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Shenqiang Ren

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14. ABSTRACT

In this project, we aim at combining material-by-design and bottom-up assembly strategies to discover and explore the emerging class of organic charge-transfer (CT) superstructures, which enable coexisting magnetic and electric orders at room temperature unattainable in traditional materials, and hold great promise for flexible nanoferronic-optoelectronics. The realization of such applications using CT superstructures requires further enhancement of the multiferroic responses, which benefit greatly from the ability to screen large materials databases. Our combined

15. SUBJECT TERMS
Materials design, self-assembly, magnetoelectrics, photovoltaics

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# Report Title

Final Report: ARO-YIP (Materials By Design): Organic Photovoltaic Multiferroics

# ABSTRACT

In this project, we aim at combining material-by-design and bottom-up assembly strategies to discover and explore the emerging class of organic charge-transfer (CT) superstructures, which enable coexisting magnetic and electric orders at room temperature unattainable in traditional materials, and hold great promise for flexible nanoferronic-optoelectronics. The realization of such applications using CT superstructures requires further enhancement of the multiferroic responses, which benefit greatly from the ability to screen large materials databases. Our combined experimental and computational study reveals that the response of opto-thermo-magneto-electric and ferroic orders are sensitive to organic crystalline structures, and the essential strategy for material-by-design is the control over polymer crystallization and interfacial electron coupling. Based on this principle, remarkable magnetoconductance, and giant thermoelectric and magnetoelectric coupling are achieved for room temperature CT conductive nanoferronics. The details will be discussed in the report of this project and 8 published manuscripts over one-year award period. In addition, 1 patent application has been submitted. This project also provides unique education/outreach activities at various levels. The PI participated in the Research for High School Teacher program and recruited 3 local high school science teachers for summer research, which produces a high-profile publication after their summer project. The project has also supported two outstanding undergraduate researchers, Zunwu Zhou and Chris Birzer, both are in chemistry/engineering. Both received undergraduate awards during the project period, and Zunwu Zhou has been admitted to the graduate program of Univ. Arizona. Note: This project has been transferred to Temple University (PI’s current affiliation) after one-year award period, and the further progress will be covered in the further progress report.

## Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

### (a) Papers published in peer-reviewed journals (N/A for none)

| Received | | Paper |
|---|---|---|
| 04/30/2015 | 1.00 | Maogang Gong, Wei Qin, Xiaomin Chen, Tejas A. Shastry, Ridwan Sakidja, Guoliang Yuan, Mark C. Hersam, Manfred Wuttig, Shenqiang Ren. Multiferroicity of Carbon-Based Charge-Transfer Magnets, Advanced Materials, (01 2015): 734. doi: 10.1002/adma.201403396 |
| 04/30/2015 | 2.00 | Wei Qin, Maogang Gong, Tejas Shastry, Mark C. Hersam, Shenqiang Ren. Charge-Transfer Induced Magnetic Field Effects of Nano-Carbon Heterojunctions,<br>Scientific Reports, (08 2014): 6126. doi: 10.1038/srep06126 |
| 04/30/2015 | 3.00 | Maogang Gong, Tejas A. Shastry, Qiannan Cui, Ryan R. Kohlmeyer, Kyle A. Luck, Andrew Rowberg, Tobin J. Marks, Michael F. Durstock, Hui Zhao, Mark C. Hersam, Shenqiang Ren. Understanding Charge Transfer in Carbon Nanotube–Fullerene Bulk Heterojunctions,<br>ACS Applied Materials & Interfaces, (04 2015): 7428. doi: 10.1021/acsami.5b01536 |
| 04/30/2015 | 4.00 | Wei Qin, Beibei Xu, Shenqiang Ren. An organic approach for nanostructured multiferroics,<br>Nanoscale, (04 2015): 0. doi: 10.1039/C5NR01435B |
| 04/30/2015 | 5.00 | Alec Kirkeminde, Shenqiang Ren. Interdiffusion Induced Exchange Coupling of L10-FePd/a-Fe Magnetic Nanocomposites,<br>Nano Letters, (08 2017): 4493. doi: |
| 04/30/2015 | 7.00 | Jessica Lohrman, Shenqiang Ren, Yu Xie. Phase aggregation and morphology effectson nanocarbon optoelectronics,<br>Nanotechnology, (11 2014): 485601. doi: |
| 04/30/2015 | 6.00 | Maogang Gong, Tejas A. Shastry, Kyle A. Luck, Yu Xie, Marco Bernardi, Daniel Jasion, Tobin J. Marks, Jeffrey C. Grossman, Shenqiang Ren, Mark C. Hersam. Polychiral Semiconducting Carbon Nanotube/Fullerene Solar Cells,<br>Nano Letters, (08 2014): 5308. doi: |
| 06/28/2015 | 8.00 | Youpin Gong, Qingfeng Liu, Jamie Samantha Wilt, Maogang Gong, Shenqiang Ren, Judy Wu. Wrapping cytochrome c around single-wall carbon nanotube: engineered nanohybrid building blocks for infrared detection at high quantum efficiency,<br>Scientific Reports, (06 2015): 0. doi: 10.1038/srep11328 |
| **TOTAL:** | | **8** |

