

Clarification of exciton dynamics in long-range exciplex under optical and electrical excitation

ラジャカルナ アナンダ ラジャパクシャ パンディシャ ワサラ ムディヤンセ
ラゲ タリンドゥ プリヤンカラ バンダラ ラジャカルナ

<https://hdl.handle.net/2324/7329460>

出版情報：九州大学，2024，博士（工学），課程博士
バージョン：
権利関係：



2024

Doctor Thesis

Clarification of exciton dynamics in long-range exciplex under optical and electrical excitation

Rajakaruna Ananda Rajapaksha Panditha Wasala
Mudiyanselage Tharindu Priyankara Bandara Rajakaruna

Department of Applied Chemistry
Graduate School of Engineering
Kyushu University

2024.07.01

Table of Contents

Chapter 1. Introduction

1.1.	An overview of organic semiconductors.....	2
1.2.	An overview of OLEDs	3
1.3.	Excited states in organic semiconductors	4
1.3.1.	Singlet state and Triplet state	4
1.3.2.	Singlet-triplet energy gap (ΔE_{ST})	6
1.3.3.	Local excited state and charge transfer excited state	6
1.3.4.	Intersystem and reverse intersystem crossing	7
1.4.	Singlet-Triplet Utilization Mechanisms	7
1.4.1.	Phosphorescence	8
1.4.2.	Triplet-triplet utilization (TTU)	9
1.4.3.	Thermally activated delayed fluorescence (TADF)	9
1.5.	Exciplex	10
1.5.1.	Conventional exciplex.....	10
1.5.2.	Long-range exciplex	11
1.6.	OLEDs	12
1.6.1.	Principle of operation.....	12
1.6.2.	Exciplex OLEDs	13
1.7.	Motivation and purpose of this thesis	14

Chapter 2. Unveiled Exciplex Exciton Dynamics: Dual-Excitation of Donor and Acceptor Layers

2.1.	Introduction.....	19
2.2.	Experimental Section	21
2.2.1.	Materials and optical characterization of thin films.....	21
2.2.2.	Fabrication and characterization of OLEDs.....	22
2.2.3.	Photocurrent measurement.....	22

2.2.4.	Displacement current measurement	22
2.3.	Results and Discussion	23
2.3.1.	Fundamental exciplex formation characteristics between TCTA and PO-T2T.....	23
2.3.2.	Unique photophysical characteristics of D/S (dual spacer)/A configuration	27
2.3.3.	Verification of unique exciplex formation from device characteristics	32
2.4.	Conclusion	37
Chapter 3. Distance-Dependent Exciplex Exciton Dynamics in Donor/Spacer/Acceptor Layers		
3.1.	Introduction.....	39
3.2.	Experimental Section	40
3.3.	Results and Discussion	40
3.4.	Conclusion	49
Chapter 4. Summary and Outlook		
4.1.	Summary.....	52
4.2.	Future perspectives	55
References.....		58
List of Acronyms		63
List of Publication.....		65
Acknowledgment.....		66

Chapter 1

Introduction

1.1. An overview of organic semiconductors

The valence band (VB) and conduction band (CB) are the two energy bands that conventional inorganic materials exhibit for the outermost electrons. Inorganic materials are categorized as conductors, semiconductors, and insulators based on the gap between these bands.^{1,2} When the VB and CB overlap to produce a continuous band, a conductor is formed. The Fermi level is located inside an insulator's band gap, which is more than 5 eV. The Fermi level in inorganic semiconductors is located within a small band gap

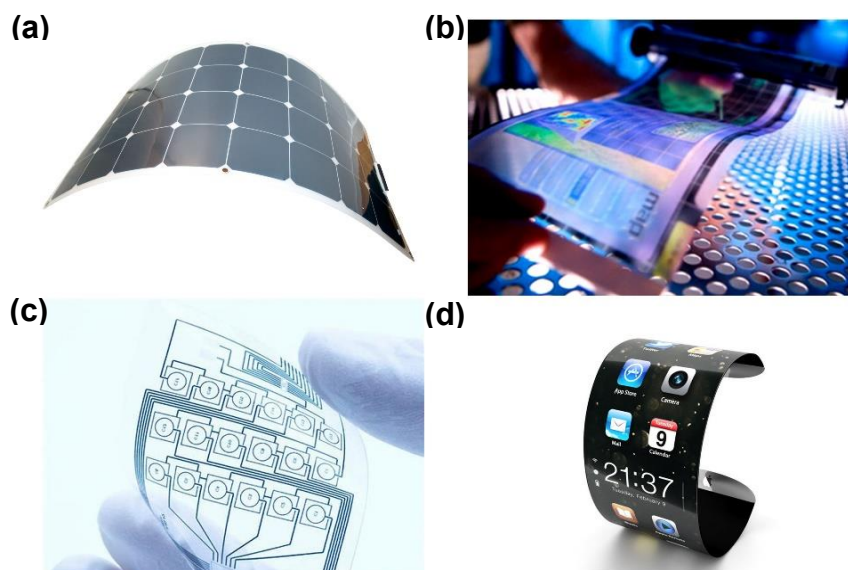


Figure 1.1. Several application fields of organic semiconductor-based devices. (a) Organic solar cells from www.happyyachting.com/sunbeam-system-solpanel-sp50-flush-1 (b) Flexible OLEDs from www.firstpost.com/tag/flexible-display (c) Flexible organic electronic circuit from <https://cordis.europa.eu/article/id/422061> (d) SAMSUNG flexible watch from www.raqwe.com/samsung-patented-flexible-hours/

(less than 4 eV). Conversely, this valence-conduction band gap is mimicked by organic semiconductors.³ Organic molecules contain the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). These MOs function in a way that is comparable to that of the CB and VB, respectively. Because electrons can be injected into or extracted from these MOs, charges can hop between organic molecules.^{4,5} During charge transport in organic

semiconductors, two different processes usually take place, often in opposition to one another. In specific, when electrons enter and exit LUMO levels, a material that is compatible with this mechanism is classified as an n-type semiconductor. In contrast, when electrons hop between the HOMO levels, it produces a positive-charge quasi-particle called a "hole." A semiconductor that prefers hole transportation is referred to as a p-type semiconductor. Nonetheless, in theory, any organic molecule should be able to transfer both electrons and holes, making it an intrinsic semiconductor.^{6,7}

Comparing organic semiconductors to inorganic-based semiconductors provides several noteworthy benefits. Organic semiconductors have relatively low sublimation temperatures since they lack

metal or ionic bonding, making them advantageous for potential low-cost film fabrication methods with low-temperature processes.⁸ Furthermore, even for large polymer chains, device manufacture based on solution methods is possible, significantly lowering costs.⁹ Additionally, a wide range of organic molecules can be designed and synthesized to meet the specifications of each semiconducting device, thanks to the semiconducting feature based on the conjugated π -system.¹⁰ Among all the applications of organic semiconductors, organic light emitting diodes (OLEDs) are one of the most widely used and currently dominate the flat panel display commercial industry systematically.

1.2. An overview of OLEDs

OLED technology has rapidly expanded dominance in the display market, replacing technologies like cathode ray tubes (CRTs) and liquid crystal displays (LCDs). These advanced displays are now widely manufactured for diverse applications such as wearable technologies, lighting, automotive, and medical displays, representing a market valued in the hundreds of millions. Continuous research in both academic and industrial sectors focuses on developing cost-effective, efficient, and dependable materials to improve OLED products.^{9,10}

Phosphorescent emitters, which are used in consumer OLED technologies today, have exceptional efficiency, they produce more than 20% external quantum efficiency (EQE) and more than 100 lumens per watt of power efficiency.^{11,12} As a result, they can compete with the best light-emitting diodes (LEDs) on the market. However, the photochemical instability of blue emitters is a serious drawback. Blue phosphorescent emitters usually fall short of reaching 1,000 hours, while red and green

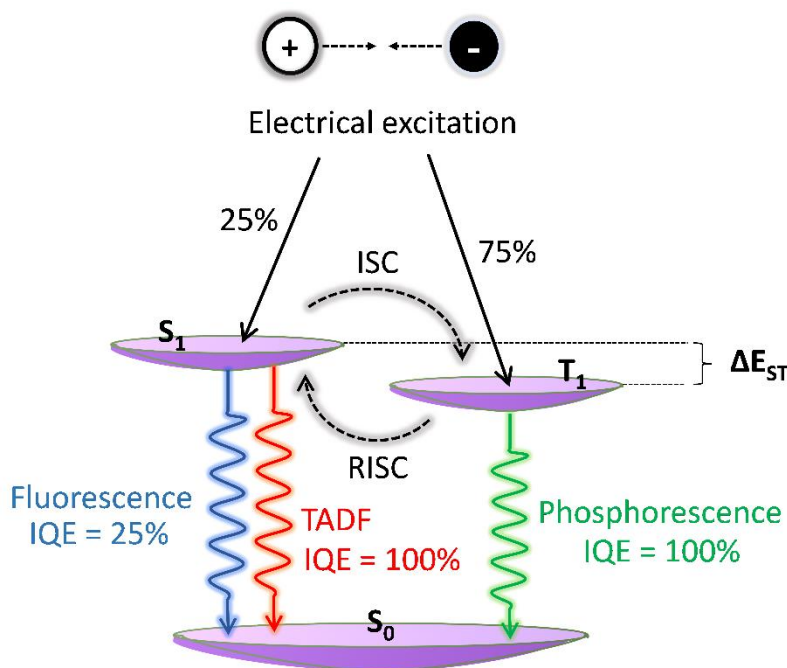


Figure 1.2. Light generation processes in fluorescence, phosphorescence, and thermally activated delayed fluorescence (TADF)-based OLEDs.

emitters have lifetimes far above the 10,000-hour industry requirement. This constraint affects how long screens made entirely of this technology last overall.¹³ To address this challenge, modern OLED displays employ a conventional fluorescent emitter for the blue component. Unfortunately, because there is no active triplet-utilizing mechanism, this choice reduces the overall efficiency of the resultant device.¹⁴

Researchers have just discovered a novel technique using thermally activated delayed fluorescence (TADF) to produce incredibly effective emitters.¹⁴ This method aims to combine the stability often associated with fluorescence emitters with the high efficiency of phosphorescent emitters (Fig. 1.2). TADF emitters are generally categorized into two groups: intramolecular and intermolecular.^{15,16} Compared to their intramolecular counterparts, TADF exciplexes have received less attention as possible emitters. Exciplexes were initially believed to be unadjustable for improved OLED performance, apart from the donor (D) and acceptor (A) materials selected at the beginning. However, research into slightly modified intramolecular TADF materials using D-A structures has since seen considerable growth.^{17,18}

1.3. Excited states in organic semiconductors

1.3.1. Singlet state and Triplet state

The electron's quantum state dictates the exciton's energy and multiplicity. This transition results in the electron being excited to the LUMO, leaving behind a positively charged hole in the HOMO. The interaction between this hole and the excited electron forms a quasiparticle known as an exciton. An exciton is a quasiparticle that is created when this hole interacts with the excited electron.¹⁹

The energy and multiplicity of the exciton are determined by the quantum state of the electron. Four quantum numbers are typically used to describe an atomic electron state: The electron's primary energy level is denoted by the principal quantum number (**n**), its orbital shape is defined by the angular momentum quantum number (**l**), its 3D orbital orientations are characterized by the magnetic quantum number (**ml**), and its angular momentum is described by the spin quantum number (**s**). The same array of quantum numbers cannot be shared by two electrons, according to Pauli's exclusion principle. Consequently, each orbital (**n, l, ml**) can host a maximum of two electrons, each with opposite spins (+1/2 ($\uparrow$ or α) or -1/2 ($\downarrow$ or β)).

The total spin angular momentum of a molecule's electrons determines its spin state. The net spin contribution to the system is zero when electrons fill orbitals in pairs with opposite spins, such as doubly filled orbitals.²⁰ Therefore, when describing an excited state configuration, it suffices to consider only the unpaired electrons, which are typically the highest energy electrons in the system.

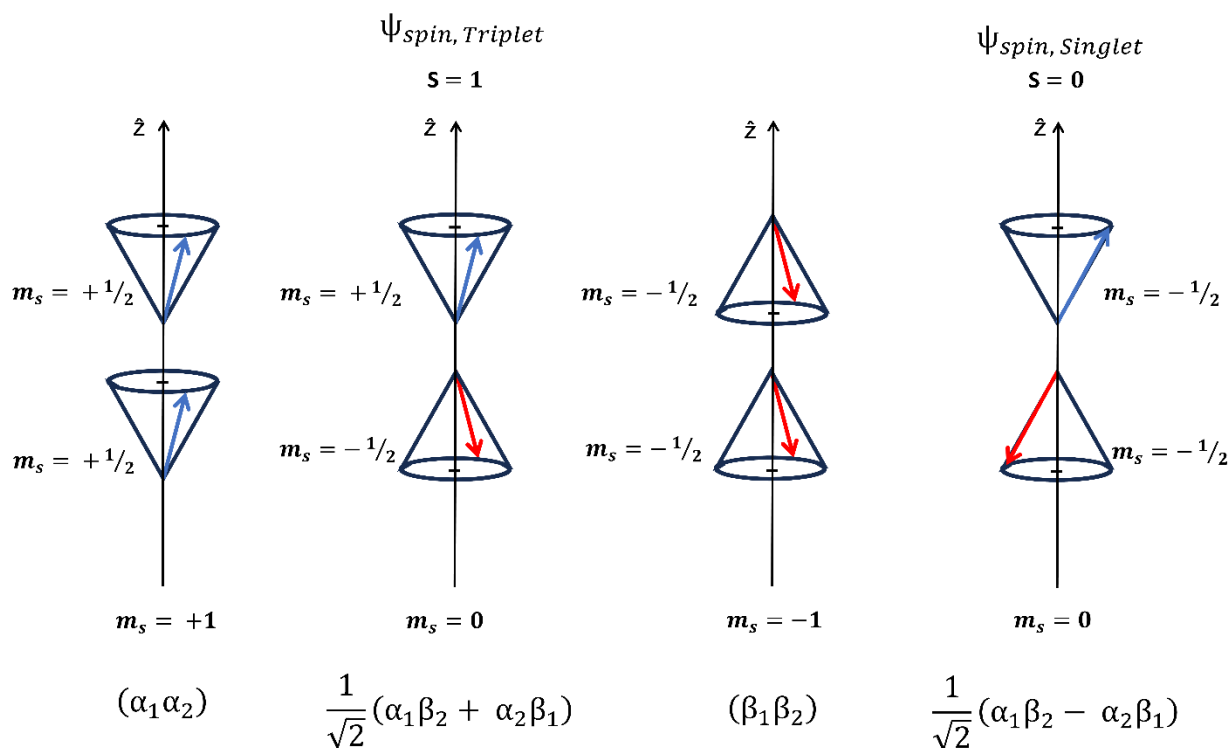


Figure 1.3. Schematic diagram of two electron system forming singlet and triplet states.

In a molecule's singlet or triplet excited state, the overall spin (S) can be either 0 or 1. This is determined by the alignment of the electron in the Lowest Unoccupied Molecular Orbital (LUMO) and the remaining electron in the Highest Occupied Molecular Orbital (HOMO), whether they are antiparallel or parallel. In the singlet state, these electrons are antiparallel, producing two electrons with opposing spins. For a given S , the number of possible values for the m_s , which describes the angular momentum projection, is $2S + 1$. These values array from $-S$ to $+S$ in increments of one. When $S = 0$, there is only one possible value of m_s , which is 0.²⁰ In the singlet state, two electrons have antiparallel spins, causing their motion around an axis to be facing opposing directions, neutralizing one another. This results in an anti-symmetric spin wavefunction. On the other hand, the triplet state comprises three equally energetic states where the spins of the two interacting electrons are aligned in all three possible combinations, leading to symmetric spin wavefunctions. In the triplet state, the m_s can take on the values -1, 0, and 1 (**Fig. 1.3**).

Conversely, an organic molecule's ground state typically aligns with a singlet state according to Pauli's exclusion principle.^{20,21}

1.3.2. Singlet-triplet energy gap (ΔE_{ST})

The singlet and triplet states exhibit distinct energy levels in systems that are more complicated than a hydrogen atom. The energy gap between these states is twofold in the exchange energy (J), as expressed in **Eq. 1.1**. This exchange energy represents the energy required to flip the spins of the two electrons to transition between these states.²²

$$J = \iint \Phi(1)\psi(2) \left(\frac{e^2}{r_1-r_2} \right) \Phi(2)\psi(1) dr_1 dr_2 \quad (1.1)$$

where Φ and ψ represent the wavefunctions of HOMO and LUMO; r_1 and r_2 are the electron coordinates, and e is the charge of an electron (1.602×10^{-19} C).

The overlap of electronic wavefunctions in molecular systems gives rise to the exchange interaction, which is crucial for TADF emitters. This overlap directly affects $2J = \Delta E_{ST}$,²² the energy gap between the singlet and triplet states. Significant overlap between the wavefunctions of the electrons in the LUMO and HOMO leads to a larger exchange interaction and, consequently, a large ΔE_{ST} (usually 0.7–1.0 eV). Since TADF emitters aim for an ΔE_{ST} as insignificant as possible, this large ΔE_{ST} is not advantageous.²³ Conversely, exciplexes benefit from having LUMO and HOMO levels on distinct molecules, where there is essentially no integral overlap of wavefunctions. Exciplexes have an advantage over other materials when it comes to satisfying the energy level alignment requirements for effective TADF emission.

1.3.3. Local excited state and charge transfer excited state

Minimizing the wavefunction overlap between the LUMO and the HOMO is crucial for achieving a small ΔE_{ST} gap that is advantageous for TADF. Separating the HOMO and LUMO spatially by positioning them on distinct parts of a bigger molecule is one such approach. This approach often results in intramolecular charge transfer (CT) states,²³ where there is significant energy separation between the HOMO and LUMO orbitals within the same molecule. Alternatively, intermolecular CT states, known as 'Exciplex' states²⁴, in which HOMO and LUMO are localized on separate molecules, can produce a similar effect. Locally Excited (LE) states, on the other hand, involve the whole molecule and usually show significant overlap between the HOMO and LUMO orbitals. **Equation 1.2** illustrates how the contributions from both LE and CT states can be integrated to explain the wave function of any electronic state.

$$\psi = c_1\psi(X_1^-X_2^+) + c_2\psi(X_1^+X_2^-) + c_3\psi(X_1^*X_2) + c_4\psi(X_1X_2^*) + c_0\psi(X_1X_2) \quad (1.2)$$

In the context of molecular interactions, X_1 and X_2 represent the two molecules involved. The superscripts (+) and (-) designate molecules that are positively and negatively charged, respectively. The *

signifies the localization of an excited electron, resulting in an excited state. In **Eq 1.2**, the initial two terms describe the influence of CT characteristics on the wave function, the subsequent two terms relate to the LE characteristics of the wave function, and the last term relates to the ground state. Notably, a stronger LE character leads to a more significant oscillator strength. LE states tend to decay rapidly through radiative pathways due to their larger ΔE_{ST} , which means that when it comes to utilizing triplet states, they are less important than CT. Conversely, CT excited states exhibit a small overlap with the ground state compared to LE, resulting in comparatively slower emission rates. However, they are highly effective in utilizing triplet states.^{23,24}

1.3.4. Intersystem and reverse intersystem crossing

Intersystem crossing (ISC) and reverse intersystem crossing (RISC) are two methods that an excited state might use to change its total spin. These processes are theoretically forbidden but occur when singlet and triplet states mix. The singlet and triplet states must mix in order for ISC and RISC to occur, allowing a partial allowable spin-flip from one state to the other. In the absence of active ISC mechanisms in the simplest theoretical model, molecules cannot transition spontaneously between singlet and triplet states. However, active mixing mechanisms enable singlet and triplet states to combine where their potential energy surfaces overlap, typically at a critical nuclear coordinate where the J value becomes negligible.²² Vibronic coupling (VC) and spin-orbit coupling (SOC) are the predominant mechanisms responsible for state mixing in OLED emitter materials. Since the intensity of SOC increases with the atomic number (Z) to the fourth power, heavy elements like Ir or Pt are common in phosphorescent materials. The ΔE_{ST} gap is a critical factor for VC and is responsible for the rise of RISC, or TADF.²⁵

1.4. Singlet-Triplet Utilization Mechanisms

Under electrical excitation, triplet states are more commonly populated (3 times more) than singlet states, despite the optical selection rules that normally prevent the direct transition from the singlet ground state during photoexcitation. However, this restriction does not apply when excitons are generated through electrical means.

Under electrical excitation, triplet states occur three times more frequently than singlet states, even though these states are typically not optically accessible due to optical selection rules that prevent the electron from transitioning out of its singlet ground state upon photoexcitation. However, this limitation does not apply when excitons are generated electrically.^{14,20} In this context, electrons and holes are injected into the organic film, enabling them to interact according to spin statistics. Therefore, for OLED applications, it is important to develop methods that utilize both singlets and triplets for light emission. Three mechanisms have been explored for utilizing singlets and triplets to produce light: phosphorescence, triplet-triplet utilization (TTU), and TADF.^{12,14,26} The photophysical processes of each mechanism are illustrated in **Fig. 1.4**.

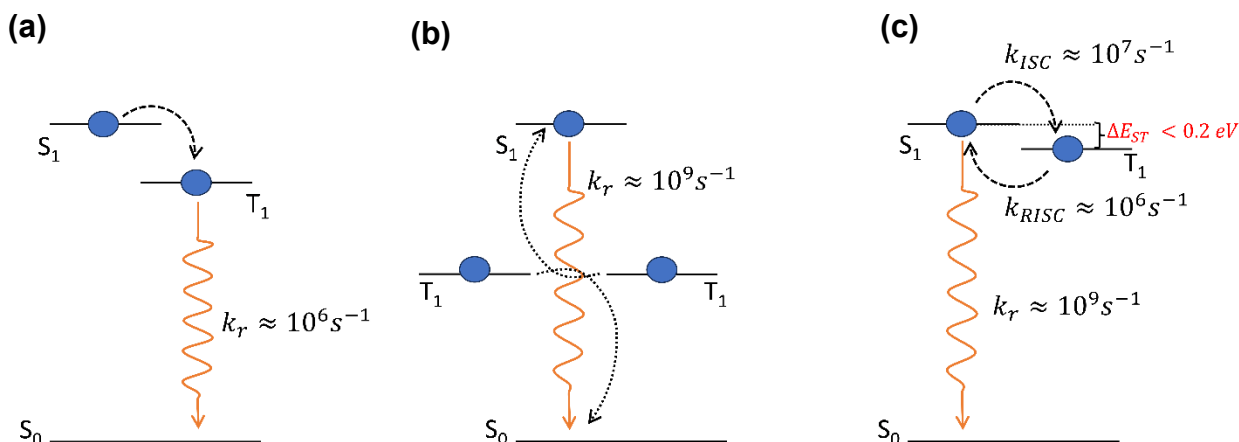


Figure 1.4. Schematic illustration of singlet-triplet utilizing methods used to maximize OLEDs efficiency, (a) Phosphorescence, (b) TTU, and (c) TADF.

1.4.1. Phosphorescence

Phosphorescence is a process where singlet states undergo Intersystem Crossing (ISC) to convert into triplets, which emit light (**Fig. 1.4a**).¹¹ This emission efficiency is improved by incorporating heavy metals into the molecular design of the emitter. These heavy elements exhibit strong SOC, facilitating the necessary spin-flip transition for direct emission from the triplet state (T1).²⁵ As a result, phosphorescence can compete with other non-radiative decay processes, enabling its observation at room temperature. Complexes containing metals such as iridium (Ir) and platinum (Pt) have shown remarkably high photoluminescence quantum yield (PLQY) values, nearing 100% at room temperature, which makes them highly suitable for applications in OLED emitters.¹²

1.4.2. Triplet-triplet utilization (TTU)

TTU is an energy transfer process involving the interaction of two molecules in their triplet excited states. When two excited triplets come together, they form an encounter complex.²⁷ In this complex, one of the triplets is promoted to the radiative singlet excited state (**Fig. 1.4b**).²⁶ This process takes place when the energy of the excited singlet state (E_{S_1}) is lesser than the combined energy of two triplet states ($2E_{T_1}$). The encounter complex involves nine distinct states, each characterized by different spin properties: singlet, triplet, or quintet, depending on the combined spins of the two interacting triplets. The singlet state is particularly desirable for OLED applications because it can lead to an excited singlet state through delayed fluorescence (DF), as described by **Eq. 1.3**. In contrast, the triplet and quintet states act as quenchers because they do not produce an excited singlet state.



