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Organic Solid - State Lasers

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Abstract: ***Various facets of human existence have been affected by lasing ap - plications. New laser technologies are in high demand to match the laser industry's evolving tendencies toward being tiny, portable, and highly integrated. Because of their simple processing procedures, ease of spectral and chemical adjustment, low refractive indexes, mechanical flexibility, and low thresholds, organic semiconductors are potential gain medium options for innovative laser systems. Organic solid - state lasers (OSSLs) open up a new horizon of simple, low - cost, time - saving, versatile, and environmentally friendly manufacturing technologies for new and desirable laser structures (micro-, asymmetric, flexible, and so on), allowing semiconductor lasers to reach their full potential in future electronics. The design of the organic gain medium is also examined in terms of opportunities, problems, and future research prospects.***

Keywords: lasers, organic semiconductors, future electronics, low-cost manufacturing, environmental friendliness

1. Introduction

Since the discovery of laser oscillation about sixty years ago[1], laser applications have spread across a wide range of fields, including scientific research, pharmaceutical manufacturing, and telecommunications. The advancement of newer laser techniques requires the creation of new materials. Organic semiconductors have gotten a lot of attention in recent years because of their large - area and low - cost manufacturing via solution processing, as well as their tunable optoelectronic properties thanks to the easy molecular design, which make them potential materials for a variety of applications like organic light - emitting diodes (OLEDs) 2 - 5 organic solar cells (OSCs) organic thin - film transistors (OTFTs) and organic solid - state lasers (OSSLs) A wide range of organic semiconductors has been investigated, paving the way for organic electronics to advance quickly. Extensive research has been done to promote OLEDs as flat - panel displays and solid - state lighting emitters in commercial applications. OSSLs, particularly organic semiconductor lasers (OSLs), as an - other significant class of organic light emitters and the anticipated successor to OLEDs, have been a new and demanding research field. Organic semiconductors are compatible with a wide range of optical resonators, and in many situations, the optical resonators can be directly combined with organic gain media, resulting in versatile and relatively low - cost laser devices.
Rest of the paper is organised as follows:

- Section 2 presents Organic semiconductor laser architectures.
- Section 3 presents organic gain media
- Section 4 challenges in electrically pumping organic lasers
- Section 5 conclusion and future work

2. Organic Semiconductor Laser Architecture

2.1 Building blocks

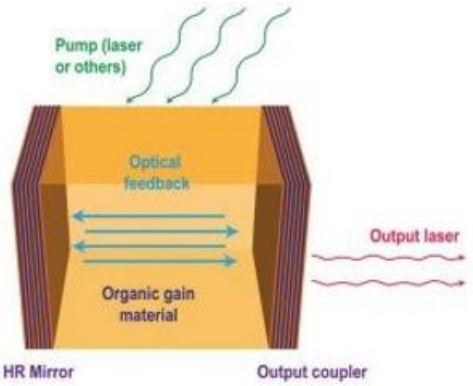

Figure 1: The principal building blocks of a laser: a pumping source, an optical feedback structure, and a gain medium

Organic lasers, like all other lasers, are made up of three main components: a pumping source, an optical feedback structure, and a gain medium. The basic characteristic of an organic laser is the organic gain medium, which is usually a p - conjugated organic molecule. Organic molecules are intensively researched as optical gain media for organic lasers to fully explore the potentials of organic lasers, such as simple processing, mechanical flexibility, and bio - compatibility. Gain media with specified geometries can, in fact, operate as optical feedback structures on their own. As far as we're concerned, light trapped within the feedback structure needs to be amplified for laser operation, which is essential to reduce any loss involved in the entire process. A traditional laser design, as shown in fig 1, comprises of two mirrors for optical feedback and organic gain media filling the interior area. Organic semiconductors' spontaneous emission could be reflected back and forth between the mirrors in a little amount. Light can induce stimulated emission and hence be enhanced by the interactions of excitons in organic gain media in their excited states. A continuous photon avalanche will occur if the light amplification exceeds the optical losses that are normally caused by cavity defects and gain medium absorption.

