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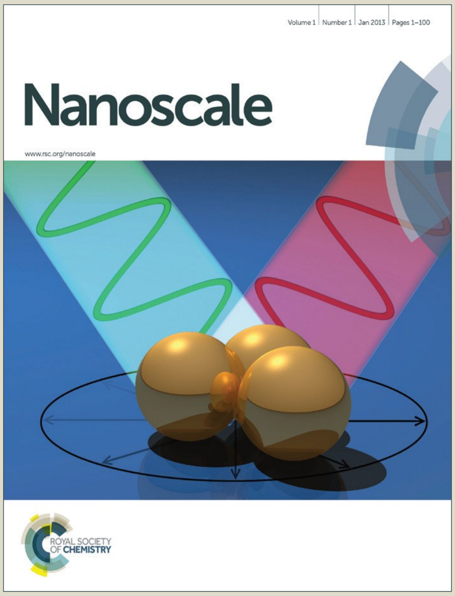

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An Organic Approach for Nanostructured Multiferroics

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Abstract

Multiferroics are materials that simultaneously exhibit more than one ferroic order parameters, such as ferroelectricity, ferroelasticity and ferromagnetism. Recently, multiferroicity has received a significant revival due to the colossal magnetoelectric coupling effect for the development of nano-ferronics. In this mini-review, we focus on the recent study of ferroelectricity, magnetism and magnetoelectric coupling within the newly discovered organic charge-transfer complexes. A systemic understanding on the origin of organic ferroelectricity and magnetism is provided. Furthermore, based on the recent mechanism of magnetoelectric coupling effect: spin-ordering-induced electric polarization and ferroelectricity-induced spin alignment, we further present a recent progress of organic charge-transfer multiferroics and metal-organic framework multiferroics. The coexistence of polarization and magnetism at room temperature of organic charge-transfer complexes will be critical for the development of all-organic multiferroics.

1. Introduction

In 1894, Pierre Curie predicted that the magnetoelectric coupling (ME) effect could occur in certain classes of materials, known as multiferroics, which was confirmed later in chromium oxide (Cr_2O_3) compound.[1, 2] Multiferroicity has recently received a significant revival (Fig. 1), due to its potential to add new functionalities into electromagnetic devices, and its ability to couple magnetic and electric order parameters. Striking examples include inorganic $BiMnO_3$[3-6] and $BiFeO_3$[7-12] compounds, as room-temperature multiferroic materials. They exhibit a spontaneous polarization and magnetic moment at room temperature, where the *d* electrons of transition metal (Fe, Mn) contribute to the ferromagnetism and the lone-pair 6*s* electron of Bi ions induced interaction between Bi ions and O ions drives the lattice off-central symmetry for ferroelectricity.[11-13] The discovery of the magnetoelectric effect in manganite, such as $TbMnO_3$[14], $GdMnO_3$[15, 16], $MnWO_4$[17-19] and $Ni_3V_2O_8$[20], has also paved a way towards a new family of non-collinear multiferroic manganites, where the spiral moments induce polarization through spin-orbit coupling due to the Dzyaloshinskii–Moriya effect.[21-25] In addition, collinear multiferroic structures do not require the presence of spin-orbit coupling, where these materials are based on their magnetostriction effect, such as $HoMnO_3$[26, 27] $YMnO_3$[28, 29] and $RMnO_5$[30] (R is a rare earth ion). The ferroelectricity is originated from the Mn sites that are inequivalent by the crystallographic structure: a magnetically driven spontaneous distortion that makes bonds unequal and breaks inversion symmetry.

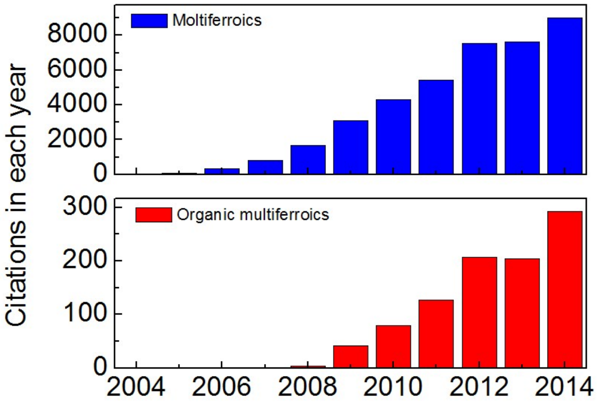

Figure 1. The citation trend of multiferroics and organic multiferroics in the last

decade (The data is obtained from Web of Science).

