Recent advances in solid-state organic lasers

Sébastien Chénais* and Sébastien Forget*

Abstract

Organic solid-state lasers are reviewed, with a special emphasis on works published during the last decade. Referring originally to dyes in solid-state polymeric matrices, organic lasers also include the rich family of organic semiconductors, paced by the rapid development of organic light-emitting diodes. Organic lasers are broadly tunable coherent sources, potentially compact, convenient and manufactured at low cost. In this review, we describe the basic photophysics of the materials used as gain media in organic lasers with a specific look at the distinctive features of dyes and semiconductors. We also outline the laser architectures used in state-of-the-art organic lasers and the performances of these devices with regard to output power, lifetime and beam quality. A survey of the recent trends in the field is given, highlighting the latest developments in terms of wavelength coverage, wavelength agility, efficiency and compactness, and towards integrated low-cost sources, with a special focus on the great challenges remaining for achieving direct electrical pumping. Finally, we discuss the very recent demonstration of new kinds of organic lasers based on polaritons or surface plasmons, which open new and very promising routes in the field of organic nanophotonics.

© 2011 Society of Chemical Industry

Keywords: organic lasers; microcavities; spasers; organic photonics

INTRODUCTION

Since the first demonstration of laser oscillation, now more than fifty years ago,1 applications using lasers have spread to very many areas, e.g. research, medicine, technology and telecommunications. The variety of available laser sources is large and covers a wide span in terms of attainable wavelengths, output powers and pulse durations. Although they can have various aspects, lasers are always composed of three essential building blocks (Fig. 1): a gain medium, a pump source and a resonator. The gain medium can be a gas, a liquid or a solid in which amplification of optical waves occurs by stimulated emission of radiation. This fundamental process is dominant over absorption provided that a population inversion is realized, which is the role attributed to the pump source. The resonator provides feedback and defines the spatial and spectral coherence of the beam.2

Among the various kinds of laser materials, π-conjugated molecules or polymers are of foremost interest and form the rich family of so-called ‘organic lasers’. The history of organic lasers is almost as long as that of lasers themselves: liquid dye lasers, based on solutions of π-conjugated highly luminescent (dye) molecules, were demonstrated as early as in the mid-1960s,3 and are still today popular sources of tunable visible radiation, in spite of the cumbersome designs and the inconvenience linked to toxic solvents. Very early (in 1967) it was proposed to incorporate dyes in solid-state polymeric matrices4 which appeared to be a promising route to build broadly tunable sources that would have the benefits of being compact, convenient and able to be manufactured at low cost. Although there is still today active research on dye-doped polymer lasers, these devices have not managed, from then up to the present, to enter the marketplace: the main reason is probably that there is a fundamental contradiction between the inherent bad photostability of organic molecules and the high cost of the pump source, in general a pulsed laser. Subsequent efforts then naturally went in the direction of improving the dye and host matrix photostability, and/or decreasing the required pump threshold intensity so that alternatives to pulsed lasers may be found. The history of solid-state organic lasers reached its turning point with the advent of organic semiconductors (OSCs), paced by the development of organic light-emitting diodes.5 Very low thresholds could be demonstrated in thin-film-based OSC lasers; furthermore the devices turned out to be easy-to-handle and compact, while keeping all the advantages of organic materials.6,7 The question was then whether an organic laser diode would be ever realized, that is, a device pumped with an injected current rather than with an optical source, in the same way as inorganic semiconductor lasers work. This issue drove considerable efforts and is still now a major inspiration route for organic laser research, although no demonstration of such a device has been reported yet.

What are the targeted applications for organic solid-state lasers? The natural playground associated with organic lasers is spectroscopy. In this case, the modest output power is not problematic, whereas the broad tunability is a strong advantage and short pulses allow time-resolved studies. The simplicity of the fabrication process makes organic sources attractive for integration into miniature spectroscopic systems. In a similar way, organic lasers are potentially useful for chemical sensing. An interesting achievement was the detection of trinitrotoluene using conjugated polymer films.8 The mechanism is based on the observation of fluorescence quenching which results from the presence of a trinitrotoluene molecule on the polymer. Even if this detection is possible with simple fluorescence, it has been...
could be used in a similar way to detect specific DNA sequences.12 OSC lasers may be attributed to artefacts or mistaken identification of laser action.25 Electrical excitation have been published, but they were later made between a ‘dye’ and an ‘organic semiconductor’ from a special focus on lasers and light-emitting diodes. atm/online whereas some claims of apparent gain or lasing action under supplementary losses brought by electrical excitation; surprisingly, some claims of apparent gain or lasing action under electrical excitation have been published, but they were later attributed to artefacts or mistaken identification of laser action. These aspects are reviewed in this paper. In the meantime, new and advanced trends, particularly in the field of device physics, has received his PhD from Paris 11 university (Institut d’Optique) in 2003 for his work on new solid-state lasers systems. He joined the Lasers Physics Laboratory (CNRS/Paris 13 University) in 2005 as an assistant professor. His current area of research is organic photonics, with a special focus on lasers and light-emitting diodes.

Dr. Sébastien Forget has received his PhD in optics and photonics from the Paris 11 university (Institut d’Optique) in 2003 for his work on new solid-state lasers systems. He joined the Lasers Physics Laboratory (CNRS/Paris 13 University) in 2005 as an assistant professor. His current area of research is organic photonics, with a special focus on lasers and light-emitting diodes.

Dr. Sébastien Chénais received his PhD from Paris 11 university (Institut d’Optique) in 2002, studying thermal effects in ytterbium-doped solid-state lasers in Patrick George’s group. Since 2003, he has been assistant professor at the Lasers Physics Laboratory (CNRS/Paris 13 University), working on organic photonics and laser physics.

In this paper, organic solid-state lasers are reviewed. The reader will find several very comprehensive and top-quality reviews on this subject published during the last decade. Therefore, this paper is not intended to be a complete survey of every aspect of organic lasing; it is instead written with the purpose of drawing a picture of the field as it appears to us at the beginning of 2011, emphasizing the latest advances and trends, particularly in the field of device physics.

This paper is structured as follows. In the next section we briefly review the different types of organic solid-state materials used for lasers, and comment on the distinction that can be made between a ‘dye’ and an ‘organic semiconductor’ from a laser physics point of view. The section after that is devoted to an overview of existing organic laser architectures, with a special emphasis on devices employing thin films. We then attempt to analyse recent research trends. Relying on papers published during the last decade, a few general tendencies can be sketched. First, the quest of the ‘organic laser diode’ remains a key that drives the scientific community. Many insights contributed to a better understanding of the bottlenecks caused by the supplementary losses brought by electrical excitation; surprisingly though, some claims of apparent gain or lasing action under electrical excitation have been published, but they were later attributed to artefacts or mistaken identification of laser action. These aspects are reviewed in this paper. In the meantime, new and alternative concepts came about. Optically pumped organic lasers ceased to be regarded as intermediate steps before achieving a future – maybe unlikely – electrically pumped device; instead they started to be regarded as interesting devices in their own right, as far as cheap pump sources, such as diode-pumped solid-state microlasers, laser diodes or even light-emitting diodes, could be used. In the penultimate section we highlight the recent progress made in this direction with optically pumped organic lasers, either in terms of lowering the threshold, increasing the wavelength coverage (to the deep red or infrared (IR) and to the ultraviolet (UV)), improving the wavelength agility, enhancing the lifetime of the devices, or improving the conversion efficiency, output power and beam quality. The final section is devoted to the newest, and maybe the most unexpected trend in the field: using organic gain media in devices that are no longer classical lasers, or ‘photon lasers’, but rather devices based on quasiparticles such as exciton–polaritons (mixing of photon states and excitons) or surface plasmons (and surface plasmon polaritons). Two recent breakthroughs illustrate this tendency: the demonstration of an organic crystal microcavity polariton laser, which may open a novel path towards electrically driven lasers, and the first experimental proof of an organic-based ‘spaser’ (i.e. surface plasmon amplification by stimulated emission of radiation). The latter represents a real step forward as it breaks the supposedly ‘unbreakable law’ stating that the minimum size for a laser has to be half an optical wavelength. Being a truly nanometric – a few tens of nanometres in size – coherent quantum generator at optical frequencies, the spaser may play the same role in nanophotonics than the laser plays in photonics, and reconcile the length scales of electronics and optics. These recent results open very exciting perspectives in the use of organic gain media both for fundamental physics and practical applications.

