the ferroelectric, which increases with the applied field frequency, as indicated by grey arrows.

Gorbunov *et al.* demonstrated resistive switching due to charge injection barrier modulation (IBM) in a self-assembling discotic material with a carbonyl-bridged triarylamine core⁸⁵. The effect is largely interfacial and can be explained by hindered/facilitated charge injection in the semiconductor due to band-bending depending on the polarization direction near the electrode, which guarantees excellent current rectification. On/off ratios in this case strongly depend on the optimization of the band diagram of the device and values higher than 10^5 can be achieved in energetically optimized devices⁹². In the ‘on’ state, the current is limited by the bulk conductivity and the device typically operates in the space-charge-limited current (SCLC) regime:

$$j(V) = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{V^2}{d^3} \exp\left(0.891 \gamma \sqrt{V/d}\right). \quad (3.8.1)$$

Here V is the applied voltage, d is the layer thickness, μ_0 is the zero-field mobility, γ is a phenomenological parameter quantifying the mobility enhancement by the applied electric field and $\epsilon_0 \epsilon_r$ is the dielectric permittivity of the material. The ‘off’ state current is determined by the

height of the injection barrier, resulting in injection-limited conductivity, which typically grows exponentially with voltage, see Fig. 23b. The transition between the ‘off’ and ‘on’ states occurs at the coercive voltage of the ferroelectric. The device is in its low-conductivity ‘off’ state when the directions of the polarization and field oppose and turns to the high-current ‘on’ state when the polarization flips to align along the field. This type of resistive switching was previously observed in organic phase-separated ferroelectric-semiconductor polymer blends^{92,93}.

Another, fundamentally different switching mechanism, resulting in *J-V* loops with opposite sense as those discussed above, was found in different molecules of a similar core-shell ‘semiconductor-ferroelectric-tail’ structure and was referred to as the bulk conductivity switching (BCS)⁸⁶. As discussed, molecular dipoles (=amides) self-assemble in a head-to-tail manner, which creates an asymmetric, ratchet-like potential for charges transported in the core. Depending on the relative directions of the applied field and polarization, *i.e.* the orientation of the ratchet-shaped potential landscape with respect to the field, the charge mobility at finite field is enhanced or reduced. Oppositely to the case of injection barrier modulation, the high-conductivity ‘on’ state occurs when the field and the polarization directions are antiparallel, while the low-conductivity ‘off’ state occurs when the directions match. In this case, as no injection barrier related effects are at play, conduction in both the ‘on’ and ‘off’ states is expected to be bulk-limited, typically SCLC or Ohmic, see Fig. 23a. Again, in *J-V* curves the turning point sits at the coercive field of the ferroelectric.

Both discussed mechanisms are directly related to the ferroelectricity-semiconductivity interaction and are fundamentally different from other kinds of resistive switching like filament formation, transient doping and other conventional resistive switches^{83,94}. There is no fundamental restriction for these two resistive switching mechanisms to appear in the same material. Yet, despite having been found in similar material systems, they were never observed in the same material. Moreover, devices based on these compounds typically required elevated operation temperatures, leading to short polarization retention times of the order of minutes, precluding actual application^{85,86}. Recently, we have demonstrated how resistive switching behaviour can be influenced by band-diagram engineering in devices based on a new supramolecular semiconducting ferroelectric, see Article V. For that, our colleagues synthesized a dipolar benzotrithiophene-cored discotic molecule. Columnar discotic liquid-crystals with a conjugated benzotrithiophene (BTT) core are known to have very high ($\sim 10^{-3}$ cm²/V/s) mobilities of photogenerated charge carriers⁹⁵. Due to the combination with the excellent ferroelectric functionality of the supramolecular materials with amide moieties,

including ‘infinite’ retention at room temperature, our BTT-cored trisamide proved to be the first material to show continuous tunability from injection- to bulk-limited conductivity modulation, driven by the unique coupling between the ferroic and semiconducting properties of the molecule.

4 Materials

Collective dipolar switching leading to spontaneous and robust ferroelectric polarization requires certain conditions related to the material structure. Namely, the system must possess two stable opposing, ideally equipotent states with a defined energy barrier between them which can be overcome by an applied electric field. Here the beauty of the materials science reveals itself by providing a multitude of methodologies and techniques to achieve this bistability in diverse classes and structures of (synthetic) inorganic⁹⁶, organic^{97–99} and hybrid^{100,101} materials.

The first recognized ferroelectric was the hydrogen-bonded Rochelle salt containing organic tartrate ions (1921, Valasek³). Purely inorganic synthetic perovskite structure ceramics were only discovered several decades later^{102,103}, yet this did not hinder them to secure a strong position in the ferroelectric market, which was assured by their exceptionally high performance. Despite the rapid development of both lead-based and lead-free inorganics, the progress of the field tends to saturate²³. Organics, contrarily, are currently emerging, with new materials of different structure being constantly added to the list alongside the first fully organic ferroelectric, thiourea¹⁰⁴. The versatility of organic synthesis offers a broad spectrum of designs for polarization generation as compared to the conventional ion displacement in inorganics. Specifically, the necessary symmetry breaking can be established using different approaches^{98,99}: flipping/rotation of permanent molecular dipoles in single-^{104,105} and multi-component¹⁰⁶ (supra)molecular structures as well as porous frameworks¹⁰⁷, proton transfer in hydrogen-bonded systems¹⁰⁸ and dimer formation in charge-transfer complexes¹⁰⁹ in addition to the separation/movement of (lattice) ions^{3,101}. A large fraction of organic ferroelectrics are crystalline molecular materials. These, while demonstrating record-breaking piezo- and ferroelectric parameters in the bulk^{22,110}, face difficulties when brought into thin-film shape. Alternative to these are polymer¹¹¹, liquid-crystalline¹¹² and other soft organics⁹⁹ that are not only easily-processable, cost-efficient and typically eco-friendly, but also lightweight, flexible and even self-healing, which opens prospects to transparent, conformable (bendable, foldable) or even disposable electronics.

4.1 Inorganic ferroelectric materials

The dominating materials in the field of piezo/ferroelectrics remain the inorganic perovskite structure ceramics and their thin films. These ABX_3 composition materials with differently sized A and B cations and an anion (in most cases oxygen) X demonstrate excellent ferroelectric switching in the non-centrosymmetric tetragonal phase (see Figure 24). Prototypic ferroelectric perovskites often come as solid solutions, for example, lead zirconite-titanite $Pb(Zr,Ti)O_3$ (PZT), strontium bismuth tantalate $SrBi_2Ta_2O_9$ (SBT) or variations of barium titanite $BaTiO_3$ (BTO)¹¹³. The piezo- and ferroelectric properties of these materials depend strongly on their elemental composition and mostly on the ratio of the cations. The composition that is close to the morphotropic phase boundary (MPB) with coexisting tetragonal and rhombohedral ferroelectric phases leads to an unprecedented boost of ferroelectric and especially piezoelectric performance in ferroelectric perovskites like PZT.¹¹⁴ As a result, the remnant polarization can reach $>1000 \text{ mC/m}^2$, the dielectric constant >10000 , and the piezoelectric constant $>1000 \text{ pm/V}$. The coercive fields are comparatively low and range between $0.1\text{--}10 \text{ V}/\mu\text{m}$ due to the underlying ion displacement mechanism with relatively low energy barriers for polarization switching. These materials can be easily doped, which allows for additional tuning of their mechanical, dielectric, thermal or fabrication properties¹¹⁵. However, this does not solve the problem of high density, mechanical rigidity and brittleness of both bulk ceramics and epitaxial layers.

Toxicity (*e.g.* lead-poisoning) and the usage of rare elements has raised environmental concerns that have been attempted to address by synthesizing lead-free materials. Yet, the current lead-free piezo/ferroelectric technology with remnant polarizations $\sim 500 \text{ mC/m}^2$, piezo-coefficients $<1000 \text{ pm/V}$ and reduced Curie temperatures has not yet reached the high performance level set by the PZT²³. In addition, perovskite ferroelectrics are notoriously sensitive when it comes to fatigue and especially imprint problems or the performance-limiting substrate/electrode influence (clamping, etc.)²⁴. This, together with the high characteristic processing temperatures ($>1000^\circ\text{C}$) that create integration issues with the silicon technology, limits the possibilities of inorganic perovskites to be integrated in our everyday electronics and brightens the future of easy-processable organic materials.

Figure 24. General structure of perovskite crystal lattices with the BX_6 octahedron framed by A cations.

4.2 Symmetry breaking in organics

Ferroelectricity in organic materials can be established through a plethora of molecular designs (Fig. 25). The most intuitive design principle utilizes polar molecules or their segments (including proton transfer), yet recent research has demonstrated switchable remnant polarization also in systems of nonpolar materials via cation-anion displacement and charge-transfer induced dimerization. Non-covalent interactions, which organics are famous for, provide a new degree of freedom for engineering ferroelectrics. Thus, material designs at both the molecular as well as the supramolecular level are possible, which suggests a near-infinite number of conceivable organic ferroelectrics, most of which are undisclosed at present.

Figure 25. Three main approaches leading to ferroelectric ordering in organics: proton transfer in hydrogen-bonded systems (*e.g.* croconic, squaric acid), relative displacement of charged entities (*e.g.* dimerized nonpolar charge-transfer complexes) and dipole reorientation by flipping/rotation/bending (*e.g.* PVDF, odd-numbered nylons, BTAs, fluorinated PPE¹¹⁶).

