Organic donor-acceptor cocrystals for multiferroic applications

Wang, Zongrui; Zhang, Qichun

2020

Wang, Z. & Zhang, Q. (2020). Organic donor-acceptor cocrystals for multiferroic applications. *Asian Journal of Organic Chemistry*, 9(9), 1252-1261.
<https://dx.doi.org/10.1002/ajoc.202000024>

<https://hdl.handle.net/10356/154244>

<https://doi.org/10.1002/ajoc.202000024>

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[a] Dr. Z. Wang, Prof. Dr. Q. Zhang
School of Materials Science and Engineering
Nanyang Technological University
50 Nanyang Avenue, 639798, Singapore (Singapore)
E-mail: qc Zhang@ntu.edu.sg

Abstract: *Cocrystallization strategy has provided an efficient route to fulfill the room temperature magnetoelectricity in single phase due to the long-range ordered π - π stacking (donor-acceptor assembled) network, long-lived excitons (with μ s lifetime), spin orders ($\pm 1/2$ spin) and charge transfer (CT) dipoles in the assembled crystal lattice. Together with the superiorities in cost-effective, easy tailorability, light weight, mechanical flexibility and large-scale integration of organic materials, research direction on organic CT multiferroics has become a rising star. In this minireview, we present the recent progress in the fundamental understanding and designing of multiferroics and highlight the advance of organic CT compounds in exploring the magnetoelectronic (ME) coupling effect ranging from experimental to theoretical investigations. Moreover, the challenges existing in this area are also put forward as well as some perspectives for the future development.*

1. Introduction

Exploration of novel organic multifunctional materials is the eternal theme in organic electronics, due to their indispensable role in advancing the modern engineering to consumer market including electronics, mechanics, and artificial intelligence as well as their remarkable superiorities in excellent molecular designable capability, large-area integration, flexibility and cost-effective processability compared with inorganic materials.^[1-3] In recent years, a burgeoning strategy based on the assembly principle to design/construct the organic multifunctional materials have gained considerable attentions, i.e., cocrystal engineering, which combines two or more different components in the same crystal lattice through noncovalent interactions (charge transfer (CT) interactions, π - π interactions, hydrogen bonds or halogen bonds). It has provided an efficient and versatile strategy towards novel functions including but not limited to the simply assembled properties of constituent units due to the synergistic effects.^[4-6]

Actually, real concerns on this area can be emerged from charge-transfer compounds (CTC), one type of hybrid materials that consist of charge-donating (D) and charge-accepting (A) components with π -electron orbitals, which hold an extremely important position in cocrystal engineering. They were first found to possess the striking tunability of electronic properties ranging from insulator to superconductor. The most famous example should be the first organic metallic cocrystal TTF·TCNQ discovered in 1973, which was assembled with the non-metallic components of tetrathiafulvalence donor and 7,7,8,8-tetracyanoquinodimethane acceptor.^[7] Later, the first organic superconductivity was firstly fulfilled in organic salt (TMTSF)₂PF₆ containing di-(tetramethyltetraselenafulvalene) (D) and hexafluorophosphate (A) units in 1980.^[8] Likewise, CTC strategy is widely applied as a powerful tool to regulate semiconducting

characteristics. For example, cocrystals of (BEDT-TTF)·(TCNQ) were reported in 2004 to exhibit ambipolar charge-transport at low temperature.^[9] Besides the electronic applications, recent investigations also indicated their extraordinary and exciting optoelectronic and photonic properties with the wide applications in photoconductivity,^[10-11] photovoltaics,^[12] nonlinear optics,^[13] white-light emitting,^[14-15] room-temperature phosphorescence^[16] and optical waveguide.^[14] Some excellent reviews have been published to highlight these directions.^[4-6]

