FUNDAMENTAL CONCEPT OF PHOTOLUMINESCENCE SPECTROSCOPY

Abstract

A general introduction to photoluminescence spectroscopy is covered in this chapter. The technique of studying how electromagnetic radiation interacts with materials to disclose compositional or structural features is called molecular spectroscopy. It employs quantum numbers to discern between various energy states and divides radiation energy into areas. Using the Jablonski diagram, we covered the foundations of photophysics in the first section of the chapter. This article provides a brief overview of certain radiative transitions, such as phosphorescence and fluorescence, as well as non-radiative ones, such as internal conversion (IC), spin-forbidden intersystem crossover (ISC) processes, and vibrational relaxation (VR). The energy levels required for the absorption and emission of luminous materials are shown by the Jablonski energy diagram.. Stokes shift is one of the significant aspects of luminescence spectroscopy that we have covered. Energy loss and non-radiative transitions are involved in the processes of fluorescence and Stokes shift. We talked about thermally activated delayed fluorescence (TADF) in the next section. The TADF process's concept for design and mechanism have been thoroughly examined. The chapter's last section provides a brief overview of room-temperature phosphoresce (RTP). This section contains a brief explanation of El-Sayed's rule and the fundamentals of phosphorescence. Furthermore, a review was conducted on the thorough descriptions of the many approaches that have been employed in the literature to generate room-temperature phosphorescence (RTP).

Keywords: Photoluminescence Spectroscopy.

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I. INTRODUCTION

The study of how electromagnetic radiation interacts with materials (atoms or molecules) to create an absorption pattern that aids in deducing structural or compositional information is known as molecular spectroscopy. Electromagnetic radiation (EM) is divided into distinct regions according to the radiation energy of various molecular processes, as shown in Figure 1. In increasing frequency order, all energy states are quantized as discrete values. The sets of quantum numbers typically aid in the identification of the number and its relative energies in various regions of the electromagnetic spectrum.[1] Other discussions of quantum mechanics are outside the purview of this chapter, aside from the fact that the sets of quantum numbers determine the atomic and molecular energy.

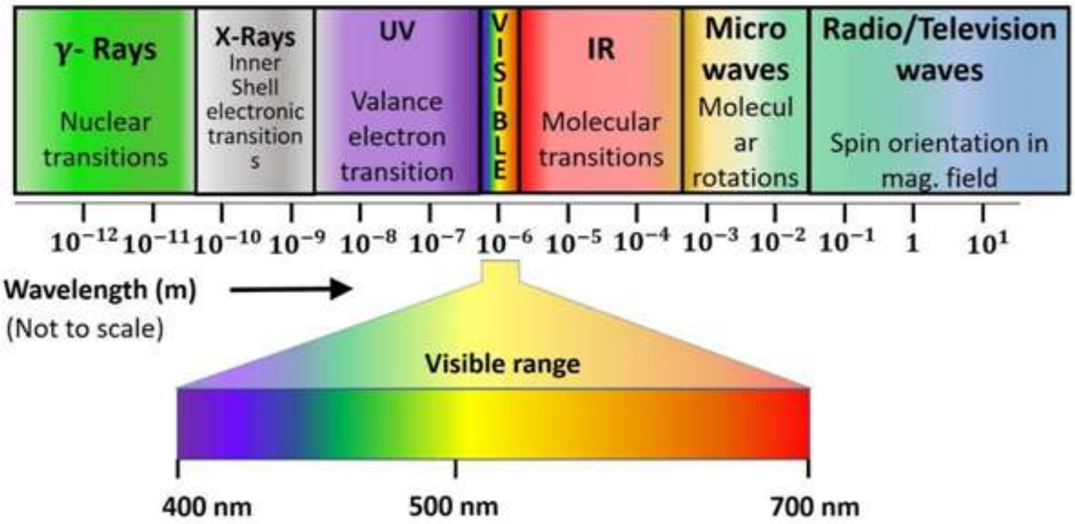

Figure 1: Electromagnetic Spectrum. The Visible Range is Zoomed in

A Jablonski energy diagram (Figure 2), so named in honor of the Polish physicist Professor Alexander Jablonski, serves as a general representation of the various energy levels required in the absorption and emission of luminescent materials [2] fundamentally, a Jablonski diagram is an energy diagram with the energy levels arranged along a vertical axis. For a specific species, each column depicts a different spin multiplicity (singlet or triplet). Straight arrows signify radiative transitions, while dotted, squiggly arrows signify non-radiative transitions. S0, S1, and S2 in figure 2, represent the singlet ground state, first excited singlet state, and second excited singlet state, respectively. Each electronic energy state contains a number of vibrational energy states that could be coupled with the electronic state (rotational energy states are disregarded).

