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Introducing Magneto-Optical Functions into Soft Materials

Chia-Liang 'Charlie' Cheng
National Dong Hwa University
No 1 Sec 2 Da Hsueh Rd
Shoufeng, 97401
TW

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Report on Introducing Magneto-Optic Properties into Soft Materials

Chia-Liang Cheng, National Dong Hwa University, Hualien, Taiwan
Bin Hu, University of Tennessee, Knoxville, TN 37996, USA

This project intends to introduce magneto-optical properties in soft materials including organic and bio materials by using magnetic nanomaterials. This final report includes the successful developments of magneto-optical properties in both organic and bio magnetic nanocomposites during the project period of three years.

PART I: Enhanced π-d electron coupling in excited state in magnetic-organic nanocomposite γ-FeO_x-C_{60}(>DPAF-C_9)

1. Objective

The objective is to understand the π-d electron coupling in magnetic-organic nanocomposite γ-FeO_x-C_{60}(>DPAF-C_9) in both ground and excited states. The goal is to illustrate the fundamental mechanisms of π-d electron coupling, providing a physical understanding for magneto-electronic coupling in the magnetic-organic nanocomposite and developing a new approach to realize magneto-electronic coupling for various applications.

2. Experimental Results

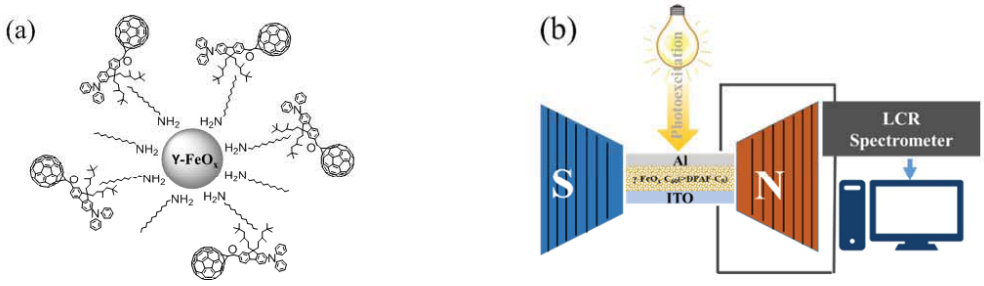

Figure 1, (a) Chemical structure of γ-FeO_x-C_{60}(>DPAF-C_9). (b) Experiment setup for magnetocapacitance measurement.

The experimental studies on π-d electron coupling have been performed in the magnetic-organic nanocomposite γ-FeO_x-C_{60}(>DPAF-C_9) as shown in Figure 1 (a). π electrons and d electrons are provided by the organic composite C_{60}(>DPAF-C_9) and magnetic composite γ-FeO_x accordingly. They are found to interact with each other through magneto-current measurement.[1] Here, the experimental measurement was based on magnetic field effect of capacitance (magnetocapacitance). This measurement was carried out by putting the device with the structure of ITO/γ-FeO_x-C_{60}(>DPAF-C_9):PMMA/Al in to the electromagnet as illustrated in Figure 1(b). This experimental measurement allowed us to explore magneto-electric coupling in both ground and excited states by measuring the capacitance as a function of magnetic field without and with photoexcitation respectively.

2.1 π-d electron coupling in ground state

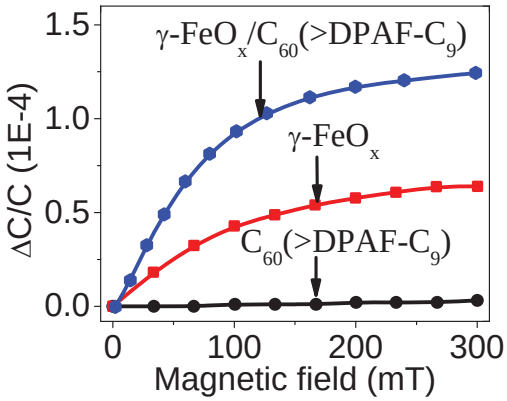

Figure 2. π-d electron coupling in ground state demonstrated by magnetocapacitance

It is obvious in Figure 2 that the magnetocapacitance in pure C_{60}(>DPAF-C_9) is relatively negligible while the magnetocapacitance in pure γ-FeO_x shows a positive magnetocapacitance in ground state. In addition, the amplitude and the line-shape of magnetocapacitance of γ-FeO_x-C_{60}(>DPAF-C_9) is enhanced and narrowed respectively. Such enhancement and narrowing is clearly due to the interaction between π electron in C_{60}(>DPAF-C_9) and d electron in γ-FeO_x. The spin and polarization of d electrons are coupled to generate magnetocapacitance. With the interaction between π electron and d electron, the applied magnetic field can further enhance the

capacitance through C_{60}(>DPAF-C_9). This experiment result undoubtedly indicates the interaction between π electron and d electron in ground state.