2.2 Quasi four - level laser structure of organic semiconductors

To accomplish effective population inversion, multiple -

level lasing systems must be built in order to realize efficient lasing output from an integrated optical feedback structure. Because of their intrinsic quasi four - level lasing systems, organic gain mediums are often beneficial. As seen in Fig.2, organic materials are often high in energy

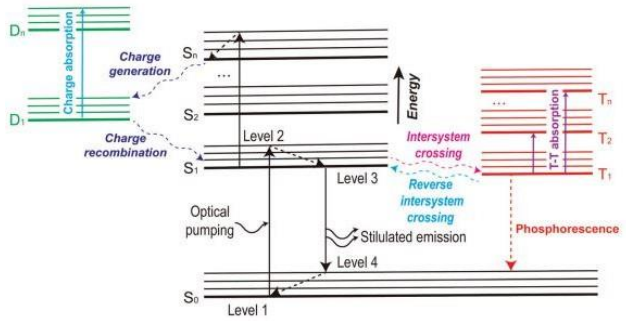

Figure 2: Energy level diagram of an organic semiconductor, showing singlet excitons, triplet excitons and charges.

levels, resulting in the formation of numerous stimulated radiative channels as a result of electronic vibration coupling. In fact, most organic emitters have a system that is similar to a four - level system. The excitons are excited from the electronic ground state (S0, level 1) to the initial electronic excited state (S1, level 2), followed by a quick vibrational relaxation process to the lowest vibrational level of S1 in the case of optical pumping (level 3). The population inversion commonly happens from level 3 to one of the upper vibrational levels of S0 due to the short lifetime from level 2 to level 3 (less than a picosecond) (level 4). It takes a long time for vibrational relaxation to return to level 1, which precludes any major exciton population from forming in level 4. Given the inevitability of optical loss in gain media and integrated optical devices, organic emitters' intrinsic four - level structure is significantly more beneficial for ensuring ini - tial sufficient optical gain for creating effective lasing output. Cavity scattering, ground - state self - absorption, charge absorption, triplet excited state absorption, and other undesirable losses exist. These losses can cause absorption in the lasing/amplification wavelength area, lowering lasing output energy and/or halting it altogether. As shown in fig2, singlet excitons can flip their spins to the lowest triplet excitation state (T1) via intersystem crossing (ISC), which is generally lower in energy and allows them to accumulate due to the significantly longer triplet - state lifetime than S1. Unfortunately, the triplet–triplet absorption band overlaps the singlet fluorescence emission band and is rather large. Due to triplet–triplet absorption and S1 population reduction via singlet–triplet annihilation, long - lived triplet excitons can cause optical losses for light amplification.

2.3 Amplified spontaneous emission (ASE)

ASE characterisation is a quick and easy way to compare the gain characteristics of different materials without having to worry about cavity effects. The stimulated emission amplification happens in the gain medium without the use of an optical feedback structure when the population inversion is generated in the quasi four - level system. Through further stimulated emission, a photon avalanche known as ASE will occur. Without an optical feedback structure, ASE characterizations can be performed to estimate the available gain. Aside from that, the variable stripe length (VSL) approach collects ASE intensity from the sample's edge as a function of stripe length. Shaklee et al. originally reported it in the nitrogen laser. To examine the gain characteristics of organic gain media, the VSL approach has been widely employed. The usual gains of organic gain medium measured with the VSL method vary from 100 to 102 cm^{-1}.

3. Organic Gain Media

For decades, organic dyes dissolved in liquid solvents have been investigated for lasing applications. Close packing of organic pigments, on the other hand, frequently causes luminescence to self - quench. OSSLs can also be made by doping colors into non - conjugated polymers like polystyrene (PS) and PMMA. Because "organic dye lasers" and "OSLs" have essential similarities, it is critical to identify these materials. The search of electrically pumped lasers has historically prompted the differentiation between dyes and organic semiconductors. The majority of organic laser pumping sources are still optical devices, and their semiconducting properties have not been completely investigated. In certain instances, it appears that distinguishing dyes from organic semiconductors based on their electrical characteristics is pointless. In this review, we use Samuel et al classification. 's system to classify organic dyes and organic semiconductors. To build a division for organic semiconductors, three properties are proposed: I facile processing in thin film pro - duction, (ii) high PLQY even in tidy film, and (iii) charge transfer capability. This section explains the development of organic gain media, including organic dyes, fluorescent organic semiconductor emitters etc.