**MATERIALS**

**Overview of molecular materials suitable for organic lasing**

Dye molecules dissolved in liquid solvents have been for decades the most popular scheme for organic lasers. The first attempts to make solid-state organic lasers naturally consisted of using the same compounds. A dye can be defined as a \( \pi \)-conjugated molecule with a high quantum yield of fluorescence. It can be either neutral or ionic: typical examples are xanthene (rhodamine and fluorescein families), coumarins, oxazines or pyromethenes. Even though a given dye molecule can be a very good light emitter in a dilute form, it will be less efficient or even completely non-emissive at high concentrations because of intermolecular interactions arising between nearby molecules, an effect referred to as concentration quenching. In the solid state, a straightforward strategy to avoid quenching is to incorporate dye...
molecules as dopants into solid matrices. Solid hosts can be either polymers – essentially poly(methyl methacrylate) (PMMA) and its derivatives34 – or glasses and hybrid organic–inorganic materials prepared by sol–gel techniques.35–38

Also, OSCs have been identified as suitable for lasing. The term refers to their electrical semiconducting properties, although the physics of electrical conduction in organics differs notably from that of inorganic semiconductors.39 Based on structural considerations, one can distinguish three categories of OSCs: organic crystals, small molecules and polymers.

Organic single crystals of anthracene or pentacene40,41 resemble inorganic crystals, and their transport properties can be defined in terms of bands. In practice, the high voltage needed to get light from those crystals limits their practical interest and their difficult growth limits their lasing applications as well. In addition, high molecular-crystal packing provides high mobilities which is generally in contradiction to a high quantum yield of fluorescence.42 Single crystals are, however, being considered for light-emitting transistors,43 which may be of interest for organic lasers as discussed in a later section.

Small-molecule OSCs are at the origin of the astonishing development of commercial thermally evaporated organic light emitting diodes (OLEDs)5,44 In such OSCs, which are mostly amorphous, transport occurs by hopping between localized sites, with a probability that critically depends on the orbital intermolecular overlap. Any neat film of a π-conjugated compound will then have semiconducting properties to some extent. However, the tendency to intermolecular π–π stacking and dipole–dipole interactions between units lead a priori to severe quenching and is detrimental for lasing: many OSCs turn out to be either non-emissive or may emit fluorescence but are not suitable for lasing. Many efforts in molecular design have hence been directed towards improving the luminescence properties of OSC films. This can be done by designing molecular geometries where fluorophore units are kept apart and/or π–π stacking much reduced.45–47 Dendrimers for instance are good candidates for organic lasing: the dendrimer structure48,49 consists of a chromophore (e.g. pyrene50) located in the core of a highly branched structure ended with surface groups. The core defines the optical properties such as emission wavelength, whereas the surface groups confer solubility and act as spacers to limit π–π stacking. Similarly, the spiro-linkage used to couple two oligomers in spiro-compounds51–53 enables definition of a twisted geometry54 in which the optical properties of the individual moieties are conserved. However, the easiest way to eliminate concentration quenching is still to physically separate the emissive units; it is possible, however, to give to the host an active role with guest–host systems. The archetypal example is Alq3:DCM (Fig. 2).55,56 In this case, the pump light is absorbed by the higher energy gap host material (Alq3; Fig. 2(a)), which very efficiently transfers its energy to the lower energy gap guest (DCM; Fig. 2(d))
The other major category of semiconducting organic molecules is formed by conjugated polymers.\textsuperscript{58} Conjugated polymers can exhibit high photoluminescence yields even in the solid state. Lasing has been demonstrated in a large number of such macromolecules, especially in poly(phenylene vinylene) (PPV)\textsuperscript{18,59,60} and polyfluorenes\textsuperscript{61,62} (Figs 2(b) and (c)). While it is generally difficult to make homogeneous blends of polymers, host–guest systems composed of two polymers have been recently investigated for laser action, e.g. based on MEH-PPV doped into F8BT\textsuperscript{63} (Figs 2(e) and (f)).

Recently, new materials have emerged as good candidates for organic lasing: this is the case for liquid crystals,\textsuperscript{64} whose self-organized structure forms photonic bandgaps that can be exploited for lasing. The gain unit can be a classic dye incorporated into a neat small-molecule thin film of molecular density \( n \approx \rho \times N_A/M = 1.3 \times 6.10^{23}/460 \approx 10^{21} \text{ cm}^{-3} \) (where \( \rho \) is the film density, \( N_A \) the Avogadro number and \( M \) the molar mass, numerical values here are those of Alq\textsubscript{3})\textsuperscript{71}, incident light will be absorbed over a typical length scale of \( L_{\text{abs}} = (\sigma_{\text{abs}} n)^{-1} \sim 100 \text{ nm} \). A first consequence is the possibility to make very thin devices, with a strong impact on resonator design (discussed in a later section).

A subsequent point is the correlated high gain: as stimulated emission cross-sections and absorption cross-sections are linked and of comparable magnitude, very high optical gains are possible in organic media (gain cross-sections of \( 10^{15} \text{ cm}^2 \) are reported in conjugated polymers\textsuperscript{27}).

Another remarkable feature of organic molecules is their very broad fluorescence spectra, leading to a possible tuning of the emission wavelength (achieved, for instance, by using a dispersive element added inside the laser cavity\textsuperscript{28}), and making them capable of ultrashort pulse generation.\textsuperscript{74} Furthermore, it is relatively easy to modify the emission spectrum by changing the chemical structure, giving birth to a wide range of materials emitting from the near-UV to the near-IR, in contrast to inorganic semiconductors where the emitted wavelength is limited by the available materials and lattice-matching restrictions. There are several strategies to chemically tune the emission of a given molecular unit. For instance, one may vary the effective conjugation length, i.e. the average size of the \( \pi \)-orbital cloud on the molecule or the segment, which basically defines the colour in the same way as the size of a quantum dot relates to its spectrum.\textsuperscript{75} An archetypal example is given by the polyacene series, where the adjunction of phenyl rings from benzene to pentacene leads to a red-shift of the absorption spectrum.\textsuperscript{76} Another interesting way of chemical tuning consists of altering the strength of intramolecular charge transfer, as illustrated for the unsymmetric push–pull triarylamine-based compounds shown in Fig.5. As the strength of the electron-withdrawing group increases, a higher dipole moment arises in the exited state: when the material is in the form of a neat film or through a Förster mechanism\textsuperscript{57} (Fig. 3). Compared to DCM doped into a passive matrix (like PMMA), the host–guest structure enables a much higher absorption of the pump; the material obtained is furthermore able to transport charges through Alq\textsubscript{3}. Finally, the Stokes shift between absorption and emission wavelengths is increased, which consequently reduces self-absorption (i.e. re-absorption of the emitted laser light).

