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Magneto-optical studies on organic-magnetic Nanocomposites

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Traditional study on magnetic optical phenomenon are mostly focused on incorporation of magnetic structures in bulk semiconducting materials under high magnetic field. However, magnetic-optical properties at well-defined magnetic/semiconducting interface are rarely explored. Fundamental studies on the underlying mechanism of magneto-optical phenomenon generation through excited states are also highly demanded. This project is proposed to experimentally explore unique magneto-optical properties in excited states for newly developed organic magnetic nanocomposites, organic light emitting materials, up-conversion nanocrystals, and organic/ferromagnetic interface. The goal is to obtain insightful understanding of the coupling mechanisms between magnetic and optical properties in excited states, and develop new guidelines for designing next-generation magneto-optical nanomaterials. This research effort presents a unique research area to generate superior magnetic optical properties for application to Air Force technologies. The US, Japan, China, France, Germany, Brazil and Korea, etc. have been investing in the areas of novel magnetic materials, organic magnetic nanocomposites synthesis, molecular spin physics, and magnetic structure-property characterizations in both ground and excited states. Clearly, organic-magnetic nanomaterials and multi-functional materials are expected to become a critical component in next-generation sensing, navigation, and renewable-energy technologies.

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Magneto-optical Studies on Organic-magnetic Nanocomposites

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I. Objective

Traditional study on magnetic optical phenomenon are mostly focused on incorporation of magnetic structures in bulk semiconducting materials under high magnetic field. However, magnetic-optical properties at well-defined magnetic/semiconducting interface are rarely explored. Fundamental studies on the underlying mechanism of magneto-optical phenomenon generation through excited states are also highly demanded. This project is proposed to experimentally explore unique magneto-optical properties in excited states for newly developed organic magnetic nanocomposites, organic light emitting materials, up-conversion nanocrystals, and organic/ferromagnetic interface. The goal is to obtain insightful understanding of the coupling mechanisms between magnetic and optical properties in excited states, and develop new guidelines for designing next-generation magneto-optical nanomaterials. This research effort presents a unique research area to generate superior magnetic optical properties for application to Air Force technologies. The US, Japan, China, France, Germany, Brazil and Korea, etc. have been investing in the areas of novel magnetic materials, organic magnetic nanocomposites synthesis, molecular spin physics, and magnetic structure-property characterizations in both ground and excited states. Clearly, organic-magnetic nanomaterials and multi-functional materials are expected to become a critical component in next-generation sensing, navigation, and renewable-energy technologies.

In this project, the international collaborations have made the following significant progress on (i) optically tunable magnetization in excited states based on 2D graphene nanoparticles, (ii) optically controllable magnetization in van der Waals heterostructures, (iii) using magnetic nanoparticles to control light-emitting states in organic materials (iv) magneto-photoluminescence based on two-photon excitation in up-conversion nanocrystals, and (v) unique method to couple semiconducting and magnetic properties through interaction between optically-generated charge-transfer states and magnetized charge-transfer states.

II. Achievements

1. 2D materials magneto-optics: Optically tunable magnetization in excited states based on 2D graphene nanoparticles [Nanoscale 9, 2017: 2563-2568]

Optically tunable magnetic properties present as a unique phenomenon that is highly demanded for developing multifunctional materials in sensing, detection, and renewable-energy technologies. However, the generation of optically tunable magnetic properties is of great challenge, which

requires novel semiconducting/magnetic system design, and new detection method for experimental analysis. In this collaborative study we have found that upon photoexcitation, fluorinated graphene nanoparticles can possess stronger magnetization as compared to ground state. Theoretically, doped graphene such as fluorinated graphene nanoparticles can exhibit semiconducting properties due to the delocalized π induced by surface-mediated charge-transfer or bulk defects. Theoretical and experimental studies have indicated that defects such as vacancies, adatoms, and zigzag edges can introduce localized magnetic moments by the formation of unpaired spins in defective graphene and functionalized graphene. With the delocalized π electrons and localized spins, the fluorinated graphene nanoparticles can demonstrate excited state and magnetization, allowing the studies on the magnetization in excited state.

