

**Experimental Studies on Extremely Slow Phonon Dynamics and Circularly
Polarized Excitonic Emission in Organic Multi-functional Materials**

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

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May 2025

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ACKNOWLEDGEMENTS

Firstly, I would like to express my heartfelt gratitude to my Ph.D. advisor, Dr. Bin Hu, whose unwavering support, insightful guidance, and valuable advice have been instrumental to my research. I would also like to thank my Ph.D. dissertation committee members, Dr. David Mandrus, Dr. David J. Keffer, Dr. Haixuan Xu, and Dr. Huibo Cao, for their constructive comments and valuable advice on my Ph.D. proposal and dissertation.

I also wish to acknowledge my collaborators, Dr. Prem Prabhakaran at Hannam University, Dr. Kunio Awaga at Nagoya University, and Dr. Tetsuro Kusamoto at Osaka University, for their significant help in providing the materials and discussing the results to support my studies. My sincere thanks go to Dr. Jong Keum at Oak Ridge National Laboratory for his exceptional support and guidance in performing experimental studies, analyzing data, and discussing results involving X-ray diffraction and reflection.

I am particularly grateful to my former lab mates, Dr. Miaosheng Wang, Dr. Yixuan Dou, and Dr. Bogdan Dryzhakov, for helping me in my Ph.D. research studies. My gratitude also goes to the present group member, Tatenda Kanyowa, for his great help and friendship.

Finally, I owe my deepest thanks to my parents, Weifeng Tang and Changli Ma, for their boundless love and unwavering support during my Ph.D. journey, and to my dear friend Kedun, Bingqilin, and their friends, whose kindness and encouragement sustained me through the most challenging days.

ABSTRACT

Understanding and controlling exciton behavior in molecular and hybrid crystalline systems is pivotal to advancing next-generation optoelectronic technologies. This dissertation investigates exciton dynamics, spin–orbit coupling (SOC), and circularly polarized luminescence (CPL) across four interrelated material systems: donor–acceptor (D–A) type organic crystals, chiral metal–organic frameworks (MOFs), luminescent radicals, and chiral perovskite crystals. Chapter 1 introduces these materials along with the concepts of extremely slow phonon dynamics and circularly polarized excitonic emission.

Chapter 2 explores the role of phonon dynamics in polar organic crystals with D–A configurations. Through time-resolved photoluminescence and structural characterization, we discovered that ultra-slow phonon interactions prolong excited-state lifetimes via a triplet-based charge transfer mechanism. This manifests as super-delayed fluorescence, revealing a novel phonon-assisted luminescence pathway.

Chapter 3 focuses on spin–orbit coupling effects in chiral MOFs. Structural chirality induces Rashba-type band formation and non-degenerate spin states. By correlating SOC-driven optical transitions with luminescence lifetimes, we demonstrate that chiral MOFs enable spin-selective emission, highlighting their potential for chiral optical devices.

Chapter 4 investigates spin-dependent behavior of circularly polarized excitons in organic radical-doped crystals. The doublet states in radicals circumvent traditional spin statistics limitations to enable excited-state luminescence. Significant CPL signals were observed experimentally, with magnetic field application enhancing both intensity and degree of

polarization. This magnetic enhancement verifies synergistic interactions between doublet states, SOC, and spin-mixing processes.

Chapter 5 examines spin–orbit coupling ordering in chiral perovskite crystals. Through CPL and magneto-optical spectroscopy at low temperatures, we observed magnetic field-enhanced circularly polarized excitonic emissions. The combination of chirality-induced Rashba bands and helically arranged SOC enables magnetic field modulation of excited-state behavior, providing direct evidence of excitonic spin ordering.

Chapter 6 provides a comprehensive summary of this dissertation and discusses the implications from the perspective of future applications. It focuses on overcoming traditional limitations in light emission using open-shell radical systems, chiral material design, and spin-polarization mechanisms. The experimental findings presented in this work—including the suppression of non-radiative losses, regulation of electron–phonon coupling, and realization of efficient circularly polarized light emission via chiral architectures—offer a solid foundation for the development of next-generation spintronic optoelectronic devices and quantum information technologies.

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Chapter 1 Introduction

1.1 Organic Multi-Functional Materials

1.1.1 Organic Multi-Functional Materials

Organic luminescent functional materials play an important role in modern optoelectronic technologies, finding extensive applications in displays, lighting systems, and sensing devices. Recent advancements have significantly enhanced their performance and functionality through the incorporation of novel structural designs and emerging material systems. This section presents several representative categories of organic luminescent materials, including donor-acceptor (D-A) molecules, radical light emitters, metal-organic frameworks (MOFs), and chiral organic-inorganic hybrid perovskites.

1.1.2 Donor-Acceptor Molecules

The remarkable luminescent performance of donor–acceptor (D–A) materials can be fundamentally attributed to their distinct charge-transfer mechanisms and dynamic characteristics. In such systems, electron-rich donor moieties (e.g., triphenylamine or carbazole derivatives) spontaneously transfer electrons to electron-deficient acceptors (e.g., cyano groups or benzothiadiazole), establishing stable charge-separated states with establishing a charge-separated state where the donor bears a partial positive charge and the acceptor a partial negative charge^{1,2,3,4,5,6}. The D-A architecture enhances exciton utilization efficiency through effective charge transfer and recombination processes. Particularly in Thermally Activated Delayed Fluorescence (TADF) materials, this configuration theoretically achieves near-unity (100%) exciton utilization, thereby significantly improving luminous efficiency. Conventional fluorescent materials are constrained by the participation of only 25% of singlet excitons in light emission. In

contrast, D-A molecules enable triplet excitons to contribute to emission through reverse intersystem crossing (RISC) under thermal activation by minimizing the energy gap between singlet (S_1) and triplet (T_1) states ($\Delta E_{ST} < 0.2$ eV). This mechanism theoretically achieves 100% internal quantum efficiency (IQE)^{7,8}. For instance, non-fullerene organic photovoltaic devices (OPVs) based on PM6:Y6 systems have demonstrated power conversion efficiencies exceeding 18%⁹. Another notable example is the green-emitting material (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (abbreviated as 4CzIPN), which exhibits exceptional external quantum efficiency (EQE) exceeding 30%¹⁰. This breakthrough highlights the potential of D-A architectures in overcoming the limitations of traditional luminescent systems through optimized charge transfer dynamics and energy level engineering.

Beyond the molecular scale, the solid-state packing and supramolecular organization of D-A molecules also influence their optical and electronic properties. In thin films or crystalline states, molecular arrangements may enhance or suppress charge-transfer (CT) interactions. For example, face-to-face stacking can lead to excimer formation, typically exhibiting broad, red-shifted, and low-efficiency emission^{11,12}. In contrast, ordered aggregation can promote desirable traits such as aggregation-induced emission (AIE), where restricted intramolecular motion in aggregated states suppresses non-radiative decay¹³. Thus, controlling aggregation patterns and molecular orientation is crucial in the design of D-A materials.

Furthermore, D-A structures have been shown to enable spin-flip transitions via spin-orbit coupling (SOC), as shown in **Figure 1-1**, which governs the interaction between an

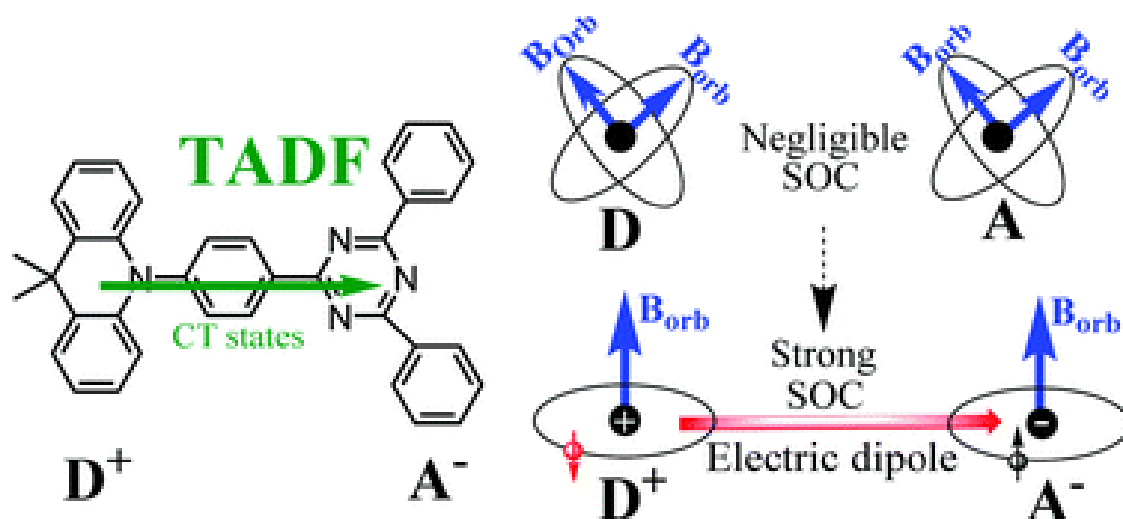


Figure 1-1 Illustration showing SOC generated by polarizing orbitals due to the electrical dipole between D⁺ and A⁻ within a CT state¹⁷.

electron's spin and orbital angular momentum, profoundly influencing optoelectronic and quantum behaviors^{14,15,16,17}. Intermolecular charge-transfer donor-acceptor dipoles can function as an unconventional method to create a SOC, by passing the conventional method of using heavy elements to generate SOC. Through molecular engineering, SOC effects in D-A systems can be modulated to facilitate transitions from non-radiative triplet states to radiative singlet states, resulting in OLED applications.

1.1.3 Metal-Organic Frameworks

Figure 1-2 illustrates the structure of metal-organic frameworks (MOFs), which are an exciting class of crystalline, porous materials composed of metal ions or clusters coordinated with organic ligands. This modular assembly creates extended networks with highly tunable pore sizes, large surface areas, and diverse chemical functionalities.

Because of these attributes, MOFs have attracted widespread attention across multiple disciplines—from gas storage and separation to catalysis, sensing, and even optoelectronics. In multifunctional material applications, MOFs offer a unique platform that combines structural versatility with incorporating additional functional properties, such as luminescence, magnetism, and conductivity.

In the realm of optoelectronics, MOFs are being explored for their potential in light-emitting and photovoltaic devices. When MOFs are designed with conjugated organic linkers or with luminescent metal centers (such as lanthanides), they can exhibit strong fluorescence or phosphorescence^{18,19,20}. The rigid framework provided by the MOF can also suppress nonradiative decay processes—often associated with molecular vibrations—thereby enhancing the luminescent quantum yield^{21,22}. Such characteristics

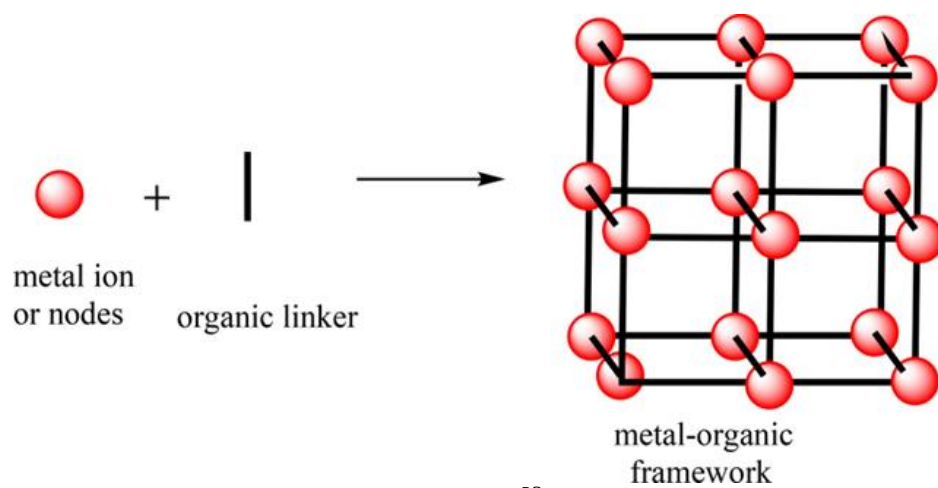


Figure 1-2 Illustration of the structure of MOFs²³.

are particularly attractive for the development of sensors and displays^{24,25,26}.

1.1.4 Radical Light-Emitting Materials

Radical light-emitting materials have emerged as a promising class of organic emitters for light-emitting diodes (LEDs) and other optoelectronic applications. Unlike conventional organic emitters that rely on closed-shell molecules with singlet and triplet excited states, radical emitters are based on open-shell systems containing one or more unpaired electrons. This fundamental difference gives rise to a unique doublet spin manifold in both the ground and excited states. Because transitions within this doublet manifold are spin-allowed, radical light-emitting materials can, in principle, achieve nearly 100% internal quantum efficiency without the need for additional processes—such as intersystem crossing—to harvest dark triplet excitons²⁷.

As shown in **Figure 1-3**, at the core of radical emitters is the presence of a singly occupied molecular orbital (SOMO). In a radical molecule, the SOMO lies energetically between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of an equivalent closed-shell system. When a radical absorbs a photon, an electron is promoted from a fully occupied orbital (or, in some cases, from the SOMO itself) to a higher unoccupied orbital, creating an excited doublet state (commonly denoted as D_1). The subsequent radiative decay from this excited doublet state to the ground doublet state (D_0) is a spin-allowed process. This direct “doublet emission” mechanism circumvents the spin statistics that limit conventional organic light-emitting diodes (OLEDs) to 25% efficiency, because in typical closed-shell systems, only 25% of excitons generated as singlets are emissive while 75% of excitons, formed as

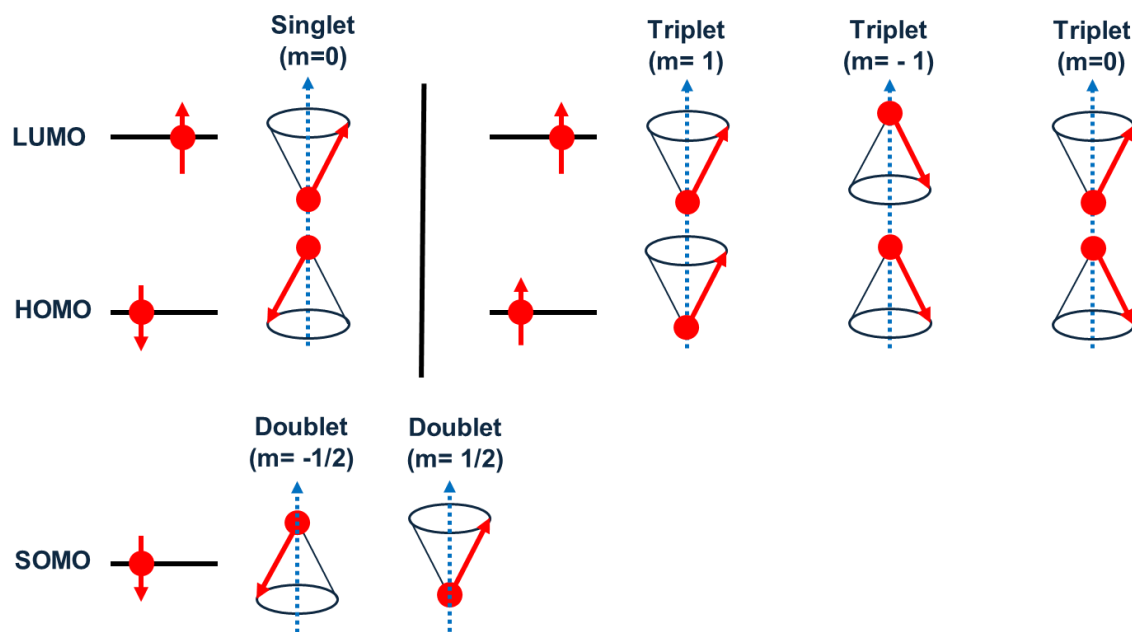


Figure 1-3 Schematic diagram of triplet states, singlet state, and doublet states.

triplets, are often lost through nonradiative decay or require heavy-metal complexes to become emissive.

To design efficient radical light-emitting materials, researchers must address two main challenges: achieving high photoluminescence quantum yield (PLQE) and ensuring the long-term stability of the radical species. The inherently reactive nature of open-shell species has historically limited the practical use of radicals in devices. However, through careful molecular engineering—such as incorporating sterically demanding substituents and designing rigid molecular frameworks—chemists have developed stable organic radicals that resist dimerization and degradation under ambient conditions. For example, derivatives of tris(2,4,6-trichlorophenyl)methyl (TTM) and related motifs have demonstrated both excellent thermal and photo-stability while retaining strong doublet emission in the visible to near-infrared (NIR) spectral regions²⁸.

In addition to molecular design, the photophysical behavior of radical emitters is highly dependent on its environment and the host materials in which they are embedded.

Radical-based OLEDs typically employ host–guest architectures, where the radical emitter is dispersed within an organic semiconductor matrix. The host material must not only be chemically compatible but also enable efficient energy transfer and balanced charge injection to maximize device performance. For instance, by selecting hosts with appropriate energy levels and good charge transport properties, researchers have demonstrated radical OLEDs with external quantum efficiencies (EQEs) exceeding 10% and, in some reports, approaching 27% for deep-red and NIR emissions²⁹. Such achievements are particularly exciting because they showcase the potential of radical

emitters to deliver high brightness, fast response (with emission lifetimes in the nanosecond range), and low-efficiency roll-off at high current densities.

In summary, radical light-emitting materials represent a paradigm shift in the design of organic optoelectronic materials. Their unique doublet spin characteristics allow for highly efficient, fast emission that bypasses the traditional limitations imposed by singlet–triplet exciton dynamics.

1.1.5 Organic-Inorganic Hybrid Metal Halide Perovskites

Figure 1-4 illustrates the formation of organic–inorganic hybrid metal halide perovskites with the general ABX_3 crystal structure^{30,31}. The A site is generally a monovalent cation such as methylamine ion (MA^+), formamidinium ion (FA^+), and inorganic cations Cs^+ , Rb^+ . The B-site is usually a divalent transition metal cation, exemplified as Pb^{2+} , Sn^{2+} , Cu^{2+} , Eu^{2+} , and Yb^{2+} . The X sites are generally halogen ions, including Cl^- , Br^- , and I^- . The B-site metal cation is coordinated with six X-site anions to form a BX_6^{4-} octahedral structure, and the A-site ion can be wrapped in a BX_3 cage to create a 3D crystalline structure of ABX_3 by an angle-shared connection. Organic-inorganic hybrid metal halide perovskites can be prepared by spin-coating method to form polycrystalline films. On the other hand, they can also be prepared into high-quality single crystals by solution processing methods including anti-solvent crystallization, seed-solution growth, solvothermal method and interface crystallization^{32,33,34,35}. The perovskite single crystals can be prepared with different crystallographic structures including the cubic phase such as $MAPbBr_3$ and $FAPbI_3$ ^{36,37}, the tetragonal phase such as $MAPbI_3$ and $MASnI_3$, the orthorhombic phase such as $TMA_2NaInCl_6$, and the triclinic phase such as

SOC effects

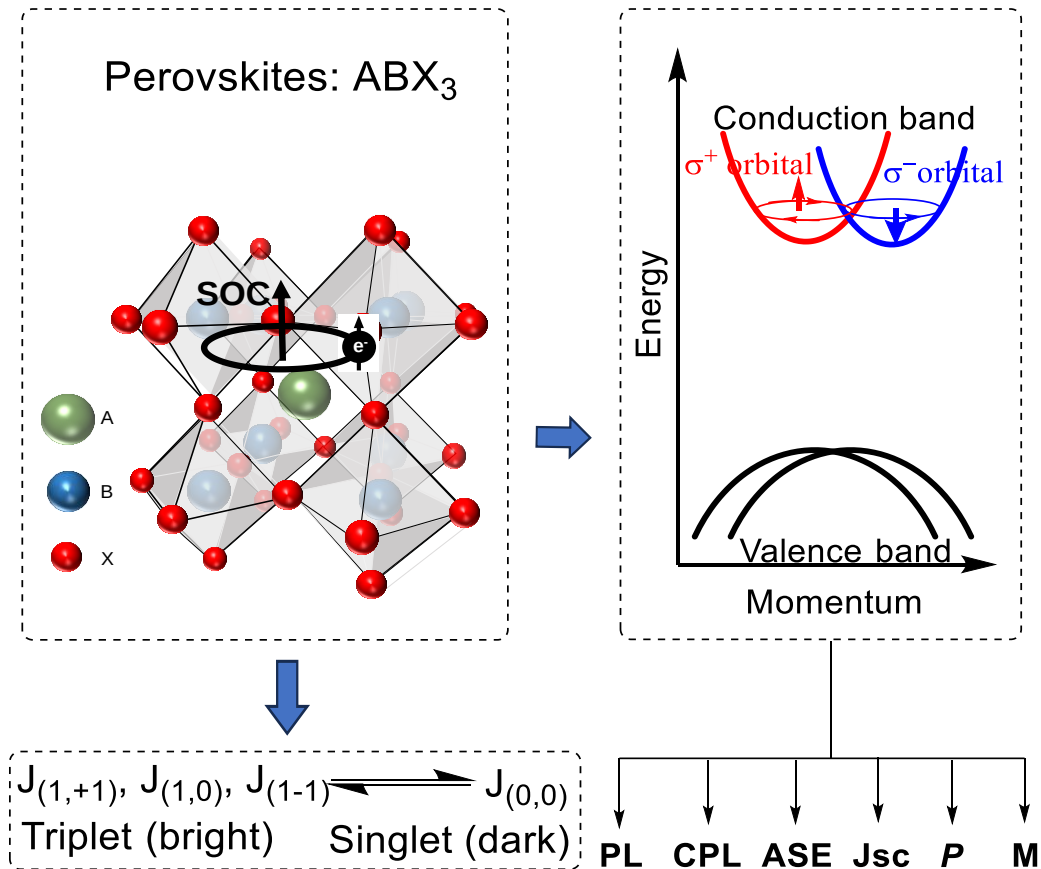


Figure 1-4 Organic-inorganic hybrid metal halide perovskites (OIHMHP) are multifunctional semiconductors carrying both orbital and spin momentum towards forming strong spin-orbital coupling (SOC)³⁸.

(MBA)₂PbI₄^{33,34,39,40}. Importantly, organic-inorganic hybrid metal halide perovskites have shown significant potential for applications in light-emitting diodes (LEDs), solar cells, and detectors due to facile solution-processing capabilities, high-quality thin-film formation, and large tuning capabilities of energy levels. The development of these materials in optoelectronics began with the perovskite compound, (C₆H₅C₂H₄NH₃)₂PbI₄ (PAPI), which demonstrated an electroluminescent (EL) in LED design as early as 1994⁴¹. Since then, advancements have been made by employing strategies such as incorporating high-mobility hole-transport and electron-transport layers, addressing uncoordinated perovskite defects, and introducing additives to refine the structures and increase exciton binding energies^{42,43,44,45,46,47,48}. Consequently, the perovskite LEDs have achieved high external quantum efficiencies (EQE) of up to 30%^{49,50,51}.

In 2009, the organic-inorganic hybrid perovskites such as CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ were initially applied in quantum dot-sensitized solar cells, leading to the development of the first perovskite solar cells, achieving the external quantum efficiency (EQE) of 3.8%⁵². In 2012, a hole-conducting material, spiro-MeOTAD, was introduced in the (CH₃NH₃PbI₃) nanoparticles to fabricate solid-state solar cells, achieving an EQE of 9.7% and successfully working 500 hours.^[53] Furthermore, a new deposition method was developed by introducing the PbI₂ into a nanoporous titanium-dioxide film and then converted into CH₃NH₃I perovskite upon exposure to CH₃NH₃I₃, enabling better control on the film morphology⁵⁴. This technique has shown significant improvements and reproducibilities, increasing the EQE to 15%. On the other hand, a low-temperature vapor-assisted solution process was adopted to create high-quality polycrystalline

perovskite films with excellent surface coverage, low roughness, and microscale grain size, achieving a high EQE of 12.1% in planar heterojunction solar cells⁵⁵.

The heavy elements provide an experimental hypothesis that such hybrid perovskites possess a strong SOC. Therefore, the hybrid perovskites can be named as strong SOC semiconductors with solution-processing, large-area formation capabilities, and facile property-tuning features by changing chemical elements or structural symmetries.