**Number of Papers published in peer-reviewed journals:**

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## (b) Papers published in non-peer-reviewed journals (N/A for none)

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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## (c) Presentations

1) Jessica Lohrman and Shenqiang Ren, Ratio Influence on morphological and physical properties of P3HT-C60 all-conjugated block copolymer systems, 249th ACS National Meeting, Denver, CO, March 22, 2015.
2) Shenqiang Ren, All polymeric nanoferronics, Materials Research Society (MRS) meeting, Boston, MA, Dec. 2nd, 2015
3) Shenqiang Ren, High energy product magnetic nanostructures, Materials Research Society (MRS) meeting, Boston, MA, Dec. 1st, 2015

**Number of Presentations:** 3.00

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## Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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## Peer-Reviewed Conference Proceeding publications (other than abstracts):

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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## (d) Manuscripts

Received Paper

**TOTAL:**

**Number of Manuscripts:**

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## Books

Received Book

**TOTAL:**

Received Book Chapter

**TOTAL:**

## Patents Submitted

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## Patents Awarded

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## Awards

PI:
Shenqiang Ren (2015 NSF CAREER award, 2014 Emerging Investigator of the Royal Society of Chemistry).

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Student participants:
Christopher Birzer (University Scholars Program Scholarship, Honors General Chemistry Book Award)
Zunwu Zhou (K. Barbara Schowen Chemistry Scholarship).

## Graduate Students

| NAME | PERCENT_SUPPORTED | Discipline |
|---|---|---|
| Jessica Lohrman | 0.50 | |
| Daniel Jasion | 0.50 | |
| **FTE Equivalent:** | **1.00** | |
| **Total Number:** | **2** | |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| Beibei Xu | 1.00 |
| **FTE Equivalent:** | **1.00** |
| **Total Number:** | **1** |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|---|---|---|
| Shenqiang Ren | 0.10 | |
| **FTE Equivalent:** | **0.10** | |
| **Total Number:** | **1** | |

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED | Discipline |
|---|---|---|
| Chris Birzer | 0.50 | |
| Zunwu Zhou | 0.50 | |
| **FTE Equivalent:** | **1.00** | |
| **Total Number:** | **2** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ...... 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 1.00

## Names of Personnel receiving masters degrees

| NAME | |
|---|---|
| Daniel Jasion | |
| **Total Number:** | **1** |

## Names of personnel receiving PHDs

| NAME | |
|---|---|
| Alec Kirkeminde | |
| **Total Number:** | **1** |

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

### Sub Contractors (DD882)

## Inventions (DD882)

# Scientific Progress

Experimental advances:

- Supramolecular assembly enabled polymeric charge-transfer superstructures
- Integration between optoelectronics, thermoelectrics and magnetoelectrics in all polymeric nanoferronics
- External stimuli controlled optical, electronic and magnetic properties.

Theoretical advances:

- Charge transfer effect on organic magnetism
- Polymer side chain in polymer crystallization and charge transfer
- Crystalline packing effect on molecular electronics.

Scientific progress and accomplishments:

Topic 1: All carbon design and assembly for extraordinary energy harvesting and magnetic field sensing

The objective of this task is to explore exciton dynamics, charge transport, and optoelectronics in all carbon assemblies, consisting of the chirality-selective single wall carbon nanotubes (SWCNTs, 1D), fullerenes (0D), and graphene derivatives (2D). The integration of noncovalent supramolecular assembly with all carbon material design lays the foundation for achieving unprecedented optoelectronic and ferroic properties within 3D carbon percolation networks. This is particularly noteworthy because, presently, little is known about the fundamental physical processes governing nanocarbon assemblies with heterogeneous energy levels and exciton binding energies. Without well-defined interfaces in blended structures, it is extremely challenging to understand the underlying physical processes governing their optoelectronic operation. Novel strategies of self-assembly will not only offer solutions to some of the current challenges in solar energy harvesting, but also discoveries of new phenomena. Fundamental understanding of how mechanical strain influences the electric and optical properties of the assemblies on both the molecular and structural level is an essential step toward the improvement of their optoelectronic and magnetic field sensing performance.