3.1 Organic dyes

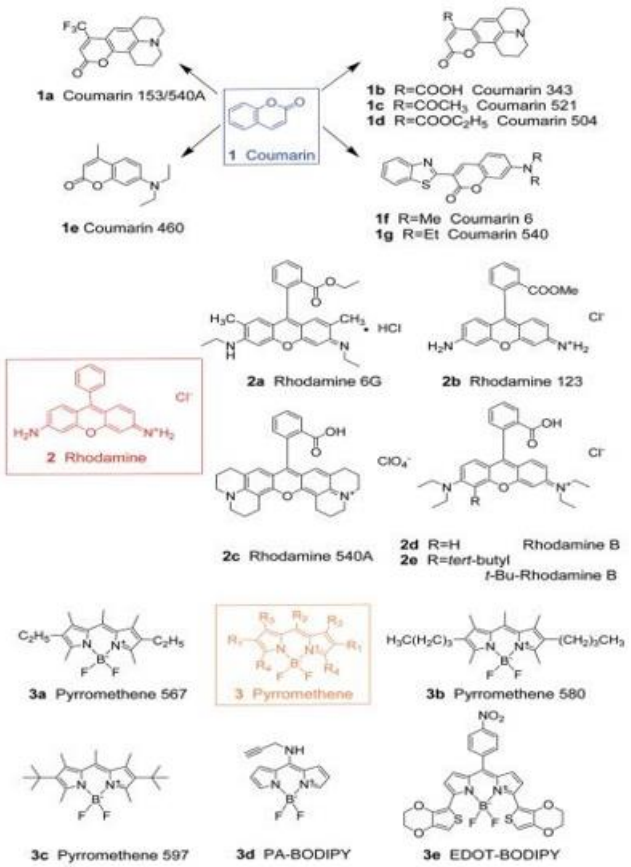

Figure 3: Dye examples, including coumarin dyes, rhodamine dyes and pyrromethene dyes

In the traditional meaning, an organic dye is a substance that may color another substance. Organic dyes have a spectral absorption band that ranges from ultraviolet (UV) to near - infrared (NIR). Mul - tiple conjugated double bonds are present in all of these compounds, which substantially limit their spectral characteristics and chemical reactivities. The large variety of chemical configurations that can operate as laser dyes is one of the major reasons for the emergence of dye lasers. Laser dyes emit light across the whole visible spectrum, as well as the near UV and NIR spectral regions. The categories based on their chemical structures are usually used as laser dyes. The main laser dye series are coumarins (1), xanthenes (2), and pyrromethenes (3).

The xanthene family, particularly the high - efficiency rhodamine dyes, has been frequently employed throughout history (rhodamine 640, rhodamine 6G, etc.). Dyes have been studied more extensively for lasing applications with improved performance and photostability in recent decades. Coumarin dyes are a significant family since their emission ranges from violet to green. A generic coumarin is made up of a cyclobenzene and a pyrone, with numerous substituents connected to the basic core, as shown in figure 3. Xanthenes are a class of dyes including rhodamines, eosins and fluorescein. These molecules emit with high efficiency and good photostability in the green to red spectral region.

Two benzene rings with a pyran ring in the middle make up the fundamental core of rhodamine dyes (2a–2e) (see in Scheme 1). Rhodamine 6G (2a) is one among them, and it's frequently used as a benchmark for other laser dyes. Rhodamine 6G has a strong singlet– singlet absorption, with a molar extinction coefficient of 1.1 105 l mol1 cm1 at 540 nm. However, triplet–triplet absorption, which is one of the primary difficulties for organic lasers, is insignificant.

Pyrromethene dyes (3a–3e) are a novel type of laser dye that was developed recently. Figure 3 illustrates their chemical structures. The fundamental unit structure is made up of two pyrroles joined by a BF2 group and a stiff methylene. Pyrromethene dyes surpass rhodamine 6G in terms of solubility in organic solvents (or polymer matrixes), thermal stability, and PLQYs (40.9). They also have lower rates of intersystem crossing (2a). Furthermore, pyrromethene dyes have a wide range of functional locations, and the connected end - cappers have a considerable impact on fluorescence and stimulated emission characteristics.

Organic semiconductors are far more suitable for lasing applications than organic dyes, thanks to their ease of chemical functionalization, low lasing thresholds, and semiconducting electrical characteristics. Various organic semiconductors have been examined and explored for lasing applications, which will be covered in detail in the following section. Organic dyes are a convenient and unique choice for generating controllable coherent radiation in the visible and near - infrared spectrum bands due to their ease of synthesis. Nanowire lasers, random lasers, and multi - photon pumped lasers have all been described recently using doped laser dyes as emitters.