Consequently, such hybrid perovskites have demonstrated attractive optoelectronic functionalities, originally triggered by their fascinating photovoltaic actions in the solution-processing thin-film solar cells^{52,56,57}. We should emphasize that these optoelectronic functionalities mainly result from the unique band structures, namely Rashba band structures, derived from SOC effects in combination with symmetry breaking in the hybrid metal halide perovskites. In 1959, Soviet-American physicist Emmanuel I. Rashba reported the fundamental studies on the symmetry of the energy bands in wurtzite lattice crystals, establishing the Rashba effects^{58,59}. In 2013, utilizing the density functional theory and $\mathbf{k} \cdot \mathbf{p}$ modeling, the loss of inversion symmetry in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ was predicted³⁹. At the same time, the Rashba band structures were initially proposed for the organic-inorganic hybrid metal halide perovskites (β -MAPbI₃, β -MASnI₃, and ortho-MASbBr₃)⁶⁰. Naturally, combining SOC and symmetry breaking provides the necessary condition to form Rashba band structures. The formation of Rashba band structures in the hybrid perovskites was supported by the experimental phenomena of superior long lifetimes of photogenerated carriers involved in photovoltaic actions and also circular photogalvanic effects where right-handed and left-

handed circularly-polarized photoexcitations generate different photocurrents. Essentially, when symmetry breaking acts on SOC, Rashba band structures are split into two non-degenerate conduction bands carrying right-handed and left-handed circularly-polarized orbital momentum. In contrast, the valence band still shows a negligible splitting in momentum space due to their symmetry-like wavefunctions. This leads to a fundamental scenario in which Rashba band structures carry an indirect bandgap when SOC and symmetry breaking are combined in the hybrid metal halide perovskites. This scenario of indirect band gap in Rashba band structures has been used to interpret the superior long lifetimes of photogenerated carriers benefiting the photovoltaic actions in perovskite solar cells^{32,61,62}. On the other hand, the hybrid perovskites can demonstrate high PL quantum yield (PLQY) values^{63,64,65,66,67,68,69}. For example, using the room-temperature ligand-assisted reprecipitation (LARP) method has led to the perovskite CsPbBr₃ nanocrystals with a high PLQY of 92.3%⁶⁸. Applying in-situ PbBr₆⁴⁻ octahedra passivation strategy, the PLQY of CsPbBr₃ nanoplatelets has been increased to 96%⁶⁶. Utilizing the improved synthesis method involving trioctylphosphine–PbI₂ (TOP–PbI₂) as a reactive precursor, nearly 100% of room-temperature PLQY from the CsPbI₃ quantum dots was reported⁶⁵. This experimental phenomenon implies that there exists a mechanism to realize efficient radiative recombination in the indirect band structures in such hybrid perovskites. More interestingly, perovskite light-emitting diodes have shown high external quantum efficiencies (EQE) of > 20 % which refers to the internal quantum efficiencies (IQE) approaching 100 %. This experimental demonstration provides an important indication that the **J** excitons can all be converted into light-emissive excitons

through internal conversion, namely intersystem crossing. The aim of this review article is to analyze the experimental results and provide a critical understanding of the SOC effects occurring in spontaneous emission, ASE, and CPL regimes.

1.2 Slow Phonon Dynamics of Excitonic Emission in Organic Multi-functional Materials

1.2.1 Excited States of Organic Multi-functional Materials

Research on excited states plays an important role in the performance and functionality of organic multifunctional materials. In organic semiconductors, the relatively low dielectric constant and the strong Coulomb attraction between electrons and holes lead to tightly bound excitons^{70,71}. These excitons are critical for applications such as organic light-emitting diodes (OLEDs), organic photovoltaics, and photodetectors^{72,73,74}. Molecular structure and aggregation strongly influence exciton emission efficiency, color purity, and dynamic behavior^{75,76}.

Furthermore, additional regulation of excitonic properties is critical to advancing organic multifunctional material performance. Self-assembly and crystallization can induce synergistic effects - such as exciton delocalization or aggregation-induced emission (AIE) - that further modify photophysical behaviors^{77,78,79}. External stimuli like temperature and electric/magnetic fields enable modulation of exciton dynamics by influencing intersystem crossing rates, energy transfer pathways^{80,81,82,83}.

1.2.2 Electron-Phonon Coupling

Electron-phonon coupling is generated from the perturbation of the electronic potential caused by lattice vibrations⁸⁴. Its Hamiltonian can be divided into two parts⁸⁵:

- Deformation Potential: a local potential change induced by lattice distortions, which dominates electron scattering in nonpolar semiconductors (such as silicon).
- Fröhlich Interaction: A long-range Coulomb interaction in polar crystals, which governs electron-phonon coupling in ionic crystals (such as halide perovskites).

This interaction is fundamental to the electrical, thermal, and optical properties of materials and underpins phenomena such as superconductivity, electrical resistivity, and thermal conductivity^{86, 87, 88}.

In semiconductors, electron–phonon interactions are equally critical. They not only affect carrier mobility but also serve as a key mechanism for nonradiative recombination processes that compete with radiative transitions⁸⁹. In organic light-emitting diodes (OLEDs), strong electron-phonon coupling can result in spectral broadening and reduced device efficiency due to nonradiative losses^{90,91}. Moreover, in semiconductor devices, electron–phonon interactions contribute to the thermalization process: when an electron is excited to a high-energy state, it rapidly loses energy by emitting phonons and eventually relaxes back to the band edge⁹². This process, traditionally believed to occur on ultrafast timescales—from femtoseconds to picoseconds, plays a decisive role in the performance of photovoltaic and light-emitting devices^{93,94,95}.

Electron-phonon coupling is typically described using perturbative methods. For example, the Fröhlich Hamiltonian is widely used to describe the interaction between electrons and longitudinal optical phonons in polar crystals⁹⁶. For more complex materials, first-principles calculations based on density functional theory (DFT) have become indispensable^{97,98}. These computational methods enable researchers to determine

electron-phonon coupling constants and to predict the impact of such interactions on carrier mobility, lifetimes, and other material properties.

Experimentally, a variety of techniques are employed to study electron-phonon coupling. Angle-resolved photoemission spectroscopy (ARPES) can directly reveal electron self-energy effects, displaying the electronic band structure associated with electron-phonon coupling⁹⁹. Raman spectroscopy and inelastic neutron scattering are also widely used to study phonon modes and their interactions with the electronic system^{100,101}.

In organic functional materials, electron-hole pairs formed by Coulomb attraction are significantly influenced by the vibrational modes of the molecules^{102,103}. Regulating the degree of electron-phonon coupling can enhance exciton emission, prolong exciton lifetimes, and even induce phenomena such as thermally activated delayed fluorescence (TADF), which is applied in high-efficiency OLEDs¹⁰⁴. By reducing nonradiative decay rates—for example, through molecular design or by improving crystal quality to “slow” phonon dynamics—exciton harvesting can be made more efficient, thereby increasing the external quantum efficiency of light-emitting devices¹⁰⁵.

1.2.3 Phosphorescence and Fluorescence

In the field of optoelectronic materials, phosphorescence and fluorescence—two fundamental luminescence mechanisms—have long been at the forefront of scientific research and technological development¹⁰⁶. Fluorescence refers to the process in which a material, upon absorbing photons, rapidly returns from an excited singlet state (S_1) to the ground state (S_0) while emitting photons, with typical emission lifetimes on the order of nanoseconds¹⁰⁷. In contrast, phosphorescence involves the transition of electrons from a

triplet state (T_1) to the ground state; due to the spin-forbidden nature of this transition, the emission lifetime is significantly longer, often reaching the microsecond or even millisecond regime¹⁰⁸. In recent years, with the continual emergence of novel organic luminescent materials, achieving efficient room-temperature phosphorescence and improving exciton utilization through molecular design have become challenges in the optoelectronic device sector. Techniques such as room temperature phosphorescence (RTP) and thermally activated delayed fluorescence (TADF) have emerged as innovative solutions for high-efficiency, optoelectronic devices.

Room temperature phosphorescence (RTP) is a phenomenon that overcomes the traditional constraint that organic materials only exhibit phosphorescence under cryogenic or rigid-state conditions where organic materials only exhibit phosphorescence under low-temperature or strictly solid-state conditions^{109,110,111}. RTP materials not only broaden the application spectrum of organic luminescent materials—for instance, in low-power displays, glow-in-the-dark applications, and bioimaging—but also provide new experimental platforms for investigating the dynamics of triplet excitons^{112,113,114}.

Simultaneously, thermally activated delayed fluorescence (TADF) has attracted widespread attention in the realm of organic light-emitting diodes (OLEDs). TADF materials are engineered to possess an extremely small energy gap between the singlet (S_1) and triplet (T_1) states (typically $\Delta E_{ST} < 0.2$ eV), enabling triplet excitons to be thermally upconverted via reverse intersystem crossing (RISC) to the singlet state for radiative recombination. This mechanism overcomes the conventional fluorescence limitation of utilizing only 25% of excitons which is shown in **Figure 1-5** and can

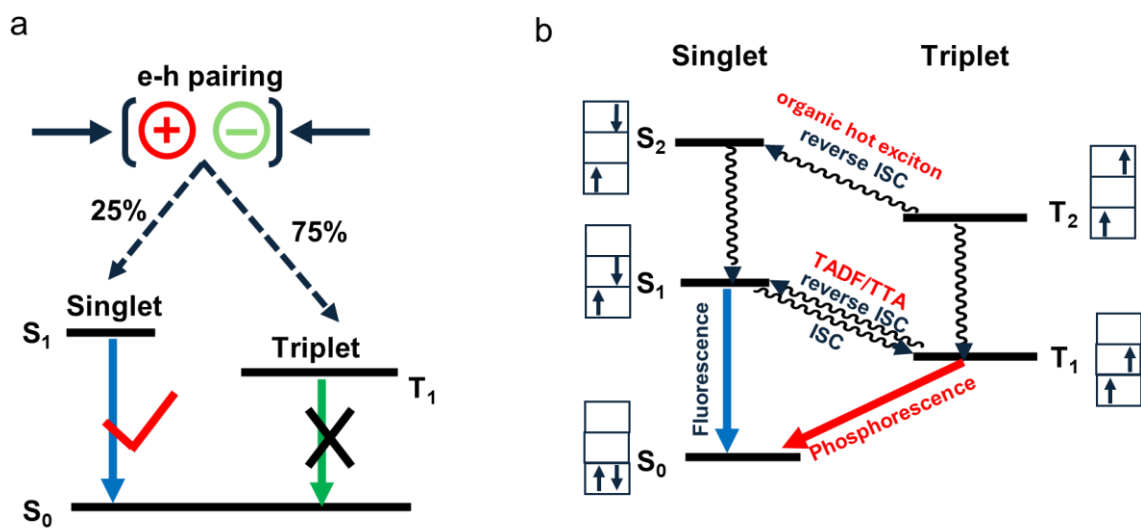


Figure 1-5 (a) Schematic energy level diagram for free charges, electron-hole pairs, and excitons in OLEDs. (b) Jablonski diagrams of fluorescence and phosphorescence.

theoretically achieve internal quantum efficiencies approaching 100%^{115,116}. Recent advances in molecular conformation regulation, optimization of conjugated systems, and the design of intermolecular interactions have endowed TADF materials with not only exceptional luminous efficiency but also remarkable advantages in terms of color purity and response speed, thereby laying a robust foundation for the development of high-performance OLED devices^{117,118}.

In recent years, continuous progress in donor-acceptor engineering, dynamic molecular coordination, and microstructural control have paved the way for the progressive enhancement of the performance of light-emitting devices composed of multifunctional organic materials.

1.3 Circularly Polarized Excitonic Emission in Organic Multi-functional Materials

1.3.1 Circularly Polarized Luminescence

Circularly polarized luminescence (CPL) is an intriguing and increasingly important phenomenon in organic multifunctional materials. Unlike conventional luminescence—where the emitted light is generally unpolarized or linearly polarized—circularly polarized luminescence (CPL) refers to the preferential emission of left- or right-handed circularly polarized light¹¹⁹. This property not only provides additional information about the chiral nature of the material but also offers unique opportunities in applications such as three-dimensional displays, optical information storage, enantioselective sensing, and spintronics^{120,121,122,123}.

The degree of circular polarization is quantified by the luminescence dissymmetry factor, g_{lum} , defined as:

$$g_{lum} = 2 \frac{I_R - I_L}{I_R + I_L} \quad (1)$$

where I_R and I_L are the intensities of the left- and right-circularly polarized emissions, respectively.

The generation of CPL in organic systems is fundamentally linked to the chirality of the molecular structure or the supramolecular assembly. In many cases, the design of donor-acceptor (D–A) molecules can be adapted to introduce chiral centers or induce chiral conformations upon aggregation. Such molecules can exhibit strong intramolecular charge transfer (ICT) characteristics and pronounced chiroptical responses^{124, 125}. When these D–A systems aggregate, they may form chiral nanostructures that amplify the circular polarization of the emitted light through cooperative interactions.

Characterizing CPL involves a combination of spectroscopic techniques. Circular dichroism (CD) spectroscopy is often employed to assess the chiroptical properties of a material in its ground state, while CPL spectroscopy directly measures the differential emission of left/right-circularly polarized light^{126, 127}. Advances in time-resolved CPL spectroscopy have also begun to unravel the dynamics of chiral excitons and the interplay between radiative decay and non-radiative processes¹²⁸.

Moreover, the development of high-performance CPL emitters is also influencing the field of organic light-emitting diodes (OLEDs). By harvesting both the singlet and triplet excitons in a controlled fashion, and by tuning the chiroptical response, it is possible to fabricate OLEDs with enhanced efficiencies and novel functionalities, such as polarized light emission for advanced display applications^{129, 130}.

1.3.2 CPL of MOFs

The integration of chirality into MOFs represents a promising strategy for developing advanced CPL-active materials. Chiral MOFs, prepared by using enantiopure ligands or by post-synthetic modification, can display circularly polarized luminescence (CPL). CPL is of growing interest for applications in three-dimensional displays, optical data storage, and enantioselective sensing. The ordered and tunable structure of MOFs makes them an excellent platform to achieve high dissymmetry factors in CPL, potentially surpassing those of conventional organic or inorganic materials.

In 2020, a pair of chiral MOF crystals was reported. Through biomimetic hydrogen bonding interactions, achiral fluorophores were anchored onto the inner surface of the helical channels of host MOFs, thereby inheriting the chiral characteristics of the hosts. This strategy significantly enhanced the luminescence dissymmetry factor of the resulting composite system ($g < \pm 1.50 \times 10^{-3}$) of the original CMOFs to ± 0.0115 ¹³¹. In 2024, researchers successfully fabricated Chiral Liquid Crystalline MOF (CLCMOF) thin films by layer-by-layer crosslinking of chrysene-based chiral liquid crystals with a chrysene-containing MOF, followed by UV irradiation. The resulting CLCMOF films exhibited strong chirality, pronounced photochromic fluorescence, and outstanding circularly polarized luminescence (CPL) performance, with dissymmetry factor reaching up to 0.4 ¹³². In 2025, researchers embedded CsPbX₃ (X = Cl, Br, I) perovskite quantum dots (PeQDs) into amino acid co-assembled chiral metal–organic frameworks (CMOFs), developing solid-state CPL nanohybrids that combine full-color CPL with excellent stability. By in situ generation of PeQDs within L/D-ZIF-8 CMOFs, they successfully

prepared solid-state CPL nanohybrid systems (L/D-ZIF-8 $\supset$ PeQDs) with a maximum luminescence dissymmetry factor g_{lum} of 1.41×10^{-3} and a photoluminescence quantum yield (PLQY) as high as 13%. The chiral microenvironment provided by the CMOFs enhanced CPL performance and effectively suppressed anion exchange and aggregation-induced quenching¹³³.

1.3.3 CPL of Radicals

To achieve circularly polarized luminescence (CPL) in organic radicals, the key lies in introducing molecular chirality while maintaining radical stability. Recent advances in molecular design have proposed multiple strategies:

Designing inherently chiral asymmetric radical molecules enables intrinsic chiroptical emission. For example, a Spanish research team developed propeller-shaped triphenylmethyl radical derivatives, whose enantiomers exhibit CPL signals in solution, with left-/right-handed emission corresponding to opposite CPL spectral signs. This marks the first report of intrinsic CPL from purely radicals driven by chirality, with a measured luminescence dissymmetry factor g_{lum} of approximately $0.5\text{--}0.8 \times 10^{-3}$ ^[134].

Hybridizing stable luminescent radical units with chiral ligands or substituents can induce global molecular chirality. For instance, Japanese researchers bridged two stable triarylmethyl radicals (PyBTM groups) with a chiral binaphthyl axis to create what is reported as the first axially chiral diradical emitter¹³⁵. The molecule displays pronounced chiroptical activity in solution, with observable circular dichroism (CD) and CPL signals. Even achiral radicals can exhibit CPL when dispersed in chiral environments, such as polymer films or cholesteric liquid crystals, which transfer chirality to the emissive

species. Recent work demonstrated that embedding radical molecules into chiral liquid crystals (LCs) to form composite films significantly amplifies CPL signals, achieving a g_{lum} enhancement to the order of 10^{-2} in the LC medium¹³⁶.

1.3.4 CPL in Perovskite

Organic-inorganic hybrid metal halide perovskites can be prepared with chiral structures with right- or left-handedness. The structural chirality can be introduced by chiral organic ligands such as: MBA (methylbenzylammonium), MPEA (β -methylphenethylammonium), 3APD (R-3-aminopiperidine), NEA (1-(1-naphthyl)ethylammonium), DACH (1,2-diaminocyclohexane), and CMBA (1-(4-chlorophenyl)ethylammonium) or chiral distortions in the inorganic frameworks.^[35,40,137,138,139,140,141,142] **Table 1** summarizes the different chiral perovskites and the CPL performance in different dimensionalities (0D,1D,quasi-2D,2D, and 3D). For example, the chiral 2D perovskite (R/S)-MBA)₂PbI₄ was successfully synthesized by incorporating chiral molecules, leading to the CPL with the degree of polarization (DOP) of 9.6 % (DOP defined by: $DOP = \frac{I_R - I_L}{I_R + I_L} \times 100 \%$) at 77 K.^[78] This gives rise to a large g factor of 0.2. By altering the position of the Br atom on the aromatic ring from para to meta site, it was found that the chiral 3BrMBA₂PbI₄ possesses largely distorted crystalline structures with enhanced chiroptical properties as compared to the chiral 4BrMBA₂PbI₄. Consequently, the chiral-structured 3BrMBA₂PbI₄ perovskite demonstrated a strong CPL with the DOP reaching 52 % under linear excitation at room temperature, which corresponds to $g = 1.04$.^[143] Furthermore, circularly-polarized electroluminescence (CP-EL) was successfully developed from chiral-structured

Table 1. Chiral-structured perovskites with different dissymmetry g factors and applications³⁸.

Perovskites Chemical formula	Dimensionality		applications	g factor ^{a)}
(S-/R-MBA) ₄ Bi ₂ I ₁₀ (ref)	0D		CPL	$g_{lum} \approx 0.18$ at 78 K
(R/S-MBA) ₄ Cu ₄ I ₄ (ref)	0D		CPL	$g_{lum} \approx 0.01$
(R/S-4MBA)(Gua) ₂ In _{0.99} Sb _{0.01} Cl ₆ • H ₂ O (ref)	0D		CPL	$g_{lum} \approx 0.01$
(S-MBA)PbI ₃ (ref ¹⁴⁵)	1D		CP-Photodetector	$g_{res} = 0.31$
(R-/S-NEA)PbI ₃ (ref ¹)	1D		CP-Photodetector	$g_{res} = 1.85$ / $g_{res} = 0.294$
(RR/SS-DMPZ)PbBr ₄ (ref)	1D		CPL	$g_{lum} \approx 0.0232$
(S-/R-MBA) ₂ MA _{nc-1} Pb _{nc} Br _{3nc+1} $n_c = 2$ to 5 (ref)	Quasi-2D		CPL	$g_{lum} \approx 0.008$
(PEA _x S-/R-NEA _{1-x}) ₂ MA _{n-1} Pb _n I _{3n+1} (x is the ratio of PEA, and n is the number of [PbI ₆] ⁴⁻ sheet) (ref ¹⁴⁴)	Quasi-2D		CPL/CPEL	$g_{lum} \approx 0.0021$ and $g_{EL} \approx 0.004$
(R-/S- β -MPA)EA ₂ Pb ₂ Br ₇ (ref)	Quasi-2D		CP-Photodetector	$g_{res} = 0.03$
(R/S-MBA) ₂ Pb _{0.9} Sn _{0.1} I ₄ (ref)	2D		CP-Photodetector	$g_{res} = 0.44$
(R/S)-3BrMBA ₂ PbI ₄ (ref ¹⁴³)	2D		CPL	$g_{lum} = 1.04$
(R/S)-MBA) ₂ PbI ₄ (ref ⁴⁰)	2D		CPL	$g_{lum} = 0.2$ at 77 K
(R/S)-MBA) ₂ PbI ₄ with (+/-)TADDOLs ^{b)} (ref)	2D		CP-Photodetector	$g_{res} = 1.16$
(R-/S- α -PEA)PbI ₃ (ref ¹⁴⁷)	2D		CP-Photodetector	$g_{res} = 0.1$
MAPbBr ₃ with chiral (S-/R-) BinapO ^{c)} (ref ¹⁴⁶)	3D		CPEL	$g_{EL} \approx 0.18$
MAPbBr ₃ with chiral structure (ref)	3D		CP-Photodetector	$g_{res} = 0.38$
R-/S-[dimethylamine]PbCl ₃ (ref)	3D		CP-Photodetector	$g_{res} = 0.296$

a) g factors are shown for circular polarized PL, or EL, or absorption defined as g_{lum} , or g_{EL} , or g_{res} .

b) (+/-)TADDOLs refers to [2*S*,3*S*/2*R*,3*R*]-2,3-*O*-isopropylidene-1,1,4,4-tetraphenyl-1,2,3,4-butanetetrol.

c) phosphine oxide ligand S- or R-[1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphine oxide)

perovskite LEDs. When using quasi-2D perovskite incorporated with both achiral PEA and chiral S/R-1-(1-naphthyl)ethylammonium iodide (S/R-NEAI) to fabricate perovskite LEDs, the CP-EL was observed with the g factor of 4.0×10^{-3} .^[144] In 2024, utilizing situ-formed MAPbBr₃ perovskite film passivated by the chiral phosphine oxide ligand S- or R-[1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphine oxide) (S- or R-) BinapO, the CP-EL was demonstrated with a large g factor of 0.18 based on the device architecture of ITO/PEDOT:PSS/Poly-TPD/perovskites/TPBi/LiF/Al.^[145]

It should be noted that the chiral structures can demonstrate different absorption coefficients to right-handed and left-handed circularly-polarized lights due to handedness-governed optical polarization effects, leading to chirality-distinguished optical absorption. This provides a fundamental principle for designing circularly-polarized photodetectors. Here, the dissymmetry g_{res} factor of absorption coefficients is

$$g_{\text{res}} = 2 \frac{R_R - R_L}{R_R + R_L} \quad (2)$$

where, the R_R and R_L are the responsivity under right-handed and left-handed circularly-polarized light intensities.

The photodetector based on the quasi-2D chiral perovskites, [(R)- β -MPA]₂MAPb₂I₇[(R)- β -MPA=(R)-(+)- β -methylphenethylamine) demonstrated a dissymmetry factor g of 0.2 with high responsivity up to 1.1 AW⁻¹ and detectivity of 2.3×10^{11} Jones.^[146] By introducing chiral organic cations of R/S- α -phenylethylamine (α -PEA) with (PbI₆)⁴⁻ octahedral chains, the chiral perovskites [(R- and S- α -PEA)PbI₃] were successfully prepared. The (R- and S- α -PEA)PbI₃ photodetectors were then fabricated, demonstrating a maximum g_{res} of 0.1 at the wavelength of 395 nm along with responsivity of 797 mA

W^{-1} and detectivity of 7.1×10^{11} Jones.^[147] Furthermore, the R/S-1-(1-naphthyl)ethylamine (R- and S-NEA⁺) were selected as chiral cations in the 1D perovskites. This design considers that the large π -conjugated naphthalene skeleton in NEA⁺ can interact with neighboring molecules to strongly affect the helicity of the (PbI₆)⁴⁻ octahedral chains. The (R/S-NEA)PbI₃ device [transparent conducting oxide (TCO)/SnO₂/chiral perovskites/bathocuproine(BCP)/Ag] demonstrated the highest polarization discrimination ratio of 25.4 ($g_{\text{res}} = 1.85$) in the detection of CPL.