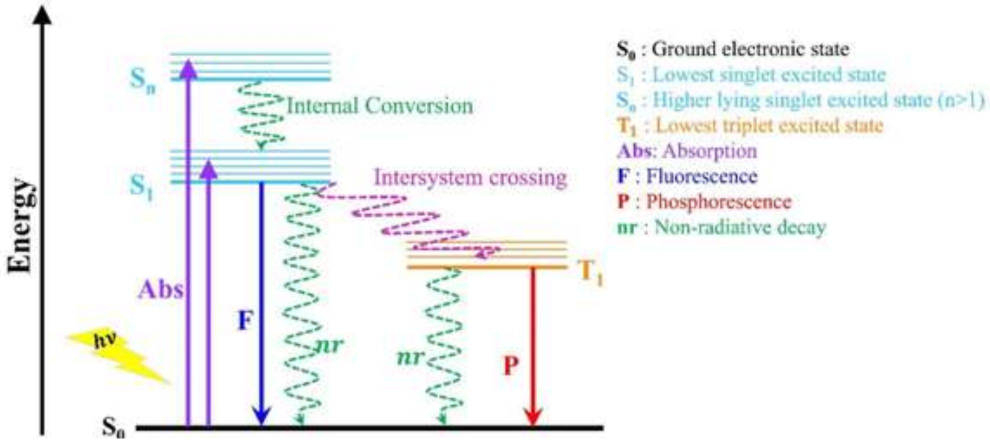

Figure 2: Schematic Representation of Jablonski Diagram

When a molecule is exposed to photons, light is quickly absorbed (femtosecond time regime). The molecule will move to a higher singlet excited state after being photo excited, but it won't be in an equilibrium state. Finally, it will release the energy it had built up and return to its relaxed state near the ground. It reaches the lowest vibrational level of the first excited state through a variety of non-radiation transitions like vibrational relaxation (VR) and internal conversion (IC), which is a radiationless transition between spins with the same multiplicity (Table 1). Fluorescence is the term used for a phenomenon where molecules deactivate from this state through a radiative transition. Stoke's shift is caused by the energy lost before fluorescence as a result of different non-radiative transitions, where absorption happens at a shorter wavelength than fluorescence.

Intersystem crossing, also known as ISC (A non-radiative transition between isoenergetic vibrational levels to different spin multiplicity), is another non-radiation transition that a photon can go through. ISC is, in theory, a spin-prohibited process. However, it is only marginally permitted due to spin-orbit coupling (SOC) between the orbital angular momentum and the Table 1. The lifetimes of various Transition. spin angular momentum. ISC is a very slow transition when compared to other depopulation transitions (Fluorescence or IC). However, following the ISC process, phosphorescence is the term used to describe any radiative transition from the triplet excited state to the ground state.[3] According to Kasha's rule, "luminescence (fluorescence or phosphorescence) only occurs with appreciable yield from the lowest excited state of a given multiplicity," emission typically takes place from the lowest excited state.[4-5]

Table 1: The Lifetimes of Various Transition

Transition	Timescale	Type
Absorption	10^{-15} s	Radiative
Vibrational relaxation (VR)	$10^{-12} – 10^{-10}$ s	Non-radiative
Internal conversation (IC)	$10^{-11} – 10^{-9}$ s	Non-radiative
Fluorescence	$10^{-10} – 10^{-7}$ s	Radiative
Intersystem crossing (ISC)	$10^{-10} – 10^{-6}$ s	Non-radiative
Phosphorescence	$10^{-6} – 10$ s	Radiative