Photophysical properties relevant for laser action

Many photophysical aspects of \( \pi \)-conjugated systems are relevant for lasing. Conjugated organic molecules are intrinsically four-level systems (Fig. 4). The excited state (or manifold) \( S_1 \) and the ground state \( S_0 \) are both coupled to a multitude of vibronic states: the absorption line is between the ground state of the \( S_0 \) manifold and a vibrational high-lying state of the \( S_1 \) manifold, while the laser transition occurs between the lowest-energy vibrational state of the \( S_1 \) manifold and one of the vibrational states of \( S_0 \). This four-level system guarantees low-threshold lasing since no minimum pump power is required to achieve population inversion, provided that the lower level of the laser transition is above the ground state by several times \( kT \).\textsuperscript{68} An important aspect related to lasing is the presence of triplet states (Fig. 4). Molecules in the first singlet excited state \( S_1 \) may flip their spin through intersystem crossing and end up in the \( T_1 \) triplet state, generally lower in energy, where they can accumulate because of a high triplet-state lifetime. Unfortunately, the \( T_1 \) \( \rightarrow \) \( T_2 \) absorption band is very broad and overlaps the singlet fluorescence emission band.\textsuperscript{69} Hence, solid-state organic lasers can indeed only emit short pulses (in contrast to liquid dye lasers which can run in continuous-wave mode because the circulation of the fluid allows continuous refreshing of the medium). Recent reports have shown the termination of lasing a few nanoseconds\textsuperscript{63} after pump turn-on in polymer host-guest systems or after a few tens of nanoseconds\textsuperscript{70} in small-molecule lasers in the case of long-pulse pumping: these aspects are essential in the context of electrical pumping and are reviewed in more detail in a later section.

Absorption cross-sections (\( \sigma_{\text{abs}} \)) in organics are among the highest of all laser media, typically of the order of \( 10^{-16} \text{ cm}^2 \). In a neat small-molecule thin film of molecular density \( n \approx \rho \times N_A/M = 1.3 \times 6.10^{23}/460 \approx 10^{21} \text{ cm}^{-3} \) (where \( \rho \) is the film density, \( N_A \) the Avogadro number and \( M \) the molar mass, numerical values here are those of Alq\textsubscript{3}), incident light will be absorbed over a typical length scale of \( L_{\text{abs}} = (\sigma_{\text{abs}} n)^{-1} \sim 100 \text{ nm} \). A first consequence is the possibility to make very thin devices, with a strong impact on resonator design (discussed in a later section).
in a polar environment, the Stokes shift increases accordingly and the emission is red-shifted.

Finally, we mention that the photophysics of organic gain media will be different in neat films from that in dilute solutions, due to the importance of intermolecular interactions (see the next subsection).

It is possible to make a short list of the qualities that are required to make a good organic laser material. They pertain both to the fluorophore alone and to its environment (the host matrix for instance):

- Compounds are stable against oxygen and moisture, and photostable against pump photons (pumping at low photon energies greatly relaxes this constraint).
- The quantum yield of fluorescence, measured in the solid state, is high (low quenching, weak π–π stacking, etc.).
- Losses at the laser wavelength are minimized (low re-absorption of the fluorophore and low absorption/scattering losses of the environment).
- The Stokes shift is low (reduces the fraction of pump energy converted into heat, and thus enables an increase of the conversion efficiency and photostability). Note that this requirement is in contradiction to the previous point.
- Stimulated emission cross-section \( \sigma_{\text{em}} \) is high (governs the local gain \( g = \sigma_{\text{em}} N \Delta N \) and then the pump threshold).
- A combination of low intersystem crossing rate, low triplet–triplet absorption cross-section, low spectral overlap of optical gain with triplet absorption and eventually low triplet state lifetime is desirable (all these parameters are often not known but strongly limit the repetition rate and pulse duration obtainable from optically pumped organic lasers).
- In host–guest systems based on Förster resonant energy transfer, a large Förster radius of several nanometres is desirable (good overlap of donor emission with acceptor absorption, high cross-sections, etc.).

In order to certify a given material for lasing applications, amplified spontaneous emission (ASE) experiments are often carried out to measure the optical gain, especially for thin-film devices when light can be waveguided inside the active material. The pump beam is tailored in the form of a thin stripe: when net gain is present in the film, light emerging from the edge of the stripe exhibits a spectrum much narrower than the fluorescence spectrum, often referred to as ‘mirrorless lasing’. Also, the edge intensity varies superlinearly with the stripe length, and simple data processing allows extraction of the net gain: this technique is referred to as the variable stripe length (VSL) method.46,77,78 Typical gains measured in organic gain media with the VSL technique are in the range \( 10^{0} – 10^{2} \) cm\(^{-1}\). In conjugated polymers, transient femtosecond pump/probe experiments reveal gains that can locally increase up to 2000 cm\(^{-1}\) in ladder-type methyl-poly(p-phenylene)79 or 12 000 cm\(^{-1}\) in polyfluorene.80

**Classification of materials: dyes versus organic semiconductors?**

Is there a way to classify these different materials (dyes in inert matrices, host–guest systems, conjugated polymers, small molecules, dendrimers, etc.) in classes that would be relevant for the laser physicist?

A first distinction can be drawn on the basis of processing techniques, leading to the differentiation between bulk gain media and thin films. **Bulk gain media** are millimetric to centimetric rods that are intended to be set in macroscopic laser cavities after being polished to optical quality;29 the rods are fabricated by inserting an organic emitter into a monomer (such as methyl methacrylate) before polymerization29,34 or into a glass by a sol–gel process.81 In contrast, **thin films** are somewhat easier to implement, either through thermal evaporation or solution processing. Small molecules (including dyes) can be evaporated provided that they are neutral, while polymers are too heavy to do so. Solution processing includes techniques such as spin-coating,82 dip-coating, doctor-blading83 or ink-jet printing.84 Many conjugated polymers are solution-processable, as well as small-molecule compounds, provided that they are soluble. Some insoluble polymers may be made solution-processable via, for example, side-chain functionalization or main-chain copolymerization with soluble segments. Non-conjugated polymers such as PMMA are also readily solution-processable, making dye-doped polymeric lasers also suitable for thin-film devices.

Beyond this ‘technological’ classification, a long-admitted distinction is traditionally made between dyes and OSCs, and it is useful to wonder what the foundations of such a differentiation are. Following Samuel and Turnbull,22 three properties are often argued to make a division: lasing OSCs, as opposed to dyes, (i) have a high photoluminescence quantum yield even in neat films, (ii) can be processed in the form of thin-film structures and (iii) are capable of charge transport. These criteria are, however, sometimes ambiguous, as some molecules hardly fall into one category exclusively: they may have high quantum yields of fluorescence in solution (complying with the classic definition of a dye) but keep their luminescent and lasing properties in neat films, whereby they acquire semiconducting properties. For instance, the unsymmetric starburst triarylamine derivatives introduced by Ishow et al.45 (shown in Fig. 5) exhibit quantum...
yields of fluorescence that are in the range 0.2–0.8 both in cyclohexane solution and in thin solid films, they can be used as neat films in low-threshold optically pumped lasers and can also be incorporated in OLEDs in the form of 20 nm thick pure layers, proving that they are capable of charge transport; they can be evaporated but are also solution-processable, for example by spin coating. Such compounds comply with both definitions of dyes and OSCs and highlight the overlap between these two classes. Historically, the dyes versus OSC separation was motivated by the admitted goal of achieving electrical pumping. Nowadays, many recent advances (described in the following) pertain to optically pumped devices, in which semiconducting properties are not used; in those cases making a distinction based on electrical properties seems irrelevant.