In addition to the inorganic counterparts, it should be noted that organic multiferroics have been attracting significant interests, due to their low temperature solution processing for the fabrication of all-organic multifunctional smart materials.[31-33] Recently, room temperature ferroelectricity, magnetism and magnetoelectric coupling have been shown in organic charge-transfer complexes,[34, 35] where a supramolecular design allows the electron donor and acceptor molecules to assemble into the ordered charge-transfer networks for room temperature ferroelectricity. For example, the charge-transfer crystals between a pyromellitic diimide-based acceptor and derivatives of pyrene-based donor show a polarization as high as 6 μC/cm^2 under 10 KV/cm electric field.[35] Moreover, room temperature magnetism has also been shown in the crystalline charge-transfer complexes.[36-40] The coexistence of ferroelectricity and magnetism in metal-organic frameworks further enrich the area of organic multiferroics.[41-49] In this mini-review, we present the recent understanding of ferroelectricity, magnetism and magnetoelectric coupling within organic charge-transfer complexes. The unique characteristics of organic multiferroics could further enable the structural and external field stimuli control. In the following, we begin with the review on the strategies for the development of organic ferroelectricity and magnetism, and then proceed with the analysis of the magnetoelectric coupling effect of organic multiferroics.

2. Organic ferroelectricity and magnetism

Ferroelectric materials are of importance and interest in both fundamental scientific research and technological applications. Compared to their inorganic counterparts, organic ferroelectrics represent a new family of molecule-based crystals resulted from the emerging field of molecular electronics with non-uniform microscopic origin of electrical polarization. In general, ferroelectrics have been classified into two different types: displacement transition and order-disorder transition.

2.1 Molecular ferroelectrics

One type of molecular ferroelectrics is based on the halogen family compounds, such as diisopropylammonium bromide[50, 51] and diisopropylammonium chloride,[52] which exhibit a spontaneous polarization of 23 μC/cm^2 (Curie temperature of 426K), remarkable piezoelectric response, low dielectric loss and well-defined ferroelectric domains. As shown in Fig. 2a, the emergence of the spontaneous polarization is driven by a cooperative atomic distortion at molecular sites that break the mirror symmetry plane of each single diisopropylammonium bromide molecule, resulting in an asymmetric arrangement of the charges. To confirm the existence of spontaneous polarization, ferroelectric hysteresis loops are measured under different temperatures, as shown in Fig. 2b. In addition, temperature dependent dielectric constant confirms that the transition temperature is above room temperature in these molecules, while low frequency is beneficial for the improvement of dielectric constant (Fig. 2c). Moreover, the entropy transitions between paraelectric and ferroelectric (Boltzmann's formula $\Delta S = R\ln N$) are comparable for both diisopropylammonium bromide and diisopropylammonium chloride, where S entropy and R universal gas constant, being of the order of 1.43 J mol^{-1} K^{-1} (diisopropylammonium bromide) and 1.14 J mol^{-1} K^{-1} (diisopropylammonium chloride), [51] respectively, which is much smaller than two-site position model (displacement phase transition 5.76 J mol^{-1} K^{-1}). Therefore, the order-disorder transition contributes to the main origin of the spontaneous polarization in the halogen family compounds.

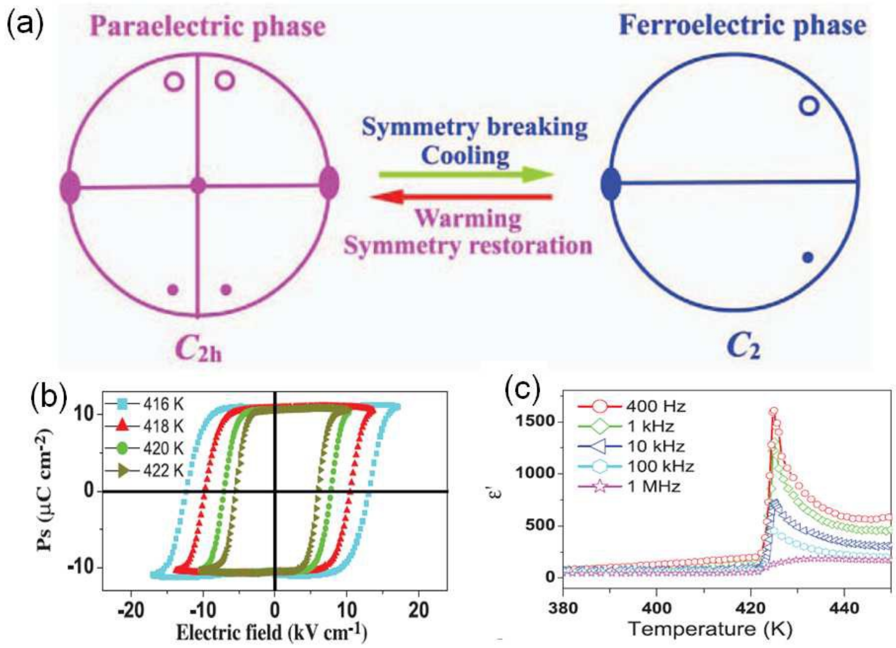

Figure 2. (a) Schematic figure of the order-disorder phase transition. (b) Ferroelectric hysteresis loops of diisopropylammonium bromide under different temperature. (c) Temperature dependent dielectric constant under different frequencies. Reproduced from reference[50] with the permission of American Association for the Advancement of Science.