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From the perspective of energy consumption, electroluminescence materials have garnered a lot of attention in the field of lighting technology in recent decades. The first electroluminescence (EL) device based on the 8-hydroxy aluminum (Alq3) combination with an external quantum efficiency (EQE) of less than 1% was reported by Tang and VanSlyke in 1987.[6] Spin statistics have revealed that upon electrical excitation, 25% singlet and 75% triplet excitons are produced. [7] Emission from the triplet excited state is crucial for capturing 75% of the available triplet excitons. By utilizing the strong spin-orbit coupling (SOC) of iridium (III), an efficient electro-phosphorescence device was produced in 1999 that had an effective decay rate of 106 s^{-1}. After that, there's an internal EL efficiency of 100% The internal EL efficiency of these complexes was quickly increased to 100%.[8] Despite the fact that this research achieved 100% external quantum efficiency, their practical utility is limited by cost and toxicity. Alternative, less expensive organic materials have been created that can capture triplet excitons under ambient circumstances in order to get around this problem. In the first section of this chapter, we covered a number of techniques for extracting singlet and triplet excitons from pure organic materials based on donor (D) and acceptor (A) conjugates, including thermally activated delayed fluorescence (TADF), room-temperature phosphorescence (RTP), dual emission, and mechanically altering the singlet-triplet energy gap (□EST).

II. THERMALLY ACTIVATED DELAYED FLUORESCENCE (TADF)

For molecular fluorescence, there are two unimolecular emission mechanisms: prompt fluorescence (PF) and delayed fluorescence (DF). Perrin was the first to observe DF in 1929 and gave them the names phosphorescence and longer-lasting fluorescence.[9] Later, DF was also noted in fluorescein, eosin, and aromatic hydrocarbons, respectively, by Magel et al.(1941), Hatchard et al. (1961), and Horrocks et al. (1968).[10-12] This long-lasting fluorescence was known as TADF in 1968 by Wilkinson and Horrocks.

In 1995, Harris and colleagues noticed that DF had dissolved in Acridine yellow in a hard saccharide glass.[13] In a 2007 study of DF in C70 fullerene, Berberon-Santos et al. demonstrated the inborn kinetics of the TADF emission. [14] Additionally, they noticed an increase in emission intensity in poly (tert-butyl methacrylate) (PtBMA) film up to 100 °C. In addition, they noticed an increase in emission intensity in the poly (tert-butyl methacrylate) (PtBMA) layer under an oxygen-free environment up to 100 °C. Six tin(IV)-porphyrin complexes (Figure 3) that demonstrated TADF and phosphorescence as a result of little energy splitting between the lowest ΔEST to harness TADF in these molecules were reported by Adachi et al. in 2009.[15]