4.2.1 Ferroelectric proton tautomerism

In order to achieve remnant polarization, effective relative charge separation must be induced in materials. One way to do so is by using the proton transfer ability of hydrogen-bonded materials due to cooperative proton tautomerism (interconversion of the single and double bonds)¹¹⁰. Certain organic moieties like O=C-OH, O=C-NH or N=C-NH can form intermolecular hydrogen bonds that are further strengthened by conjugation. In high-quality (co)crystals this creates a channel for cooperative directional transfer of protons, leading to ferroelectric polarization. This approach gives ferroelectric materials with the highest recorded polarization in organics so far and relatively low coercive fields due to the moderate energy barrier for proton transfer, compared to, for example, macrodipole rotation that includes steric effects. The leading proton-transfer type compound is croconic acid^{110,117} with a remnant polarization of ~200–300 mC/m² and a coercive field of ~2 V/μm. Yet, with some exceptions, these materials function away from room temperature¹¹⁸. In addition, their best performance is achieved in rigid single crystals that require careful preparation with repeated purification. This not only increases technological costs but also limits their applicability in thin-film devices.

4.2.2 Molecule-displacive ferroelectricity

The most prevalent type of ferroelectricity in inorganics is the displacive-type, caused by the relative movement of ions in the unit cell of inorganic perovskites that was introduced previously in the text (see section 4.1). A conceptually similar effect has been shown in organics using dimerized charge-transfer complexes formed by small (typically) planar nonpolar conjugated molecules^{109,119}. The effect is enabled by the molecular charge redistribution between paired donor and acceptor molecules. Though resulting in very high ~550 mC/m² remnant polarization at liquid helium temperatures (~7 K)¹⁰⁹, significantly lower polarization values are observed at room temperature^{109,119}, ranging 10⁻³–20 mC/m². As these conjugated compounds are typically semiconducting, this type of ferroelectrics suffer from high dielectric losses⁹⁸. The problem is especially evident at higher (room) temperature, which hampers most ferroelectric applications.

4.2.3 Permanent dipole reorientation

Seemingly one of the most robust polarization generation methodologies, which in most cases guarantees proper room-temperature ferroelectricity and advantageous physical properties, is the introduction of field-switchable permanent dipoles in the materials structure. In this way

ferroelectricity has been established in the first small-molecular organic ferroelectric thiourea¹⁰⁴ as well as in the first polymer ferroelectric polyvinylidene fluoride (PVDF)¹²⁰. The necessary molecular mobility for the dipole flipping can be provided using free-to-rotate single covalent bonds or weak van der Waals interactions, while the collective dipole reorganization (effective charge separation) is assured by dipole-dipole coupling (sometimes also hydrogen-bonding) throughout the supramolecular network. Though such systems are characterized by a lower remnant polarization that is limited by their permanent dipole density ($\sim 120 \text{ mC/m}^2$ for strongly poled P(VDF:TrFE)) and the highest coercive fields ($\sim 10\text{--}100 \text{ V}/\mu\text{m}$) from all materials discussed herein, they provide easy-processability, cost-efficiency, lightness and flexibility. These properties are strongly desired for cheap and flexible memory devices that are the missing element on the way towards a break-through in bendable/conformable or disposable electronics.

4.2.3.1 *Ferroelectric polymers*

Polymer science has emerged as a tool to solve practical problems like making rubber less sticky or creating waterproof plastics, all at low cost and in industrial amounts. Driven by similar principles, polymers with electronic functionality come with a strong claim to revolutionize solar energetics¹²¹ and other spheres of plastic electronics based on organic (semi)conductors¹²². It is thus not surprising that the only commercially available organic ferroelectrics that have led to actual working devices are polymeric, with the famous example of the P(VDF:TrFE) copolymer. Other similar structure macromolecules comprising switchable dipolar moieties have been investigated^{116,123}: poly(thio)ureas, polyimides, nylons, etc. However, they did not provide the required polarization/piezoresponse and stability levels as did the fluorinated polymers.

To become ferroelectrically switchable, the prototypic fluorinated polymer polyvinylidene fluoride (PVDF) must be brought to the ferroelectric phase, where all its difluoro-ethylene ($-\text{CH}_2\text{-CF}_2-$) dipoles face the same direction (*i.e.* full trans configuration or β -phase[§]). For the PVDF homopolymer this procedure is rather cumbersome and requires application of a mechanical stretching force, an elevated temperature, a high electric field or all three combined. Yet, if a certain amount of trifluoroethylene ($-\text{CHF-CF}_2-$) is introduced, the resulting P(VDF:TrFE) copolymer enters the ferroelectric β -phase with ease due to induced steric hindrance between the fluorene atoms. Naturally, this slightly reduces the theoretical saturated polarization as the net molecular dipole density decreases, yet the produced films become easily

[§] A more exotic ferroelectric δ -phase has also been found, see Ref. 148.

conditioned for the final application. The intensity of the ferro/pyro/piezoelectric response relies on a high level of crystallinity ($\gg 50\%$) of the polymer film¹². P(VDF:TrFE) is semi-crystalline in nature which means that segments with orderly packed polymer chains (*i.e.* crystallites) are surrounded by amorphous, chaotically arranged material, see Figure 6. Crystallinity is typically enhanced by annealing the prepared films above the Curie temperature $\sim 130\text{--}140^\circ\text{C}$ for a couple of hours at ambient atmosphere. Properly conditioned and electrically poled, P(VDF:TrFE) will demonstrate exemplary room-temperature ferroelectric operation ($P_r \approx 60\text{--}120 \text{ mC/m}^2$, $E_c \approx 50 \text{ V}/\mu\text{m}$) in capacitor⁸⁰ as well as hybrid ferroelectric-semiconductor memory^{87,124} devices. For piezoelectric applications P(VDF:TrFE) can offer relatively high $|d_{33}| \approx 30\text{--}60 \text{ pm/V}$ owing to the possibility to tune its performance by composition.¹²⁵

Figure 26. Possible polarization switching progression in a single ferroelectric polymer chain (an example of PVDF)⁸⁷.

4.2.3.2 *Ferroelectric liquid crystals*

The success of polymer ferroelectrics has proven that, due to their great film-forming and other advantageous physical properties, macromolecular organics can compete with inorganics, depending on the application. However, a lesser control of molecular synthesis, an often limited tunability of the molecular structure, and a difficulty to achieve high crystallinity levels remain unsolved problems of polymeric materials. An alternative to polymers are small-molecular-mass compounds. So far, small-molecules with ferroelectric functionality are usually characterized in large, carefully grown single-crystals or (epitaxial) thin-films using highly controlled deposition processes. Solution-processability would therefore bring a great advantage, but this might well compromise high-quality molecular ordering. Small-molecular liquid-crystalline materials therefore come to the fore as a highly viable alternative to polymer ferroelectrics. Liquid-crystalline molecules are soluble, and their structure can be easily controlled and manipulated by synthetic methods. Furthermore, their liquid-like properties assure sufficient molecular mobility for molecular dipole rotation, while their spontaneous self-ordering solves the poor crystallinity issue and even makes the materials self-healing.

The liquid-crystalline properties arise from the core-shell architecture of the molecules, see Figure 27. The aromatic, frequently conjugated core determines the shape of the molecule: rod-, banana-, bowl-, umbrella-, disk-like, etc. The molecular dipole can be created using two main methodologies: (1) due to the asymmetric shape of the core, as in bent-core or bowl-shaped mesogens, and (2) by introduction of a dipolar molecular switch/rotor, that is a free-to-rotate/bendable moiety with a permanent dipole, like in BTAs. This dipolar moiety can be placed at practically any part of the molecule – between the core and the tail⁵⁸ or in the tail¹²⁶, as well as in the core itself^{127,128}. And, while in case (1) the whole molecule must change its direction to switch polarization (see Figure 27, right)^{129,130}, case (2) leads to typically more stable ferroelectric phases as only segments of the molecule are responsible for the ferroelectric switching. The core in turn takes a role in stabilizing the self-assembled supramolecular structure with the help of non-covalent interactions like hydrogen-bonding or π - π stacking that is characteristic to aromatic/conjugated systems. In fact, these interactions would be strong enough to result in a high-rigidity crystalline ordering, and it is the task of the flexible peripheral sidechains to introduce extra kinetics in the system, leading to the liquid-crystallinity. These, *e.g.*, paraffinic alkyl tails or their variations, act like spacers and influence the packing peculiarities of the molecules and largely determine the phase transition temperatures, including the ferroelectric-to-paraelectric critical point³⁰, see section 5.1 for details. This way, these tails

can control the geometrical dipole density^{58,128} (*i.e.* the polarization) and the operational temperature range of the ferroelectric, despite the fact that they do not (with rare exceptions¹²⁶) contain any active groups. Planar-cored liquid-crystals are typically found in columnar phases^{131,132} where molecules self-organize in a head-to-tail manner – *i.e.* they stack axially like magnets, as compared to, for example, bent-core or rod-like mesogens that tend to form smectic, nematic or cholesteric structures. Such columnar discotic liquid-crystals demonstrate significantly improved – in fact record – polarization stability among the ferroelectric liquid-crystals.^{30,57}

Figure 27. Typical structure of ferroelectric liquid-crystalline mesogens with examples: aromatic (conjugated) core (rod-, bowl-, disc-, banana-shaped, etc.), hydrogen-bonding/dipolar moieties, flexible solubilizing tails. A C3 symmetry case is depicted on the left, yet any symmetry C1, C2, C3, C4, C5, C6, etc., is possible, as shown by the core examples. Schematic polarization switching mechanisms for bowl-, rod- and banana-shaped mesogens are shown on the right.

5 Rational design of organic ferroelectric discotics

Small-molecular liquid-crystals (LCs) are dynamic molecular systems with various degrees of molecular mobility that depend on temperature (thermotropic LCs) or LC concentration in presence of solvent (lyotropic LCs). To be operational, most conventional LCs require omnidirectional spatial constraints due to their fluidity, therefore closed (for optical applications transparent) liquid-crystal cells are used – LCD technology is based on this kind of LC behaviour. When it comes to solid-state applications, some LCs are better than others. There is an emerging class of thermotropic LCs – the ferroelectric columnar discotic mesogens – that sustain themselves even at high temperatures and no substrate stabilization is needed, owing to several self-organization and self-stabilization mechanisms.