1.4.3. Thermally activated delayed fluorescence (TADF)

Effective RISC occurs when the ΔE_{ST} is sufficiently small, often around or less than 0.2 eV (**Fig. 1.4c**).^{14,15} From the beginning, scientists thought that TADF occurred between the charge transfer singlet state (^1CT) and charge transfer triplet state (^3CT). This assumption is challenged by El-Sayed's rule, which emphasizes that a considerable rate of intersystem crossover (k_{ISC}) requires a change in orbital type (ISC is not allowed between states that have the same orbital character).²⁸ Therefore, the locally excited triplet state (^3LE) is essential for enabling the Reverse Internal Conversion (RIC) process (**Eq. 1.4**), which shows a balance between the ^3LE and ^3CT influence with VC. Additionally, RISC is mediated by the ^3LE and ^1CT energy gap. These two processes are pivotal to the TADF mechanism, as later demonstrated by Gibson et al. through simulation. **Eq. 1.5** illustrates how the presence of ^3LE always facilitates the coupling between ^3CT and ^1CT .²⁹

$$k_{IC} = \frac{2\pi}{\hbar} |\langle \psi_{3CT} | \hat{H}_{vib} | \psi_{3LE} \rangle|^2 \delta(E_{3CT} - E_{3LE}) \quad (1.4)$$

$$k_{RISC} = \frac{2\pi}{\hbar} \left| \frac{\langle \psi_{1CT} | \hat{H}_{SOC} | \psi_{3LE} \rangle \langle \psi_{3LE} | \hat{H}_{vib} | \psi_{3CT} \rangle}{E_{3CT} - E_{3LE}} \right|^2 \delta(E_{1CT} - E_{3LE}) \quad (1.5)$$

where k_{RISC} and k_{IC} represent the rates of reverse intersystem crossing and internal conversion, respectively; $\hbar$ denotes the Planck's constant ψ_{1CT} , ψ_{3CT} , ψ_{3LE} are the wavefunctions of the charge transfer singlet, charge transfer triplet, and locally excited triplet states, respectively; $\hat{H}_{vib}$ and $\hat{H}_{SOC}$ are the Hamiltonians for vibronic coupling and spin-orbit coupling; E_{3LE} , E_{1CT} and E_{3CT} represent the electronic energy of the ^3LE , ^1CT , and ^3CT , respectively; $\delta(E_{3CT} - E_{3LE})$ and $\delta(E_{1CT} - E_{3LE})$ are Kronecker deltas.

The degree of the k_{RISC} is also strongly dependent on the ΔE_{ST} (**Eq. 1.6**).³⁰

$$k_{RISC} \propto e^{-\Delta E_{ST}/k_B T} \quad (1.6)$$

Although the previously mentioned works were conducted on intra-molecular TADF systems, exciplexes can also benefit from comparable discoveries on the inter-molecular TADF mechanism.

1.5. Exciplex

1.5.1. Conventional exciplex

An exciplex forms as an excited complex between two different conjugated molecules (monomers) when one of them is in an excited state, even though they do not interact in their ground states. An exciplex is formed by pairing an electron-donating (D) with an accepting (A) molecule. Excitation can occur in either the D* or the A*, causing localized excitation at the interface between D and A. This localized excitation leads to the creation of a CT exciplex state. When either the D or A component is photoexcited, electron transfer (ET) occurs, as illustrated in **Fig. 1.5a**.^{18,31} The existing wavefunction of the exciplex ($\psi[DA]^*$) (**Eq. 1.7**), can be expressed similarly to **Eq. 1.2**, with X_1 representing the D and X_2 representing the A.

$$\psi([DA])^* \approx c_1\psi(D^*A) + c_2\psi(DA^*) + c_3\psi(D^+A^-) + c_0\psi(DA) \quad (1.7)$$

where c_x denotes the coefficients, c_0 : the ground state, c_1 and c_2 : the excited and ground LE states of D and A and c_3 : the ground CT state, respectively.

Previous studies have shown that not every D-A pair necessarily forms an exciplex. Exciplex formation requires a driving force for ET, which is governed by the energy disparity between the HOMO and LUMO levels of both the D and A (**Fig. 1.5b**). The essential condition for exciplex can be summarized as follows: $E_{LUMO}^A - E_{LUMO}^D > 0$ and $E_{HOMO}^A - E_{HOMO}^D > 0$. ET is not energetically favorable if these requirements are not satisfied.^{32,33}

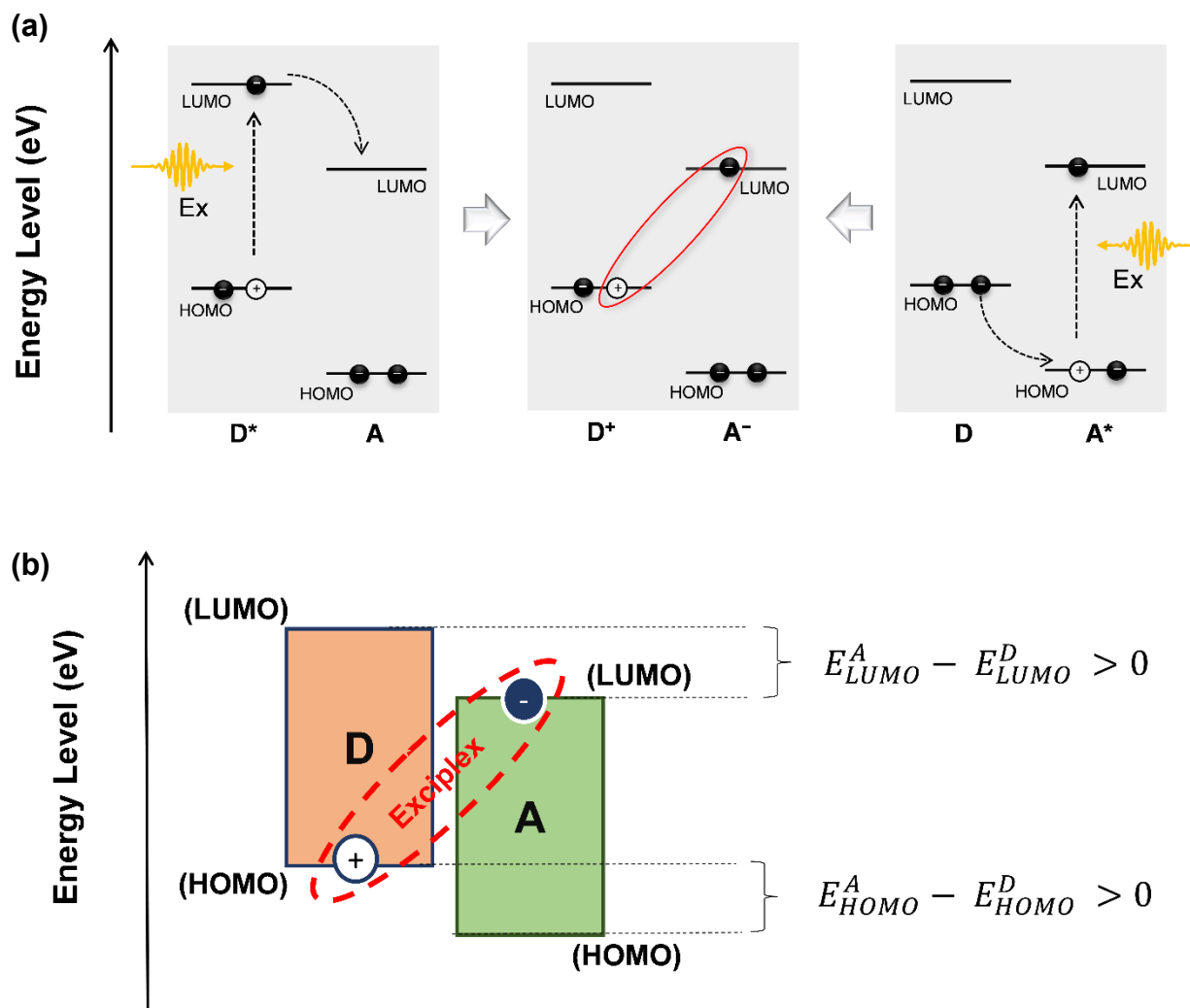


Figure 1.5. (a) Schematic energy diagram exciplex formation through electron transfer in the D or A excitation. (b) Schematic diagram of D and A with appropriate energy levels to efficient ET for exciplex formation.

1.5.2. Long-range exciplex

Generally, exciplexes were thought to occur over short distances only around the D-A interface. However, recent researchers have revealed something remarkable: long-range exciplex emissions.³⁴ These exciplex emissions occur even when the donor and acceptor molecules are separated by substantial distances.^{34,35,36}

At the interface between the electron D and A, long-range exciplex emission also occurs as shown in Fig. 1.6. The maximum theoretical energy of this exciplex can be approximated as the disparity between the LUMO (E_{LUMO}^A) and the HOMO (E_{HOMO}^D) of the A and D respectively.³⁶ Additionally, a significant

contribution to the total exciplex energy arises from the Coulomb D-A pair (Eq. 1.8).³⁷ Therefore, exciplex energy can be expressed as;

$$E_{Exciplex} = E_{LUMO}^A - E_{HOMO}^D - E_C(r) \quad (1.8)$$

Here, as shown in Eq. 1.9, the greater the physical separation between the D-A couple, the more blueshift arises due to the reduction of the Coulomb attraction energy term ($E_C(r)$).³⁷

$$E_{C(r)} = e^2 / (4\pi\epsilon\epsilon_0 r) \quad (1.9)$$

where e is the charge, ϵ is the relative permittivity of organic materials, ϵ_0 is the permittivity of the vacuum, and r is the distance between the charges, respectively.

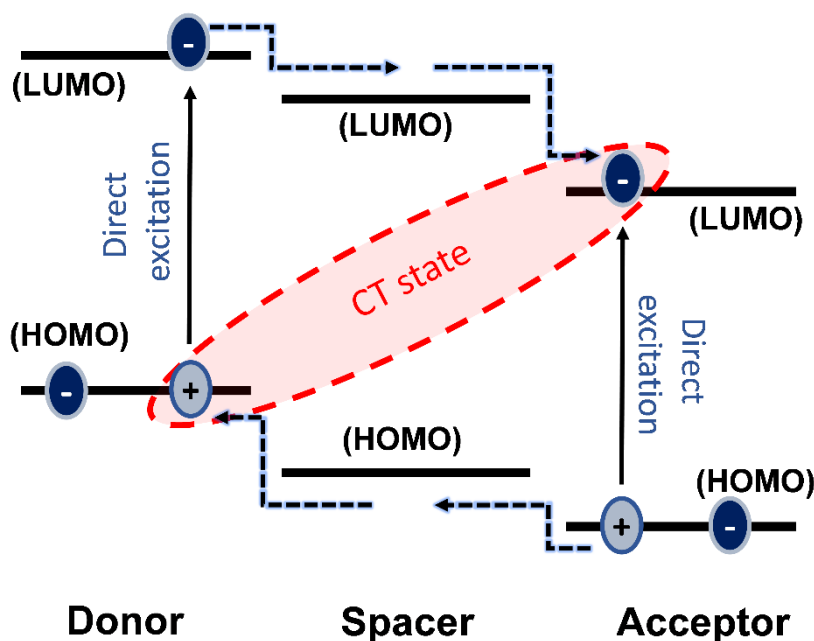


Figure 1.6. Schematic diagram of long-range exciplex system.

1.6. OLEDs

1.6.1. Principle of operation

An OLED functions as an optoelectronic device that emits light through electroluminescence (EL) by combining injected holes and electrons. Unlike traditional LEDs (which rely on inorganic semiconductors), OLEDs use organic molecules.⁹ Early in the 1950s, André Bernanose noticed this phenomena in organic materials,²⁴ and Tang and Van Slyke introduced the first effective multilayer OLED.¹⁰

By recombining electrically injected charge carriers (holes and electrons), these organic semiconductors produce light. Consequently, Frenkel-type excitons with high exciton binding energy (0.5–1.0 eV) radiatively decay in the emissive layer.^{12,14}

Figures 1.7a and b illustrate a typical multilayer OLED structure and the corresponding energy level alignment of its various layers. In this structure, electrons are injected into the device from the cathode, which is typically made of a metal with a low work function(ϕ_C). To enter the electron transport layer (ETL), these electrons must overcome the electron injection barrier (ΔE_e) Conversely, holes are introduced into the device from the anode, typically made of transparent high Φ_A metal oxides. Holes must pass through a hole injection barrier (ΔE_h), to enter the hole transport layer (HTL).³⁸ Minimizing these injection barriers and facilitating efficient carrier transport to the emissive layer (EML) are key objectives of the ETL and HTL. Electrons and holes can recombine in the EML after being injected into the device and generate excitons, which then radiatively decay to produce EL. Any extra processes signify channels for loss of energy during OLED operation.

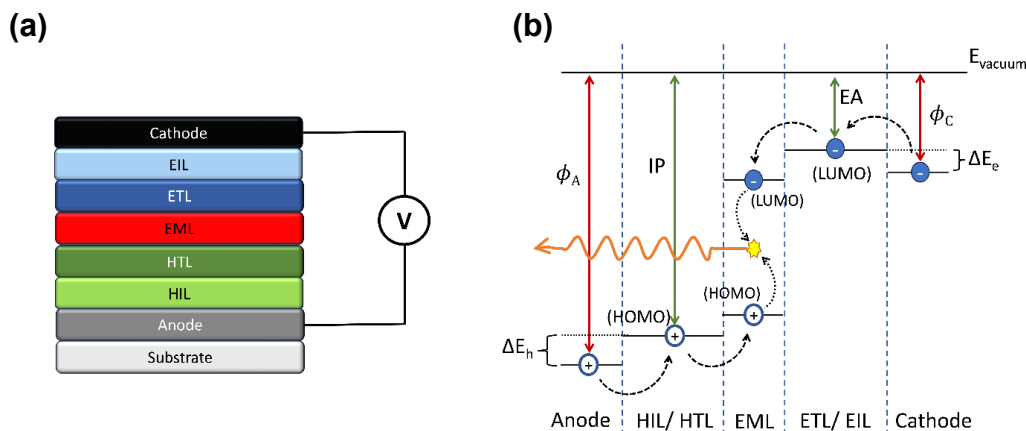


Figure 1.7. (a) Schematic representation of the universal device architecture of OLED. (b) A schematic depicting the standard alignment of energy levels in an OLED.

1.6.2. Exciplex OLEDs

In the earlier stage, interfacial exciplexes were viewed as problematic in OLED structures due to perceived efficiency losses, considered a design flaw. However, they also offer a captivating opportunity: the potential to develop OLEDs using just two organic materials, as an exciplex generally consists of an ETL and an HTL material.³⁹ This opens up the possibility of designing HTL|Exciplex|ETL structures (**Fig.**

1.8). Significantly beneficial practical benefits are provided for commercial scaling up by this simplified and effective framework.

Exciplexes were widely used as hosts even before they were considered viable candidates for the EML because of their excellent exciton confinement capabilities and ability to take advantage of ET to the emitters.⁴⁰ Within an organic substance, the energy gaps between the LUMO and HOMO causes an electron and a hole to separate, resulting in the production of an exciplex. When an electron and hole approach each other closely, they can combine to create an exciplex, which is a bound state with lower energy than that of

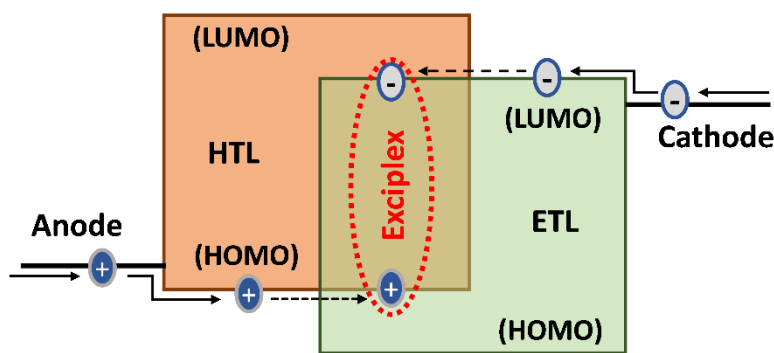


Figure 1.8. Schematic diagram of an OLED architecture with HTL|Exciplex|ETL structure

the individual electron and hole. This unique capability confines excitons effectively. The offsets between HOMO-HOMO and LUMO-LUMO stabilize the exciplex system and prevent current leaking into adjacent layers in the

OLED stack. This localization ensures the confinement of

these excitons for the radiative process inside the EML.¹⁷ Exciplexes as emitters became more prevalent after it was revealed that triplets could be extracted *via* TADF.⁴¹ Dos Santos et al. studied strategies to enhance efficiency in exciplex OLEDs. They underlined the importance of the triplet energy level alignments of the D and A close to the energy of exciplex to increase RISC, achieved by minimizing the ΔE_{ST} .⁴² Furthermore, Kim et al. demonstrated that by minimizing non-radiative emissions, lowering an exciplex OLED's temperature may improve exciplex efficiency.⁴³

1.7. Motivation and purpose of this thesis

This thesis aims to enhance a general understanding of the photophysical and electrical aspects of exciplex and long-range exciplex phenomena. The goal is to leverage this understanding to enhance the potential applications of exciplex-based OLEDs for future generations. Thus far, exciplex researchers have primarily concentrated on optimizing material combinations to enhance performance. Furthermore, the primary objective of long-range exciplex research is to maximize the extent of separation between the D and A. However, the underlying mechanisms governing exciplex systems remain elusive, and there are evident gaps in our understanding of this field of study. Consequently, this work aims to reveal the

underlying phenomena of exciplex behavior by investigating long-range exciplex systems. My ultimate goal is to develop efficient and effective next-generation OLED devices based on this newfound understanding.

In the realm of exciplex formation, interactions between D and A are frequently encountered. Conventionally, exciplexes were thought to arise from excited states like $(D^* \dots A)$ or $(D \dots A^*)$. In **Chapter 2**, I revealed that D and A molecules can be simultaneously excited without undergoing an electron transfer process. This dual stimulation leads to the creation of long-range exciplexes within the D/S/A structure, particularly when bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO)/ 1,4-bis(triphenylsilyl)benzene (UGH2) dual spacer layers are involved. Consequently, I deduce that the exciplex wavefunction is influenced by the component of the $(D^* \dots A^*)$ state.

Chapter 3 delves into an in-depth investigation of the kinetics of the long-range exciplex system. Specifically, I focus on the interaction between the singlet-triplet energy difference (ΔE_{ST}) and activation energy (E_a), considering the spatial separation of the D and A components. This analysis confirms the existence of an optimal separation distance for long-range exciplex systems. This distance ensures optimal energy alignment and overlap. Importantly, this ideal separation is influenced by both the E_a of the exciplex system and the ΔE_{ST} . Fundamentally, it's a delicate balance that maximizes exciplex efficiency.

In the final chapter, I will summarize this study and outline the research roadmap for the future. Based on our work, we anticipate significant implications for practical applications over the long term.

Specifically, radical-pair reactions, crucial for magnetic field sensing, illustrate the potential of quantum technology applications.⁴⁴ These reactions, involving singlet-triplet coherence of electronic spins, are reported to enhance magnetoreception efficiency.⁴⁴ Magnetic interactions, like exchange interaction and electron-nuclear entanglement, play a significant role in promoting this coherence. Optimizing exchange couplings is key to maximizing the quantum advantage of singlet-triplet coherence.⁴⁵ This study illustrates that dual excitation exciplex systems possess unique spectral properties with the possibility of higher radical pairs generation and offer the potential for artificial manipulation of ΔE_{ST} through D-A partial separation mechanisms. This control facilitates rapid interconversion between singlet and triplet states of radical pairs, influencing the spin Hamiltonian. Based on these factors, I believe that the outcome of this work is opening up a new direction to enhance the real-world application of quantum sensing, particularly in geophysics and geomagnetism in the future.

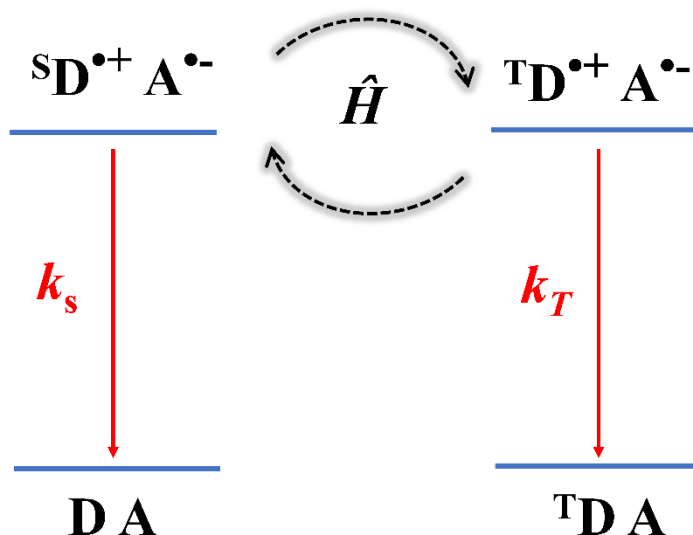


Figure 1.9. Radical-pair reaction dynamics. A charge transfer following the photoexcitation of a donor-acceptor dyad DA produces a singlet state radical-pair $^S\text{D}^{\bullet+} \text{A}^{\bullet-}$, which is coherently converted to the triplet radical pair, $^T\text{D}^{\bullet+} \text{A}^{\bullet-}$, due to magnetic interactions embodied in the spin Hamiltonian $\hat{H}$. Simultaneously, spin-selective charge recombination leads to singlet and triplet neutral products with respective rates k_s and k_T . (Reproduced with permission from ref. 44. Copyright 2020, American Physical Society.)

Free radicals are versatile and reactive intermediates that enable synthesis and applications under mild conditions in both chemical and biological systems. To enhance their utility, developing electron D-A pairs that sustain charge-separated (CS) states with extended lifetimes, avoiding energy loss through complex electron-transfer processes, is crucial.⁴⁶ Prolonging the CS state's duration is essential for generating radical ions *via* electron-transfer reactions, effectively competing against back electron transfer to the ground state.⁴⁶ Recent studies propose that adjusting the distance between donor and acceptor molecules can elongate the CS state's lifetime.⁴⁷ This approach is still demonstrated with intramolecular systems. However, there have been no

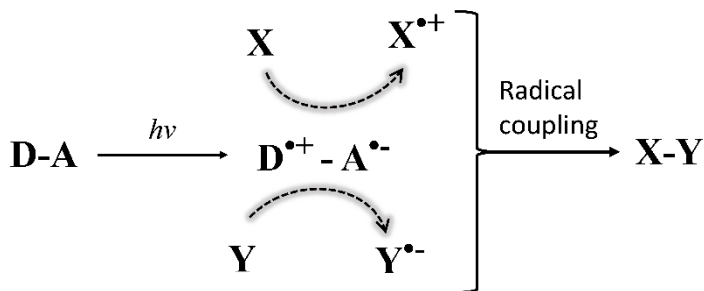


Figure 1.10. Radical coupling reaction of $\text{X}^{\bullet+}$ and $\text{Y}^{\bullet-}$ produced by electron-transfer reactions of substrates (X and Y) with the CS state of an electron donor-acceptor dyad (D-A). (Reproduced with permission from ref. 46. Copyright 2012, John Wiley & Sons, Ltd.)

reports applying this strategy with intermolecular systems. Therefore, exploring this concept with long-range exciplexes, where no charge transfer between D and A, could lead to new approaches for designing

durable CS systems. This advancement holds promise for enhancing the efficiency of technologies such as OPVs, which depend on effective charge separation mechanisms.