Apart from the above-mentioned charming properties in CT systems, very recently, research interests are located at ferroelectric and ferromagnetic behaviors, due to the tunable polar dimerization and spin density waves induced by the long range ordered crystalline DA networks and largely delocalized π -electrons in CT compounds. Several CT systems have been successfully obtained as organic ferroelectrics (e.g. TTF-based CTC)^[17-18] and ferromagnets (e.g. C₆₀-based CTC).^[19-20] Some even show these properties under ambient conditions,^[21-22] which have been systematically presented in several published reviews.^[23-26]

Recently, scientists believe that organic multiferroics would be designed/achieved in CT systems by coupling both ferroelectricity and ferromagnetism, where the exchange interactions resulted from charge-spin coupling and delocalized π -electrons could endow them exhibiting magnetoelectric properties. As a matter of fact, the research focusing on organic multiferroics has only been conducted for 10 years, since the first all-organic multiferroic TTF·BA (BA, *p*-bromanil) was reported experimentally by Kagawa *et al* in 2010.^[27] Even though their fascinating physical properties and significant potential for technology applications, the research on either novel material exploitation or the fundamental mechanisms of organic CT multiferroics are still in the primary stage. However, some innovative and breakthrough researches have been obtained and significantly boosted the development of this field.^[25, 27-37]

Although many other systems such as polymers,^[38a, 38b] covalent organic frameworks (COFs),^[38c] or metal-organic frameworks (MOFs)^[38d-38f] have been demonstrated to show multiferroics properties, we only discuss recent progress in organic donor-acceptor cocrystals for multiferroic applications in this minireview. We begin with a brief description of multiferroics including the definition, history, evolution, significance, category and fundamental research to build a basic knowledge framework on the field, and then proceed with the presentation of the progress in experimental and theoretical investigations on organic CT multiferroics in the past decade. Furthermore, we summarize and describe the representative organic CT multiferroic systems, and a systematic understanding of the origin of magnetoelectronic (ME) coupling is also provided. Finally, we give a brief discussion and put forward the open issues existing in this area and outline some perspectives and the inspiration for the future development.

Scheme 1. Donors and acceptors of organic CT compounds discussed in this review.

Zongrui Wang received her B.S. degree in Chemistry in 2010 from the School of Chemistry and Chemical Engineering at Inner Mongolia University, and then received her Ph.D. from Institute of Chemistry, Chinese Academy of Science in July 2016 under the co-supervision of Professors Huanli Dong and Wenping Hu. After that, she joined the group of Associate Professor Qichun Zhang in Nanyang Technological University as a Research Fellow in October 2016. Her present research interest focuses on organic electronics including the design, assemble technology and optoelectronic properties of organic cocrystals.

Qichun Zhang is an Associate Professor at the School of Materials Science and Engineering and at Nanyang Technological University, Singapore. His research focuses on conjugated rich carbon materials and applications. Currently, he is an associate editor for J. Solid State Chemistry, Advisory board members of Materials Chemistry Frontiers, Chemistry - an Asian Journal, Journal of Materials Chemistry C, and Inorganic Chemistry Frontiers. He also is a fellow of the Royal Society of Chemistry. In 2018 and 2019, he has been recognized as one of highly cited researchers (top 1%) in cross-field in Clarivate Analytics. Till now, he has published more than 346 papers (H-index: 70) and 4 patents.

((Author Portrait))

2. Brief Description of Multiferroics

Multiferroics are species coexisting at least two states of ferroic orders in a single phase such as ferromagnetic, ferroelectric or ferroelastic states, which have aroused great concern due to their fascinating physic-chemical properties and broad application prospects in the past decades. In multiferroic materials, by applying the suitable external driving “forces” (i.e., magnetic field, electric field or mechanical stress), the cross-coupling between the order parameters including the spontaneous magnetization M_s , spontaneous electric

polarization P_s and spontaneous deformation ϵ_s can give extremely wide and interesting properties such as piezo-magnetism, piezo-ferroelectricity, magneto-electric coupling, electrostriction, and magnetostriction (Figure 1a). This field covers many aspects ranging from fundamental research to technological applications including sensors,^[39–40] microwave devices,^[41–42] random access multi-state memories,^[43–44] energy transformation,^[45] thermal energy harvesting,^[46] gyration,^[47] magnetic recording^[48] and solid-state refrigeration.^[49–53] The research interest in multiferroic materials is mainly settled on two aspects: (1) these materials offer an opportunity to exploit functionalities with various orders, like a four-state memory element with both a magnetic bit and an electric bit; and (2) the coupling of different states can induce novel functionalities that might not exist in either state alone, and benefit for the more efficient technologies (e.g., the reduced heat and time waste in the reading and writing process for a magnetic bit instead of the directly-applied magnetic field through the voltage bias).