However, a distinction can still be made at the macroscopic scale of the gain medium rather than at the molecular scale, based on the occurrence of intermolecular interactions, and their influence on laser performance. In a first category, including neat films and host–guest systems (which can be identified with OSCs), exciton–exciton annihilation, exciton diffusion, photogeneration of charges and related phenomena can quench the excited-exciton picture discussed above. This has been shown extensively in conjugated polymers and this is also true in guest–host systems: for instance, in the Alq3:DCM blend, the fast laser dynamics are affected by the Förster transfer dynamics as well as by quenching of the guest (DCM) singlets on photogenerated Alq3 triplets. In contrast, when an emitter is dissolved in a passive matrix, intermolecular effects are less and laser physics somewhat simpler. In that sense, the difference between dyes in optically evaporated, a technique that provides excellent control over thickness and optical quality. The most natural resonator geometry for thin-film organic lasers is consequently the two-dimensional planar waveguide. We will focus in the following paragraphs on those ‘thin-film’ lasers, and give a brief review of some of the most frequently used resonator geometries.

Waveguides
In a planar waveguide, the resonator axis is parallel to the film plane: the photons travel a long way (several millimetres) through the active medium during a round trip, leading to high overall gain. In this geometry, the light is waveguided in the high-refractive-index organic layer, sandwiched between, typically, a low-index substrate (glass or silica) and air. As the typical order of magnitude for an organic layer thickness is ca 1 μm, single-mode waveguides are easily achieved. Optical feedback can be obtained in several ways, as reviewed below.

Fabry–Perot waveguides
A convenient and low-cost arrangement used in inorganic semiconductor diode lasers to form the cavity mirrors is to cleave the semiconductor to obtain flat facets. Indeed, the crystalline structure of the semiconductor allows clean and almost perfect facets, with a reflectivity as high as 30% due to the very high refractive index of the active medium. Things are not so simple with organic materials, as the refractive index is typically two times lower, leading to a reflectivity of only a few percent. Moreover, it is technically very difficult to obtain good-quality edges with organic films because of the amorphous structure of the material. However, Kozlov et al. demonstrated such a Fabry–Perot resonator with a 1 mm long Alq3:DCM layer as the active medium. As expected from the long interaction length between the laser wave and the gain medium, the lasing threshold was low (around 1 μJ cm−2) and the quantum slope efficiency remains one of the highest ever reported (70%). However, the spatial quality of the emerging beam is low and its divergence is high because of the subwavelength aperture at the end of the waveguide.

Distributed feedback lasers
A very attractive way to avoid the ‘facet drawback’ together with increasing the mirror reflectivity is to use diffractive structures. In this case, a periodic diffraction grating is used to provide feedback with a very high efficiency for a given wavelength range. These gratings can be easily integrated onto planar waveguides and thus avoid the need for cleaved facets. In such structures, the high reflection coefficient ensured by the periodic grating is combined with the potential long interaction between the laser wave and the gain medium to ensure low-threshold lasing. One can classify the periodic surface corrugation into two categories, namely distributed Bragg resonators (DBRs) and distributed feedback (DFB) structures.
of the corrugation, the diffraction process and surface emission (Fig. 7(a)). Such second-order structures can be diffracted perpendicular to the waveguide plane, leading to a second-order grating (Fig. 6). For first-order diffraction process ($m = 1$), the resonant wavelength is $\lambda / n_{\text{eff}}$, where $\lambda$ is the period of the corrugation, and $n_{\text{eff}}$ is the effective refractive index of the waveguide. For first-order diffraction process ($m = 1$), we obtain $\lambda = \lambda / (2n_{\text{eff}})$. An issue encountered with such a structure is light extraction through highly reflective Bragg mirrors, together with high divergence due to the small transverse size of the waveguide. To circumvent both problems, a second-order grating ($m = 2$) is of particular interest. Indeed, in this configuration the resonant wavelength is $\lambda = n_{\text{eff}} \lambda$. The grating diffraction condition for this order means that some light is diffracted perpendicular to the waveguide plane, leading to surface emission (Fig. 7(a)). Such second-order structures can provide an efficient way to extract the light from the cavity, even if second-order gratings typically lead to a higher lasing threshold compared to first-order gratings.95,96

Simple one-dimensional DFB organic lasers have been reported in a huge set of materials (both polymers27,60,82,97 and small molecules26,50,98–101) covering almost all the visible spectrum. Another advantage of DFB lasers is that their wavelength can be relatively easily tuned by changing the thickness of the organic layer (hence the effective refractive index) or the period of the modulation (as discussed in a later section). The concept of DFB lasers can also be extended to two-dimensional systems. This type of periodic structure (where either the thickness or the refractive index is modulated in two dimensions) is referred to as a two-dimensional photonic crystal structure.102,103 There is a growing interest in such structures, with square, hexagonal or circular concentric geometries. In such resonators, optical feedback is applied in several directions in the plane of the film. This opens the way toward photonic bandgap engineering where the spectral and spatial characteristics of the laser beam can be controlled with a high degree of accuracy. For example, it has been demonstrated by Samuel’s group that a clear enhancement of the spatial beam quality can be obtained through the use of two-dimensional DFB structures104–106 (even if the far-field pattern generally follows the grating geometry, for example forming a cross in a square-lattice photonic crystal or an azimuthally polarized annular profile in the case of a 2D DFB structure106 together with an important decrease of the threshold.105

**DBR lasers**

One potential difficulty with a DFB structure is that the thickness modulation can induce incoherent scattering associated with surface irregularities brought by the patterning process, and consequently a high level of losses. Lower threshold can be obtained through the use of so-called DBR geometries.107 The term usually applies to a stacking of quarter wavelength layers with alternating high and low indices (in dielectric mirrors for examples). The same principle could be applied in the waveguide plane by corrugating the layer with a periodic pattern with a half wavelength period. The laser then consists of an organic waveguide in which two outer areas are nanopatterned to ensure Bragg reflection46,108 (Fig. 7(b)). Each of the corrugated areas acts as a Bragg mirror, and reflects light for the chosen wavelength. The advantage of such a structure is that the gain medium located between the mirrors remains uncorrugated, which limits losses induced by scattering.

**Microcavities**

**Organic vertical cavity surface-emitting lasers**

Another natural arrangement for an organic laser, inspired by stacked OLEDs, consists of a planar sandwich of the organic material between two mirrors to form a Fabry–Perot microcavity.
in the vertical direction (resonator axis perpendicular to the film plane; Fig. 8(a)). This kind of configuration has already been successfully used for crystalline solid-state lasers and for inorganic diode lasers which are known as vertical cavity surface-emitting lasers (VCSELs). The organic VCSEL (OVCSEL) geometry was the one used by Tessler et al.6 to demonstrate optically pumped organic lasing in PPV. Using a highly reflective broadband DBR mirror and a partially transmitting silver mirror as an output coupler, very high quality factor $Q$ could be achieved.109 The 100 nm thick PPV layer was simply spin-coated onto the DBR mirror and the silver layer was evaporated on top. Only a few longitudinal modes are supported by a microcavity, and when the pump power exceeds the lasing threshold (200 $\mu$J cm$^{-2}$ in this case), a single mode dominates the emission spectrum of the laser. Following this pioneering work, several planar microcavities with various organic media were reported. The microcavity $Q$-factor (and thus the lasing threshold) can be improved by sandwiching the polymer between two DBR mirrors,110 or by directly growing the top DBR mirror at low temperature onto the polymer.111 Another option is to change the lasing medium to use small molecules instead of polymers. Lasing with the archetypal Alq$_3$:DCM blend in DBR–metal$^{109}$ or DBR–DBR$^{91}$ microcavities was reported. Recently, Sakata and Takeuchi$^{112}$ realized such a microcavity laser with a cheap and compact UV laser diode as a pump source.

