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Candidate Materials as Gain Media in Organic, Triplet-Based, Room-Temperature masers Targeting the ISM Bands

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Abstract

While lasers have enjoyed greater popularity, masers—which emit coherent radiation in the microwave spectrum—are also of critical importance to a variety of applications. Recently, an organic gain medium has been developed, which allows emission at room temperature without the traditional encumbrances of cryogenic cooling or an externally applied magnetic field, at vastly improved power efficiency. This discovery opens up new avenues for applications that were previously impractical. However, further investigation is still required for frequency tuning of the device, through the selection of alternate gain media beyond the original choice of pentacene-doped *p*-terphenyl and some linear acenes similar to the pentacene prototype. This chapter outlines some of the essential criteria necessary to achieve masing with an organic semiconductor gain medium, including zero-field splitting (ZFS), triplet sublevel division, and metastable population inversion. Three tables of possible candidate materials are presented based on this roster of criteria, particularly targeting emission in one of the industrial, scientific, and medical (ISM) bands. A selection of preferred guest molecules is recommended for in-situ testing as room-temperature masers gain media candidates.

Keywords: room-temperature maser, organic semiconductors, triplet sublevels, zero-field splitting, metastable population inversion, candidate

1. Introduction

The maser, the microwave analogue of the laser, has long been a device of considerable interest [1, 2]. With emission frequencies between 0.3 and 300 GHz, masers have had several significant applications, including precision frequency references for atomic clocks [3–5],

radio astronomy [6, 7], space and long-distance communication [8–11], radar [12, 13], remote sensing [14], ultrasensitive magnetic resonance spectroscopy [15], and medical imaging [14]. However, widespread use of such devices has been limited by low efficiency and complex technical requirements. Recent advances in room-temperature masers [16–19] have revitalized interest in its potential uses. Particularly, the work of Oxborrow [16, 20] using pentacene *p*-terphenyl as the masing material has opened up a whole new direction of experimental research, through spin manipulation in organic semiconductor materials. Without the traditional encumbrances of cryogenic cooling or an externally applied magnetic field, these new avenues pave the way for a new generation of miniaturized ultra-low-noise high-gain amplifiers, oscillators, and transceivers.

Of particular interest for a variety of applications are materials which have demonstrated emission in the range of 2.4–2.5 GHz, one of the industrial, scientific, and medical (ISM) bands. ISM frequencies are designated as unlicensed and reserved internationally for experimental and short-range applications such as microwave ovens, cordless phones, military radar, and industrial heaters. The ISM bands have seen a dramatic increase in usage over the past decade for wireless connectivity devices [21], including Bluetooth [22], Zigbee and WLAN [23], and Hiperlan, among others [24]. These bands represent an important frequency range for future internet-of-things applications. Although there have been significant advances in recent years, the only viable room temperature masing demonstrated thus far, from pentacene *p*-terphenyl, is limited to a single emission frequency well away from this desirable application range [16]. Additionally, the conversion efficiency (i.e. the energy output in microwaves compared to the energy input in visible light) at the laboratory scale is still only around 3% [20]. To move beyond this prototype material, a comprehensive examination of the necessary features for room temperature masing using organic semiconductors is required.

In this chapter, we examine a few of the essential criteria necessary to achieve masing with an organic semiconductor gain medium, including triplet zero-field splitting (ZFS), metastable population inversion, and triplet lifetime. We enumerate numerous organic compounds as alternative candidates, based on advantageous conditions for these three criteria. Specifically, we target materials with ZFS values favorable to emission in the ISM band, as well as highlighting other interesting materials with desirable properties.

1.1. masers

MASER stands for microwave or molecular amplification by stimulated emission of radiation. Like its counterpart, the LASER (light amplification by stimulated emission of radiation), the maser converts an input of electrical or optical energy into a coherent, focused beam of photons. Both devices operate along similar lines and require the stimulation of atoms to elevate electrons to excited states. The electrons migrate to higher orbital levels if the atoms are “pumped,” that is, receive energy from an external source. As those electrons lose their energy (after 10^{-8} seconds), they emit photons by emission and retreat to a lower energy level. If this process occurs naturally, it is referred to as spontaneous emission, whereas if it occurs by design, it is called stimulated emission. Stimulated emission occurs when a photon strikes an electron already suspended at an excited state level: the electron releases its energy and the

exiting photon will be in phase with the striking photon. That is, the two photons will travel away coherently, with the same wavelength, frequency, and vector.

Key to coherent emission is the maintenance of stable population inversion. The pump must keep a greater percentage of electrons at the excited states, at a rate faster than the natural relaxation rate to the ground state. Excited state electrons must maintain their stimulated position long enough to allow incident photons to strike and cause coherent cascade emission. For masers, due to the small gap between the excited and ground states (1×10^{-6} to 1×10^{-3} eV), it is relatively easy to produce a high ratio of atoms in the excited state. Additionally, as the ratio of the Einstein coefficients (A, spontaneous emission and B, stimulated emission) varies with the cube of the frequency [25–27], spontaneous emission can generally be neglected for the microwave part of the spectrum.