2.2 π-d electron coupling in ground state

Figure 3 clearly shows that the magnetocapacitance of γ-FeO_x-C_{60}(>DPAF-C_9) increase significantly from the ground state to the excited state. It should also be noted the magnetocapacitance of γ-FeO_x-C_{60}(>DPAF-C_9) is composited by two parts: the slow increasing with a small slope under small magnetic field (<20 mT) and the fast increasing with a large slope when the magnetic field exceeding 20 mT. Therefore, both the increased value and line-shape change of magnetocapacitance indicate that the interaction between π electron and d electron is enhanced in the excited state.[2]

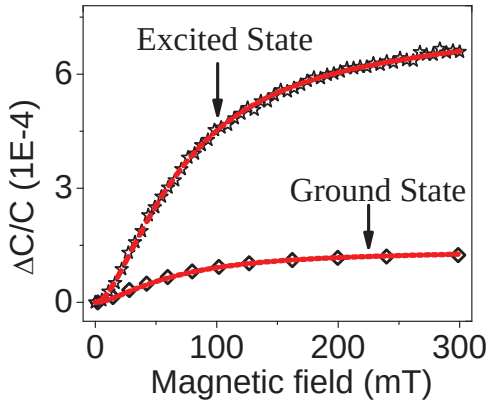

Figure 3, Magnetocapacitance of γ-FeO_x-C_{60}(>DPAF-C_9) in ground state and excited state. The excitation light is CW 405nm laser with 31.25mW/cm^2.

2.3 Tuning the π-d electron coupling by changing the intensity of π electrons

π-d electron coupling is the key effect for realizing the magneto-electronic coupling in magnetic-organic nanocomposite γ-FeO_x-C_{60}(>DPAF-C_9). Now we use the intensity of π electron as a parameter to control the coupling between π electron and d electron through tuning the photoexcitation intensities. Figure 4 clearly depicts that increasing the photoexcitation intensities leads to a narrower line-shape of magnetocapacitance. Additionally, the amplitude of

the magnetocapacitance increases with the higher photoexcitation intensity as shown in inset of Figure 4. These experiment results demonstrate that photoexcitation intensity can tune the coupling between π electron and d electron based on the density change of π electrons. This enhancement is due to the Coulomb interaction between π electron and d electron through the dipole-dipole interaction between them.

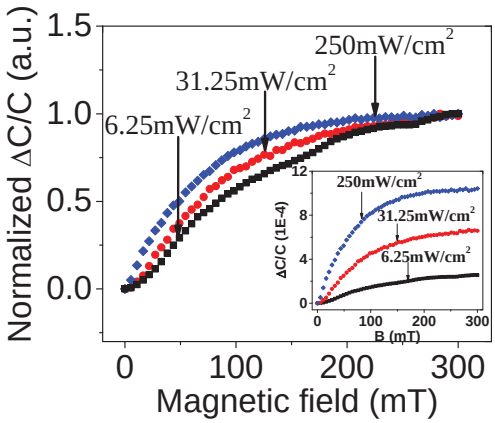

Figure 4, (a) Normalized magnetocapacitance curves for γ-FeO_x-C_{60}(>DPAF-C_9) with increasing photoexcitation intensities; inset: absolute value of magnetocapacitance from γ-FeO_x-C_{60}(>DPAF-C_9).