The fluorinated graphene nanoparticles were suspended in organic solvent. A magnetization force can be introduced upon applying magnetic field due to intrinsic magnetic properties of fluorinated graphene nanoparticles. This magnetization force can cause an orientation or alignment for the suspended nanoparticles, changing light scattering signal, leading to magnetic field effect of light scattering (Figure 1a). It can be seen in Figure 2b that, a magnetic field can change the light scattering from the suspended fluorinated graphene nanoparticles, generating a magnetic field effect of light scattering signal with the amplitude of 60% at 900 mT. More importantly, in excited state the suspended nanoparticles exhibit an enhanced magnetic field effect of light scattering with amplitude of 69%. The increased magnetic field effect of light scattering signal upon applying photoexcitation shows that the excited state possesses a stronger magnetization in the fluorinated graphene nanoparticles as compared to ground state. Clearly, our study provides first experimental evidence of realizing optically tunable magnetization in doped graphene derivatives through the interaction between delocalized semiconducting π electrons and localized spins.

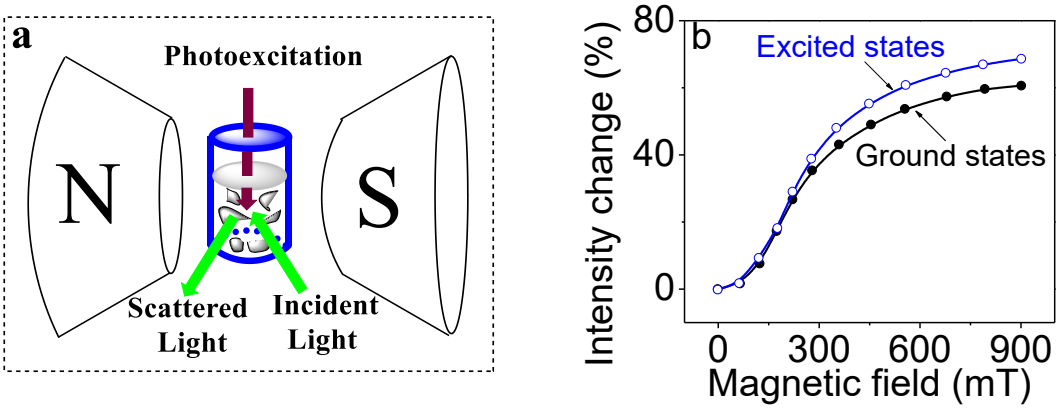

Figure 1 a. Schematic setup for measuring magnetic field effect of light scattering in excited state. **b.** magnetic field effect of light scattering signal from fluorinated graphene nanoparticle suspension in ground state and excited state.

2. Nanohybrid magneto-optics: Optically controllable magnetization in van der Waals heterostructures [The Journal of Physical Chemistry C 122, 2018: 6912-6917]

Photoexcitation-controllable magnetization offers a unique principle of developing magneto-optical properties in multifunction materials. However, it is challenging to design well balanced semiconducting/magnetic materials systems with mutually coupled semiconducting and magnetic properties. Based on the successful experience of magnetic field effect of light scattering study on optically tunable magnetization in doped graphene, the international collaboration between Bin Hu (USA) and Kwang-Sup Lee (Korea) have adopted a new approach: realizing the photoexcitation-controllable magnetization by chemically linking the magnetic γ-Fe_2O_3 nanoparticles and 2-D graphene based on magnetic field effect of light scattering.

The MYG nanohybrid was synthesized by coupling 0D magnetic nanoparticle(MNP) γ-Fe_2O_3 and 2D semiconducting graphene through π-conjugated ligand Y in *N*-methyl pyrrolidone (NMP) solvent (Figure 2a). We can see that in Figure 2b, MYG suspension shows magnetic field effect of light scattering with amplitude of 12.2%, whereas pristine graphene suspension and magnetic nanoparticles shows MFE_{LS} with lower amplitude of 7% and 3%, respectively. However magnetic field effect of light scattering of superparamagnetic γ-Fe_2O_3 MNP shows much narrower line-shape, revealing that MNP possesses a larger magnetic susceptibility giving rise to a faster magnetic response. By coupling MNP with graphene flakes through ligand Y, narrower MFE line-shape and increase in MFE amplitude can be observed in MYG suspension, indicating an enhancement of magnetic properties.