2.2 Organic charge-transfer ferroelectrics

The second type of organic ferroelectrics is based on the charge-transfer complexes, such as lock arm supramolecular ordering (LASO),[35] tetrathiafulvalene-p-chloranil (TTF-CA)[53-55] and tetrathiafulvalene-2-bromo-3,5,6-trichloro-p-benzoquinone.[56] Within the LASO systems, the structure of acceptor (1) and donor (2, 3 and 4) are shown in Fig. 3a. The assembly of acceptor and donor by non-covalent bonding interactions: π-π stacking, hydrogen-bonding and van der Waals forces contribute to the formation of supramolecular charge-transfer complexes, as shown in Figs. 3b-3d. Interestingly, room temperature ferroelectric polarization measurements reveal the spontaneous polarization of these three donor-acceptor complexes. As shown in Fig. 4, for the complexes of 1·2, 1·3 and 1·4, the remnant polarization (P_r) exceeds 1μC/cm^2. At a low temperature, the saturation polarization for the complex 1·4 was remarkably large and the remnant polarization for this supramolecular crystal was found to be approximately as high as 55 μC/cm^2 under 10 KV/cm applied electric field, which is much larger than that of the complexes 1·2 (5 μC/cm^2 under 10 KV/cm) and 1·3 (6 μC/cm^2 under 10 KV/cm). Within the stacked charge-transfer LASO, the ionicity is characterized by measuring the extent of electron transfer to investigate how its magnitude influences ferroelectric behavior. At room temperature, the ionicity for LASO complexes 1·2, 1·3 and 1·4 (the crystals shown in Figs. 3b–d) are 0.68, 0.89 and 0.43, respectively (non-ionic state with 0.5 ionicity value). Therefore, both the donor-acceptor dimerization induced structural non-symmetry and electron transfer resulted ionic states lead to ferroelectricity within these stacked charge-transfer polar crystals. In organic charge-transfer TTF-CA ferroelectrics,[53-55] a partial electron transfer between the TTF and CA molecules and the symmetry along the stacking axis broken due to the formation of weakly bound TTF-CA dimmers both contribute to the origin of ferroelectricity, exhibiting a polarization of 8 μC/cm^2.[53]

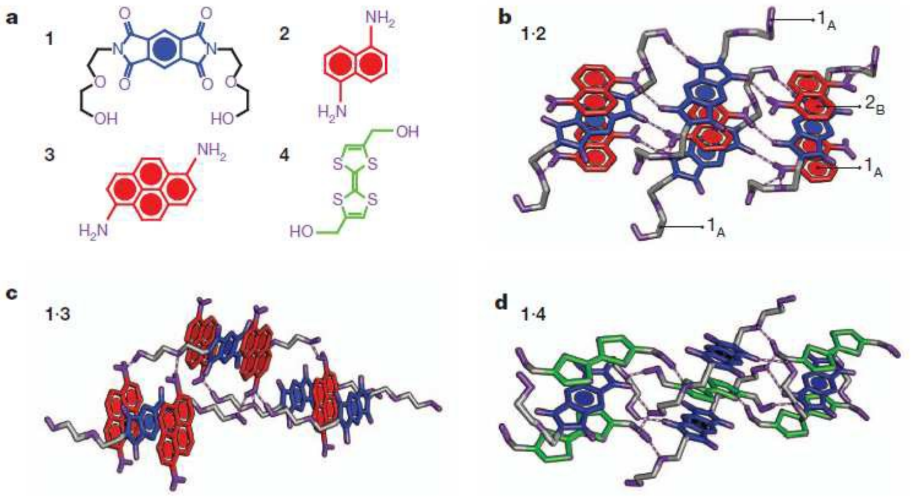

Figure 3. (a) Structural plot of electron donor (2, 3, 4) and acceptor (1) molecules. Compound 1 is a pyromellitic diimide. Compounds 2 and 3 are aromatic electron donors. Compound 4 is tetrathiafulvalene derivative. (b), (c) and (d) are combination of 1·2, 1·3 and 1·4, respectively. Reproduced from reference [35] with the permission of Nature Publishing Group.