2.4 Tuning the π-d electron coupling by changing the intensity of d electrons

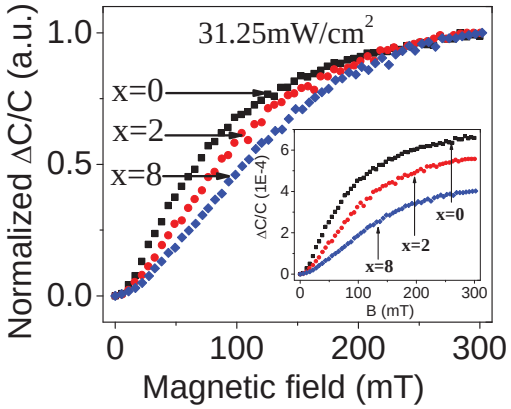

Figure 5, Normalized magnetocapacitance curves for γ-FeO_x-C_{60}(>DPAF-C_9) mixed with iron oxide nanoparticles with different weight ratios under 31.25mW/cm^2; inset: absolute value of magnetocapacitance from γ-FeO_x-C_{60}(>DPAF-C_9) mixed with iron oxide nanoparticles.

It is also possible to tune the π-d electron coupling by changing the density of d electrons. Figure 5 describes the magnetocapacitance of γ-FeO_x-C_{60}(>DPAF-C_9) changing with the concentration of γ-FeO_x. Obviously, increasing the concentration of γ-FeO_x broadens the line-shape of magnetocapacitance. Meanwhile, the value of magnetocapacitance decreases as the increasing concentration of γ-FeO_x. This results shows the evidence that increasing the concentration of d electrons weakens the π-d electron coupling, which is ascribe to the spin interaction between π-d electron and d electrons.

2.5 Mechanisms for the π-d electron coupling

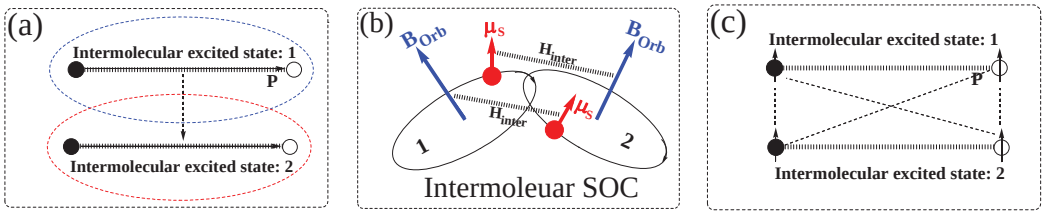

Figure 6, (a) Long-range Coulomb interaction, (b) Mid-range spin-orbital coupling and (c) Short-range spin interaction.

In this study we have found that the π-d electron coupling can be realized through three different channels: long-range Coulomb interaction, intermediate-range spin-orbital coupling, and short-range spin-spin interactions between semiconducting π conjugated structures C_{60}(>DPAF-C_9) and magnetic nanoparticles γ-FeO_x in organic-magnetic composites γ-FeO_x-C_{60}(>DPAF-C_9). The long-range Coulomb interaction is due to the dipole-dipole interaction from π electrons and d electrons. The middle-range spin-orbital coupling originates from the interaction between electron spin from π/d electrons and the orbital magnetic field from d/π electrons. The short-range spin-spin interaction derives from the adjacent π electrons and d electrons.

In summary, we studied the π-d electron coupling in the magnetic-organic nanocomposites γ-FeO_x-C_{60}(>DPAF-C_9) through magnetocapacitance. An enhancement of π-d electron coupling is observed in the excited state, demonstrated by the amplitude increase and line-shape change of magnetocapacitance. In addition, this coupling is proved to be controllable by changing the densities of π electrons and d electrons. This interaction is ascribe to the long-range Coulomb interaction, middle-range spin-orbital coupling and short-range spin-spin interaction. As a general conclusion, the π-d electron coupling promise the existence of photo-adjustable magneto-electric coupling, paving the way for the realization of magneto-electric-optical applications.

3. Future research plan

In general, three further works based on this research should be carried out: (i) revealing π-d coupling mechanisms by changing the distance between them, (ii) demonstrating π-d coupling induced multiferroic effects with optically controllable magnetic properties and magnetically controllable optic and electric properties, and (iii) developing new guidelines for designing next-generation magneto-optical polymers by using π-d coupling in excited states.

PART II: Magneto-Electric Coupling between Fe_3O_4 Magnetic Nanoparticles and Human Serum Albumin (HSA) in Ground and Excited States

1. Objective

The objective is to understand the magneto-electric coupling between Fe_3O_4 magnetic nanoparticles and Human Serum Albumin (HSA) in both ground and excited states. The goal is to elucidate the fundamental mechanisms of magneto-electric coupling in bio/magnetic composites. It is expected that the magneto-electric coupling can provide a new approach to develop magneto-optic properties in bio materials for various applications.