Furthermore, the MFE amplitude increases from 12.2% to 14.8% in MYG suspension under 250mW/cm^2 photoexcitation, and the line-shape become narrower (Figure 2c). This enhanced MFE signal and narrower line-shape provide evidences that the magnetization becomes stronger under photoexcitation in the MYG nanohybrid. Specifically, in the MYG nanohybrid, graphene can interact with γ-Fe_2O_3 nanoparticles through the coupling between π electron in semiconducting graphene and d electron in magnetic nanoparticles, leading to enhanced magnetic properties in excited states. Our study present a practical method to develop photoexcitation-controllable magnetization based on chemically linked magnetic-semiconducting hybrid materials through d-π electron coupling.

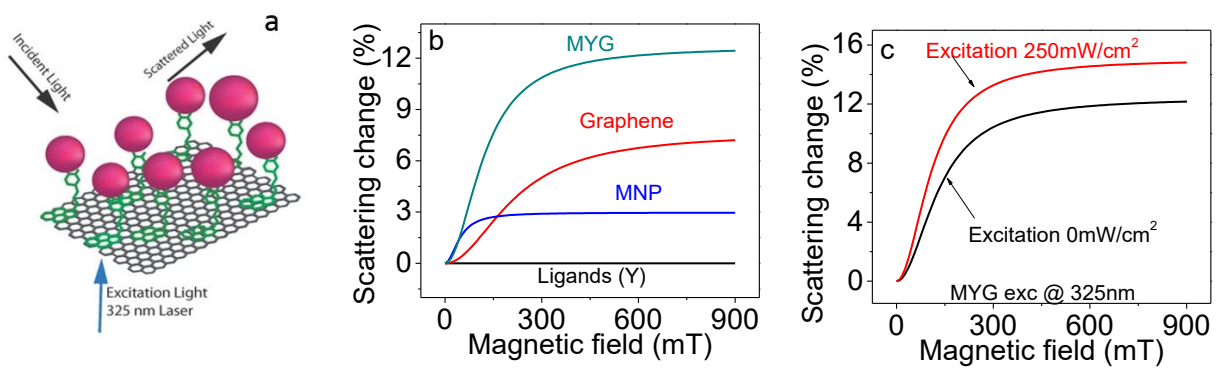

Figure 2a. Schematic setup for measuring magnetic field effect of light scattering in excited state. **b**. magnetic field effect of light scattering signals from coupled sample (MYG) and separated components (MNP, graphene, organic molecules). **c**, magnetic field effect of light scattering signals from MYG suspension in ground state and excited state.

3. Organic light emission: Using magnetic nanoparticles to control light-emitting states in organic materials [submitted to Nature Communication]

Thermally activated delayed fluorescence (TADF) presents as a unique mechanism to boost the light-emitting efficiency for next generation organic light-emitting diodes (OLEDs). TADF emitters generally contain the donor-acceptor structure with charge-transfer states (CT states) to have small energy difference between singlets and triplets (ΔE_{ST}) (Figure 3a). Therefore, previous experimental studies have been mainly focused on tuning energy parameter to increase the TADF efficiency by reducing the energy barriers ΔE_{ST}. However, it remains as a significantly unaddressed issue on how the spin flipping mechanism is involved in the TADF process. This collaborative study investigates the two major parameters, namely exchange interaction and spin-orbital coupling, responsible for spin-conserving and spin-mixing respectively in TADF process. We found that magnetic nanoparticle doping can be used as a convenient method to tune the exchange interaction and spin-orbital coupling in TADF to control the efficiency of delayed fluorescence. Here, the magneto-photoluminescence is used to study the spin-specific TADF process based on DMAC-TRZ molecule in toluene solutions. Figure 3b shows the magneto-photoluminescence in TADF from DMAC-TRZ toluene solution. We can see that photoluminescence intensity gradually increases and then becomes saturated with the applied magnetic field, leading to the positive magneto-photoluminescence in TADF. Meanwhile, the magneto-photoluminescence signal is negligible for non-TADF system with Frenkel exciton as the excited state.