There are four main factors inducing self-assembly and keeping the molecules together in columnar discotic mesophases: electrostatic dipole-dipole interactions, hydrogen-bonding, π - π stacking of conjugated cores and intercalation of sidechains. Depending on the exact molecular structure, the balance between these effects may vary. Thus, to avoid overgeneralization we will analyse the specific example of the archetypal self-assembling discotic ferroelectric trialkylbenzene-1,3,5-tricarboxamide or BTA (see Figure 28). As shown in the molecular structure template given on the left of Figure 27, it has a planar conjugated benzene core to which three freely rotatable amide groups, followed by flexible alkyl chains are attached. The aggregation of BTAs (similarly to any columnar discotic) proceeds via several steps. First, molecules stack into one-dimensional columns that grow in a highly cooperative fashion^{48,133}, forming a hydrogen-bonded triple-helical network of microdipoles. The out-of-plane rotation angle of the dipolar groups depends on the size of the core¹³⁴, the length of the dipolar moiety, temperature, applied field and even stack length, and is around 30–40° for BTA^{30,133}. This defines the helical pitch of the stack, being 6 molecules for BTA (yet can be different for other cores⁹⁵) which implies that each joining molecule is rotated by 60° with respect to the previous one.

This step of self-assembly can be visualized using an analogy to magnets. Let us imagine flat round fridge magnets put face-down and arranged tightly and orderly on the kitchen table. It will not take long to discover that even the smallest perturbation will start a vivid chain-reaction of self-assembly into various length columns. Dipolar discotic molecules behave in a similar way in solution, the only difference being the electrostatic and not the magnetic fields being at play. It was in fact this magnificent act of self-assembly observed in diluted solutions that

initially triggered scientists to investigate these and similar molecules. It was noticed that long, quasi one-dimensional helical self-assembled structures – supramolecular polymers¹³⁵, very similar to DNA – are formed with tail-controlled chiral-preference¹³⁶.

Figure 28. Primary, secondary and tertiary structure of an archetypal columnar discotic liquid-crystal benzene-1,3,5-trisamide (BTA). Self-assembly of the dipolar disk-shaped molecules into columns with the axial macrodipole and consequent columnar-hexagonal packing leads to ferroelectric bistability and remnant polarization.

In high concentrations and in the solid-state, a second step of self-assembly is observed that extends into the other two dimensions when these molecular columns conglomerate to form a tight, typically hexagonal (or also rectangular) lattice. The peripheral tails of the adjacent molecules intercalate to minimize the occupied area, see rightmost panel of Figure 28. When deposited from solution (by spin-coating, drop-casting, etc.), molecular stacks will lie horizontally on the substrate. This arrangement profits in-plane device geometries, *e.g.* interdigitated electrode devices, as the polarization appears along the stack axis. To be able to operate in out-of-plane geometries, the initial molecular arrangement must be reconfigured to perpendicular/normal to the substrate, or homeotropic, alignment of the molecular stacks. Here, the benefits of the liquid-like properties of these materials manifest by allowing to manipulate the supramolecular ordering with the help of an applied electric field at lower viscosity (elevated temperature) conditions. This homeotropic alignment procedure can be directly observed using polarized light microscopy (POM) with crossed polarizers as darkening of the image, see the insets of AFM micrographs in Figure 29. The initial and final surface topographies obtained by the AFM reveal a clear change in directionality of the molecular self-assemblies. As the level of homeotropic alignment corresponds to the geometrical dipole density and thus to the polarization, the dynamics of the procedure can be indirectly measured

as the growth of the ferroelectric signal, see middle panel of Figure 29. The inset shows a gradual rise of the remnant polarization value during the alignment, which eventually saturates when all available molecular dipoles are oriented along the field lines at the electrode area. The process is very similar to the nucleation-and-growth mechanism observed in (ferroelectric) crystals and likely proceeds via several steps as was depicted in Fig. 17, which explains a clearly Gaussian alignment kinetics (blue solid line in Fig. 29).

Figure 29. Field-driven molecular alignment procedure (middle) during which in-plane bundles (left) are forced to stand homeotropically (right, taken from Ref. 105) to form out-of-plane geometry devices. AFM micrographs are of $2 \times 2 \mu\text{m}^2$ and $1 \times 1 \mu\text{m}^2$, respectively. Insets are polarized light microscopy images with crossed polarizers. A schematic side-view of the capacitor devices is given underneath for each case. Alignment speed is calculated as the derivative of the P_r trace.

The final hexagonal arrangement of the molecular columnar macrodipoles determines the available ferroelectric polarization in the layer, *vide infra* Fig. 30 for examples. Interestingly, many authors claim that it is the hexagonal packing itself that induces ferroelectric ordering in the columnar phases. Intuitively, such columnar ordering could lead to a cancellation of the net polarization due to the antiferroelectric ($\uparrow\downarrow\uparrow\downarrow$) interactions between the adjacent macrodipoles. Yet, extensive 2D/3D Ising⁸⁸ and (kinetic) Monte Carlo^{60,137,138} simulations reveal that due to the particular ratio of intercolumnar steric and electrostatic interactions and geometric frustration of the adjacent hexagonally (Δ triangularly) packed columns, when two oppositely oriented columnar dipoles leave the third electrostatically ‘confused’, columnar hexagonal phases lead to a truly ferroelectric phase. It was shown by dielectric relaxation spectroscopy (DRS) on BTAs⁴⁴, the temperature at which this ferroelectric ordering collapses (=Curie point) is very close to, but not exactly equal to the melting temperature of the material. This is an

expected behaviour of a ferroelectric based on the Curie-Weiss law introduced earlier in the text (section 3.2). The further melting, or isotropization, temperature marks a moment when all non-covalent interactions – π - π stacking and H-bonding – are broken and the liquid-crystal becomes just liquid.

Another relevant characteristic temperature of liquid-crystals is the one at which the material loses most of its molecular mobility and enters a pure crystalline state. This usually happens when the flexible fatty/oily (typically long alkyl chains) tails ‘freeze’ and crystallize. Hence, the three typical physical phases of thermotropic LCs are the crystalline, the liquid crystalline (with possible intervening higher order plastic phases) and the isotropic phase. The exact temperature of these phase transitions can be observed as a heat energy transfer – consumption upon entering and release upon leaving a higher energy state – during differential scanning calorimetry (DSC) measurements. The resultant thermograms display distinct heat-flow peaks around the points of transition from one to another fashion of molecular packing. The exact details of the packing must, nevertheless, be examined using additional techniques such as small- (SAXS) or wide-angle (WAXS) X-ray scattering, where the features of molecular ordering are extracted based on interpretation of distances between Bragg peaks corresponding to different Bragg reflections, etc.

All the principles, methods and properties discussed above are characteristic to all columnar (hexagonal) discotic ferroelectric liquid crystals – the highly-ordered materials with electric polarization along the self-assembled columnar axis. It is now time to find out how to make these substances demonstrate their unique behaviour and (sometimes quite literally) reveal their individual colours. The way to do so is through rational chemical structure modifications, based on the balancing of distinct functions of each architectural unit in the molecule. Ultimately, that should guide the optimization of the molecule for particular purposes. The rarity of comprehensive studies of structure-property relations is a key motivation for this review.

5.1 Tail engineering

The most straightforward means of influencing the properties of ferroelectric discotics is by peripheral tail modification. The idea of tuning different material characteristics through variation of the flexible side-chains has been alive for long in the field of liquid crystals, firstly for semiconducting¹³⁹ and electro-optical applications. This methodology applies to ferroelectric liquid-crystals as well and has a surprisingly strong impact on the final material properties like remnant polarization and its stability, coercive field, operational temperature range, Young's modulus and piezoelectric response.

Dipole density

As discussed previously in the text, the role of the flexible tails is typically passive, implying that introduction of dipolar units and other functionalization occurs elsewhere in the molecular structure. Thus, tails mainly act as an insulating spacer between the adjacent molecular columns in supramolecular assemblies. The shorter the spacer, the more columnar macrodipoles can fit in a unit volume. The actual geometrically available dipole density can be calculated from the inter-disc c and inter-columnar a molecular packing parameters (measured by XRD techniques⁵⁸) and a geometrical area filling factor k for a certain type of packing (*e.g.* 0.9069 for hexagonal, 0.7854 for square lattice) in combination with the average dipole moment per molecule μ , which for BTA comprising three amide groups is $3 \times 4 = 12$ Debye¹³³. This way, $P_{\text{geom}} = 4k\mu/(\pi ca^2)$. This leads to a rapid growth of available polarization for shorter tails (Fig. 30a, solid line), as the intercolumnar distance increases linearly with every added carbon to the tail (dashed line), and interdisc spacing being mostly tail-length independent. This dipole density varies together with the molecular packing parameters upon changing temperature and typically increases for cooling. This P_{geom} control methodology led to a boost in the remnant polarization from ~ 6 mC/m² to ~ 10 mC/m² for ferroelectric ureas¹²⁸ and from ~ 20 mC/m² to ~ 60 mC/m² for BTAs⁵⁸ by shortening the tail length from -C₁₆H₃₃ to -C₄H₉ and -C₁₈H₃₇ to -C₆H₁₃, respectively. See Article I for further discussion.

Phase diagram

Having most degrees of freedom for motion, the peripheral tails strongly affect the overall molecular mobility (or viscosity) of the system and hence (co-)determine the phase transition temperatures. Gradual changes in the phase diagram have been observed both for ferroelectric ureas¹²⁸ and BTAs⁵⁸ with varying tail lengths. For BTAs, shortening of the tails leads to extended liquid-crystalline phases and the operating temperature range moving to room

temperature and below: from above 50°C for BTA-C18 to ~0° for BTA-C10 and slightly increased ~38°C for BTA-C6 due to a competing packing effect⁵⁸. The isotropization or clearing (breaking non-covalent bonds) temperature remains around 200°C for all linear-tailed BTA homologues. Though favourable, liquid-crystallinity is not the ultimate requirement for ferroelectricity, as it was previously thought^{33,99}. The high molecular mobility in the LC phase is indeed of great service for molecular alignment during the device conditioning, *vide supra*. Yet, ferroelectric switching can also be established in higher-order plastic phases, as observed in branched-tailed BTA homologues³⁰, while short-tailed BTA-C6 is perfectly switchable in the crystalline state, probably due to the low molecular mass of the tail.