3.2 Fluorescent organic semiconductor materials

Tang and Van Slyke of Kodak invented the first thin - film OLED with Alq3 as the emitter in the late 1980s. The rapid advancement of OLEDs has transformed our understanding of the link between molecular architectures and optoelectronic capabilities of organic

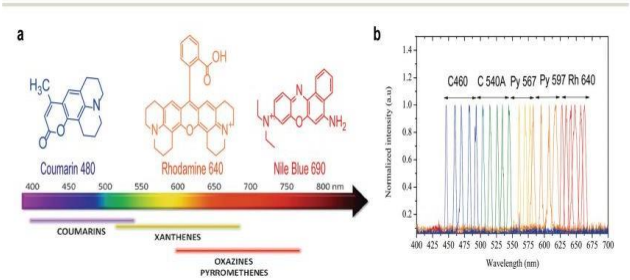

Figure 4: (a) Wavelength tunable range for some dye families. (b) Tunable lasing results from five doped - emitters, i. e., coumarin 460 (C 460), coumarin 540 A (C 540A), pyrromethene 567 (Py 567), pyrromethene 597 (Py 597), and a blend of rhodamine 640 (Rh 640) and C 540A

semiconductor materials, resulting in extraordinary advances in OSLs. A variety of materials have been identified as organic gain medium thus far. Organic crystals, amorphous tiny molecules, dendritic starburst molecules, conjugated polymers, and other fluorescence materials for OSLs are the most common.

In the sections that follow provides an overview of recent achievements and highlight fluorescent organic gain materials with exceptional behavior and performance. T We describe the emission wave - lengths, needed energy densities

at thresholds (areal energy densities, areal power energy densities), and gain values of the gain media based on data gathered from most papers. The section also discusses about gain materials, focusing on crucial optoelectronic parameters such as PLQY, full width at half maximum (FWHM), ASE/lasing energy density at threshold, optical gain, and the other necessary values.

3.2.1 *Organic crystals*

Organic crystals, as opposed to amorphous materials, have long - range molecular order, which allows for high anisotropy and a well - defined crystalline structure to form a self - laser cavity, resulting in improved thermal and photochemical stability, superior charge - carrier transport properties, larger refractive indexes, and polarized emission. Most current organic crystals, such as oligothiophenes, oligophenylenes, thiophene–phenylene co- oligomers (TPCOs), oligophenylene vinylenes (nPVs), fluorene/ phenylene co - oligomers, cyano derivatives, etc., have poor ASE or lasing capabilities. Crystal quality, molecule stacking, and intermolecular interactions may all play a role in amplification (or lasing) behaviour in organic crystals.

3.2.2 *Amorphous small molecules*

Column chromatography can produce fluorescent small molecular compounds with well - defined molecule structures and high purities (i. e., without evident catalyst residues, side products, or chemical flaws). Thermal evaporation can be used to make small molecular films since their molecular weights are low (typically less than 1000 Da). The obtained tiny molecules are ideally suited for creating amorphous smooth films by solution method with good uniform optical and waveguide properties due to the incorporation of suitable solubilizing side groups.

3.3 Triplet gain media and triplet sensitizers

Fluorescence, phosphorescence, and TADF are the three basic emission mechanisms for organic light sources that are currently available for attaining efficient light output. Fluorescent materials dominate the existing organic gain media. In carrier recombination, a 1: 3 ratio