Non-degenerate Rashba band structures carrying right-handed and left-handed circularly-polarized orbital momentum provide a fundamental platform for developing CPL. When non-degenerate spin-up and spin-down Rashba band structures are selectively excited to generate right-handed or left-handed circularly-polarized excitons, a CPL can then be observed if the circularly-polarized orbital momentum can conserve their circular polarizations within the PL lifetime. For example, the CPL was observed with the DOP of 4.8 % ($g = 0.097$) at 10 K in achiral 2D Ruddlesden-Popper perovskites (BA)₂(MA)_{n-1}PbI_{3n+1} (where MA = CH₃NH₃ and BA = CH₃(CH₂)₃NH₃).^[148] Clearly, non-degenerate spin-up and spin-down Rashba band structures carrying right-handed and left-handed circularly-polarized orbital momentum provide a convenient mechanism to develop CPL. It should be emphasized that Rashba band structures are also formed in the chiral perovskite single crystals: (S/R-3AMP)PbBr₄, which enhances the device performance of CPL detection.^[149] The PL intensity of (R-3AMP)PbBr₄ measured under right-handed (σ^+) excitation is 9.1 % higher than that under left-handed (σ^-) excitation. Particularly, the PL intensity can be decreased by 11.8 % in the (S-3AMP)PbBr₄ when

changing from right-handed (σ^+) excitation to left-handed (σ^-) excitation at 77 K. This presents a strong detection of circularly-polarized light by monitoring PL intensity. Importantly, this detection method leads to a much larger responsivity to circularly-polarized light, as compared to anisotropy-circular dichroism (0.037 % at 405 nm). This indicates that the Rashba band structures are indeed formed in the (S/R-3AMP)PbBr₄ single crystals. Therefore, Rashba band structures involved in chiral perovskites provide an additional mechanism to tune circularly-polarized optical properties.

1.3.5 Chirality-Induced Spin Selectivity (CISS) in perovskite

Electrical spin injection provides a new mechanism to generate CP-EL in LEDs. It was demonstrated that spin-polarized holes injected from a ferromagnetic semiconductor GaMnAs layer can recombine with unpolarized electrons from the n-GaAs substrate to form circularly-polarized excitons in the light-emitting InGaAs layer to generate a CP-EL^[150]. The CP-EL was shown with a DOP of 8 % at the spectral peak of 1.35 eV (918 nm) under 6 K and a magnetic field of 100 mT.

It should be noted that CP-EL can be developed by using chirality-induced spin selectivity (CISS) through chiral-structured materials. As shown in **Figure 1-6**, a chiral-structured hole-transport layer can provide circularly-polarized holes into achiral light-emitting layer. Simultaneously, non-polarized electrons are injected into achiral light-emitting layer. The recombination of circularly-polarized holes with non-polarized electrons can essentially form circularly-polarized excitons, as demonstrated by CP-EL. Clearly, the CP-EL confirms that the chiral structures can indeed activate CISS

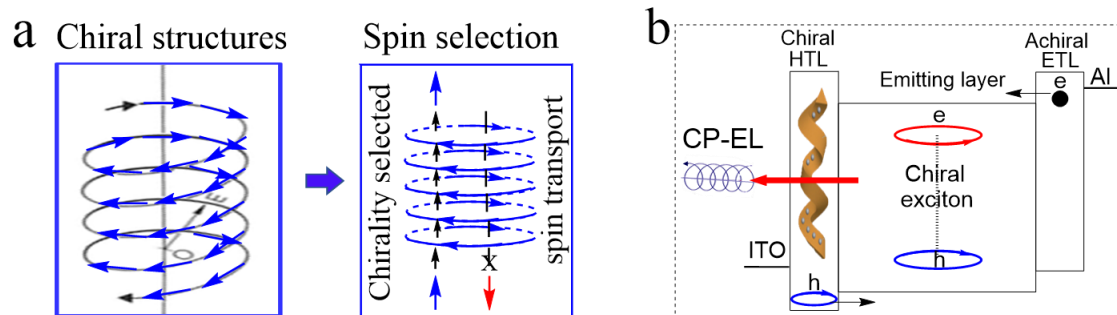


Figure 1-6 Chirality induced spin selection: CISS. (a) Schematic diagram for CISS; (b) CISS LEDs to demonstrate CP-EL by using circularly-polarized holes injected from chiral-structured hole-transport layer (HTL) and non-polarized electrons from achiral electron-transport layer (ETL)³⁸.

phenomena. It was demonstrated that the chiral-structured (R/S-MBA)₂PbI₄ leads to the room-temperature CP-EL with the DOP of $\pm 2.6\%$ ($g \approx 0.052$) within the spectral range between 660 nm and 700 nm based on CISS¹⁵¹. In this study, the chiral perovskite (R/S-MBA)₂PbI₄ film serves as the hole transport layer that injects the circularly-polarized holes into the adjacent achiral perovskite emitting layer to recombine with non-polarized electrons to form circularly-polarized excitons. Furthermore, the chiral-structured perovskites (R/S-MBA)₂PbI₄ were also utilized to provide circularly-polarized holes to the achiral III–V light-emitting (Al_xGa_{1-x})_{0.5}In_{0.5}P layer formed with multiple quantum wells. This device design has led to a CP-EL with a high DOP of $15 \pm 4\%$ ($g \approx 0.3$)¹⁵². Notably, this high CP-EL indicates that the circularly-polarized holes provided by the chiral perovskite layer must have a longer spin lifetime (~ 100 ps) in the III-V (Al_xGa_{1-x})_{0.5}In_{0.5}P light-emitting layer. This prolonged spin lifetime of circularly-polarized holes allows the overlap with PL lifetime, required for developing CP-EL with enhanced circular polarization. Clearly, chiral-structured metal halide perovskites have become an interesting class of materials to enable CISS with facile structure-property tuning capabilities.

**Chapter 2 Extremely Slow Phonon Dynamics Enabled by Crystalline-Assembling
Donor-Acceptor Molecules**

2.1 Abstract

Phonon dynamics are a critical factor to control the optical properties of excited states in light-emitting materials. Here, we report an extremely slow relaxation of photoexcited lattice vibrations enabled by assembling the donor-acceptor (D-A) molecules [2-(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide], namely AC molecules, into dipolar crystal. By using photoexcitation-modulated Raman spectroscopy, we find that the crystalline-lattice vibrations monitored by Raman-scattering laser beam of 785 nm demonstrate an un-usual slow relaxation in the time scale of seconds after ceasing photoexcitation beam of 343 nm in such dipolar crystal. This presents extremely slow phonon dynamics enabled by crystalline-assembling the D-A molecules into a dipolar crystal. Simultaneously, the photoluminescence (PL) exhibits a prolonged behavior, lasting 10 ms after ceasing photoexcitation in dipolar AC crystal. This phenomenon provides an experimental hypothesis that the slow phonon dynamics function as an important mechanism to un-usually prolong excited states dynamics upon crystalline-assembling the D-A molecules into dipolar crystal. This hypothesis can be verified by directly suppressing the phonon dynamics through freezing D-A molecular liquid into dipolar crystalline solid at 77 K to largely prolong the PL to 1 second after removing photoexcitation. Clearly, crystalline-assembling D-A molecules provide the necessary conditions to enable slow phonon dynamics towards prolonging excited states dynamics.

2.2 Introduction

Phonons originate from the lattice vibrations when individual molecules are orderly-assembled into crystalline structures, known as crystals. Because organic molecules possess strong electron-phonon coupling due to low dielectric constants, phonons can inevitably cause nonradiative emission of excited electrons in light-emitting materials^{153,154,155,156}. Essentially, the excited electrons can quickly relax from high-energy to low-energy levels in excited states by partially releasing their energies to phonons through electron-phonon coupling mechanism, leading to rapid dynamics of excited states normally with the time scale of nano/micro-seconds. This quick relaxation can inevitably cause an optical loss, forming a fundamental challenge to utilize the high-energy excited electrons in generating optoelectronic outcomes. Therefore, phonon dynamics are a critical factor in controlling excited state dynamics towards advancing optical properties. It has been commonly observed that, when the phonon dynamics are suppressed at low temperatures, the excited state dynamics can be substantially prolonged with high PL quantum yields in organic light-emitting molecules. Interestingly, it has been observed that the excited state dynamics can be prolonged much beyond the traditional time window of nano/micro-seconds at room temperature, exemplified as persistent luminescence in organic materials^{157,158,159,160,161,162,163}. On the other hand, it has been widely observed that assembling donor-acceptor molecules can lead to aggregation-induced emission known as AIE phenomenon at room temperature^{164,165,166,167,168}. This AIE phenomenon has indicated that assembling donor-acceptor molecules provides the necessary condition to suppress molecular vibrations

towards breaking normal electron-phonon coupling effects to advance light-emitting properties^{169,170,171}. Furthermore, assembling the D-A molecules into crystalline structures has been found to demonstrate extremely long PL lifetimes, shown as persistent and afterglow luminescence at room temperature^{172,173,174,175,176,177}. Here, our experimental observation presents an important scenario that crystalline assembly of D-A molecules provides a fundamental platform to develop un-usual phonon dynamics in advancing optical properties.

In this study, we utilize photoexcitation-modulated Raman spectroscopy together with time-resolved PL measurements and magnetic field effects to explore un-usual slow phonon dynamics in dipolar organic crystal prepared by crystalline-assembling the D-A molecules [2-(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide], known as AC molecules. The AC molecules were assembled into three different formats: (1) orderly-assembling into crystal, (2) randomly-assembling into amorphous film, (3) freezing liquid solution into crystalline solid in liquid nitrogen. The photoexcitation-modulated Raman spectroscopy combines light-scattering laser beam of 785 nm and excitation-laser beam of 343 nm. The light-scattering laser beam generates Raman signals from lattice vibrations while the excitation-laser beam excites the lattice vibrations. Remarkably, the phonon dynamics can be illustrated by continuously monitoring the Raman signals from lattice vibrations under the light-scattering beam of 785 nm after ceasing the excitation-laser beam of 343 nm. The time-resolved PL measurements were used to characterize the excited state dynamics while enabling un-

usual slow phonon dynamics. Magnetic field effects were applied to elucidate the spin states involved in un-usual slow phonon dynamics.

2.3 Materials and Methods

2.3.1 Materials Synthesis

The reagents were purchased from Sigma-Aldrich, TCI chemicals, and SAMCHUN chemicals, and used without further purification. The synthesis process of intermediates during material synthesis was confirmed through Thin Layer Chromatography (TLC).

The purification process of the formed material was performed through column chromatography, and the stationary phase used at this time was Merk's silica gel 60 (70-220 mesh). Proton NMR spectra of the synthesized molecules were characterized using ^1H -NMR (Bruker Biospin AVANCE III HD 400) to confirm the chemical structures.

The synthesis of the donor molecule and the TADF molecule AC is shown in **Figure 2-1**.

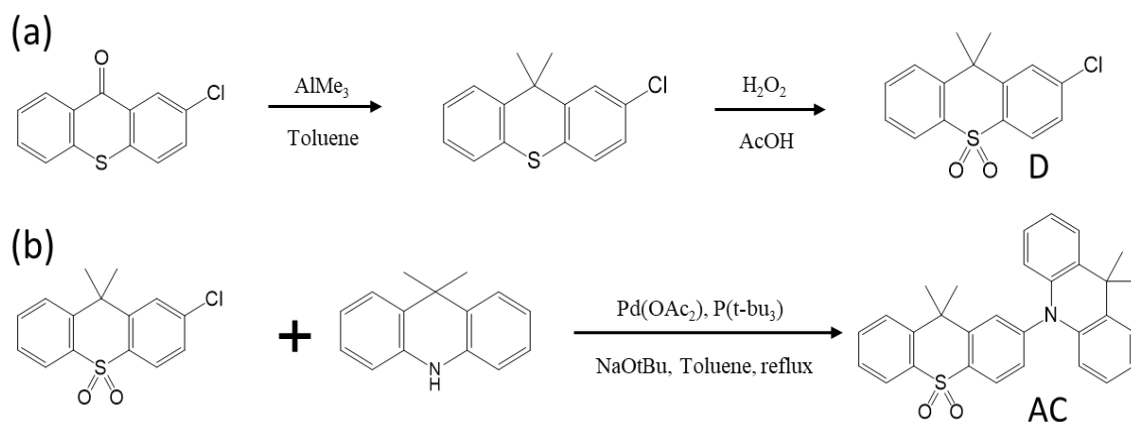


Figure 2-1 Synthesis of donor D and TADF molecule AC

Synthesis of acceptor molecule:

2-chloro-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (D) (3.00 g, 11.5 mmol) was mixed with 85 ml acetic acid in a 250 ml 2-neck flask. Then, 34% hydrogen peroxide (20 mL) was added into the flask. The temperature of the reactant was set at 120 °C and stirred under reflux for 12 hours. After completion of the reaction, the reactant was cooled to room temperature, extracted with MC and water, dried over MgSO₄ in an evaporator. A white solid was obtained by purification through column chromatography (MC/n-haxane) with the yield of 2.4 g (71%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): 8.09 (t, 2H, J=7.6 Hz), 8.03 (s, 1H), 7.98 (d, 1H, J=8 Hz), 7.76 (t, 1H, J=7.4 Hz), 7.71 (dd, 1H, J=8.2, 1.4 Hz), 7.64 (t, 1H, J=7.4 Hz), 1.83 (s, 6H).

Synthesis of 2-(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (AC):

In a 250 ml 2-neck flask, acceptor D (1 g, 3.41 mmol), 9,9-dimethyl-9,10-dihydroacridine (0.82 g, 4.09 mmol), and 70 ml Toluene were mixed. The mixture was degassed for 10 minutes while stirring. Then the acetic acid palladium (II) (38.3 mg, 0.125 mmol) was added into the flask under nitrogen atmosphere. The sodium tert-butoxide (1.63 g, 17 mmol) and tri(tert-butyl) phosphine (68.8 mg, 0.17 mmol) were added to the flask at the temperature 110 °C and stirred under reflux for 8 hours. After completion of the reaction, the mixture was cooled to room temperature and filtered through celite. A white solid was obtained by purification through column chromatography (ethyl acetate/n-haxane) with the yield of 0.73 g (46%). ¹H-NMR (400 MHz, CDCl₃, ppm): 8.47 (d, 1H, J=8 Hz), 8.26 (d, 1H, J=7.6 Hz), 7.77 (d, 1H, J=8 Hz), 7.72 (s, 1H), 7.65 (t, 1H, J=7.6 Hz), 7.57

(m, 1H, J=7.6 Hz), 7.50 (m, 3H), 6.98 (m, 4H, J=7.2 Hz) 1.89 (s,6H), 1.71 (s, 6H)

2.3.2 AC Crystal Preparation

20 mg AC powder was added into a 4 mL glass vial, then 500 μ L toluene and 500 μ L chloroform were added into the glass vial. The liquid solution, after being filtered, was stirred for about 8 h at 60 °C. The AC crystals were grown by evaporating the solvent at ambient conditions.

2.3.3 AC Frozen Liquid Preparation

10 mg AC powder was mixed with 1 ml Chloroform in a 4 mL glass vial. The liquid solution was stirred for about 1 h at room temperature. The frozen AC liquid was prepared by placing the liquid solution into a clear 4 mL glass vial into liquid nitrogen. This frozen liquid serves as an analogue to AC crystal to explore phonon dynamics effects of persistent luminescence.

2.3.4 Characterizations and Measurement

The optical images of micro-crystals were captured by using a Horiba Xplora Plus system. Photoluminescence in steady and dynamic regimes was measured by the Horiba SPEX Fluorolog 3 spectrometer. As shown in **Figure 2-2 a**, photoexcitation-modulated Raman spectroscopy was performed using a Horiba Xplora Plus confocal Raman microscope with a built-in 785 nm laser beam in combination with an external photoexcitation of a pulsed laser beam (343 nm) generated through a harmonic generator from a Pharos laser system (Light Conversion, 100 kHz, 1025 nm, 290 fs). To minimize interference from photoluminescence (PL) in the Raman signal, two long-pass filters (FGL550S >550 nm, FGL610S >610 nm) were placed in front of the Raman detector. The setup diagram for

magnetic field effects is shown in **Figure 2-2 b**. Essentially, the magnetic field effects were measured by monitoring PL intensity at peak wavelength as a function of a magnetic field. The amplitude for magnetic field effects is defined as $MFE = \frac{I_B - I_0}{I_0}$, where I_0 and I_B are signal intensities recorded without and with magnetic fields, respectively. The second harmonic generation (SHG) and infrared-to-visible up-conversion photoluminescence measurements were conducted by using a 1025 nm excitation beam from the same Pharos laser (Light Conversion, 100 KHz, 1025 nm, 290 fs). The long-pass filter (> 850 nm, 10CGA-850, MKS) was placed in the excitation beam path, and the filter (pass range 300-800 nm, FSQ-KG5, MKS) was added into the emission beam path to increase optical detectivity.

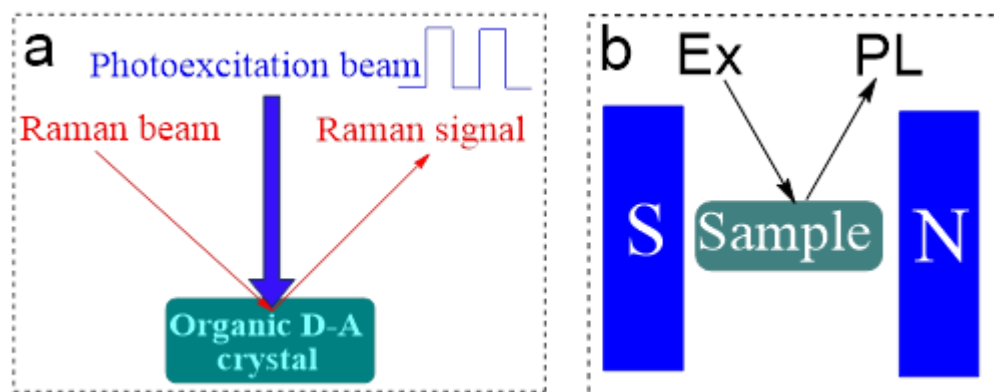


Figure 2-2 The diagrams illustrate experimental setups. (a) Photoexcitation-modulated Raman spectroscopy, Raman beam: 785 nm (continuous wave), photoexcitation beam: 343 nm (mechanically modulated waves), Raman signals from lattice vibrations were recorded as photoexcitation beam was modulated by using mechanical shutter with on/off time scale of 100 ms; (b) Magnetic field effects of PL, Ex: excitation wavelength of 343 nm, PL signal was monitored while scanning magnetic field.

2.4 Results and Discussion

2.4.1 Slow Phonon Dynamics Enabled by Crystalline-Assembling D-A Structures into Dipolar Crystal

The AC molecule consists of 2-chloro-9,9-dimethyl-9H-thioxanthene 10,10-dioxide and 9,9-dimethyl-9,10-dihydroacridine serving as donor and acceptor units to generate strong D-A interaction (**Figure 2-3**). The BBOT molecule includes 5-(tert-butyl)benzo[d]oxazole) and thiophene structures with symmetric design, leading to negligible donor-acceptor interaction. **Figure 2-3 b** displays the XRD patterns of the AC and BBOT crystals, which exhibit well-defined and sharp diffraction peaks indicating the high crystallinity. The optical images shown as the inset in **Figure 2-3 b** represent the AC and BBOT crystals prepared with sub-millimeter sizes by slowly evaporating the mixed organic solvent of toluene and chloroform at room temperature.

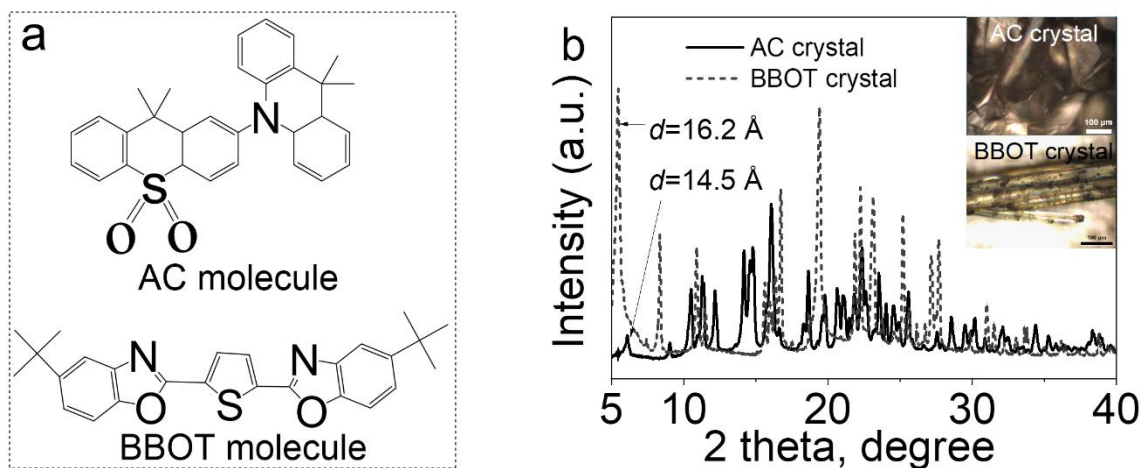


Figure 2-3 Basic information for dipolar AC crystal with strong donor-acceptor interaction as compared to BBOT crystal with negligible donor-acceptor interaction. (a) Chemical structure of AC molecule; (b) X-ray diffractograms of AC and BBOT crystals (Inset: crystal images).

Figure 2-4 shows the dynamic characteristics of Raman signals generated by the light-scattering laser beam of 785 nm, recorded at different time scales after ceasing the excitation-laser beam of 343 nm for the AC crystal with strong donor-acceptor interaction as compared to the BBOT crystal with negligible donor-acceptor interaction. The phonon dynamics were characterized by continuously monitoring the Raman signals from lattice vibrations at different delay times after ceasing the photoexcitation beam of 343 nm.