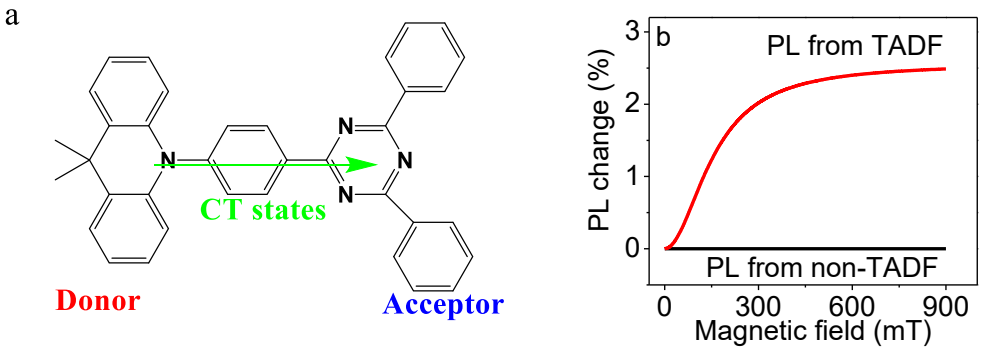

Figure 3a. Molecular structures of DMAC-TRZ, where DMAC and TRZ serve as electron-donating and electron-accepting part respectively; **b.** Magneto-photoluminescence from TADF and non-TADF process.

The key parameters in controlling the spin specific TADF process have been explored by intentionally changing the exchange interaction and spin-orbital coupling via the doping of magnetic Fe_3O_4 nanoparticles. In particular, we monitor the line-shape and TADF rate with the doping concentration of magnetic nanoparticles. The line-shape narrowing and broadening can be related to spin-orbital coupling and exchange interaction, respectively. By combining the TADF rate, we can elucidate how exchange interaction and spin-orbital coupling affect the TADF. Figure 4a depicts the normalized magneto-photoluminescence curves from DMAC-TRZ toluene solution with low doping concentration. We can see that increasing the doping concentration from 0 to 1 wt% causes a line-shape narrowing in magneto-photoluminescence. Specifically, the line-shape reflects how fast singlet/triplet ratio can be changed with external magnetic field through perturbing the singlet-triplet intersystem crossing in CT states. We know that exchange interaction and internal magnetic interactions disallows and allows singlet-triplet intersystem, respectively. The competition between exchange interaction and internal magnetic interaction dynamic equilibrium in singlet/triplet ratio. The magnetic field can influence the internal magnetic interaction to break this dynamic equilibrium and generate magneto-photoluminescence. In typical TADF system, the spin-orbital coupling is the dominate spin mixing mechanism. Thus, exchange interaction and spin-orbital coupling are two intrinsic spin parameters functioning as resistance force and driving force for TADF, respectively. The line-shape narrowing reflects that low concentration magnetic nanoparticles doping can increase the spin-orbital coupling as the driving force to facilitate the TADF through spin mixing process.

On contrast, at high concentration doping, the line-shape becomes broadening with the increase of the concentration, as shown in Figure 4b. This line-shape broadening indicates that at high doping concentration magnetic nanoparticles can enhance the exchange interaction, therefore increasing the resistance force for TADF. Our magneto-photoluminescence studies on DMAC-TRZ based TADF emitter reveals the spin-orbital coupling as the major mechanism for efficient spin mixing process in TADF. The magnetic Fe_3O_4 nanoparticles doping was found can increase (reduce) the

TADF efficiency in low (high) doping concentration through enhancing the spin-orbital coupling (exchange interaction).

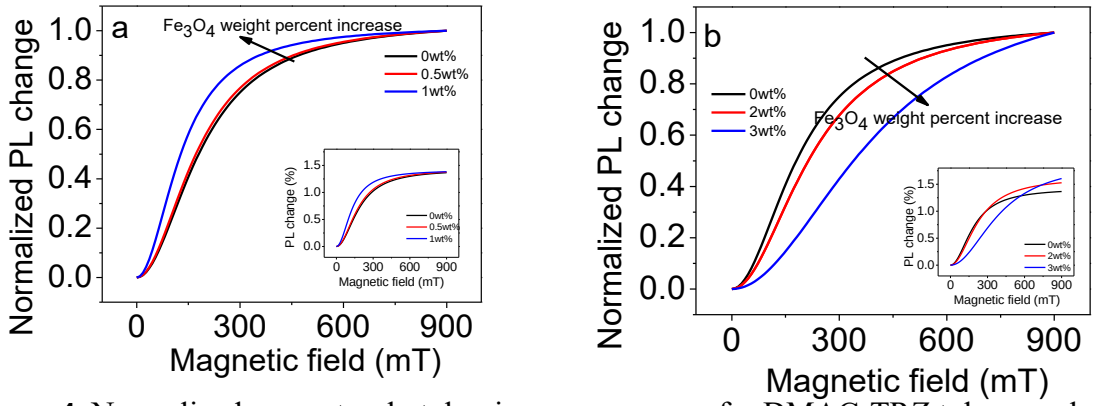

Figure 4. Normalized magneto-photoluminescence curves for DMAC-TRZ toluene solution with low concentration (0.5 and 1wt%) **a.** and high concentration (2 and 3wt%) **b.** magnetic Fe_3O_4 nanoparticles doping. The inset shows the absolute magneto-photoluminescence values.