Charles Townes and co-workers showed the first working maser using NH_3 gas as the gain medium [28]. In such a system, the two energy levels used are the two vibrational states of the ammonia molecule given by the oscillation of the nitrogen atom [1]. The difference between the wave function of the two configurations with N above and below the plane of hydrogen atoms yields an output radiation at 1.25 cm wavelengths [28]. By applying an electric field, the electric dipole moment in the ammonia molecules can be used to separate the two molecular configurations, maintaining a stable population inversion. This first maser proved very effective as a low-noise amplifier and was proposed as the first atomic clock standard by the National Institute of Standards and Technology (NIST) [29]. Further developments of gas [30], and then solid state masers [31, 32], focused on providing population inversion through the manipulation of spin states.

1.2. Disadvantages of traditional masers

Although it is relatively easy to produce population inversion with microwave emission, the major bottlenecks for its effective use in most applications are low power efficiency and complex operational requirements.

For the traditional gas or molecular masers, the modes that yield microwaves, either through conformational changes as in ammonia or spin states as in hydrogen [30], are inherently stable and require only physical separation to maintain stable population inversion. However, the population of molecules in the quantum state of interest is relatively low [33]. They also require high vacuum to prevent gas scattering collisions [28, 30, 33]. With a high vacuum, however, the gas molecules are spatially separated to such an extent that effective stimulation is limited, and the power output of gas-based masers is relatively low (pico to nanowatts) [33].

For solid state materials, the limitations are the opposite. If there are non-degenerate spin states, there can be a large population of atoms in the excited state, as thermal energy is generally sufficient to effectively pump the molecules across the small energy gaps. However, the lifetimes of such excited spin states are very short. Spin-lattice relaxation rates increase exponentially with rising temperature [34] to the degree that at room temperature, spin-relaxation times for many solid materials are in the nanosecond range due to rapid phonon scattering [35]. Additionally, the spin population inversion decreases at higher temperatures [16, 36].

Therefore, most solid state masing materials require cryogenic temperatures to maintain stable population inversion and sufficient lifetimes [10, 35, 37].

The requirement of non-degenerate spin states also limits the applicability of masers. If there is no naturally occurring split within the microwave frequency range, magnetic fields must be applied to induce Zeeman splitting of the degenerate energy states. Many gaseous and solid state materials require the application of large magnetic fields in order to emit at desirable frequencies [38–40].

1.3. Organic masers

One method of overcoming the major bottlenecks of room temperature masing is to use a material that has long excited state lifetimes and natural zero-field splitting, such as an organic semiconductor. Despite having low mobility and complex transport properties, organic semiconductors have significant advantages over inorganic semiconductors as a gain medium.

Lifetimes of spin excited states in organics are substantially longer than inorganic materials, microseconds instead of pico or nanoseconds [41]. In some aromatic molecules, lifetimes have been observed as high as milliseconds or even full seconds [42–45]. The long lifetime in organics is due to the weak spin-orbit coupling (SOC), as a result of the low molecular weight of the materials involved, such as carbon and hydrogen in small molecule arrangements (low Z value) or π -conjugated polymers [41]. The strength of spin-orbit interaction is proportional to Z^4 [46].

Oxborrow et al. demonstrated the only room-temperature solid state maser observed thus far based on a pentacene-doped *p*-terphenyl molecular crystal, where the spin lifetime can reach 135 μ s at room temperature [16]. This result relies on the excitonic route to forming stable states with suitable separation for microwave emission. The organic maser functions by photoexciting a solid state gain medium composed of an organic guest molecule within a solid polymer crystal (which taken together comprise a Shpolskii matrix [47]) and then emitting photons by exciton decay within the triplet sublevels. Radiative emission is then guided and amplified by a resonance cavity to form a coherent pulsed or continuous maser beam [16].

The gain medium chosen by Oxborrow et al. [16, 20] was the well-studied molecule pentacene, a polycyclic aromatic hydrocarbon with five benzene rings, embedded in a *p*-terphenyl matrix [48–56]. Dispersing a small amount of this guest molecule within the polymer host matrix separates the guest molecules from one another to prevent quenching. Additionally, incorporating pentacene into a matrix frustrates the rotational degrees of freedom and splits the usually degenerate triplet states [48] allowing microwave emission at room temperature.

The key to the long lifetime is the formation of the triplet exciton state, which is quantum mechanically forbidden to decay to the ground state. As shown in **Figure 1**, emission from such a gain medium is based on optical excitation into the dipole-allowed singlet state, followed immediately by an intersystem crossing to the metastable triplet state, and then a return to the ground state (often through phosphorescence). Materials which additionally have non-degenerate triplet states can, as an intermediate step, have transitions between triplet states to produce the required microwaves.