Regarding branched, swallow-tailed homologues (*e.g.* with 2-ethylhexyl, 1-hexylheptyl chains), strongly promoted axial self-assembly is observed⁴⁸ which leads to higher quality, longer supramolecular aggregates and therefore increased clearing temperatures (see compounds labelled 6/2 and 7/6 in Fig. 30b). A synergistic effect in isotropization temperature was observed in 1:1 mixtures of BTA-C7/6 and BTA-C12, where 250°C was found for the mixture as compared to 203°C and 236°C for neat BTA-C12 and BTA-C7/6, respectively³⁰. Recently, a continuous tuning of the crystalline-to-LC transition temperature has been demonstrated for mixtures of pyrene-cored tetraamides with linear and chiral tails¹⁴⁰. The study was inconclusive about the effect of mixing on the ferroelectric properties, though.

Figure 30. (a) Effect of a macrodipole packing density on the geometrically available polarization (solid line, right axis) for different alkyl chain lengths. An example of BTA. Inset: relative area that molecular column occupies based on the intercolumnar packing distances measured by X-ray diffraction techniques (dashed line, left axis). (b) Phase transition temperatures of different BTA homologues. (c) Small-signal piezoelectric coefficient¹⁰ measured for different BTA homologues. The dotted line is a fit using Eq. 2.1.1.

Polarization retention and coercive field

Tail-related facilitated self-aggregation into larger supramolecular units affects the level of structural disorder in the layers, which, as shown for BTAs experimentally³⁰ and by simulations⁶⁰, has a remarkable effect on the stabilization of the ferroelectric polarization. Based on the thermally activated nucleation-limited switching theory (section 3.4.4), polarization reversal is promoted by formation of oppositely oriented nuclei (or ‘defects’) that are of sufficient volume to start a back-switching avalanche. For the external field induced polarization switching the level of structural disorder is of lesser importance as it is mostly initiated at the electrode interface⁶⁰. This explains why coercive fields only vary by several times (less than an order of magnitude) when comparing different homologues. Further propagation of the domain walls will intuitively be quicker in more ordered films, which results in shorter polarization switching times^{26,30,58}. However, the most significant effect of increased structural order is when spontaneous depolarization is considered, as it starts at defects that sit in the bulk⁶⁰. Fig. 31 summarizes the polarization retention data in an Arrhenius activation plot for various linear-, branched-tailed and mixed BTA homologues. A clear improvement in retention, reaching 5–7 orders of magnitude (*cf.* 2–5 times increase in coercive fields) is observed when linear tails are changed for branched or in their mixtures (see BTA-C7/6:C12 case) due to synergetic effects. The 10-year limit is overcome already at high temperatures, which is promising for memory applications. This entirely tail-induced polarization stabilization can be explained by the reduced number of structural defects that in turn is caused by high cooperativity during self-assembly. See Article II for further discussion.

The influence of the tail length on the coercive field value (and polarization stability) is rather counterintuitive, as, despite their larger molecular mass and thus expected stronger hindrance for switching, longer, bulkier tails result in reduced coercive field values and faster depolarization. This has been observed experimentally in phthalonitrile-based ferroelectrics¹²⁷, where the longer-tailed homologue was successfully switchable while for the shorter-tailed homologue the polarization was non-invertible, likely due to a too high coercive field. The trend is even clearer for BTAs, where the coercive field at the same conditions (70°C, 5 Hz) drops from more than 50 V/ μm to below 25 V/ μm when comparing hexyl and octadecyl tails. Higher molecular mass tails, bringing more disorder and kinetics to the system, are the reason why this experimental observation does not agree with molecular dynamics simulations³⁰.

Figure 31. Depolarization activation plot – depolarization time constant vs. reciprocal temperature – of different BTA homologues (electrical measurement in real devices) as compared to other organic ferroelectrics P(VDF:TrFE) (own data) and phthalonitrile-based umbrella-like liquid-crystal PN-C2 (black star, SHG spectroscopy¹²⁷).

Young's modulus and piezoelectric response

Another interesting opportunity to tune the material properties by changing the peripheral tail length appears when turning from ferroelectric to piezoelectric behaviour. We recently showed that two different regimes of electromechanical response manifest in the same BTA material with different length alkyl chains (see Article IV)¹⁰. While short-tailed BTA-C6 and BTA-C8 demonstrate textbook-like negative piezoelectricity (see section 2.1.3), molecules with C10 and longer tails show unique elastomer-like actuation with strong amplification of the response around the coercive field, which is caused by a change in mechanical stiffness of the layer upon polarization switching. This unusual behaviour disappears under small-signal conditions, where again close-to-ideal piezoelectric behaviour is observed. The magnitude of the piezoelectric constant at these conditions follows a neat growing trend with shortening of the alkyl chains, see Fig. 30c. This trend can be explained by the gradually decreasing remnant polarization, dielectric constant and piezoelectric coupling parameter for longer tails, which outcompete the effect of lower Young's moduli (1.5, 1.2, 0.95, 0.75, 0.3 GPa at 60°C for C6 to C18, respectively) that would hypothetically lead to higher piezoelectric response for the same polarisation. The trend of increasing mechanical stiffness with shorter tails has been observed in purely crystalline compact-tailed BTAs as well, reaching 3.3 GPa for the toughest.¹⁴¹

5.2 Dipolar moiety engineering

To gain ferroelectric functionality, discotic liquid crystals must be equipped with switchable moieties comprising a permanent dipole moment. This is different from the bent-core or bowl-like liquid-crystals where polarity arises from the asymmetry of the core. The planar non-polar conjugated cores of discotics requires additional functionalization in the shell, which brings certain advantages due to separation of different functions in a molecule, see section 3.8, yet requires additional synthetic steps. The choice for the polar motif is broad – starting with chemical functional groups and moving towards various heterocycles as substituents, yet for maximum performance (*e.g.* in hybrid-function applications) the optimum variant must be picked.

A large permanent dipole moment of the substituent is the main requirement. The magnitude of the molecular dipole moment μ essentially depends on a distance r between constituting atoms (*i.e.* bond lengths) and differences in their effective electronegativity (relative distribution of partial molecular charges q): $\vec{\mu} = \sum q\vec{r}$. Organics offers a whole list of oxygen, nitrogen, sulphur, fluorene-containing dipolar groups with dipole moment varying between 0–10 D for combinations with the most and least electronegativity¹⁴². The most popular dipolar moieties, due to the high dipole moment, easy accessibility of synthons and, likely, historical tradition, remain (thio)amide (3.8–5.1 D), (thio)urea (4.6–4.9 D)¹⁴³, ester (~1.8 D), and vinylidene fluoride (as in PVDF, 2.1 D). These potentially electrically switchable dipolar groups are often introduced in the molecular structure to promote non-covalent interactions and self-assembly¹³², and thus are found in supramolecular polymers, gelators, self-healing materials and liquid-crystals, without even considering the ferroelectric functionality. Their strong dipole-dipole interactions and possible hydrogen-bonding (as in Kevlar or nylon) are exploited to achieve outstanding physical material properties. Newer dipolar substituents include diverse heterocyclic moieties like azoles or (thio)furans, that typically possess a lower dipole moment¹⁴⁴ but also allow hydrogen bonding. An increasing amount of evidence proves the indisputable importance of these non-covalent interactions for successful ferroelectric switching.

1,2,3-triazole

A quite recent attempt to create a ferroelectric liquid crystal was by employing the previously untested 1,2,3-triazole heterocycle with a maximum dipole moment of 4.55 D and a H-bonding capability¹⁴⁵. The molecular core of choice – naphthalene – was tried originally as well, while

the tails remained the classical 3,4,5-tris(octyloxy)phenyl (Fig. 32). The final design resulted in a C₂-symmetry molecule that enters a LC phase at elevated temperatures and self-assembles in helical columnar structures consisting of cisoid conformers. The compound proved to be ferroelectrically switchable within a relatively narrow 100–120°C temperature window. The polarization hysteresis loops were measured in liquid-crystal cell (LCC) devices with considerable leakage currents that are likely due to the conjugated structural elements and with double-peak features observed. These two peaks were attributed to dipolar and ionic switching by the authors, though subsequent flipping of each of the two dipolar groups might be an alternative explanation. With all effects included, a remnant polarization of around 16 mC/m² was achieved, which was of the same range as the calculated geometrically expected value. The coercive field was around 30 V/μm at 105°C, which is similar to other dipole-flipping ferroelectrics and corroborates the hypothesized ferroelectricity due to the rotation of the 1,2,3-triazole, and excluding ion transport with much lower characteristic fields. Other attempts to observe polar switching in a series of columnar phases with 1,2,3-triazole dipolar motif remained unsuccessful¹⁴⁶.

Figure 32. Examples of 1,2,3-triazole-based molecules, of which only the left-most has been shown to enable ferroelectric switching¹⁴⁵. Molecules on the right demonstrated no polarization reversibility¹⁴⁶.