Organic long-persistent luminescence (LPL) systems have gained attention for their unique optical properties. Exciplex formation typically involves strong CT states induced by internal electron D and A pairs under external excitation.⁴⁸ This process generates free radical cations and anions that transfer electrons through receptor molecules to form stable CS states. Radicals are crucial for extending the lifetime of CT states essential to LPL, storing energy and releasing it gradually over time.⁴⁹ Thus, radicals significantly influence exciton trapping, charge transfer dynamics, and the efficiency of luminescence. Optimizing radical densities is critical to enhancing these properties for practical applications like glow-in-the-dark materials and optoelectronic devices. Utilizing a long-range exciplex system without D-A charge transfer could potentially increase radical production. Moreover, fine-tuning the separation distance between optimal D and A moieties can control transfer dynamics, further enhancing the LPL process.

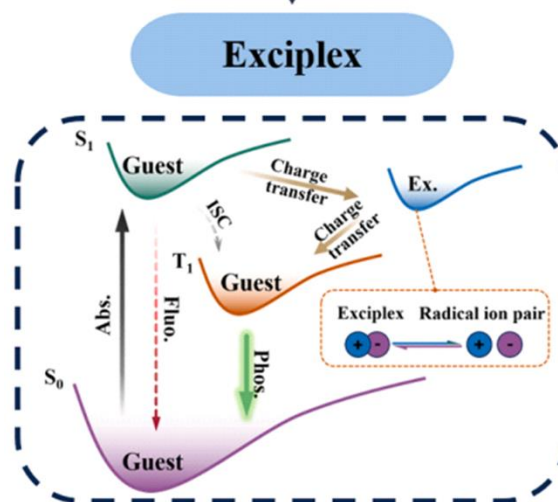


Figure 1.11. Schematic diagram of exciplex architecture involved LPL (Reproduced with permission from ref. 49. Copyright 2024, Elsevier B.V.)

Chapter 2

Unveiled Exciplex Exciton Dynamics: Dual-Excitation of Donor and Acceptor Layers

2.1. Introduction

In recent decades, organic optoelectronic devices—specifically OLEDs and organic photovoltaics (OPVs)—have emphasized the critical role of intramolecular and intermolecular CT processes.^{14,50,51} These processes are led by exciplexes, which play a crucial role in charge recombination and separation. In OLEDs, while exciplexes have been annoyed with the long-term issues of low PLQYs with redshifted emissions, TADF emitters have made significant strides. By exploiting the small ΔE_{ST} within CT states, TADF emitters achieve impressive EQEs exceeding 20%.^{11,52} Additionally, OPVs have demonstrated remarkable power conversion efficiencies (PCEs) of over 18% through well-designed D and A structures.^{53,54}

Exciplexes are often regarded as intermediate-excited CT complexes because of the partial electron transfer that occurs between the photoexcited D and A molecules. Following radiative and nonradiative transitions, the produced CT species form an exciplex and proceed through consecutive charge separation in OPVs.⁵⁵ Additionally, because of the special energy structures that allow them to capture all electrically generated excitons for light emission, exciplexes have been frequently used in OLEDs. The Coulomb interaction between the external electrical bias and the CT state can be the reason for these opposing characteristics of charge separation and recombination. Therefore, regulating the gap between the hole-electron pair has a significant impact on CT behaviors. Looking back at previous exciplex-based OLED studies, it undoubtedly emphasizes improving exciplex systems for advanced OLEDs.^{42,56}

After either D or A molecule is at an excited state (D^* or A^*) by photon absorption, the CT formation of ($D^{\delta+} \dots A^{\delta-}$) occurs, leading to the formation of an intermolecular excited state, exciplex ($D-A$)*.⁵⁷ As shown in **Eq. 2.1**, an exciplex wave function is given by a linear combination of LE, CT, and ground states.⁵⁸

$$\psi([DA]^*) \approx c_3\phi(D^*A) + c_2\phi(DA^*) + c_1\phi(D^+A^-) + c_0\phi(DA) \quad (2.1)$$

where c_x denotes the coefficients, c_0 : the ground state, c_1 : the ground CT state, c_2 and c_3 : the excited and ground LE states of D and A, respectively. Generally, since the ground-state factor, c_0 , on the exciplex state can be neglected, **Eq. 2.1** can be commonly expressed as follows (**Eq. 2.2**),

$$\psi([DA]^*) \approx c_3\phi(D^*A) + c_2\phi(DA^*) + c_1\phi(D^+A^-) \quad (2.2)$$

Here, the energy level of the intermolecular CT state can be expressed as follows (**Eq. 2.3**),

$$E_{CT} = IP_D - EA_A - E_b = \Delta E_{DA} - E_b \quad (2.3)$$

where IP_D is the ionization potential of a D, EA_A is the electron affinity of an A, and E_b is the binding energy of a CT state.^{59,60}

Recently, an advanced concept of the exciplex through a long-range distance has been proposed.³⁴ The long-range electron-hole pair coupling between spatially separated D and A molecules, or D/spacer (S)/A layers, that can occur even at a distance of more than 10 nm was initially described by Nakanotani et al. and Al'Attar et al. later reported on a D/S/A system that was comparable to this one, emphasizing the impact of an external electric field on the carrier separation of interfacial exciplexes.^{34,35,61}

In this chapter, I explored a fascinating phenomenon: the simultaneous dual excitation of D and A molecules, both optically and electrically. This unique approach leads to the creation of a through-space exciplex, without direct electron transfer between them. To demonstrate that, the long-range exciplex system was built by inserting unique S layers with large energy barriers between the adjacent D and A molecules. In detail, tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (**Fig. 2.1a**) and 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) (**Fig. 2.1b**) were employed as a D and an A, respectively, while UGH2 (**Fig. 2.1c**) with a deep HOMO of -7.2 eV and DPEPO (**Fig. 2.1d**) with a shallow LUMO of -2.0 eV were served as the components of the dual-insulating spacer layer.^{62,63} Notably, the large energy gaps between the D/S and S/A layers interface enabled sufficient suppression of the exciton formation through the conventional direct electron transfer between D and A. Instead, a long-range exciplex was formed by simultaneous exciting D and A layers optically and electrically.

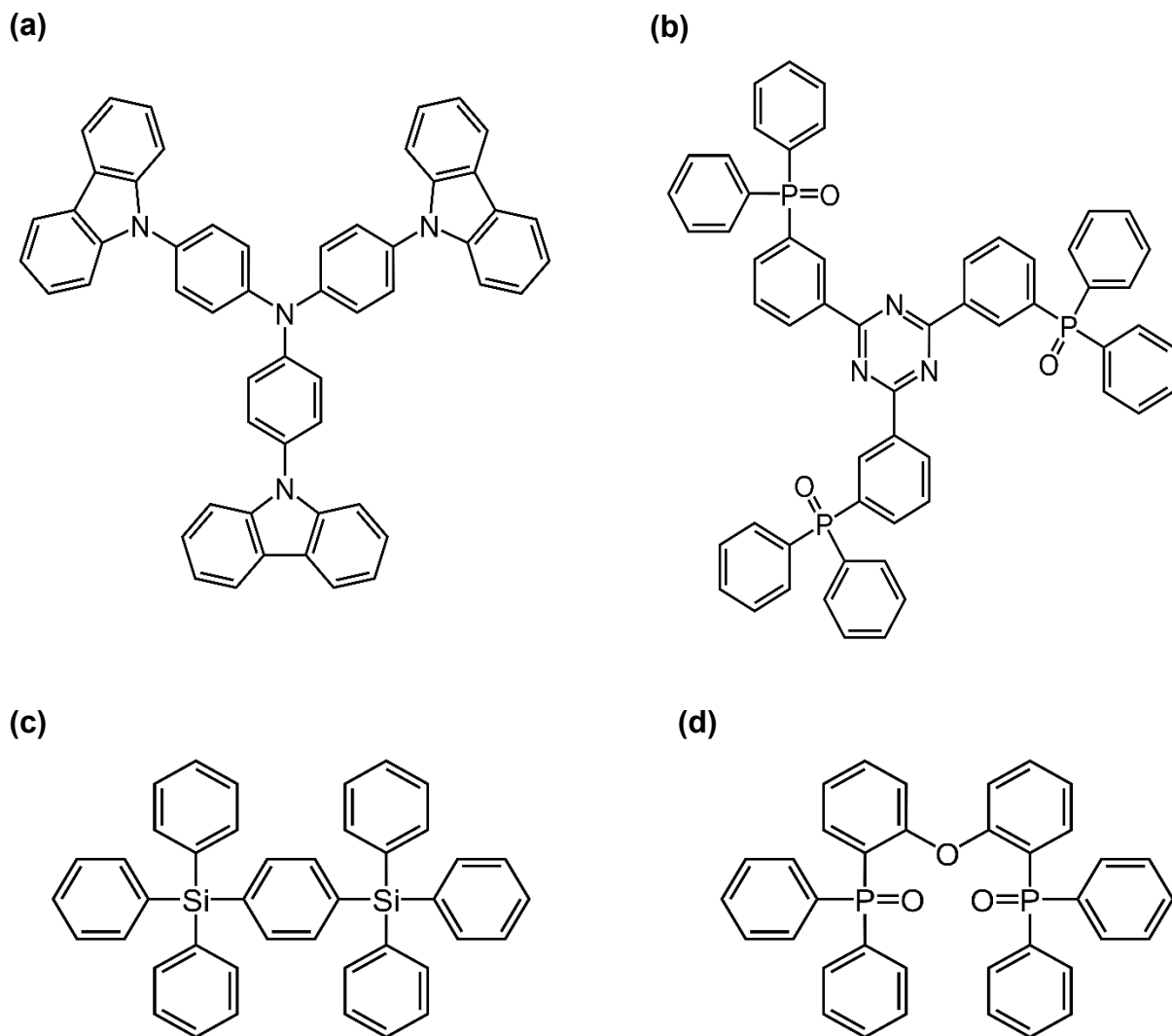


Figure 2.1. The molecular structures of organic materials used in this work (a) TCTA, (b) POT2T, (c) UGH2, and (d) DPEPO.

2.2. Experimental Section

2.2.1. Materials and optical characterization of thin films

All chemicals were purchased from Luminescence Technology Co. Thermal evaporation was used to form organic thin films on clean quartz and silicon substrates at pressures around 2×10^{-4} Pa. The substrates were cleaned with acetone and isopropanol, and then exposed to UV/ozone before use. Optical

characterizations were performed using an ultraviolet–visible–near-infrared spectrometer (Perkin-Elmer LAMDA 950-PKA) and a spectrophotometer (FP-8600, JASCO). PLQY was assessed using an absolute PLQY measurement device (C13534-01, Hamamatsu Photonics). The HOMO levels were determined by photoelectron spectroscopy (Riken Keiki, AC-3).

2.2.2. Fabrication and characterization of OLEDs

I used pre-patterned 100 nm thick tin-doped indium oxide (ITO) as a bottom electrode. After being successively ultrasonically cleaned in acetone, detergent (Semico clean), distilled water, and isopropanol. The substrates were dried using isopropanol vapor before being exposed to UV/ozone to remove impurities that had been adsorbed. At a pressure of around 2×10^{-4} Pa, thermal evaporation was conducted for organic layers and metal electrodes. The devices were promptly encapsulated with glass lids using epoxy glue in a glove box filled with nitrogen ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). Using a source meter (Keysight B2911A, Keysight Technologies) and a luminance meter (CS-2000, Konica Minolta, Japan) at a constant DC current at room temperature, the current-density-voltage-luminance (*J-V-L*) properties of OLEDs were assessed. By evaluating at least three separate times, the present device performance repeatability was verified.

2.2.3. Photocurrent measurement

Photocurrent measurements were performed using a computer-controlled Keithley 2400 source unit under simulated AM1.5G solar illumination from a Xe lamp-based solar simulator (SRO-25 GD, Bunko-Keiki) with a scan rate of 200 mV s^{-1} . The illumination area during the *J-V* measurements was defined at 3.24 mm^2 ($1.8 \times 1.8 \text{ mm}^2$).

2.2.4. Displacement current measurement

DCM was utilized to examine the carrier injection and accumulation characteristics in OLEDs. A voltage with triangular waveform generated by a function generator (WaveStation 2052, Teledyne Lecroy) was applied to OLEDs under a dark condition, and current responses were recorded by an oscilloscope (HDO4054A, Teledyne Lecroy) through voltage/current amplifier (CA5350, NF Corporation). The ramp rate of the triangle waveform was 100 V s^{-1} . All measurements were performed in an ambient atmosphere at room temperature.

2.3. Results and Discussion

2.3.1. Fundamental exciplex formation characteristics between TCTA and PO-T2T

As shown in **Fig. 2.2**, the TCTA layer possesses the HOMO and LUMO energy levels of -5.8 and -2.4 eV, while the PO-T2T layer possesses a much deeper HOMO and LUMO of -6.8 and -3.2 eV, respectively. Due to the distinct energy gaps ($\Delta E_{\text{HOMO}} = 1.0$ eV and $\Delta E_{\text{LUMO}} = 0.8$ eV) between them, the intermolecular interactions can induce electron-hole coupling, forming the CT state under photoexcitation.^{64,65}

The photophysical properties of TCTA and PO-T2T neat films (20 nm), a TCTA/PO-T2T bilayer film (10/10 nm), and a TCTA:PO-T2T co-deposited film with a molar ratio of 1:1 (20 nm) were investigated in order to clarify the exciplex formation between TCTA and PO-

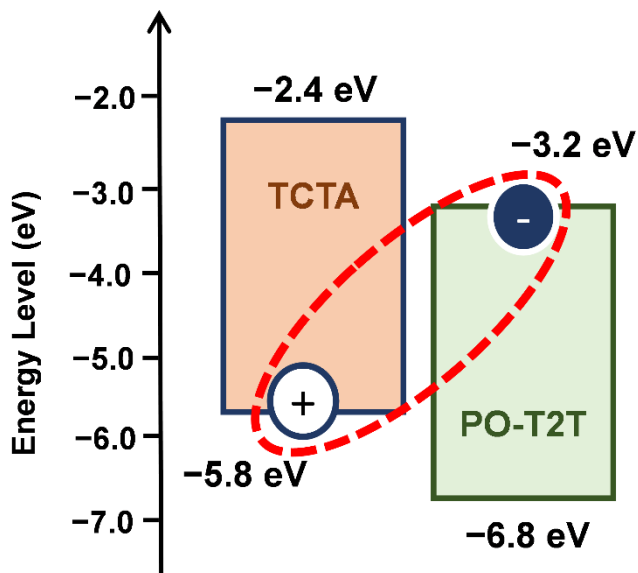


Figure 2.2. Energy level diagram (HOMO and LUMO) of TCTA and PO-T2T layers.

T2T. Four solid-state films' absorption spectra are displayed in **Fig. 2.3a**. TCTA neat film's absorbance peaks were located at around 290 nm and 340 nm. On the other hand, PO-T2T neat film's absorbance peak only appeared at about 280 nm, and any wavelength greater than 320 nm shows very low absorption. The absorption tendency of a TCTA neat film at a wavelength exceeding 300 nm is followed by the TCTA/PO-T2T bilayer and the co-deposited layers in this instance, suggesting that TCTA dominates photon absorption. In the meantime, at a wavelength shorter than 300 nm, the superimposed absorption of both TCTA and PO-T2T was noticed. Hence, at a shorter wavelength of 280 nm, both TCTA and PO-T2T may be adequately excited, whereas mainly TCTA can be excited at around 330 nm. Therefore, by varying the excitation wavelength, the D or A molecules' excitation can be managed. The absence of any other absorption bands in the mixed film other than those of the parent TCTA and PO-T2T films suggests that there is no intermolecular interaction occurring between TCTA and PO-T2T in their ground states.^{66,67}

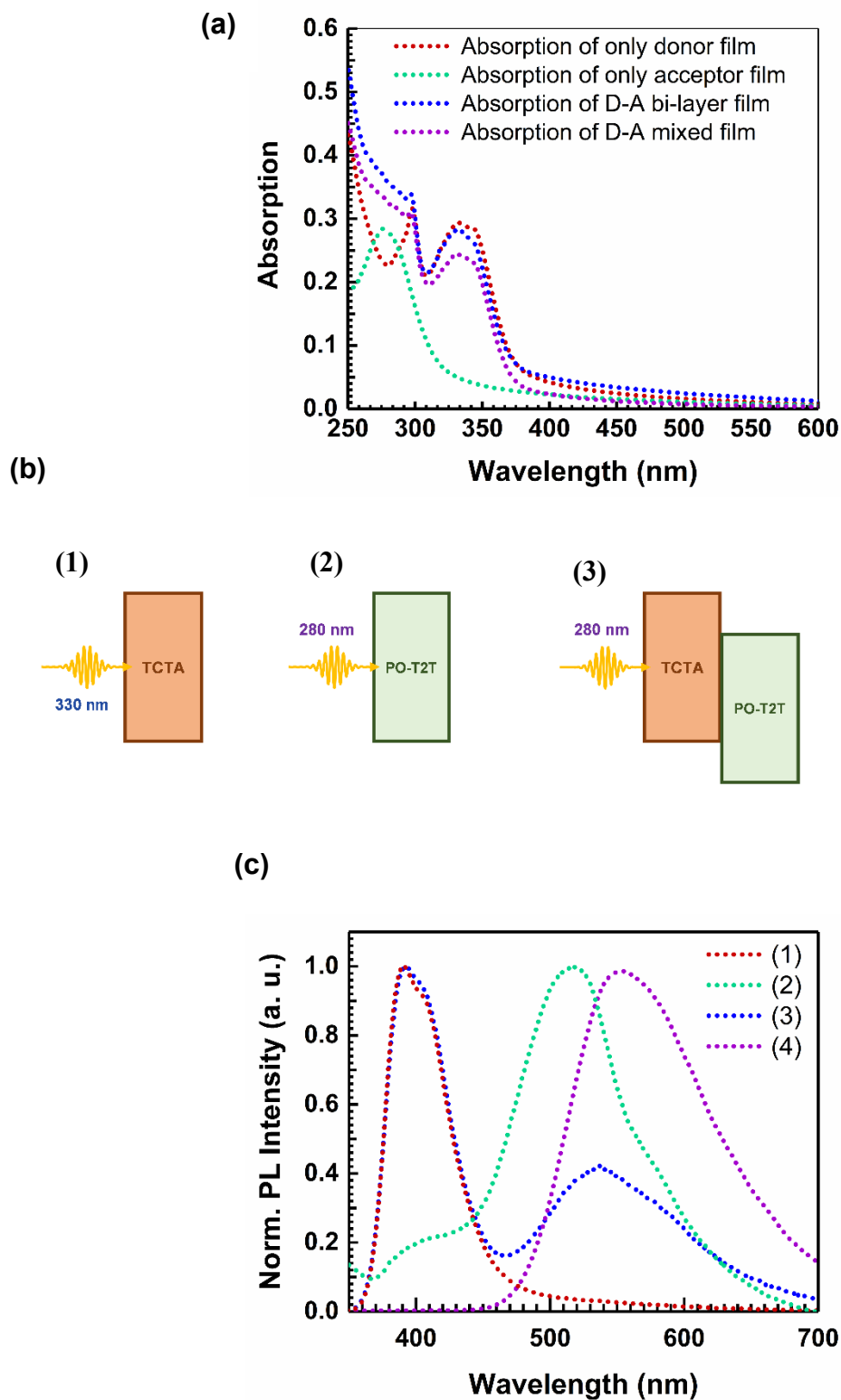


Figure 2.3. (a) UV-vis absorption spectra of four films. (b) Illustration for the excitation wavelengths and directions of (1) TCTA (donor) only, (2) PO-T2T (acceptor) only, (3) TCTA/PO-T2T bilayer, and (4) TCTA: POT2T mixed films. (c) PL spectra of TCTA, PO-T2T, and TCTA/PO-T2T bilayer.

The PL spectra of the four films with excitation modes are shown in **Fig. 2.3b** and **c**. The wavelengths at which these films were excited were 280 nm and 330 nm, respectively. The neat film of TCTA exhibited a maximum PL spectrum (λ_{max}) of 388 nm and a PLQY of $\Phi_{\text{PL}} = 8.9\%$. Conversely, a PO-T2T neat film's PL spectrum, which has an extremely low Φ_{PL} of 1.4%, can only be seen at 280 nm upon excitation. Its λ_{max} is at 510 nm, with a small shoulder peak at about 400 nm. In the mixed film, a broad and single PL spectrum was observed with $\lambda_{\text{max}}=550$ nm and a higher Φ_{PL} of 63%, indicating that the intermolecular interactions between D and A motifs lead to an efficient exciplex formation. In contrast, in the bilayer film, since the exciplexes are only formed at the D/A interface, the PL spectrum was composed of a broad emission with $\lambda_{\text{max}}=530$ nm and a rather stronger component peaked at 388 nm was observed, corresponding to the LE state emission from TCTA. The different molecular arrangements and interactions in the mixed film would be responsible for the variation in λ_{max} between the bilayer and mixed films.⁶⁸

To comprehend the formation process of the exciplexes, excitation wavelength and excitation direction-dependencies of PL properties were investigated using a quartz substrate/ TCTA (10 nm)/ PO-T2T (10 nm) film. In this instance, I selected an excitation wavelength of 280 nm ($\lambda_{\text{Ex}}=280$ nm) to allow for the simultaneous stimulation of the TCTA and PO-T2T layers, while $\lambda_{\text{Ex}} = 330$ nm was used to mainly excite a TCTA layer (**Fig. 2.4a**). As shown in **Fig. 2.4b**, the identical absorption spectra of the TCTA (10 nm)/PO-T2T (10 nm) film can be obtained with the excitation direction from either the D or A side. This suggested that the number of incident photons absorbed by the TCTA/PO-T2T film is independent of the incident direction. When the incident direction was from the TCTA side with the excitation at $\lambda_{\text{Ex}} = 330$ nm, the LE emission ($\lambda_{\text{em}} = 388$ nm) from the TCTA neat film was dominant, and the emission intensity from the exciplex was rather weak. In the case of excitation at $\lambda_{\text{Ex}} = 280$ nm, on the other hand, the exciplex emission intensity was appreciably enhanced. Further, in the case of the incident direction from the PO-T2T side with $\lambda_{\text{Ex}} = 330$ nm and $\lambda_{\text{Ex}} = 280$ nm, the proportions of the exciplex emission were significantly higher than the LE emission of TCTA. When the incident wavelength was $\lambda_{\text{Ex}} = 280$ nm, *i.e.*, the dual excitation of both TCTA and PO-T2T, the higher efficiency of exciplex production was the most pronounced (**Fig. 2.4c**).