Figure 2-4 a shows the Raman spectra of AC crystal at room temperature, generated by the light-scattering beam of 785 nm, recorded at different delay times after removing the excitation-laser beam of 343 nm. We can see a very un-usual phenomenon: the Raman signals are slowly relaxing in the time scale of seconds after ceasing the excitation-laser beam of 343 nm in the AC crystal. This phenomenon represents an extremely slow phonon dynamics enabled by crystalline-assembling the D-A structures into the crystal. We should note that assembling D-A structures can often generate aggregation-induced-emission (AIE) phenomena, shown as much-enhanced light emission in solid state as compared to liquid state^{178,179,180}. The AIE phenomena have led to the widely-recognized scenario that assembling D-A structures can largely suppress the molecular vibrations in solid state^{181,182}. Here, our photoexcitation-modulated Raman spectroscopy find a new phenomenon that the slow phonon dynamics can be enabled when crystalline-assembling the D-A structures into crystal. On contrast, the BBOT crystal with negligible D-A interaction exhibits a normal phenomenon: the Raman signals are quickly relaxed after ceasing the excitation-laser beam, lacking any detectable change at different delay times of 0.5s and 1s (**Figure 2-4 b**). **Figure 2-4 c** illustrates the dynamic comparison between

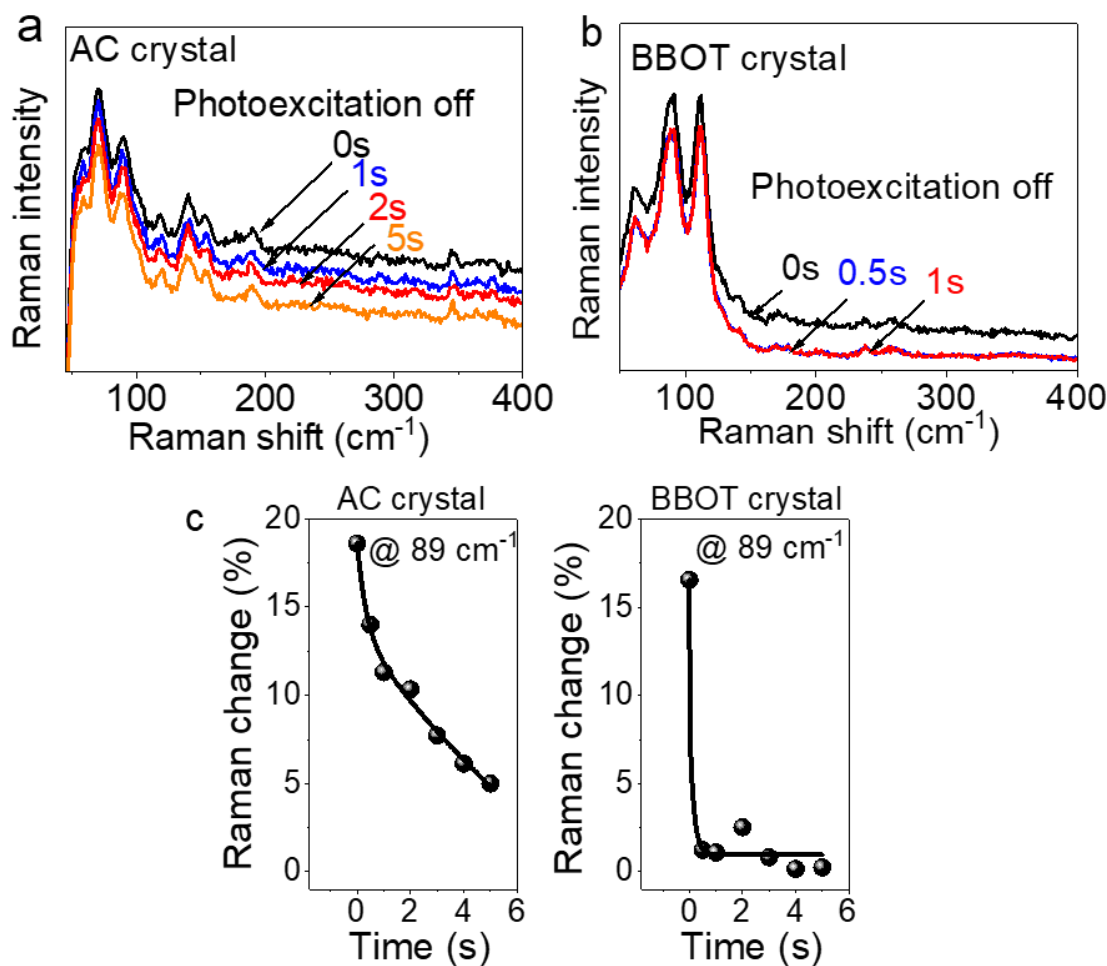


Figure 2-4 Photoexcitation-modulated Raman spectroscopy for dipolar AC crystal with strong donor-acceptor interaction as compared to BBOT crystal with negligible donor-acceptor interaction. Raman laser beam: 785 nm. Photoexcitation laser beam: 343 nm. The time resolution in dynamic Raman measurements is 100 milliseconds. (a) Raman signals were recorded for AC crystal at different time scales after ceasing photoexcitation, indicating extremely slow phonon dynamics; (b) Raman signals were recorded for BBOT crystal after ceasing photoexcitation, lacking slow phonon dynamics; (c) Slow and fast relaxations of lattice vibrations at 89 cm⁻¹ for AC and BBOT crystals after ceasing photoexcitation, respectively.

the AC and BBOT crystals with slow and quick relaxations of Raman signal of lattice vibrations at 89 cm^{-1} . Clearly, the AC crystal with strong D-A interaction demonstrates extremely slow phonon dynamics from lattice vibrations enabled by crystalline-assembled D-A structures. However, the BBOT crystal with negligible D-A structures exhibits quick phonon dynamics of excited lattice upon removing the photoexcitation. We should note that the crystalline-assembled D-A molecular structures can generate optical phonons, known as phonon waves, through lattice vibrations in dipolar crystals. The un-usual slow phonon dynamics reflect that the D-A molecular structures must be crystalline-assembled in such way to enable the opposite phase relations between optical phonon waves, consequently leading to a large suppression of optical phonons. We can expect that the suppression of optical phonons yields two outcomes: (1) the reduced density of optical phonons, commonly indicated aggregation-enhanced light emission, (2) the slow relaxation of excited lattice vibrations to exhibit slow phonon dynamics. Nonetheless, our photoexcitation-modulated Raman spectroscopy find that crystalline-assembling D-A molecular structures can enable the un-usual slow phonon dynamics in dipolar AC crystal.

We should note that thermal diffusion processes in the laser-heated samples may also influence the Raman spectra, and thermal diffusion can occur on timescales of milliseconds. Here are the details to remove the thermal effects: as we can see in the following **Figure 2-5** that heating (65°C) decreases the Raman signal amplitude from crystalline molecular lattice (below 100 cm^{-1}), which is opposite to the experimental phenomenon that photoexcitation increases the Raman signal amplitude from crystalline

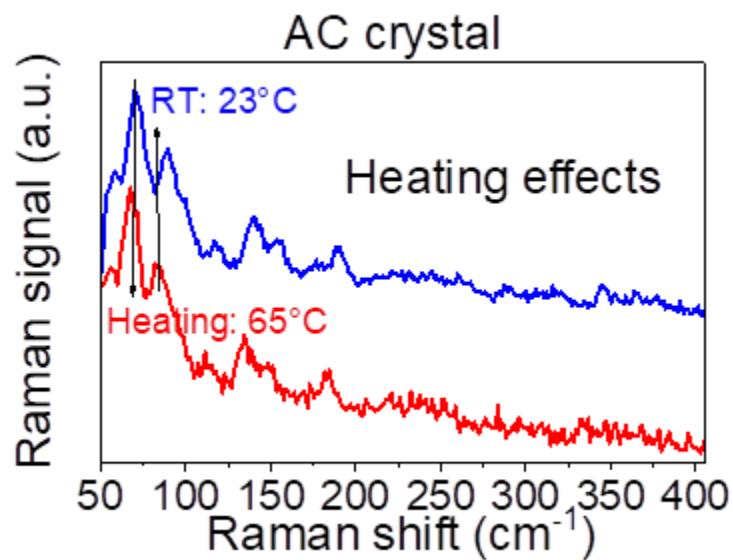


Figure 2-5. Raman spectra of AC crystal were measured with heating to 65 °C and cooling down to room temperature (23 °C), shown as heating-decreased density of lattice vibrations in dipolar AC crystal.

molecular lattice. In addition, after removing the heating (65°C), the Raman signal can be fully recovered. This heating effect is illustrated in **Figure 2-5**.

2.4.2 Prolonging Excited States Dynamics by Crystalline-assembling D-A Structures into Dipolar Crystal

Figure 2-6 shows the PL characteristics for the AC crystal with strong D-A interaction as compared to the BBOT crystal with negligible D-A interaction. We can see in Figure 2-6a that crystalline and amorphous assembling the AC molecules generate slightly different PL spectra with the peak positions at 431 nm and 445 nm for the crystal and spin-cast film, respectively. Interestingly, the AC crystal formed by crystalline assembling the D-A structures demonstrates a long-lasting PL reaching 10 ms after ceasing the photoexcitation, presenting prolonged excited states dynamics at room temperature. On contrast, amorphous-assembling the AC molecules into spin-cast film (AC dispersed in PMMA matrix) completely lacks prolonged excited states dynamics, shown by a much shorter PL lifetime of 9.8 μ s, where the average lifetime is defined by

$$\tau_{ave} = \frac{\sum_{i=1}^n \alpha_n \times \tau_n^2}{\sum_{i=1}^n \alpha_n \times \tau_n}.$$

Clearly, crystalline-assembling the D-A structures simultaneously

leads to extremely slow phonon dynamics and prolonged excited states dynamics in the dipolar AC crystal. This presents an experimental hypothesis that the slow phonon dynamics enabled by crystalline-assembling the D-A structures function as a fundamental mechanism to prolong the excited states dynamics in organic crystal. In contrast, the BBOT crystal with negligible D-A interaction demonstrates a typical fluorescence with the PL peaked at 480 nm and the lifetime of 126 μ s (**Figure 2-6 b and c**), lacking

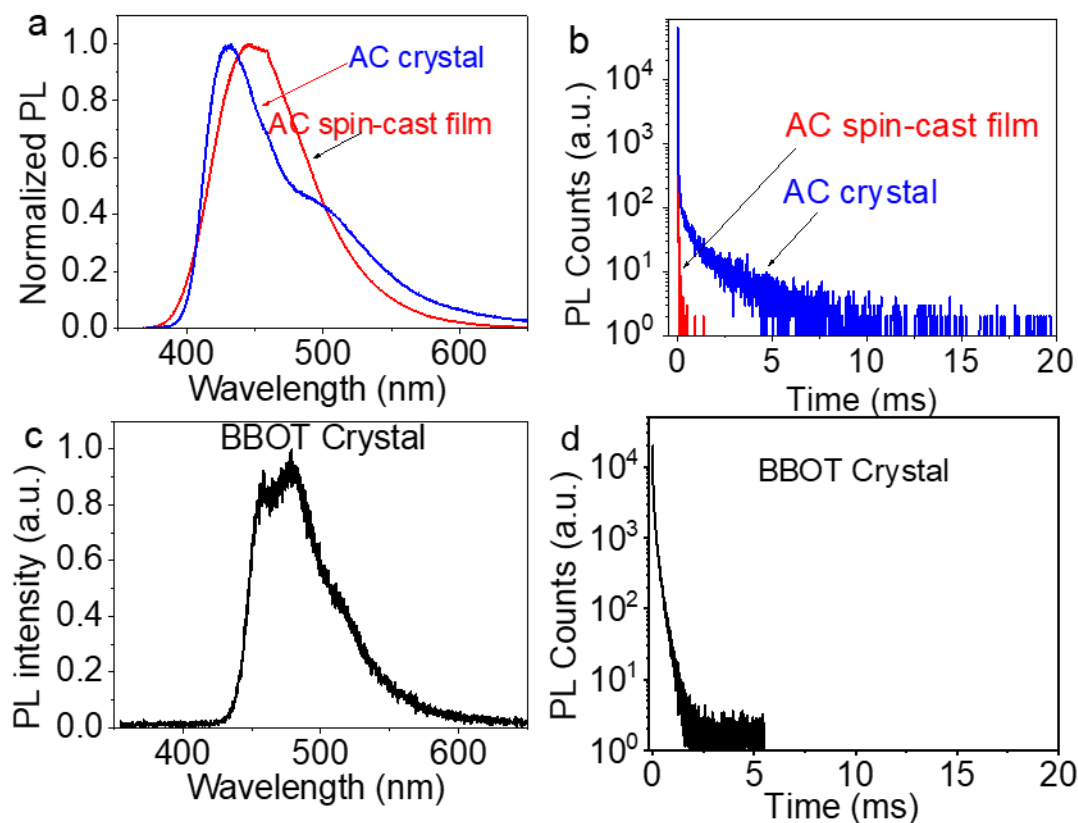


Figure 2-6 PL characteristics of AC and BBOT crystals under 343 nm pulsed laser excitation at room temperature. (a) PL spectra measured from AC crystal compared with AC spin-cast film (AC molecules dispersed in PMMA matrix); (b) PL lifetimes from AC crystal at 432 nm and AC/PMMA spin-cast film at 450 nm; (c) PL spectra measured from BBOT crystal; (d) PL lifetime at the peak wavelength of 480 nm for BBOT crystal.

prolonged excited states dynamics at the absence of slow phonon dynamics (**Figure 2-4 c**).

To verify this experimental hypothesis, we manually suppress the phonon dynamics by freezing the AC liquid solution in liquid nitrogen (77 K) to form a frozen liquid serving as a crystalline solid. The liquid solution was prepared in chloroform solvent with a concentration of 10 mg/ml. **Figure 2-7 a** shows the PL spectra for the AC frozen liquid at 77 K and the solution at room temperature (298 K). The frozen liquid gives rise to a blue-shifted PL with a peak of 450 nm as compared to the room-temperature solution with a PL peak of 478 nm. Particularly, the frozen liquid demonstrates a strong second harmonic generation (SHG) peaked at 512 nm, accompanied by broad infrared-to-visible up-conversion PL under 1025 nm excitation (**Figure 2-7 b**). This SHG signal verifies that the frozen liquid can indeed form the dipolar crystalline structures, leading to an analog to the crystal prepared by the orderly assembly of the AC molecules with strong D-A interaction. Interestingly, the frozen AC liquid demonstrates a largely prolonged PL lasting about 1 second after ceasing the 343 nm excitation when manually suppressing the phonon dynamics at liquid-nitrogen temperature, as illustrated in **Figure 2-7 c**. In contrast, the room-temperature AC liquid solution exhibits a prompt PL with a PL lifetime of 16 ns.

Clearly, the long-lasting PL that occurred in frozen liquid provides experimental evidence that the slow phonon dynamics serve as a vital mechanism to prolong the dynamics of the excited state in a dipolar crystal formed with a strong D-A interaction.

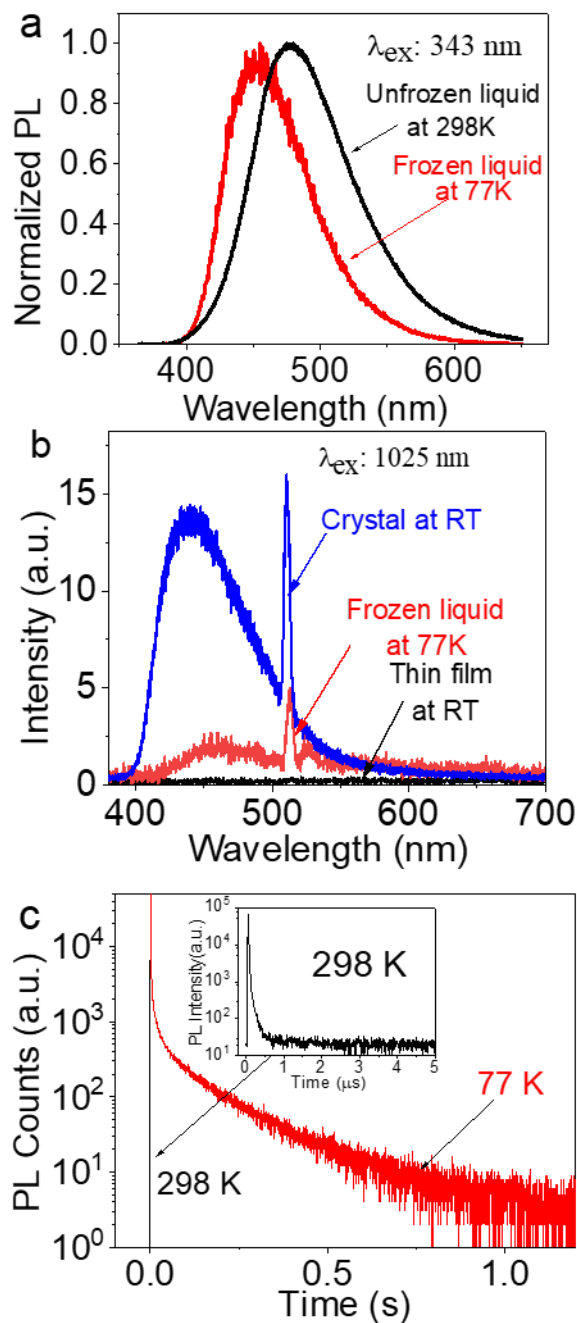


Figure 2-7. PL characteristics for AC frozen liquid in liquid nitrogen (77 K) and unfrozen AC solution under 343 nm excitation at room temperature (298 K). (a) PL spectra from AC un-frozen and frozen liquids; (b) Second Harmonic Generation (SHG) signal peaked at 512 nm from frozen liquid associated with infrared-to-visible up-conversion PL (broad spectrum) under 1025 nm excitation as compared to crystal with orderly-assembled D-A molecules and spin-cast film with randomly-assembled D-A molecules; (c) PL lifetimes for frozen (at 77 K) and unfrozen (at RT) liquids at 478 nm excitation.

2.4.3 Spin States Involved in Slow Phonon Dynamics to Prolong Excited States

Dynamics

We should note that inorganic chromophores can often give rise to much prolonged PL with lifetimes reaching seconds, minutes, and even hours, shown as long-lasting luminescence at room temperature, known as afterglow luminescence. The afterglow luminescence can be normally observed when the excited electrons are trapped in shallow traps and then slowly de-trapped via thermal energies. Thus, thermally de-trapping the trapped electrons has become a popular mechanism to generate afterglow luminescence in inorganic chromophores. Notably, similar afterglow luminescence induced by thermally de-trapping trapped excitons can also be observed in organic materials. Here, we emphasize that the prolonged PL dynamics only occur when the AC molecules with strong D-A interaction are crystalline-assembled into dipolar crystals while amorphous-assembling the AC molecules completely lacks the prolonged PL. This experimental phenomenon removes the possibilities of de-trapping trapped excitons in the prolonged PL dynamics induced by crystalline-assembling AC molecules since amorphous assembling would lead to higher probabilities to form traps to facilitate de-trapping-enabled prolonged PL dynamics, which is opposite to our experimental observation. In addition, our magnetic field effects indicate that the prolonged PL are not from localized trap states (discussed in **Figure 2-8**). Therefore, the prolonged PL dynamics can be attributed to the slow phonon dynamics when orderly assembling the D-A molecules into dipolar crystals.

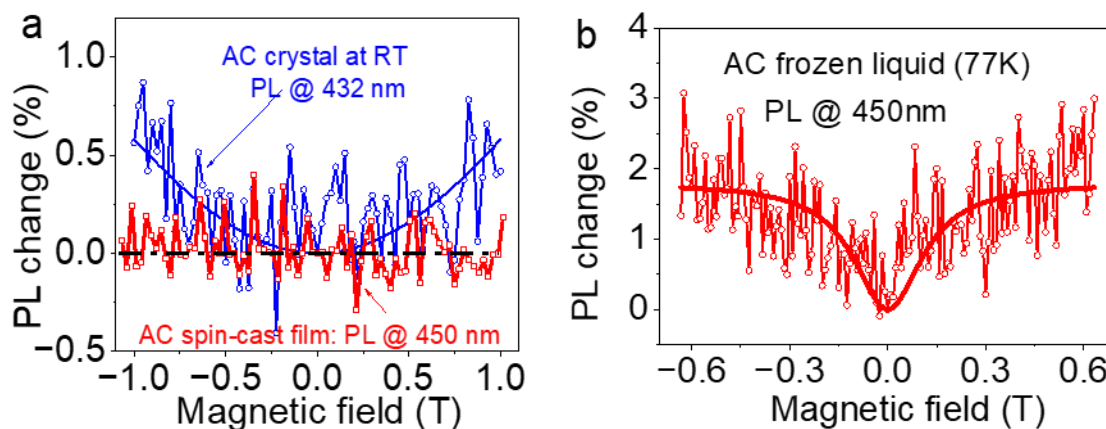


Figure 2-8. Magnetic field effects were measured to indicate spin singlets responsible as light-emitting states with prolonged lifetimes for dipolar AC crystal at room temperature (298 K) and AC frozen solution in liquid nitrogen (77 K) under 343 nm excitation. Magnetic field effects were recorded by monitoring PL peak intensity as a function of a magnetic field. (a) Magnetic field effects are shown for AC crystal at room temperature. AC spin-cast film lacks magnetic field effects; (b) Magnetic field effects are illustrated for AC frozen liquid in liquid nitrogen.

Now we discuss the spin states involved in slow phonon dynamics. It is noticed that the prolonged luminescence have been widely assumed as long-lived phosphorescence from triplet emission, named as room-temperature phosphorescence (RTP). However, it still lacks the spin signature to define the spin states of proposed RTP in aggregated organic molecules. Here, we performed the experimental measurements of magnetic field effects for the AC crystal, frozen liquid, and spin-cast film. **Figure 2-8 a** shows that the prolonged PL in the AC crystal gradually increases in intensity with increasing magnetic field at room temperature, leading to magnetic field effects with positive amplitude. Similar magnetic field effects can also be observed in the frozen AC liquid with long-lasting PL (**Figure 2-8 b**). Here, the positive amplitude of magnetic field effects provides an experimental indication that the light-emitting states are indeed the spin singlets but involves the triplet-to-singlet intersystem crossing. It should be emphasized that positive magnetic field effects of PL can be commonly observed when an external magnetic field increases the triplet-to-singlet intersystem crossing, namely reverse intersystem crossing (RISC), in electron-hole pairs such as charge-transfer states. Specifically, an external magnetic field can flip electron spins in excited states through spin scattering. Whether spin flipping occurs determines whether an intersystem crossing can be activated. Once the spin flipping occurs, the intersystem crossing can be activated from a higher-energy state to a lower-energy state. When the triplets have a higher energy than the singlets, an external magnetic field induces a triplet-to-singlet intersystem crossing, leading to positive magnetic field effects of PL in the case where the singlets are light-emitting states. When the triplets have a lower energy than the singlets, an external magnetic field

causes a singlet-to-triplet intersystem crossing, giving rise to negative magnetic field effects of PL. We should note that the triplet-to-singlet intersystem crossing must require spin flipping to occur. Our early studies found that the D-A structures can enable the spin flipping through electric-magnetic coupling mechanism in organic light-emitting system. By comparing the curve shapes of magnetic field effects between AC crystal and frozen liquid, we can see that applying magnetic field can more easily change the intersystem crossing in the frozen liquid than the crystal. This indicates that the intersystem crossing is easier to occur in the frozen liquid than the crystal. However, the frozen liquid with easier intersystem crossing demonstrates a much longer PL lifetime as compared to the crystal. Clearly, the prolonged excited states dynamics in the frozen liquid are not originated from intersystem crossing, which further supports that the slow phonon dynamics are serving as the responsible mechanism for prolonging the excited states dynamics upon crystalline-assembling the D-A molecules into dipolar crystal. It should be noted that the triplets have higher energy than the singlets in electron-hole pairs such as charge-transfer excitons. Through the triplet-to-singlet intersystem crossing, spin singlets become the responsible light-emitting states with prolonged dynamics. Clearly, suppressing the lattice vibrations upon orderly-assembling the D-A molecules provides the necessary condition to develop slow phonon dynamics in dipolar crystal. As illustrated in **Figure 2-9**, the photoexcitation generates electrons and holes, namely photogenerated carriers, in dipolar crystals. The photogenerated electrons and holes recombine into both spin-singlet and spin-triplet electron-hole pairs through Coulomb capture. Our magnetic field effects of PL shown in **Figure 2-8** indicates that the triplet

Orderly-assembling D-A molecular structures into dipolar crystals

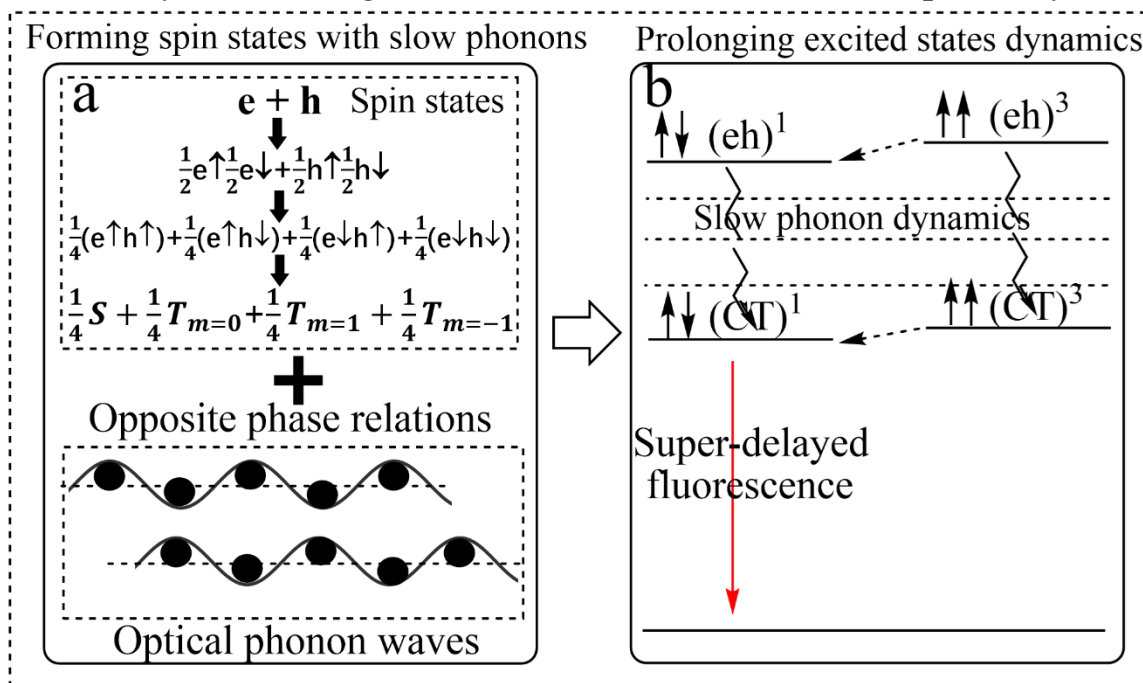


Figure 2-9. Slow phonon dynamics enable prolonged excited states dynamics when orderly-assembling D-A molecular structures into dipolar crystals. (a) Spin-singlet and spin-triplet electron-hole pairs are formed by recombining photogenerated electrons and holes through Coulomb capture in dipolar crystals formed with slow phonon dynamics due to opposite phase relations between optical phonons. (b) Through electron-phonon coupling, the electron-hole pairs experience slow relaxations to evolve into charge-transfer excitons, leading to slow phonon dynamics. When spin-singlet charge-transfer excitons undergo radiative emission, prolonged PL can be observed to exhibit super-delayed fluorescence, shown as prolonged excited states dynamics in dipolar crystals.

electron-hole pairs can be internally converted into singlet electron-hole pairs through intersystem crossing in dipolar AC crystal, commonly observed in organic materials. Simultaneously, orderly-assembling the D-A molecular structures enables the slow phonon dynamics in dipolar crystal by having the opposite phase relations between optical phonon waves from lattice vibrations. The optical phonons, namely polarized phonons, are ready to generate electron-phonon coupling, which is prominent phenomenon in organic materials intrinsically carrying low-dielectric constants. Through electron-phonon coupling, the electron-hole pairs can experience slow relaxations to evolve into charge-transfer excitons, leading to un-usual slow phonon effects in excited states. When the spin-singlet charge-transfer excitons undergo radiative emission, the prolonged PL lifetimes can be observed to demonstrate the so-called super-delayed fluorescence at room temperature. Clearly, orderly-assembling D-A molecular structures into dipolar crystals provides the necessary condition to enable the un-usual slow phonon dynamics by suppressing optical phonons, and consequently prolonging the excited states dynamics in dipolar crystals.