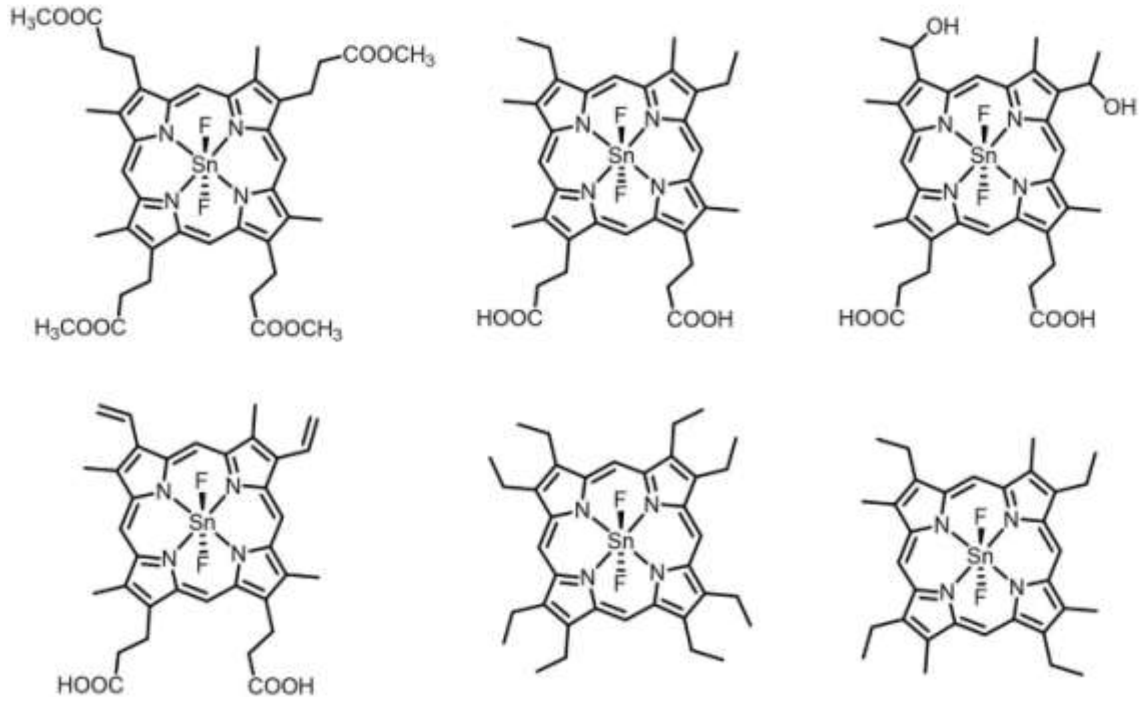

Figure 3: Molecular Structures of Tin (IV)-Porphyrin Complexes

III. MECHANISM AND DESIGN PRINCIPLE OF TADF MATERIALS

The quick fluorescence process and the inherent mechanism of TADF differ slightly. When T_1 is populated by ISC from S_1 to T_1, TADF occurs by reverse intersystem crossing (rISC) from T_1 to S_1 (Figure 4). The energy differential (ΔE_{ST}) between the S_1 and T_1 states is essential to the fundamental TADF process. Due to the high electron exchange energy between these levels, ΔE_{ST} is typically high for pure organic systems (0.5 to 1.0 eV). In accordance with equations 1 and 2, reducing EST will result in an efficient ISC or rISC rate.

$$k_{ISC} \propto \rightarrow \frac{<S_1|H_{SO}|T_1>}{\Delta E_{ST}} \qquad (1)$$

$$k_{rISC} \propto \rightarrow \frac{-\Delta E_{ST}}{k_B T} \qquad (2)$$

Low ΔE^{ST} can be attained by spatially separating D and A units coupling. The standard photophysics has been altered by this design method for harvesting triplet excitons through delayed fluorescence, which has also advanced the field of optoelectronic research.

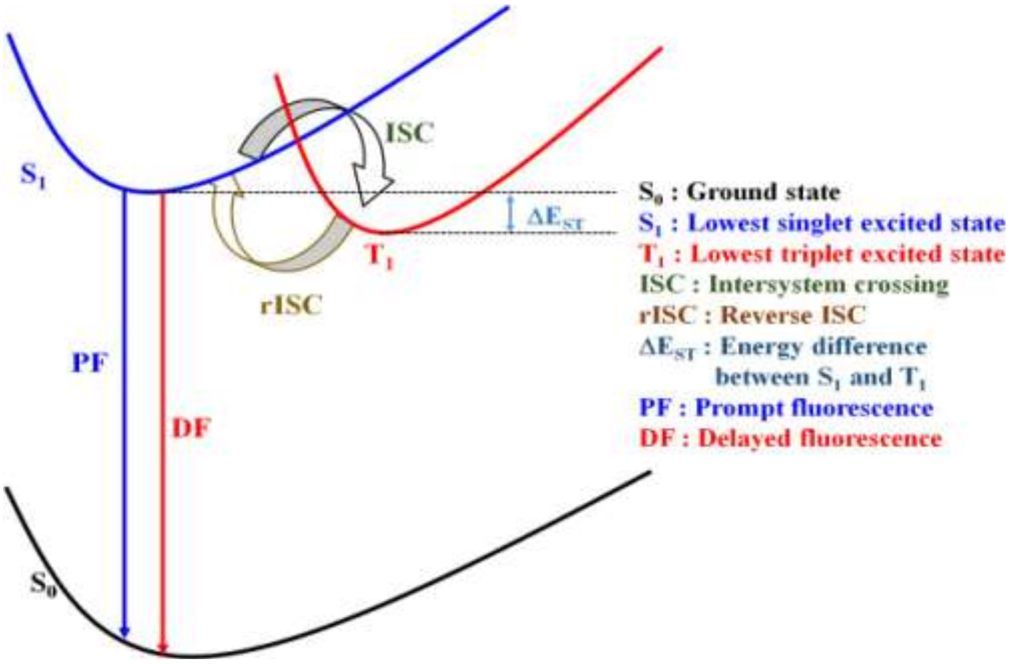

Figure 4: Jablonski Diagram of TADF

A general design approach and mechanism for the effective TADF materials were put forth by Adachi et al. in 2012.[16] Using carbazole as the donor and dicyanobenzene as the electron acceptor, a series of novel D-A conjugates with the TADF property were developed in this research and employed in EL devices (Figure 5).