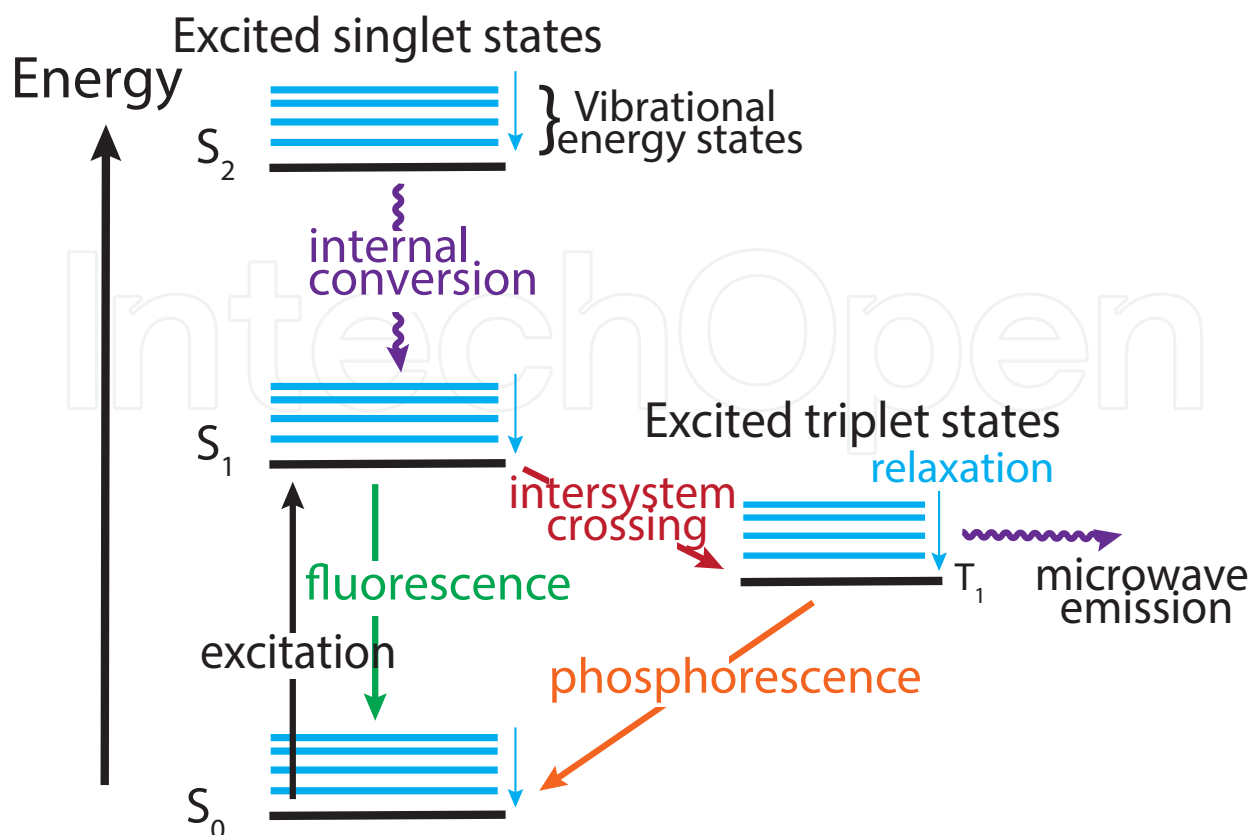


Figure 1. A Jablonski diagram showing the possible transitions that can occur for an organic-based maser.

The mechanism of electron transport in organic semiconductors also makes them advantageous as a gain medium. Semiconduction in organic molecules occurs in a π -conjugated system, where π orbitals are delocalized over some or all of the molecules. Transport of electrons through the π -orbital electrons also further suppresses both SOC and the hyperfine interaction (“HFI”, the interaction between electron spin and the adjacent atomic nuclei) [57, 58]. As both singlet and triplet states in organic semiconductors result from room-temperature stable exciton spin pairs [59, 60], emission lifetimes can be substantially longer than those observed in inorganic systems.

Organics are generally cost-effective, easy to fabricate and test, versatile, flexible, plentiful, and lightweight [61–63]. Spin manipulation in organics—for improved optoelectronic devices, for spintronics, for spectroscopy—also has a long history [34, 41, 61, 64–70]. There are many candidate materials to investigate across the vast spectrum of organic molecules, providing numerous choices for applications.

2. Criteria for room-temperature, organic, triplet-based maser

As described above, organic semiconductors provide a new avenue for efficient solid state masers. Though pentacene *p*-terphenyl is the first successful room-temperature organic maser, it still suffers from some limitations. It is limited to a single output frequency of

1.45 GHz, its spin-relaxation lifetime is only 135 μs , its power conversion efficiency is only around 3% [20], it can only operate for pulses of about 300 μs [2], and the molecular crystal is unstable under high-power pumping and at high temperatures. Bogatko et al. [71], building on the success of pentacene, recently identified several possible new candidate materials based on a computational molecular design strategy. Focusing on the linear acenes and some of their derivatives, they were able to suggest new directions to overcome some of these limitations. However, a vast body of organic semiconductors beyond the linear acenes exists that can be explored and optimized as a gain medium, at a variety of emission frequencies, to expand the possibilities of room-temperature maser applications.