With so many benefits, therefore, the exploration of novel multiferroic materials retains great significance. Based on this view, it comes to the first envisioned expectation: *what is required to ensure the simultaneous occurrence of multiple-ferroic properties in a single phase?*^[54] Firstly, it mandatorily requires the adequate structural building blocks to generate multiple electrostatic potential wells to allow ferroelectric-like ionic motion. Meanwhile, the paramagnetic ions are also desirable to ensure the efficient ionic shift and magnetic coupling (e.g., Ni in nickel boracites). Besides, the magnetic interaction pathways should be guaranteed to permit the direct exchange or super-exchange interactions.^[55–56] Secondly, it needs the simultaneous breaking of the spatial-inversion and time-reversal symmetry, which is intimately related to the co-existence of ferroelectricity and ferromagnetism. However, in the early trial, the materials satisfying these conditions are rare. Even on the theoretical level, only 11 groups among 122 Shubnikov-Heesch point groups possibly allow a simultaneous M_s , P_s and ϵ_s in the same phase.^[57]

Nowadays, the scope of multiferroics has been expanded to the inclusion of antiferroic order and the current trend has excluded the ferroelasticity, where it is always referred to the magnetoelectric multiferroics with the simultaneous ferroelectric and magnetic states in single- or multicomponent materials. Although the pioneering work in this area can be traced back to 1950s,^[58] the surge of research interests has been frustrated for over half of a century because of the theoretical “ d^0 vs d^n ” problem” obstructing the ferromagnetism and the ferroelectricity in perovskite structure materials. Normally in these materials, people believe that “ d^0 ” favors ferroelectricity, while it conflicts to the magnetism which needs partially filled d shells.^[51] However, with the exploration of high-quality practical multiferroic materials (especially for the non-collinear multiferroic manganites) and the theoretical framework perfection (such as spin-orbit and spin-lattice coupling) in recent decades, a revival explosion on this area has been appeared.^[59] Generally speaking, the multiferroics can be classified into two types (Figure 1b):^[60] type-I represents that the magnetic and ferroelectric orders occur independently (two orders have different microscopic origins) and type-II describes that the ferroelectric and magnetic transitions emerge jointly (they inhabit strong magneto-electric coupling). Specifically, for type-II multiferroics, the ferroelectricity not only can be caused by a unique type of magnetic spiral, but also appears even for collinear magnetic structure. The explored

multiferroic family can be summarized as several branches based on the driven mechanisms (Figure 1c).^[50]

1). *Lone pair ferroelectricity, d-electron magnetism*, in which materials contain two cations respectively providing ferroelectricity and magnetism, like the prototypical multiferroic BiFeO_3 .^[61]

2). *d^0 ferroelectricity, f-electron magnetism*, the same single component with two-cation materials as the first case, but with the magnetism from *f* electrons and ferroelectricity from d^0 -ness. The leading example is EuTiO_3 .^[62]