2.5 Summary

In summary, we find that orderly-assembling the donor-acceptor AC molecules into dipolar crystal demonstrates an un-usual phenomenon that the photoexcited lattice vibrations are slowly relaxing in the time scale of seconds after ceasing the photoexcitation by using photoexcitation-modulated Raman spectroscopy. This phenomenon represents extremely slow phonon dynamics occurred in the dipolar AC crystal. Essentially, the slow phonon dynamics can be enabled in crystalline-assembled

D-A structures with suppressed lattice vibrations when the optical phonons have opposite phase relations in dipolar crystals. Interestingly, the AC crystal can simultaneously exhibit the prolonged excited states dynamics shown by the long-lasting PL up to 10 ms after removing the photoexcitation, when slow phonon dynamics occur. This leads to an experimental hypothesis that the slow phonon dynamics function as a fundamental mechanism to prolong the excited states dynamics when crystalline-assembling D-A structures into dipolar crystals to suppress lattice vibrations. This hypothesis can be validated by artificially suppressing the lattice vibrations by freezing AC liquid solution into dipolar crystalline solid. Particularly, when freezing the AC liquid solution into dipolar crystalline solid in liquid nitrogen (77 K) to artificially suppress the lattice vibrations, the PL can last up to 1 second after ceasing photoexcitation. This confirms that suppressing the lattice vibrations provides a vital mechanism to realize slow phonon dynamics upon crystalline-assembling the D-A structures into dipolar crystal.

Consequently, the excited states dynamics can be substantially prolonged, shown as the extended PL lasting 10 milliseconds in AC dipolar crystal and 1 second in dipolar frozen AC liquid after removing photoexcitation. In general, realizing slow phonon dynamics requires three necessary conditions. First, the dipolar D-A molecular structures must be crystalline-assembled into a dipolar crystal, which is a prerequisite for generating optical phonons from crystalline lattice vibrations that mediate electron-phonon coupling. Second, the crystalline-assembled dipolar D-A molecular structures must be arranged in such way that the optical phonons have opposite phase relations within dipolar AC crystal, leading to a large suppression of optical phonon waves. Third, this phonon

suppression produces dual effects: (1) the reduction in the optical phonon density known as aggregation-enhanced emission, and (2) the slow relaxation of the excited optical phonons to exhibit slow phonon dynamics towards prolonging the excited states dynamics shown as prolonged PL lifetime through electron-phonon coupling in dipolar AC crystal. Furthermore, our magnetic field effects indicate that the light-emitting states with extended lifetime are indeed spin singlets but involve reversible triplet-to-singlet intersystem crossing, leading to the so-called super-delayed fluorescence in the dipolar AC crystal. This result reveals that the slow phonon dynamics are, in effect, occurred in spin-singlet states to generate prolonged excited states dynamics when crystalline-assembled D-A structures suppress the lattice vibrations. Therefore, crystalline-assembling the D-A structures into dipolar crystal provides an interesting platform to establish unusual slow phonon dynamics to prolong the excited states dynamics in developing advanced optical properties.

Chapter 3 Spin-Orbital Coupling Effects in Chiral structured Metal-Organic Frameworks

3.1 Abstract

Metal-organic frameworks (MOFs) are known as an important platform to explore multifunctional properties through molecular and coordination designs. This letter reports spin-orbital coupling (SOC) effects of light-emitting dynamics in chiral-structured MOFs [Ru(ppy)₃][Zn₂(ox)₃] and [Ru(ppy)₃][Mn₂(ox)₃] prepared with right-handedness configuration, namely $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals with weaker and stronger SOC, respectively. Both chiral-structured $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals possess non-central symmetric polarizations, identified by Second Harmonic Generation (SHG), leading to circularly polarized luminescence (CPL) under one-photon and two-photon excitations at room temperature. Here, SOC formed with non-central symmetric polarizations leads to the suggestion that spin-up and spin-down band structures become nondegenerate, providing the precondition to form Rashba band structures within chiral-structured MOFs. We observe that the chiral-structured $\Delta\Delta$ Mn crystal carrying stronger SOC demonstrates a much faster light-emitting transitions determined by the shorter photoluminescence (PL) lifetime of 10.8 ns as compared to the chiral-structured $\Delta\Delta$ Zn crystal carrying weaker SOC shown with the longer PL lifetime of 100 ns. This observation provides an experimental indication that SOC serves as a key parameter to accelerate light-emitting transitions by satisfying the momentum conservation through exciton-lattice coupling within Rashba band structures in chiral-structured MOFs. Furthermore, the higher-energy excitons selected from shorter emitting wavelength at 573 nm in the chiral-structured $\Delta\Delta$ Zn crystal illustrate a faster light-emitting transition with the PL lifetime of 30.5 ns while the lower-energy excitons selected from longer

emitting wavelength at 614 nm display a slower light-emitting transition with the PL lifetime of 100 ns. Because higher-energy and lower-energy transition dipoles correspond to stronger and weaker SOC, this phenomenon confirms that increasing SOC can essentially accelerate light-emitting transitions through Rashba band structures in chiral-structured MOFs. Furthermore, circularly polarized luminescence (CPL) measurements under both one-photon and two-photon excitations confirm the establishment of a helical ordering of transition dipoles via lattice-assisted momentum conservation.

3.2 Introduction

Metal-organic frameworks (MOFs) have become highly attractive multifunctional materials that can demonstrate light-emission, lasing actions, nonlinear optical behaviors, electrical conduction, magnetic properties, and chemical sensing capabilities^{183,184,185,186,187}. Essentially, MOFs combine organic π -conjugated molecular frameworks with metal ions through coordination connections. This presents ultimate possibilities on tuning the multifunctional properties through rational design of organic frameworks and metal ions. Recently, our collaborators have successfully separated right-handed and left-handed chiral-structured MOFs by using ruthenium complexes $[\text{Ru}(\text{ppy})_3]^{2+}$ and metal-centered Δ and Λ chiralities.¹⁸⁸ Specifically, the $[\text{Ru}(\text{ppy})_3]^{2+}$ complexes act as 3D-chiral frameworks carrying optical properties to formulate chiral-structured MOFs $[\text{Ru}(\text{ppy})_3][\text{M}_2(\text{ox})_3]$ (ox=oxlate) where the metal ions simultaneously incorporate ionic and spin properties. Our chiral-structured MOFs have shown circularly polarized luminescence (CPL) at room temperature. In general, when the electronic transition dipoles establish a helical order within chiral structures, the emitted photons

can carry circular angular momentum in the situation where the helical order of electronic transition dipoles can be conserved within PL lifetime^{189,190,191}. This leads to chirality-induced CPL based on chiral structures. On the other hand, combining SOC with symmetry breaking configurations can split spin-up and spin-down band structures in momentum space, leading to the precondition to form spin-nondegenerate Rashba band structures with fundamental possibilities of spin-dependent orbital-helical order in semiconductor crystals^{17,59,192,193,194,195}. Consequently, light-emitting excitons can demonstrate a CPL with right-handedness or left-handedness upon selecting different handedness of circularly polarized photoexcitation^{149,196,197,198,199,200,201,202}. Lifting spin degeneracy in momentum space can inevitably break momentum conservation in electronic transitions in chiral-structured MOFs carrying SOC and non-central symmetric polarizations. Therefore, SOC effects become a critical issue in determining light-emitting properties in chiral-structured MOFs. In this work, we select two chiral-structured MOFs [Ru(ppy)₃][Zn₂(ox)₃] and [Ru(ppy)₃][Mn₂(ox)₃] crystals with same right handedness but different SOC, namely $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals, to explore the SOC effects of light-emitting transitions.

3.3 Materials and Methods

3.3.1 Materials Synthesis

Chiral-structured MOFs [Ru(ppy)₃][Zn₂(ox)₃] and [Ru(ppy)₃][Mn₂(ox)₃] were synthesized by using previously-published procedures^{203,204,205,206}. The synthesis was focused on (1) the chiral resolution of [Ru(bpy)₃]I₂ and (2) the homo-chiral [Δ -Ru(bpy)₃][Δ -Zn₂(ox)₃] and [Δ -Ru(bpy)₃][Δ -Mn₂(ox)₃]. The H₂O-DMF (3:1, 8 mL)

solution of $[\Delta\text{-Ru}(\text{bpy})_3]\text{I}_2$ (41 mg, 0.05 mmol), zinc acetate dihydrate (22 mg, 0.10 mmol) or manganese (II) acetate tetrahydrate, oxalic acid (13 mg, 0.14 mmol), and hydrochloric acid (12 M, 0.5 mL) in a screw-capped vial was heated in an oven at 80°C. After 5 days, the reaction mixture slowly cooled to room temperature. The crystals were filtered, washed well with water and DMF, and dried. $[\Delta\text{-Ru}(\text{bpy})_3][\Delta\text{-Zn}_2(\text{ox})_3]$ and $[\Delta\text{-Ru}(\text{bpy})_3][\Delta\text{-Mn}_2(\text{ox})_3]$ single crystals were harvested with the size about 1 mm³[188].

3.3.2 Characterization and Measurement

PL in steady and time-dependent states were measured by the Horiba SPEX Fluorolog 3 spectrometer. The photoexcitation source was from a pulsed laser (343 nm and 1030 nm) generated through a harmonic generator (Ultrafast Systems LLC, second harmonic) with a Pharos laser (Light Conversion, 1100 kHz, 1030 nm, 290 fs).

The Time-resolved SHG spectra were measured by a pulsed laser (1030 nm) under a frequency of 100 KHz, an 850 nm long-pass cutoff filter (Newport) was placed on the excitation beam path before the sample, an FSQ-KG5 short-pass filter (300–800 nm, Newport) was placed on the emission beam path after the sample.

The circular polarized luminescence measurements were measured by the FLAME-T-XR1-ES spectrometer, CPL were measured upon switching the excitation and emission between left-handed and right-handed circular polarizations by rotating a quarter waveplate with -45° and +45° relative to a linear polarizer, as shown in **Figure 3-1**.

In CPL measurements, samples were excited by a pulsed laser (343nm or 1030 nm). Both chiral-structured MOFs $[\text{Ru}(\text{ppy})_3][\text{Zn}_2(\text{ox})_3]$ and $[\text{Ru}(\text{ppy})_3][\text{Mn}_2(\text{ox})_3]$ were measured at room temperature under the transmitting mode.

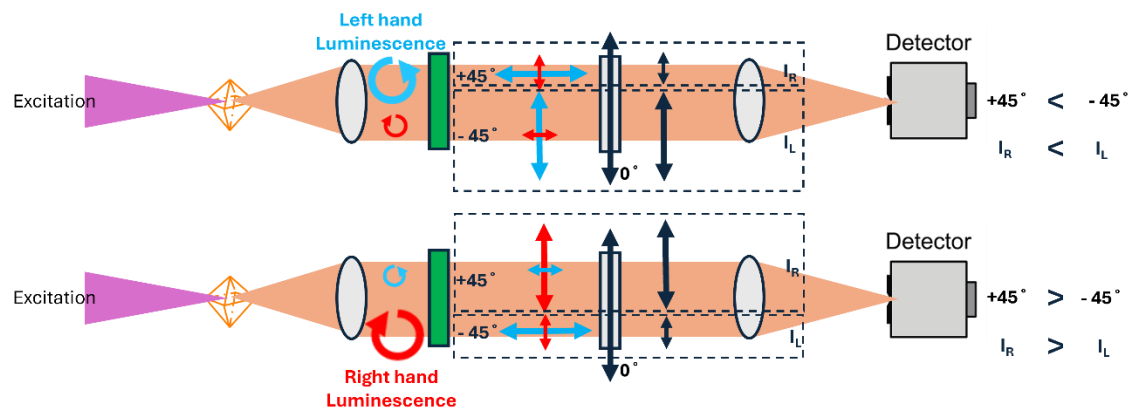


Figure 3-1 The diagrams illustrate experimental setups for CPL detection.

3.4 Results and Discussion

3.4.1 Photoluminescence and Nonlinear Optical Properties of Chiral-Structured

Ruthenium-Based MOFs

Figure 3-2 shows the PL characteristics at room temperature for Ruthenium complexes-based MOFs [Ru(ppy)₃][Zn₂(ox)₃] and [Ru(ppy)₃][Mn₂(ox)₃] shown as $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals. The $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals have very similar PL spectra with well-resolved peaks at 573nm/614nm and 507nm/607nm. Moreover, as shown in **Figure 3-2 c and d** both $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals demonstrate Second Harmonic Generation (SHG) in addition to two-photon up-conversion PL detected by time-dependent measurements under the pulsed laser excitation of 1030 nm. The SHG appears in the time window of sub-nanoseconds while the two-photon up-conversion PL dominates after sub-nanoseconds. The SHG indicates that $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals possess noncentral-symmetric polarizations. Clearly, the $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals are high-quality chiral-structured MOFs with both down-conversion and up-conversion light-emitting properties.

3.4.2 Circularly Polarized Luminescence in Chiral-Structured Ruthenium-Based MOFs

We can see in **Figure 3-3 a and b** that the chiral-structured $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals exhibit a right-handed σ^+ CPL with the degree of polarization (DOP) of 0.8 % and 1.6 % at room temperature under right-handed circularly polarized laser excitation of 343 nm. Here, the CPL can be described by its circular polarization degree, namely the degree of polarization (DOP) defined by

$$DOP = \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-} \quad (3)$$

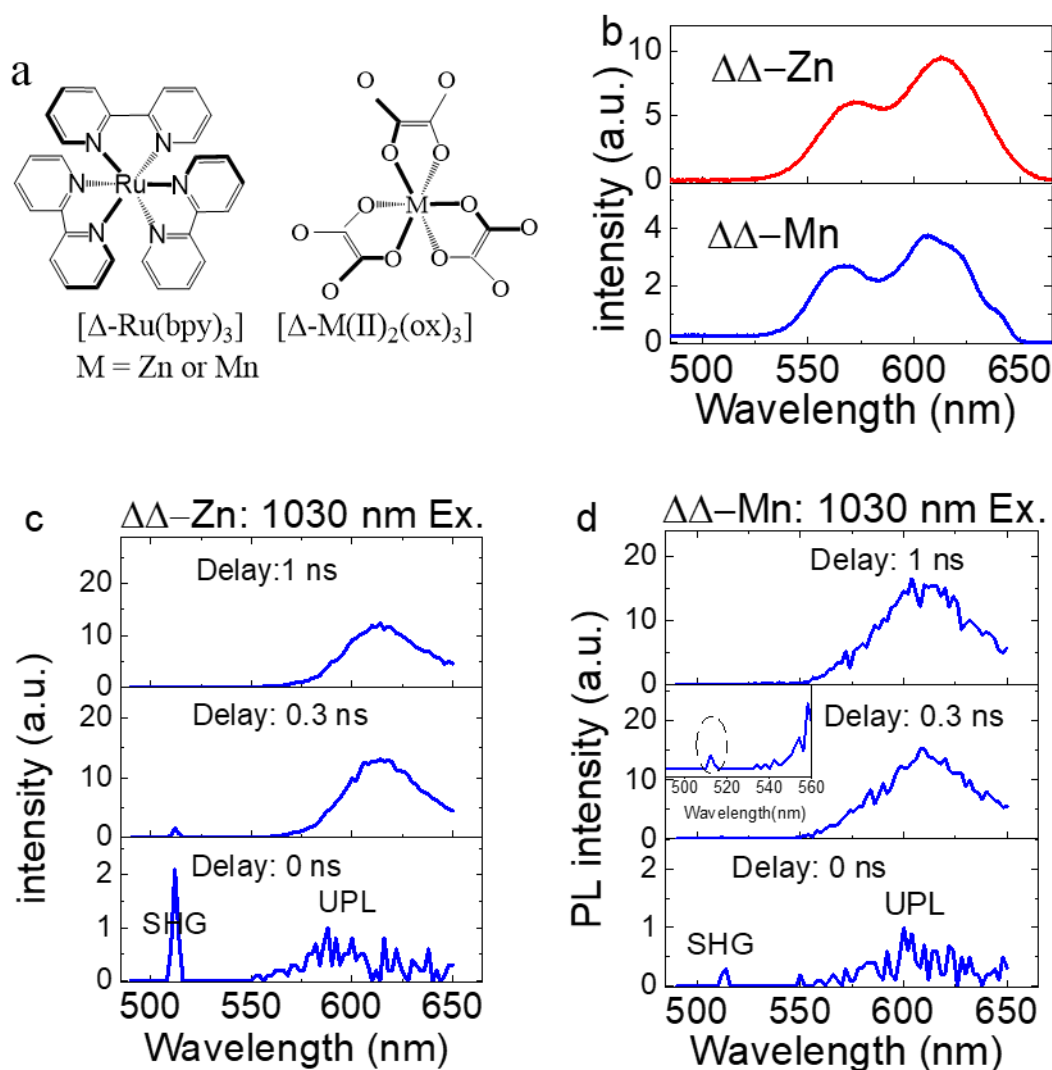


Figure 3-2 Optical properties of chiral-structured (Zn and Mn) MOFs with right handedness. (a) Chemical structures; (b) PL spectra under 343 nm excitations; (c) Time-resolved SHG with up-conversion PL (UPL) under 1030 nm laser beam for $\Delta\Delta\text{-Zn}$ MOF; (d) Time-resolved SHG with up-conversion PL (UPL) under 1030 nm laser beam for $\Delta\Delta\text{-Mn}$ MOF.

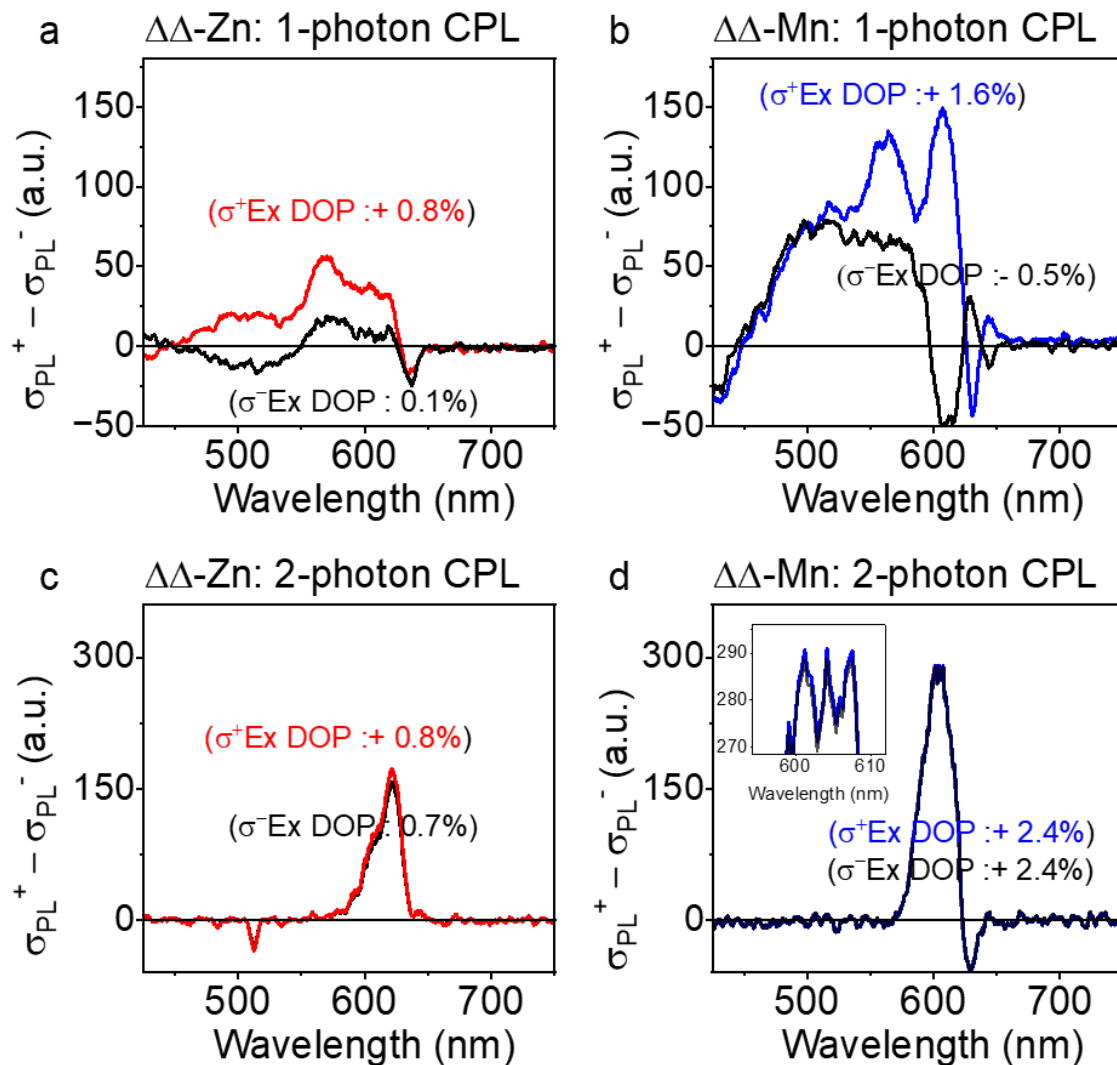


Figure 3-3 CPL characteristics at room temperature in right-handed chiral-structured $\Delta\Delta$ Zn and $\Delta\Delta$ Mn crystals under right-handed (σ^+) circularly polarized photo-excitations and left-handed (σ^-) circularly polarized photo-excitations (343 nm and 1030 nm). (a) Subtracted spectra ($\sigma^+ - \sigma^-$) of $\Delta\Delta$ Zn crystal measured under 343 nm laser excitation. (b) Subtracted spectra ($\sigma^+ - \sigma^-$) of $\Delta\Delta$ -Mn crystal measured under 343 nm laser excitation. (c) Subtracted spectra ($\sigma^+ - \sigma^-$) spectra of $\Delta\Delta$ -Zn crystal measured under 1030 nm laser excitation. (d) Subtracted spectra ($\sigma^+ - \sigma^-$) of $\Delta\Delta$ -Mn crystal measured under 1030 nm laser excitation.

It is known that chiral-structured MOFs can commonly demonstrate a CPL at room temperature^{131,207,208,209}. Here, we should note that the chiral-structured MOFs are designed with the dipolar donor-acceptor structures between Ruthenium complexes and metal ions. Essentially, the dipolar donor-acceptor structures are formed with helical configuration, functioning as helical dipolar polarizations in the chiral-structured crystals. We can expect that the helical dipolar polarizations provide the necessary condition to establish the helical order of electronic transition dipoles to generate a CPL in chiral-structured MOFs. It is noted that, when the circularly polarized photoexcitation is selected with the handedness (σ^-) opposite to chirality (σ^+) of chiral-structured MOFs, the $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals exhibit much reduced CPL with the DOPs (**Figure 3-3 a and b**). This implies that the circularly polarized photoexcitation with the handedness opposite to the chirality of chiral-structured MOFs has a difficulty to establish the helical order of dipolar polarizations and consequently disables the helical order of electronic transition dipoles. We should also note that chiral MOFs could possess a birefringence phenomenon due to anisotropic polarizations^{210,211}. The birefringence can often lead to a CPL, giving rise to birefringence-induced CPL^{212,213}. Here, switching the circularly polarized photoexcitation between right-handedness and left-handedness suggests that the helical order of light-emitting excitons can be indeed established. Furthermore, CPL can be also observed in $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals at room temperature under 2-photon excitation (**Figure 3-3 c and d**). Interestingly, both right/left-handed circularly-polarized excitations give rise to similar DOP (0.8%/0.7% and 2.4%/2.4%) in the $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals under 2-photon excitation. This phenomenon implies that two phonons can

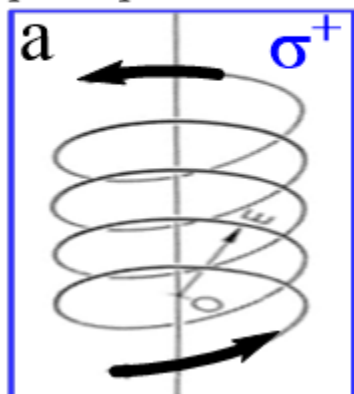
provide sufficient orbital momentum to establish the helical order of electronic transition dipoles when the excitation handedness is opposite to the chirality of chiral-structured MOFs. Clearly, the 2-photon up-conversion CPL indicate that the $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals are formed as high-quality chiral-structured MOFs.