4. Two photon magneto-optics: magneto-photoluminescence based on two-photon excitation in up-conversion nanocrystals [Small 13, 2017: 1603363]

Magneto-photoluminescence is a typical magneto-optical effect based on mutually coupled magnetic and optical properties in multifunctional materials. It has been largely demonstrated in excitonic light emitting materials based on spin dependent excited states. However, it remains an un-addressed issue on whether magneto-photoluminescence can be generated in non-excitonic light emitting materials. To respond this great challenge, the international collaboration has been exploring the possibility of realizing magneto-photoluminescence in lanthanide doped up-conversion nanocrystals by considering the spin-dependent transition dipoles.

Traditional efforts have been focusing on incorporating magnetic ions with lanthanide doped up-conversion materials which can decrease the up-conversion luminescence efficiencies. Recently, our study has developed new concepts by considering the spin-dependent transition dipole formed between excited electron and ionic core of lanthanide ion, together with operative spin mixing between antiparallel and parallel spins under high intensity photoexcitation. It can be noted in Figure 5a that magneto-photoluminescence can be observed in the Y_2O_2S: Er, Yb crystals under two-photon excitation of 980 nm laser beam only if the excitation exceeds the critical intensity of 2080mW/cm^2. Specifically, the two-photon excitation generates spin-antiparallel transition dipoles based on spin selection rule in doped Er3+ ions. When the photoexcitation exceeds the critical intensity, the Coulomb screening can decrease the exchange interaction, allowing spin mixing to occur under the influence of SOC. The competition between between spin mixing and spin conserving can lead to an equilibrium in populations on antiparallel and parallel dipoles. An external magnetic field can then disturb the equilibrium modifying the populations on antiparallel and parallel dipoles, consequently generating magneto-photoluminescence (Figure 5b). Clearly,

our study provides new insight to generate magneto-optical effects in up-conversion materials under low magnetic field at room temperature.

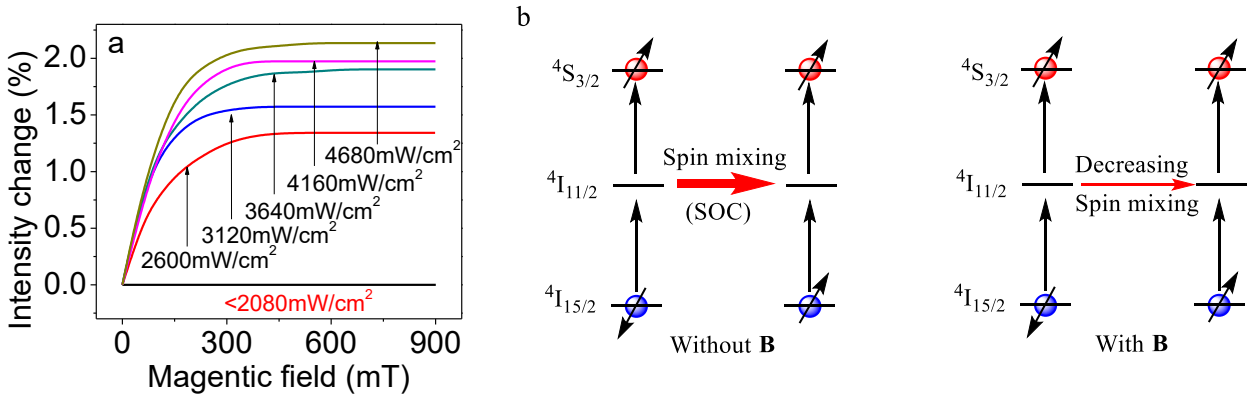

Figure 5a. Magneto-photoluminescence of Y_2O_2S: Er, Yb under high intensity 980nm IR laser excitation. **b**. schematic of generating magneto-photoluminescence in two photon up-conversion process by magnetically disturb the balance of population of transition dipoles with different spin states.