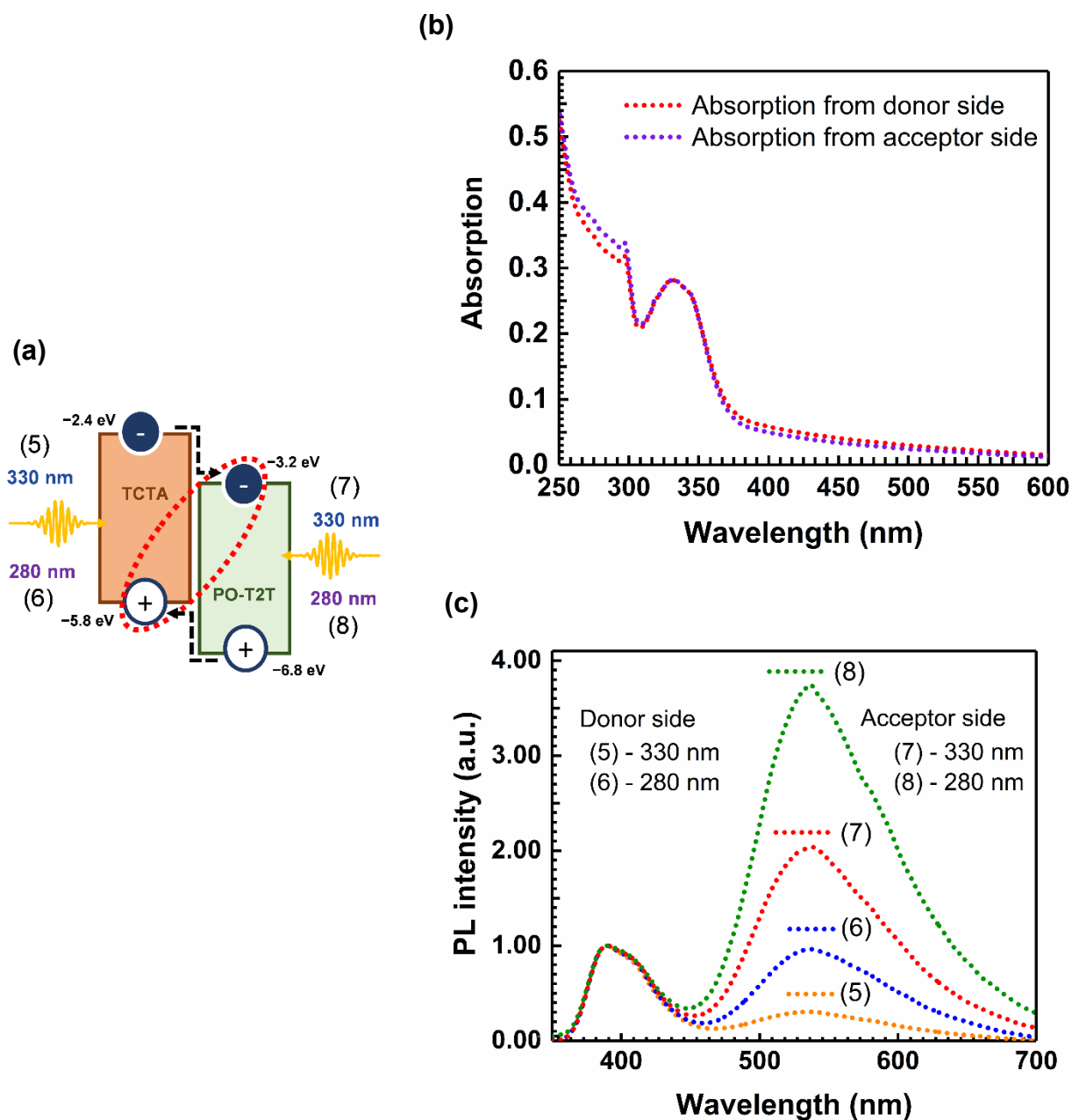


Figure 2.4. (a) Illustration of four different types of excitations: (5) 330 nm and (6) 280 nm excitation from donor side and (7) 330 nm and (8) 280 nm excitation from the acceptor side. (b) Absorption spectra of a TCTA/PO-T2T bilayer film excited from two different sides at 280 nm (c) PL spectra excited from donor and acceptor sides with 330 and 280 nm.

I evaluated the number of photons that contribute to the formation of exciplex under the assumption that photons absorbed near the interface of TCTA (1 nm)/PO-T2T (1 nm) thin films result in the formation of exciplex in order to comprehend the cause of the intense exciplex appearance with the acceptor side excitation at $\lambda_{ex} = 280$ nm. According to quantitative analysis, photons irradiated from the TCTA side, the

number of photons absorbed near the interface are $1.22 \times 10^{13} \text{ m}^{-2} \text{ s}^{-1}$ at 330 nm and $2.14 \times 10^{13} \text{ m}^{-2} \text{ s}^{-1}$ at 280 nm. From the acceptor side irradiation, the numbers of photons absorbed at 330 nm and 280 nm are $3.43 \times 10^{13} \text{ m}^{-2} \text{ s}^{-1}$ and $5.82 \times 10^{13} \text{ m}^{-2} \text{ s}^{-1}$, respectively. This result denotes that the exciplex intensity variation in **Fig. 2.4c** can be simply ascribed to the difference in the number of incident photons that could reach the TCTA/PO-T2T interface.

2.3.2. Unique photophysical characteristics of D/S (dual spacer)/A configuration

Next, I devised a multilayer structure involving D, S, and A layers to manipulate the exciplex formation process. My focus was on the unique role of dual excitation from the D and A layers. The exciplex formation *via* a long-range D...A pair was designed in this experiment. Specifically, I aimed to address a drawback observed in previous long-range exciplex studies: the relatively shallow HOMO and deep LUMO energy levels of the spacers compared to the D and A components.^{34,35,64} This mismatch led to ineffective blocking of both holes and electrons, resulting in direct electron transfer through the S layers. To overcome this, I employed DPEPO with a very shallow LUMO energy level (-2.0 eV) and UGH2 with a very deep HOMO energy level (-7.2 eV) as the dual-layer spacer. My strategy aimed to strictly inhibit direct charge transfer by ensuring sufficient blocking of both charge carriers by the S layers. Additionally, both DPEPO and UGH2 possess a high triplet energy level (over 3.0 eV), effectively preventing triplet energy loss in the exciplexes formed during the process.^{62,63}

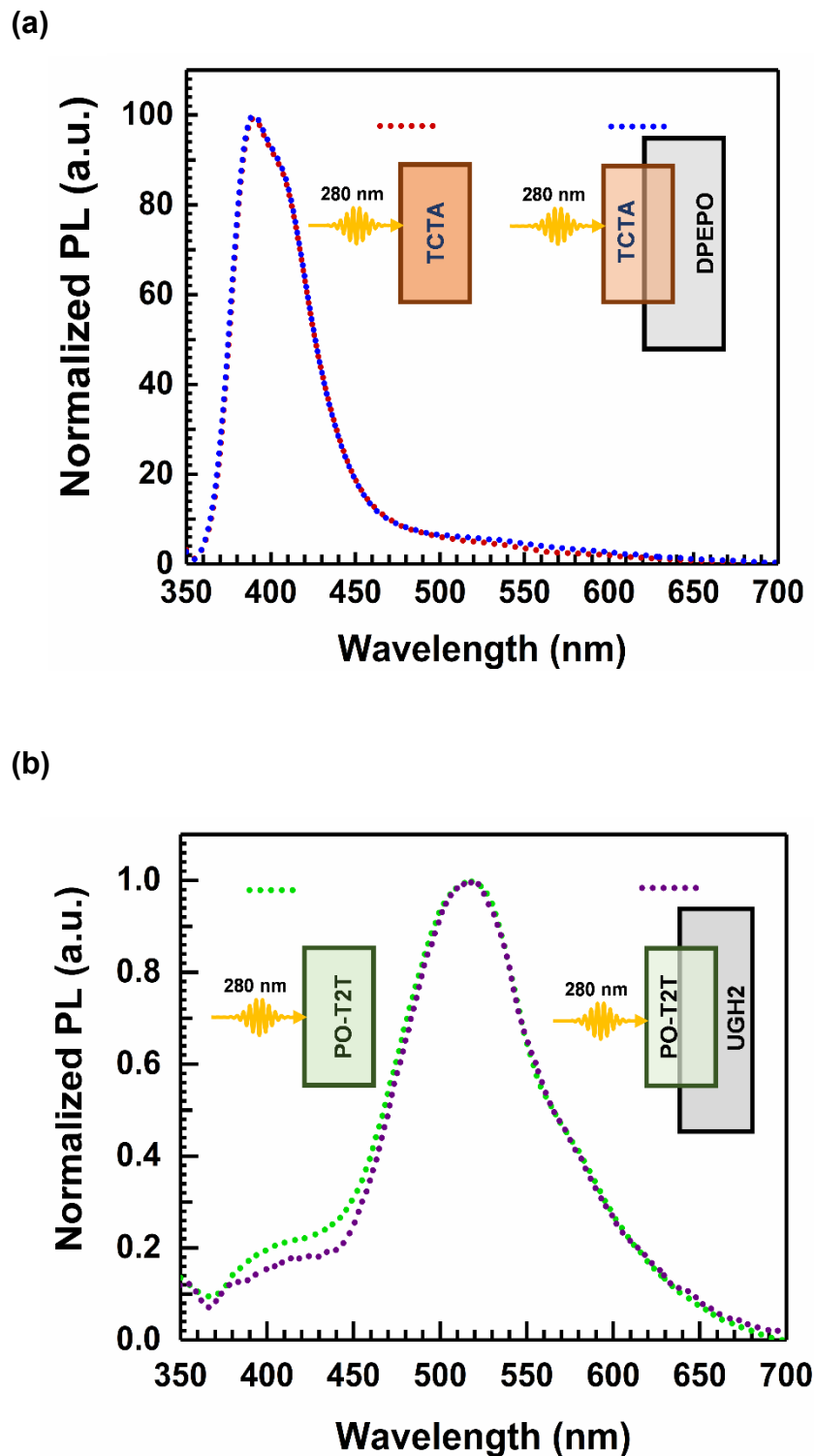


Figure 2.5. (a) PL spectra of TCTA and TCTA/ DPEPO codeposited films. (b) PL spectra of PO-T2T and PO-T2T/UGH2 co-deposited films. No shift or additional emission peaks, which confirm that there is no intermediate exciplexes formation between the donor and insulator or the acceptor and the insulator.

First, each co-deposited film was fabricated to ensure that there was no exciplex formation between TCTA: DPEPO and UGH2: PO-T2T. As illustrated in **Figs. 2.5a** and **b**, except for the LE emissions from TCTA ($\lambda_{\text{Em}}=388$ nm) and PO-T2T ($\lambda_{\text{Em}}=510$ nm) neat films, no additional emission appeared in these mixed films, indicating that the appreciable molecular interactions between the TCTA/DPEPO and UGH2/PO-T2T interfaces can be excluded. In this instance, better carrier confinement necessitates the dual-layer configuration. When considering the photo-induced electron transfer (PIET) in TCTA/UGH2/PO-T2T layers with the excitation of the TCTA layer, the cascade electron transfer would happen through the LUMO levels of TCTA, UGH2, and PO-T2T, since the LUMO (-2.8 eV) of UGH2 locates between the LUMO (-2.4 eV) of the TCTA and the LUMO (-3.2 eV) of PO-T2T (**Fig. 2.6a**). On the other hand, regarding the PIET with the excitation of the DPEPO system, since the HOMO (-6.1 eV) of DPEPO locates in the middle of the HOMO (-6.8 eV) of PO-T2T and the HOMO (-5.8 eV) of TCTA, the cascade hole transfer would happen through the HOMO levels of PO-T2T, DPEPO, and TCTA (**Fig. 2.6b**).^{70,71} Thus, the perfect carrier confinement within each D and A layer cannot be fully achieved, contrary to previous reports.

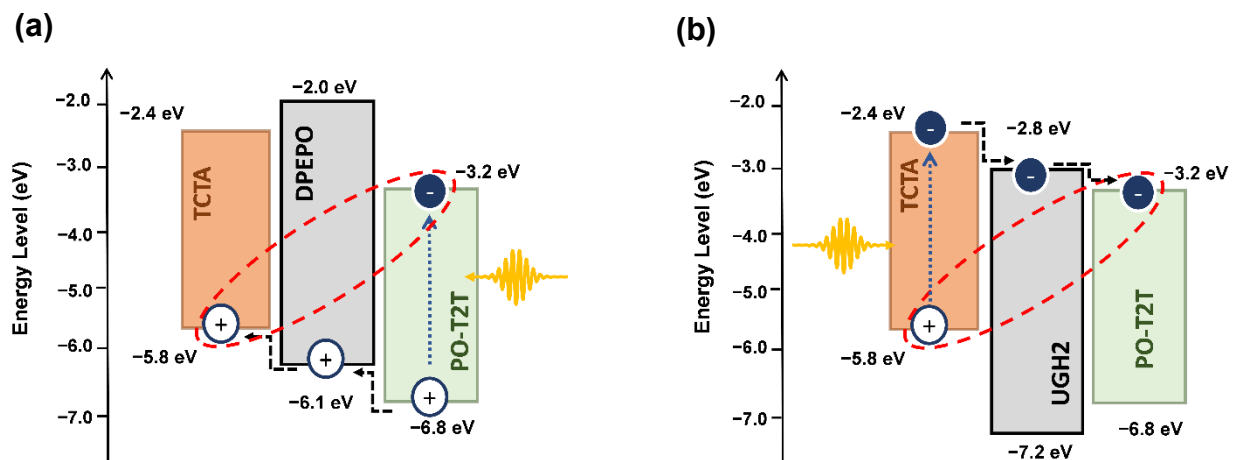


Figure 2.6. (a) Schematic energy diagram of TCTA/ UGH2/ PO-T2T single layer insulator system. The excited donor electrons are transferred to the acceptor through the spacer layer by photo-induced electron transfer (PIET) from the donor since the UGH2's LUMO level locates between the LUMO levels of TCTA and PO-T2T (b) Schematic energy diagram of TCTA/ UGH2/ PO-T2T single layer insulator system. The excited donor electrons are transferred to the acceptor through the spacer layer by photo-induced electron transfer (PIET) from the donor since the UGH2's LUMO level locates between the LUMO levels of TCTA and PO-T2T.

Here, the steady-state photoluminescence (PL) spectra of the exciplex formed between the TCTA and PO-T2T layers through the single spacer layer of UGH2 or DPEPO showed a noticeable blueshift compared with that of the TCTA/PO-T2T layer (**Figs. 2.7a, b, c, and d**). This blueshift becomes more pronounced as the thickness of the spacer film increases. The blueshift in exciplex energy can be attributed to a decrease in the electron-hole Coulombic binding energy.³⁴

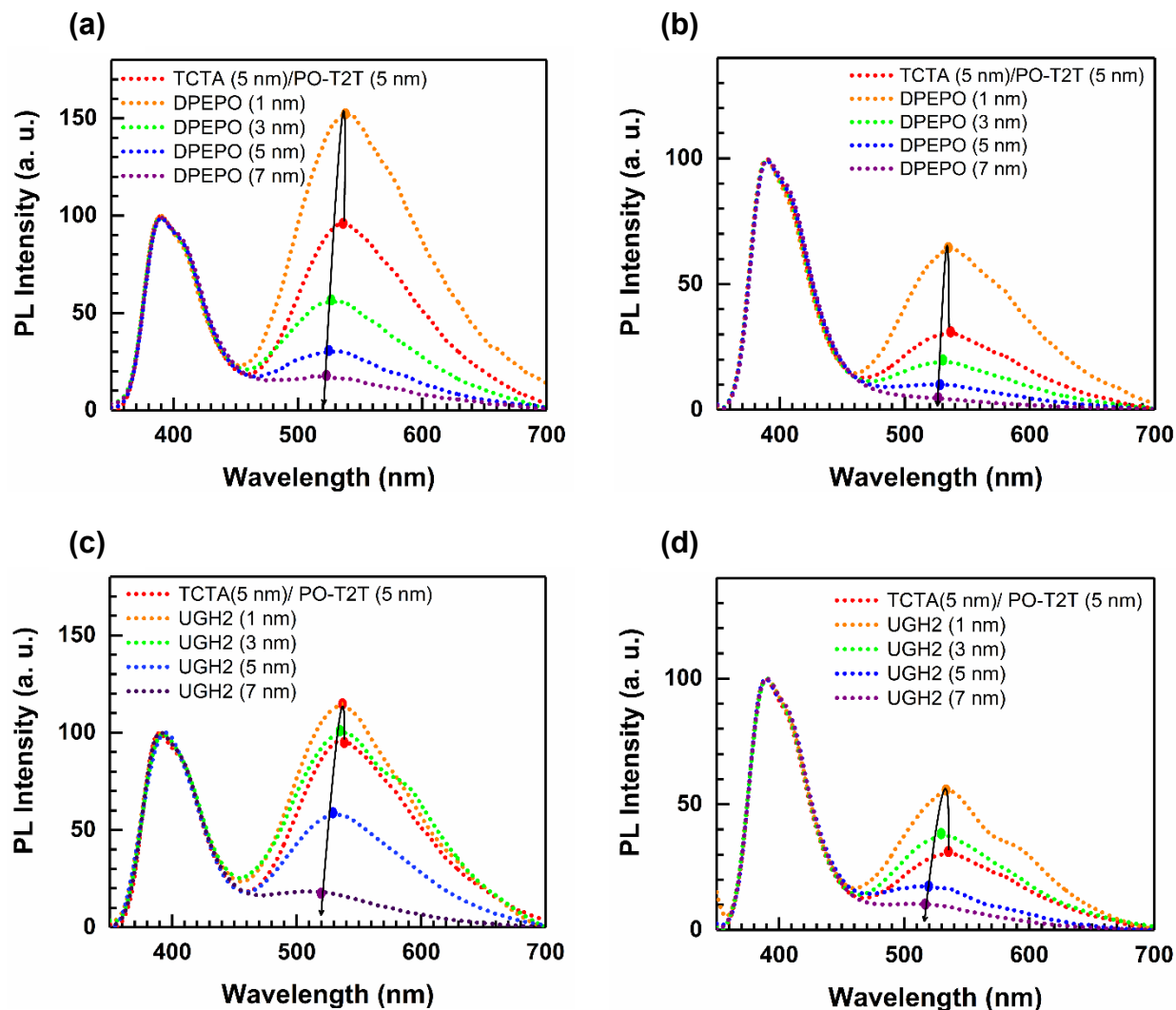


Figure 2.7. Steady-state PL spectra of the exciplexes formed between TCTA and PO-T2T layers through a single DPEPO spacer with (a) both donor and acceptor excitation, and (b) only donor excitation. Steady-state PL spectra of the exciplexes formed between TCTA and PO-T2T layers through a single UGH2 spacer with (c) both donor and acceptor excitation and (d) only donor excitation.

Next, I introduced a double-spacer layer of UGH2 and DPEPO, as illustrated in **Fig. 2.8**. The primary purpose of this layer was to block direct electron transfer between the D and A layers. **Figures 2.9a**

and **b** show the PL spectra under two different excitation scenarios from the only TCTA (D) excitation with $\lambda_{\text{Ex}} = 330$ nm and dual excitation with $\lambda_{\text{Ex}} = 280$ nm, respectively. The donor-only excitation resulted in weaker exciplex emissions than those of the dual excitation. Further, the exciplex emissions almost disappeared when the total thickness of the S was over 4 nm (**Fig. 2.9a**). Thus, it indicates that the substantial electron transfer from D to A layers through the S layer is prohibited beyond 4 nm. In the case of dual excitation, interestingly, long-range exciplex emission was observed up to 7 nm. Notably, when the S thickness was 4 nm, the exciplex emission intensity was most pronounced, surpassing that of the reference TCTA/PO-T2T film.

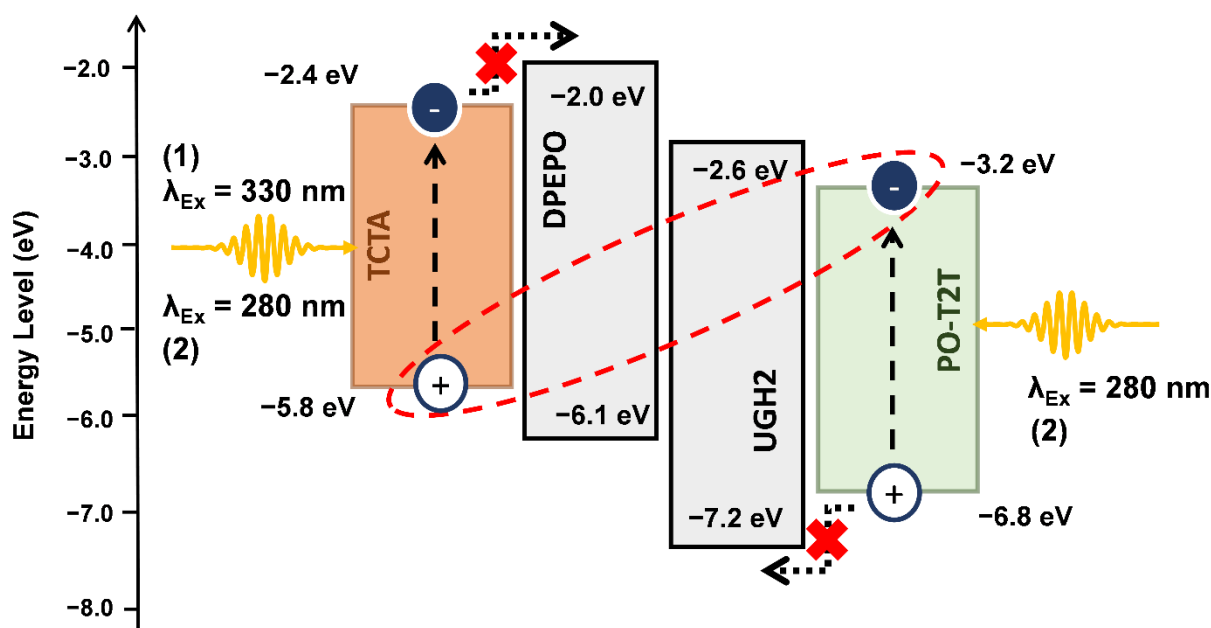


Figure 2.8. Energy level diagram of TCTA, DPEPO, UGH2, and PO-T2T layers with schematic energy diagram of dual insulator system suppressing photo-induced electron transfer (PIET) processes.

Here, I discussed the potential mechanism of exciplex generation based on this distinctive exciplex formation. Based on the Boltzmann distribution, the ET between the LUMOs of TCTA and DPEPO may be challenging in the case of only D excitation over the energy gap ($E = 0.4$ eV). Therefore, the observed ET would be due to the tunneling effect through the spacer layers and significantly reduced over 4 nm. However, in the situation of dual excitation, since D and A are excited at the same time, it would be able to induce the electronic coupling, even over a distance of 4 nm, between the hole in TCTA and the electron in

PO-T2T, creating the exciplex. These findings suggest that exciplex production can occur in a novel way *via* dual excitation which is not possible with single excitation.

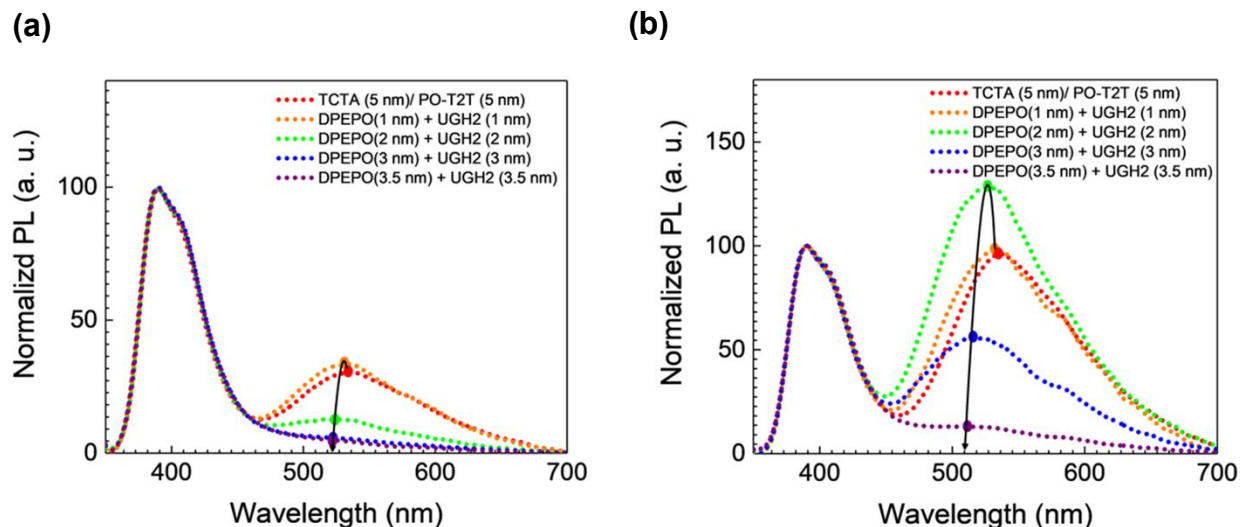


Figure 2.9. Steady-state PL spectra containing the exciplex formed between TCTA and PO-T2T having a double-insulator system with excitation by (a) only donor layer, and (b) both donor and acceptor layers.