3.4.3 Spin-Orbit Coupling-Induced Rashba band structures and accelerated Electronic Transitions in Chiral-Structured MOFs

We should emphasize that the SOC and noncentral-symmetric polarizations formed in chiral-structured MOFs provide the possibilities to split the spin-up and spin-down band structures in momentum space. This presents an interesting scenario that the chiral-structured MOF crystals possess Rashba band structures, as illustrated in **Figure 3-4**. Rashba band structures can be commonly expected in semiconductor crystals when SOC and non-central symmetry are co-existed^{214,215}. Notably, lifting spin-up and spin-down band structures in momentum space can inevitably cause an indirect bandgap between the minimal-energy state of conduction band and the maximal-energy state of valence band. The transition dipoles must require lattice-assisted momentum conservation in chiral-structured MOFs in order to generate a helical ordering of light-emitting excitons towards generating a CPL.

To explore lattice-assisted momentum conservation effects of light emission, we monitored the PL lifetimes from the chiral-structured $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals. **Figure 3-5 a** shows the PL lifetimes for the weak-SOC $\Delta\Delta\text{Zn}$ and the strong-SOC weaker-SOC $\Delta\Delta\text{Mn}$ crystals. We can see that weak-SOC $\Delta\Delta\text{Zn}$ and strong-SOC $\Delta\Delta\text{Mn}$ crystals demonstrate much longer and shorter PL lifetimes. This indicates that increasing SOC

Helically-configured
dipolar polarizations



Rashba band structures
circularly polarized orbitals

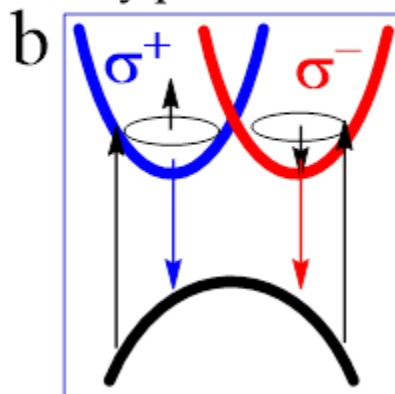


Figure 3-4 Helically-structured dipolar polarizations and Rashba band structures in chiral-structured MOFs. a. Right-handed helical order (σ^+) of dipolar polarizations. b. Rashba band structures carrying circularly polarizable orbital momentum (σ^+ and σ^-) with right-handed and left-handedness. When SOC is weak, helical order of dipolar polarizations dominates CPL. When SOC is strong in symmetry breaking configuration, Rashba band structures involve in CPL.

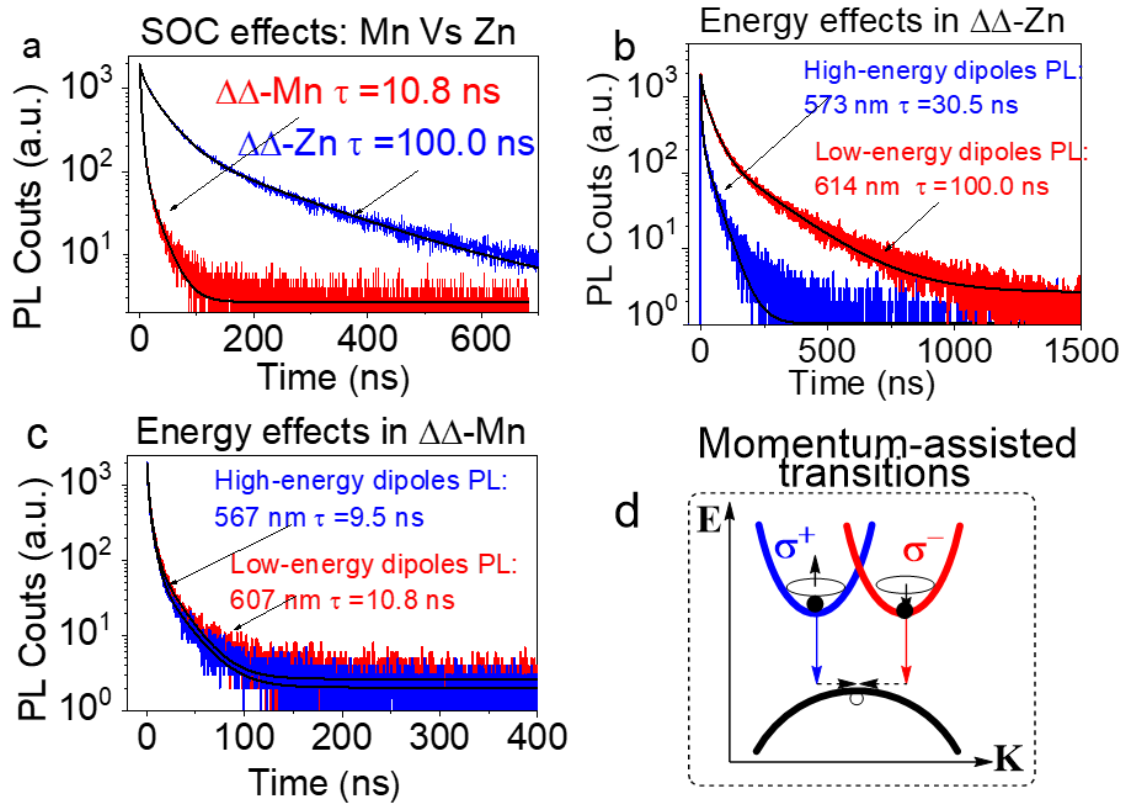


Figure 3-5 SOC effects in weak-SOC $\Delta\Delta\text{Zn}$ and strong-SOC $\Delta\Delta\text{Mn}$ crystals. (a) Faster and slower PL lifetimes for $\Delta\Delta\text{-Zn}$ (PL at 614 nm) and $\Delta\Delta\text{-Mn}$ (PL at 607 nm) under 343 nm excitation. (b) Reduced and extended PL lifetimes for high and low-energy transition dipoles (PL: 573nm and PL: 614nm) in weak-SOC $\Delta\Delta\text{Zn}$, respectively. This means that high-energy dipoles have a stronger SOC, accelerating electronic transitions in weak-SOC MOF. (c) Similar PL lifetimes for high and low-energy transition dipoles (PL: 567nm and PL: 607nm) in strong-SOC $\Delta\Delta\text{Mn}$ MOF. This means that increasing SOC through high transition dipoles does not further affect already-accelerated electronic transitions in strong-SOC MOF. d. Rashba band structures carry indirect gaps. Electronic transitions require momentum conservation.

can essentially accelerate the electronic transitions, shown by the shorter PL lifetime in strong-SOC $\Delta\Delta\text{Mn}$ as compared to weaker-SOC $\Delta\Delta\text{Zn}$. This SOC-accelerated electronic transitions can be confirmed by the reduced and extended PL lifetimes from high-energy and low-energy transition dipoles with PL peaks at 573 nm and 614 nm in the weaker-SOC $\Delta\Delta\text{Zn}$ (**Figure 3-5 b**). We should note that high-energy and low-energy transition dipoles possess stronger and weaker SOC, respectively. Here, we can see in the $\Delta\Delta\text{Zn}$ that the high-energy transition dipoles (PL peak: 573 nm) carrying stronger SOC give rise to a much reduced PL lifetime of 18.35 ns as compared to the extended PL lifetime of 44.33 ns for low-energy dipoles (PL peak: 614 nm) carrying weaker SOC. On contrast, the strong-SOC $\Delta\Delta\text{Mn}$ demonstrates similar PL lifetimes (8.47 ns and 9.21 ns) for high-energy and low-energy transition dipoles with the PL peaks at 567 nm and 607 nm (**Figure 3-5 c**). Clearly, increasing SOC can largely accelerate the electronic transitions in chiral-structured MOFs. This presents a fundamental scenario that the lattice-assisted momentum conservation is essentially realized by chiral-structured SOC, leading to SOC-accelerated light-emitting transitions in chiral-structured MOFs.

3.5 Summary

In summary, our work demonstrates that the differences of spin-orbit coupling (SOC) significantly accelerate electronic transitions in chiral-structured MOFs. Particularly, the $\Delta\Delta\text{Zn}$ and $\Delta\Delta\text{Mn}$ crystals demonstrate a SOa SOC-dependent light-emitting transition non-central symmetric polarizations, identified by the PL lifetimes from light-emitting excitons carrying weaker and stronger SOC. This leads to an interesting scenario that the spin-up and spin-down light-emitting excitons become non-degenerate in momentum

space, presenting an analogue similar to Rashba band structures. This scenario implies that light-emitting transitions must require lattice-assisted momentum conservation upon lifting spin degeneracy in momentum space in chiral-structured MOFs. This scenario is supported by the experimental phenomenon that weaker and stronger SOC lead to slower and faster light-emitting transitions, respectively. Specifically, the stronger-SOC $\Delta\Delta\text{Mn}$ crystal exhibits an accelerated light-emitting transition with the shorter PL lifetime of 10.8 ns, as compared to the weaker-SOC $\Delta\Delta\text{Zn}$ crystal with slower light-emitting transition and longer PL lifetime of 100.0 ns. Furthermore, we observed that higher-energy excitons carrying stronger SOC selected from shorter PL wavelength demonstrate a much accelerated light-emitting transition as compared to lower-energy excitons carrying weaker SOC selected from longer PL wavelength. Clearly, SOC serves as the key parameter to accelerate light-emitting transitions through lattice-assisted momentum conservation in chiral-structured MOF crystals.

Chapter 4 Spin-dependent Behaviors of Circularly-Polarized Exciton in Light-emitting Radicals

4.1 Abstract

This work reports that crystalline doublet states can enable circularly-polarized spin-orbital coupling (SOC) effects, shown by magnetic field effects of circularly-polarized luminescence (CPL) in radicals-doped crystal (PyBTM_{0.001}:*aH*-PyBTM_{0.999}) with photoluminescence quantum efficiency of 86%. Specifically, applying 1.4 T magnetic field changes the circular polarization of CPL from 0.76 % to 0.63 % under right-handed σ^+ excitation and from 0.35 % to 0.25 % under left-handed σ^- excitation, presenting magnetic field effects of CPL. Here, magnetic field effects of CPL indicate that crystalline doublet states are essentially formed with Rashba-like band structures carrying right-hand (σ^+) and left-hand (σ^-) circularly polarizable orbital momentum in radicals-doped crystalline structures. Clearly, forming crystalline doublet states provides a fundamental platform to explore circularly-polarized SOC effects through Rashba-like band structures in radicals-doped crystal.

4.2 Introduction

Radical molecules are intrinsically formed with doublet states carrying spin momentum that can fundamentally impact the advancements of spin-electronic, chiroptical, and orbitronic materials^{216,217,218,219,220,221,222,223,224}. In general, radical molecules can lead to amorphous and crystalline doublet states by forming random and ordered morphological structures. In amorphous doublet states, the radical molecules have shown the possibilities of lifting spin restrictions towards achieving 100 % spin-allowed excitons^{29,225,226,227,228}. Therefore, amorphous doublet states have become an emerging platform to explore unique light-emitting properties enabled by spin radicals in organic

molecules. Furthermore, introducing spin radicals into organic molecules has been pursued to demonstrate attractive magnetic, chirality, photoluminescence, and electroluminescence properties²²⁹. However, the crystalline doublet states carrying internally-coupled spin-orbit coupling (SOC) and nonlinear optical polarization demand much effort to explore emerging spin-optical properties enabled by internally coupled spin-orbital coupling and nonlinear optical polarization.

Here, we explore circularly-polarized SOC effects enabled by crystalline doublet states formulated by dispersing the spin radicals (PyBTM) into the donor-acceptor (*aH*-PyBTM) crystalline matrix to form radicals-doped crystal (PyBTM_{0.001}:*aH*-PyBTM_{0.999}) with photoluminescence quantum efficiency of 86%. The radicals-doped crystals were prepared with the size of ~ 0.5 millimeters by using room-temperate solution growth method. Magnetic field effects of CPL were used to identify the circularly-polarized SOC effects. In this work, circularly-polarized SOC effects were explored in crystalline doublet states by using magnetic field effects of CPL based on radicals-doped crystal (PyBTM_{0.001}:*aH*-PyBTM_{0.999}) with high quantum efficiency of 86%.

Magnetic field effects of CPL were conducted by monitoring the circular polarization of CPL upon applying an external magnetic field. Essentially, magnetic field effects of CPL indicate that crystalline doublet states are formed with Rashba-like band structures carrying right-handed and left-handed circularly-polarized orbital momentum to enable circularly-polarized SOC effects in radicals-doped crystalline structures.

4.3 Materials and Methods

4.3.1 Materials Synthesis

The radicals-doped dipolar crystals were prepared with a size of ~ 0.5 millimeters by using a room-temperate solution growth method²³⁰. 0.1wt% PyBTM-doped αH -PyBTM crystals used for the optical investigations were prepared according to the procedure reported previously with slight modification, where acetone was used in place of dichloromethane as the solvent.⁴

4.3.2 Characterization and Measurements

Powder X-ray diffraction study confirmed that the doped crystals are phase-pure and isostructural to parent αH -PyBTM crystals, consistent with the previous report.⁴ The doping concentration of the samples were estimated to be 0.08~0.1 wt% by absorption spectroscopy.⁴ PL in steady and dynamic regimes was measured by the Horiba SPEX Fluorolog 3 spectrometer. The time-resolved photoexcitation source was from a pulsed laser beam (343 nm) generated through a harmonic generator (Ultrafast Systems LLC, third harmonic) with a Pharos laser (Light Conversion, 25 kHz, 1025 nm, 290 fs). The SHG spectrum was measured by the same excitation source as the time-resolved photoexcitation source under a frequency of 100 kHz, an 850 nm long-pass cutoff filter (Newport) was placed on the excitation beam path before the sample, an FSQ-KG5 short-pass filter (300–800 nm, Newport) was placed on the emission beam path after the sample. CPL was measured by the FLAME-T-XR1-ES spectrometer under circularly polarized detection and excitation selected with right-handedness or left-handedness. The right-handed and left-handed circular polarizations were set by rotating a quarter wave

plate with -45° and $+45^\circ$ relative to a linear polarizer. In CPL measurements, samples were excited by a continuous-wave (CW) laser beam of 375nm.

4.4 Results and Discussions

4.4.1 Photoluminescence and Nonlinear Optical Properties in Radicals-Doped Crystals

Figure 4-1a shows the PL spectra at different excitation intensities ($34 \mu\text{J}/\text{cm}^2$ and $160 \mu\text{J}/\text{cm}^2$) of 343 nm laser beam at room temperature for the radicals-doped crystal ($\text{PyBTM}_{0.001}:\text{aH-PyBTM}_{0.999}$) containing 0.1 wt% radical molecules (PyBTM) dispersed into dipolar *aH*-PyBTM crystalline matrix. The PL spectral similarity between 0.1% radicals-doped crystal and liquid solution verifies that the radicals (PyBTM) function as monomer emitters to generate light emission in the 0.1% radicals-doped crystal ($\text{PyBTM}_{0.001}:\text{aH-PyBTM}_{0.999}$). **Figure 4-1b** illustrates the absorption and PL spectra for the radical molecules (PyBTM) and matrix (*aH*-PyBTM) in liquid solution. The crystal structure of the radicals-doped crystal can be confirmed by the X-ray diffraction (XRD) data shown in **Figure 4-1c**. Here, the radicals-doped crystal can give rise to crystalline doublets. Interestingly, increasing the excitation intensity generates a slower PL lifetime of $0.73 \mu\text{s}$ while only a faster PL lifetime of 84 ns is shown at low excitation intensity, as illustrated in **Figure 4-1d**. The faster and slower PL lifetime components indicate that the light emission from the crystalline doublet states combines two light-emitting components, suggesting prompt non-spin-mixing prompt and delayed spin-mixing processes in the radicals-doped crystal ($\text{PyBTM}_{0.001}:\text{aH-PyBTM}_{0.999}$).

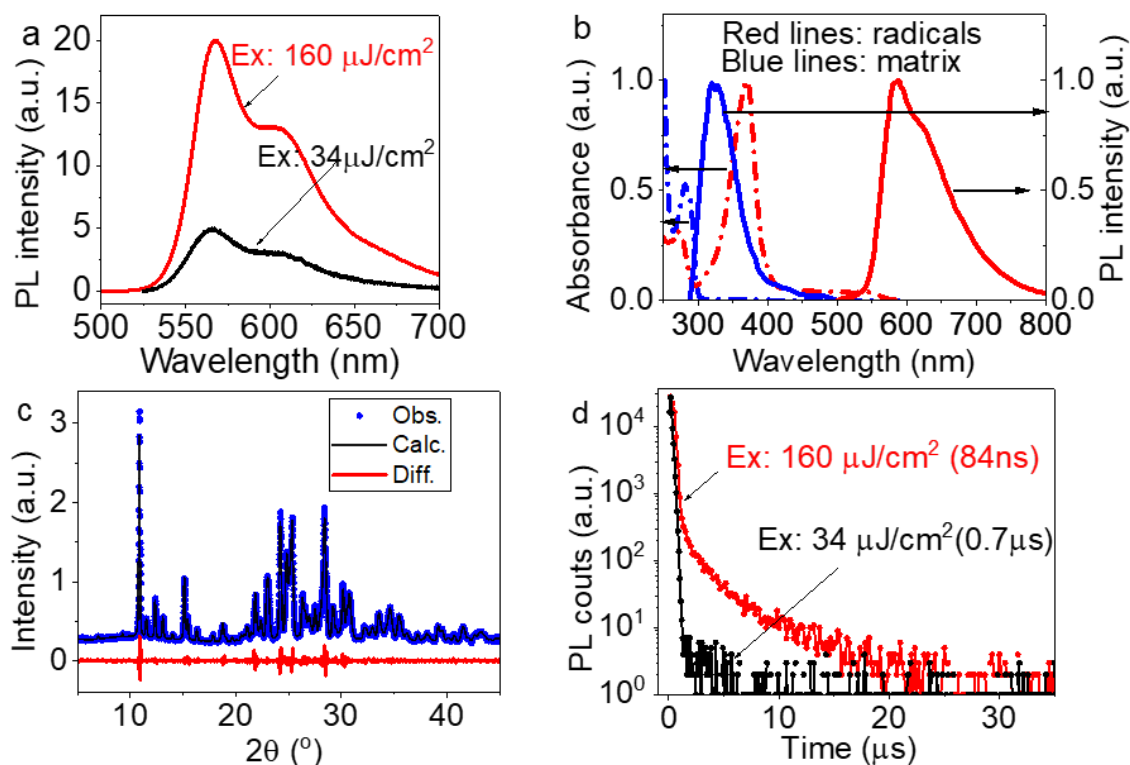


Figure 4-1 PL characteristics for radical emitters. (a) PL spectra at lower and higher excitation intensities; (b) PL and absorption spectra for 0.1% radicals-doped dipolar crystal ($\text{PyBTM}_{0.001}:\alpha H\text{-PyBTM}_{0.999}$) and its liquid solution. (c) Observed (blue dot) and calculated (black line) powder X-ray diffraction profiles for the Pawley refinement of 0.1 wt% radicals-doped dipolar crystal ($\text{PyBTM}_{0.001}:\alpha H\text{-PyBTM}_{0.999}$). The calculation was conducted based on the crystallographic data of $\alpha H\text{-PyBTM}$. The bottom red curve represents the difference between the two profiles. (d) Different PL lifetimes at 568 nm occurred in nanosecond and microsecond time windows under low and high excitation intensities from 343 nm pulse laser beam. Higher excitation generates both nanosecond and microsecond PL lifetimes while low excitation only gives rise to nanosecond PL lifetime.

The radical monomer emitters are known as unpaired spins carrying intrinsic spin momentum in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}), as shown in **Figure 4-2 a**. Consequently, dispersing the 0.1 % radical molecules carrying intrinsic spin momentum into the crystalline matrix forms a light-emitting system with spin momentum, as illustrated in **Figure 4-2 b**. Essentially, radicals with unpaired spins provide an opportunity to introduce a SOC in organic molecule^{231,232,233}. Furthermore, the 0.1 % radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}) demonstrates the Second Harmonic Generation (SHG) accompanied with 2-photon up-conversion luminescence (UPL), measured with time-resolved spectroscopy at room temperature (**Figure 4-2 c**). The time-resolved spectral measurements indicate that the SHG signal is quickly established while the UPL is gradually developed into a dominant component. It should be noted that the radicals-doped dipolar crystal is formed as triclinic structure with the symmetry of P-1 space group²³⁴. The observed SHG presents the scenario that the radicals cause a distortion of polarization wavefunctions through electric-magnetic coupling mechanism, leading to symmetry breaking in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}). It should be noted that the efficient triplet-singlet intersystem crossing occurred in highly-efficient organic delayed fluorescence^{235,236} imply that SOC can be widely existed in organic molecules designed with charge-transfer states in the absence of heavy elements. However, the SOC reflected by delayed fluorescence in the organic molecules designed with charge-transfer states are formed in amorphous structures. Here, we should emphasize that simultaneously activating SOC and nonlinear optical polarization in crystalline structures provides the necessary condition readily to form

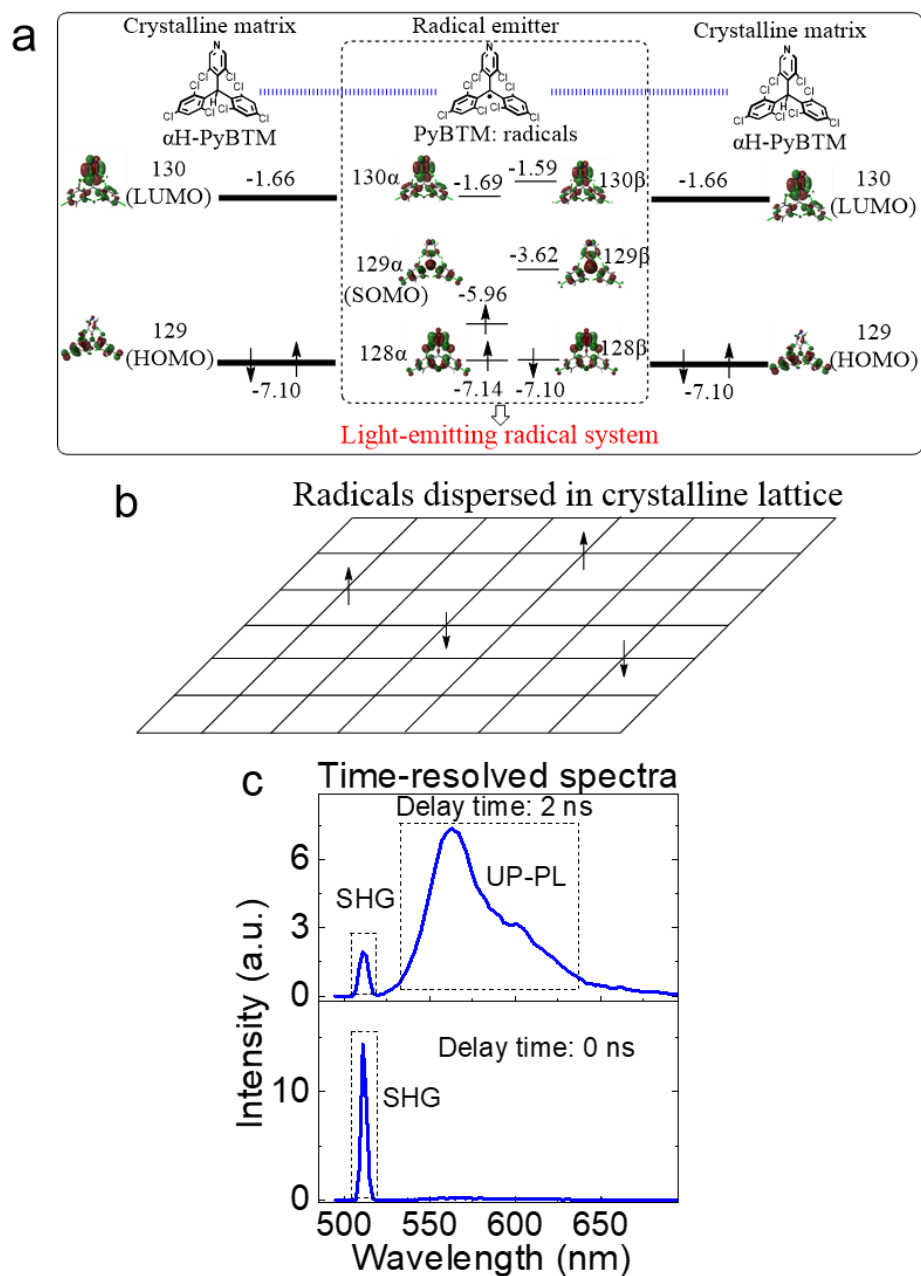


Figure 4-2 Spin effects in radicals-doped dipolar crystal. (a) Radical molecules functioning as monomer emitters are dispersed into crystalline dipolar matrix to form doublet states. (b) Radical monomers (PyBTM) are dispersed in crystalline (αH -PyBTM) matrix to form dipolar light-emitting system carrying spin momentum. (c) Time-resolved SHG and UPL at different delay times (0 ns and 2 ns) in 0.1% radicals-doped dipolar crystal (PyBTM_{0.001}: αH -PyBTM_{0.999}) under 1025 nm laser beam.

circularly-polarized orbital momentum with spin-up and spin-down configurations, similar to Rashba-like band structures, in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}).