To date, there have been few studies of all carbon assembly. All carbon nanocomposites typically involve covalently linking the individual components or extensive surface functionalization to improve their processability. However, such strategies often deteriorate or contaminate the functional carbon surfaces thus compromising their performance. The strategy – noncovalent self-organization – benefits from self-assembly nature inherent to all carbon (sp2) nanomaterials. This opens up new possibilities for making all carbon assemblies without the need for any surface functionalization or dispersing agents for SWCNTs. All carbon assemblies can absorb and exchange energy through different physical mechanisms depending on the length scale. The charge and energy transfer and other attributes of interest can be related to all carbon donor and acceptor combinations, well-defined interfaces and morphologies. The molecular scale arrangement has been shown to dramatically affect the donor-acceptor charge transfer and overall device performance. With the control of their self-assembled morphology and interface, we demonstrate a polychiral semiconducting carbon nanotube-fullerene solar cell with a power conversion efficiency of 3.4% - a record for a cell using carbon nanotubes as a photoactive component. Using light-induced electron paramagnetic resonance, light-intensity dependent current-voltage scans, and ultrafast pump-probe techniques, we have achieved a thorough understanding of charge transfer dynamics within the SWCNT-fullerene blend at the interfaces. Furthermore, self-assembled nanocarbon system displays a high level of photodetectivity (D*) of 9 ×1011 Jones that is more than 30 times higher than the D* of the single-chirality (6,5)-rich SWCNT based nano-carbon photodetector at the same wavelength (860 nm). In addition to demonstrate the figure of merit for superlative optoelectronics, magnetic field effects on self-assembled carbon heterojunctions are explored. Room temperature magnetic field effects have not been observed in either single-walled carbon nanotubes or C60 under a small magnetic field due to their weak hyperfine interaction and slight difference of g-factor between positive and negative polarons. We demonstrate charge-transfer induced magnetic field effects in self-assembled SWCNT and fullerene heterojunctions at room temperature, where the mechanism of magnetic field effects is verified using excited state transition modeling. By controlling SWCNT concentrations and interfacial interactions, self-assembled carbon heterojunctions exhibit tunability of charge-transfer density and room temperature magnetoconductance of 2.8 % under 100 mT external magnetic field. External stimuli, such as electric field and photoexcitation, also play an important role in controlling the magnetic field effects of self-assembled carbon heterojunctions, which suggests that these findings could enable the control of optoelectronic properties of carbon heterojunctions. This enables a discovery of carbon charge-transfer magnet, consisting of the fullerene electron acceptor and SWCNT electron donor, where room temperature magnetism and the magnetoelectric (ME) coupling is controlled by the electron donor-acceptor interactions. Electron spin resonance is used to investigate the unpaired spin resonance within the fullerene acceptor. An external electric field is shown to effectively tune the magnetization of carbon charge-transfer complex. Furthermore, it is demonstrated that magnetic field dependent dielectric constant and current density can be tuned through the ratio between singlet and triplet charge-transfer.

Topic 2: Rational design and assembly of organic charge-transfer crystals for room temperature flexible nanoferronics

We report the first example of multiferroicity in centimeter-sized crystalline polymeric charge-transfer superstructures that grow at the liquid-air interface and are controlled by non-covalent interaction through supramolecular assembly. The charge order–driven ferroic mechanism reveals spontaneous and hysteretic polarization and magnetization at the donor-acceptor interface. The charge transfer and ordering in the ferroic assemblies depend critically on the self-organizing and molecular packing of electron donors and acceptors. The ability to control the dimensions of three-dimensional charge-transfer networks allows us to manipulate the structural packing at the molecular scale (the crystalline structure has been identified using high resolution synchrotron radiation with the collaboration of Argonne national laboratory). It is the first time to demonstrate three-dimensional supramolecular assembly and co-crystallization of thiophene donor and polymerized fullerene acceptor as the prototypical supramolecular charge-transfer co-crystals (SCTCs). The overall dimensions of SCTCs require a hierarchical organization and long-range non-covalent interactions between the thiophene donor and C60 acceptor, where the segregation stacking between the donor and acceptor molecules can be adjusted by the polar solvent loading ratios. The crystallized thiophene donor exhibits the monoclinic structure with the lattice constant a=1.660 nm, b=0.780 nm and c=0.863 nm, while the polymerized C60 acceptor adopts face-centered cubic (fcc) structure with the lattice constant 1.415 nm. To our knowledge, this is the first time to demonstrate a rational control on the co-crystallization of semiconducting polymers to enable exotic physical properties. Furthermore, charge-transfer controlled magnetism is observed in SCTCs, and the magnetic measurements were employed to elucidate the anisotropy of magnetization within SCTCs between in-plane (easy axis) and out-of-plane (hard axis) directions. The charge-lattice coupling within the crystallized thiophene nanowire chain gives rise to the spin density wave leading to the spontaneous magnetization of SCTCs. A strong (weak) charge-lattice coupling would induce a narrow (wide) spin cone, which promotes the alignment of spins within the narrow (wide) spin cone along easy (hard) axis. Room-temperature ferroelectricity of SCTCs is confirmed using the ferroelectric hysteresis loops. Furthermore, under photoexcitation, more excitons are introduced in SCTCs to enhance the polarization, resulting in the light intensity dependent polarization behavior. The SCTCs exhibit an unusual temperature dependent susceptibility tendency: two characteristic peaks are observed at 100 K and 200 K. The susceptibility transition at 100 K is consistent with our previous observation of the competing mechanism between Curie’s law (decreasing susceptibility with T) and thermally excited triplet bipolarons (increasing susceptibility with T) in thiophene nanowires. The susceptibility transition at 200 K can be ascribed to the thermally induced transition from singlet bipolarons to triplets within the polymerized C60. To understand the origin of magnetism in SCTCs, simulations were carried out by the spin unrestricted density functional theory (DFT) framework with the GGA-PBE functionals implemented in the VASP package. The C60 intercalation between the side chains of the thiophene enhances charge-transfer interactions to increase the density of charges in thiophene nanowires. Our results indicate that the observed magnetism likely originates from the charged crystalline thiophene nanowires. The ground state is spin-unpolarized due to the degenerate spin up and spin down energy levels. By introducing positive charges into the thiophene crystal through charge-transfer, a splitting of energy level between spin up and spin down, which results in a net magnetic moment. The invention described here not only represents a new coupling mechanism of magnetic and electric ordering but also creates a new class of emerging all-organic nanoferronics.