Phthalonitrile

A quite exotic and one of the first attempts to induce robust polarization in columnar phases was proposed by a group led by Takuzo Aida, where, together with dipolar amides (which were initially considered as self-assembly promoting agents), a highly polar phthalonitrile (PN) motif was used in fan-like asymmetric molecules¹²⁷. The proposed molecules (Fig. 33) differ from the others discussed in this section because the molecular disc, or a ‘pizza’ in this case, is formed

by self-assembly of four of these fan-like ‘pizza slices’, which adds an extra step in molecular aggregation in comparison with the conventional discotics. Dipolar switching was intended to originate from a ‘flapping’ movement of the phthalonitriles facing the centre of the molecule. The required molecular mobility for this is provided by flexible alkyl linkers between the phthalonitriles and the rest of the molecule. The length of these $-(CH_2)_n-$ linkers was optimized to $n = 2$, as $n = 3$ resulted in paraelectric behaviour. The peripheral sidechains were varied as well from bulky 3,4,5-tris(dodecyloxy)phenyl to even bulkier wedge-like tails, where the latter were found to be the optimal, as the former did not provide enough molecular mobility for dipole flipping (or insufficient fields were applied). The self-assembled umbrella-like layers pack in a columnar hexagonal lattice. After homeotropic alignment one of the four tested molecular structure variants – the bulky-tailed short-linked PN-C2 – was ferroelectrically switchable with a remnant polarization of $\sim 17 \text{ mC/m}^2$.

The coercive field of $0.23 \text{ V}/\mu\text{m}$ at 120°C , though unnaturally low compared to similar materials, can be explained by the extremely slow field-sweeping speed ($<0.008 \text{ Hz}$) that was used to reach full poling of the material. Intuitively, higher applied fields would have solved the slow switching problem, but likely caused electrical breakdown. Thus, the full polarization saturation was only reached in several minutes at relatively high (120°C) temperatures and even longer at 60°C , which limits any memory applications for this type of compounds. The polarization stability though is relatively good and exceeds 1000 minutes at 60°C , as measured using optical second-harmonic generation (SHG) method for a corona-poled free-standing film. Two relaxation pathways can be distinguished, the faster of which is related to amide direction randomization ($\sim 1/4$ of the total polarization) while the longer is attributed to back-bending of PNs¹⁴⁷. Thus, though initially it was thought that amides refrain from switching in these umbrella-like structures with the phthalonitrile cores, later studies confirmed their contribution to field-induced polarization inversion.

Figure 33. Supramolecular materials based on dipolar phthalonitrile (PN) moiety. Optimized structure molecules (*i.e.* 2a) demonstrate ferroelectric switching. Figure reproduced from Ref. 127 with permission.

Oligo-vinylidene fluoride

Polyvinylidene fluoride (PVDF) and especially its copolymers with polytrifluoroethylene (PTrFE) remains one of the most famous ferroelectrics¹¹¹. This can be explained by it being a non-capricious workhorse which, though lagging behind the best inorganic analogues, gets work done when mechanical flexibility and low cost are critical. As introduced above (section 4.2.3.1), PVDF has two ferroelectric phases – the exotic δ -phase¹⁴⁸ and the commonly used all-trans conformation β -phase, to which it must be forced externally by temperature, field, tension etc. or by composition, typically via partial hydrogen-to-fluorene substitution. There is however an alternative approach – employment of shorter (degree of polymerization smaller than 10) oligomer chains – the result of which is the material entering the β -phase spontaneously, in turn leading to higher typical remnant polarizations.¹⁴⁹ These short oligovinylidene fluoride (OVDF) chains make for a perfect candidate for, *e.g.*, discotic liquid-crystal functionalization. This approach has for the first time been demonstrated with benzene, perylene bisimide (PBI) and phthalocyanine (Pc) core discotics (Fig. 34), which was also the first demonstration of a covalent coupling between OVDF and another organic molecule, thus clever synthetic procedures had to be accommodated¹⁵⁰. As a result, ferroelectrically switchable materials with

PBI and Pc cores were obtained. In contrast, the BTA-based molecule, though having the highest degree of β -phase, did not show any switching, likely due to competing amide and OVDF motifs or layer morphology problems. PBI-OVDF in turn gave a remnant polarization of $\sim 5 \text{ mC/m}^2$ with a coercive field of $23 \text{ V}/\mu\text{m}$ at 50°C . The result might be improved if higher crystallinity and molecular ordering levels could be achieved. The most expressed ferroelectric behaviour was observed in Pc-OVDF layers, that were characterized by close-to-ideal polarization hysteresis loops with $\sim 37 \text{ mC/m}^2$ remnant polarization and $\sim 20 \text{ V}/\mu\text{m}$ coercive field. Though in none of the cases the pure OVDF polarization levels ($\sim 90 \text{ mC/m}^2$) were achieved, which is at least in part due to ‘dilution’ of the dipolar OVDF segments with the cores and paraffinic tails, the coercive fields were reduced almost fivefold (*cf.* $115 \text{ V}/\mu\text{m}$ for pure OVDF layers¹⁴⁹). The differences in achieved ferroelectric parameters between PBI- and Pc-based molecules can be explained by different columnar packing parameters, number of OVDF motifs and, likely, different levels of homeotropic alignment. What is more, both materials were found to give rise to a previously unobserved resistive switching mechanism originating from the hybridization of semiconducting and ferroelectric properties, see section 5.3 for further details.¹²⁶

Figure 34. Molecular structure of OVDF-functionalized discotic liquid-crystals with benzenetrisamide (BTA), perylenebisimide (PBI) and zinc phthalocyanine (Pc) cores¹⁵⁰.

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Amides

Despite multiple attempts to introduce new functional groups that would be responsible for polar switching in a molecular structure, amides remain a safe, classical way to go. Though forming hydrogen-bonded networks, the ferroelectricity of amide-based materials arises from physical rotation of the dipolar moieties and not the proton transfer, as confirmed by ferroelectric and dielectric relaxation spectroscopy (DRS) tests on deuterated BTA molecules.⁵⁵ Amides were first complemented by simple benzene cores and alkyl chains^{62,105}, which was already enough to disclose a huge potential of the molecular design to bring a new functionality to discotic liquid-crystals. Now, more and more different cores are being decorated with amides which leads to florescence of the field of ferroelectric discotics.

– Amides: the core

The function of the core is firstly stabilization of the one-dimensional axial ordering due to noncovalent π - π stacking, which allows for the breaking of the hydrogen bonded network upon reversal of the microdipoles without losing the axial order. The importance of this role can be illustrated with the example of two similar mesogens – one with a planar conjugated thus π - π stacking benzene core benzene-trisamide (BTA), another with a similar nonconjugated non-planar cyclohexane core cyclohexane-trisamide (CTA). Though entering the same columnar-hexagonal LC phase with almost identical packing¹⁵¹, BTA is one of the best organic ferroelectrics with P_r reaching 60 mC/m² while CTA does not demonstrate any ferroelectric switching (unpublished). This holds for compounds with thioamides as well (unpublished), the only difference being higher achievable remnant polarizations due to a larger dipole moment of thioamides ~5.1 D compared to ~4 D of amides. The absence of a ferroelectric signal in a non-planar triphenylamine-cored trisamide, which showed neither liquid-crystal phases nor dielectric anomaly¹⁵², and in non-planar tetraphenyl-ethylene (TPE)-cored¹⁵³ as well as tetra[2,3]thienylene-cored¹⁵⁴ tetraamides supports the hypothesis (Fig. 35). Only sources that explicitly reported the lack of ferroelectric signal are used here, omitting the ones that studied potentially switchable compounds but did not pursue ferroelectric characterization.

Figure 35. Molecular structures of materials that, except of the leftmost (thio)BTA, do not demonstrate ferroelectric switching. This is likely caused by the non-planar molecular cores that fail to provide sufficient stabilization during polarization switching.

Nevertheless, in a non-planar yet conjugated helicene derivative ferroelectric switching was observed¹⁵⁵. In contrast to the conventional discotics with a 1D polarization axis (columnar phase), Anetai *et al.* attempted to create a 2D hydrogen-bonded network of amides (lamellar phase) using a (racemic mixture of) croissant-shaped 4-helicenes as a core, to which two tetradecyl tails were attached via amides. Though ferroelectric switching was demonstrated at elevated temperatures (70–150°C), the acquired high remnant polarization value of ~110 mC/m² could not be validated by the reported geometrically available dipole density of 31 mC/m² that was calculated for the particular packing parameters measured using XRD techniques. The coercive field was normal for amide-based ferroelectrics: ~20 V/μm at 150°C and 0.5 Hz. The study also attempted to introduce chiral preference by introducing a defined chirality helicene core, yet the materials appeared non-switchable. In spite of that, a very useful observation was reported based on a comparison of amide-based (Fig. 36 left) and ester-based (right) helicene derivatives. By lack of ferroelectric response in non-H-bonding ester-based compounds, as compared to successful polarization switching in the H-bonding amide-based analogue (blue *Rac*-1), the authors prove the importance of the hydrogen bonding in the ferroelectric switching process, which is essentially caused by facilitated self-assembly and stabilization of the polar state.

Figure 36. Amide- and ester-substituted helicene derivatives tested in the study by Anetai *et al.* Only devices based on the racemic mixture of amide-equipped compound (blue, *Rac*-1) demonstrated ferroelectric switching in the bilayer lamellar liquid-crystal phase (inset). Its chiral analogue and ester-based materials were non-switchable.

Returning to flat conjugated cores, a number of variants to benzene have been proposed that became successful ferroelectrically switchable materials. Studied by Akutagawa *et al.* (Fig. 37), a pyrene-cored liquid-crystal with four tetradecylamides⁹¹ (PTeA-C14) yielded a remnant polarization below 15 mC/m^2 with a coercive field of $\sim 1.5 \text{ V}/\mu\text{m}$ at 220°C . An analogous structure with a larger tetraphenylporphyrin core (TppTeA-C14)¹⁵⁶ gave similar values $\sim 11 \text{ mC/m}^2$ and $2 \text{ V}/\mu\text{m}$ at 230°C , while the remnant polarization of another massive-cored hexaphenyltriphenylene-hexamide³³ with tetradecyl tails (HptpHA-C14) was impossible to determine due to an excessive leakage input in the polarization hysteresis loops. For details on fluorescent and semiconductor-like properties of these and other conjugated-cored compounds, see section 5.3.