2. Experimental Results

The experimental studies on magneto-electric coupling have been performed by combining surface-modified soluble Fe_3O_4 magnetic nanoparticles and Human Serum Albumin (HSA) in liquid solutions. The experimental measurement was based on magnetic field effect of light scattering.[3] This experimental measurement allowed us to explore magneto-electric coupling in both ground and excited states by measuring the light scattering intensity as a function of magnetic field.

Figure 7, Bio molecules: Human Serum Albumin (HSA) and magnetic/bio composite.

2.1 Magneto-electric coupling revealed by Magnetic Field Effect of Light Scattering

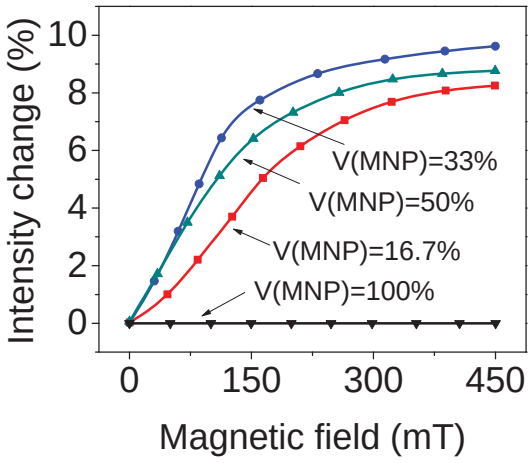

Figure 8. Magnetic field effect of light scattering (MFE_{LS}) on the HSA + Fe_3O_4 composite.

It is demonstrated in Figure 8 that the magnetic field effect of light scattering (MFE_{LS}) in pure Fe_3O_4 nanoparticles solution is relatively negligible. However, when the Human Serum Albumin (HAS) is added into the solution, the MFE_{LS} is significantly enhanced. Such enhancement is undoubtedly owing to the existing interaction between HSA and Fe_3O_4 nanoparticles.[4] With applied magnetic field, re-alignment of HSA molecule occurs due to the

anisotropic interaction between Fe_3O_4 magnetic nanoparticle and HSA. Through the interaction with Fe_3O_4 nanoparticles, the HSA molecules can be dragged to rotate under magnetic field and then MFE_{LS} is enhanced. This experimental result suggests the first evidence that the magnetic nanoparticles can Coulombically interact with the bio molecules, leading to a magneto-electric coupling between the magnetic nanparticles and bio molecules.

2.2 Time-resolved dynamics of MFE_{LS} in ground states of HSA/Fe_3O_4 nanoparticle composites

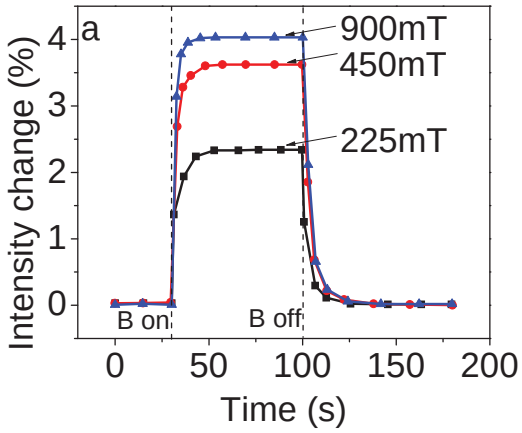

Figure 9. Time-dependent MFE_{LS} of 16.7% Fe_3O_4 nanoparticles concentrations at different magnetic field strengths.

Figure 9 clearly shows that in the HSA/Fe_3O_4 nanoparticle composites with 16.7% Fe_3O_4 concentrations, with the magnetic field increasing, the MFE_{LS} signal becomes larger at the 532nm scattering light. With the rise of magnetic field, the re-alignment of HSA molecule becomes more pronounced due to the Coulombic interaction between Fe_3O_4 magnetic nanoparticles. This demonstrates that stronger magnetic field leads to more complete orientation of HSA/Fe_3O_4 nanoparticle composites, and thus a higher magnitude in MFE_{LS} signal. This experimental result confirms that the magneto-electric coupling exists between the magnetic particles and bio molecules.