**Microrings, microdiscs and microspheres**

The easy processing of organic materials allows for the realization of new geometries that are impossible to obtain with classic inorganic semiconductors. A first example is the microring laser, where a polymeric film is deposited around an optical fibre or even a metallic wire$^{113}$ (Fig. 8(b)). This can simply be achieved by dipping the fibre into a solution of the polymer.114 The waveguide created around the fibre forms a ring microcavity where the light bounces through total internal reflections on the interface between the polymer and the surrounding medium. As the diameter of the fibre is typically around several micrometres, the light travels through a long path to make a round trip, which is associated with a complex mode pattern, mixing whispering gallery modes and waveguide modes.$^{115}$ As a consequence, very low thresholds can be achieved with such structures$^{116}$ (ca 1 $\mu$J cm$^{-2}$). The pumping of these lasers can be done transversally or through the core of the fibre, leading to a more uniform pumping pattern.$^{117}$

In a similar way, microdisc lasers$^{10,116}$ can be realized by lithographically patterning and etching an organic film to form circular discs of several micrometres in diameters (Fig. 8(c)). The microdisc supports whispering gallery modes comparable to those observed in microring lasers, but also possible Fabry–Perot resonances. With more complex shapes$^{118}$ (squares, pentagon, stadiums, etc.) a wide variety of mode patterns are possible, which offers a tool to study quantum chaos or chaotic lasing. The regular comb-like spectrum obtained even with complex shapes enables one to infer the dominant periodic orbits in such structures$^{119}$ (Fig. 9).

Finally, the microsphere structure$^{120}$ is the three-dimensional generalization of the microdisc. It can be formed by superimposition and melting of several microdiscs on a lyophobic surface to form droplets. A common property shared by these geometries is the ‘messy’ output, since light is emitted in many radial directions.
obtained with DFB structures (usually a few percent or less).

emission have been reported: Yokoyama
breakthroughs. Other claims of electrically driven stimulated
history of scientific misconduct rather than the history of laser
yet. In 2000, Schön
of extremely compact, tunable, cheap, flexible lasers: it remains
worth targeting, potentially opening the way to a new class
strategy to obtain a diffraction-limited circular output beam
was demonstrated in 1996,7 an electrically pumped organic
laser was demonstrated in 1996,7 an electrically pumped organic
laser mode and gives rise to a TEM00 diffraction-limited transverse
This unusual output may be tailored upon adjusting on the shape
Vertical external cavity surface-emitting organic laser
(VECSOL) concept
A major drawback shared by DBR/DFB, microdisc/ring and
microcavity organic lasers is the asymmetric and/or highly
diverging profile of the output beam, which strongly limits
the potential applications of such laser sources. In contrast, circular and diffraction-limited beams (i.e. with the minimum
beam divergence obtainable from a beam of given transverse size,
governed by diffraction laws) can be obtained with external bulk
resonators using dye-doped polymer blocks, but at the expense
of compactness and with longer and more complex fabrication
processes than organic thin films. A recently demonstrated strategy to obtain a diffraction-limited circular output beam from
an organic thin-film laser is the VECSOL,121 which is the
organic counterpart of the inorganic vertical external cavity
surface-emitting laser.122 A VECSOL is composed of a plane
mirror coated with a thin film of the organic material and a
remote concave mirror to close the cavity. The macroscopic (up
to several centimetres) cavity defines the spatial geometry of the
laser mode and gives rise to a TEM00 diffraction-limited transverse
profile (Fig. 10). This laser architecture also leads to record optical
conversion efficiency for thin-film organic lasers (more than 50%)
has been reported123) together with respectable output energies
(>30 μJ). This contrasts with the relatively low slope efficiencies
obtained with DFB structures (usually a few percent or less).

PROSPECTS FOR ELECTRICAL PUMPING

Soon after an optically pumped organic solid-state semiconductor
laser was demonstrated in 1996,7 an electrically pumped organic
laser, or ‘organic laser diode’, became an important breakthrough
worth targeting, potentially opening the way to a new class
of extremely compact, tunable, cheap, flexible lasers: it remains
today a hot topic as no such organic laser diode has been reported
yet. In 2000, Schön et al.124 reported such an achievement in a
tetracene crystal, but this paper (and others by the same author)
was later retracted,125 a story which unfortunately entered the
history of scientific misconduct rather than the history of laser
breakthroughs. Other claims of electrically driven stimulated
emission have been reported: Yokoyama et al.126 observed a
spectral narrowing of the edge emission of an OLED as well as
an intriguing superlinear dependence of the emission on the
electrode length, which was attributed to the presence of
stimulated emission. Tian et al.24 observed the same features but
suggested that a misalignment of the collecting optics could be the
reason for the observed superlinear dependence instead of
gain. In both cases, the spectral narrowing can be well accounted
for by a resonant leaky mode at the cut-off frequency.126 Another
intriguing claim of lasing with an unrealistically low threshold
under electrical pumping in a microcavity OLED was reported by
Liu et al.23 Those recent reports, however, are probably not lasing,
as shown and discussed by Samuel et al.25 It can be added that
stimulated emission has been claimed126 under continuous-wave
excitation, which is a strong indication against lasing: continuous-wave
operation under optical pumping would actually be quite a
breakthrough in itself (such a report by Nakanotani et al.127 is
questionable for the same reasons and is probably only due to a
resonant leaky mode).

The challenges to realize direct electrical pumping of an
organic laser device are numerous and complex,70,128,129 and are
much better understood now than 15 years ago. Unfortunately,
the astonishing progress made in OLED technology in the past
10 years, in terms of luminance and efficiency, is not straight-
forwardly transferable to organic lasers. A good illustration of a
breakthrough for OLEDs that is not useful for lasers is triplet energy
harvesting through the use of phosphorescent materials.130 This
new class of materials led to an approximately fourfold increase
of efficiency as 75% of the excitons created by carrier recombinan
treplets. However, phosphorescence is not suitable for lasing
(at least attempts to observe ASE in highly efficient phospho-
rescent emitters Ir(ppy)3 or Btp2Ir(acac) have failed131,132) since
the excited state T1 → Tn (n > 1, a dipole-allowed transition
associated with high absorption cross-sections σT1→Tn absorption
band spectrally overlaps the T1 → S0 emission band, associated
with low stimulated emission cross-sections.

The key difference between an OLED and a laser is that lasing
requires net gain (i.e. light amplification surpassing all kinds of
losses, due to both the material and the environment), whereas
fluorescent emission is a linear threshold-less phenomenon:
because π-conjugated systems have short excited-state lifetimes
(a few nanoseconds), a high exciton recombination rate will be
required to run a laser, much more than in a standard operating
OLED. It is instructive to seek an estimation of what would be the
current density threshold of an organic laser diode if the losses
were the same as in an optical pumping configuration. Starting from
optically pumped DFB laser data, a value of ca 100 A cm−2 can thus
be obtained: this estimation was obtained from a DCM : Alq3 active
medium sandwiched between two cladding layers of Alq3, as
well as from a PPV polymer laser.21 Importantly, this figure has to
be understood as a lower limit. Indeed, higher current densities
of the order of kA cm−2 have been achieved in pulsed OLEDs134 or
in light-emitting field-effect transistor (LEFET) devices135 without
ever observing lasing, and values as high as 128 kA cm−2 have
been reached in a thin film of copper phthalocyanine.136 This
makes clear that electrical driving brings extra losses, due to the
presence of metallic electrodes, and also because of absorption
and quenching attributed to charge carriers (polarons) and triplet
excitons. We briefly review these aspects below.