In the spirit of Oxborrow's original inspiration [2], we have examined the literature on organic semiconductors to present a list of additional potential gain medium candidates. First, we identify candidates that show solid state microwave emission over a variety of possible emission frequencies without an externally applied magnetic field. Then, we discuss the population inversions and triplet lifetimes that exist in such systems. Finally, we touch on some potential promising candidates that exhibit favorable conditions if a suitable host material can be found to operate effectively at room temperature.

2.1. Emission from triplet state

Fundamentally, to perform masing, photons must first be emitted by stimulation from a gain medium at a desired frequency (or wavelength). The designation of "microwave" applies to electromagnetic waves with wavelengths between 1 m and 1 mm, with frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm) [72].

In contrast to inorganic semiconductors, the excited states of organic molecules are highly localized. Rather than acting as free carriers, electrons or holes are bound to a molecule, forming a polaron. A polaron consists of the excited state molecule, its internal geometric distortion, and the distortion field with respect to its neighboring molecules, due to the addition or loss of charge. When positive and negative polarons (holes and electrons) interact, they form a room-temperature stable electron-hole pair (exciton) localized on one or a few molecules. This localization and the consequently large exchange splitting generate two distinct states, referred to as singlets (S_1 spin 0) and triplets (T_1 spin 1), depending on the spin interaction of the two carriers. In a singlet state, excitons have opposite spin orientations and the electronic energy levels do not split when the molecule is exposed to a magnetic field. In a triplet state, the electron has the same spin orientation (parallel) as the hole and energy-level splitting becomes possible.

As the name *triplet* implies, there are *three* distinct symmetric spin states, which arise from the interaction of charge carriers with parallel spins (see **Figure 2**). Usually, these levels are degenerate but can be split either through the application of a magnetic field (Zeeman effect) or through the molecular geometry (zero-field splitting).

As the α and β spin states respond oppositely to an applied magnetic field, the Zeeman effect (**Figure 2**) results in a tunable energy separation of the two spin states, which increases proportional to the applied magnetic field according to the expression [73]:

$$E = g\beta M_s H \quad (1)$$

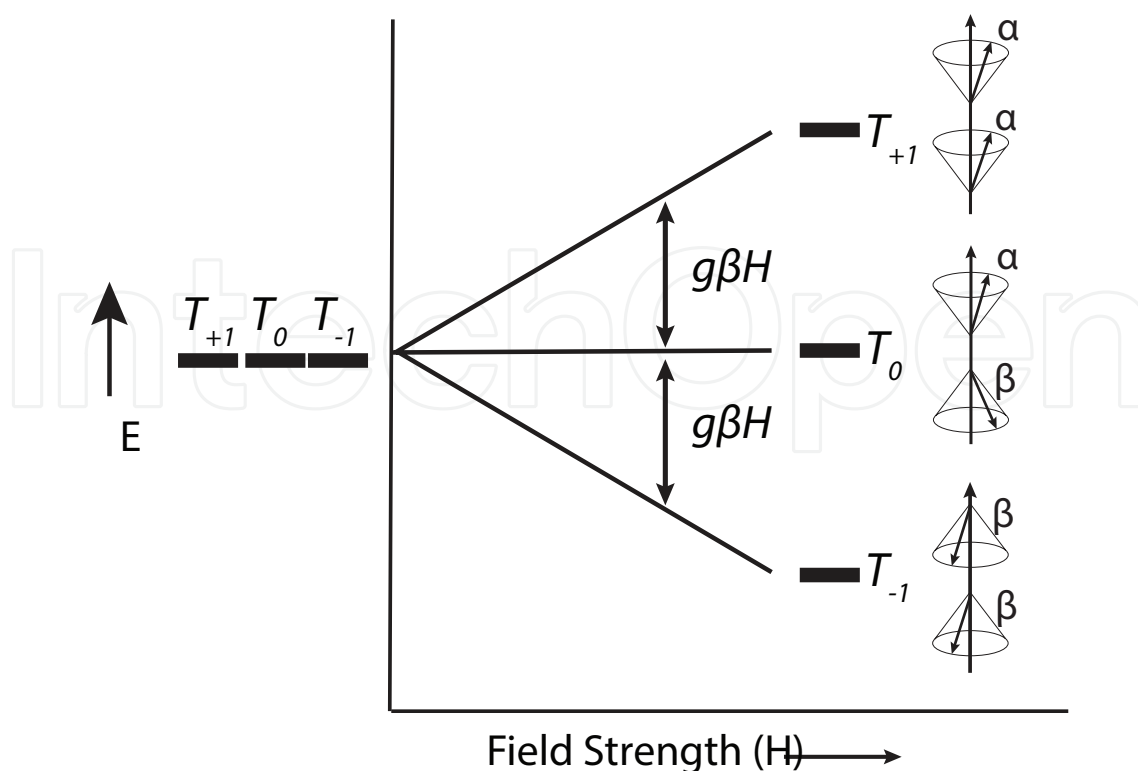


Figure 2. An energy diagram showing the splitting of the degenerate triplet sublevels under an applied magnetic field. Insets show the spin configuration for each of the triplet sublevels.

where g is the electronic g factor, β is the Bohr magneton, M_s is the spin quantum number, and H is the applied field.