## Technology Transfer

My group is currently collaborating with ARL scientists: Drs. Asha Hall and Raymond Brennan (both serve as my scientific liaison on my project), on high frequency dielectric measurement of self-assembled organic crystals, and the structural characterization/modeling of alumina, respectively.

# 1. Foreword

Title: ARO-YIP (Materials by Design): Organic Photovotaic Multiferroics

Keywords: Materials design, self-assembly, magnetoelectrics, photovoltaics

PI: Shenqiang Ren

Student Participants: Alec Kirkeminde (Graduate student, Univ. Kansas), Jessica Lohrman (Graduate student, Univ. Kansas), Daniel Jasion (Graduate student, Univ. Kansas), Beibei Xu (Postdoc, Univ. of Kansas), Chris Birzer (Undergraduate, Univ. Kansas), Zunwu Zhou (Undergraduate, Univ. Kansas)

Abstract:

In this project, we aim at combining material-by-design and bottom-up assembly strategies to discover and explore the emerging class of organic charge-transfer (CT) superstructures, which enable coexisting magnetic and electric orders at room temperature unattainable in traditional materials, and hold great promise for flexible nanoferronic-optoelectronics. The realization of such applications using CT superstructures requires further enhancement of the multiferroic responses, which benefit greatly from the ability to screen large materials databases. Our combined experimental and computational study reveals that the response of opto-thermo-magneto-electric and ferroic orders are sensitive to organic crystalline structures, and the essential strategy for material-by-design is the control over polymer crystallization and interfacial electron coupling. Based on this principle, remarkable magnetoconductance, and giant thermoelectric and magnetoelectric coupling are achieved for room temperature CT conductive nanoferronics. The details will be discussed in the report of this project and 8 published manuscripts over one-year award period. In addition, 1 patent application has been submitted. This project also provides unique education/outreach activities at various levels. The PI participated in the Research for High School Teacher program and recruited 3 local high school science teachers for summer research, which produces a high-profile publication after their summer project. The project has also supported two outstanding undergraduate researchers, Zunwu Zhou and Chris Birzer, both are in chemistry/engineering. Both received undergraduate awards during the project period, and Zunwu Zhou has been admitted to the graduate program of Univ. Arizona. Note: This project has been transferred to Temple University (PI’s current affiliation) after one-year award period, and the further progress will be covered in the further progress report.

## 2. List of Illustrations

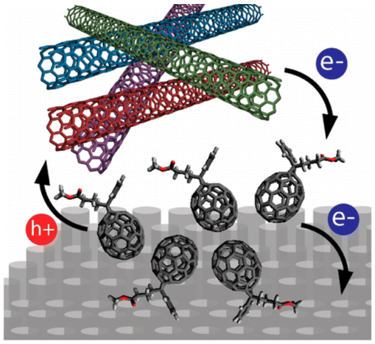

Figure 1. All carbon charge-transfer assembly

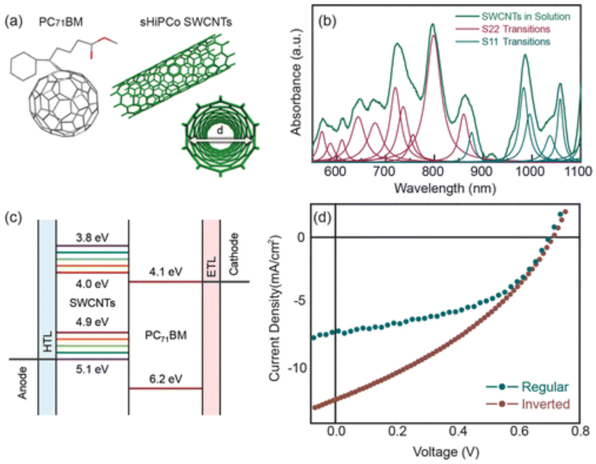

Figure 2. Materials, device structure, and performance of all carbon optoelectroncis. (a) Structure of all carbon nanomaterials. (b) Optical absorption spectra of the semiconducting carbon nanotubes. (c) Schematic structure of energy diagram for all carbon assembly. (d) Current–voltage curves in the dark and under AM 1.5 illumination, providing a power conversion efficiency of 2.5% and 3.1%, respectively.