Figure 37. Molecules with pyrene⁹¹, tetraphenylporphyrin¹⁵⁶ and hexaphenyltriphenylene³³ cores decorated with tetradecylamides, studied by the group of Akutagawa. All the compounds demonstrated ferroelectric and fluorescent properties.

Guilleme *et al.* synthesized a discotic liquid-crystalline trisamide¹⁵⁷, unique due to its sub-phthalocyanine core with an axial non-invertible boron fluoride (BF) dipole in the centre¹⁵⁸ (Fig. 38 left). Owing to its large charge transport-promoting core, SubPc-trisamide not only demonstrated ferroelectric polarization reversal, but also a previously unobserved bulk resistive switching mechanism due to hybridization of both the functionalities (section 3.8). A moderate $P_r \approx 1.3 \text{ mC/m}^2$, which could potentially be improved by higher homeotropic alignment levels, and a normal coercive field $\sim 25\text{--}50 \text{ V}/\mu\text{m}$ were found at elevated temperatures around $\sim 130^\circ\text{C}$.¹²⁶

An analogous approach employing a carbonyl-bridged triarylamine (α -CBT) core with three amide groups (Fig. 38 middle) led to a larger, yet likely interfacial polarization of 9 mC/m^2 and a coercive field of $\sim 15 \text{ V}/\mu\text{m}$ at $\sim 130^\circ\text{C}$.⁸⁵ Again, because of a combination of a 1D charge transport channel in the molecular core¹⁵⁹ and the surrounding strong permanent amide dipoles another – interfacial – resistive switching mechanism was observed, that was previously only found in phase-segregated ferroelectric-semiconductor blends of P(VDF:TrFE) and conjugated polymers like P3HT (section 3.8).¹³⁴ The measured polarization retention in drop-casted gold-electrode α -CBT capacitor devices was below 10 minutes at elevated temperatures (130°C). Similar polarization retention was found for discotic liquid-crystals functionalized with oligo-vinylidene fluoride chains¹²⁶ before alkyl-tail optimization³⁰, see Table 1.

Obviously, for memory device applications both the (related) moderate retention and the high-temperature operation problem must be solved. Hence, García-Iglesias *et al.* proposed a novel molecular design of a ferroelectric discotic liquid-crystal with a semiconducting benzotrithiophene (BTT) core, see Article V.¹⁶⁰ The molecular architecture was simplified to basic structural elements with a single dodecyl tail connected to each of the three amides at the 1, 6, 11 positions of the BTT (Fig. 38 right). The resulting molecule not only was easily synthesizable, but also demonstrated extreme polarization retention that exceeded the commercial 10-year requirement for memory devices already at elevated temperatures, and thus became one of the best among the amide-based ferroelectrics³⁰. This came at the cost of a higher coercive field $>100 \text{ V}/\mu\text{m}$ (at 25 Hz). The remnant polarization, corresponding to the dipole density, was around 25 mC/m^2 and remained constant from strongly elevated to room temperature. In addition to this, both bulk conductivity switching and injection barrier modulation, previously only observed in different systems, were found in BTTTA-C12 devices (section 3.8).¹⁶⁰

Figure 38. Amide-based C3 symmetry semiconducting ferroelectrics that demonstrated resistive switching based on the injection barrier and/or bulk conductivity modulation.

To summarize, the central motif of the discotic molecules is responsible for a multitude of functions, including stabilization of aggregates, determination of dimensionality of the self-assembly or introduction of semiconductivity. Depending on the symmetry of the core and the available chemical bonding positions, the number of accommodatable dipolar moieties is also influenced. As discussed in the following section, this can also affect the ferroelectric properties.

– Amides: the number of dipolar motifs

Some authors have declared a desire to introduce as many dipolar units in the structure as possible, hoping for stronger self-assembly and higher achievable polarization levels^{33,34,161}. However, in addition to the number of dipolar branches (*e.g.* amide moieties), the spacing between them and the symmetry of the molecule influences the outcome as well; and while odd-numbered compounds like benzene-bisamides (BBA-C14), -trisamides (BTA-C14) or -pentaamides (BPA-C14) do show ferroelectric behaviour, benzene-tetraamides (BTaA-C14) and -hexamides (BHA-C14) are found to be paraelectric (Fig. 39)¹⁶². This may originate from lack of electrostatic frustration within molecular columns (which is characteristic to odd-numbered benzene-amides and, macroscopically, hexagonal lattices, see Fig. 39 left) and/or steric hindrance between the closely packed dipolar units and a resultant antiferroelectric ordering. The situation changes if the compact benzene is changed to larger molecular cores, leading to ferroelectrically switchable pyrene-tetraamide (PTaA-C14)^{91,163} or hexaphenyltriphenylene-hexamide (HHA-C14)³³. Interestingly, benzothienobenzothiophene substitution for benzene in a bisamide configuration (BtbtBA-C14) led to a loss of ferroelectric function likely due to the absence of axial self-assembly³³.

Figure 39. Benzene-cored molecules with different number of alkylamide moieties. While BBA, BTA and BPA demonstrate ferroelectric switching, BTeA and BHA do not, likely due to the balanced dipolar arrangement (left). BTBT-cored bisamide (right) does not form molecular stacks which prevents ferroelectric behaviour.

Unfortunately, an increased number of dipolar groups does not straightforwardly convert into increased polarization, see Table 1. Based on a study of Akutagawa *et al.*, benzene-cored derivatives with 2, 3, 4, 5 and 6 amides followed by tetradecyl -C₁₄H₂₉ tails resulted in 13, 8, 0, 10 and 0 mC/m² remnant polarization, respectively¹⁶². Hence, with some exceptions^{33,91,127,155}, derivatives with three amide groups and a planar conjugated core^{30,58,85,126,157} remain in principle the only combination with a guaranteed ferroelectric response^{88,89}. If desired, the dipole density can be further tuned by the peripheral tails, see section 5.1.

Urea

Thiourea was the first entirely organic compound characterized as ferroelectric¹⁰⁴. Since then, sulfur (thio-) and oxygen based ureas (see Fig. 40) have been exploited as dipolar and hydrogen-bonding moieties in liquid-crystalline frameworks, in most cases granting a polar switching functionality^{128,130}. However, despite a large dipole moment and textbook-like hydrogen bonding, urea-based ferroelectric liquid crystals suffer from poor polarization stability with sub-minute retention times at elevated temperatures⁶¹. The reason to this might hide in the molecular architecture of the reported urea derivatives that, instead of being used as dipolar rotors, *cf.* amide-based ferroelectrics, the urea group has the dual role of a dipole-switching core. As discussed previously in the text (see – *Amides: the core*), the most successful ferroelectric operation is observed in materials with a stabilizing core and dipolar switching functions separated. Thus, yet ferroelectrically uncharacterised BTA-like molecular designs as the one reported by Li *et al.*, where one of the amides is substituted for urea, might have a large potential.¹⁶⁴

Figure 40. Examples of urea-based liquid-crystals: columnar diphenylurea (DPU) with a switchable ‘core’¹²⁸; and columnar discotic benzeneureabisamide (BUBA) the ferroelectricity of which is yet to be demonstrated¹⁶⁴.

5.3 Integrated functionalities – semiconducting properties

Columnar discotic liquid-crystals with large conjugated cores are well known in the field of organic semiconductors as they allow to achieve rapid charge transport due to the high-quality self-ordering. Axial self-assembly promoted by the π - π stacking of the aromatic cores creates one-dimensional channels with high interdisc orbital overlap for efficient charge hopping through the stacks. Charge transport mobilities in such systems reach more than $1 \text{ cm}^2/\text{V}\cdot\text{s}$, which is at least 5 orders of magnitude higher than for typical semiconducting polymers and is approaching the values obtained for organic molecular crystals^{165,166}. These molecules typically do not comprise dipolar motifs, unless they are employed as hydrogen-bonding agents for enhanced self-assembly¹⁶⁵. In this case, local electrostatic fields arising from these adjacent dipoles leads to additional energetic disorder that in turn most likely causes the reduced mobility of the charges flowing through the core as compared to the no-dipole case¹⁶⁷. As the dipole directions are normally randomized (characteristic operation fields of semiconducting devices are much lower than the coercive fields for ferroelectric/dipolar switching), no asymmetry of response can be expected. Only when operating at high applied fields enabling polarization reversal, the bulk conductivity switching can be observed in materials with hybridized semiconducting and ferroelectric functionalities, as it was discussed in section 3.8. Charge transport mobilities in this case have been shown to reach $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ for well-aligned devices in the high-conductivity ‘On’ state¹⁶⁰. Setting the ferroelectric functionality aside, the facilitated self-assembly and high conjugation levels of the cores positively influence other properties like luminescence and energy transfer¹⁵⁹.

Due to their small size benzene-cored molecules absorb in the deep UV with a peak around 230 nm ¹⁶⁸. This is due to the deep HOMO and shallow LUMO level leading to optical band gap

of around 4–6 eV. Though suggested to provide separate paths for electron and hole transport that would lead to photovoltaics without p-n junctions^{169,170}, the high required excitation energies and the unavoidable extreme sensitivity to structural disorder prohibit its practical implementation. The situation changes when larger cores are introduced. Some examples with luminescence spectra shifting from UV to the visible region are given below.

Benzenetrithiophene-trisamide¹⁶⁰ (BttTA-C12, Fig. 38 right) with a HOMO of –5.5 eV, a LUMO of –2.1 eV, a resulting band gap of 3.4 eV and emission peak at around 400 nm is a considerable improvement in comparison to BTAs, see Article V.

Hexaphenyltriphenylene-hexamide³³ HptpHA-C14 (Fig. 37 right) demonstrated fluorescent properties on the UV-Vis boundary as well, with a spectral peak at around 394 nm and a quantum yield of 17.5%. Concentration- and solvent-dependent properties could not be examined in HptpHA-C14 due to solubility problems.