However, some materials, particularly organic molecules, exhibit a splitting of the triplet states without an applied magnetic field due to the anisotropic electron distribution from the delocalized orbitals over the molecule [73], as shown in **Figure 3**.

Many organic semiconductors show this type of molecular splitting, with the energy gap described by the zero-field splitting parameters D and E . Generally, shortening along one spatial direction will lead to a decrease in the triplet energy, as seen in **Figure 3(b)** where T_z is lower for a planar symmetric molecule, such as coronene. Conversely, elongating the electrical field distribution along a spatial direction will increase the energy, as for pentacene, which has a long and short axis in the x - y plane. Along the backbone (oriented along X in our example), the triplet energy T_x will be slightly higher than along the transverse direction, T_y . This arises because the orbitals are distributed over the entire molecule for many organic semiconductors, resulting in an asymmetric electron energy distribution. D is defined as the energy difference between T_z and degenerate energy states as in (b) or between T_z and the average of the two other energy states as in (c). It can be positive or negative, depending on whether there is confinement or elongation of the electron distribution over the molecule. The parameter E is half the energy difference of the T_x and T_y energy states or the gap between X or Y and the degenerate energy level [73].

Of particular interest for a variety of applications are materials which have demonstrated emission in the range of 2.4–2.5 GHz, one of the ISM bands. These bands represent an impor-