First, the electrodes used for electrical injection are problematic.
The lowest thresholds in optically pumped devices have been
obtained with waveguide lasers (such as DFB lasers), because
they enable a long interaction with the gain medium, and are
consequently a natural design choice for a future organic laser
diode. However, the guided mode leaks outside the high-index
active part and overlaps with the absorbing metallic electrodes, a
feature which is amplified by the fact that all organic films tend to

Figure 10. Schematic of a VECSOL.121 The left-hand mirror is highly
transparent (HT) for the pump wavelength and highly reflective (HR)
for the laser radiation. The radius of curvature and reflectivity of the output
coupler are optimized to yield the highest output energy in a single
transverse mode.
have similar refractive indices, not helping optical confinement. As a result, the threshold is greatly increased, as has been shown by optically pumping a structure with massive metallic contacts.\textsuperscript{137} It is possible to carefully design the contact geometry so that the overlap between the optical mode and the electrodes is reduced as far as possible,\textsuperscript{138} for instance by putting the contacts in the node of a TE\textsubscript{2} waveguide mode,\textsuperscript{139} by using thick charge-transport conducting polymers to keep the mode away from the electrode\textsuperscript{140} or by using transparent conductive oxides for both electrodes.\textsuperscript{141,142}

The second and troublesome source of losses associated with electrical pumping is the presence of the charge carriers themselves (polarons) which have broad absorption bands overlapping the emission and can then absorb laser photons or quench singlet excitons.\textsuperscript{143} Little quantitative information has been available up to now about polaron absorption: Rabe \textit{et al}.\textsuperscript{144} made a precise and unambiguous measurement of a polaron absorption cross-section in a hole-transporting spiro-bifluorene compound and found a low value ($\sigma = 2.6 \times 10^{-13} \text{ cm}^2$ between 560 and 660 nm), confirming the idea that polarons more certainly interact through polaron–exciton quenching\textsuperscript{86} than through direct photon absorption.

Both the electrode and the polaron issues are in fact directly related to the low mobility of OSCs. Indeed, the mobilities of amorphous OSCs are in the range $10^{-5} - 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which means that achieving a high current flow will mobilize a high number of polarons. A low mobility also means a high resistivity, so that achieving a high current flow will mobilize a high number of polarons. A low mobility also means a high resistivity, so that electrodes must be set close to each other to provide a high electric field. A promising laser architecture in this context is the organic LEFET (OLEFET),\textsuperscript{145} which shows potential for solving the electrode and polaron problems simultaneously. The key idea is that the field-effect mobility is higher than the bulk mobility measured in a planar OLED structure,\textsuperscript{146} so that higher current densities can be obtained (values in the region of several kA cm\textsuperscript{-2} have been reported in OLEFETS\textsuperscript{135,147}). This configuration also makes it possible to position the emission zone far away from the metallic contacts. Recently, optically pumped lasing was demonstrated in a LEFET structure with a DFB grating.\textsuperscript{148} The structure and the lasing results are detailed in Fig. 11. Although OLEFETS are now able to outperform the equivalent OLEDs,\textsuperscript{149} no laser action has been shown yet.

The presence of triplet excitons is the third impediment towards organic laser diodes, and it is certainly the most difficult to overcome. Triplets are more abundant than singlet excitons under electrical excitation: first, because of the 3 : 1 unfavourable creation probability ratio; second, because their much longer lifetime (of the order of milliseconds\textsuperscript{150}) makes them pile up, at least in a long-pulse or high-repetition-rate regime (which makes short pulses always preferable\textsuperscript{151}). Under optical pumping, triplets are only created through intersystem crossing, and are not deleterious provided that the device is operated with short pump pulses. Triplets cause issues because they will absorb laser photons (triplet absorption (TA), meaning increased cavity loss), and/or because they will quench singlets through a Förster-type non-radiative dipole–dipole interaction referred to as singlet–triplet annihilation (STA).\textsuperscript{70} These effects are not radically different in nature since they are both related to the triplet–triplet absorption cross-section $\sigma_{\text{T-T}}$ and the spectral overlap between the singlet emission band and the triplet excited-state $T_1 \rightarrow T_n$ absorption band (the same feature that makes organics unsuitable for continuous-wave lasing). In contrast to polaron-related phenomena, triplet issues can be studied under optical excitation with long-pulse pumping. Based on the observation of complete lasing suppression a few tens of nanoseconds after pump turn-on in Alq$_3$:DCM and BCzVBi:CBP lasers, Giebink and Forrest\textsuperscript{70} concluded that STA between guest singlets and host triplets was the dominant mechanism, compared in particular to TA. Lehnhardt \textit{et al}.\textsuperscript{153} showed conversely that STA and TA both play an important role in a polymer–polymer (F8BT–MEH-PPV) guest–host system, based on experiments revealing that lasing persists for only a few nanoseconds, regardless of the pump duration. Numerical simulations\textsuperscript{70} led to the conclusion that, even in an ideal case where polaron quenching would be totally absent, triplets hinder lasing in a guest–host system at any current density.

As a conclusion, 15 years after the first demonstration of an OSC laser, achieving an organic laser diode seems as challenging as it was at the very beginning, but the bottlenecks are now much better understood. The additional losses brought about by electrical excitation are now well identified and are being assessed.

![Figure 11](image-url)
RECENT TRENDS IN OPTICALLY PUMPED ORGANIC LASER RESEARCH

Facing the numerous challenges discussed above towards the realization of an organic laser diode, some have started to wonder whether the future of compact organic lasers would not be instead an ‘indirect’ electrical pumping scheme, in the sense that charge carriers are not directly injected into the conjugated material but to a laser diode or a LED which in turn would optically pump the material. This application-driven approach reminds us what is the basic ambition for organic lasers: to become cheap, practical, compact alternatives to complex tunable laser technologies. Here, the distinction between a dye (in a polymeric or a semiconductor matrix like Alq3) and an OSC is useless, since their different photophysical properties (discussed in a previous section) are not exploited. Below, we briefly review some recent routes explored towards the improvement of optically pumped organic lasers. All these developments may not be gathered in a single device (e.g. a low threshold will hardly be compatible with a high output energy) but all contribute to the flourishing of the field.

Indirect electrical pumping strategy: loosening the constraint on the pump source

The concept of indirect electrical pumping is to use an electrically pumped light source to (optically) pump an organic laser. This pumping light source must be cheap, compact and efficient, in contrast to expensive flashlamp-pumped Nd: YAG lasers, nitrogen lasers or titanium–sapphire lasers which have been the most widely used pump sources so far. This approach is then justified by the important progress made in solid-state coherent light sources technology. Very compact pulsed microchip solid-state lasers have hence been used for the pump, leading to organic sources having the size of a small shoebox. A microchip laser remains, however, a complex light source, composed of an inorganic IR laser diode and a laser crystal coupled to a saturable absorber emitting IR light in a pulsed mode, followed by frequency conversion stages to reach the UV–blue wavelengths suitable for pumping most organic lasers. A major advance in terms of reducing costs and improving compactness was triggered by the release in 1996 by Nichia Corp. of blue InGaN laser diodes. Since then, output powers have been scaled up and have become suitable for directly pumping organic lasers.

Going still further in simplification, Yang et al. demonstrated an OSC laser pumped by an inorganic incoherent LED, creating a highly compact organic source (Fig. 12). This approach opens the way towards highly integrated hybrid organic–inorganic photonics.

Extending the wavelength coverage

π-Conjugated systems are essentially destined to emit visible light. At longer wavelengths, non-radiative decay channels compete with fluorescence, resulting in a quantum yield of fluorescence that tends to decrease with the emitted wavelength. On the short-wavelength side, blue or UV emitters suffer from a reduced photostability as small π-conjugated cores often lack rigidity, and are generally pumped with deep-UV highly energetic photons (although there has been a demonstration of two-photon pumping of a blue polyfluorene laser). Because of the large potential interest for spectroscopy, substantial efforts have been made to look for efficient UV emitters. Silafluorenes or spiro-compounds are good candidates for this purpose: the lowest lasing wavelength achieved to date directly from an OSC film is 361.9 nm, obtained with a thermally evaporated spiro-terphenyl film. Telecommunications, biomedical applications (e.g. deep-tissue imaging) and probably in the near future plasmonics (discussed in the next section) will continue to motivate research towards efficient deep-red or IR gain materials and lasers. Lasing operation has been reported.

