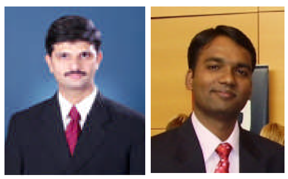
Laser Dyes

G S Shankarling and K J Jarag

This article is a short review of organic colorants used in dye lasers. The basic principle of a dye laser, requirements of a dye for good laser activity, and different types of dyes used for laser applications are discussed.



(left) G S Shankarling is an Associate Professor in the Dyestuff Technology Department of Institute of Chemical Technology, Mumbai. He is also in-charge of Perfumery and Flavour Technology. His research interest focuses on design and development of functional colorants, perfumery chemicals, green methods for fine chemical synthesis, process development for pigments and textile dyes.

(right) K J Jarag is pursing PhD under the guidance of Dr G S Shankarling in the Dyestuff Technology Department of Institute of Chemical Technolgy Mumbai since 2007. His doctoral research involves the synthesis of novel colorants for functional applications.

Keywords
Lasers, dyes, photostability, liquid-state dye lasers.

1. Introduction

Applications of lasers are wide and varied today. They are found in communication techniques, in microsurgery and in many spectroscopic applications such as Raman spectroscopy for following photochemical reactions and ultra fast reaction kinetics, in isotope separations, and in trace analysis, eg., detection of sodium atoms in concentrations as low as 0.003ng cm^{-3}. Dye lasers are the most versatile and one of the most successful laser sources known today due to their significant contribution to basic physics, chemistry, biology and other fields. The first laser dye was reported in 1966.

Traditional laser technology utilises a variety of inorganic materials to produce the required emission. Several different types of inorganic lasers have been developed to emit in ultraviolet, visible or infrared region of the electromagnetic spectrum. Though inorganic lasers are of low cost and robust devices, they have some drawbacks. They emit only at very few specific wavelengths and in very narrow bands, whereas dye lasers cover the entire visible and near IR region and have far greater tunability compared to inorganic lasers. Dye lasers are contributing greatly to the progress in laser technology.

The aim of this review is to give an overview of the different types of dyes used in laser technology application. We have focused on recent developments in liquid-state dye laser technology.

2. Principle

The term LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. A laser is a device used for the amplification or generation of coherent light waves in the UV, VIS, and near IR region.

The principle of stimulated emission (*Figure* 1) is explained here.

a) Light absorption brings molecules from the ground state S_0 to the excited state S_1.

b) The absorbed energy is lost, e.g., by fluorescence which leads to no phase relationship between the emitted photons.

c) When the excited molecules are irradiated by a light flash corresponding to the energy difference between S_1 and S_0, stimulated emission occurs within the average lifetime of excited state S_1. This means that the excited molecule, when hit by such a photon, emits a second photon of the same energy, intensity, phase and direction (polarization).

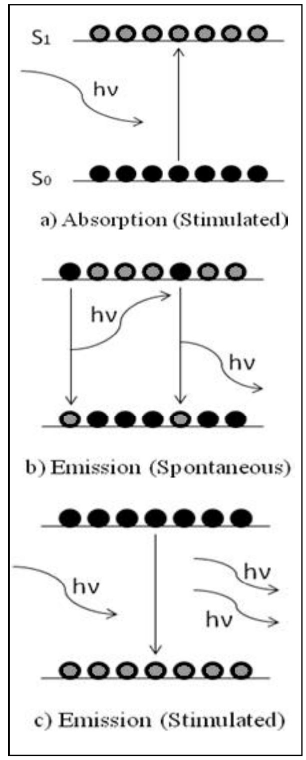
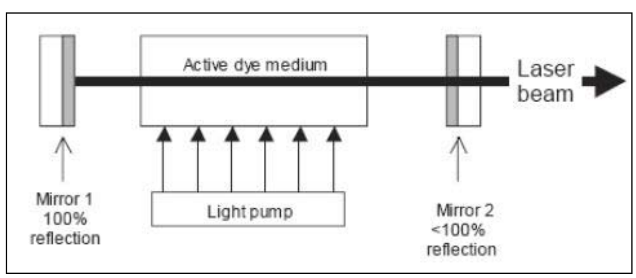


Figure 1. Principles of light absorption and emission.