5. **Magneto-electric coupling between charge transfer states: Unique method to couple semiconducting and magnetic properties through interaction between optically-generated charge-transfer states and magnetized charge-transfer states [The journal of physical chemistry letters 6, 2015: 4319-4325.]**

Coupling between semiconducting and magnetic properties presents potential opportunities of generating mutually tunable magnetic-optical-electric effect in multifunctional materials and devices. It requires well-defined semiconducting/magnetic system to generate the mutual coupling, and unique experimental approach to analyze the underlying mechanism. In this international collaborative study, we have demonstrated optically tunable spin interface by combining optically generated charge transfer states and magnetized charge transfer (CT) states based on thin-film design. In general, optically generated CT states are electrical dipoles generated by photoexcitation through a charge-transfer process in organic semiconductors. Using Optically generated CT states presents a unique approach to develop magneto-optic and magneto-electric properties in excited states. Whereas, magnetized CT states can form at 2D ferromagnetic/semiconducting interface through direct charge transfer or wave function hybridization. Magnetized CT states can offer a mutual tuning mechanism between magnetic and electric properties based on a ferromagnetic/semiconducting interface. Coupling between optically generated CT states and magnetized CT states presents potential approach of mutual tuning between magnetic optical and electric properties in multifunctional thin film devices.

The coupling between optically generated CT states and magnetized CT states was studied by using magneto-dielectric effects based on thin-film devices with the architecture of ITO/TPD:BBOT/TPD/Co/Al. It can be noted that device with combination of optical CT states and magnetized CT states exhibits a larger amplitude (Figure 6a) and narrower line-shape (Figure 6b) in magneto-dielectric signal as compared to devices with only optical CT states or magnetized CT states. This result presents critical evidence of interaction between the optically induced CT states and magnetized CT states. Importantly, our analysis indicates that this interaction between the optically generated CT states and magnetized CT states is due to (i) Coulomb interaction and (ii) spin−orbital interaction. Specifically, increasing optically generated CT states by increasing photoexcitaion intensity, can enhance the Coulomb interaction and reduce the spin-orbital interaction, leading to a narrower magneto-dielectric line-shape and a larger magnitude (Figure 6c). Whereas, increasing the distance between optical CT states and magnetized CT states by increasing TPD layer thickness weakens the Coulomb interaction and spin-orbital interaction, leading to a broader line-shape and larger amplitude (Figure 6d). Therefore, our results provide a new mechanism to realize magneto-electric coupling by combining optically generated CT states and magnetized CT states based on ferroelectric/organic interfaces for future electric, magnetic, and optic applications in excited states.