2.3.3. Verification of unique exciplex formation from device characteristics

In dual excitation, after the exciplex decays radiatively or non-radiatively, the counter hole and electron are left in each layer. To justify the dual excitation process, these residual carriers need to be identified. For that, I studied the effect of the S layer under the operation mode of photo-electric conversion. Here, I prepared two sets of devices, as shown in **Figs. 2.10a** and **b**; Device A (reference): anode/D/A/cathode [ITO (100 nm)/ TCTA (20 nm)/ Copper phthalocyanine (CuPc): Fullerene (C60) (1: 1 molar ratio) (30 nm)/ PO-T2T (20 nm)/ Al (100 nm)] having a mixed CuPc: C60 carrier generation layer and Device B anode/ D/ S/ A/ cathode [ITO (100 nm)/ TCTA (20 nm)/ DPEPO (2 nm)/ UGH2 (2 nm)/ PO-T2T (20 nm)/ Al (100 nm)]. The current density (J) – voltage (V) measurements were done under the irradiation of the white light (AM1.5G).

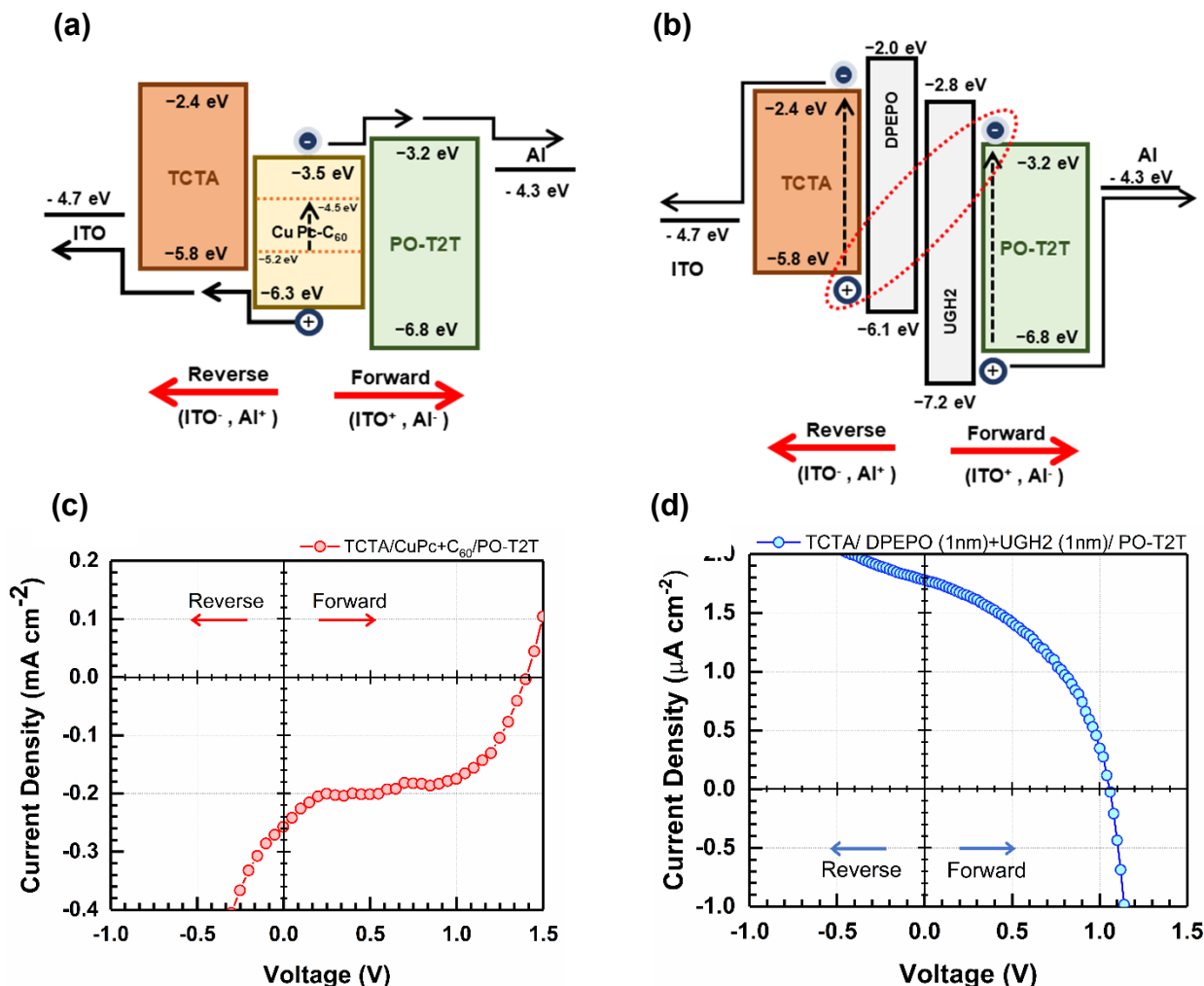
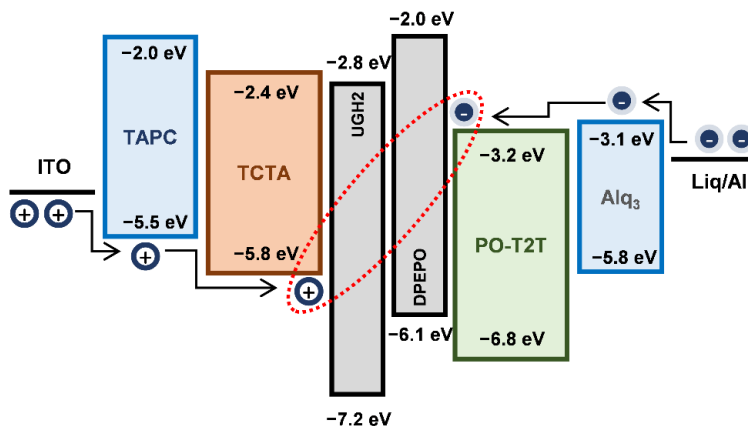


Figure 2.10. Schematic energy diagram of CT process of (a) Conventional type solar cell with CuPc/C₆₀ active layer, (Device A). (b) double insulating system, (Device B). (c) J-V characteristics of Device A. (d) J-V characteristics of Device B.

I observed conventional carrier generation flow in Device A (Fig. 2.10a), where holes and electrons are extracted from the ITO anode and the Al cathode, respectively. This is consistent with the direction of current flow in a forward (p-i-n) biased solar cell (Fig. 2.10c).⁷² Consequently, the photo-generated excitons underwent charge separation at the CuPc: C₆₀ layer, resulting in electron and hole transport by PO-T2T and TCTA layers, respectively.⁷³ However, it's interesting to note that Device B showed the output of an opposite current flow, suggesting that holes and electrons are removed from the Al and ITO electrodes, respectively (Fig. 2.10d), verifying the occurrence of the long-range exciplex formation by dual excitation.

(a)



(b)

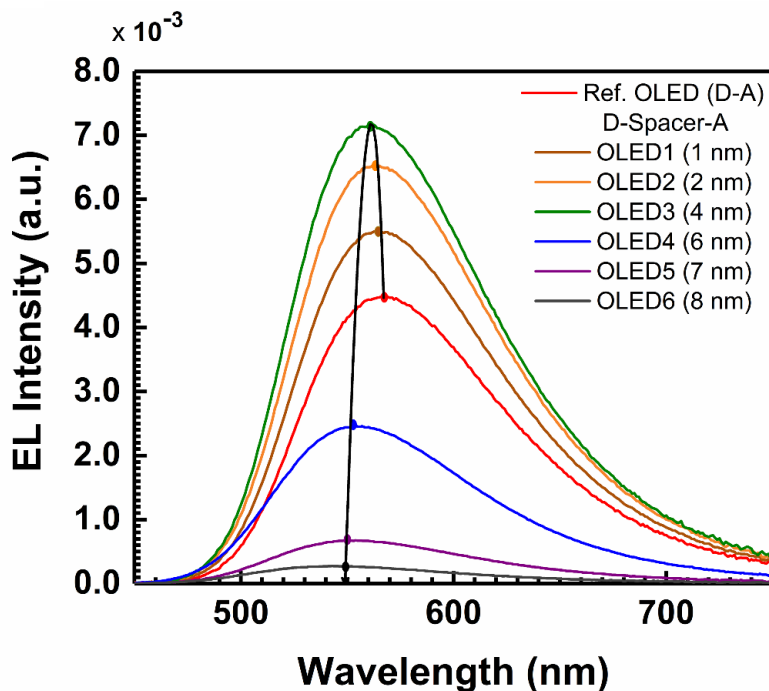


Figure 2.11. (a) Schematic energy diagram of OLED with dual insulating layers (b) EL spectra of OLEDs with different D-A distances. (OLED1 = UGH2 0.5 nm + DPEPO 0.5 nm, OLED2 = UGH2 1.0 nm + DPEPO 1.0 nm, OLED3 = UGH2 2.0 nm + DPEPO 2.0 nm, OLED4 = UGH2 3.0 nm + DPEPO 3.0 nm, OLED5 = UGH2 3.5 nm + DPEPO 3.5 nm and OLED6 = UGH2 4.0 nm + DPEPO 4.0 nm).

Furthermore, I fabricated OLEDs with varying spacer thicknesses between the TCTA and PO-T2T layers in order to comprehend the long-range exciplex behavior under electrical excitation (**Fig. 2.11a**). The device structure is ITO/ 4,4-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) (30 nm)/

TCTA (10nm)/ S (UGH2/DPEPO) (x nm)/ PO-T2T (10 nm)/ tris(8-hydroxyquinolino)aluminum (Alq₃) (30 nm)/ Liq (2 nm)/ Al (100 nm), where the distance between D and A was precisely controlled by the double-spacer (UGH2 1:1 DPEPO) thicknesses. Here, holes were injected from an ITO electrode into the HOMO of the TCTA layer (−5.8 eV) through the TAPC layer, and electrons were injected from an aluminum electrode into the LUMO level of the PO-T2T layer (−3.2 eV) through the Alq₃ layer (−3.1 eV). The holes and electrons are forced to accumulate at the interfaces of TCTA/UGH2 and DPEPO/PO-T2T, respectively, due to their large energy barriers for carrier injections ($\Delta E_{\text{HOMO}} = 1.4$ eV for hole injection and $\Delta E_{\text{LUMO}} = 1.2$ eV for electron injection, respectively). Here, I also prepared the reference device without a S layer, ITO/ TAPC/ TCTA/ PO-T2T/ Alq₃/ Liq/ Al with the same thicknesses. The device exhibited the EL at 100 $\mu\text{A cm}^{-3}$ current density with only a single wavelength peak at 538 nm, implying the exciplex formation at the D-A interface, which is consistent with that under photoexcitation.

After the UGH2/DPEPO layer is inserted, electrons and holes accumulate at the TCTA/UGH2 and PO-T2T/DPEPO interfaces, respectively, making direct electron transfer between TCTA and PO-T2T almost prohibited. Nevertheless, the exciplex can be created by the through-space interaction. As seen in **Fig. 2.11b**, a notable blueshift of the exciplex ELs with an increasing D-A distance (d) was noted. The change in the Coulombic potential energy [$E_C(r)$] between the electron/hole pairs in the CT state is related to this spectrum shifting.^{34,35} In **Eq. 2.4** that follows,

$$E_C(r) = \frac{e^2}{4\pi\epsilon_0\epsilon r} - eF \cdot r \quad (2.4)$$

where r is the distance between an electron and a hole, e is the electron charge, F is the electric field, and ϵ_0 and ϵ are the permittivity in the vacuum and in the medium, respectively. Thus, the EL intensities originated from $^1(\text{D}^{\delta+} \text{A}^{\delta-})^*$ gradually increased, then weakened with increasing the S thickness and disappeared entirely over a wavelength of 7 nm. This outcome is in agreement with the PL spectra's tendency. The absence of extra EL components from the LE states of $1(\text{D})^*$ or $1(\text{A})^*$ is noteworthy. This would suggest that the UGH2/DPEPO spacer entirely blocks the carrier injection and transport, leading to the dominant contribution only from $\phi(\text{D}^* \text{A}^*)$.

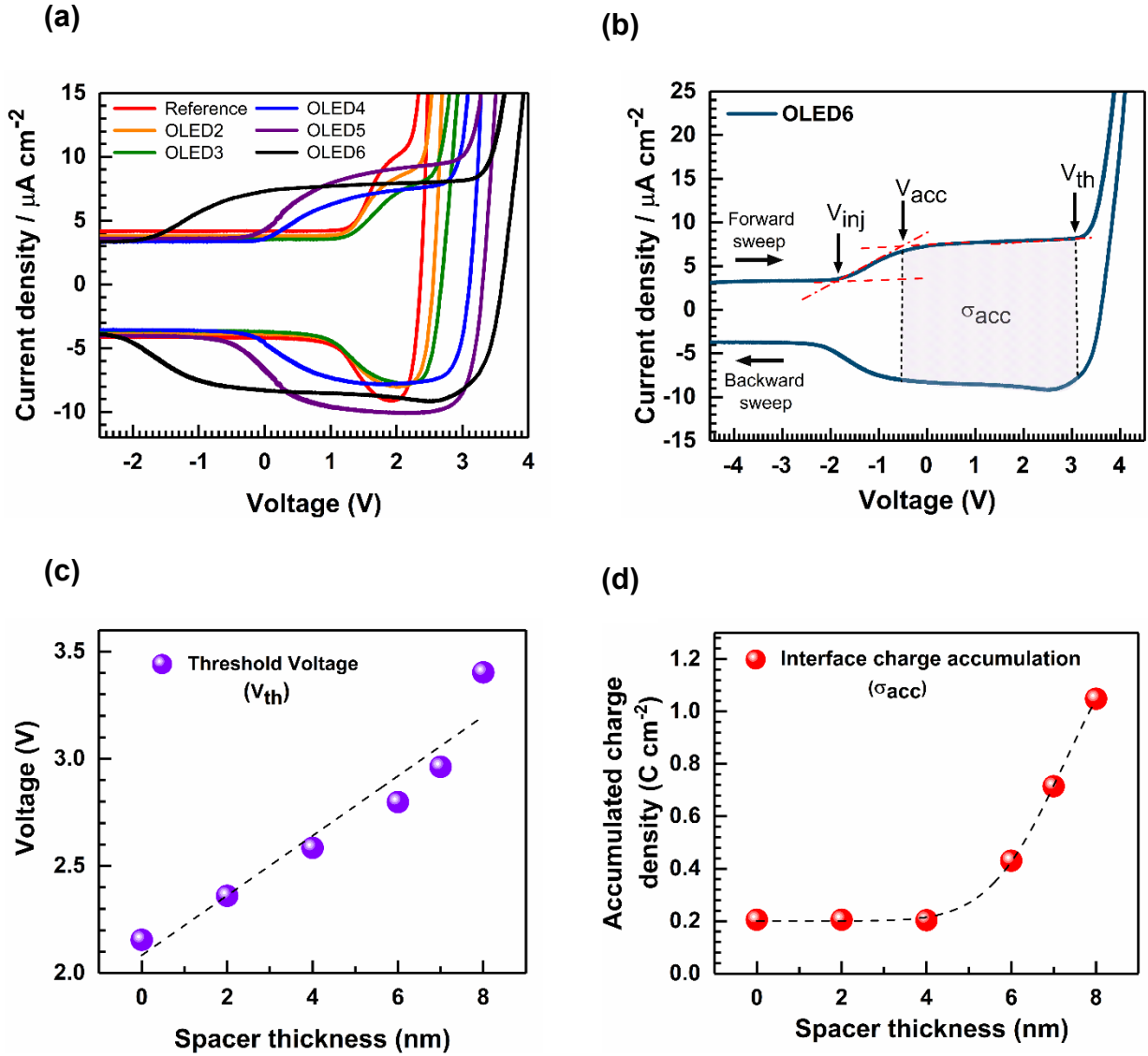


Figure 2.12. (a) DCM characteristics of OLED with double insulating layers of UGH2/DPEPO. (b) Schematic illustration of the DCM characteristics of OLED6, Injected voltages (V_{inj}), accumulation voltage (V_{acc}), and threshold voltages (V_{th}) are defined by the intersection of the extended lines. (The amount of accumulated charges at the interface (σ_{acc}) is proportional to the highlighted area.) (c) Threshold voltage of OLEDs with different D-A distances (d) Interface charge accumulation of OLEDs with different D-A distances.

In addition, displacement current measurement (DCM) was used to study charge accumulation behavior under electrical excitation. DCM is a type of current density-voltage (C-V) measurement where the device is subjected to a triangle wave voltage and the current responses, including displacement and actual currents, are measured.⁷⁴ It is feasible to evaluate the charge injection and accumulation characteristics of the device since the displacement current is proportional to the device's apparent capacitance. In DCM, the measured current (i_{DCM}) can be expressed as **Eq. 2.5**,

$$i_{DCM} = i_{act} + C_{app} \frac{dv}{dt} \quad (2.5)$$

where C_{app} is the apparent capacitance of the device, $\frac{dv}{dt}$ is applied triangular voltage and i_{act} is the actual current response. The OLEDs' threshold voltages (V_{th}), as seen in **Figs. 2.12a** and **b**, were proportionate to their D/A distance (S thickness), indicating the S layers' adequate charge carrier blocking.⁷⁵ However, the equivalent charge density (σ_{acc}) showed distinct characteristics. When the D/A distance is shorter than 4 nm, the accumulated charge density was a very small value ($\sim 20 \mu A cm^{-2}$), suggesting the charge accumulation did not substantially occur at the interface between D/A and S layers due to the consumption as exciplex. On the other hand, the σ_{acc} increased drastically as the S thickness increased when the D/A distance was more than 4 nm. With extending the S thickness, implying the injected charges were mainly accumulated at the interfaces, and charge hopping or tunneling was entirely suppressed. This suggests that the injected charges were substantially accumulated at the interfaces and that charge hopping or tunneling was completely suppressed.

2.4. Conclusion

In this research, I explored an unexplored route for exciplex formation. Unlike the traditional ($D^* \dots A$) or ($D \dots A^*$) mechanisms, I discovered that dual excitation of D and A molecules, without direct electron transfer between them, can lead to exciplex formation. Specifically, the D/S/A formation with the DPEPO/UGH2 spacer layer enabled long-range exciplex formation by exciting both D and A layers simultaneously. The charge separation behavior under reverse photocurrent flow and the accumulation of charges with sufficient S thickness indicated that the electrons and holes generated in the D/S/A layers confirmed the presence of the dual excitation process. Therefore, I conclude that the component of the (D^*A^*) state would significantly contribute to the exciplex wavefunction. This insight prompts a modification of the exciplex equation, emphasizing the significance of $D^* \dots A^*$ coupling in manipulating exciplex formation (**Eq. 2.6**):

$$\psi([DA]^*) \approx c_4 \phi(D^*A^*) + c_3 \phi(D^*A) + c_2 \phi(DA^*) + c_1 \phi(D^+A^-) + c_0 \phi(DA) \quad (2.6)$$

Chapter 3

Distance-Dependent Exciplex Exciton Dynamics in Donor/Spacer/Acceptor Layers

3.1. Introduction

When light strikes electron D or A molecules, it triggers an intriguing phenomenon: the formation of CT complexes, commonly known as exciplexes. These entities are generated by the transfer of electrons between adjacent D and A molecules.^{76,77,78} Exciplexes are not merely theoretical constructs; they are abundant in nature, especially within photosynthetic systems. Moreover, they find practical applications in organic optoelectronic devices, including OPVs and OLEDs, where the heterojunctions between D and A molecules are exploited.⁴² Recently, exciplexes have been actively used as TADF emitters in OLEDs by taking advantage of a small ΔE_{ST} , resulting in highly efficient exciton harvesting for light emission.⁷⁹ Additionally, exciplexes have also been widely used as host materials in OLEDs, aiming for low driving voltage, balanced holes, and electron transport, and reduced efficiency roll-off. Unlike the localized Frenkel excitons generated in conventional organic aromatic compounds, intermolecular CT excitons within exciplexes exhibit broader delocalization.^{80,81} These excitons spread across both electron-accepting and electron-donating molecules, resulting in weaker exciton binding energies (E_b) compared to Frenkel excitons. Recently, researchers have extended the exciplex concept by introducing a S layer between the D and A layers in OLED architectures. This innovative approach opens up new possibilities for optimizing device performance and exploring novel applications.^{34,35}

In the realm of intramolecular exciplexes, such as those found in TADF molecules, scientists can precisely determine the spacing between the D and A.⁸² However, things get more complex with intermolecular exciplexes, those formed between separate molecules within thin films. In these thin films, it is challenging to precisely control the distance between the D and A due to the distance distribution depending on the steric structure of the molecules. In this chapter, I focus on multilayered long-range exciplex systems by finely controlling the distance between D and A. To achieve this, we insert an ultra-thin S layer between the D and A.^{34,35,72} This precise control allows us to clarify the characteristic photophysical behavior with time-dependent dynamics of exciplexes over varying distances. In previous studies, Graves et al. attempted to explain how the inhomogeneity of D and A molecules in films affected the distribution of ΔE_{ST} .⁶² Kim et al. then reported on computational techniques to demonstrate that the effective ΔE_{ST} and k_{RISC} in exciplex blends are ultimately determined by the distribution of singlet and triplet energies.⁴⁴ Here, I present an in-depth study of a long-range exciplex system by examining how the distance between the D and A molecules affects the behavior of the activation energy (E_a) and ΔE_{ST} .

3.2. Experimental Section

All chemicals were purchased from the Luminescence Technology Co. and used as received. Thermal evaporation was used to form organic thin films on clean quartz and silicon substrates at 2×10^{-4} Pa. Before the deposition, the substrates underwent cleaning with acetone and isopropanol, followed by exposure to UV/ozone. Absorption and PL spectra of organic thin films were measured using an ultraviolet–visible–near-infrared spectrometer (Perkin-Elmer LAMDA 950-PKA) and a fluorescence spectrophotometer (FP-8600, JASCO), respectively. PLQY was measured using an absolute PLQY measurement system (C13534-01, Hamamatsu Photonics). Additionally, transient PL decay was measured using Hamamatsu Photonics Quantaaurus-Tau C11367. Delayed PL lifetime fitting was performed using single exponential fitting of $y = y_0 + A_1 e^{-x/t_1}$ formula from 1.5 μ s to 10 μ s time range. Using the obtained delayed PL lifetime (τ_D), prompt-PL lifetime (τ_P) was calculated based on double exponential decay fitting of $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$ from 13 ns to 100 ns time range. The HOMO levels were determined by the photoelectron spectroscopy (Riken Keiki Co., AC-3). A cryostat (PS-HT-200, Nagase Techno-Engineering Co.) and a high-power Xenon lamp (MAX-303, Asahi spectra Co.) were used to analyze the temperature dependency of PL spectra under vacuum conditions with the excitation wavelength of 340 nm. The time-resolved PL decay was measured using a transient emission spectrometry setup with an excitation source of third harmonic wave generation from Nd:YAG/YVO laser at 355 nm, pulse duration 30 ps, EKSPLA PL-2250, and the streak camera of C10910-01, Hamamatsu Photonics.