3). *Novel ferroelectricity, d-electron magnetism*, where the magnetism relies on the conventional *d* electrons, while the ferroelectricity is induced via an improper route, which includes i) *geometrically driven multiferroics* that the rotations of

coordination polyhedral surrounding the A-site cation can induce the polar distortion, ii) *magnetically induced ferroelectrics* that a centrosymmetric magnetic ordering (such as a spin spiral) can break the inversion symmetry and induce a spontaneous polarization mainly through three routes like inverse Dzyaloshinskii-Moriya (DM) interaction, the Heisenberg-like exchange striction and spin-dependent *p-d* hybridization, and iii) *charge-order driven ferroelectrics* which has been well established in organic charge-transfer complexes that exhibit spin-induced electric polarization or ferroelectricity-induced spin alignment.^[25, 37] Herein, we only give a brief description on the multiferroics since some excellent reviews have elaborately and explicitly present in the overall development of ferroelectricity,^[23-24, 63] ferromagnetism^[26, 56, 64-65] and multiferroics.^[50-51, 53, 66-70]

Figure 1. a) Schematic illustration of possible cross-couplings in multiferroic materials, where P, M and ϵ refer to electric polarization, magnetization and mechanical strain, respectively. Reprinted with permission from Ref.[59]. Copyright Materials Research Society 2017. b) Schematic diagram of two types of magnetoelectric multiferroicity. Reprinted with permission from Ref.[51]. Copyright 2016 Springer Nature. c) Schematic illustration of several representative mechanisms driving the ME coupling in a single phase. Reprinted with permission from Ref.[51]. Copyright 2016 Springer Nature.

3. Organic Multiferroic Complexes

Although substantial achievements on the multiferroics have been witnessed both on scientific research and technological applications in recent decades, the vast majority of studying subjects are inorganic matters. Until very recently, organic cocrystals (or charge-transfer crystals (CTC)), has become a novel force to be reckoned due to their potential in exploiting room-temperature multiferroics and their inherent strengths in cost-effective, easy tailorability, light weight, mechanical

flexibility and large-scale integration.^[25, 28, 71] Organic cocrystals are the complexes that co-assemble charge-donating (D) and charge-accepting (A) components together into ordered one-, two-, or three-dimensional network via noncovalent interactions, inducing unique physicochemical properties beyond the simple sum of properties of constituted components.^[4-6] More importantly, the controllable polar dimerization by the long-range supramolecular ordering interactions and spin density wave within tightly packed CT lattices in CTC has offered a promising pathway to endow them with ferroelectric or ferromagnetic

properties.^[72-73] For instance, the canonical mixed-stack CT system, tetrathiafulvalene (TTF) with halogenated quinones, e.g., TTF-chloranil (TTF-CA), undergoes a ferroelectric phase transition (ionic/ferroelectric phase) owing to the molecular displacement and rearrangement of the molecular-charge distribution along the CT chain.^[24, 74-75] Besides, CT crystals with ferroelectric Curie temperature above room temperature based on a pyromellitic diimide-based acceptor and derivatives of naphthalene-, pyrene- and TTF-based donors have also been developed, which is critical for the practical application.^[76] Moreover, fullerene (C_{60})-based CT complex tetrakis(dimethylamino)ethylene- C_{60} (TDAE- C_{60}) was observed as ferromagnets, where the ferromagnetism could be attributed to the distribution of localized spin order on C_{60} molecules (induced by the merohedral disorder).^[19-20] On this basis, it is also anticipated to couple the magnetic and electric order parameters through CT behavior due to the long-range localized spin and charge ordering.^[77] Since Kagawa *et al* reported the first experimentally all-organic multiferroic CTC (i.e., TTF-BA), in 2010,^[27] the research on organic CT multiferroics has come into the focus for almost ten years. Some intriguing fruits have been made. In the following, we will outline the reported representative organic CT multiferroic systems and identify the origin of ME coupling in these systems.

3.1. Characterization of Multiferroic Properties

To characterize the potential magnetoelectric materials can be but is not limited to the independent polarization (P - E) and magnetic (M - H) hysteresis loop measurements. That's because the co-existence of both properties does not indicate their coupling effect. The best way in principle is through direct methods, that is, recording the variation of polarization under the presence of applied external magnetic field and/or the changes of magnetization with the external applied electric field. Besides, indirect methods can also provide the valid information to determine the characteristics of multiferroic properties, such as, the variation of dielectric property with the magnetic field, the anomalies of magnetic (electric) susceptibility at the Curie temperature for ferroelectric (magnetic) transition, the structural change, the magnetic state characterized from Raman spectroscopy (to characterize the phase transition and symmetry change), nuclear magnetic resonance (NMR, to determine the local structure and dynamics of nonmagnetic and magnetic solids) and electron paramagnetic resonance (EPR, to determine the electronic and magnetic state in the materials), as well as other strategies like theoretical investigation and etc. The specific characterizations could be detailedly explained in the following sections.