2.3 Tuning magneto-electric coupling between Fe_3O_4 magnetic nanoparticles and bio molecules by modifying the surface charge density

The Coulombic interaction in the HSA/Fe_3O_4 nanoparticle composites is a key factor for the magneto-electric coupling composites. To probe magneto-electric coupling in the ground state of bio/magnetic nanoparticle composites, we first select to tune the coupling through the modulation of surface charge in the HSA. Thus, light scattering intensity under different magnetic field is systematically investigated, as a stronger MFE_{LS} signal indicates pronounced magneto-electric coupling in the composites (Figure 10).

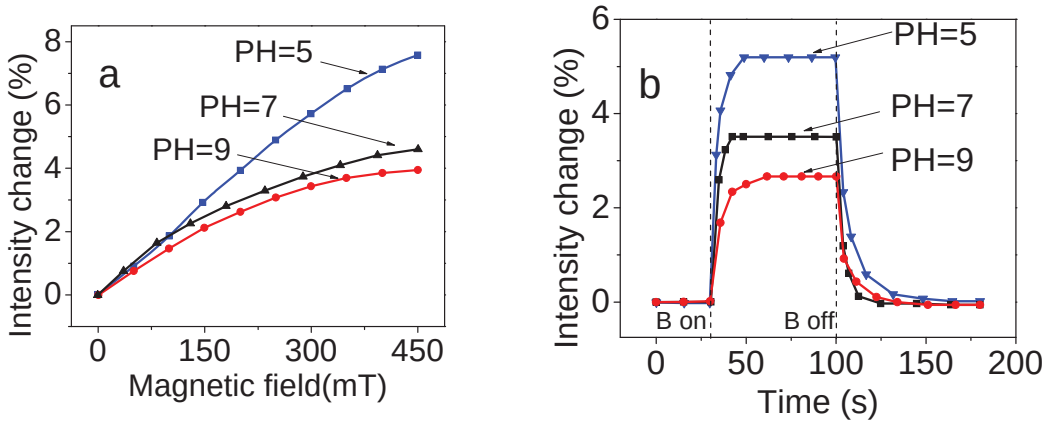

Figure 10. Magnetic field effect of light scattering for HSA + Fe_3O_4 composite with different PH values in suspended solution. a: MFE_{LS} as a function of magnetic field. b: Time dependent MFE_{LS} profiles at a fixed magnetic field of 900 mT.

The surface charge of the HSA/Fe_3O_4 nanoparticle composites is modulated through the PH value of the solution. Since the isoelectric point (pI) of HSA is around 4.7, HSA have positive charge below pI and negative charge above pI. The isoelectric point (pI) of Fe_3O_4 nanoparticles is around PH 6.8. Thus, at PH 5, HSA have negative charge while Fe_3O_4 nanoparticles have positive charge, this can promote the electrostatic attraction between HSA and Fe_3O_4 nanoparticle.[5] As a result, Figure 10 illustrates that stronger Coulombic interaction induces enhanced magneto-electric coupling in the HSA/Fe_3O_4 nanoparticle composites: at PH 5, the MFE_{LS} presents significant enhancement compared to the system with PH7 and PH9. At PH 9,

HSA and Fe_3O_4 nanoparticles both have negative charge, the electrostatic repulsion does not favor the adsorption of HSA on Fe_3O_4 nanoparticles thus leads to the decrease of MFE of light scattering. The PH effect on MFE of light scattering indicates that Coulombic interaction plays an important part in the magneto-electric coupling in the HSA/Fe_3O_4 nanoparticle system.

2.4 Magneto-electric coupling in excited states in HAS+Fe_3O_4 system

We study the magneto-electric coupling of the HSA/ Fe_3O_4 system by measuring MFE of light scattering with a photoexcitation beam of 285nm to analyze the excited states effect on the magnetic polarization and HSA/ Fe_3O_4 interaction. It has been shown that adding a photoexcitation into light scattering experiment can present as a powerful measurement to elucidate the effects of excited states.[6] Figure 11 shows the magnitude of MFE increases from 3.6% to 4%. This enhancement is possibly owing to magnetic polarization in the excited states of the HSA, which promotes the magneto-electric coupling.[7]