A condition for stimulated emission to occur is that the number of molecules in the excited state S_1 is higher than that in the ground state S_0 at the moment of flash. The situation in which molecules exist predominantly in an excited state rather than ground state is known as population inversion and is brought about by pumping the system with a source of energy.

A simple schematic representation of a technical laser is presented in *Figure* 2. The active medium (AM) is the system that is responsible for stimulated emission. The light energy pump (EP) provides the energy for the inversion of the population, and Mirror 1 and Mirror 2 are parallel mirrors that amplify the stimulated emission by multiple passages through the laser cavity. A small fraction of the laser light leaves the cavity through Mirror 2 and is used for the given application.

Figure 2. Basic elements of laser.



There are several ways in which we can classify the different types of lasers. They can be classified on the basis of their mode of operation or according to what material is used as the active medium. Depending on their mode of operation, lasers are classified as

- Continuous wave (CW) lasers and
- Pulsed wave lasers.

Lasers are also broadly divided into four categories on the basis of the material used as an active medium. They are

- Solid lasers
- Liquid lasers
- Gas lasers
- Semiconductor lasers.

Dye lasers belong to the family of liquid lasers. The active material is a dye dissolved in a liquid solvent. The approximate working ranges of various laser dyes are shown schematically in *Figure* 3.

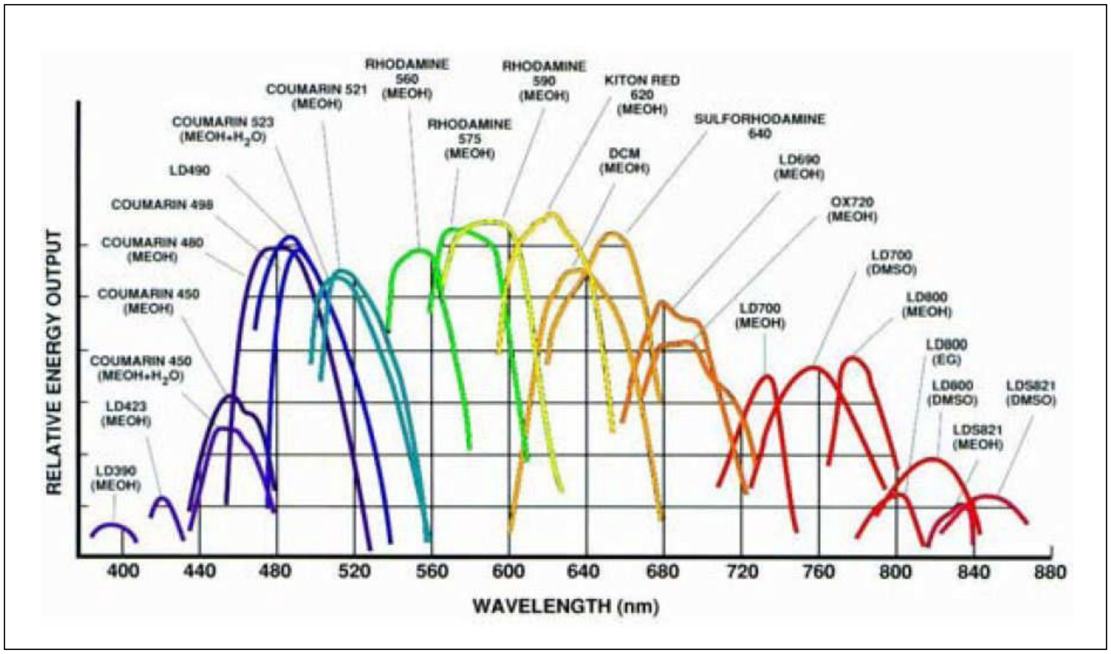


Figure 3. Dye spectral emission characteristics.