3.3. Results and Discussion

As shown in **Figs. 3.1a** and **b**, TCTA, composed of electron-donating carbazole and triphenylamine (TPA) moieties, was used as a donor, whereas PO-T2T, composed of electron-accepting triazine and diphenylphosphine units, was used as an acceptor. Because of the distinct energy gaps between the HOMOs and LUMOs, i.e., $\Delta E_{\text{HOMO}} = 1.0$ eV and $\Delta E_{\text{LUMO}} = 0.8$ eV, the exciplex formation occurred by photo-excitation. To understand the through-space CT formation between TCTA and PO-T2T, I prepared the multilayered structure of D/S/A. My selection for a S material is UGH2, which has a large energy gap compared with those of TCTA and PO-T2T layers (**Fig. 3.1c**); high triplet energies and optical and UV transparency of UGH2 also give an additional advantage for photophysical studies.⁶⁴

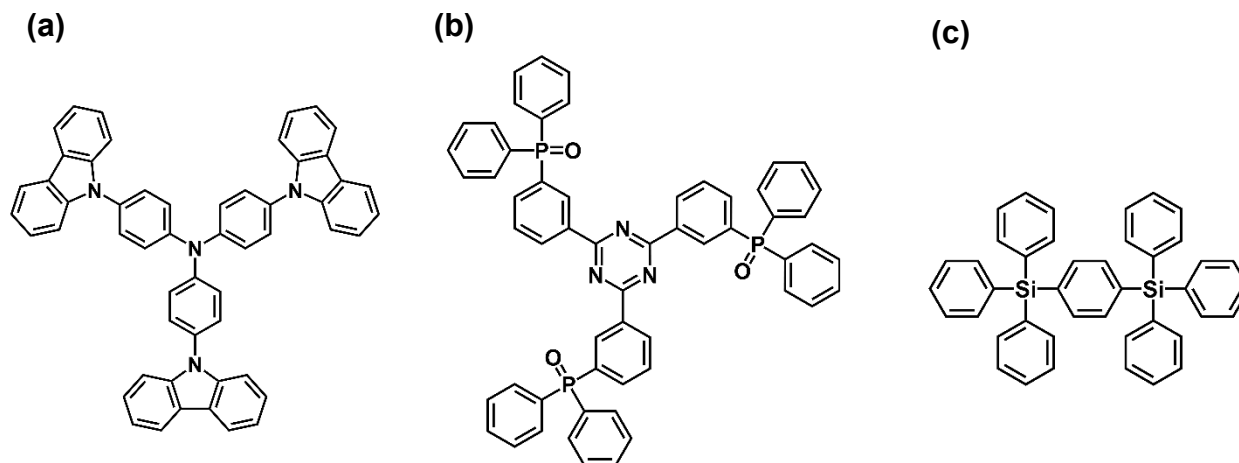


Figure 3.1. Molecular structures of the material used in this work (a) TCTA, (b) PO-T2T, and (c) UGH2.

Figure 3.2 shows the alignment of organic layers' energy levels (HOMO and LUMO). To ensure consistency throughout the entire study, I maintain D excitation for the formation of exciplex, due to the limitation of temperature-dependent transient emission spectrometry, where the excitation source of the third harmonic wave generation is the Nd:YAG/YVO laser at 355 nm. Since the LUMO level (-2.8 eV) of UGH2 is located deeper than the LUMO level (-2.5 eV) of the TCTA layer, the excited donor electrons are transferred to the acceptor through the S layer by PIET from the D (UGH2's LUMO level locates between the LUMO levels of TCTA and PO-T2T).⁸³

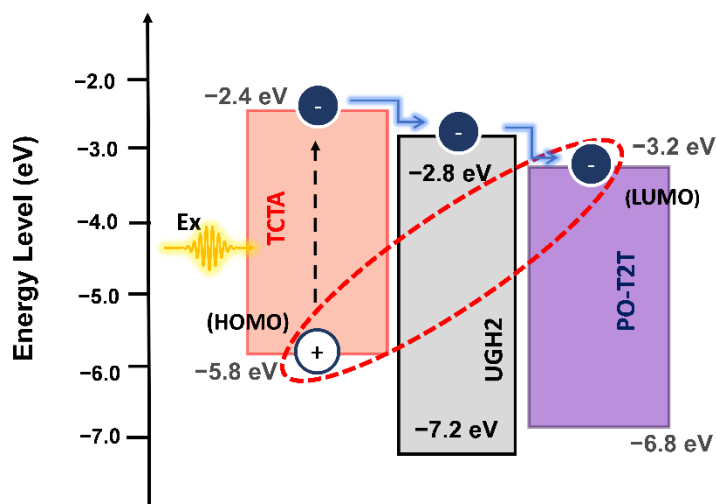


Figure 3.2. Schematic energy diagram (HOMO and LUMO) of TCTA, PO-T2T, and UGH2 and mechanism of the long-range exciplex in which excited donor electrons are transferred to the acceptor through the spacer layer.

First, the photophysical characteristics of vacuum-deposited neat and codeposited thin films with a thickness of 20 nm were examined in order to comprehend the interactions between D and A under photoexcitation. The absorption and photoluminescence (PL) spectra of the neat TCTA, PO-T2T, and codeposited TCTA:PO-T2T (1:1 in molar ratio) films are shown in **Figs. 3.3a and b**. The absorption

of a TCTA neat film extends between 250 to 340 nm, while that of a PO-T2T film is located mainly at a wavelength shorter than 300 nm and at wavelengths greater than 300 nm. Both the TCTA/PO-T2T bilayer and the mixed films follow the superimposed spectra of both components. Besides, this bilayer and codeposited films showed no extra absorption bands, suggesting no ground state interactions between them.

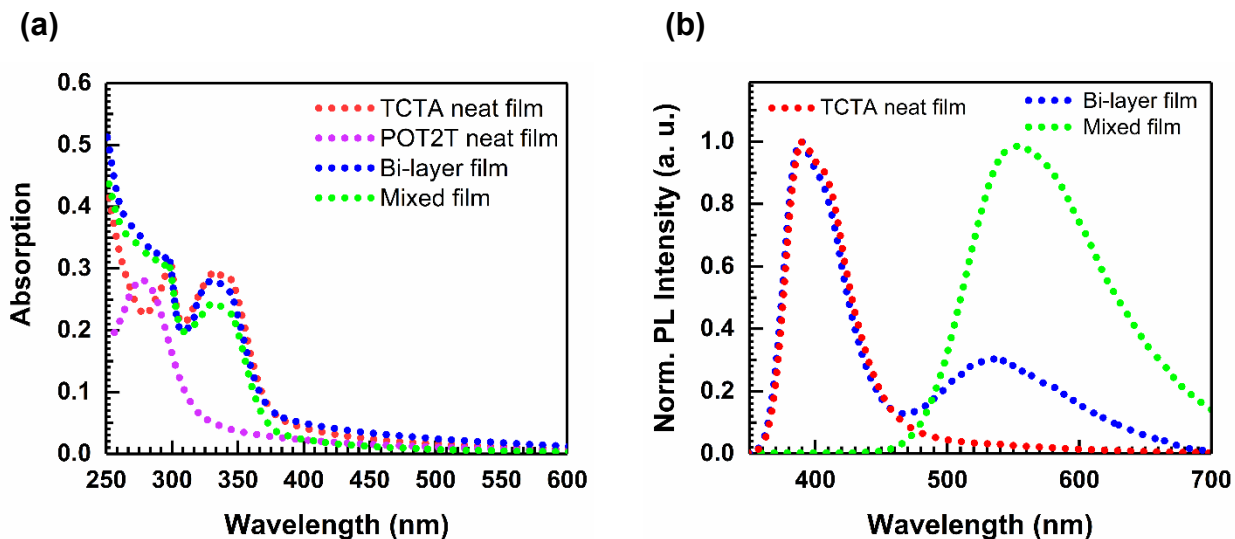


Figure 3.3. (a) UV-vis absorption spectra of TCTA (donor) only, PO-T2T (acceptor) only, TCTA/PO-T2T bilayer, and TCTA:PO-T2T mixed films. (b) PL spectra of TCTA, TCTA/PO-T2T bilayer, and TCTA: PO-T2T mixed films.

Here, mainly donor excitation at the wavelength longer than 300 nm was used to excite the TCTA layer. **Figure 3.3b** shows the PL spectra of a TCTA neat film, a bilayer D:A film, and a codeposited D:A film with an excitation wavelength of 330 nm. (When the PO-T2T neat film was excited at 330 nm, there was no discernible emission because of the acceptor's poor absorption over 300 nm.) In the bilayer film, the exciplex contribution at $\lambda_{\text{max}}=530$ nm was found to be relatively small, and a dominant component corresponding to the LE state emission from TCTA was observed at around 390 nm. Conversely, in the mixed film, a single broad PL spectrum with the $\lambda_{\text{max}}=550$ nm was observed, indicating efficient exciplex formation.

Further, to confirm no intermediate exciplex formation between the D/S and S/A, two codeposited films of TCTA:UGH2 and PO-T2T:UGH2 with each thickness of 20 nm were fabricated. As shown in **Fig. 3.4**, except for the emissions from TCTA ($\lambda_{\text{max}}=388$ nm) and PO-T2T ($\lambda_{\text{max}}=510$ nm) neat films, no additional emission appeared in these mixed films, indicating no CT interactions between TCTA/UGH2 and PO-T2T/UGH2 layers.

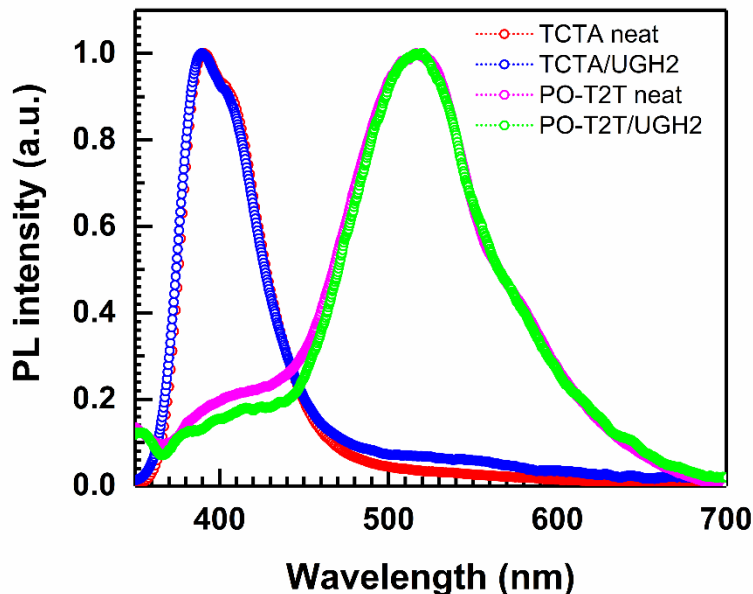


Figure 3.4. PL spectra of TCTA neat, TCTA/UGH2 codeposited, PO-T2T neat, and PO-T2T/UGH2 codeposited films.

Next, I investigated how the photophysical characteristics of TCTA (5 nm), UGH2 (x nm), and PO-T2T (5 nm) were affected by the D-A separation. **Figure 3.5** shows the steady-state PL spectra with varying the UGH-2 spacer thicknesses. Here, I assume that the number of incident photons absorbed by the films is independent of the S thickness since the UGH2 layer is transparent at the excitation wavelength of 330 nm. As shown in **Fig. 3.5** and **Table 3.1**, a slight blueshift of the exciplex emissions was identified with the thickness increase. This blueshift can be explained by decreased electron-hole Coulombic attraction energy due to the longer distance of D-A molecules, leading to higher CT energy.^{34,35} Simultaneously, the parent TCTA emission at 388 nm becomes gradually dominant with increased S thickness, suggesting decreased exciplex production with the separation. Interestingly, the maximum exciplex emission intensities were observed at the 1 nm D-A distance, indicating that 1 nm is the optimal separation distance for exciplex formation. When the S thickness becomes large, the exciplex's ΔE_{ST} and oscillator strength decrease.⁸⁴ Thus, the compatibility of the small ΔE_{ST} and the adequate oscillator strength formation was realized at the spacer thickness of 1 nm.

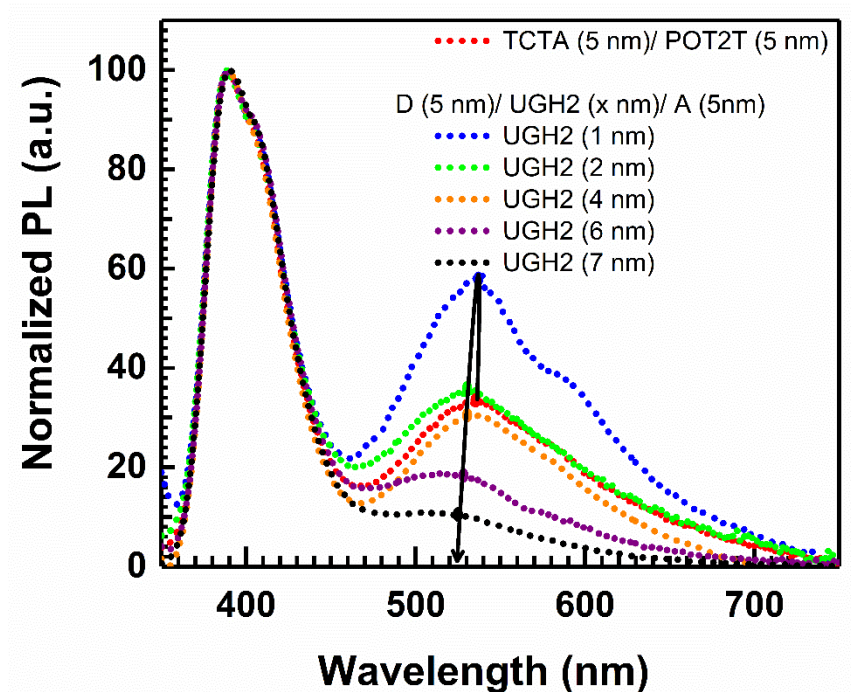


Figure 3.5. Steady-state PL spectra of TCTA (5 nm)/UGH2 (x nm)/PO-T2T (5nm) films with different spacer thicknesses.

Table 3.1. Photophysical properties of TCTA (5 nm)/UGH2 (x nm)/PO-T2T (5 nm) system with different spacer thicknesses.

UGH2 thickness (nm)	PL maximum (nm)	PLQY Air/ N ₂	τ_P (ns)	τ_D (μ s)	k_r (10^5 s^{-1})	k_{ISC} (10^7 s^{-1})	k_{RISC} (10^6 s^{-1})
-	539	0.030/ 0.033	44.4	1.17	6.8	6.0	3.4
1.0	536	0.034/ 0.038	40.6	1.00	6.8	6.2	3.5
2.0	533	0.032/ 0.035	38.9	1.59	6.5	9.8	3.7
4.0	531	0.027/ 0.031	34.3	1.71	6.2	9.3	3.5
6.0	529	0.023/ 0.025	31.1	1.23	5.4	8.5	3.1
7.0	526	0.020/ 0.021	26.1	0.74	4.0	8.0	2.9

Then, using an excitation wavelength of 340 nm at room temperature, I investigated the time-resolved photoluminescence (TRPL) properties of TCTA (5 nm), UGH2 (x nm), and PO-T2T (5 nm) films with varying S thicknesses (**Figs. 3.6a** and **b**). The TRPL characteristics showed not only a prompt (τ_P) component but also a long-lived delayed component (τ_D), which is the characteristic behavior of exciplex-based TADF.^{42,85}

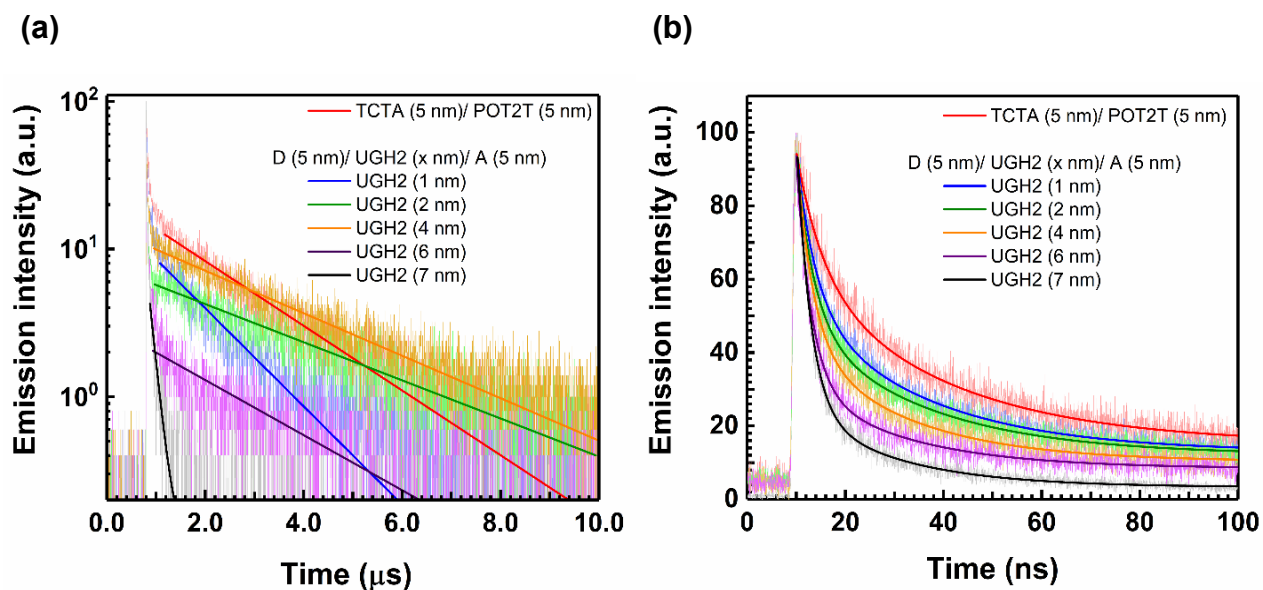


Figure 3.6. (a) Room-temperature transient PL characteristics of a TCTA (5 nm)/spacer (UGH2, x nm)/PO-T2T (5 nm) thin films with ms time scale. (b) Room-temperature transient PL characteristics of TCTA (5 nm)/spacer (UGH2, x nm)/PO-T2T (5 nm) thin film with ns time scale.

Also, the prompt and delayed emission spectra of the 2 nm and 4 nm spacer film are shown in **Figs. 3.7a** and **b**, indicating that the prompt and delay emission coincides with the exciplex spectrum, but there is a slight redshift between the prompt and delayed components, due to the relaxation of exciplex confirmation after the reverse ISC process.^{42,86}

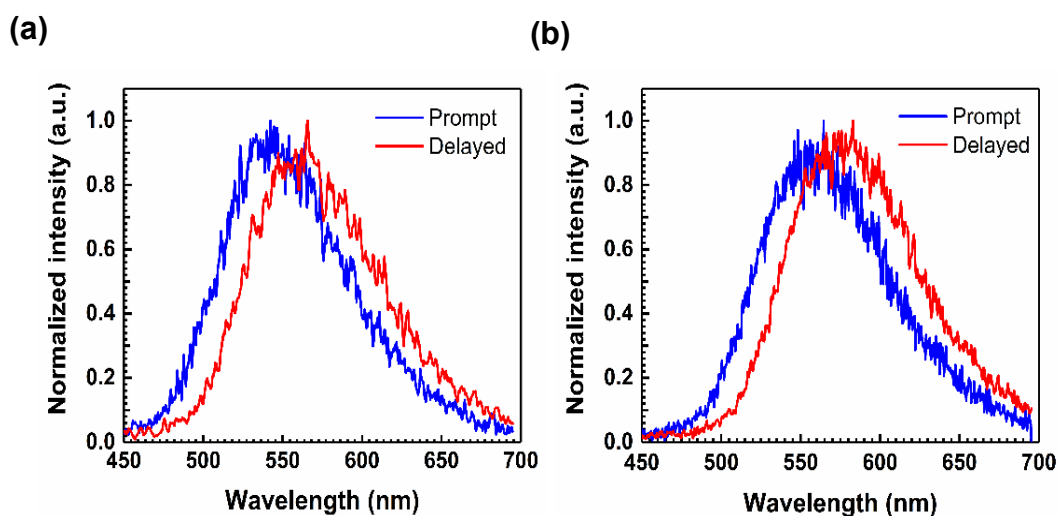


Figure 3.7. (a) Prompt and delayed PL spectra of (a) TCTA (5 nm)/spacer (UGH2, 4 nm)/PO-T2T (5 nm) and (b) TCTA (5 nm)/spacer (UGH2, 4 nm)/PO-T2T (5 nm) thin films.

Next, using the double exponential decay functions in the log–log scale to fit the decay curves, I investigated the S thickness dependency of τ_P and τ_D , as shown in **Table 3.1**. It was also determined whether the delayed fluorescence is due to TADF and not TTU by looking at how the delayed emission intensity depends on excitation power (**Fig. 3.8**). This is confirmed by the linear relationship between laser power and emission intensity, which rules out TTU involvement.⁸⁷

In contrast to τ_D , which showed the characteristic D-A distance dependence, τ_P gradually decreased as the D-A distance increased. In specific, the shortest τ_D was observed at the 1 nm separation, indicating the ideal energy alignment and orbital overlap for the exciplex emission. At the thicknesses of 2–6 nm, on the other hand, the increase in τ_D is indicative of the reduced Coulombic interaction. Further, at the thicknesses of 6–7 nm, τ_D

rapidly decreases, indicating a decrease of exciplex production with the enhancement of the nonradiative decay processes. To understand the cause of the observed deviation in τ_D , I also measured the absolute PLQYs of the films (**Table 3.1**). The PLQY increased for all films when ambient oxygen was removed, indicating the contribution of the delayed emission *via* the RISC process from the triplet state.^{42,88} At the S layer of 1 nm, the PLQY showed the maximum and decreased with the thicker spacer layers. Due to a reduction in the HOMO and LUMO orbital overlap, this observation is compatible with the steady decrease of the radiative decay rate (k_r) with the D-A separation. The characteristic τ_D and PLQY behaviors suggest that 1 nm separation is an optimal distance where the balance between small ΔE_{ST} , proper oscillator strength, and the suppression of nonradiative decay maximize the exciplex emission.

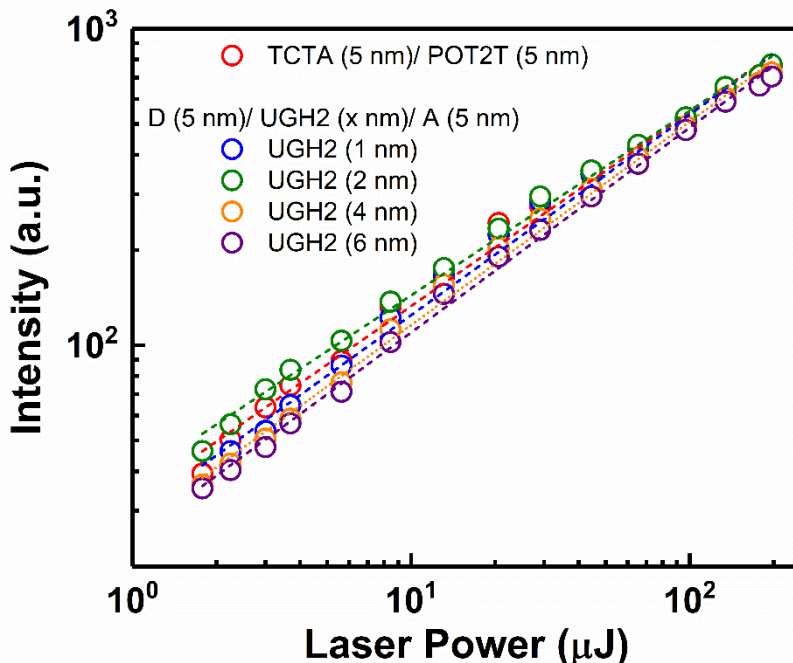


Figure 3.8. A linear fit of delayed intensity vs. excitation power of TCTA (5 nm)/spacer (UGH2)/PO-T2T (5 nm) films with log-log plot.