3.2. TTF based CT Multiferroics

Considering that TTF-quinone-based system were the earliest and most widely investigated ferroelectric CT complexes, they were regarded as the first potential candidates to possess the simultaneous ferroelectricity and magnetism. On this basis, after ME coupling for TTF-CA was theoretically predicted in 2009,^[78] the first organic CT multiferroic complex TTF-BA was experimentally identified in 2010 (Figure 2).^[27] Different from the traditionally magnetically induced ferroelectric through antisymmetric Dzyaloshinskii-Moriya interaction in inorganic matters, the ME coupling in TTF-BA was based on the spin-lattice coupling (spin-Peierls instability), that is, a one-

dimensional (1D) polarization can be achieved through the dimer-singlet formation of the ionic TTF donor (D^+) and BA acceptor (A^-) when the space group changes from nonpolar (P-1) to polar (P1) under its Curie temperature (T_c) of 53 K (Figure 2b). Specifically, the ionic states of $D^+A^-D^+A^-...$ mixed stacks can be regarded as one dimensional Heisenberg chain with 1/2 spin, which involves the spin-Peierls instability that can host a polar singlet-dimer. The ferroelectricity resulted from the spin-Peierls instability was experimentally verified by the vanished spontaneous polarization with the suppression of the singlet state by a magnetic field and also confirmed by the theoretically simulation.^[79]

Figure 2. a) Upper: schematic structure of ionic $D^+A^-...$ chain with mixed stack in TTF-BA at high- and low-temperature phases. The arrow, underline and ellipsoid denote spin -1/2, a dimer and a singlet state, respectively; Bottom: crystal structure of TTF-BA. b) P - E hysteresis loop of TTF-BA along b axis under different temperatures. Inset: the temperature dependent polarization. c) Magnetic-field-induced transition from the ferroelectric nonmagnetic phase to the paraelectric paramagnetic phase in TTF-BA. Reprinted with permission from Ref. [27] Copyright 2010 Springer Nature.

3.3. C_{60} -based CT Multiferroics

C_{60} -based CTC was one of the most extensively studied organic multiferroic systems, especially in term of the exploration of room temperature multiferroicity. C_{60} -based CT compounds have been widely investigated as the prototypical ferromagnets owing to the strong exchange interaction of unpaired spins within fullerene molecules^[80] and the merohedral disorder.^[19-20] For example, room temperature ferromagnetism was found in hydrogenated C_{60} due to the structure peculiarities with the controllably electron-accepting behaviors of carbon pentagons and hexagons,^[81] and so is the remarkable CT complex of TDAE- C_{60} aforementioned.^[19-20] The Ren group has done lots of explorations on the C_{60} -based organic CT multiferroics.^[29-34, 77, 82] A segregated-stack cocrystal with a long-range ordered CT network based on the electron donor TTF and acceptor C_{60} was observed to display an unusual multitude of external stimuli-controlled ferroic properties, due to the modulation of charge-spin composite orders (Figure 3a, b).^[34] The density of singlet and triplet CT can be tuned by the magnetic field owing to the formation rate of spin-parallel and spin-antiparallel states for the competition of spin-conserving and spin-mixing. In TTF- C_{60} CT crystal, an external magnetic field could result in intersystem