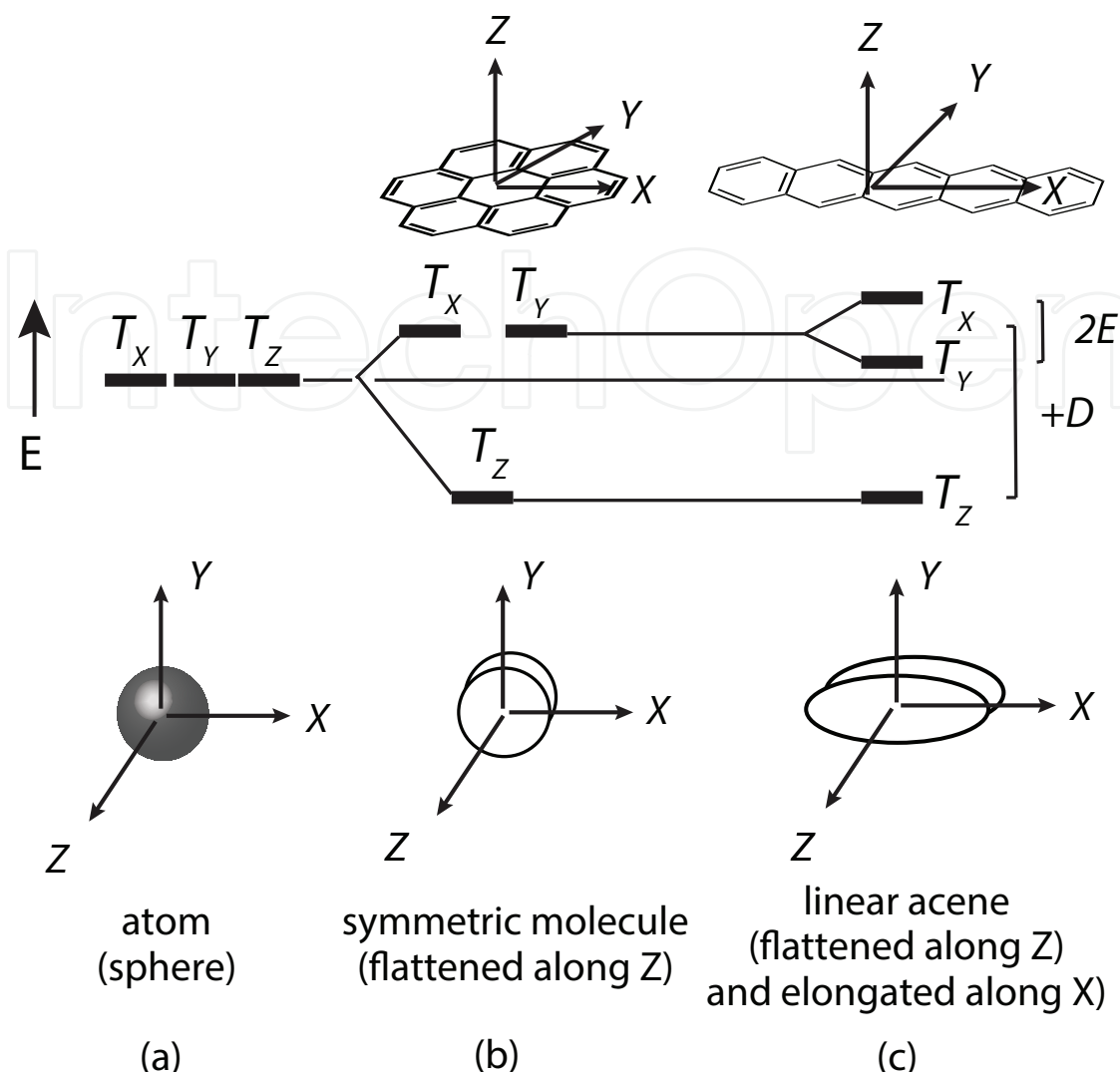


Figure 3. An energy diagram showing the splitting of the degenerate triplet sublevels with changes in molecular conformation. (a) A spherically symmetric electron distribution has degenerate triplet states in three dimensions. (b) A symmetric planar molecule, such as coronene, is symmetric in the x - y plane but has one non-degenerate level from shortening along the Z -axis. (c) An asymmetric planar molecule, such as pentacene, has three split states. As the molecule is elongated along the X axis, T_x has higher energy than T_y . The zero-field splitting parameters D and E describe the separation between the triplet states.

tant frequency range for future internet-of-things applications. Candidate guest materials with 2.4–2.5 GHz emission are presented in **Table 1**, along with other candidates with values slightly below that region. Due to the Zeeman effect, discussed above, these materials could also become viable candidates with application of a modest external magnetic field to open up the triplet energy gap.

The organic molecules presented in **Table 1** have calculated triplet emission frequency based on their reported zero-field splitting coefficients D and E (cm^{-1}). Many of the results are taken from data for randomly oriented molecules in a glassy solution, which only yield the absolute value of the ZFS coefficients [74]. As D and E can take on positive or negative values, we present two emission frequencies, by either adding to or subtracting E from D , before converting to frequency. In some of the literature, single emission frequencies were reported without

Guest	Host	ZFS (GHZ)		Ref.
		High	Low	
Azulene	Phenazine	2.191	1.778	[75]
3,4-benzopyrene	EPA or methanol ^a	2.272		[76]
3,4-benzopyrene	Glasses plastics	2.272		[42]
3,4-benzopyrene		2.278		[77]
Fluoroanthene	Glasses plastics	2.278		[42]
Fluoroanthene	Glasses plastics	2.449		[42]
Fluoroanthene	PMMA	2.449		[45]
Fluoroanthene	Ethanol glass	2.458	2.159	[78]
Phenazinium	Sulfuric acid-ethanol ^a	2.317	1.718	[79]
1,2-benzanthracene	Rigid glass	2.368		[77]
Triphenylamine	PMMA	2.401		[45]
Naptho[2,3-a]coronene	Decane ^a	2.413	1.856	[80]
Cata-hexabenzocoronene	PMMA	2.463	2.423	[81]
Aeridine-b9	Biphenyl	2.49	1.959	[80]
Dibenzo[a,g]coronene	Octane ^a	2.491	1.292	[80]
1,3-diazaazulene	Phenazine	2.494		[75]

The high and low ZFS correspond to the absolute difference between positive and negative values of D and E . For entries where either ZSF parameter values were not reported or the molecule was symmetric (hence $E = 0$), the single emission frequency is given under "high."

^aAn experiment performed at or near cryogenic or liquid N₂ temperatures to ensure host is a solid matrix.

Table 1. Candidate materials for organic semiconductor gain medium sorted by zero-field splitting emission frequency.

giving D and E values and are accordingly represented as one value here in the high column. If the molecule was symmetric about the x - y plane, yielding a 0 value for E , the single emission wavelength is listed also in the high column. Though the table is mostly sorted by "high" ZFS emission values, some variation was found in the reported values for a single material, due potentially to variation in temperature, host material, or experimental setup. For clarity, we have grouped molecules from different sources together rather than sorting them by their reported value. Note that we have made our calculations based on the values given in the referenced sources, even if the experiments were originally reported elsewhere.

2.2. Triplet relative population inversion

For masing action, a system must have a top-heavy population imbalance with more excitons in the upper states than lower states. Such a configuration will allow for stimulated emission of the heavily populated upper states, with plenty of openings within the lower states where excitons can decay down. For organic molecules, numerous examples exist of high ratio excitons in the

highest triplet sublevel, with a vastly smaller population in the lowest triplet state. For example, pentacene in *p*-terphenyl has a demonstrated a ratio of 0.76:0.16:0.08 relative population in the $T_X:T_Y:T_Z$ sublevels. Other examples of notable population inversion are presented in **Table 2**.