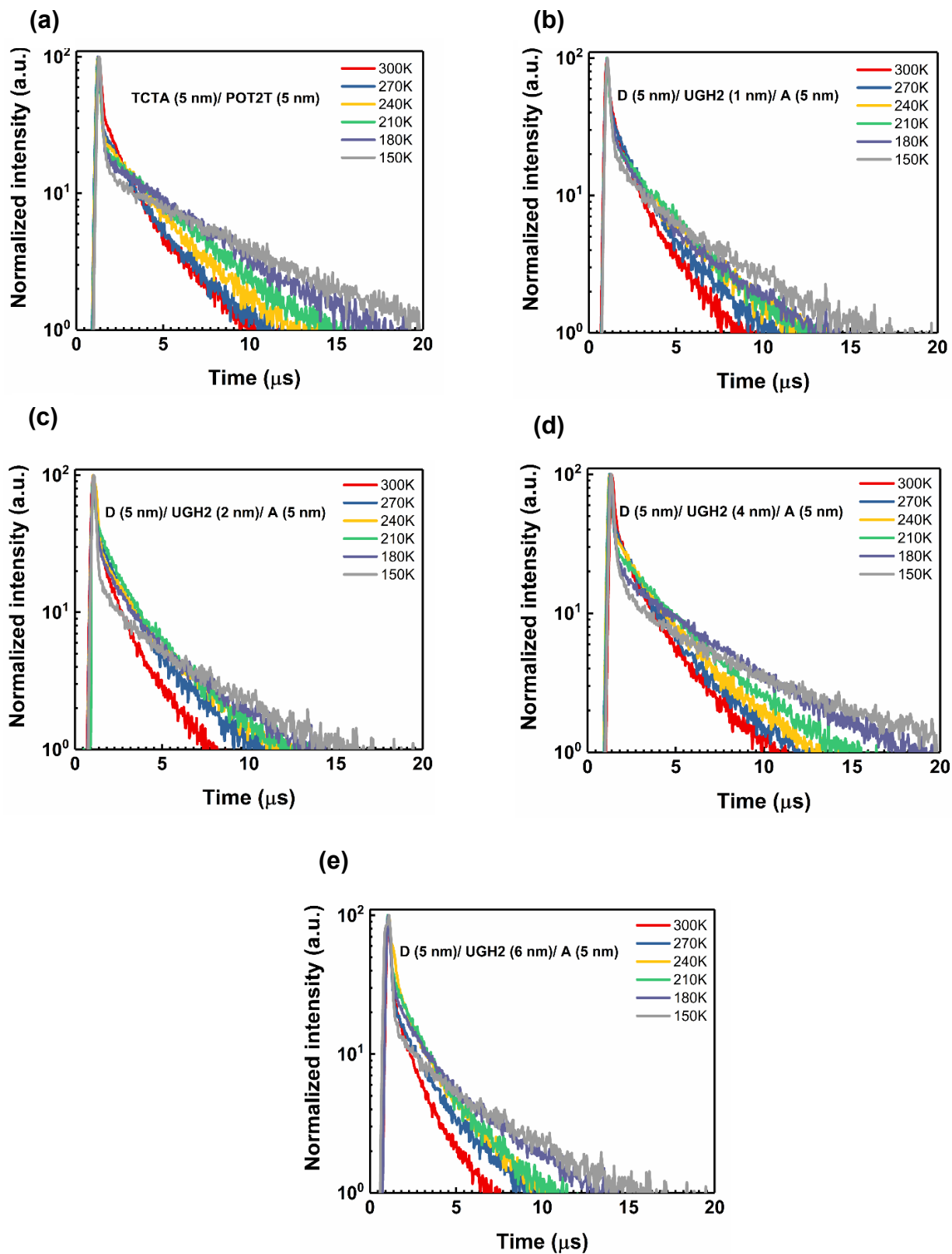


Figure 3.9. Temperature dependence of transient PL at 150–300 K for different spacer thicknesses (a) $x=0$ nm, (b) $x=1$ nm, (c) $x=2$ nm, (d) $x=4$ nm, and (e) $x=6$ nm.

To further understand the kinetic behavior of the through-space exciplexes, I conducted temperature-dependent TRPL (**Fig. 3.9**) and analyzed it with the Marcus' equation for the temperature dependence of intersystem crossing (ISC) rate (k_{ISC}) and reverse ISC rate (k_{RISC}) as following,⁸⁹

$$\ln(k_{(RISC \text{ or } ISC)} \cdot \sqrt{T}) = -\frac{E_a}{k_B} \cdot \frac{1}{T} + \ln A \quad (3.1)$$

where T is the absolute temperature, E_a is the activation energy, k_B is the Boltzmann constant, and A is the pre-exponential factor, respectively. The activation energies of RISC (E_a^{RISC}) and ISC (E_a^{ISC}) were calculated from **Figs. 3.10a** and **b**. It indicates that both E_a^{RISC} and E_a^{ISC} gradually increased with increased S thickness.

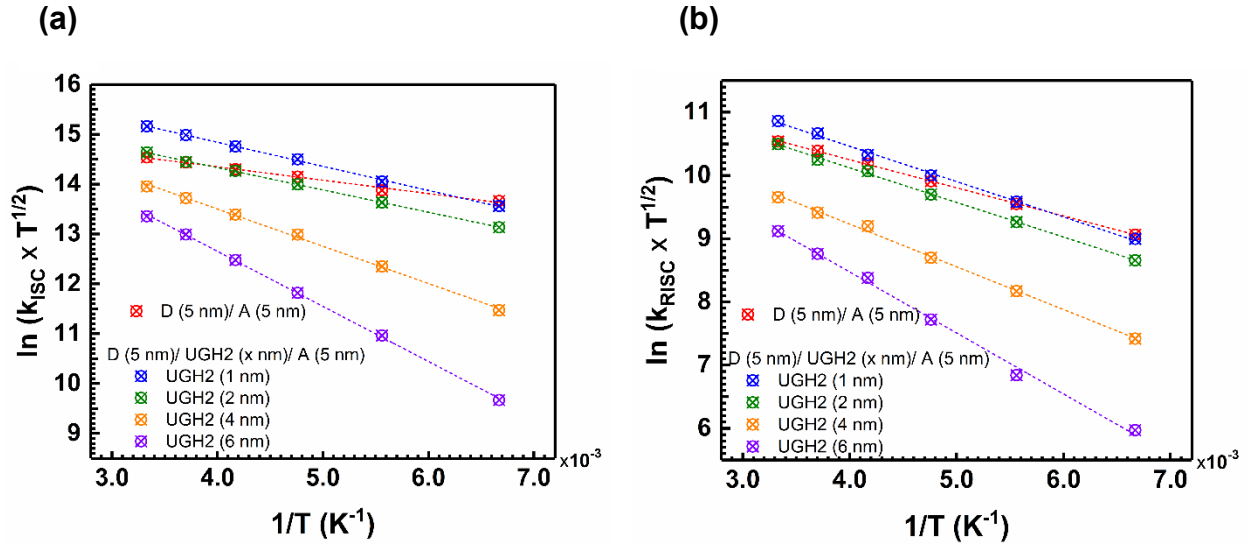


Figure 3.10. (a) Temperature dependence of k_{ISC} with the different spacer thickness. (b) Temperature dependence of k_{RISC} with different spacer thickness.

Using the obtained activation energies of E_a^{RISC} and E_a^{ISC} , I estimated the spacer dependence of ΔE_{ST} .⁹⁰ Here, we assumed that the RISC and ISC processes proceed through the same intermediate energy level (i.e., T_2) as shown in **Fig. 3.11a**. Thus, the ΔE_{ST} is given by the following equation,

$$\Delta E_{ST} = E_a^{RISC} - E_a^{ISC} \quad (3.2)$$

where E_a^{RISC} is the activation energy in the RISC process and E_a^{ISC} is the activation energy in the ISC process.

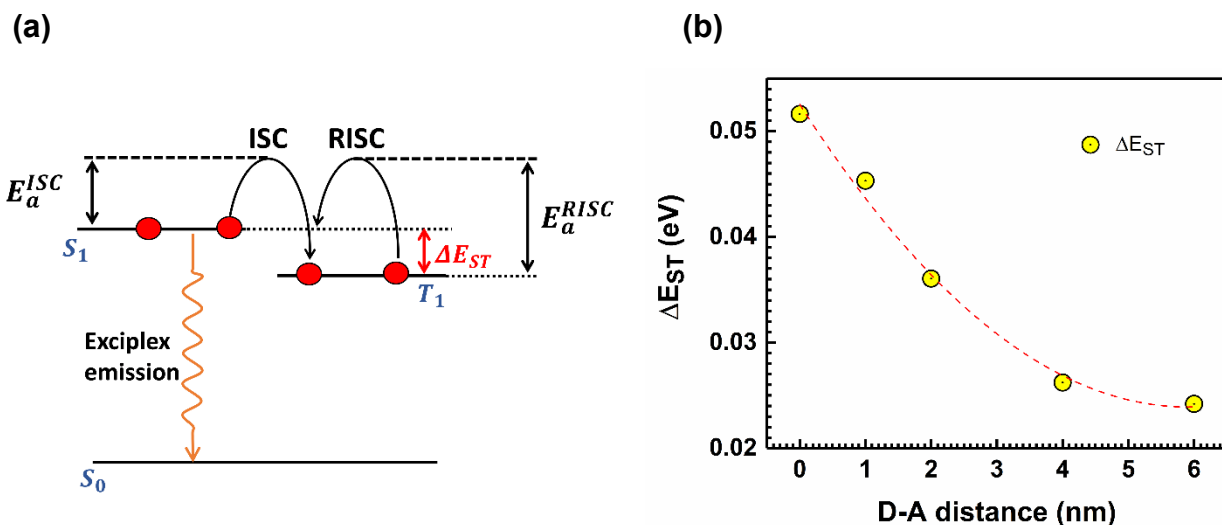


Figure 3.11. (a) The schematic energy diagram of exciplex with the possible route of ISC and RISC processes. (b) Estimated ΔE_{ST} with different spacer thicknesses.

Based on the ΔE_{ST} evaluation (**Fig. 3.11b**), I deliberate the characteristic behavior of through-space exciplex. In the case of $x=0$ nm, while the oscillator strength is rather large due to the relatively large overlap integral between the HOMO and LUMO, the ΔE_{ST} becomes large, resulting in a small k_{RISC} . With increasing the distance between the D and A layers, the electrostatic attraction gradually weakens and the smaller overlap integral between the HOMO and LUMO resulted in the decrease of ΔE_{ST} . Therefore, with the 1 nm separation, the balanced high k_{RISC} and ΔE_{ST} provided the highest PLQY in this system. Regarding 2 nm separation, k_r started to decrease, while k_{RISC} started to increase due to the smaller ΔE_{ST} . With a further increase of the S distance, k_r and k_{RISC} progressively decreased. In the case of 4 nm separation, a slight decrease of k_{RISC} suggests that triplets can overcome the activation barrier, resulting in the singlets effectively. However, slower k_{RISC} results in a long delay lifetime. Over the 4 nm separation, k_{RISC} steeply decreased, resulting in higher E_a . Due to the low k_r and k_{RISC} , triplets decayed nonradiatively.

3.4. Conclusion

In this research, I investigate the formation of an exciplex between TCTA and PO-T2T following the insertion of a UGH2 inert spacer layer. The interplay of k_r , k_{RISC} , ΔE_{ST} , and E_a resulted in a systematic change of exciplex characteristics in photophysical parameters, which I observed as the distinctive emission behavior. ΔE_{ST} becomes large when there is a big overlap integral between HOMO and LUMO, which places the D and A close to each other. Conversely, when the distance between the D and A molecules

increased, ΔE_{ST} decreased due to the smaller overlap integral between the HOMO and LUMO. However, further increasing the distance between them, k_r and k_{RISC} progressively decreased, suggesting an increase in the activation energy. At the 1 nm separation, the balanced k_r and ΔE_{ST} facilitated the appearance of the highest exciplex emission in this system.

Chapter 4

Summary and Outlook

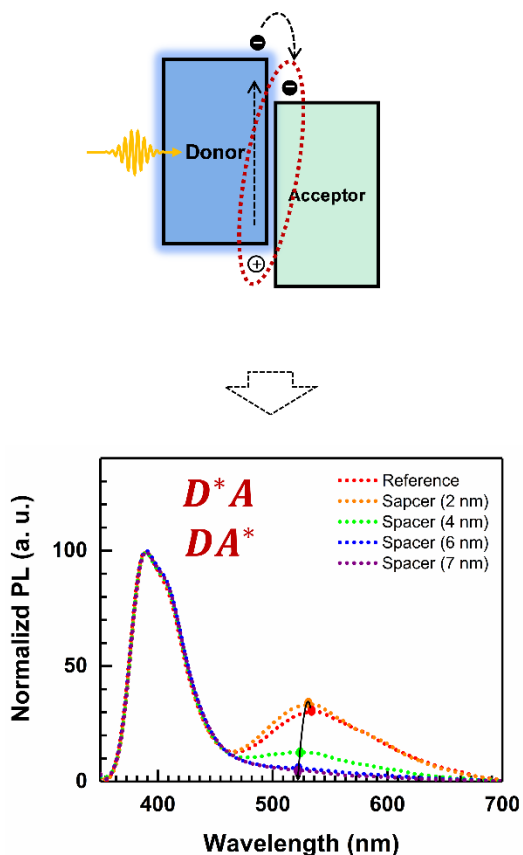
4.1. Summary

In summary, this thesis aimed to deepen the understanding of exciplex and long-range exciplex phenomena to enhance our comprehension and encourage engagement in inter-molecular charge transfer research. Through thorough examination and analysis, this study has provided valuable insights into the sophisticated mechanisms governing these phenomena, illuminating the fundamental principles underlying inter-molecular interactions and charge transfer processes. By clarifying the dynamics of exciplex formation and long-range exciplex behavior, this research emphasizes the significance of inter-molecular charge transfer as a critical phenomenon across various scientific disciplines, such as organic electronics, OPVs, and optoelectronic devices. The findings presented in this thesis not only advance our theoretical understanding but also carry substantial implications for the development of innovative technologies with enhanced functionalities and performance. Moreover, this thesis highlights the importance of collaborative endeavors and interdisciplinary approaches in pushing the boundaries of inter-molecular charge transfer research. In conclusion, it is expected that the findings of this study will renew interest and exploration in the scientific community, spurring more investigation into inter-molecular charge transfer. This could lead to significant progress in fields like materials science and chemistry.

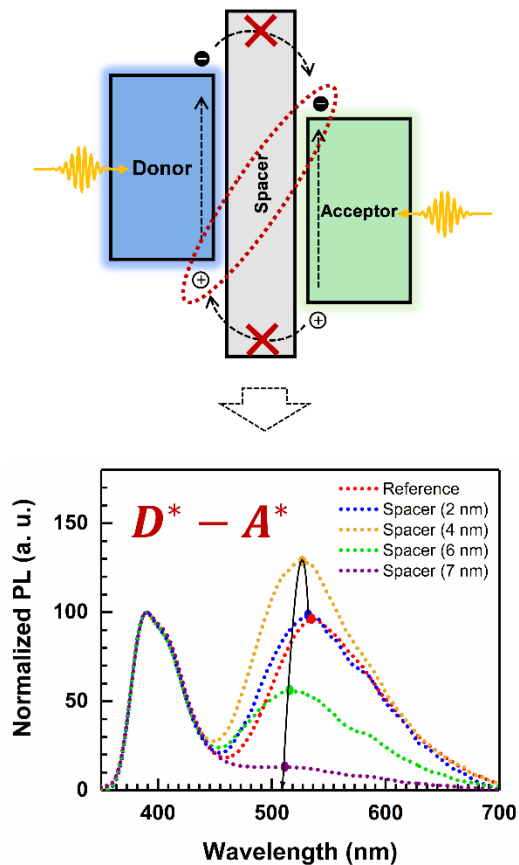
In Chapter 2, I aimed to evaluate the existing comprehension of exciplex systems and identify any shortcomings within the current exciplex framework. Through my analysis, I recognized a limitation in the current exciplex formula. Consequently, I introduced a novel term to enrich the existing exciplex equation and rectify this inadequacy. I validated a pioneering pathway for exciplex formation. This pathway arises from the simultaneous excitation of D and A molecules without direct electron transfer between them. Specifically, the utilization of a dual spacer layer comprising DPEPO/UGH2 facilitated the generation of a long-range exciplex *via* the simultaneous excitation of the D and A layers. My investigation involved the analysis of charge separation under reverse photocurrent flow. Additionally, I observed charge accumulation with sufficiently thick insulator layers. These observations provided compelling evidence supporting the occurrence of the dual excitation mechanism. This was further verified by the accumulation of electrons and holes within the D/S/A layers. Overall, the findings presented in **Chapter 2** contribute to advancing our understanding of exciplex formation mechanisms. By identifying and addressing limitations in the current exciplex framework, and by proposing and verifying a novel exciplex formation pathway, I believe I can enhance the ongoing scientific discussion on inter-molecular charge transfer phenomena. Thus, the component of the ($D^* \dots A^*$) state contributes to the exciplex wavefunction, leading to a modification of the exciplex equation as follows:

$$\psi([DA]^*) \approx c_4 \phi(D^* A^*) + c_3 \phi(D^* A) + c_2 \phi(DA^*) + c_1 \phi(D^+ A^-) + c_0 \phi(DA)$$

Conventional exciplex mechanism



Novel exciplex mechanism



$$\underbrace{\psi([DA]^*)}_{\text{Advanced description}} \approx \underbrace{c_4 \phi(D^*A^*)}_{\text{New term}} + \underbrace{\psi([DA]^*)}_{\text{Conventional description}}$$

Figure 4.1. Graphical representation of Chapter 2's result.

In **Chapter 3**, my primary focus lies in revealing the kinetics underlying long-range exciplex phenomena. While **Chapter 2** has utilized a long-range exciplex configuration to provide a novel perspective on exciplex formation, our understanding of the exciton dynamics in such systems remains limited. In this study, I delved into the behavior of a long-range exciplex system, particularly exploring the dynamics between D and A molecules' separation distances. Through detailed analysis, I identified distinctive emission characteristics resulting from the interplay of k_r , k_{RISC} , ΔE_{ST} , and E_a . This

comprehensive examination unveiled systematic alterations in exciplex properties across a spectrum of photophysical parameters. Significantly, my findings highlighted that at a separation distance of 1 nm, a delicate balance between k_r and ΔE_{ST} facilitated the appearance of exciplex emission within this system. This observation underscores the elaborate interplay between molecular dynamics and environmental factors in shaping the behavior of long-range exciplex systems, thereby enriching our understanding of these complex phenomena.

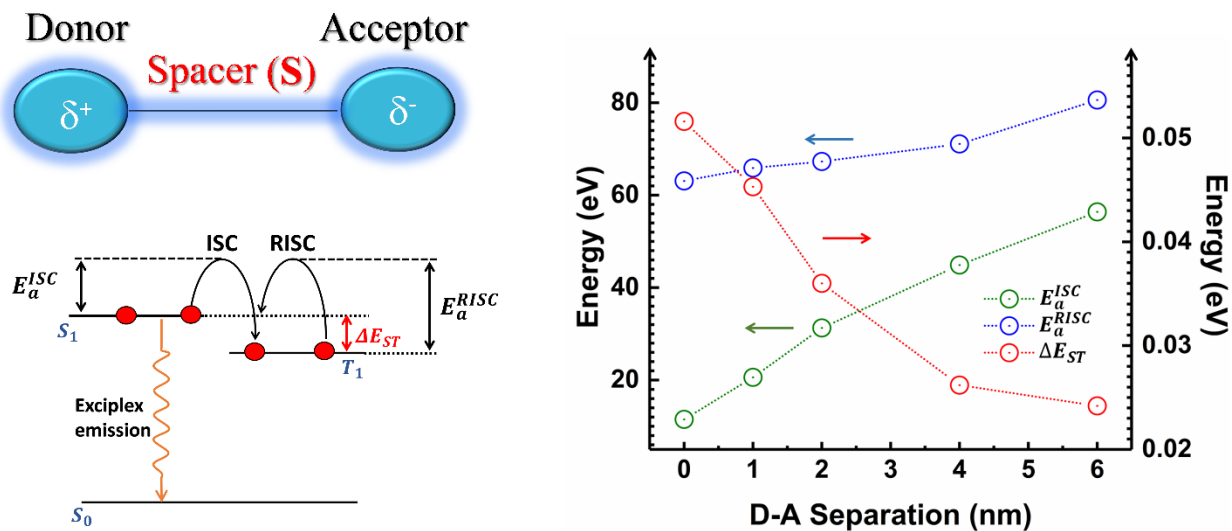


Figure 4.2. Graphical representation of Chapter 3's result.

4.2. Future perspectives

In the future, it is crucial to deepen our understanding of exciplex dynamics. Despite some progress, many aspects of long-range exciplexes formation and the exciton dynamics remain unclear. Future studies could use advanced spectroscopic and theoretical methods to uncover the optoelectronic characteristics involved in exciplex formation, such as charge separation and recombination. By gaining a better understanding of these processes, researchers can clarify fundamental aspects of exciplex behavior, which could lead to better control and use of these phenomena in different applications such as OPVs and OLEDs.

Until now, the literature on long-range exciplexes has failed to offer clear explanations for the different observations and inconsistencies associated with the selection of donor and acceptor materials. Consequently, future strategies should involve modifying donor-acceptor material pairings according to diverse optoelectronic characteristics, such as the spontaneous orientation polarization (SOP) effect, to better understand their impact on exciplexes and long-range exciplexes.

In **Chapter 2**, the recombination process in long-range exciplex systems highlights the significance of tunneling. Specifically, dual excitation scenarios are emphasized, yet there is a noticeable absence of prior research assessing the tunneling effect within these systems. Nevertheless, I hypothesize that tunneling represents a crucial factor contributing to the observed efficiency enhancements in exciplex systems characterized by short D-A separations. Therefore, I focus on conducting a comprehensive investigation into the tunneling effect specifically within long-range exciplex systems as part of my forthcoming research. From that work, I aim to provide a generalized understanding of the factors influencing long-range exciplex systems.

In **Chapter 3**, we utilized a single UGH2 spacer system to investigate the photophysical dynamics in a long-range exciplex system. However, our findings in **Chapter 2** highlighted the necessity of identifying the real exciplex phenomena, that effectively suppress charge transfer between the D and A through the spacer layer is essential. Because of that, to gain an accurate understanding of long-range exciplex dynamics, it is crucial to modify the excitation wavelength for temperature-dependent studies involving both D and A excitations. Because of that, in order to generalize findings from **Chapter 3**, I want to assess and contrast photophysical dynamics studies of dual excitation systems with suppressed charge transfer between D and A in the future.

Throughout this work, I contend with the persistent challenge concerning the low overall efficiency observed in exciplex emission. This limitation primarily stems from our focus on interface exciplex systems driven by the necessity for precise control over the D-A distance. The low efficiency of

previous studies on interface exciplexes has been a recurring problem.^{34,35} Researchers have suggested tandem architectures with several D-A interfaces to overcome the constraint.⁴⁷ By increasing charge generation and balancing, decreasing exciton quenching, increasing light extraction efficiency, optimizing charge transport, and providing material selection flexibility, tandem exciplex OLEDs have proven to be more efficient than bilayer systems.⁴⁷ Thus, my next research goal is to

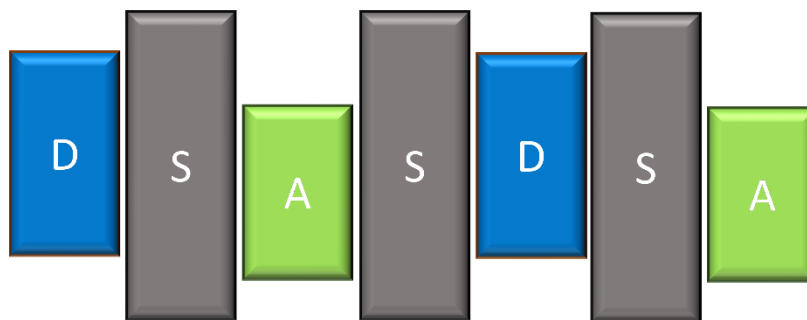


Figure 4.3. Graphical representation of tandem architecture to achieve maximum efficiency with precisely controlling D-A distance.

investigate a potentially useful strategy: using a tandem D/S/A/S/D/S/A architecture as a long-range exciplex system with precisely controlled S thicknesses (**Fig. 4.3**). I believe from this strategy I can clearly understand and clarify the D-A separation effect with highly efficient systems by enhancing efficiency further by improving the dynamics of charge generation and transport within the OLED structure. This research direction seeks to scientifically advance our understanding and capabilities in optimizing exciplex-based OLEDs, which could lead to breakthroughs in the use of long-range exciplex OLED technology across various disciplines.