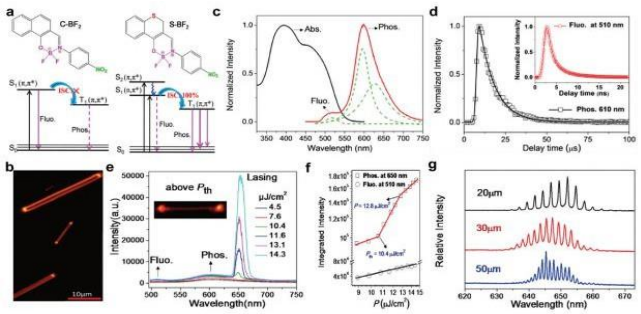

Figure 5: (a) Chemical structures and energy level diagrams of S - BF2 and C - BF2. (b) PL microscopy image of S - BF2 nanowires. (c) Absorption and PL spectra of S - BF2 nanowire. (d) Transient PL of S - BF2 nanowire monitored at the fluorescence region (red, inset) and the phosphorescence region (black). (e) Emission spec - tra under different pump densities in a single 38 mm length S - BF2 nanowire. (f) Dependence of output intensity on pump - ing density in the fluorescence band and the phosphorescence band, monitored at 510 nm and 650 nm, respectively. (g) High - resolution lasing spectra for S - BF2 nanowires with lengths of 20, 30, and 50 mm. Reproduced with permission from ref.40.
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for singlet and triplet excitons is expected, implying that 75 percent of produced excitons are blocked for the contribution of the singlet population in fluorescence emitters, according to spin statistics. As a result, under current injection, internal electroluminescence (EL) quantum efficiency (IQE) in organic light - emitting devices, such as OLEDs, would be limited to a maximum of 25 Phosphorescent and TADF materials are especially intriguing since all generated excitons, including singlet and triplet excitons, might theoretically be captured as EL. To achieve electrically pumped OSSLs, a very high current density (a few kA cm^{-2}) is required. If the 75 percent triplet excitons could be efficiently used, the injected current density beyond the lasing threshold for electrically pumped OSSLs might be greatly reduced. In most circumstances, no ASE occurs during the pumping process because the value of the excited - state absorption cross - section for phosphorescent (or TADF) emitter is substantially bigger than the maximum stimulated emission cross - section.

Yu et al. reported the single example of phosphorescence laser. Unlike most phosphorescent metal - complex molecules, the phosphorescence was obtained by (E) - 3 - ((4 - nitrophenyl) - imino) methyl) - 2H - thiochroman - 4 - olate BF2 (S - BF2, 255), a sulfide substituted difluoroboron compound (Fig.5a).

S - BF2 reversed the lowest singlet p–p* electronic transition by n–p* transition as compared to the non - substituted molecule (E) - 2 - ((4 - nitrophenyl) vimino) methyl) - naphthalen - 1 - olate BF2 (C - BF2) (Fig.5a). In stark contrast to C - prohibition BF2's of ISC from S1 (p, p*) to T1 (p, p*), T1 (p, p*) 'S1 (n, p*) ISC was found in S - BF2 with 100 percent efficiency. With the help of the nitro moiety, the ICT character was inserted into S - BF2, resulting in a moderate phosphorescence efficiency of 10 percent. Solution self - assembly was used to make S - BF2 single - crystalline nanowires.

The nanowires emitted a strong yellow - red emission and operated as an effective optical waveguide with vivid PL from the end tips, as illustrated in Fig.5b and c. With a PL peak at 510 nm (Fig.5d), which corresponds to fluorescence emission, a fast decay lifespan of 2.3 ns was measured. Phosphorescence emission was attributed to another emission peak of S - BF2 nanowire at 610 nm with a decaying lifespan of 9.3 ms (Fig.5d). The fabrication of the Fabry–Perot microcavity in the nanowire resulted in a lasing output of 650 nm in the 30 mm length nanowire (Fig.5e).

At 10.4 mJ cm2, the development from phosphorescence radiation to narrowed spontaneous emission began, and as the pumping energy increased above 12.8 mJ cm2, lasing oscillation ensued (Fig.5f). Individual cavity mode FWHM was around 0.76 nm, with a lasing peak around 650 nm, yielding a cavity quality factor of Q E. By extending the nanowire lengths, more modes in the nanowire lasing spectra were observed (Fig.5g). The value of mode spacing as a

function of 1/L was shown to have a linear relationship (L is the twice fold of nanowire length). Exploring phosphorescence gain medium for tackling the problems of OSL diodes was a significant step forward in this research (OSLDs).

3.4 Summary

This section summarizes current developments in the field of organic gain media, such as organic dyes, fluorescent semiconductor emitters, triplet gain media, and so on. The vast majority of gain media are fluorescent semiconductor emitters. On the basis of several specific building blocks, such as fluorene units, p - phenylene vinylenes, and others, promising optical features, such as low ASE/lasing thresh - olds, have been proven. However, there is currently no general principle for determining if an organic material is acceptable for use as an organic gain medium in lasing applications.

Developing effective ways to investigate robust gain media for OSSLs, particularly for electrically pumped OSLs, is still highly desirable but extremely difficult. Stimulated emission is essentially predicated on the creation of a quasi four - level lasing system.

Theoretical calculations could be used to investigate the funda - mental mechanism of stimulated emission. To get insight into ASE phenomena, the vibrational levels of the electronic ground states are simulated. The creation of the quasi four - level energy system is hampered by the low - frequency modes, which result in uncontinuous energy levels corresponding to discrete sidebands. The distinct quasi four - level energy system resulted in increased vibration strength and vibronic peak intensity of high - frequency modes, which benefits population inversion and lowers the ASE threshold. The ratio of high - frequency to low - frequency modes in organic gain medium would bring new knowledge.