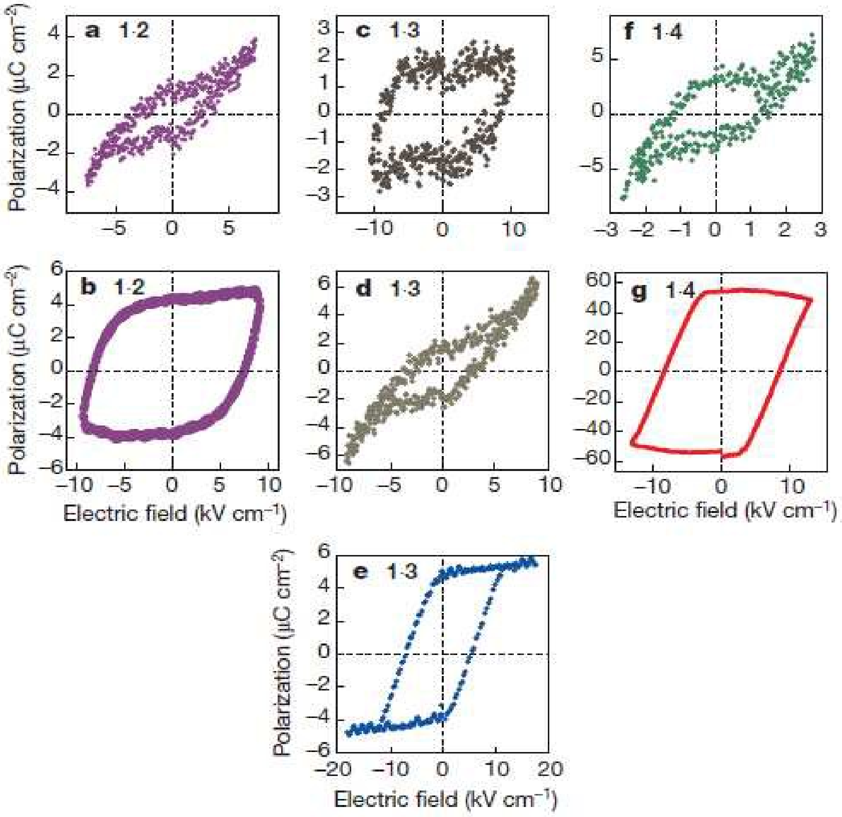

Figure 4. (a) and (b) are the polarization versus electric field curves for LASO complexes 1·2 at 300 K and 74 K. Complex 1·3 at 300 K (c, d) and 7 K (e), and complex 1·4 at 300 K (f) and 7 K (g). Reproduced from reference[35] with the permission of Nature Publishing Group.

2.3 Metal-organic framework ferroelectrics

Metal-organic frameworks (MOFs), such as $[NH_4]M(HCOO)_3$[46, 57] and $[(CH_3)_2NH_2]M(HCOO)_3$,[45, 58-61] M=Zn, Mn, Fe, Co and Ni, have shown the promising spontaneous polarization due to their order-disorder transition. Under order-disorder transition, the ammonium (or dimethylammonium) cations change from a disordered state of high-temperature phase to an ordered state of low-temperature phase. It is notable that the NH_4^+ and $(CH_3)_2NH_2^+$ ions form hydrogen bonds to the O atoms of the metal formate framework. The NH_4^+ ($(CH_3)_2NH_2^+$) cations exhibit the displacive shift at 110 K, which is thought to be closely related to the low-temperature polar structure and its origin of ferroelectricity. The entropy change of NH_4^+ and

$(CH_3)_2NH_2^+$ based MOFs are 2 J mol^{-1} K^{-1}[57] and 0.9 J mol^{-1} K^{-1}[45], respectively, which suggest the main contribution of ferroelectric transition from the order-disorder transition. More details on the ferroelectricity of MOF structures have been reviewed by Xiong *et al.*[62, 63]

2.4 Polymeric magnets

Since the discovery of quasi-one-dimensional organic superconductors and conductors, low-dimensional conjugated polymer systems have attracted much interest. Several organic ferromagnets have been reported in the past with a low Curie temperature (10 K), such as poly-BIPO,[64-67] pyro-PAN[68] and macrocyclic S=2 combined cross-linking S=1/2 organic polymers.[69] Although many attempts have been made to synthesize new organic ferromagnets, it is still challenging to understand the origin of ferromagnetism in these polymeric materials. Particularly, the existence of transition-metal impurities during the synthesis could enable the magnetic properties from strong correlation between localized *d* electrons.

Within the poly-BIPO system, the magnetism has been achieved by Ovchinnikov *et al*[64] and Cao *et al.*[67] The main zigzag chain consists of carbon atoms, and the side radical contains an unpaired electron. In order to illustrate the magnetic properties of poly-BIPO, the π electrons along the main carbon chain were treated as an antiferromagnetic spin distribution, which is based on the assumption that there are antiferromagnetic interactions between the main chain π electron spin and the residual spin of radical. All of the residual spins of the radicals tend to form ferromagnetic spin chain, which plays an important role in the ferromagnetic order in this kind of material. Another type of organic magnets is the macrocyclic S=2 combined cross-linking S=1/2 polymer.[69] This type of polymer is designed with a large density of cross-links and alternating connectivity of radical modules with unequal spin quantum numbers, macrocyclic S=2 and cross-linking S=1/2 modules, which permit a large net spin polarization through exchange coupling between the modules.