The ultimate objective of this endeavor is to comprehend the mysterious facets of exciplex phenomena and use the insights gained to create extraordinarily effective OPVs, (**Fig. 4.4a**) and OLEDs (**Fig. 4.4b**) utilizing exciplex principles. With this endeavor, I hope to make a substantial contribution to our understanding of exciplex dynamics and apply this understanding to engineer next-generation photovoltaic and display technologies with enhanced performance and functionality.

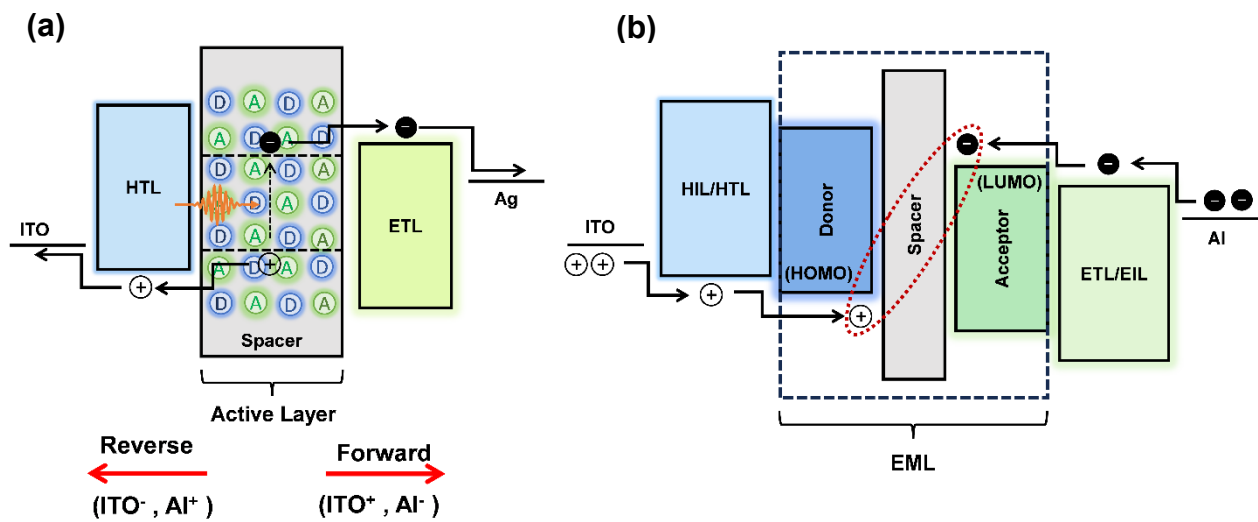


Figure 4.4. A schematic illustration of the (a) OPVs and (b) OLEDs architecture will be fabricated to enhance the performance and functionality.

References

- [1] Pierret, R. F. *Advanced Semiconductor Fundamentals*, Second Edition, vol. **1** (Pearson Education, Inc., 2003).
- [2] Sparkes, J. J. *Semiconductor Devices*. (Van Nostrand Reinhold (UK) Co. Ltd., 1987).
- [3] Sofo, J. O. & Mahan, G. D. *Phys. Rev.* **B 49**, 4565–4570 (1994).
- [4] Brütting, W. *Physics of Organic Semiconductors*. (Wiley-VCH, 2005).
- [5] Gaspar, D. & Polikarpov, E. *OLED Fundamentals: materials, devices, and processing of organic light-emitting diodes*. (CRC press, 2015).
- [6] Anthopoulos, T. D., Markham, J. P. J., Namdas, E. B., Samuel, I. D. W., Lo, S. C. & Burn, P. L. *Appl. Phys. Lett.* **82**, 4824–4826 (2003).
- [7] Chang, C. C., Hsieh, M. T., Chen, J. F., Hwang, S. W. & Chen, C. H. *Appl. Phys. Lett.* **89**, 253504 (2006).
- [8] Hager, M. D., Esser, B., Feng, X., Schuhmann, W., Theato, P., Schubert U. S. *Adv. Mater.* **32**, 2000587 (2020).
- [9] Schols, S. *Device Architecture and Materials for Organic Light-Emitting Devices*. (Springer, 2011).
- [10] Ha, J. M., Hur, S. H., Pathak, A., Jeong, J. E. & Woo, H. Y. *NPG Asia Mater.* **13**, 1–36 (2021).
- [11] Song, W. & Lee, J. Y. *Adv. Opt. Mater.* **5**, 1600901 (2017).
- [12] Sun, J., Ahn, H., Kang, S., Ko, S. B., Song, D., Um, H. A., Kim, S., Lee, Y., Jeon, P., Hwang, S. H., You, Y., Chu, C. & Kim, S. *Nat. Photon.* **16**, 212–218 (2022).
- [13] Chen, H. F., Yang, S. J., Tsai, Z. H., Hung, W. Y., Wang, T. C. & Wong, K. T. *J. Mater. Chem.* **19**, 8112–8118 (2009).
- [14] Uoyama, H., Goushi, K., Shizu, K., Nomura, H. & Adachi, C. *Nature* **492**, 234–238 (2012).
- [15] Sarma, M. & Wong K. T. *ACS Appl. Mater. Interfaces* **10**, 19279–19304 (2018).
- [16] Zhang, Z., Dou, D., Xia, R., Wu, P., Spuling, E., Wang, K., Cao, J., Wei, B., Li, X., Zhang, J., Bräse, S. & Wang, Z. *Sci. Adv.* **9**, eadf4060 (2023).
- [17] Yersin, H. *Highly Efficient OLEDs: Materials Based on Thermally Activated Delayed Fluorescence*. (Wiley-VCH, 2018).

- [18] Tanaka, H., Shizu, K., Miyazaki, H. & Adachi, C. *Chem. Commun.* **48**, 11392–11394 (2012).
- [19] Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, Third Edition (Springer-Verlag US 2006).
- [20] Su, Y., Wang, X., Wang, L., Zhang, Z., Wang, X., Song, Y. & Power, P. P. *Chem. Sci.* **7**, 6514–6518 (2016).
- [21] Turro, N. J., Ramamurthy, V., Ramamurthy, V. & Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction; University science books.* (2009).
- [22] Chen, T., Zheng, L., Yuan, J., An, Z., Chen, R., Tao, Y., Li, H., Xie, X & Huang, W. *Sci. Rep.* **5**, 10923 (2015).
- [23] Eng, J. & Penfold, T.J. *Commun. Chem.* **4**, 91 (2021).
- [24] Guo, J., Zhen, Y., Dong, H., & Hu, W. *J. Mater. Chem. C* **9**, 16843–16858 (2021).
- [25] Zhao, W., Cheung, T.S., Jiang, N., Huang, W., Lam, J. W. Y., Zhang, X., He, Z. & Tang B. Z. *Nat. Commun.* **10**, 1595 (2019).
- [26] Ieuji, R., Goushi, K. & Adachi, C. *Nat. Commun.* **10**, 5283 (2019).
- [27] Bossanyi, D.G., Sasaki, Y., Wang, S., Chekulaev, D., Kimizuka, N., Yanai, N. & Clark, J. *JACS Au* **1**, 2188 – 2201 (2021).
- [28] El-Sayed, M. A. *Acc. Chem. Res.* **1**, 8–16 (1968).
- [29] Gibson, J., Monkman, A. P. & Penfold T. J. *Chem. Phys. Chem.* **17**, 2956 –296 (2016).
- [30] Tang, X., Cui, L. S., Li, H. C., Gillete, A. J., Auras, F., Qu, Y. K., Zhong, C., Jones, S. T. E., Jiang, Z. Q., Friend, R. H. and Liao & L. S. *Nat. Mater.* **19**, 1332–1338 (2020).
- [31] Oh, C. S., Kang, Y. J., Jeon, S. K. & Lee J. Y. *J. Phys. Chem. C* **119**, 22618– 22624 (2015).
- [32] Jankus, V., Data, P., Graves, D., McGuinness, C., Santos, J., Bryce, M. R., Dias, F. B. & Monkman, A. P. *Adv. Funct. Mater.* **24**, 6178–6186 (2014).
- [33] Moon, C. K., Butscher, J. F. & Gathe M. C. *Adv. Mater.* **35**, 2302544 (2023).
- [34] Nakanotani, H., Furukawa, T. & Adachi, C. *Sci. Adv.* **2**, e1501470 (2016).
- [35] Pu, Y. J., Koyama, Y., Otsuki, D., Kim, M., Chubachi, H., Seino, Y., Enomotoa, K. & Aizawa, N. *Chem. Sci.* **10**, 9203-9208 (2019).
- [36] Weissenseel, S., Gottscholl, A., Bönnighausen, R., Dyakonov, V. & Sperlich, A. *Sci. Adv.* **7**, eabj9961 (2021).

- [37] Shao, J., Chen, C., Zhao, W., Zhang, E., Ma, W., Sun, Y., Chen, P. & Sheng, R. *Micromachines* **13**, 298 (2022).
- [38] Tang, C. W. & Van Slyke, S. A. *Appl. Phys. Lett.* **51**, 913–915 (1987).
- [39] Hong, G., Gan, X., Leonhardt, C., Zhang, Z., Seibert, J., Busch, J. M. & Bräse, S. *Adv. Mater.* **33**, 2005630 (2021).
- [40] Tamoto, N., Adachi, C. & Nagai, K. *Chem. Mater.* **9** (5), 1077–1085 (1997).
- [41] Wang, Q., Tian, Q. S., Zhang, Y. L., Tang, X. & Liao L. S. *J. Mater. Chem. C* **7**, 11329–11360 (2019).
- [42] Goushi, K., Yoshida, K., Sato, K. & Adachi, C. *Nat. Photon.* **6**, 253 (2012).
- [43] dos Santos, P. L., Ward, J. S., Bryce, M. R. & Monkman, A. P. *J. Phys. Chem. Lett.* **7**, 3341–3346 (2016).
- [44] Kominis, I. K. *Phys. Rev. Res.* **2**, 023206 (2020).
- [45] Wiltchko, R. & Wiltchko, W. *Biosensors*, **4**, 221–242 (2014).
- [46] Fukuzumi, S. & Ohkubo, K. *Photoinduced Reactions of Radical Ions via Charge Separation. In Encyclopedia of Radicals in Chemistry, Biology and Materials* (Wiley-VCH, 2012).
- [47] Palmisano, G., Augugliaro, V., Pagliaro, M. & Palmisano, L. *Chem. Commun.* **33**, 3425–3437 (2007).
- [48] Liu, D., Song, Y., Wang, H., Zhou, Z., Liu, Z. & Wang, T. *J. Mol. Struct.* **1313**, 138745 (2024).
- [49] Kabe, R. & Adachi, C. *Nature*, **550**, 385(2017).
- [50] Kim, K. H., Yoo, S. J. & Kim, J.J. *Chem. Mater.* **28**, 1936–1941 (2016).
- [51] Izumi, S., Higginbotham, H. F., Nyga, A., Stachelek, P., Tohnai, N., de Silva, P., Data, P., Takeda, Y. & Minakata, S. *J. Am. Chem. Soc.* **142**, 1482–1491 (2020).
- [52] Wu, T. L., Huang, M. J., Lin, C. C., Huang, P. Y., Chou, T. Y., Cheng, R. W. C., Lin, H. W., Liu, R. S. & Cheng C. H. *Nat. Photon.* **12**, 235–240 (2018).
- [53] Sarma, M., Chen, L. M., Chen Y. S. & Wong K. T. *Mater. Sci. Eng. R* **150**, 100689 (2022).
- [54] Cui, Y., Xu, Y., Yao, H., Bi, P., Hong, L., Zhang, J., Zu, Y., Zhang, T., Qin, J., Ren, J., Chen, Z., He, C., Hao, X., Wei, Z. & Hou, J. *Adv. Mater.* **33**, 2102420 (2021).
- [55] Yu, G., Gao, J., Hummelen, J. C., Wudl, F. & Heeger, A. J. *Science* **270**, 1789–1791 (1995).

- [56] Grosso, G., Graves, J., Hammack, A. T., High, A. A., Butov, L. V., Hanson, M. & Gossard, A. C. *Nat. Photon.* **3**, 577–580 (2009).
- [57] Yin, Y., Lai, X., Ma, Q., Ma, H., Zhu, W., Lee, J. Y. & Wang, Y. *Adv. Mater.* **36**, 2313656 (2024).
- [58] Moon, C. K., Suzuki, K., Shizu, K., Adachi, C., Kaji, C. & Kim, J. J. *Adv. Mater.* **29**, 1606448 (2017).
- [59] Kavarnos, G. J. & Turro, N. J. *Chem. Rev.* **86**, 401–449 (1986).
- [60] Kim, D. J. *Phys. Chem. C* **119**, 12690–12697 (2015).
- [61] Hontz, E., Chang, W., Congreve, D. N., Bulović, V., Baldo, M. A. & Van Voorhis, T. *J. Phys. Chem. C* **119**, 25591–25597 (2015).
- [62] Al Attar, H. A. & Monkman, A. P. *Adv. Mater.* **28**, 8014–8020 (2016).
- [63] Zhang, Q., Li, B., Huang, S., Nomura, H., Tanka, H. & Adachi, C. *Nat. Photon.* **8**, 326–332 (2014).
- [64] Holmes, R. J., D’Andrade, B. W., Forrest, S. R., Ren, X., Li, J. & Thompson, M. E. *Appl. Phys. Lett.* **83**, 3818–3820 (2003).
- [65] Graves, D., Jankus, V., Dias, F. B. & Monkman, A. P. *Adv. Funct. Mater.* **24**, 2343–2351 (2014).
- [66] Moon, C. K., Huh, J. S., Kim, J. M. & Kim, J. J. *Chem. Mater.* **30**, 5648–5654 (2018).
- [67] Lin, T. C., Sarma, M., Chen, Y. T., Liu, S. H., Lin, K. T., Chiang, P. Y., Chuang, W. T., Liu, Y. C., Hsu, H. F., Hung, W. Y., Tang, W. C., Wong, K. T. & Chou, P. T. *Nat. Commun.* **9**, 3111 (2018).
- [68] Gu, J., Tang, Z., Guo, H., Chen, Y., Xiao, J., Chen, Z. & Xiao, J. L. *Mater. Chem. C* **10**, 4521–4532 (2022).
- [69] Al Amin, N. R., Kesavan, K. K., Biring, S., Lee, C. C., Yeh, T. H., Ko, T. Y., Liu, S. W. & Wong, K. T. *ACS Appl. Electron. Mater.* **2**, 1011–1019 (2020).
- [70] Binbin, L., Gan, L., Cai, X., Li, X. L., Wang, Z., Gao, K., Chen, D., Cao, Y. & Su, S. J. *Adv. Mater. Interfaces* **5**, 1800025 (2018).
- [71] Yinghua, G., Lei, Y., Xuhong, Q., Youjun, Y. & Xiao, L. *Anal. Chem.* **95**, 9722–9728 (2023).
- [72] Menzel, J. P., de Groot, H. J. M. & Buda, F. *J. Phys. Chem. Lett.* **10**, 6504–6511 (2019).

- [73] Zhou, R., Jiang, Z., Yang, C., Yu, J., Feng, J., Adil, M. A., Deng, D., Zou, W., Zhang, J., Lu, K., Ma, W., Gao, F. & Wei, Z. *Nat. Commun.* **10**, 5393 (2019).
- [74] Roth, F., Borgwardt, M., Wenthaus, L., Mahl, J., Palutke, S., Brenner, G., Mercurio, G., Molodtsov, S., Wurth, W., Gessner, O. and Eberhardt, W. *Nat. Commun.* **12**, 1196 (2021).
- [75] Noguchi, Y., Miyazaki, Y., Tanaka, Y., Sato, N., Nakayama, Y., Schmidt, T. D., Brütting, W. & Ishii, H. *J. Appl. Phys.* **111**, 114508 (2012).
- [76] Noguchi, Y., Brütting, W. & Ishii, H. *Jpn. J. Appl. Phys.* **58**, SF0801 (2019).
- [77] He, S. J., Wang, D. K., Jiang, N., Tse, J. S. & Lu, Z. H. *Adv. Mater.* **28**, 649–654 (2016).
- [78] Liu, X. K., Chen, Z., Zheng, C. J., Liu, C. L., Lee, C. S., Li, F., Ou, X. M. & Zhang, X. H. *Adv. Mater.* **27**, 2378–2383 (2015).
- [79] Baldo, M. A., O’Brien, D. F., Thompson & M. E., Forrest, S. R. *Phys. Rev. B* **60**, 14422–14428 (1999).
- [80] Xia, Q., Xiang, Y., Gong, Y., Li, S., Wu, Y., Wang, Z. & Fu, H. *J. Mater. Chem. C* **11**, 635 (2023).
- [81] Sun, J. W., Lee, J. H., Moon, C. K., Kim, K. H., Shin, H. & Kim, J. J. *Adv. Mater.* **26**, 5684–5688 (2014).
- [82] Seino, Y., Inomata, S., Sasabe, H., Pu, Y. J. & Kido, J. *Adv. Mater.* **28**, 2638–2643 (2016).
- [83] Wang, Z., Wang, C., Zhang, H., Liu, Z., Zhao, B. & Li, W. *Org. Electron.* **66**, 227–241 (2019).
- [84] Ermilov, E.A. & Röder, B. *Photoinduced Electron and Energy Transfer. In Fundamentals of Porphyrin Chemistry.* (eds P.J. Brothers and M.O. Senge 2022).
- [85] Sun, N., Jiang, C., Li, Q., Tan, D., Bi, S. & Song, J. *J Mater. Sci.: Mater. Electron.* **31**, 20688–20729 (2020).
- [86] Schleper, A.L., Goushi, K., Bannwarth, C., Haehnle, B., Welscher, P. J., Adachi, C. & Kuehne, A. J. C. *Nat. Commun.* **12**, 6179 (2021).
- [87] Gould, I. R., Young, R. H., Muellern, L. J. & Farid, S. *J. Am. Chem. Soc.* **116**, 8176–8187 (1994).
- [88] Colella, M., Danos, A. & Monkman, A. P. *J. Phys. Chem. Lett.* **10** (4), 793–798 (2019).
- [89] Yersin, H., Czerwieniec, R., Mataranga-Popa, L., Mewes, J. M., Cheng, G., Che, C. M., Saigo, M., Kimura, S., Miyata, K. & Onda, K. *Adv. Funct. Mater.* **32**, 2201772 (2022).
- [90] Kim, H. B. & Kim, J. J. *J. Inf. Disp.* **20**, 105–121 (2019).

List of Acronyms

• A	Acceptor
• CB	Conduction band
• CRT	Cathode ray tube
• CT	Charge transfer
• D	Donor
• DCM	Displacement current measurement
• DF	Delayed fluorescence
• E_a	Activation energy
• EL	Electro luminescence
• EML	Emissive layer
• EQE	External quantum efficiency
• ET	Electron transfer
• ETL	Electron transport layer
• HOMO	Highest occupied molecular orbital
• HTL	Hole transport layer
• ISC	Inter system crossing
• k_{ISC}	Inter system crossing rate
• k_{RISC}	Reverse intersystem crossing rate
• LCD	Liquid crystal display
• LE	Locally excited
• LED	Light emitting diode
• LUMO	Lowest unoccupied molecular orbital
• MO	Molecular orbital
• Nd:YAG	Neodymium doped yttrium aluminum garnet
• OLED	Organic light-emitting diode
• OPV	Organic photovoltaic
• PCE	Power conversion efficiency
• PIET	Photo-induced electron transfer
• PL	Photoluminescence

- PLQY Photoluminescence quantum yield
- RIC Reverse internal conversion
- RISC Reverse intersystem crossing
- S Spacer
- SOC Spin orbital coupling
- TADF Thermally activated delayed fluorescence
- TTA Triplet-triplet annihilation
- VB Valency band
- VC Vibronic coupling
- ΔE_{ST} Singlet triplet energy gap

List of Publication

• Papers

- **Rajakaruna, T. P. B.**, Tang, X, Nakanotani, H., and Adachi, C. Unexplored Exciplex Formation Process by Dual Excitation of Donor and Acceptor Layers Optically and Electrically

Adv. Opt. Mater. 2401237 (2024). <https://doi.org/10.1002/adom.202401237>

- **Rajakaruna, T. P. B.**, Tang, X, Nakanotani, H., and Adachi, C. Spacer Dependence of Exciplex Dynamics in Donor/Spacer/Acceptor Layers

Chem. Phys. Lett. **848**, 141390 (2024). <https://doi.org/10.1016/j.cplett.2024.141390>

▪ Collaboration paper

- Tang, X., Tsagaantsooj, T., **Rajakaruna, T. P. B.**, Wang, K., Chen, X. K., Zhang, X., Hatakeyama, T., and Adachi, C. Stable pure-green organic light-emitting diodes toward Rec.2020 standard

Nat. Commun. **15**, 4394 (2024).

• Conference presentation/posters

- **Rajakaruna, T. P. B.**, Tang, X., and Adachi, C. Japan Society of Applied Physics (The 71st JSAP Spring Meeting 2024), Setagaya Campus, Tokyo City University, Setagaya, Tokyo (March 22 – 25, 2024). (Oral presentation).
- **Rajakaruna, T. P. B.**, Tang, X., and Adachi, C. KJF International Conference on Organic Materials for Electronics and Photonics 2023 (KJF-ICOMEF 2023, Centennial Hall, Kyushu University School of Medicine, Fukuoka, Japan (August 30 - September 2, 2023). (Poster presentation).

Acknowledgment

I wish to extend heartfelt gratitude to all individuals who have contributed to the completion of this thesis.

First and foremost, I would like to express my sincere gratitude to my supervisor, Professor Chihaya Adachi for his invaluable guidance, support, and encouragement throughout the entire research process. His expertise, insightful feedback, and unwavering commitment have been instrumental in shaping this work. I also would like to express my gratitude toward my co-supervisor Research Assistant Professor Xun Tang for his supervision, insightful discussions, and important suggestions throughout the research.

I am also grateful to the former members of the Adachi research group, now serving as a Professor at Sabaragamuwa University of Sri Lanka, who initially suggested and introduced me to the Adachi laboratory. It is truly a privilege for me to be associated with Adachi Laboratory.

I sincerely thank Professor Noritada Kaji and Professor Ken Onda for generously dedicating their time to review my work.

I am also indebted to Associate Professor Hajime Nakanotani, Research Associate Professor Yoichi Tsuchiya, Assistant Professor Kenichi Goushi, and Dr. Buddhika Karunathilaka for their collaboration, assistance, and expertise, which enriched the research outcomes.

I am grateful to all the Opera members for their encouragement, support, and fruitful discussions that have contributed to my academic growth and development.

Furthermore, I would like to acknowledge the Japanese Government for the financial support provided through the Monbukagakusho (MEXT) scholarship which compensates for all my expenditures and allows me to focus on my studies full-time.

Last but not least, I want to express my deepest gratitude to my parents, relatives, and friends for their unwavering love, encouragement, and understanding throughout this journey. Their support has been my source of strength and motivation.

Thank you all for your contributions, guidance, and support. This work would not have been possible without your support.

Tharindu P. B. Rajakaruna