Because 75 percent triplet excitons might theoretically be used for stimulated emission, the development of efficient triplet gain medium and triplet harvesters could aid in the development of electrically pumped organic lasers.

4. Challenges

Since Friend and Heeger at al, discovered the first OSLs in 1996 a lot of work has gone into this field, including gain media design, high - quality feedback structures, encapsulation technologies, CW lasers, and so on. Although optically pumped OSLs have come a long way in the last two decades, developing electrically driven OSLs remains a difficulty. Adachi's team announced the development of electrically pumped OSLs in 2019. The following section would discuss the challenges and breakthrough recent efforts in electrically - driven OSLs.

4.1 Design and Effect of metal electrode

Under the conditions of high current injection, the excitons would suffer from various channels for nonradiative transition, which would be a difficulty for OLED as a laser diode structure. The excitons may be eliminated by polaron interactions in a high electric field, but they can diffuse and quench in the presence of neighboring metal electrodes. The opaque metal electrode layer of the OLED structure also has a significant potential for absorbing the emitted photons. The efficiency roll - off is observed in the OLEDs at high excitation density, contributed by all of these factors. Estimating the excitation density to reach the lasing threshold, injected current density as high as 1 kA cm^{-2} is required. However, the operational current density of most OLEDs is still far below 1 A cm^{-2}. OLED devices exhibit substantial Joule self heating under high current densities due to the limited conductivity of organic semiconductors, which could lead to device thermal breakdown. Solwik et al. have proposed a new OLED concept that uses a restructured layer sequence to concentrate and maximize current flow in the metal - free emission region As a result, parasitic absorption by metal electrodes is avoided, and dissipation power is dramatically decreased. However, the potential of this new concept in resonator geometries, such as microcavities, needs to be further examined, and the viability of this device structure for electrically driven OSLs has yet to be determined.

4.2 Impact of dipoles and charge absorption

For electrically pumped organic lasers, carriers are a major cause of loss. Laser photons could be absorbed or singlet excitons could be quenched due to their large absorption band, which could cover the emission. It's still uncommon to find a quantitative explanation for dipole absorption. To carefully quantify the dipole absorption cross- sections, Rabe et al. employed spiro - bifluorene as the hole - transporting material. They discovered that the dipole absorption cross - section was extremely low, ranging from 560 nm to 660 nm. The results showed that dipole interactions were primarily dipole - exciton quenching rather than direct photon absorption. Organic semiconductors have low mobilities due to the presence of electrodes and dipoles. Charge - induced absorption is another severe optical loss that occurs when electrical pumping is used. Due to the lengthy lives of the charges benefiting from considerable population build - up and the region overlapping of the charge - induced absorption and the stimulated emission, absorption from charge excited states could impede stimulated emission and gain.

4.3 Effects of triplet excitons

The occurrence of triplet excitons is perhaps the greatest barrier in developing organic laser diodes. According to spin statistics, triplets account for 75 percent of the excitons generated. Because the broad triplet–triplet absorption band and the singlet fluorescence emission band overlap, the long - lived triplet excitons result in the quenching of light amplification via triplet–triplet absorption and the lowering of the S1 population by STA. Long pulse optical excitation can be utilized to investigate the difficulty created by triplet excitons.

Giebink and Lehnhardt's experiments showed that in the guest–host systems (Alq3: DCM and F8BT: MEHPPV), lasing was completely inhibited within tens of nanoseconds after the optical pumping began, implying that triplet–singlet annihilation and triplet–triplet absorption were the dominant

factors in optical losses in electrically - driven devices. The usual technique for removing the impact of triplet excitons is to introduce triplet quenchers, such as small molecule triplet scavengers (e. g., cyclooctatetraene and anthracene derivatives), and metal nanoparticles embedded in the gain medium.

5. Conclusion

The paper summarized a research in the field of organic solid state gain media. Organic dyes, fluorescent semiconductor emitters, triplet gain media, and biological materials have all been described as gain materials, with wavelengths ranging from UV to NIR. Some gain me - dia, such as laser dyes, are already commercially available, such as TDAF - 1 (79), PFO (203), F8BT (225), MEH - PPV (238), and so on.

Also in the field of organic gain media significant achievements such as high PLQYs, low ASE/lasing thresholds, good thermal/optical stabilities, high gain values, and improved charge carrier mobilities are made. Although the first optically pumped OSL was described in 1996, it was not until 2019 that the electrically pumped OLSD was realized. Despite prominent device designs and the potential for direct integration on flexible substrates, efficient and robust organic gain media for electrically driven OSLs remain limited.

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