2.5 Fullerene based ferromagnets

Since the discovery of fullerene based charge-transfer complex tetrakis(dimethylamino)ethylene-C_{60} (TDAE-C_{60}),[70-76] π-electron ferromagnetism of carbon materials has shown the ordering transition temperature towards the ferromagnetic state T_C = 16 K. Significant progress has been occurred in the understanding of structural, magnetic and electronic properties in this fullerene based charge-transfer magnets. The magnetism disappears when the electron acceptor C_{60} is replaced by C_{70},[77] while the replacement of TDAE by another electron donor (cobaltocene) results in a similar magnetic property. Ferromagnetism below 19 K in a cobaltocene-doped fullerene derivative was shown due to the unpaired spins within fullerene molecules,[78] which has been confirmed by using electron spin resonance technique.[75] The merohedral disorder of C_{60} molecules gives rise to the distribution of localized spin order of C_{60} molecules, leading to the ferromagnetism in the TDAE-C_{60} complex. In addition to the C_{60} based charge-transfer ferromagnetism, hydro-fullerene,[79-82] defective fullerenes[83] and polymerized fullerenes under the pressure of oxygen[84] could also induce magnetism. After the oxidation or hydrogenation of fullerenes, the excess spin is delocalized within the host fullerene to promote spin exchange interaction and spin alignment, which acts as the magnetic origin of the oxidized or hydrogenated fullerenes molecules.[79] The other effective method for inducing the magnetism of C_{60} molecules is based on the partially opened intermediate fullerene cage structures. A zigzag arrangement of edge atoms in the defective fullerene cage creates the dangling bonds, which lead to magnetic stabilities in isolated molecules and magnetism in the solid.[83]

3. Organic multiferroics

3.1 Organic multiferroics based on spin induced polarization

In 2010, one-dimensional organic charge-transfer magnetism, tetrathiafulvalene-p-bromanil (TTF-BA), is reported and its structure is shown in Fig. 5a and 5b.[41] Due to its spin-peierls instability (spin-lattice interaction), the polarization could be induced under its Curie temperature (53 K). The magnetic hysteresis (M-H) loops and polarization measurements further confirm the multiferroic properties of this donor-acceptor complex (Fig. 5c). It should be noted that TTF-BA is different from organic charge-transfer tetrathiafulvalene-p-chloranil ferroelectrics (TTF-CA, as mentioned in Section 2.2). In comparison to the ferroelectricity observed in TTF-CA, the TTF-BA complex shows a coexistence of spontaneous ferromagnetism and ferroelectricity under Curie temperature, where the potential magnetoelectric coupling has been studied in TTF-BA.[41] In addition, the TTF and BA molecules are always ionic states within TTF-BA systems, while the TTF-CA complex has a neutral-ionic states transition at the temperature of 84 K[85]. If the ferroelectricity originates from the spin-peierls instability, the polarization should vanish when the singlet state is suppressed by a magnetic field. These characteristics indicate a breakdown of the singlet state at one critical magnetic field (56 T). As shown in Fig. 5d, the polarization at 50 K and 52 K is almost extinguished around external 56 T magnetic field due to the singlet suppression induced disappearance of donor-acceptor dimerized ferroelectricity. At lower temperatures, polarization does not vanish up to 56 T and the partial suppression is still obvious at 40 K. Therefore, the donor-acceptor dimerized ferroelectricity is primarily due to the spin-peierls instability, which has been further confirmed by theoretical simulation.[86]