The emission of pyrene-tetramide⁹¹ PTeA-C14 (Fig. 37 left), independently of the (chiral) tail substituents¹⁴⁰, was found to sit in a visible region with the concentration-dependent emission peak ranging between 400–500 nm with 510 nm for the solid material. Based on DFT calculations a HOMO of –5.63 eV, a LUMO of –2.18 eV and a bandgap E_g of 3.45 eV were found⁹¹.

A larger carbonyl-bridged triarylamine-cored trisamide α -CBT⁸⁵ (Fig. 38 middle) allowed even further shift towards visible wavelengths with absorption peak at ~500 nm and a fluorescence maximum at 555 nm in thin-films. The energy diagram for this compound was obtained by combining the optical spectrometry and cyclic voltammetry and resulted in a HOMO of –5.7 eV, a LUMO of –3.2 eV and an E_g of 2.5 eV.

Naturally, molecules based on the well-known bulky chromophores tetraphenylporphyrin-tetramide¹⁵⁶ (TppTeA-C14, Fig. 37 middle), PBI-OVDF^{86,150} (Fig. 34 top), SubPcBF-trisamide^{86,158} (Fig. 38 left), and Pc-OVDF^{86,150} (Fig. 34 bottom) have strongly red-shifted absorption spectra with peaks at around 420 nm, 485–520 nm, 560 nm and 470–700 nm, respectively, and even further red-shifted emission, caused by narrow band gaps in range of 1.6–2 eV.

Owing to their promising semiconducting properties accompanied by ferroelectric switching, these materials may become suitable for the next-generation resistive switching-based memory devices^{85,86,91,160} or light-driven power generators based on a possible anomalous bulk photovoltaic effect in organic materials (Fig. 41). For the latter, the discussed compounds would

bring a strong advantage firstly due to the significantly lower band-gap going down to ~ 1.5 eV compared to (the lower boundary) ~ 2.2 – 2.8 eV of popular inorganic materials for this purpose, *e.g.* BFO^{171,172}. The one-dimensional columnar assembly of ferroelectric discotics also strongly promotes charge transport allowing much higher mobilities, as compared to, for example, polymer materials. From the material design perspective, the physical separation of ferroelectric (in dipolar motifs) and semiconducting (in cores) functionalities may offer novel degrees of freedom, as compared to the case of inorganics where the same lattice is responsible for both the effects.

Figure 41. Artistic impression of the bulk conductivity switching⁸⁶ (left) and the anomalous bulk photovoltaic effect¹⁷³ (right), both arising from the charges moving through the asymmetric sawtooth-like potential landscape created by the head-to-tail arrangement of the dipolar motifs in molecular columns of discotic self-assembling semiconducting ferroelectrics.

Table 1. Summary of ferroelectric and piezoelectric properties of the most popular columnar discotics. Data for other ferroelectric materials is given for reference.											
Core	Dipolar groups, no.	Tail	Symmetry	Material***	P_r , mC/m ²	E_c , V/ μ m	OTR; MP, °C	Retention, s*	LS d_{33} , pm/V	SS d_{33} , pm/V	Ref.
-	-	-	-	BTO	200 (RT ❖)	0.1–1 (RT)	<130	>10 ⁶	<700	<500	54,113
-	-	-	-	PZT	600 (RT ❖)	1–8 (RT)	<360	>10 ⁶	<1000	<400	14,113
-	-	-	-	DIPAB	~230 (50°C ❖)	0.5–2 (145°C)	<150	-	-	360	101
-	-	-	-	Croconic acid	~200–300 (RT ❖)	1–3	<175	-	+15	-	22
-	VDF, TrFE	-	-	P(VDF:TrFE) (*)	60–120 (RT)	50 (RT)	<120	>5·10 ⁵ (RT, el.)	-38	-25	10,12, 59
Zinc phthalocyanine	oVDF, 8	oVDF	C4	Pc-oVDF	33 (40°C ●)	30 (40°C, 1 Hz)	<110	~200 (50°C, el.)	-	-	86,150
PBI	oVDF, 6	oVDF	C2	PBI-oVDF	5 (50°C ●)	23 (50°C, 1 Hz)	<112	~100 (50°C, el.)	-	-	86,150
Benzene	Amide, 3; oVDF, 3	oVDF	C3	BTA-oVDF	NS	NS	<93	NS	-	-	150
Sub Phthalocyanine BF	Amide, 3	3,4,5-tris(dodecyloxy)phenyl	C3	SubPc-amide	1.3 (130°C ●)	50 (130°C, 1 Hz)	<250	-	-	-	86,157
Carbonyl-bridged triphenylamine	Amide, 3	3,4,5-tris(octyloxy)phenyl	C3	α -CBT	9 (130°C ●)	15 (130°C)	-	~300 (130°C, el.)	-	-	85,159
Benzene	Amide, 3	Hexyl	C3	BTA-C6	60 (RT ●)	42 (70°C, 5 Hz)	<195	7·10 ⁶ (RT, el.)	-21	-4.5	10,58
Benzene	Amide, 3	Octyl	C3	BTA-C8	45 (RT ●)	37 (70°C, 5 Hz)	<202	2·10 ⁶ (RT, el.)	-8	-2.8	10,58

Table 1. Summary of ferroelectric and piezoelectric properties of the most popular columnar discotics. Data for other ferroelectric materials is given for reference.											
Core	Dipolar groups, no.	Tail	Symmetry	Material***	P_r , mC/m ²	E_c , V/μm	OTR; MP, °C	Retention, s*	LS d_{33} , pm/V	SS d_{33} , pm/V	Ref.
Benzene	Amide, 3	Decyl	C3	BTA-C10	37 (RT $\star$)	32 (70°C, 5 Hz)	<200	5·10 ⁵ (RT, el.)	-	-1.8	10,58
Benzene	Amide, 3	Dodecyl	C3	BTA-C12	32 (RT $\star$)	30 (70°C, 5 Hz)	<203	2·10 ⁵ (RT, el.)	-	-1.5	10,58
Benzene	Amide, 3	Octadecyl	C3	BTA-C18	22 (50°C $\star$)	25 (70°C, 5 Hz)	>50;<211	~100 (70°C, el.)	-	-0.7	10,58
Benzene	Amide, 3	2-ethylhexyl	C3	BTA-C6/2	42 (RT $\star$)	120 (70°C, 5 Hz)	<278	7·10 ⁶ (RT)	-	-	30
Benzene	Amide, 3	1-hexylheptyl	C3	BTA-C7/6	34 (50°C $\star$)	180 (70°C, 5 Hz)	50–90; <236	>3·10 ⁸ (75°C, el.)	-	-	30
Benzene	Amide, 3	1-hexylheptyl; dodecyl	C3	BTA-C7/6;C12	32 (RT $\star$)	100 (70°C, 5 Hz)	<250	>3·10 ⁸ (70°C, el.)	-	-	30
Benzotrithiophene	Amide, 3	dodecyl	C3	BTTTA-C12	25 (RT $\star$)	300 (RT, 25 Hz)	<267	>3·10 ⁸ (120°C, el.)	-	-	160
Cyclohexane	Amide, 3	Dodecyl	C3	CTA-C10	NS	NS	-	NS	-	-	-
Benzene	Thioamide, 3	Dodecyl	C3	BTS-C12	40 (50° $\star$)	60 (50°C, 5 Hz)	<254	-	-	-	174
Cyclohexane	Thioamide	Dodecyl	C3	CTS-C12	NS	NS	-	NS	-	-	-
Benzene	Amide, 2	tetradecyl	C2	BBA-C14 (2BC)	13.3 (150°C $\blacksquare$)	42 (150°C)	<180	-	-	-	162
Benzene	Amide, 3	tetradecyl	C3	BTA-C14 (3BC)	8 (70°C $\blacksquare$)	25 (160°C)	<194	-	-	-	162

Table 1. Summary of ferroelectric and piezoelectric properties of the most popular columnar discotics. Data for other ferroelectric materials is given for reference.											
Core	Dipolar groups, no.	Tail	Symmetry	Material***	P_r , mC/m ²	E_c , V/ μ m	OTR; MP, °C	Retention, s*	LS d_{33} , pm/V	SS d_{33} , pm/V	Ref.
Benzene	Amide, 4	tetradecyl	C2	BTeA-C14 (4BC)	NS	NS	-	NS	-	-	162
Benzene	Amide, 5	tetradecyl	C1	BPA-C14 (5BC)	10 (180°C ■)	15 (160°C)	-	-	-	-	162
Benzene	Amide, 6	tetradecyl	C6	BHA-C14 (6BC)	NS	NS	-	NS	-	-	162
Pyrene	Amide, 4	tetradecyl	C2	PTeA-C14 (4PC)	7.4 (120°C ■)	2.6 (120°C, 0.1 Hz)	<200	-	-	-	162
Hexaphenyltriphenylene	Amide, 6	tetradecyl	C3	HppHA-C14 (6TP)	? (leakage, 240°C ■)	40 (240°C, 1 Hz)	<312	-	-	-	162
Tetraphenylporphyrin	Amide, 4	Tetradecyl	C4	TppTeA-C14	10 (230° ■)	2 (230°C, 0.1 Hz)	<290	-	-	-	156
4-helicene, racemic	Amide, 2	tetradecyl	C2	HeBA-C14 (<i>Rac</i> -1)	25, 111 (70°C, 150°C ■)	20 (70°C, 150°C 0.5 Hz)	<151	-	-	-	155
4-helicene, chiral	Amide, 2	tetradecyl	C2	HeBA-C14 (<i>P</i> -1)	NS	NS	<138	NS	-	-	155
4-helicene, racemic	Ester, 2	tetradecyl	C2	HeBE-C14 (<i>Rac</i> -2)	NS	NS	<63	NS	-	-	155
4-helicene, chiral	Ester, 2	tetradecyl	C2	HeBE-C14 (<i>P</i> -2)	NS	NS	<51	NS	-	-	155
tetraphenyl-ethylene	Amide, 4	tetradecyl	C2	TTeA-C14 (4TPE)	NS	NS	-	NS	-	-	33,153