3. Requirements of Dyes for Laser Application

For effective performance, dye molecules should have the following characteristics:

- Strong absorption at excitation wavelength and minimal absorption at lasing wavelength, i.e., minimum overlap between absorption and emission spectra.
- High quantum yield (0.5–1.0).
- Good photochemical stability.
- A short fluorescence lifetime (5–10 ns).
- Low absorption in the first excited state at the pumping and lasing wavelengths.
- Low probability of intersystem crossing to the triplet state.
- Laser dyes have to be very pure since impurities frequently quench the laser output.

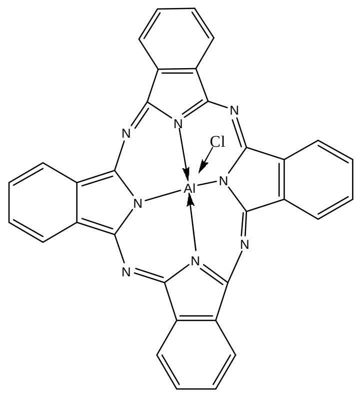
By appropriate dye selection it is possible to produce coherent light of any wavelength from 320 to 1200 nm.

4. Different Classes of Laser Dyes

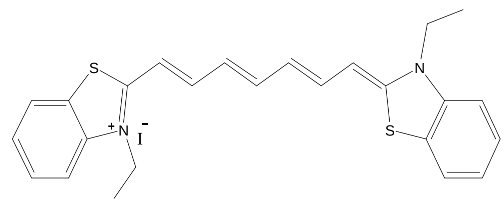
Generally, laser dyes are complex molecules containing a number of ring structures, which lead to complex absorption and emission spectra. The laser dyes can be categorized into different classes by virtue of their structures that are chemically similar. Common examples are the coumarins, xanthenes and pyrromethenes. The structure and composition of the molecule has an important influence on spectral emission.

Laser dyes are complex molecules containing a number of ring structures, which lead to complex absorption and emission spectra.

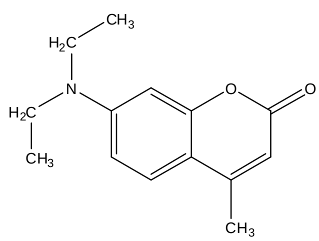
The laser activity of dyes was first observed from chloro-aluminium-phthalocyanine (**1**) by Sorokin and Lankard and from 3,3′-diethylthiatricarbocyanine (**2**) by Schmidt and Schafer.



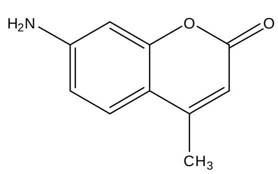
(1) Chloro-aluminium-phthalocyanine.



(2) 3,3′-diethylthiatricarbocyanine.



(3) 7-Diethylamino-4-methyl-coumarin (coumarin 125)



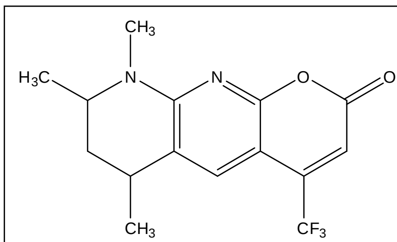
(4) 7-amino-4-methyl-coumarin (coumarin 120)

4.1 *Coumarin Laser Dyes*

A group of widely used laser dyes emitting in the blue-green region of the spectrum are derived from coumarins by substituting 7-position with auxochromes such as –OH, $–OCH_3$, $–NH_2$, $–NHCH_3$, $–N(CH_3)_2$ and other electron-donating substituents. The first coumarin laser dye was 7-diethylamino-4-methylcoumarin (**3**) which exhibits laser action at about 460 nm under flash lamp excitation.