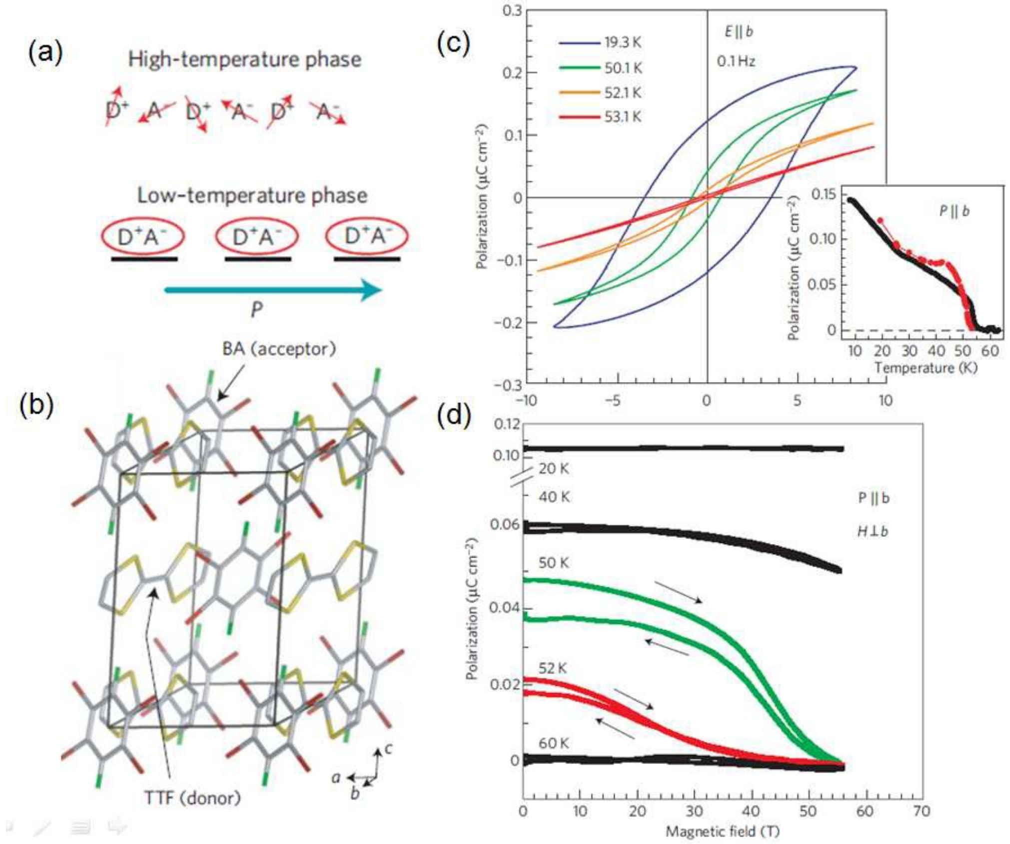

Figure 5. (a) Schematic structure of ionic donor (TTF) and acceptor (BA) mixed stacks in high and low temperature. P denotes electric polarization. (b) Crystal structure of TTF–BA. (c) P-E loops of TTF-BA under different temperature, the inset shows temperature dependent polarization. (d) The tunability of polarization by magnetic field. Reproduced from reference[41] with the permission of Nature Publishing Group.

Besides TTF-BA charge-transfer multiferroics, another organic multiferroics of spin-driven polarization is the crystalline thiophene-C_{60} charge-transfer complex. By utilizing supramolecular assembly strategy to build electron donor thiophene and acceptor C_{60} co-crystals, room temperature magnetism and spontaneous polarization were observed, as shown in Fig. 6.[36, 38] By transferring electrons from thiophene nanowire to C_{60}, ferromagnetism is possessed due to the crystalline thiophene nanowire structure induced unpaired spin alignment. In addition, through charge-transfer dissociation, light illumination induced unpaired spin within thiophene nanowires could result in an enhanced magnetization. To confirm spin induced polarization of thiophene-C_{60} complex, an external magnetic field is applied to tune the ratio between singlet and triplet charge-transfer states due to their small exchange interaction.[87-90] The applied magnetic field could induce less spin mixing, which leads to more triplet charge-transfer[88, 89] to translate into triplet excitons subsequently.[69, 70] Triplet excitons (dipoles) could contribute to the ferroelectric polarization of charge-transfer complex due to their long lifetime (~μs).[91, 92] Therefore, thiophene-C_{60} and TTF-BA charge-transfer complexes present a similar phenomenon that ferroelectric polarization could be tuned by external magnetic field. The magnetoelectric coupling within these two charge-transfer complexes is based on the spin-driven polarization. As a comparison, thiophene-C_{60} charge-transfer complex is a type of excited states (charge-transfers or excitons) dependent magnetoelectric material, while TTF-BA is a lattice dependent magnetoelectric material (spin-peierls instability derived lattice displacement).