4.4.2 Rashba-Like Band Structures of Radicals-Doped Crystals

Rashba-like band structures consist of spin-up and spin-down bands with right-handed and left-handed circularly-polarized orbital momentum. The light-emitting excitons possess both orbital and spin momentum, known as **J** states (**J** = **L** + **S**, where **L** and **S** are orbital and spin momentum). When right-handed and left-handed circularly-polarized excitations separately excite the spin-up and spin-down band structures, right-handed and left-handed circularly-polarized excitons can be generated in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}), as illustrated in **Figure 4-3 a**. When the circularly-polarized excitons conserve their circular polarization within PL lifetime, a CPL can then be observed. It is noted that forming radical molecules (trityl-based radical chlorinated derivatives) into chiral structures to form chiral organic radical emitters can lead to a CPL in CCl₄ solution at - 20 °C^[134]. It has been also reported that doping radicals into PMMA and chiral liquid crystal can give rise to a CPL. Here, we utilize magnetic field effects of CPL to explore circularly-polarized excitons in the crystalline doublet states formed by orderly dispersing radical molecules into regular lattice. **Figure 4-3 (b and c)** shows the CPL from the 0.1 % radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}) excited by right-handed and left-handed circularly polarized excitations at room temperature. The CPL give rise to the right-handed circular polarization, shown as σ^+ CPL with the circular-polarization degrees of 0.76 % and 0.35 % at room temperature under

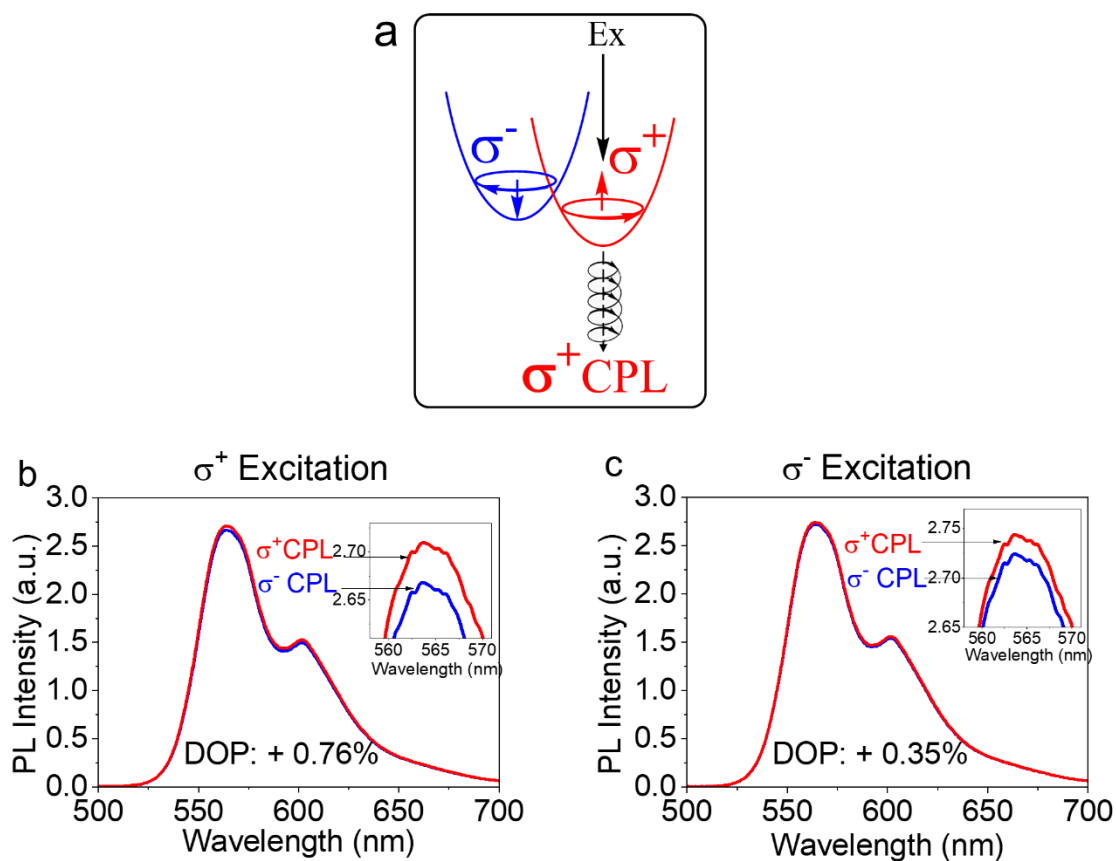


Figure 4-3 CPL performance of Radicals-Doped Crystals. (a) Rashba-like band structures with circularly polarized orbital momentum to generate CPL in 0.1% radicals-doped dipolar crystal ($\text{PyBTM}_{0.001}:\alpha\text{H-PyBTM}_{0.999}$). Circular polarization of CPL is defined by degree of polarization (DOP), given by $\frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-}$. σ^+ and σ^- refer to right-handed and left-handed circular polarizations. (b) Right-handed circularly polarized σ^+ excitation generates a right-handed σ^+ CPL with the DOP of +0.76 %; (c) Left-handed circularly polarized σ^- excitation still generates a σ^+ CPL with DOP of +0.35 %.

right-handed and left-handed circularly polarized excitations, respectively.

We should note that crystalline structures can be often formed with birefringence due to structural anisotropy. The birefringence can then give rise to a synthetic CPL by combining fast and slow optical propagating components with a certain phase difference²³⁷. Essentially, the birefringence functions as a waveplate which generates a certain phase difference between the fast and slow optical axis in crystalline structures. When the phase difference reaches $\frac{\pi}{2}$ between fast and slow optical axis, a CPL can then be observed, leading to the so-called dichroism-induced CPL, as distinguished from the CPL generated by circularly-polarized excitons in Rashba-like band structures. Therefore, it becomes a challenging issue to completely remove the birefringence effect from the CPL generated by circularly-polarized excitons.

4.4.3 Magnetic Field Effects of CPL in Radicals-Doped Crystals

Here, we utilize magnetic field effects of CPL to probe circularly-polarized excitons towards exploring Rashba-like band structures in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}). Because the dichroism-induced CPL are insensitive to magnetic field, magnetic field effects of CPL become a unique method to detect circularly-polarized excitons to avoid birefringence effect towards understanding circularly-polarized SOC effects. **Figure 4-4** shows an interesting phenomenon: an external magnetic field of 1.4 T can clearly decrease the circular-polarization degree of right-handed σ^+ CPL at room temperature. Here, the CPL are identified by measuring the σ^+ and σ^- light-emitting intensities at spectral peak-wavelength under circularly polarized excitation.

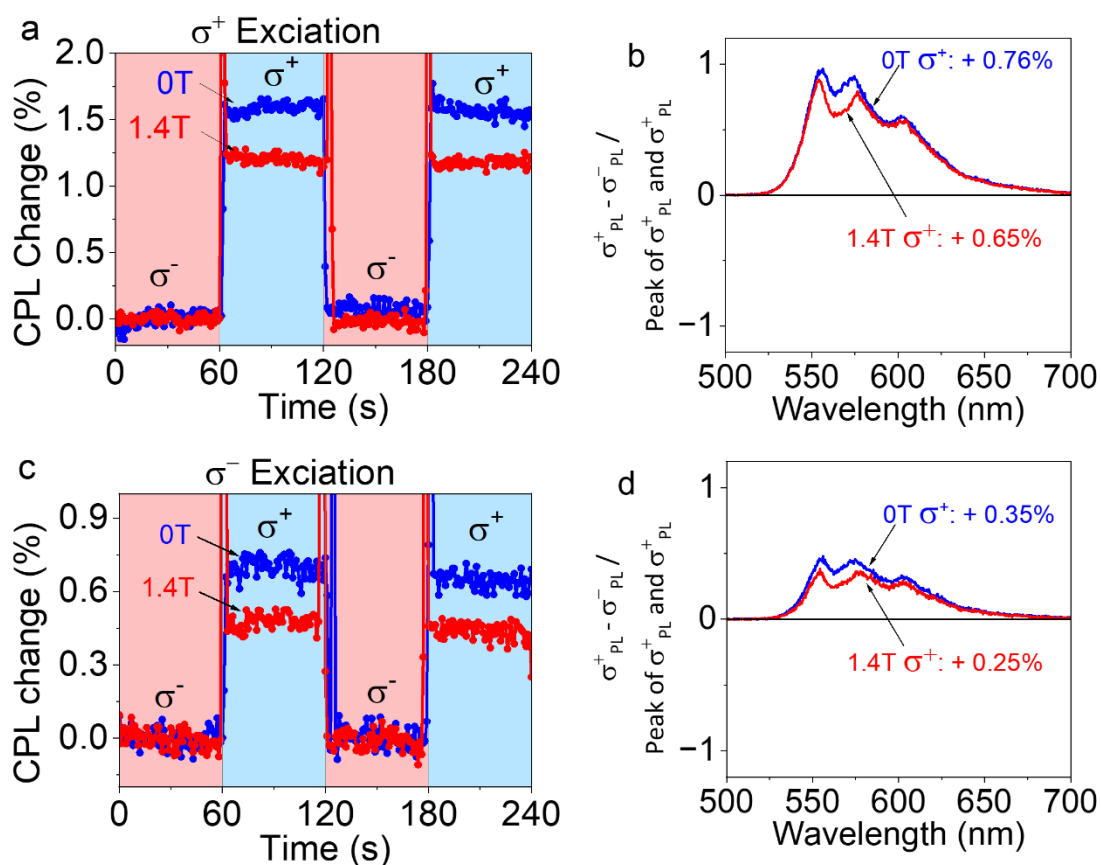


Figure 4-4 Magnetic field effects of CPL for radical monomer emitters in 0.1% radicals-doped dipolar crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}). (a) Under Right-handed circularly polarized excitation, CPL at the spectral peak of 563 nm was separately detected at right-handedness and left-handedness under a 1.4T magnetic field as compared to 0T. (b) Under right-handed circularly polarized excitation, CPL spectra were recorded under 1.4T magnetic field relative to 0T. (c) Under left-handed circularly polarized excitation, CPL at the spectral peak of 563 nm was separately detected at right-handedness and left-handedness under 1.4 T magnetic field as compared to 0T. (d) Under left-handed circularly polarized excitation, CPL spectra were recorded under a 1.4T magnetic field relative to 0T.

When the σ^+ output is stronger than the σ^- output, the CPL becomes right-handed, shown as σ^+ CPL. For non-circularly polarized light emission, σ^+ and σ^- detections give rise to the same intensity. Therefore, the difference between the σ^+ and σ^- light-emitting outputs can identify the occurrence of CPL. Here, the 0.1 % radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}) demonstrates a σ^+ CPL at room temperature under either right-handed or left-handed circularly polarized excitation. Very interestingly, the 1.4 T magnetic field can appreciably decrease the circular polarization degree of σ^+ CPL from 0.76 % to 0.65 % under right-handed circularly polarized excitation (**Figure 4-4 a and b**) and from 0.35 % to 0.25 % under left-handed circularly polarized excitation (**Figure 4-4 c and d**), presenting magnetic field effects of circular polarization of CPL. We should emphasize that magnetic field effects have been widely observed on photoluminescence (PL) intensity, shown as magnetic field effects of PL in organic materials^{238,239,240}. Essentially, magnetic field effects reflect that an external magnetic field introduces spin flipping through spin scattering and consequently changes the intersystem crossing between singlet and triplet excitons. Eventually, this redistributes the singlet and triplet populations, leading to a change on PL intensity upon applying an external magnetic field. This generates the so-called magnetic field effects of PL in organic materials. Here, an external magnetic field changes the circular polarization of CPL, shown as magnetic field effects of CPL indicated by magnetic field-modulated difference between σ^+ and σ^- CPL intensities in CPL measurements. Clearly, magnetic field effects of CPL provide three critical understanding. First, the observed CPL are indeed originated by circularly-polarized excitons, rather than dichroism effects. This implies that the crystalline doublet

states are essentially formed with circularly-polarized excitons in the radicals-doped crystalline structures. Second, the circularly-polarized excitons possess circularly-polarized SOC. This leads to the hypothesis that Rashba-like band structures can be formed with right-handed and left-handed circularly polarized orbital momentum in the radicals-doped dipolar crystal. Third, an intersystem crossing can inevitably occur between right-handed and left-handed circularly-polarized Rashba-like band structures. Notably, the intersystem crossing requires a spin flipping for circularly polarized excitons to transfer between spin-up and spin-down band structures.

4.5 Summary

The crystalline doublet states demonstrate a right-handed σ^+ CPL observed at room temperature when the radicals are dispersed into nonlinear-optically polarizable lattice matrix to form the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}), known as crystalline-type radical light-emitting platform. This observation provides the first-hand scenario that the crystalline doublet states are formed with light-emitting excitons carrying circularly polarized orbital momentum in the radicals-doped crystal (PyBTM_{0.001}: α H-PyBTM_{0.999}). More importantly, the observed CPL shows magnetic field effects where applying 1.4 T magnetic field can appreciably change the circular polarization of CPL from 0.76 % to 0.65 % under right-handed circularly polarized excitation and from 0.35 % to 0.25 % under left-handed circularly polarized excitation at room temperature. Here, magnetic field effects present the unique indication that the circularly-polarized SOC are formed in the crystalline doublet states. This leads to an important hypothesis that the crystalline doublet states are formed with Rashba-like band

structures under the influence of co-existed SOC and nonlinear optical polarization in the radicals-doped crystal. Essentially, Rashba-like band structures carry right-handed and left-handed circularly-polarized orbital momentum, giving rise to circularly-polarized excitons in the crystalline doublet states. This discovery highlights the unique optical properties from crystalline doublet states enabled by internally coupled spin, polarization, and symmetry parameters in radical light-emitting molecules.

**Chapter 5 Probing Spin-Orbital Coupling Ordering Effects in Chiral Perovskite
Crystals Based on Magnetic Field Effects of Circularly Polarized
Photoluminescence**

5.1 Abstract

Chiral-structured semiconductors have become interesting multifunctional materials with the promise to function as optically-active artificial magnetic materials with circularly polarized excitons and spin selection activities. It can be hypothesized that chiral-structured semiconductors are formed with spin-orbital coupling ordering effects to provide the necessary condition towards enabling circularly polarized excitons and spin selection activities. Here, we utilize magnetic field effects of circularly polarized photoluminescence (MFE-CPL) to probe spin-orbital coupling ordering effects based on chiral-structured metal-halide hybrid perovskite films where the chiral-structured 1D S-MBAPbBr₃ dispersed in nonchiral-structured 3D MAPbBr₃ matrix. The chiral-structured perovskites can demonstrate right-handed (σ^+) and left-handed (σ^-) CPL upon applying right-handed and left-handed circularly polarized excitations. This observation indicates that right-handed/left-handed circularly polarized lights can selectively excite the respective handed chiral structures. Interestingly, applying the magnetic field of 0.9 T can clearly increase the circular polarization of CPL at 5 K. Here, these magnetic field effects provide three fold critical information. First, light-emitting excitons can indeed exhibit circularly polarized orbital momentum, leading to circularly polarized excitons in the chiral perovskite structures. Second, the chiral structures are essentially formed with circularly-ordered spin-orbital coupling (SOC), presenting spin-orbital coupling ordering effects towards generating CPL. Third, applying a magnetic field enhances the SOC ordering effects, consequently increasing the circular polarization of CPL by decreasing the dephasing of circularly polarized excitons in chiral structures. Therefore, SOC

ordering effects play an important role in developing circularly polarized excitons in chiral structures.

5.2 Introduction

Chiral materials have shown amazing phenomena in interacting electron spins exemplified as spin selection, leading to the so-called chirality-induced spin selection (CISS). CISS presents an un-conventional approach to generate spin activities, by passing the conventional approach of utilizing ferromagnetic metals^{151,152,241,242}. However, it still demands much effort to elucidate the underlying mechanisms accountable for the dynamic interactions between chiral structures and electron spins. Parallel to understanding the underlying mechanisms of CISS, we should emphasize the classic mechanism of interacting electron spins by using spin-orbital coupling (SOC). Essentially, SOC provides a prominent mechanism to interact with electron spins, leading to spin flipping phenomena in organic molecules^{14,15,16,17}. It has been widely observed that electron spins can be effectively flipped by SOC, evidenced by SOC-enabled intersystem crossing between spin singlets and triplets in organic light-emitting molecules. Here, SOC functions as random spin-scattering centers. Nonetheless, SOC provides an important mechanism to interact with electron spins, generating spin scattering phenomena. This is known as SOC-enabled spin scattering phenomena. Furthermore, we found that optically-induced orbital order in organic-inorganic hybrid perovskites known as strong SOC semiconductors can directly interact with the spin order on ferromagnetic cobalt surface, leading to optically-induced magnetization at room temperature. This optically-induced magnetization provides a critical evidence that

the orbital order can serve as an effective mechanism to selectively interact with electron spin order.

In this work, we utilize magnetic field effects of circular polarization of CPL to explore orbital ordering effects of circularly-polarized excitons in the chiral-structured perovskite prepared by growing chiral-structured 1D S-MBAPbBr₃ in nonchiral-structured 3D MAPbBr₃ matrix. The chiral-structured 1D perovskites in nonchiral-structured 3D perovskite matrix consists of both right-handed and left-handed structures which can be respectively excited by right-handed and left-handed circularly polarized laser beams. CPL was used to identify the photoexcited chiral-structured 1D perovskites. The constant magnetic field of 0.9 T was applied to the CPL to show the effects of magnetic field on the circular polarization of CPL towards revealing the SOC ordering effects in the chiral-structured perovskite. Specifically, magnetic field effects of circular polarization of CPL were determined by measuring the degree of circular polarization (DOP), $DOP = \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-}$, before and after applying the constant magnetic field of 0.9 T. Here, σ^+ and σ^- represent the right-handed and left-handed CPL intensities. We should note that the light-emitting excitons are **J** states carrying both orbital and spin momentum in the chiral-structured perovskite. Forming J excitons are formed in chiral structures provides the fundamental hypothesis that the orbital momentum becomes helically ordered, leading to helically ordered SOC to demonstrate a CPL. However, chiral materials are often formed with structural anisotropy, giving rise to birefringence. The birefringence can be involved in CPL measurements, presenting a dichroism-induced CPL^{212,213}. Here, we utilize magnetic field effects to explore the helically-ordered SOC. Specifically, magnetic field effects can

distinguish whether the CPL originates from circularly-polarized excitons or dichroism-induced polarization effects in the chiral-structured perovskite. If the CPL were originated from dichroism-induced polarization effects rather than circularly-polarized excitons, magnetic field effects of circular polarization of CPL would be completely absent. If the CPL were generated by helically-ordered SOC of circularly-polarized excitons, magnetic field effects of circular polarization of CPL can then be observed. Therefore, magnetic field effects of circular polarization of CPL provide a powerful experimental method to explore SOC ordering effects in chiral structures.

5.3 Materials and Methods

5.3.1 Materials Synthesis

Synthesis and bulk growth of (S)-MBAPbBr₃ single crystals

The synthesis and crystal growth method of (S)-MBAPbBr₃ crystal was carried out according to that previously reported²⁴³. (S)-MBA (0.6059g, 0.0050 mol) and PbO (1.116 g, 0.0050 mol) were dissolved in 10 ml HBr solution at 85°C under constant stirring. Then, the solution was heated to 100 °C forming a colorless transparent solution. During cooling from 100 °C to 45 °C at a rate of 2 °C /hour, the crystals are harvested at 45 °C.

Synthesis and bulk growth of MAPbBr₃ single crystals

The synthesis and crystal growth method of MAPbBr₃ crystal was carried out according to that previously reported²⁴⁴. One molar solution containing PbBr₂ and MABr was prepared in DMF. The solution was prepared at room temperature. Then the solutions were filtered using PTFE filter with 0.2 μm pore size. Two milliliters of the filtrate were placed in a vial, and the vial was heated in an oil bath to 90 °C at a rate of 1 °C /hour.

Fabrications of 1D-anchoring-3D perovskites thin film

To fabricate the 3D@1D perovskites featuring a controllable ratio of chiral 1D to achiral 3D (4:1) perovskite, precursor solutions were prepared by dissolving the corresponding S-MBAPbBr₃ and MAPbBr₃ crystals in a solvent mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with a ratio of 4:1. Subsequently, crystalline thin films were produced using a spin-coating method²⁴⁵. Specifically, 100 μ L of the precursor solution, heated to 70 °C, was dispensed onto a substrate preheated to 100 °C. The substrate was then spun at a speed of 3000 rpm for 60 seconds. For the MAPbBr₃ film preparation, an antisolvent, methylbenzene, was applied to the spinning film after 10 seconds to initiate crystal nucleation. Following the spin-coating process, the films were annealed at 75 °C for 10 minutes to enhance their crystallinity.

5.3.2 Characterizations and Measurements

Characterizations

PL in steady and dynamic regimes was measured by the Horiba SPEX Fluorolog 3 spectrometer. The time-resolved photoexcitation source was from a pulsed laser beam (343 nm) generated through a harmonic generator (Ultrafast Systems LLC, third harmonic) with a Pharos laser (Light Conversion, 25 kHz, 1025 nm, 290 fs). CPL was measured by the FLAME-T-XR1-ES spectrometer under circularly polarized detection and excitation selected with right-handedness or left-handedness. The right-handed and left-handed circular polarizations were set by rotating a quarter wave plate with -45° and +45° relative to a linear polarizer. In CPL measurements, samples were excited by a CW laser beam of 375nm.

5.4 Results and Discussions

5.4.1 Basic Characteristics of Chiral-Structured 1D S-MBAPbBr₃ in Nonchiral-Structured 3D MAPbBr₃

Figure 5-1 shows the PL spectra and lifetimes for the crystal containing the chiral-structured 1D S-MBAPbBr₃ and dispersed in the nonchiral 3D MAPbBr₃ matrix at the temperature of 5 K. Essentially, the chiral-structured 1D S-MBAPbBr₃ functions as guests grown in the non-chiral 3D MAPbBr₃ matrix. The chiral-structured 1D S-MBAPbBr₃ gives rise to a broad PL spectrum peaked at 600 nm while the nonchiral 3D MAPbBr₃ matrix exhibits a narrow PL spectrum peaked at 540 nm. The chiral-structured 1D S-MBAPbBr₃ shows a much longer PL lifetime of 1.02 μ s, as compared to the nonchiral 3D MAPbBr₃ matrix with the much shorter PL lifetime of 25 ns. This longer PL lifetime implies that the chiral perovskite 1D S-MBAPbBr₃ possesses a slow electronic transition involved in the PL.