The amino analogue, 7-amino-4-methylcoumarin (coumarin 120) (**4**) shows laser action at 440 nm.

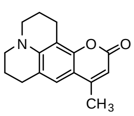
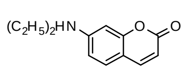
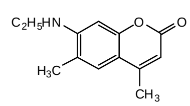
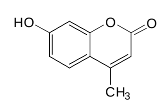
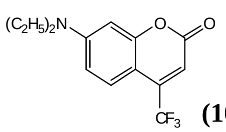
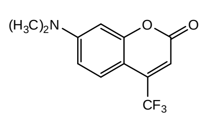
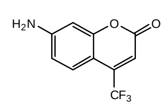
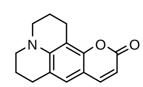
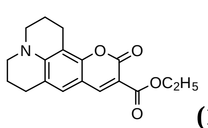
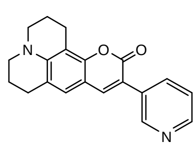
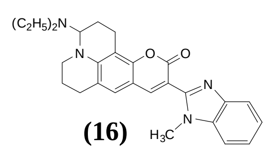
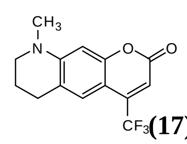
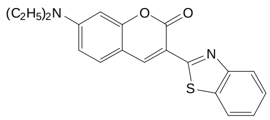
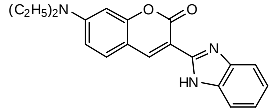
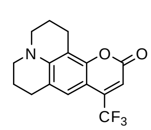
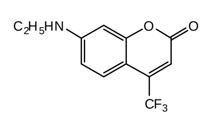
In some coumarin dyes the basic chromophore is replaced with its heterocyclic analogues like aza-coumarin, quinolone, or aza-quinolone in order to enhance the dye properties. AC3F dye (**5**) is an example for these class of dyes.



(5) AC3F Structure.

Coumarin dyes have the tendency for low photostability. Coumarins degrade due to laser light. The side products formed after degradation also absorb in the laser region which may give undesired effects. Coumarin molecule as such is non-fluorescent, but it exhibits intense fluorescence on substitution of various functional groups at different positions. In general, electron-donating substituents tend to enhance emission intensity while electron-withdrawing substituents tend to diminish it. The intensity of the dye laser beam cannot be increased over a certain range of the pump power and is limited by saturation. This is due to photo-quenching effect. Studies on the photo-quenching properties in various dyes have shown that the effect plays a crucial role in the performance of pulsed laser pumped dye laser systems. Some of the commercial coumarin laser dyes are listed in *Table* 1.

Table 1. Examples of coumarin laser dyes

Coumarin 102  **(6)**	Coumarin 466  **(7)**	Coumarin 2  **(8)**	Coumarin 4  **(9)**
Coumarin 152A  **(10)**	Coumarin 152  **(11)**	Coumarin 151  **(12)**	Coumarin 6H  **(13)**
Coumarin 314  **(14)**	Coumarin 510  **(15)**	Coumarin 30  **(16)**	Coumarin 522  **(17)**
Coumarin 6  **(18)**	Coumarin 7  **(19)**	Coumarin 153  **(20)**	Coumarin 500  **(21)**

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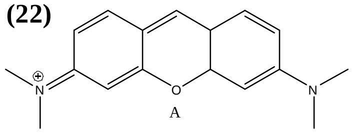

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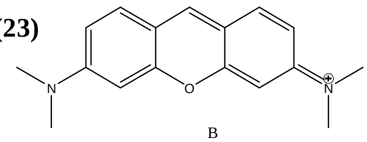
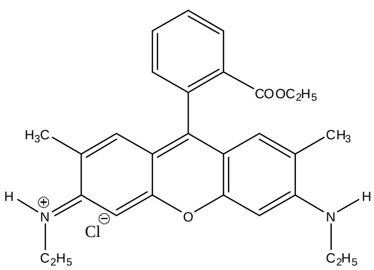
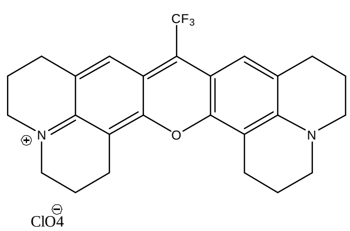


The π-electron distribution in the chromophore in the xanthenes dyes.