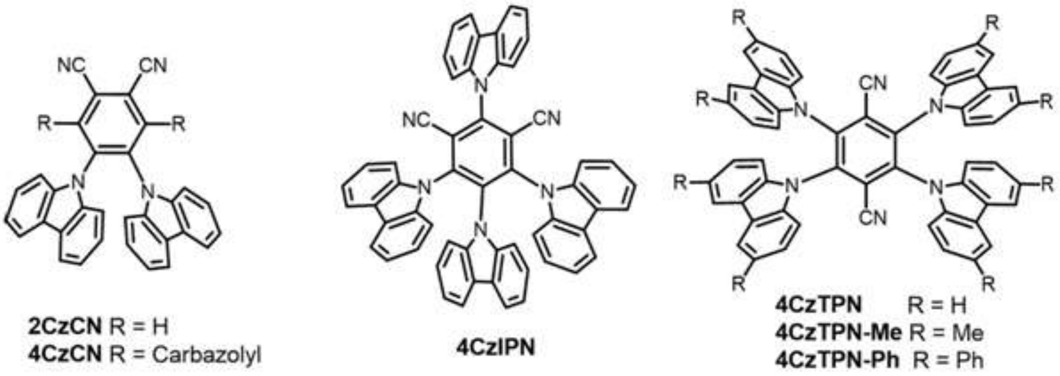

Figure 5: Molecular Structures of Czcn Moieties

Huang et al. provided a summary of a few design guidelines for D-A type TADF materials in 2015. [17] The authors of this article presented some recommendations for creating effective TADF materials, including: a) incorporating twist between D and A moieties to achieve small ΔEST; b) rigidifying the molecular structure to enhance radiative decay; c) -conjugation length; and d) redox potential between the D and A moieties along with the minimum conjugation between them. Additionally, when small ΔEST is taken into account, the overlap density (ρ10) distribution between the electronic wave functions of the ground state can be increased, which increases the photoluminescence quantum yield (PLQY) of the

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TADF materials, and the separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can increase the radiative decay rate from S1 to S0.[18-19] Several novel methods for separating the HOMO and LUMO of molecules with dual D and/or A units were also reported to achieve tiny ΔE^{ST} like Physical separation of D and A units, multiple resonance effect, X-shaped molecular structure, and physical separation of D and A units.[20-23]

IV. ROOM TEMPERATURE PHOSPHORESCENCE (RTP)

Due to the participation of longer-lived triplet states, which have been exploited in chemical- biological sensing, pure organic materials with RTP characteristics have drawn tremendous interest in the fields of chemistry, biology, physics, and material science. Organic light- emitting diodes (OLEDs), [24-25] security imaging[26-29], bioimaging[30-32], and photovoltaic technology[33–35] RTP materials are frequently based on inorganic oxides and heavy metal complexes[36-37], as is well known. According to photophysics, spin-forbidden transition is the source of phosphorescence. Effective ISC is necessary for the promotion of RTP to be successful. Spin-orbit coupling affects the rate of ISC.

Typically, organic phosphors display extremely weak ISC due to ineffective SOC transition, but inorganic phosphors and organometallic phosphors have fast ISC (104 s^{-1}). For organic lumiphores, the El-Sayed rule states that efficient ISC only happens in transitions from $^1(n,\pi^*)$ to $^3(\pi,\pi^*)$ and $^1(\pi,\pi^*)$ to $^3(n,\pi^*)$, when the molecular transition orbitals px and py nicely overlap under SOC. This rule is depicted in Figure 6.