crossing for the conversion of singlet to triplet CT, inducing an enhanced density of triplet excitons that could contribute to the dipole density due to the long lifetime (microseconds), and thus ultimately the polarization, indicating a room temperature ME coupling effect in TTF- C_{60} (Figure 3e, f). This magnetic-field induced ferroelectricity (spin-driven ferroelectricity) was observed with the optimum ME coupling coefficient up to $760 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ (under an external electric field of 80 kV cm^{-1} and a magnetic field of 200 mT). Magnetoconductance (MC) further gave insight of the inert spin-charge interactions and ME coupling. It exhibited a positive trend with the enhanced current density following the increased magnetic field, because an increase of triplet CT state ensures an enhanced interaction between excitons and polarons and thus arouses more triplet excitons dissociated into free charge carriers (Figure 3c).^[28] Besides, the photoexcitation and external electric field could also strengthen the ME coupling (Figure 3d), whereas higher electric field yet results in a negative MC, where the enhanced scattering interaction of polarons by the triplet excitons leads to a reduced charge carrier mobility (Figure 3d).^[29] Furthermore, millimeter-sized two-dimensional (2D) crystallized film based on CT crystal TTF- C_{60} was also obtained through the supramolecular strategy at the air-water interface.^[82] A new and unique characteristic of opto-magnetoelectric coupling is emerged in this 2D crystallized film and so did a stronger ME coupling in comparison with the bulk crystal, which is due to the ordered crystallized structure and long-range electron-phonon coupling toward more aligned charge, dipoles, and spins along the interface. Remarkably, by virtue of the advantages in simultaneously performing the magnetic-energy harvesting and multi-external-stimuli sensing functionalities, as well as the materials-by-design freedom, the organic CT multiferroic cocrystal of (BEDT-TTF) $_2C_{60}$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) was proved to be applied as a spin-charge converter that could convert spin information to electrical energy.^[33]

Figure 3. a) Optical photograph and b) crystal structure for the TTF- C_{60} charge-transfer crystal. c) Magnetoconductance change upon the electric field and magnetic field. d) Magnetization tuned by the electric field and

photoexcitation. e) The charge and spin configuration in CT complex with the 1D interacted chain between molecules. f) The enhanced both polarization and magnetization when applied electric field along the chain. Reprinted with permission from Ref.[34] Copyright 2016, John Wiley & Sons, Inc.

Another typical C_{60} -based CT multiferroics system is the family of thiophene-based compounds, where thiophene acts as the electron-donating moiety.^[29-30, 32, 72, 77] For instance, by co-assembling thiophene donor and C_{60} acceptor together into a three-dimensional CTC with a hierarchical organization and long-range noncovalent interactions (segregated-stack), a remarkable anisotropic magnetization and room temperature multiferroicity can be achieved.^[29] In this system, the ferromagnetism likely originates from the unpaired spin alignment within charged thiophene nanowires induced by the charge transfer. As aforementioned, the room-temperature ME coupling is a result of the spin-induced polarization, that is, the ratio of singlet and triplet charge-transfer can be readily regulated by an external magnetic field with more triplet excitons arisen to generate an enhanced dipole density. A magneto-dielectric effect could be observed (an enhanced dielectric constant with the applied magnetic field), which is because of the scattered carriers by the larger density of spin-triplet excitons toward a smaller conductance (a negative MC, Figure 4b). Moreover, due to the electron-phonon (charge-lattice) coupling tightly related to the molecular assembly axes and spin cone orientation in CTC, this material exhibited anisotropic ferroelectricity, magnetization and ME coupling behavior (Figure 4).^[30] Similar phenomena are also observed in the donor-acceptor segregated-stack CT cocrystals based on fullerene and other thiophene-based derivatives.^[72, 77] To be mentioned, a magnetoelastic character can also be realized in this polythiophene (P3HT)- C_{60} system, where the saturation magnetization varies inversely with the applied static compression stress. Such external mechanical field-dependent magnetization is the result of the coupling between magnetization and macroscopic deformation mediated by charge density waves.^[32] In addition, a nanocarbon CT magnet consisting of C_{60} (A) and SWCNTs (single-walled carbon nanotubes, D) was discovered to reveal the room temperature ME effect,^[31] which is well confirmed by the electric-field-tuned magnetization and magnetic-field-controlled dielectric constant/current density.