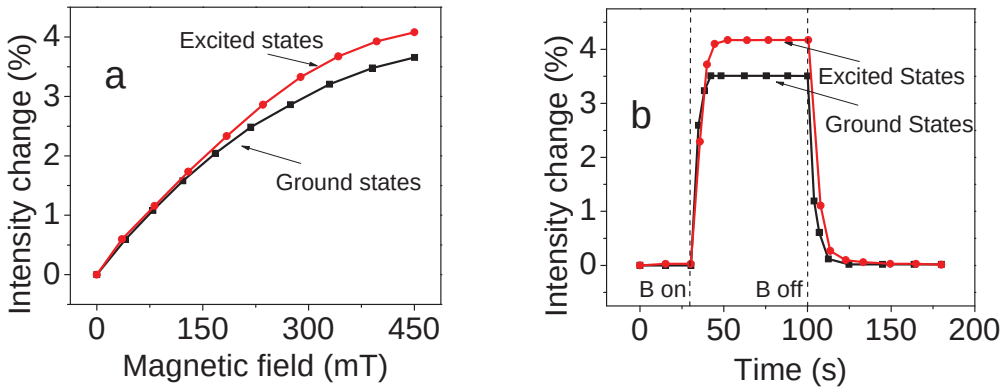

Figure 11. Magnetic field effect of light scattering in excited state for HSA + Fe_3O_4 composite. a: Magnetic field effect of light scattering in excited state as compared with ground state. b: Time dependent profiles for excited state as compared with ground state.

To investigate the effect electric polarization on the magneto-electric coupling of the system, the MFE of light scattering with and without external electric field is measured. By applying 2V electric field (Figure 12), the magnitude of MFE increases from 3% to 4%. From the time dependent MFE curve, shorter response time and relaxation time are observed under 2V electric

field. This illustrates that the excited states can enhance the magneto-electric coupling through increased electric polarization in magnetic/bio composites.

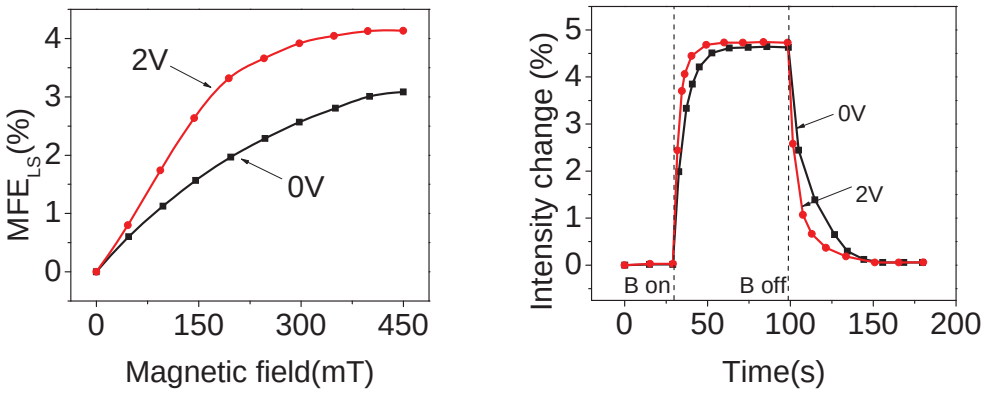

Figure 12. MFE_{LS} on HSA + Fe_3O_4 under external electric field. Time dependent MFE_{LS} profiles from HSA/Fe_3O_4 under external electric field.

In summary, we studied the magneto-electric coupling in the HSA/ Fe_3O_4 system through 1) surface charge modulation in the ground states; 2) magnetic polarization in the excited states and 3) electric polarization in the applied external electric field. Enhancements of magneto-electric coupling are observed, demonstrated by the MFE_{LS} signal under excited states and applied electric field in HSA/Fe_3O_4. As a general conclusion, the optically and electrically tunable magnetic properties of HSA/Fe_3O_4 system prove the existence of magneto-electric coupling within the interaction between HSA and Fe_3O_4 nanoparticles, which can be modulated by optical excitation through excited states.

3. Future research plan

In general, a magneto-electric coupling can be realized through three different channels: Coulomb interaction, spin-orbital interaction, and spin-spin interaction in magnetic/bio composites. We plan to use materials processing and spin-physics measurements to elucidate these three channels and to reveal the critic parameters of controlling magneto-electric coupling in magnetic/bio composites in both ground and excited states.

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