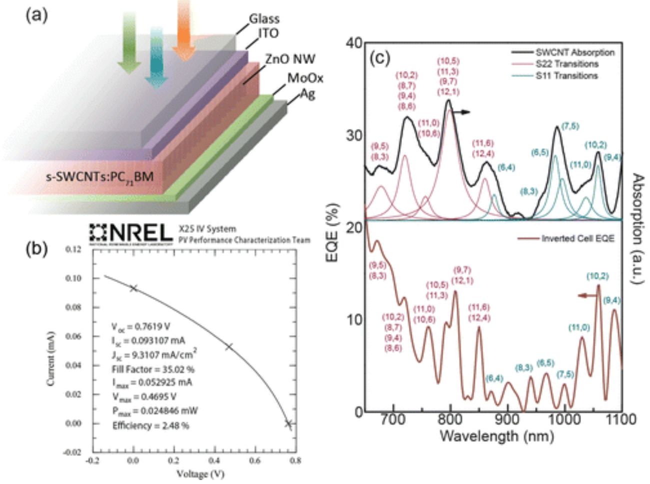

Figure 3. Structure and device performance of all carbon solar cell. (a) Schematic structure of all carbon solar cell. (b) Current–voltage curve of an NREL certified device with a PCE of 2.5%. (c) Near-IR EQE of the inverted cell.

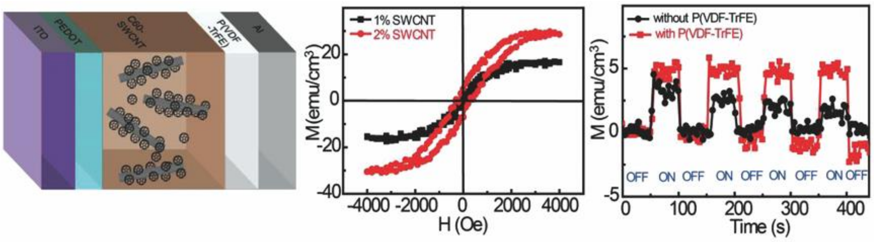

Figure 4. All carbon materials for magnetic field sensing

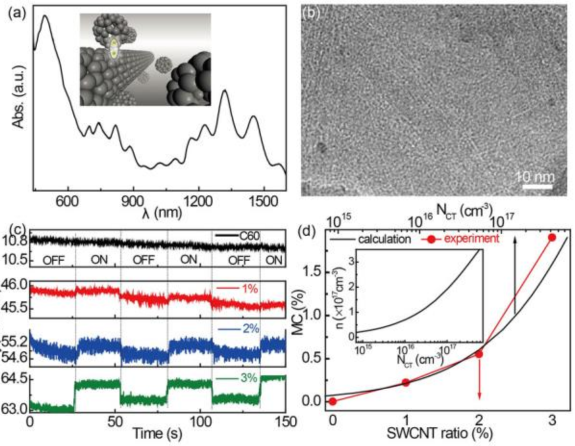

Figure 5. (a) The photoabsorption of all carbon materials. (b)TEM image of all carbon heterojunction. (c) Magnetic field effect in all carbon heterojunctions. (d) Theoretical calculation (black line) compared with the experimental result (red circle).

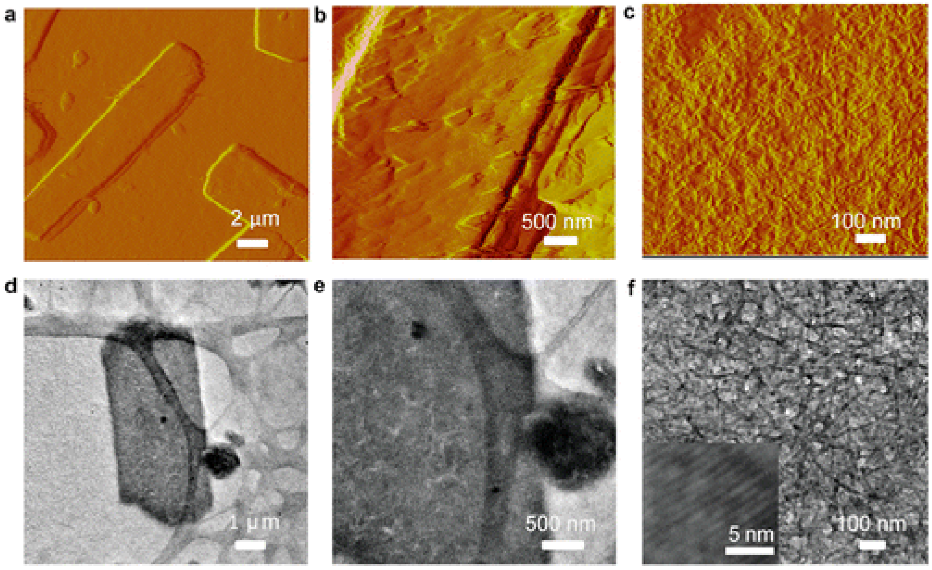

Figure 6. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of organic charge-transfer crystals. (a–c) Low-resolution and high-resolution AFM images of charge-transfer crystals. (d–f) The corresponding TEM images of charge-transfer crystals at different resolution, and the inset of (f) shows the high-resolution TEM of the well-ordered C60.