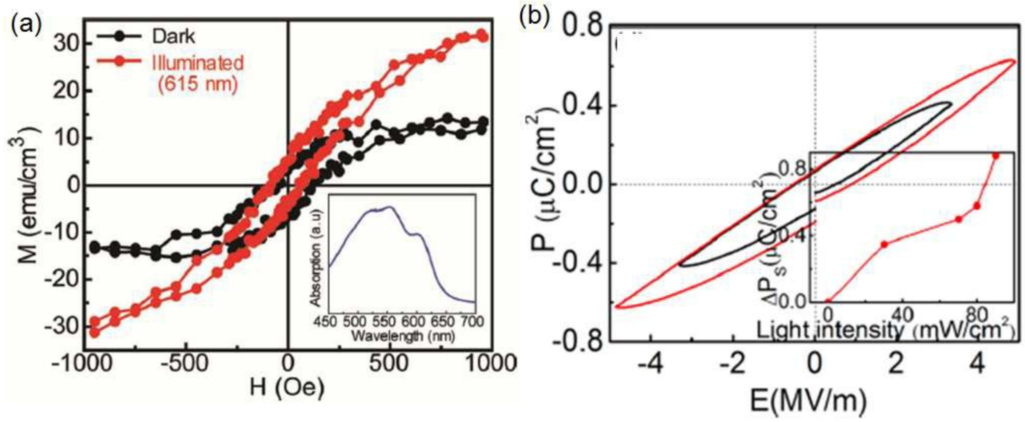

Figure 6. M-H loops (a) and P-E loops (b) of thiophene nanowire-C_{60} charge-transfer multiferroics. Reproduced from references [36, 38] with the permission of Wiley-VCH and American Chemical Society.

3.2 Organic multiferroics of charge order induced magnetism

In organic charge-transfer salt, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, where BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene, multiferroic properties could be observed under Curie temperature (25 K).[42] Within the charge-transfer salt, the electric dipoles are disordered at high temperatures with net overall polarization below T_c= 25 K (Fig. 7a). The dipoles fluctuating within the dimers at T> T_c and cooperatively locking into one molecule at T< T_c provides the origin of order-disorder type ferroelectricity, which has been confirmed through temperature dependent dielectric constant and ferroelectric hysteresis loops (Fig. 7b). The magnetism arises from the spins locating on a single dimer. The spins on average show no alignment at the center of the dimmers (T> T_c, the right schematic of Fig. 7a). However, long-range ferroelectricity implies the collective off-center positioning of spins within the dimers below T_c drive magnetic ordering (the left schematic of Fig. 7a). In contrast to the spin derived polarization systems (as discussed in Section 3.1), external magnetic field could not tune the polarization and dielectric constant of this charge-transfer salt κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl even when applying 9 T magnetic field.

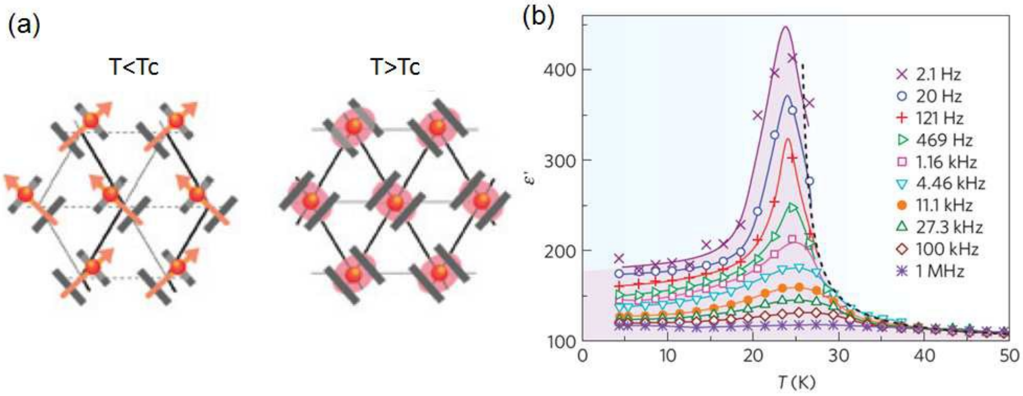

Figure 7. (a) Schematic drawings for temperatures below and above Tc of organic charge-transfer salt κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. (b) Temperature dependent dielectric constant under different frequency. Reproduced from reference[42] with the permission of Nature Publishing Group.

3.3 Metal-organic framework multiferroics

The magnetic and electric properties of MOFs start to draw much attention, because magnetic and ferroelectric orders could be achieved in single-phase MOFs.[46,]

[47, 93] In addition to the coexistence of ferroelectricity and ferromagnetism, the coupling between magnetic and electric orders is more important for the development of multiferroic MOFs. A strong magnetoelectric coupling has been achieved in $[(CH_3)_2NH_2]Fe(COOH)_3$.[43, 48] The structure of this Fe-MOF is shown in Fig. 8a, while magnetoelectric coupling effect is defined as $\Delta M/M=[M(0)-M(E)]/M(E)$, where E is electric field and M is magnetization, which is presented in Fig. 8b. In this Fe-MOF structure, Fe ions are connect with dimethylammonium cations through hydrogen bond to form the Fe–O–C–(O···HN)–Fe connections, where the ferromagnetism results from the long distance superexchange interaction between Fe ions.[94] At a high temperature, the hydrogen bonds are dynamically disordered, while the hydrogen bonds start to become ordered upon cooling below T_C. When an electric field is applied, the dipoles of hydrogen bonds tend to align along the direction of the electric field below T_C. As more hydrogen bonds are aligned along one direction, the superexchange interactions are blocked by hydrogen bonding, which results in a significant tunability of magnetization by external electric field, as shown in Fig. 8b.