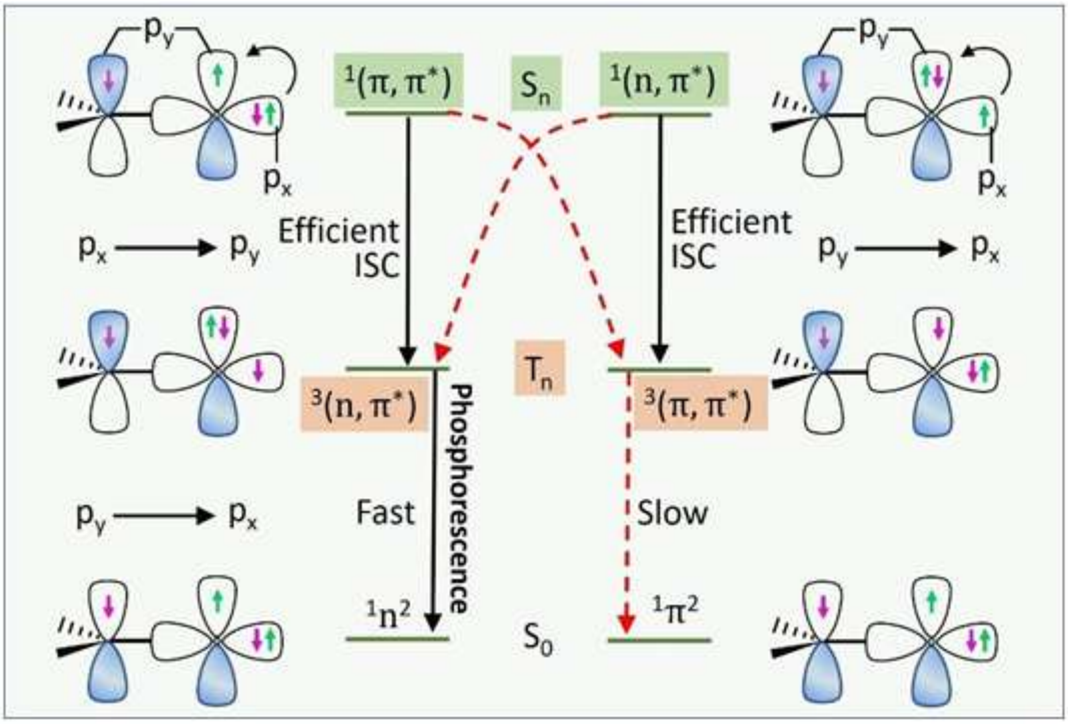

Figure 6: Schematic Representation of El-Sayed’s Rule for Efficient ISC

However, because of the ineffective SOC and inadequate orbital overlap, the ISC from $^{1}(\pi,\pi^*)$ to $^{3}(\pi,\pi^*)$ or from $^{1}(n,\pi^*)$ to $^{3}(n,\pi^*)$, is not permitted. Due to the permitted spin-flip transition from $^{1}(n,*)$ to $^{1}n^{2}$, T1 with a $^{3}(n,*)$ configuration can also quickly decay to S0, whereas T1 with a $^{3}(n,*)$ configuration has a very sluggish decay rate.

Pure organic materials without metals have recently received attention because of their affordability, low toxicity, simple processing requirements, and adaptable molecular structure. However, due to inefficient SOC and the sensitive nature of the localized triplet excitons, which easily get quenched under ambient conditions through vibrational and collisional processes as well as molecular oxygen, obtaining RTP from pure organic materials remains a bottleneck task. As a result, air-tight matrices and cryogenic (77 K) conditions are now necessary prerequisites for observing RTP.[38]

The use of dye-embedded silica gels, adsorption onto solid substrates, and the incorporation of dyes into cyclodextrins to lessen non-radiative pathways of the triplet excitons have all been used to get around these problems. These studies' weak emissions, however, put some restrictions on them.[39] Persistent RTP in difluoroboron dibenzoylmethane polylactide was reported by Zhang et al. in 2007.[40] Benzophenone and its derivatives exhibit crystalline- induced phosphorescence (CIP) at RT as Tang et al. discovered in 2010.[41] This observation further widened the scope for looking for fresh RTP content. RTP in pure organic luminogens can be made possible by halogen bonding, as demonstrated in 2011 by Kim and colleagues. [42]

Since then, it has been reported that RTP from pure organic materials can be observed through the use of crystallization, doping into rigid matrix[43], intermolecular interaction, singlet fission, etc.[44]

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