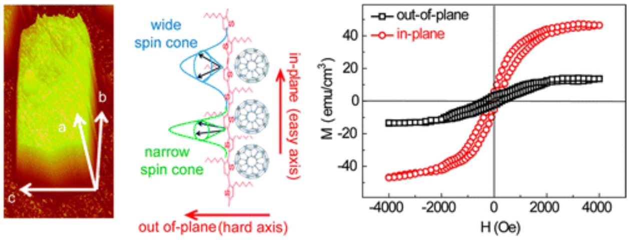

Figure 7. Organic charge-transfer superstructure induced anisotropic magnetism.

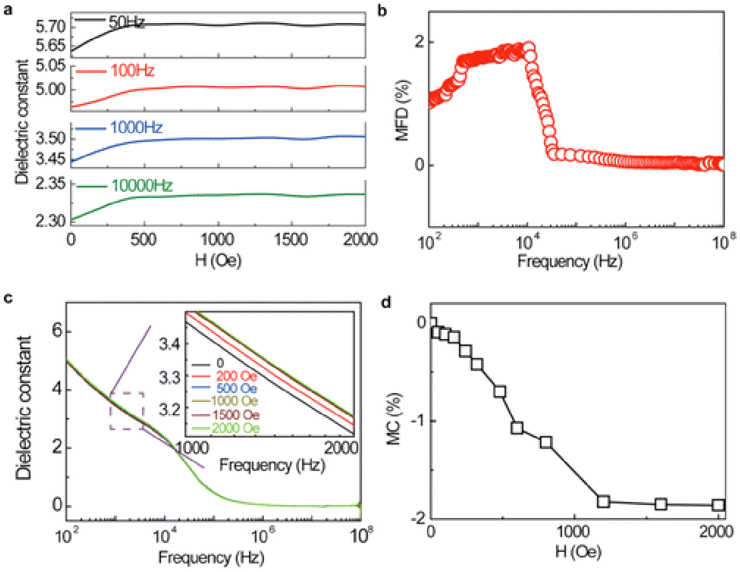

Figure 8. Magnetic field effects on dielectric constant and conductance of charge-transfer crystals. (a) Magnetic field dependent dielectric constant at different frequencies. (b) Frequency dependent dielectric constant (MFD) under the bias 1000 Oe magnetic field. (c) Frequency dependent dielectric constant under external magnetic fields. (d) Tunability of conductance by external magnetic field.

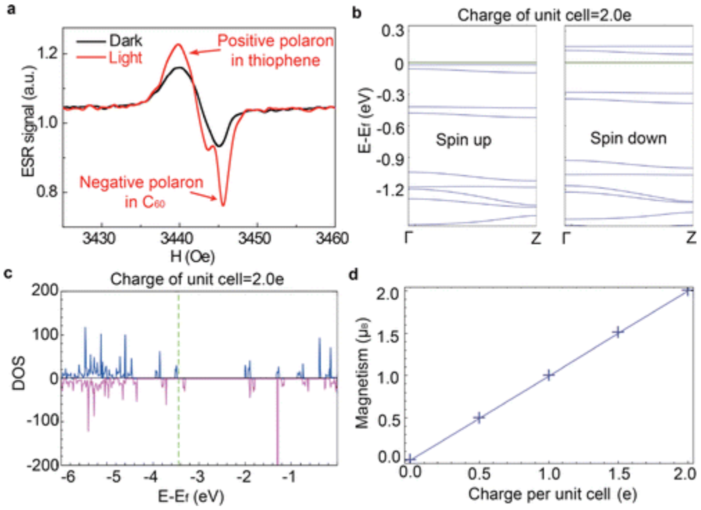

Figure 9. Electron spin resonance (ESR) and magnetic susceptibility of charge-transfer crystals. (a) ESR signals of charge-transfer crystals under dark and light environment. (b) Energy levels of spin up and spin down with 2 positive charges per unit cell. (c) Density of state with 2 positive charges in charge-transfer crystals. (d) Charge per unit cell dependent magnetization.