(24) Rhodamine 6G



(25) Rhodamine 700

4.2 *Xanthene Dyes*

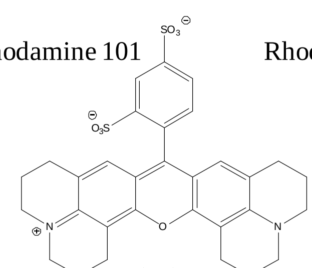
Xanthene dyes cover the wavelength region from 500 to 700 nm and are generally very efficient. Most of the commercial dye lasers are from this class – Fluorescein and Rhodamine B are the two widely used laser dyes. The electron distribution in the chromophore in the xanthenes dyes can be described by the following two identical mesomeric structures, (**22**) and (**23**).

Rhodamine 6G (**24**) shows efficient laser action in the 590nm region and lases with about one percent efficiency in most flashlamp pumped dye lasers. It is used as reference dye to measure the efficiencies of other dyes. Since Rhodamine 6G also exhibits good photostabilty, this laser dye is one of the most often used and studied. Most of the xanthene laser dyes show efficient laser action in the 560 to 800 nm region. Rhodamine 700 (**25**) is another efficient laser dye obtained by molecular engineering. This efficient dye exhibits laser action between 700 to 800 nm.

Rhodamine 700 has the 'double butterfly' structure, which enables the amino groups to become more rigid and planar (**25**). Replacing the phenyl group substituent of Rhodamine 6G by the $-CF_3$ group enhances its photostability. *Table* 2 shows some of the commercial xanthenes class laser dyes.

Table 2. Examples of Rhodamine laser dyes.

Rhodamine 101



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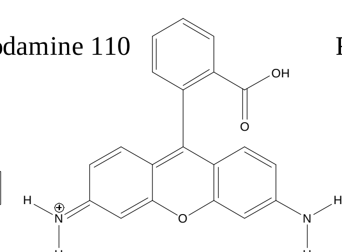
Rhodamine 110



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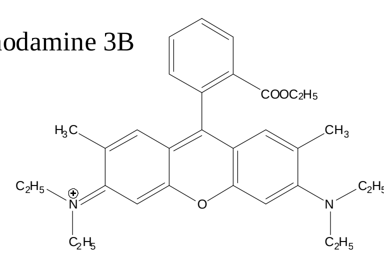
Rhodamine 3B



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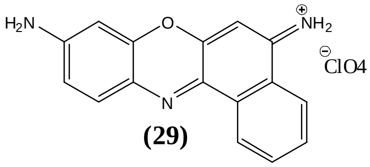
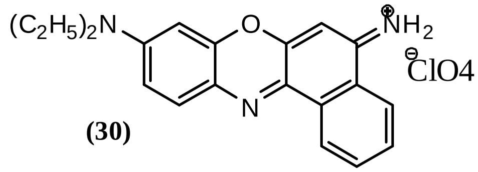
Oxazine 9



(29)

Nile Blue



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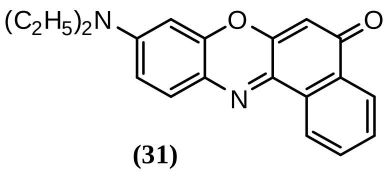
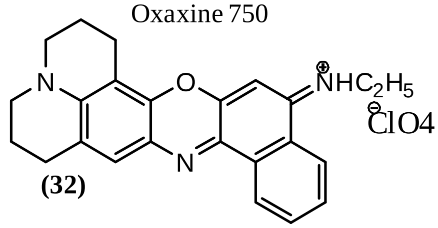
Phenoxazone