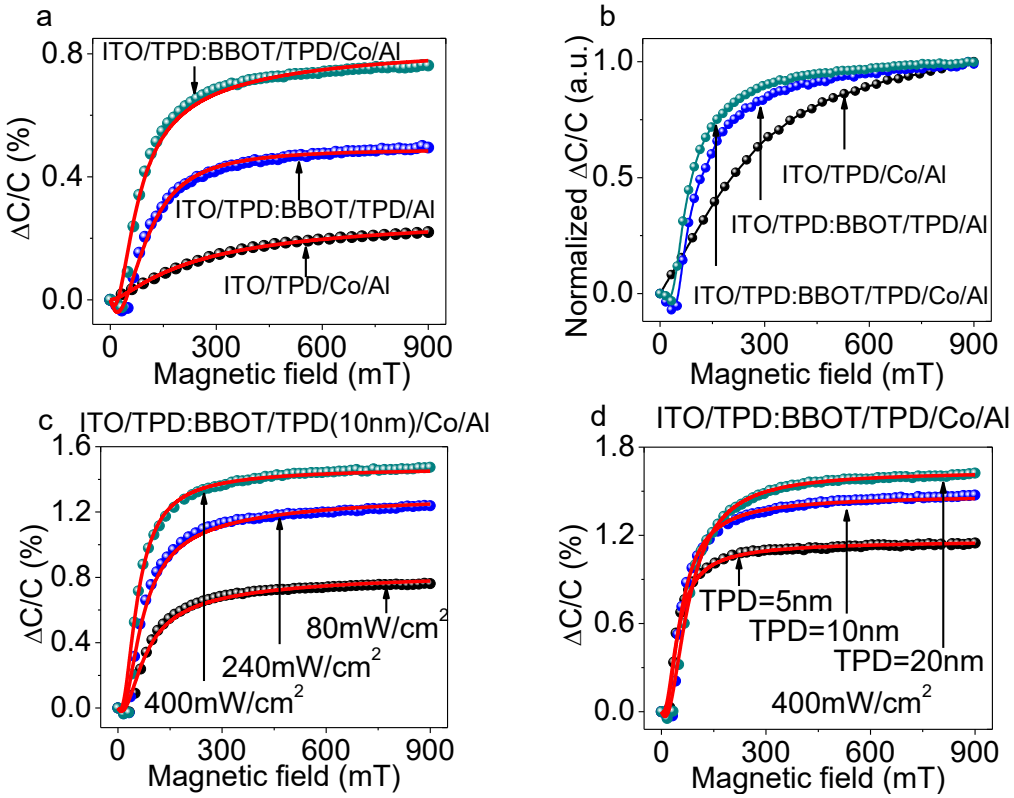

Figure 6a. Magneto-dielectric signals from devices ITO/TPD/Co/Al, ITO/TPD:BBOT/TPD/Al and ITO/TPD:BBOT/TPD/Co/Al under photoexcitation intensity of 80 mW/cm2. **b**. Normalized magneto-dielectric curves. **c.** Magneto-dielectric signals from the device ITO/TPD:BBOT/ TPD/Co/Al under different photoexcitation intensities. **d.** Magneto-dielectric signals from the device ITO/TPD:BBOT/TPD/Co/Al with different TPD thickness.

In summary, the recent international collaborations between US, Korea, and Taiwan have presented new approaches to develop optically controllable magnetic properties, coupling between magnetic and optic properties, and coupling between magnetic and electric properties. This new approach is based on combining nano-magnetic materials with organic molecules in excited state, as well as in depth understanding of spin related process in excited states. These experimental results provide the strong scenario that using organic-magnetic nano-materials in excited state presents as a novel concept to develop magnetically controllable optical, electrical, and optoelectronic processes for next generation sensing, navigation, and renewable-energy applications.

III. Preparation of graduate students

1. Yu-che Hsiao: Doctor of Philosophy, thesis title: Magnetic, optical and electrical properties of electron-hole pairs in polymer and organo-metal halide perovskite photovoltaic cells.

2. Mingxing Li: Doctor of Philosophy, thesis title: Interaction between charge-transfer states studied by magnetic field effects.

3. Ting Wu: Doctor of Philosophy, thesis title: Exploring polarization and spin effects in organic inorganic hybrid perovskites towards controlling the key optoelectronic processes.

IV. Publications

1. Lei He, Mingxing Li, Hengxing Xu, and Bin Hu. Experimental studies on magnetization in the excited state by using the magnetic field effect of light scattering based on multi-layer graphene particles suspended in organic solvents. *Nanoscale* 9, no. 7 (2017): 2563-2568. [page 1]
2. Hengxing Xu, Prem Prabhakaran, Sung Hyun Kim, Juhyung Jung, Rekha Narayan, Sang Ouk Kim, Kwang-Sup Lee, and Bin Hu. Photoexcitation-Controllable Magnetization in Magnetic–Semiconducting Nanohybrid Containing γ-Fe2O3–Graphene (0D–2D) van der Waals Heterostructure Based on Steady-State Pump–Probe Light Scattering Measurement in Magnetic Field. *The Journal of Physical Chemistry C* 122, no. 12 (2018): 6912-6917. [page 3]
3. Miaosheng Wang, Camera Foster, Ting Wu, Tanmay Chatterjee, Ken-Tsung Wong, Bin Hu. Unraveling Spin-Orbital Coupling Effects on Thermally Activated Delayed Fluorescence Based on Magneto-Photoluminescence Studies. Submitted to Nature Communication. [page 4]
4. Hengxing Xu, Wei Qin, Mingxing Li, Ting Wu, and Bin Hu. Magneto-Photoluminescence Based on Two-Photon Excitation in Lanthanide-Doped Up-Conversion Crystal Particles. *Small* 13, no. 16 (2017): 1603363. [page 6]

5. Mingxing Li, Lei He, Hengxing Xu, Ming Shao, Jeremy Tisdale, and Bin Hu. Interaction Between Optically-Generated Charge-Transfer States and Magnetized Charge-Transfer States toward Magneto-Electric Coupling. *The journal of physical chemistry letters* 6, no. 21 (2015): 4319-4325. [page 7]