Core	Dipolar groups, no.	Tail	Symmetry	Material***	P_r , mC/m ²	E_c , V/ μ m	OTR; MP, °C	Retention, s*	LS d_{33} , pm/V	SS d_{33} , pm/V	Ref.
Naphthalene	1,2,3-triazole, 3	3,4,5-tris(octyloxy)phenyl	C2	1,2,3-triazolyl naphthalene	16.2 (105°C ■)	30 (105°C)	105–120	-	-	-	145
Triazine	1,2,3-triazole, 3	3,4,5-tris(decyloxy)phenyl and others	C3	tris(triazolyl)-triazine (TTT)	NS	NS	<150	NS	-	-	146
Triazine	1,2,3-triazole, 3; ester, 3	3,4,5-tris(decyloxy)phenyl and others	C3	tris(triazolyl)-triazine (TTT)	NS	NS	<150	NS	-	-	146
Phthalonitrile, -C ₂ H ₄ -linker	Phthalonitrile, 4; amide, 8	3,4,5-tris[(4'-dodeccan-1-yloxy)benzyloxy]phenyl	C4**	PN-C2 (2a)	17 (120°C ■)	0.23 (120°C)	<140	>6·10 ⁴ (60°C, SHG)	-	-	34
Phthalonitrile, -C ₃ H ₆ -linker	Phthalonitrile, 4; amide, 8	3,4,5-tris[(4'-dodeccan-1-yloxy)benzyloxy]phenyl	C4**	PN-C3 (2b)	NS	NS	NS	NS	-	-	34
Phthalonitrile, -C ₂ H ₄ -linker	Phthalonitrile, 4; amide, 8	3,4,5-tris(dodecyloxy)phenyl	C4**	PN-C2 (1a)	NS, polarized	NS	NS	NS	-	-	34
Phthalonitrile, -C ₃ H ₆ -linker	Phthalonitrile, 4; amide, 8	3,4,5-tris(dodecyloxy)phenyl	C4**	PN-C3 (1b)	NS	NS	NS	NS	-	-	34

* El. – electrical measurement in capacitor devices; SHG – second harmonic generation. NS – non-switching or paraelectric. ‘-’ – no information.
 ** Individual molecules are C2 symmetry, while supramolecular umbrellalike layer is C4 symmetry with 8 amide and 4 phthalonitrile moieties.
 *** The original material code used in the cited articles is given in brackets.
 Device preparation and typical layer thickness: ● – spin-coating, <1 μ m; ◆ – drop-casting, <3 μ m; ■ – melt-filled liquid-crystal cell, $\geq$ 5 μ m; ♦ – bulk ceramics or (single-)crystal, $\geq$ 5 μ m.
 OTR – operating temperature range; MP – melting point

6 Conclusions

Self-assembling columnar materials enrich the field of organics due to their high-level hierarchical ordering that is facilitated by non-covalent interactions, which brings strong advantages when it comes to efficient charge transport or stable ferroelectric switching. Low toxicity, easy-processability, softness and flexibility along with the possibility of self-healing are additional highly valued properties that might eventually lead to their use in lightweight, conformable, disposable or even implantable electronics. Owing to their typical core-shell architecture, self-assembling discotics provide several pathways for molecular engineering of ferroelectric materials, simply by variation of the structural units: the (flat conjugated) core, the rotatable dipolar (hydrogen-bonding) motifs and the solubilizing peripheral tails. Many examples of different core-dipole-tail combinations are presented in this thesis pointing their advantages and shortcomings that are put in context of other organic and inorganic systems.

Small-cored (*e.g.* benzene) molecules, with the notable example of BTA (benzene-trisamide), result in textbook ferroelectric materials that can be used as model systems to understand the behaviour of the whole class of practical – polycrystalline ferroelectrics. First, we systematically pursued tuning of the molecular structure of BTAs to achieve strong and stable ferroelectric response. This was achieved by a very simple chemical structure modification – changing the peripheral tail substituents. The whole saga of BTAs started with the long-tailed BTA-C18 (corresponding to C_nH_{2n+1} alkyl chain) hoping for good solubility and strongly expressed liquid-crystalline properties. However, sparse molecular packing and highly mobile bulky tails limited the achievable dipole density, operational temperature window and stability of the polarization state. Gradual shortening of these linear alkyl tails from C18 to C12, C10, C8 and C6 led to a continuous increase in remnant polarization through a boosted dipole density, and a concomitant growth of the coercive field as well as the depolarization activation energy. The polarization retention for the shortest homologues reached several months at room temperature as compared to several minutes for BTA-C18. XRD-based techniques suggested not only a tighter molecular/columnar packing but also a lower disorder in the shorter-substituted materials, which the significant improvement in ferroelectric characteristics was attributed to.

The hypothesis was confirmed by the following study where linear tails were changed for branched substituents. Though having the same packing parameters as their linear analogues, branched-tailed materials demonstrated remarkable improvement in polarization retention of

2–8 orders of magnitude. This polarization stabilization could not be explained by electrostatic interactions nor by intermolecular steric hindrance, as studied by DFT/MD simulations. Hence, a significantly improved quality of the supramolecular nanostructures via activated and strengthened self-assembly, which has been known from previous studies in diluted solutions, was accepted as the underlying effect. This way, devices with no measurable depolarization in a wide temperature range were obtained, which could be extended by blending of certain linear and branched materials.

Having confirmed the practical usefulness of the BTAs, we demonstrated how the well-defined nanostructure of these self-assembling materials can be used to revive classical theoretical models, namely, the Preisach theory for ferroelectrics. Due to their tightly packed columnar ordering and clear nanoscopic switching mechanisms, BTAs can be imagined as a sum of ‘hysterons’ – the primitive ferroelectric particles that were hypothesized by F. Preisach back in 1935. Due to the electrostatic interactions between these hysterons, their energetic state is strongly coupled to their environment. The resulting energetic variation leads to a (typically Gaussian) distribution of the energetic states of these hysterons which can be measured experimentally if corrected for the probing conditions like field sweeping frequency, temperature, etc. We showed that in this case, the size distribution of the critical nuclei can be extracted. This distribution not only corresponds to the distribution in macroscopic coercive fields, but also leads to the dispersive polarization switching kinetics. We measured the polarization switching time for different sections of this hysteron distribution and found that ‘large’ hysterons lead to (quasi-exponentially) slower polarization switching. What is more, if ‘small’ hysterons were available, the switching was fast no matter how large the section of the distribution was probed. The ‘availability’ of hysterons was varied via turning them on/off by pre-switching them opposite to/to the probing polarity. This switching governed by the smallest available domains clearly indicated the nucleation-limited switching that previously has been shown to underly the operation of most of the (real) polycrystalline ferroelectrics. The underlying theoretical models and their alternatives were introduced and briefly discussed in this thesis. The resulting experimentally obtained log-normal distribution of characteristic nucleation times can be used to reproduce the switching dynamics in many ferroelectric systems including, but not limited to, BTAs and P(VDF:TrFE). The conclusions of the study may also provide guidelines for material engineering aiming to conventional as well as multi-bit memory applications.

Ferroelectric materials are also pyroelectric and piezoelectric because of the sensitivity of the constituting dipoles and/or their packing to temperature and mechanical deformations. It is therefore unsurprising that, being a proven ferroelectric, BTA is piezoelectrically active. Yet, in strong distinction with inorganic and other small molecular organic materials, BTAs are characterized by negative small- and large-signal longitudinal piezoelectric constants $d_{33} < 0$. This behaviour was previously observed only in two-phased materials like the semi-crystalline P(VDF:TrFE) and is based on the dimensional effect. The model considers the dipole density to be governed by the easily and anisotropically deformable (soft, amorphous, disordered) matter and not by the comparatively stiff rigid (ordered) ferroelectric phase. We show that in macroscopic devices BTAs satisfy the conditions of this effect, which also explains a clear linear increase in large-signal d_{33} for higher disorder values. Interestingly, a strong strain amplification is seen in the strain-field loops around the coercive fields regardless of the underlying mechanism – linear piezoestriction for short-tailed homologues or quadratic Maxwell stress for longer-substituted molecules. This can be explained by weakening of the hydrogen bonded network at the randomized polarization (coercive) point that leads to a gradual decrease in mechanical stiffness (=Young's modulus) and thus boosted electromechanical response. Piezoelectric applications that require flexibility would certainly profit from the comparatively high figures of merit of BTAs for actuation and energy harvesting and the possible self-healing ability.

Introducing semiconducting properties in ferroelectric materials is a leap forward from the starting point of conventional piezo/pyro/ferroelectricity. Though well-known among inorganics, semiconducting ferroelectrics are a rarely discussed topic when it comes to organic molecular materials. The previously introduced core-shell molecular design, where different functionalities can be put together in a single molecule like in a jigsaw puzzle, can be employed to yield ferroelectrically switchable materials with large conjugated cores that promote one-dimensional charge transport through the channel in the centre of the self-assembled molecular stack. As a result, unprecedented asymmetric interface/bulk conductivity can be achieved leading to resistive switching that satisfies many of the high requirements for the non-volatile memory arrays.

The celebrated multifunctionality of these self-assembling molecular materials that is also accompanied by high performance levels highlights their uniqueness in the field of materials science and potential for applications in plastic electronics. Their utilization possibilities range from various sensors to actuators, not excluding non-volatile memory devices or even

anomalous photovoltaics. It is clear that, based on the multitude of possible molecular designs, more studies must be carried to unravel the practical usefulness and pursue structural optimization of these materials.

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[§] “Fadder” is an assigned peer student to a newly arrived member at Swedish universities.

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