Figure 4. a) Atomic force microscope image and b) schematic diagram of spin cone distribution in organic CT crystal consisting of thiophene (D) and C_{60} (A) components. The exciton-lattice coupling extent and spin direction determine

the width and orientation of spin cone. b) Conductance upon the external magnetic field. c) Anisotropic magnetization and e) ME coupling in organic CTC. Inset: ME coupling coefficient upon external magnetic field. Reprinted with permission from Ref.[29]. Copyright 2015 American Chemical Society. Figure Caption.

3.4. Fluoride-based CT Multiferroics

Inorganic fluorides with transition-metal elements (such as BaMnF_4 , Na_2MAIF_7 , $(\text{NH}_2)_2\text{BeF}_4$, SrAlF_5 , $\text{K}_3\text{Fe}_5\text{F}_{15}$ and $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ families) are reported to accommodate a large number of multiferroics (or potentials), which **rank only** after oxides.^[70, 83-84] Logically, organic fluorides would be expected to be the next potential organic multiferroic system. Very recently, a new organic room-temperature CT multiferroic (mixed-stacking motif) based on F_4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, acceptor) and pyrene (donor) has been reported, which displayed anisotropic ME coupling effect and magneto-optical effect (Figure 5).^[36] In this system, compared to that with non-fluorinated acceptor (TCNQ), the fluorinated acceptor arouses an enhanced CT degree (causing closed-shell structure breaking), which indicates that more holes are generated on pyrene molecules (related to the spin polarization), thus leading to the enhanced spin density (magnetization). Besides, an anisotropic ME coupling behavior was observed, where the magnetization could be well tuned by an external electric field of different directions (horizontal and perpendicular direction) due to the anisotropy of molecular packing and CT interaction. The Cotton-Mouton effect enables this cocrystal potentially applied in opto-magnetic devices such as optical field design and magneto-optical sensors.

Figure 5. a) Image of the CT cocrystal Pyrene-F4TCNQ. b) Experimental setup of ME coupling measurement by applying electric field with different directions (E_x : horizontal, E_y : perpendicular). c) The tunability of magnetization with different electric field strengths. d) Anisotropic ME coupling in CTC. e) Schematic illustration of the relationship between electric field direction and molecular distribution. f) Magnetization change of CTC upon horizontal and perpendicular external electric field. Reprinted with permission from Ref.[36]. Copyright 2018 American Chemical Society.

3.5. Dimer-type Organic Multiferroics

Dimer-type organic molecules are predicted to be another appropriate framework for multiferroics. Different from above-mentioned organic ME coupling owing to the spin-driven polarization in microscopic mechanism, the dimer-type organic multiferroics are derived from charge-order-driven magnetism.^[37-38, 85-86] Taking a simple model of organic CT salt $(\text{TMTTF})_2\text{X}$

(TMTTF, tetramethyl-tetrathiafulvalene; $\text{X} = \text{PF}_6$, AsF_6 , and SbF_6) with 1D array of dimer units as the example,^[38, 85] it is a dimer-Mott insulator, in which the strong coupling of adjacent molecules in a dimer unit results one electron (or hole) occupying a bonding (antibonding) molecular orbital (MO). A plausible magnetic structure can be realized with the antiferromagnetic (AFM) alignment of electronic spins located at each dimer unit through inter-dimer exchange interaction (Figure 6a). Besides, inequivalent charge distribution activated by the strong inter-dimer coupling in a dimer unit can induce a dimer dipole, which could be aligned as antiferroelectric (AFE)-type order owing to the interaction between electrons in the nearest neighboring dimers. **This multiferroic AFM+AFE order is symmetric (Figure 6b),** neither invariant by the space reversal operation nor by the time reversal operation (Figure 6c). The applied external electric field along the chain can arouse the space reversal operation leading to an asymmetrically electronic charge distributions in right- and left- polarized dimers (Figure 6d). This inequivalence of electronic structure induces the different amplitudes of local spins due to the strongly entangled spins and charges, resulting in a net magnetization with the indelible up- and down-spin polarizations, that is, a linear ME coupling formation. Other significant candidates for organic dimer-based multiferroics are $(\text{BEDT-TTF})_2$ (bis(ethylenedithio)tetrathiafulvalene) type, i.e., κ -(BEDT-TTF) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ and β' -(BEDT-TTF) $_2\text{ICl}_2$.^[37, 85-86]