Lowering the threshold

The laser threshold is defined as the pumping energy where the optical gain surpasses the losses over a cavity round trip. Achieving a low-threshold laser system is a motivating goal, as it improves the global electrical-to-optical efficiency and lowers the amount of pump energy necessary to drive the laser. With a long-term view, an electrically pumped organic laser would be also obviously demonstrated more easily in a low-loss structure. For a given organic material, the lasing threshold is essentially governed by the interaction length between the laser wave and the gain medium and by the quality of the cavity mirrors. DFB/DBR lasers are intrinsically low-threshold lasers: typical thresholds values for second-order DFB lasers are a few μJ cm⁻² (Tsiminis et al.) to tens of μJ cm⁻², but results as low as 200 nJ cm⁻² (Kozlov et al.) or 150 nJ cm⁻² (Xia et al.) have been reported for small-molecule blends and 40 nJ cm⁻² for conjugated polymers. First-order gratings have the lowest thresholds (as discussed earlier), but at the expense of a degraded output beam quality. A clever approach has been proposed to combine the low threshold induced by first-order gratings with the enhanced beam quality of second-order gratings: with such a mixed structure, thresholds as low as 36 nJ cm⁻² were reported.

Figure 12. Performance of the LED-pumped organic laser proposed by Samuel’s group. The LED was manufactured by Philips (Luxeon) and driven with short current pulses to reach lasing threshold (details in Yang et al.). The inset shows a schematic of the device: the resonator is a second-order DFB grating. (Courtesy of Ifor Samuel. Reprinted with permission from Yang et al. Copyright 2011 American Institute of Physics.)
from 890 to 930 nm in a DFB structure, or even at 970 nm in a Fabry–Perot configuration, with a commercial dye (LDS 950) doped in a fluorinated polyimide waveguide. The optical gain is low in this case (1 cm⁻¹) and the lasing threshold relatively high (600 µJ cm⁻²). Gain measurements have been reported at a wavelength as high as 1.3 µm in IR1051 dye with a gain of 11 cm⁻¹ with pumping at 1064 nm.

A radically different solution to the wavelength span limit is to use the visible radiation emitted by organic systems and to convert it into UV or IR using nonlinear optics (i.e. using the nonlinear dielectric properties of matter subjected to very intense fields to generate optical harmonics). For a nonlinear process to be efficient, high peak intensities and good beam qualities (i.e. high brightness) must be achieved, which in practice makes this approach easier to implement with external resonators. Chandra et al. obtained tunable UV radiation of around 289 nm from a rotating pyromethene dye plastic disc with external frequency doubling. The same concept was applied by Mayer et al. to obtain mid-IR radiation of around 9 µm from difference frequency mixing of two solid-state dye lasers emitting at 740 nm (oxazine-1) and 803 nm (rhodamine 800). Recently, this approach was used in a thin-film organic laser with the VECSOL concept presented above.30 The authors solved the problem of low intensity (associated with thin-film organic lasers) by using an intracavity frequency doubling scheme, made possible by the open structure of the VECSOL. The proposed device is compact (1 cm long) and emits 1 µJ of diffraction-limited tunable UV monochromatic light of around 315 nm, from a rhodamine 640:PMMA active layer spun-cast onto one of the cavity mirrors (Fig. 13).

**Improving wavelength agility**

An important aspect that organic lasers must address for practical applications is the wavelength tunability or agility. In a microcavity laser, the emitted wavelength is directly related to the thickness of the active layer. Schütte et al. used this property to demonstrate an Alq₃:DCM laser continuously tunable between 595 and 650 nm made possible by a wedge-shaped microcavity structure. In this structure the material was evaporated through a rotating shadow mask to a thickness varying between 180 and 1850 nm. Similarly, Rabbani-Haghighi et al. obtained a 40 nm tunability from a VECSOL, where the spectrum is controlled by the sub-cavity formed by the active layer, making use of film thickness variations that arise naturally at the edges of a spun-cast film.

**Improving conversion efficiency and output power**

Most reports of thin-film solid-state organic lasers emphasize the spectral narrowing or threshold measurements without giving the output power obtained. The probable reason for that is the difficulty of measuring such low output powers or energies with a generally very diverging and non-homogeneous spatial beam profile. However, in some papers this information is given, and interesting slope efficiencies are obtained. For example, in an early study Kozlov et al. showed a 35% conversion efficiency (ratio of output power to input power) corresponding to a 70% quantum slope efficiency in a Fabry–Perot waveguide configuration (Fig. 8(d)) with Alq₃:DCM₂ used as a gain medium. The maximum output energy in this case was 0.9 nJ. Energies in the nanojoule range are typical for OSC lasers, essentially to a very small excitation volume. For a large number of applications, the nanojoule energy level could be sufficient anyway, as it corresponds to a watt-level peak power because of the short duration of the emitted pulses. The highest conversion efficiency was obtained recently in a VECSOL structure, where 57% optical-to-optical conversion efficiencies were obtained at the microjoule level.

**Improving beam quality**

Beam quality (or spatial coherence) was not a topic of major interest in early reports of organic lasers. As stated in a previous section,
Figure 14. Example of wavelength agility of a DFB laser through controlled mechanical stretching.169 (a) AFM image and (b) schematic of a self-organized PDMS grating used as the substrate in these experiments. (c) Example of wavelength coverage obtained versus applied strain in such a laser (grey and black lines compare the tunability obtained with a ‘cast and cure’ grating, obtained by replication onto PDMS of a wafer mater (grey), and self-organized PDMS (black); the active medium is a mixture of F8BT and MEH-PPV. (Courtesy of P. Gönn. Reprinted with permission from Gönn et al.169 Copyright 2011 John Wiley and Sons).

Figure 15. CCD image of the beam profile and $M^2$ measurement of a VECSOL121 ($M^2$ is defined as the ratio of the divergence to the theoretical diffraction-limited divergence). (Reprinted with permission from Rabbani-Haghighi et al.121 Copyright 2011 Optical Society of America).

the spatial beam quality is strongly dependent on the resonator geometry,96,106 and a typical thin-film waveguide laser may have multiple outputs and not-well-defined beams. However, it is possible to obtain a single transverse mode emission: the surface emission with a DFB structure can be near diffraction limited and exhibit relatively low divergence,104,105 even if a typical fan-shaped beam instead of a desired round homogeneous Gaussian beam is observed in 1D-DFB geometries. For edge emission, the small aperture of the waveguide as well as the poor facet quality (especially with spin-coated polymers) generally produce highly diverging and inhomogeneous beams. For vertical microcavity structures, it is relatively easy to obtain TEM$_{00}$ emission because of the symmetry of the cavity. However, the output energy is classically very low in those devices. A promising solution to combine relatively high output energies with perfect beam quality is to use an external cavity to control the transverse geometry of the laser beam121 (Fig. 15).