Guest	Host	Relative	Population		High/low ratio	Ref.
		High	Medium	Low		
Naphthalene	Naphthalene-d8	0.82	0.16	0.02	41	[82]
Naphthalene	<i>n</i> -pentane ^a	0.64	0.25	0.11	5.82	[83]
Naphthalene	Durene ^a	0.54	0.2	0.26	2.08	[84]
Pyrimidine-h4	Benzene ^a	0.92	0.05	0.03	34	[80]
Anthracene	<i>n</i> -heptane ^a	0.65	0.33	0.02	32.5	[82]
Anthracene	Biphenyl	0.39	0.55	0.06	6.5	[82]
Anthracene-d14	<i>p</i> -terphenyl-d14	0.38	0.43	0.19	2	[85]
Anthracene-h2d8	Biphenyl	0.34	0.35	0.31	1.09	[80]
Dibenzothiophene trap ^b	–	0.92	0.05	0.03	29.74	[80]
Benzophenone-b10 ^b	–	0.57	0.38	0.05	10.74	[80]
Benzophenone-b10	Benzophenone-d10 ^a	0.38	0.33	0.3	1.27	[80]
1,4-dibromonaphthalene		0.87	0.04	0.09	10	[80]
Pentacene	<i>p</i> -terphenyl	0.76	0.16	0.08	9.5	[16, 54]
<i>p</i> -dichlorobenzene	<i>p</i> -xylene ^a	0.5	0.4	0.1	4.87	[80]
Dimer	Biphenyl	0.64	0.22	0.14	4.6	[80]
Dimer	<i>p</i> -dichlorobenzene ^a	0.63	0.18	0.18	3.5	[80]
Benzene	Cyclohexane ^a	0.46	0.43	0.11	4.18	[86]
Benzene	Cyclohexane ^a	0.43	0.46	0.11	3.91	[82]

The convention of highest:middle:lowest energy Zeeman triplet line was used, and the entries are sorted in descending order of their respective ratios of high excitons, capable of emission, to low excitons, the receiving state of emitted excitons.

^aThe experiment is performed at or near-cryogenic or liquid N₂ temperatures to ensure host is a solid matrix.

^bNeat film or crystal.

Table 2. Candidate materials for organic semiconductor gain medium with triplet sub-level relative populations.

In **Table 2**, relative populations are shown for the three triplet sublevels of each material, based on a variety of sources, and sorted in descending order of their respective ratio of high excitons (capable of emission) to low excitons (the receiving state of emitted excitons). The traditional model presents these three stages as X, Y, and Z descending, but here we use the more generic (and more representative) terms high, mid, and low as X, Y, and Z may be split to differing relative energies with respect to one another in any given material (negative *D* and *E* values will determine the placement of X, Y, and Z lines). Again, the entries are grouped by molecular name.

2.3. Long triplet lifetime

An essential requirement for masing is that population inversion must be maintained consistently for a longer period of time than the ordinary excitation time scale. This is one of the most significant advantages of using an organic semiconductor as a gain medium for room temperature masing (see Section 1.3). In an organic maser, long lifetimes are achieved through the creation of the metastable triplet state, through intersystem crossing from the excited singlet. The advantage of operating within the triplet regime is that the excitons are dipole forbidden from decaying to the ground state due to the total spin moment $S = 1$. As Pauli exclusion forbids two electrons with parallel spins from occupying the same orbital, triplet excitons cannot decay to the ground state without spin flipping, phosphorescence, or nonradiative phonon perturbation. It can take significant time for those conditions to be met such that the exciton returns to the ground state (nanoseconds for pentacene and full seconds or tens of seconds for other organic molecules). This impediment to decay creates a natural metastable state, ideal for stimulated emission.

One of the most critical features for microwave emission is the spin-relaxation rate, which is substantially higher in organic materials compared to inorganic ones due to the low spin-orbit coupling in most organic molecules. For microwave emission, the most critical lifetime is the relaxation from the higher exciton sublevel (traditionally T_x and T_y) down to the lowest triplet sublevel (i.e. T_z). The triplet lifetime is also defined relative to the final decay from T_z down to the ground state. This generally is an order of magnitude longer than the desired microwave frequency of emission. **Table 3** lists the reported triplet lifetimes for a variety of materials emitting in the microwave regime.

Guest	Host	Lifetime (s)	Ref.
Coronene	PMMA	56	[87]
Coronene-d12	Octane ^a	34.5	[87]
Coronene	Rigid glass	9.4	[69]
Coronene	Alphanol 79 ^a	7.9	[88]
Coronene	PMMA	4.2	[45]
Benzophenone	Carbon tetrachloride crystal	52.1	[89]
Benzene ^b	–	26	[84]
Benzene	Cyclohexane ^a	16	[90]
Benzene	3-methylpentane sol. ^a	7	[91]
Benzene	Rigid glass	7	[69]
Phenanthrene (d)		25	[84]
Phenanthrene	Rigid glass	3.5	[77]
Phenanthrene	Rigid glass	3.3	[69]

Guest	Host	Lifetime (s)	Ref.
Triphenylene	PMMA	15.9	[69]
Triphenylene	Alphanol 79 ^a	13.3	[88]
Triphenylene	PMMA	8	[45]
s-Triazine	3-methylpentane sol. ^a	13	[91]
Biphenyl	3-methylpentane sol. ^a	8	[91]
Tryptophan	Ethylene glycol-H ₂ O ^a	5.5	[92]
1,3,5-triphenylbenzene	Alphanol 79 ^a	5.1	[88]
1,3,5-triphenylbenzene	3-methylpentane sol. ^a	4.5	[91]
Pentacene	<i>p</i> -Terphenyl	0.000135	[16]
Pentacene	PMMA	0.000045	[93]

^aAn experiment performed at or near cryogenic or liquid N₂ temperatures to ensure host is a solid matrix.