## 3. Statement of the Problem Studied

Electron transfer and the generation of a new set of $S = {}^1/_2$ spins with exchange interaction in charge-transfer (CT) complexes ($D^0A^0 \leftrightarrow D^{\delta+}A^{\delta-}$) enable a unique coupling between electric and magnetic order parameters, which is important to unlock numerous exciting technological advances in the field of flexible magnetoelectrics (ME). Over the past decades, numerous functional crystalline CT complexes with customized chemical functionality have been developed on the basis of the combination of their unique physical properties and structural stacking factors. The physical properties of crystalline CT complexes appear to be associated with the stacking arrangement (mixed- and segregated-stack) and CT degree (mixed-valence and neutral-ionic systems) between the electron donor (D) and acceptor (A). For instance, the discovery of one-dimensional metallic conductivity in segregated-stack tetrathiafulvalene-tetracyanoquinodimethane (D-A) complexes has led to the development of organic metals and superconductors in the absence of a metal atom, whereas hydrogen-bonded mixed-stack tetrathiafulvalene–pyromellitic diimide (D-A) CT complexes started the field of room temperature ferroelectric switching originating from intermolecular interactions. However, obtaining simultaneous ferroic orders and room temperature ME coupling properties in CT complexes remains challenging and represents an important topic in material scince and condensed matter science, especially for the segregated stacks, in part because of their relatively weak intermolecular interactions. In addition, the lack of scalable growth techniques for large-sized high-quality organic CT crystals represents another challenge for the development of organic multiferroics and optoelectronics. Previous studies have mainly focused on small-scale assembled nanostructures and have been concerned with structure disruption during solvent annealing, which is generally necessary to obtain long-range ordered phases. Organic CT crystals should have a long-range ordered structure, which facilitates the formation of a closely stacked structure and strong interfacial interaction for CT. The growth of large-sized CT crystals is dictated by the control of homogeneous nucleation to avoid the formation of dense nuclei and by the management of growth conditions to facilitate weak intermolecular interactions for the ordered combination of different organic molecules.

In this project, our major achievements include: 1) design and assembly of multiscale carbon materials with different dimensions, which enable a record of power conversion efficiency (3.4%) within carbon nanotube based photovoltaics, as well as room temperature ferroic properties and magnetoconductance (2.8 % under 100 mT magnetic field); 2) supramolecular assembly of organic donor-acceptor cocrystals to develop all-organic multiferroics, where room temperature organic ferroelectricity and magnetism are simultaneously coupled to exhibit ferroic ordering. The details are shown in the section 5.

## 4. Summary of the Most Important results

Topic 1: All carbon design and assembly for extraordinary energy harvesting and magnetic field sensing

The objective of this task is to explore exciton dynamics, charge transport, and optoelectronics in all carbon assemblies, consisting of the chirality-selective single wall carbon nanotubes (SWCNTs, 1D), fullerenes (0D), and graphene derivatives (2D), as shown in Fig. 1. The integration of noncovalent supramolecular assembly with all carbon material design lays the foundation for achieving unprecedented optoelectronic and ferroic properties within 3D carbon percolation networks. This is particularly noteworthy because, presently, little is known about the fundamental physical processes governing nanocarbon assemblies with heterogeneous energy levels and exciton binding energies. Without well-defined interfaces in blended structures, it is extremely challenging to understand the underlying physical processes governing their optoelectronic operation. Novel strategies of self-assembly will not only offer solutions to some of the current challenges in solar energy harvesting, but also discoveries of new phenomena. Fundamental understanding of how mechanical strain influences the electric and optical properties of the assemblies on both the molecular and structural level is an essential step toward the improvement of their optoelectronic and magnetic field sensing performance.

To date, there have been few studies of all carbon assembly. All carbon nanocomposites typically involve covalently linking the individual components or extensive surface functionalization to improve their processability. However, such strategies often deteriorate or contaminate the functional carbon surfaces thus compromising their performance. The strategy – noncovalent self-organization – benefits from self-assembly nature inherent to all carbon ($sp^2$) nanomaterials. This opens up new possibilities for making all carbon assemblies without the need for any surface functionalization or dispersing agents for SWCNTs. All carbon assemblies can absorb and exchange energy through different physical mechanisms depending on the length scale. The charge and energy transfer and other attributes of interest can be related to all carbon donor and acceptor combinations, well-defined interfaces and morphologies. The molecular scale arrangement has been shown to dramatically affect the donor-acceptor charge transfer and overall device performance. With the control of their self-assembled morphology and interface, we demonstrate a polychiral semiconducting carbon nanotube-fullerene solar cell with a power conversion efficiency of 3.4% - a record for a cell using carbon nanotubes as a photoactive component (Fig. 2 and 3). Using light-induced electron paramagnetic resonance, light-intensity dependent current-voltage scans, and ultrafast pump-probe techniques, we have achieved a thorough understanding of charge transfer dynamics within the SWCNT-fullerene blend at the interfaces. Furthermore, self-assembled nanocarbon system displays a high level of photodetectivity (D*) of $9 \times 10^{11}$ Jones that is more than 30 times higher than the D* of the single-chirality (6,5)-rich SWCNT based nano-carbon photodetector at the same wavelength (860 nm). In addition to demonstrate the figure of merit for superlative optoelectronics, magnetic field effects on self-assembled carbon heterojunctions are explored. Room temperature magnetic field effects have not been observed in either single-walled carbon nanotubes or $C_{60}$ under a small magnetic field due to their weak hyperfine interaction and slight difference of g-factor between positive and negative polarons (Fig. 4). We demonstrate charge-transfer induced magnetic field effects in self-assembled SWCNT and fullerene heterojunctions at room temperature, where the mechanism of magnetic field effects is verified using excited state transition modeling. By controlling SWCNT concentrations and interfacial interactions, self-assembled carbon heterojunctions exhibit tunability of charge-transfer density and room temperature magnetoconductance of 2.8 % under 100 mT external magnetic field (Fig. 5). External stimuli, such as electric field and photoexcitation, also play an important role in controlling the magnetic field effects of self-assembled carbon heterojunctions, which suggests that these findings could enable the control of optoelectronic properties of carbon heterojunctions. This enables a discovery of carbon charge-transfer magnet, consisting of the fullerene electron acceptor and SWCNT electron donor, where room temperature magnetism and the magnetoelectric (ME) coupling is controlled by the electron donor-acceptor interactions. Electron spin resonance is used to investigate the unpaired spin resonance within the fullerene acceptor. An external electric field is shown to effectively tune the magnetization of carbon charge-transfer complex. Furthermore, it is demonstrated that magnetic field dependent dielectric constant and current density can be tuned through the ratio between singlet and triplet charge-transfer.