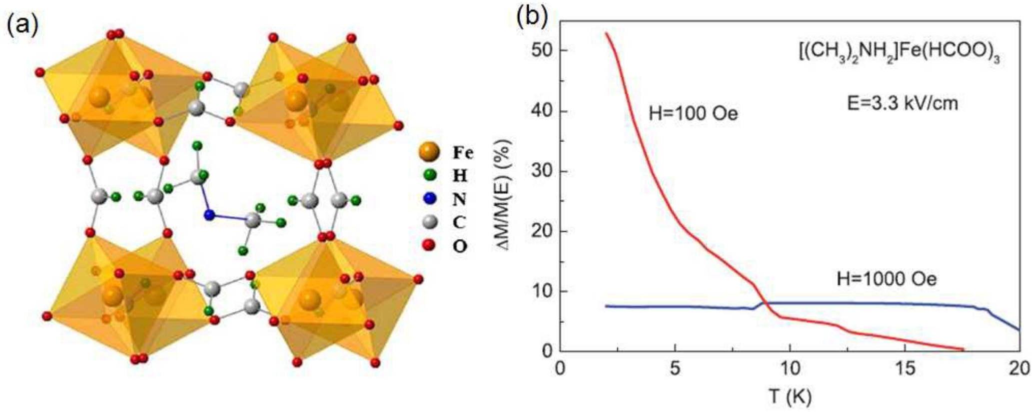

Figure 8. (a) Molecule structure of Fe-MOF. (b) tunability of magnetization by electric field. Reproduced from reference [43] with permission of Wiley-VCH.

In addition to Fe-MOF, a class of multiferroic MOFs, $[(CH_3)_2NH_2][M(HCOO)_3]$ (M= Mn, Co, Ni), was also reported with the magnetic ordering occurred at 8-36 K.[45, 58, 95, 96] In these MOF materials, hydrogen bonded dimethylammonium cations are ordered at temperatures in the range 160-185 K. With a further cooling, these materials become magnetically ordered (8-36 K), which leads to the coexisting ferroelectric and magnetic orders. To further investigate the coexistence of ferroelectricity and magnetism in this type of MOF, the replacement of a hydrogen atoms by a deuterium atoms (D) are allowed to change hydrogen bond strength through tuning N−D stretching modes.[97] In particular, it allowed for the decoupling of N−D stretching modes from the stretching modes of the CH_3 and C−H groups. As a result, different magnetic behaviors between $[(CH_3)_2NH_2][M(HCOO)_3]$ and $[(CD_3)_2ND_2][M(DCOO)_3]$ were observed, which can be attributed to the change of H-bond strength to induce a tunability of superexchange interaction of M–O–C–(O···DN)–M. In addition, by replacing $[(CH_3)_2NH_2]^+$ through $[NH_4]^+$, ferroelectric ordering occurs in the range 190-254 K, with the coexistence of magnetic and electric ordering.[46, 98] Recently, multiferroic ferroelectricity of Cu-MOFs is also observed, such as $(C_2H_5NH_3)_2CuCl_4$,[63,99] $[C(NH_2)_3]Cu(HCOO)_3$,[59,100] $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$[101]. A large remnant polarization of 37 μC/cm^2 is observed at 247 K that is comparable to classical inorganic ferroelectric oxides. The ferroelectric origin of Cu-MOFs is ascribed to the hydrogen-bond induced ordering of organic cations, while the coexistence of ferroelectricity and magnetism is induced by superexchange interactions of hydrogen-bond dependent 3*d* electrons.

4. Conclusion

In this mini-review, based on organic charge-transfer complex and MOF structure, we present the recent progress of organic multiferroics ranging from their ferroelectricity, magnetism and magnetoelectric coupling effect. Organic ferroelectricity contains three types: 1) spontaneous polarization driven by breaking the mirror symmetry plane; 2) dimerization of charge-transfer complexes; 3) spontaneous polarization induced by the order-disorder transition within MOF structures. Organic ferroelectrics have been making remarkable achievements, where room temperature polarization has reached as high as 23 μC/cm^2. However, the development of room temperature organic magnets is still lacking behind. Therefore, the future investigation on the rational design, synthesis and assembly of organic magnets will be critical for the development of room temperature organic multiferroics. Furthermore, several mechanisms of magnetoelectric coupling have been proposed, such as spin-ordering-induced polarization and ferroelectricity-induced spin alignment. The further investigation of these mechanisms will be beneficial for the development of all-organic multiferroics with giant magnetoelectric coupling coefficient.

Acknowledgements

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