Enhancing the lifetime of devices

All organic materials tend to degrade rapidly under intense excitation. Lifetime issues have been extensively studied in the field of OLEDs, and because of improvements in encapsulating techniques and materials, lifetimes up to 10 millions hours have been interpolated.172 Because high peak intensities (and often at short wavelengths) are required to attain threshold in organic lasers, the lifetime issue happens to be more critical than in OLEDs. Even though lifetime measurements are not given in many reports of organic lasers, which makes comparisons difficult between materials or structures, a typical maximum is found to be $10^5 – 10^7$ pulses before the emission intensity decreases by a factor of two (either with microcavities57 or DFB structures104,173 under vacuum). Specific encapsulation schemes can be used to enhance the operational lifetime: it has been demonstrated that a careful encapsulation can enhance the lifetime by a factor of 2500,173 The effective lifetime can thus reach hours (depending on the repetition rate), which could be enough for several applications. Another approach is to create nanocomposite materials where the fluorescent units are incorporated into a polymer host acting as an oxygen and moisture barrier.174 This also has the advantage of creating relatively thick self-supported ‘membranes’, which might be disposable and cost-effective.

IS THERE SOMETHING BEYOND ORGANIC ‘PHOTON’ LASERS? POLARITON LASERS AND SPASERS

In this last section, we highlight two recent results which might open totally new landscapes in the field of organic lasers. They have in common that they put into question the very foundation of a laser as a ‘photon’ laser. In these studies, photons are replaced by quasiparticles: either cavity exciton–polaritons or surface plasmons (SPs). While the first may be an answer to the organic laser diode problem, the second one puts organic media into the position of playing a role in the generation of optical fields at the nanoscale.

Photons in microcavities: the polariton laser

The polariton stands at the crossroads between electromagnetic and matter waves, and its coherent state is thus somewhere between a classical photon laser1,68,175 and a Bose–Einstein...
condensate (BEC).\textsuperscript{176–178} In an optical microcavity, this half-light, half-matter quasiparticle is the expression of the strong coupling between excitons and photons inside the cavity.\textsuperscript{31,179–183} Consequently, the relevant eigenstates of the whole system are no longer photons or excitons, but a linear combination of both. In the limit of a vanishing photon character and at thermal equilibrium, an exciton BEC is obtained, whereas in the limit of a vanishing exciton character and a non-equilibrium situation the polariton laser is indistinguishable from a classical photon laser.\textsuperscript{31} Observation of polaritons at room temperature is tricky because the excitonic part of the polariton dissociates when the thermal energy $k_B T$ is comparable to the exciton binding energy. Interestingly, this binding energy is much higher with Frenkel excitons that best describe organic media than with the Wannier–Mott exciton binding energy is much higher with Frenkel excitons that best describe organic media than with the Wannier–Mott exciton

Surface plasmons (SPs) are collective oscillations of the conduction electrons of a metal. Surface plasmon polaritons (SPPs) are of particular interest: they are quasiparticles associated with electromagnetic waves coupled to free electron oscillations that propagate along the interface between a dielectric and a metal with a negative real part of permittivity.\textsuperscript{187} These waves have a higher $k$-vector than in vacuum (hence, a lower wavelength) and are evanescent in both metal and dielectric, leading to an enhanced electromagnetic field near the interface.\textsuperscript{188} However, because of metal absorption, SPPs cannot propagate over long distances, which is a serious impediment to building plasmonic circuitry. Many works of the last decade have then consisted of increasing the propagation lengths of SPPs by appending gain media in the dielectric. There have been several demonstrations of net gain or ASE\textsuperscript{189–192} in plasmonic structures incorporating organic gain materials, which can be dyes in solution,\textsuperscript{192} dyes in polymer matrices\textsuperscript{190,191} or conjugated polymers.\textsuperscript{189} Red (or IR) dyes are especially relevant here, as a compromise between minimizing metal losses (the longer the wavelength the better) and maximizing material gain (in the visible; see the previous section). Gather et al.\textsuperscript{189} measured a net optical gain of $8 \text{ cm}^{-1}$ with the variable stripe length technique in a long-range SPP mode where the gain medium is a mixture of a PP derivative (MDMO-PPV) with a poly(spiro-fluorene) polymer. The study of SPP modes also provides information about organics-on-metal quenching: De Leon and Berin\textsuperscript{193} showed that only the nearest molecules (\textless;10 nm away from the metal) are quenched through a dipole–dipole interaction to the electron–hole pairs of the metals, while most of the molecules located between 10 and 100 nm feed a short-range SPP mode rather than a radiative photon mode. This idea can be pushed forward to build a ‘SPP laser’ where the oscillating mode is a SPP: such a device was demonstrated by Oulton et al.\textsuperscript{194} with an inorganic CdS nanorod on silver. The device is characterized by a tight sub-wavelength confinement of the optical mode. Bergman and Stockman\textsuperscript{195} proposed a different way of approaching subwavelength lasers with the spaser: it makes use of nanoparticle (or nanolocalized) SPP instead of SPPs, which are the quanta of the collective oscillations of free electrons in a metal nanoparticle whose dimensions are between $ca$ 1 nm and the metal skin depth ($ca$ 25 nm). When such a nanoparticle is surrounded by a gain medium, a macroscopic population of SPs is expected to build from stimulated emission. The first experimental demonstration of a spaser was provided in 2009 by Noginov et al.,\textsuperscript{32} who used spheres of 44 nm in diameter composed of gold cores of 14 nm in diameter surrounded by OG-488 dye-doped silica shells as the gain medium (Fig. 16). The nanospheres were optically pumped at 488 nm and emitted a narrow line at 531 nm, which was assigned to the emission of dye molecules into a SP mode instead of a photon mode. The interest of spasers lies in their ability to generate electric fields oscillating at optical frequencies in nanolocated areas.\textsuperscript{196} This may be useful for microscopy (such as scanning near-field optical microscopy or fluorescence imaging with single-molecule sensitivity) and nanoscale lithography,\textsuperscript{185} or serve as a basis for ultrafast nanoamplifiers that have the potential to be the future building blocks of optical computers just as metal–oxide–semiconductor field-effect transistors are the basis of today’s electronics.

Nanoplasmonics and spasers

Plasmonics is a burgeoning field defined as the study of optical phenomena at the nanoscale vicinity of metal surfaces, and offers exciting perspectives of applications in nanophotonics,\textsuperscript{188} ultrafast nanoelectronics\textsuperscript{185} or biomedical optics,\textsuperscript{186} among others. At first glance, speaking of optics at the nanoscale, and moreover with the involvement of organic gain materials, may seem doubly paradoxical: first, because it is generally admitted that photons cannot be confined to areas much smaller than half their wavelength; second, because as we saw in a previous section, metals cause very large losses, and organic fluorescence near metals is strongly quenched.
In terms of processing techniques, will play a significant role in the electron microscopy image of gold core. (c) Scanning electron microscopy image of gold/silica/dye core–shell nanoparticles. (d) Spaser mode (in false colour), with $\lambda = 525$ nm and $Q = 14.8$; the inner and the outer circles represent the 14 nm core and the 44 nm shell, respectively. The field strength colour scheme is shown on the right. (Courtesy of Mikhail Noginov. Reprinted by permission from Macmillan Publishers Ltd, Nature (Noginov et al.)

Figure 16. (a) Schematic of a hybrid nanoparticle architecture (not to scale), indicating dye molecules throughout the silica shell. (b) Transmission electron microscopy image of gold core. (c) Scanning electron microscopy image of gold/silica/dye core–shell nanoparticles. (d) Spaser mode (in false colour), with $\lambda = 525$ nm and $Q = 14.8$; the inner and the outer circles represent the 14 nm core and the 44 nm shell, respectively. The field strength colour scheme is shown on the right. (Courtesy of Mikhail Noginov. Reprinted by permission from Macmillan Publishers Ltd, Nature (Noginov et al.)

ACKNOWLEDGEMENTS

The authors are very grateful to Elena Ishow and Alain Siove for stimulating and fruitful discussions.

REFERENCES