Moreover, other exotic strategy to design/obtain organic CT multiferroics could be realized by decorating mixed stack CT crystals with organic radicals, which is also able to realize a clear tendency towards multiferroic behavior.^[87]

Figure 6. Spin and charge configurations with dimer units arrayed on a 1D chain. a) An electrically non-polarized state with charge distributed equivalently on two molecules of a dimer unit. b) An electrically polarized state with polarized charge distribution, termed as the multiferroic AFE + AFM state. c) A spin and charge configuration obtained by applying the time reversal operation or the space inversion operation to the configuration in b. d) perpendicular net magnetization (M) and parallel electric polarization (P) to the chain are induced by applying an electric field (E) along the chain direction on the polarized state in b. Herein, filled purple circles, shaded ovals, and thin red and blue arrows denote molecules, charge distributions, and spins, respectively. Shaded orange arrows represent electric dipole moments due to deformations of the charge clouds. Spins are aligned antiferromagnetically and are directed perpendicular to the chain. Reprinted with permission from Ref.[85]. Copyright 2016 Springer Nature.

4. Challenges and Perspectives

Although the research on the multiferroics has been conducted for half a century, the interest focusing on organic CT multiferroics only appeared ten years ago. Even though some innovative breakthrough have been achieved in several organic CT multiferroic systems (especially with room temperature magnetoelectricity) and a couple of microscopic frameworks demonstrating multiferroic physics, this field in practice is still at a very infancy stage and remains a set of challenges to be overcome: i) **The very weak ME coupling** in the existing organic CT multiferroics has greatly limited their fundamental research and industrial application; ii) Although several microscopic mechanisms (i.e., spin-induced polarization and charge-ordering-induced spin alignment) have been presented to illustrate the ME coupling, they are far from sufficient on designing/fabricating materials with huge ME coupling coefficients; iii) Although some possible prototype devices have been reported, the practical applications of organic CT multiferroics are still challenging at present due to both the material and technical issues. In this situation, more efforts are required urgently on the rational design, synthesis and assembly of novel organic CT multiferroics with large room temperature magnetoelectric properties. Besides, a systematically theoretical study to efficiently guide the future development should also be established.

In this mini review, we have presented the progress in the fundamental understanding and designing of multiferroics, and prominently introduced the development on organic CT multiferroics ranging from experimental to theoretical investigations in recent ten years. Remarkably, with the potential in exploiting room-temperature multiferroics and inherent strengths in cost-effective, easy tailorability, light weight, mechanical flexibility and large-scale integration, organic CT multiferroics possess enormous market potential for future. Therefore, we expect that this review would enable readers assess the current stated of this field and trigger more interests and efforts to devote on it.

Acknowledgements

Q. Z. acknowledges financial support from AcRF Tier 1 (RG 111/17, RG 2/17, RG 113/18, RG 8/16) and Tier 2 (MOE 2017-T2-1-021 and MOE 2018-T2-1-070), Singapore.

Keywords: co-crystallization • organic charge-transfer complex • room-temperature multiferroics • magnetoelectric coupling

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Entry for the Table of Contents

Organic charge-transfer (CT) multiferroics has become a novel force to be reckoned, due to their potential in exploiting room-temperature magnetoelectric coupling effect and inherent strengths for commercial application. In this Minireview, recent progress of organic CT multiferroics ranging from experimental to theoretical investigations is summarized and specifically several representative CT systems are provided.