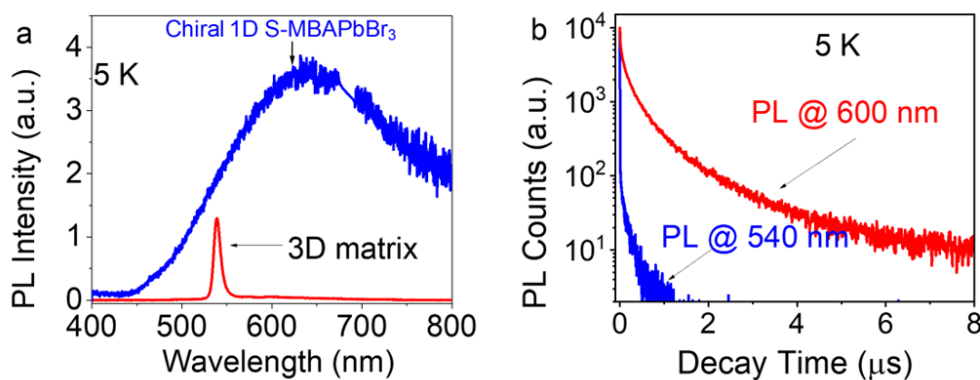


Figure 5-1 (a) PL spectra and (b) lifetime of the 1D with 3D thin film at 5K.

5.4.2 CPL Characteristics in 1D with 3D Crystalline thin film

We can see in **Figure 5-2** that the portion ranging between x nm and x nm of the PL from the chiral perovskite becomes right-handed and left-handed circularly-polarized luminescence (σ^+ and σ^-) at the temperature of 5 K under right-handed and left-handed circularly-polarized photoexcitations (343 nm), respectively. The σ^+ and σ^- CPL are shown with the degree of circular polarizations (DOP) of + 6.9 % and -6.1 %. This phenomenon indicates that there exists both right-handed and left-handed chiral structured perovskites dispersed in the nonchiral 3D MAPbBr₃ matrix. Importantly, circularly-polarized photoexcitations preferably excites chiral structures with the same handedness, leading to handedness selection rule. Essentially, this handedness selection rule reflects that the circularly-polarized laser-beam electrical field vector can selectively polarize the corresponding chiral structures with the same handedness, giving rise to electrically-polarized chiral structures. Here, electrically-polarized chiral structures provide the necessary condition to generate circularly-polarized excitons. When circularly-polarized excitons conserve their circular polarizations within PL lifetime, a CPL can be observed. Notably, the normally observed low DOP implies that the circularly-polarized excitons are largely relaxed their circular polarizations to become randomly-polarized excitons, consequently leading to quite low circular polarization of CPL. However, we should note that chiral structures are inevitably accompanied with structural anisotropy to demonstrate birefringence. This birefringence can often generate quite high circular polarizations of CPL, shown by large DOP or dissymmetry factor g, through dichroism effects, rather than circularly-polarized excitons. This causes a

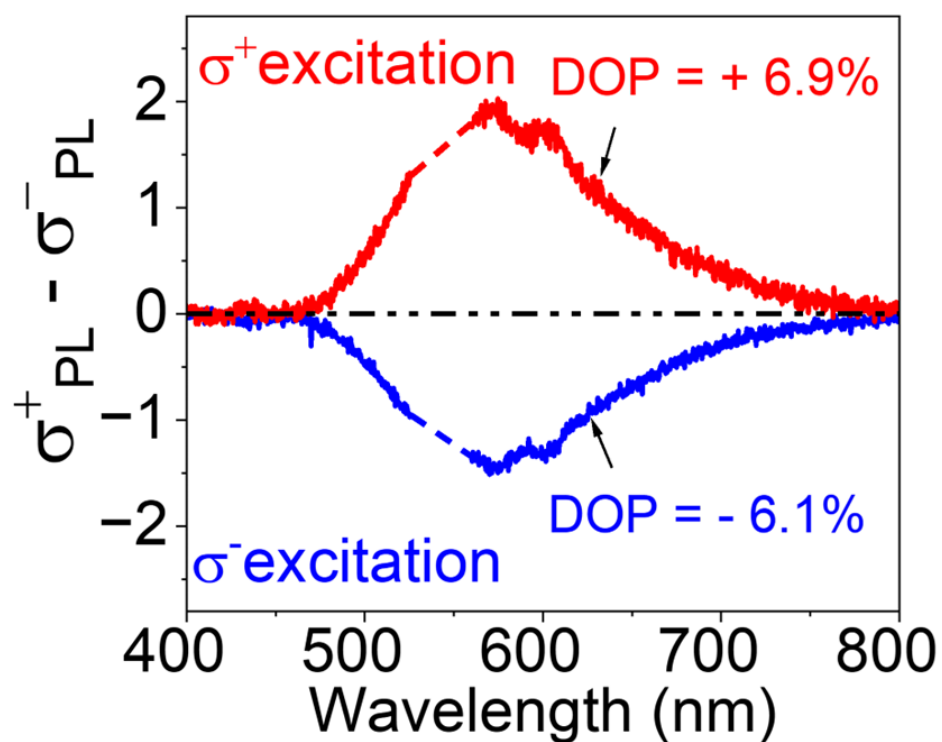


Figure 5-2 CPL characteristics at 5K in 1D with 3D thin film under right-handed (σ^+) circularly polarized photo-excitations and left-handed (σ^-) circularly polarized photo-excitations: Subtracted spectra ($\sigma^+ - \sigma^-$) of chiral 1D thin film measured with right-handed (σ^+) excitation; Subtracted spectra ($\sigma^+ - \sigma^-$) spectra of chiral 1D thin film measured with left-handed (σ^-) excitation.

difficulty to detect circularly-polarized excitons by using CPL measurements.

Experimentally, the birefringence-induced CPL can be minimized by adjusting the excitation geometry of chiral structures. But, it is still challenging to completely remove the birefringence effects from CPL measurements by adjusting excitation geometry.

Here, we use magnetic field effects of circular polarization of CPL as a unique method to explore circularly-polarized excitons based on chiral structured perovskite.

5.4.3 MFE-CPL in 1D with 3D Crystalline thin film

Figure 5-3 illustrates the CPL measured with and without the magnetic field of 0.9 T for the chiral-structured 1D S-MBAPbBr₃ dispersed in nonchiral-structured 3D MAPbBr₃ matrix at the temperature of 5 K. Here, the CPL intensities refer to the values at spectral-peak wavelength. When the σ^+ excitation (375 nm laser beam) generates a stronger σ^+ CPL and weaker σ^- CPL components to enable a net σ^+ CPL output, applying the magnetic field of 0.9 T increases the σ^+ CPL intensity while unchanging the σ^- CPL intensity (**Figure 5-3 a and b**). This phenomenon presents clear evidence that an external magnetic field increases the circular polarization degree of σ^+ CPL under σ^+ excitation, leading to magnetic field effects of σ^+ CPL when the right-handed chiral structures are excited by σ^+ excitation. The calculation based on the CPL spectra indicates that the magnetic field of 0.9 T increases the DOP of σ^+ CPL from +6.9 % to +7.5 % under σ^+ excitation. This implies that the σ^+ CPL from the right-handed chiral structures shows magnetic field effects with the amplitude of 8.7 %. Similarly, when the σ^- excitation (375 nm laser beam) induces stronger σ^- CPL and weaker σ^+ CPL component to develop

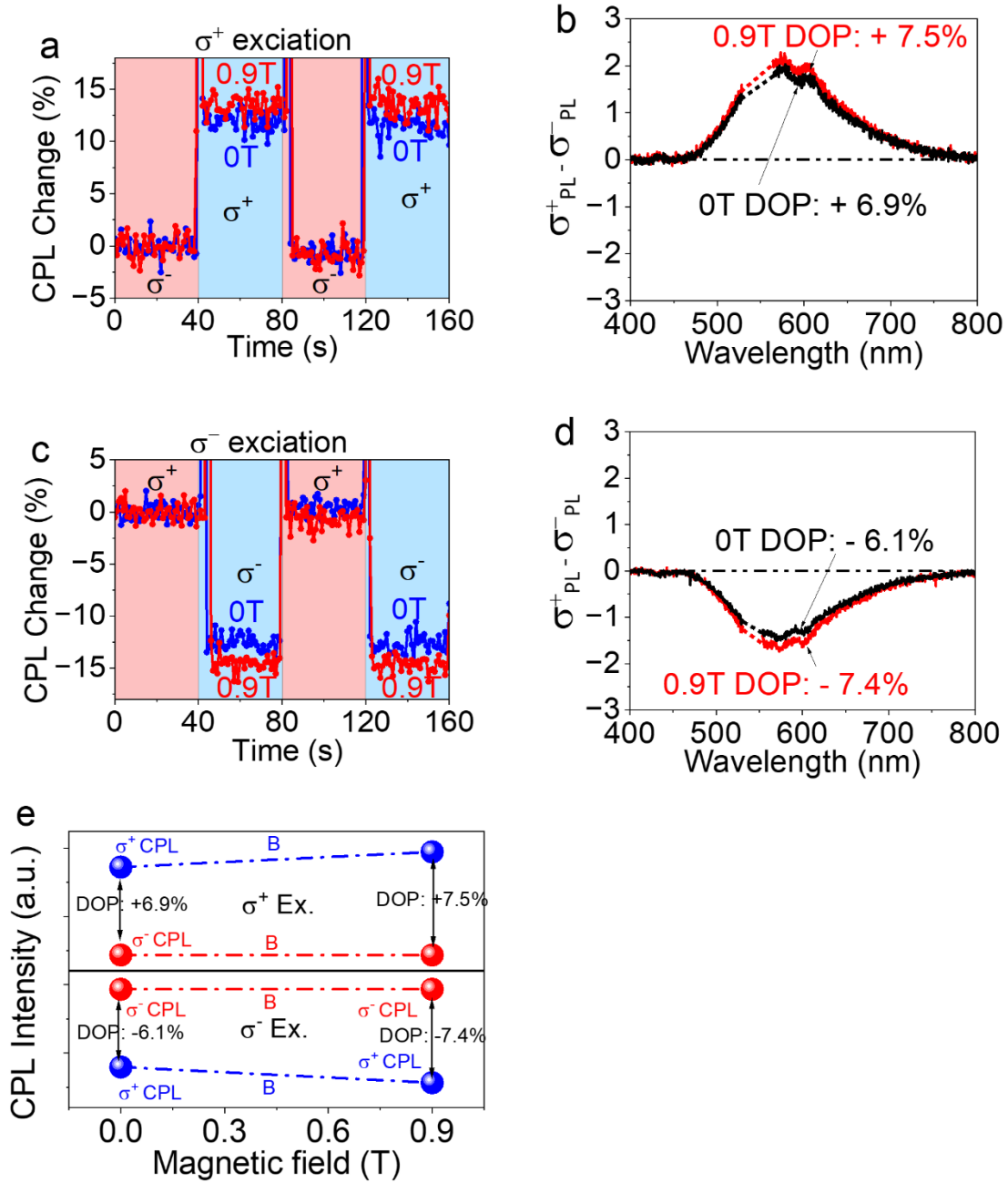


Figure 5-3 MFE-CPL characteristics at 5K in 1D with 3D thin film under (a) right-handed (σ^+) circularly polarized photo-excitations and (c) right-handed (σ^-) circularly polarized photo-excitations under 0T and 0.9T at 600 nm. (b) Subtracted spectra ($\sigma^+ - \sigma^-$) of radical crystal measured with right-handed (σ^+) excitation under 0T and 0.9T; (d) Subtracted spectra ($\sigma^+ - \sigma^-$) spectra of radical crystal measured with left-handed (σ^-) excitation under 0T and 0.9T. e) Magnetic field effects of CPL: the magnetic field increased the DOP value.

a net σ^- CPL output, applying the magnetic field of 0.9 T boosts the σ^- CPL component while leaving the σ^+ CPL intensity unchanged (**Figure 5-3 c and d**). This observation indicates that an external magnetic field can increase the circular polarization degree of σ^- CPL from -6.1 % to -7.4 % when left-handed chiral structures are excited by σ^- excitation. The calculation based on the CPL spectra shows that the σ^- CPL from the left-handed chiral structures demonstrates magnetic field effects with the amplitude of 21.3 % when the left-handed chiral structures are excited by σ^- excitation. Clearly, the CPL from both right-handed and left-handed chiral structures in the 1D S-MBAPbBr₃ are sensitive to external magnetic field, giving rise to magnetic field effects of CPL.

Here, we discuss the critical information revealed by magnetic field effects of CPL. In general, chiral structures can demonstrate CPL through circularly-polarized excitons and dichroism phenomenon due to birefringence effects, leading to two different types of CPL, namely dichroism-based CPL and circularly-polarized excitons-based CPL. The dichroism-induced CPL relies on the phenomenon that incident optical beam becomes two different polarizations due to birefringence effects. And these two different polarizations can often generate a large CPL, leading to dichroism-induced CPL. Since an external magnetic field has negligible effects on the birefringence, the dichroism-based CPL are lacking magnetic field effects. The circularly-polarized excitons-based CPL require that light-emitting excitons form helically-ordered electrical polarizations within chiral structures. With helically-ordered electrical polarizations of excitons, the electrical field vector of emitted light becomes circularly rotating, giving rise to a CPL. We should

note that the **J** excitons carry both orbital and spin momentum in metal halide perovskites.

Because circularly-polarized excitons and dichroism-induced phenomena are possible and impossible to be sensitive magnetic field, magnetic field effects provide unique method to distinguish these two types of CPL.

First, the phenomenon that CPL becomes dependent of magnetic field provides unique evidence that both right-handed and left-handed chiral structures in the 1D S-MBAPbBr₃ are indeed formed with circularly-polarized excitons carrying circularly-polarized orbital momentum, generating circularly-polarized orbital momentum-based CPL distinguished from dichroism-based CPL caused by birefringence effects. Second, CPL are indeed originated from circularly-polarized excitons.

Second, applying the magnetic field of 0.9 T increases the σ^- CPL component from -6.1 % to -7.4 % under σ^- excitation, while unchanging the σ CPL component. Similarly, applying the magnetic field of 0.9 T increases the σ^+ CPL component from +6.9 % to 7.5 % under σ^+ excitation, while leaving the σ^+ CPL component unchanged. Clearly, this phenomenon indicates that applying an external magnetic field can indeed increase the circular polarization for both σ^- CPL generated by σ^- excitation and the σ^+ CPL generated by σ^+ excitation.

5.5 Summary

The application of an external magnetic field significantly influences the Circularly Polarized Luminescence (CPL) characteristics of chiral 1D S-MBAPbBr₃, notably enhancing the degree of circular polarization. This magnetic field effect provides strong

evidence that CPL generation is primarily driven by the formation of circularly polarized excitons rather than merely resulting from birefringence-induced dichroism.

The scientific importance of this finding lies in its validation of the existence of circularly polarized excitons, which inherently carry circularly polarized orbital angular momentum in chiral perovskites. Additionally, it establishes a novel and effective method to differentiate CPL arising from excitonic mechanisms from that induced by birefringent effects.

Future research should focus on expanding this investigation to other chiral materials, exploring how magnetic fields of various intensities and orientations influence CPL.

Further understanding of these mechanisms will provide deeper insights into the fundamental processes underlying chiral luminescence phenomena.

Chapter 6 From Application to Outlook: A Concluding Perspective

Over the past three decades, organic light-emitting diodes (OLEDs) have been successfully commercialized in various display applications, including high-end smartphones and television screens. However, further enhancement of light-emission efficiency remains a core challenge for the continued expansion of their commercial use. Early studies revealed that the internal quantum efficiency (IQE) of conventional OLEDs was theoretically limited to 25%, due to the spin-forbidden nature of triplet exciton radiative transitions. Consequently, much of the research in the past few decades has focused on overcoming this limitation through various strategies, such as spin-orbit coupled fluorescence, thermally activated delayed fluorescence (TADF), triplet-triplet annihilation (TTA), and the hot exciton mechanism involving high-energy intersystem crossing.

In recent years, open-shell radical molecules have emerged as a promising alternative to circumvent the spin-statistical bottleneck. Unlike closed-shell molecules, radicals possess singly occupied molecular orbitals (SOMOs), which lead to the formation of doublet states rather than singlet or triplet states. Importantly, the SOMO $\rightarrow$ SUMO transitions in radicals are spin-allowed, thus enabling efficient radiative emission without the constraints of spin selection rules.

Despite the promising potential of radical-based systems, several fundamental questions regarding their emission mechanisms remain unresolved. We found that emissive excitons can carry both orbital angular momentum (**L**) and spin angular momentum (**S**), giving rise to so-called **J**-excitons, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$. In organic systems without spin-orbit coupling (SOC), excitons are typically in pure spin states (**S** states). However, in

radical-doped crystals, SOC lifts spin degeneracy and induces Rashba-type band structures with orbital angular momentum, effectively converting S-excitons into J-excitons. When circularly polarized light selectively excites the σ^+ or σ^- bands, the resulting recombination of J-excitons leads to the emission of circularly polarized light. This mechanism offers new insight into the emission dynamics in radical systems.

Although a theoretical IQE of 100% is achievable in some organic light emitting systems, like radicals and TADF, the external quantum efficiency (EQE) is often limited to approximately 20% due to non-radiative losses arising from electron–phonon coupling, optical waveguide effects (WGE), and surface plasmon polariton (SPP) effects. To address this challenge, donor–acceptor (D–A) structured organic crystals have been shown to suppress electron–phonon interactions through rational molecular design and crystal engineering, thereby reducing the likelihood of non-radiative transitions. For instance, organic crystalline thin films fabricated via solution-based techniques such as dip-coating have shown the potential to achieve enhanced EQEs.

Moreover, D–A organic crystals also exhibit promising applications in biological sensing and imaging. Their high selectivity in photoluminescence enables sensitive detection of specific biomolecules or ions, while long-lived phosphorescence properties contribute to prolonged observation windows, which are beneficial for real-time monitoring of biological processes.

Our studies have revealed that slow phonon modes in D–A crystals have a profound influence on the lifetime and transition pathways of excited states. When the lattice relaxation time is prolonged, excited states can persist in a quasi-equilibrium lattice

configuration, thus facilitating the formation of long-lived emissive states. Moderately strong electron–phonon coupling enhances radiative transitions by increasing the Franck–Condon factor through vibronic interactions, whereas overly strong coupling leads to exciton self-trapping and increased non-radiative decay. By suppressing high-frequency non-radiative relaxation channels, slow phonon dynamics offer an alternative strategy to enhance luminescence efficiency—distinct from conventional triplet-based storage mechanisms like TADF or phosphorescence. Instead, the slow lattice response effectively stabilizes excitons, mitigating energy loss and promoting radiative decay.

Among various organic and perovskite light-emitting systems, spin-polarized light-emitting diodes (Spin-OLEDs/Spin-LEDs) are particularly notable for their ability to emit circularly polarized light (CPL), making them highly attractive for applications in optical communication, quantum information processing, and encryption (e.g., quantum key distribution).

Recently, the chirality-induced spin selectivity (CISS) effect has provided an alternative approach to realizing circularly polarized excitons in devices without requiring two ferromagnetic electrodes. Studies have shown that even a single chiral-structured transport layer can suffice to generate spin-polarized carriers. For example, a chiral hole-transport layer can inject circularly polarized holes into an achiral emissive layer, while unpolarized electrons are simultaneously injected from the opposite side. The recombination of these carriers leads to the formation of circularly polarized excitons, as evidenced by CP-EL measurements, even in the absence of overall chiral architecture in the emissive layer.

In our work, we have proposed a theoretical framework to describe the formation of circularly polarized excitons in chiral MOFs and chiral organic/inorganic perovskites. In such systems, spin–orbit coupling (SOC) and symmetry breaking jointly induce non-degenerate spin-polarized Rashba band structures. The spin-up and spin-down Rashba bands carry right-handed and left-handed circularly polarized orbital angular momentum, respectively. Due to momentum conservation, these bands can be selectively excited by right- and left-handed circularly polarized photoexcitation.

This mechanism not only provides a fundamental understanding of how spin-polarized excitons are formed and controlled through chiral structural design but also establishes a solid theoretical basis for the development of spin-selective light-emitting devices. These insights are expected to play a critical role in the advancement of next-generation spin-polarized emitters, spin-injection devices, and quantum optoelectronic components.

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Appendix

List of Publications

1. **Yipeng Tang**, Heejae Kim, Kwang - Sup Lee, Dong Ryeol Whang, Tae - Dong Kim, Jong Keum, Prem Prabhakaran, and Bin Hu. "Abnormal Slow Phonon Dynamics Toward Prolonging Excited States Dynamics Enabled by Crystalline - Assembling Donor - Acceptor Molecules." *Advanced Materials* (2025): 2416873.
2. Liu L, **Yipeng Tang (co-first author)**, Ma Y, Hu B. Spin - Orbital Ordering Effects of Light Emission in Organic-Inorganic Hybrid Metal Halide Perovskites. *Advanced Materials*. 2024:2411913.
3. **Yipeng Tang**, Bogdan Dryzhakov, Ryota Matsuoka, Tetsuro Kusamoto*, Bin Hu*, Spin Circularly Polarized Luminescence from Crystalline Doublet States in Radicals-Doped Crystals; To be submitted.
4. **Yipeng Tang**, Kazuya Nakashima, Bogdan Dryzhakov, Rie Suizu, Kunio Awaga*, Bin Hu*, Spin-Orbital Coupling-Accelerated Light-Emitting Transitions in Chiral-Structured Metal-Organic Frameworks; To be submitted.
5. **Yipeng Tang**, Bin Hu*, Probing spin-orbital coupling ordering effects in chiral perovskite crystals based on magnetic field effects of circularly polarized photoluminescence: In preparation.
6. Lin, Chun - Yen, Chen - Han Lu, Kai - Hua Kuo, Miaosheng Wang, **Yipeng Tang**, Yixuan Dou, Bin Hu*, Chung - Chih Wu*, and Ken - Tsung Wong*. "Highly Efficient Blue Thermally Activated Delayed Fluorescence Emitters with

- a Triphenylamine - Based Macrocyclic Donor." *Advanced Optical Materials* 11, no. 5 (2023): 2202292.
7. Demangeat, Catherine, **Yipeng Tang**, Yixuan Dou, Sherrice Dale, Jakob Cielo, Eunkyong Kim, Ha - Jin Lee, Anthony d'Aléo, Bin Hu*, and André - Jean Attias*. "Necessary and Sufficient Condition for Organic Room - Temperature Phosphorescence from Host - Guest Doped Crystalline Systems." *Advanced Optical Materials* 11, no. 10 (2023): 2300289.
 8. Zhang, Jia, Jiajun Qin, Weidong Cai, **Yipeng Tang**, Huotian Zhang, Tong Wang, Artem Bakulin, Bin Hu*, Xiao - Ke Liu*, and Feng Gao*. "Transport Layer Engineering Toward Lower Threshold for Perovskite Lasers." *Advanced Materials* 35, no. 30 (2023): 2300922.
 9. Yang, Wenqiang, Seung - Hyeon Jo, **Yipeng Tang**, Jumi Park, Su Geun Ji, Seong Ho Cho, Yongseok Hong, Dong-Hyeok Kim, Jinwoo Park, Eojin Yoon, Huanyu Zhou, Seung-Je Woo, Hyeran Kim, Hyung Joong Yun, Yun Seog Lee, Jin Young Kim, Bin Hu, and Tae-Woo Lee* "Overcoming charge confinement in perovskite nanocrystal solar cells." *Advanced Materials* 35, no. 39 (2023): 230
 10. Bogdan Dryzhakov, **Yipeng Tang**, Keum Jong, Haile Ambaye, Jinwoo Kim, Tae-Woo Lee, Valeria Lauter*, Bin Hu* Spin Switchable Optical Phenomena in Rashba Band Structures through Intersystem Crossing in Momentum Space in Solution-Processing 2D-Superlattice Perovskite Film. *Nature Communications* (accepted).

Vita

Yipeng Tang was born in Changchun City, Jilin Province, China. He received his B.S. in Material Science and Engineering (2015) at Jilin University, China, and received his master's degree in Material Science and Engineering (2020) at Jilin University, China. In August 2021, he joined the Ph.D. program in the Department of Materials Science and Engineering at the University of Tennessee, Knoxville. His doctoral research focuses on the fundamental physics of semiconductors in optoelectronics, utilizing advanced optical, electrical, structural, and magnetic characterization techniques. His dissertation research for a Ph.D. degree is focused on slow phonon dynamics and circularly polarized light-emitting excitons in organic multi-functional materials.