^bNeat film or crystal.

Table 3. Candidate materials for organic semiconductor gain medium with long triplet lifetime.

2.4. Potential candidate materials

Table 4 summarizes the top candidate materials that should be studied further to exploit their long spin-relaxation lifetimes and high population inversion. Currently, complete information at room temperature is limited for these materials other than pentacene. However, as with pentacene [51], the low temperature behavior suggests that if a suitable Shpol'skii matrix [47] can be found for these molecules which preserve the ZFS, then each would be an excellent candidate for a room-temperature maser gain medium.

Guest	Host	Emission (GHz)	Sublevels			High-low ratio	Temp (K)	Lifetime (s)	Refs.
			High	Medium	Low				
Naphthalene	Naphthalene-d8	2.968	0.82	0.16	0.02	41	1.3	3 [88]	[82]
Naphthalene	<i>n</i> -pentane ^a		0.64	0.25	0.11	5.8			[82]
Pyrimidine	Benzene ^a	2.187	0.92	0.05	0.03	34	1.2	0.14, 0.017, 0.012	[80]
Anthracene	<i>n</i> -heptane ^a	2.159	0.65	0.33	0.02	32.5	1.3	0.05 [77]	[82]
Anthracene	Biphenyl		0.39	0.55	0.06	6.5			[82]
Dibenzothiophene ^b	–	3.29, 1.76	0.92	0.05	0.03	30*	1.3	9, 0.36, 0.29	[80]
Pentacene	<i>p</i> -terphenyl	1.42	0.76	0.16	0.08	9.5	RT	0.000135	[16]
Phenazine	EtOH ^a	2.236		0.9	0.1	9*	77	0.011	[79]

Guest	Host	Emission (GHz)	Sublevels			High-low ratio	Temp (K)	Lifetime (s)	Refs.
			High	Medium	Low				
Phenazinium	ETOH ^a	2.018		0.9	0.1	9 [*]	77	0.009	[79]
Phenanthrene	TBB ^a	2.384 [*]	0.1	0.28	0.62	2.8 [*]	1.6	0.26, 0.023	[80]
Triphenylene	Hexane ^a	1.443	0.4	0.43	0.17	2.34	1.2	8.3, 8.3, 27.8	[80]
Tryptophan	Glass	2.95	0.39	0.38	0.23	1.7		5.5	[94]
Tryptophan	Ethylene Glycol-H ₂ O ^a		0.282	0.347	0.371			4.17, 8.43, 26.5	[92]
Coronene	<i>n</i> -hexane	2.827	0.43	0.41	0.16	2.7 ^{**}	1.6	4.24, 3.94, 59.9	[86]
Coronene	Octane		33.3	33.3	33.3	1.0 ^{**}	1.35		[80]
Trans-stilbene ^a	–	3.79, 1.51	0.5	0.2	0.3	1.67	1.3	0.014, 0.014, 0.15	[82]

Three distinct triplet lifetimes of X (high), Y (mid), and Z (low) sublevels are reported.

^aAn experiment performed at or near cryogenic or liquid N₂ temperatures to ensure host is a solid matrix.

^bNeat film or crystal.

^{*}Emission occurs from Y down to X.

^{**}Uniform shapes (such as coronene) have degenerate X and Y, so they both emit at the same wavelength, thereby increasing the population ratio.

Table 4. Top candidate materials for an organic semiconductor gain medium.

3. Summary

With significant improvements to power efficiency and operational parameters through the selection of alternative candidate materials, the maser could expand beyond its current niche applications for use in laser-to-radio frequency (RF) or light-to-RF conversion, for coherent emission in the millimeter or centimeter wavelengths, or for coherent transmission in radio frequencies. Possible areas of application include enhanced communication security (narrow casting as opposed to broadcasting), organic radio components such as low-noise or solar-powered amplifiers, direct optical powering of transceivers without an inefficient electrical conversion stage (suitable for sensors and emerging “internet-of-things” applications), radiative diagnoses and therapy, directed energy tools and weapons for military and defense applications, and wireless power transmission over vast distances including energy to and from planetary orbit (space-based solar power).

In this chapter, we have presented a list of possible candidate materials that have zero-field triplet emission over a variety of frequencies, including technologically interesting ISM bands. We have also shown promising materials that exhibit high population inversion and long triplet lifetimes, which are required to achieve room temperature masing.

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Conflicts

The authors declare no conflicts of interest in the creation of this work.

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