Topic 2: Rational design and assembly of organic charge-transfer crystals for room temperature flexible nanoferronics

We report the first example of multiferroicity in centimeter-sized crystalline polymeric charge-transfer superstructures that grow at the liquid-air interface and are controlled by non-covalent interaction through supramolecular assembly (Fig. 6). The charge order–driven ferroic mechanism reveals spontaneous and hysteretic polarization and magnetization at the donor-acceptor interface (Fig. 7). The charge transfer and ordering in the ferroic assemblies depend critically on the self-organizing and molecular packing of electron donors and acceptors. The ability to control the dimensions of three-dimensional charge-transfer networks allows us to manipulate the structural packing at the molecular scale (the crystalline structure has been identified using high resolution synchrotron radiation with the collaboration of Argonne national laboratory). It is the first time to demonstrate three-dimensional supramolecular assembly and co-crystallization of thiophene donor and polymerized fullerene acceptor as the prototypical supramolecular charge-transfer co-crystals (SCTCs). The overall dimensions of SCTCs require a hierarchical organization and long-range non-covalent interactions between the thiophene donor and $C_{60}$ acceptor, where the segregation stacking between the donor and acceptor molecules can be adjusted by the polar solvent loading ratios. The crystallized thiophene donor exhibits the monoclinic structure with the lattice constant $a$=1.660 nm, $b$=0.780 nm and $c$=0.863 nm, while the polymerized $C_{60}$ acceptor adopts face-centered cubic (fcc) structure with the lattice constant 1.415 nm. To our knowledge, this is the first time to demonstrate a rational control on the co-crystallization of semiconducting polymers to enable exotic polarization, magnetoconductance and magnetoelectric properties (Fig. 8).

Furthermore, charge-transfer controlled magnetism is observed in SCTCs, and the magnetic measurements were employed to elucidate the anisotropy of magnetization within SCTCs between in-plane (easy axis) and out-of-plane (hard axis) directions. The charge-lattice coupling within the crystallized thiophene nanowire chain gives rise to the spin density wave leading to the spontaneous magnetization of SCTCs. A strong (weak) charge-lattice coupling would induce a narrow (wide) spin cone, which promotes the alignment of spins within the narrow (wide) spin cone along easy (hard) axis. Room-temperature ferroelectricity of SCTCs is confirmed using the ferroelectric hysteresis loops. Furthermore, under photoexcitation, more excitons are introduced in SCTCs to enhance the polarization, resulting in the light intensity dependent polarization behavior. The SCTCs exhibit an unusual temperature dependent susceptibility tendency: two characteristic peaks are observed at 100 K and 200 K. The susceptibility transition at 100 K is consistent with our previous observation of the competing mechanism between Curie's law (decreasing susceptibility with $T$) and thermally excited triplet bipolarons (increasing susceptibility with $T$) in thiophene nanowires. The susceptibility transition at 200 K can be ascribed to the thermally induced transition from singlet bipolarons to triplets within the polymerized $C_{60}$ (Fig. 9) To understand the origin of magnetism in SCTCs, simulations were carried out by the spin unrestricted density functional theory (DFT) framework with the GGA-PBE functionals implemented in the VASP package. The $C_{60}$ intercalation between the side chains of the thiophene enhances charge-transfer interactions to increase the density of charges in thiophene nanowires. Our results indicate that the observed magnetism likely originates from the charged crystalline thiophene nanowires (Fig. 9). The ground state is spin-unpolarized due to the degenerate spin up and spin down energy levels. By introducing positive charges into the thiophene crystal through charge-transfer, a splitting of energy level between spin up and spin down, which results in a net magnetic moment. The invention described here not only represents a new coupling mechanism of magnetic and electric ordering but also creates a new class of emerging all-organic nanoferronics.

## 5. Bibliography

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