(31)

Oxaxine 750



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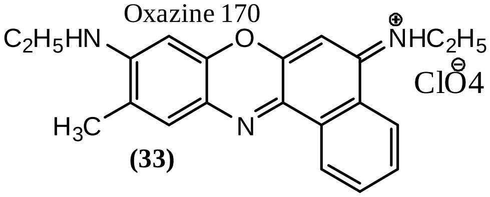
Oxazine 170



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Oxazine 1

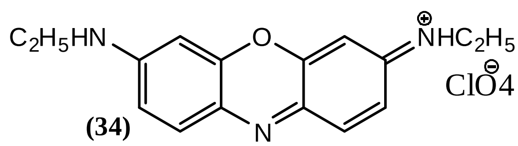

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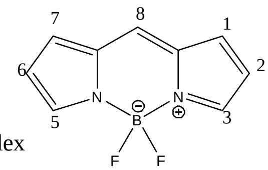
Table 3. Examples of oxazine laser dyes.

4.3 *Oxazine Dyes*

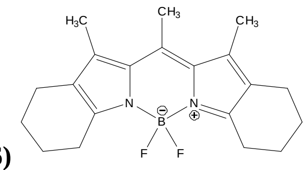
Oxazine dyes are planer and are rigid like xanthene dyes. All oxazine dyes are photochemically more stable than xanthenes. Some of the well-known oxazine laser dyes are listed in *Table* 3. A few commercial oxazine dyes such as cresyl violet, nile blue, etc., used for textile applications are also used as laser dyes. These are cationic dyes.

4.4 *Pyrromethenes*

Boron-dipyrromethene dyes, also known as BODIPY, are fluorescent dyes used for laser application. They are composed of dipyrromethene complexed with a disubstituted boron atom, typically a BF_2 unit. BODIPYs are an important class of laser dyes. They are tunable in the green–yellow visible region of the electromagnetic spectrum. They exhibit high lasing efficiency, good photostability, high fluorescence quantum yield, low rate



(35) BODIPY complex

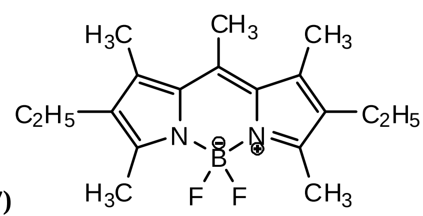


(36)

constant of intersystem crossing and large molar absorption co-efficiency. The photophysical properties of these dyes can be modulated to some extent by incorporating the adequate substitution in the molecular structure of the parent BODIPY chromophore. The general structure of BODIPY complex is shown here (**35**).

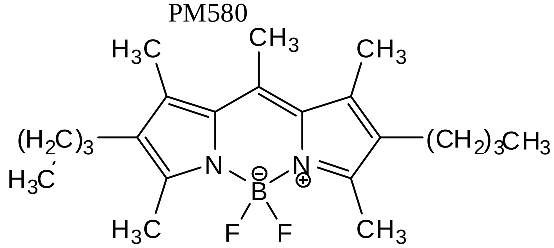
Table 4. Important BODIPY laser dyes.

PM567



(37)

PM580



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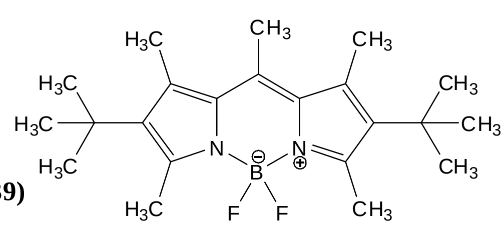
PM597



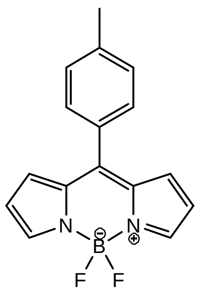
(39)

Some of the BODIPY complexes are commercially available. The 1,3,5,7,8-pentamethyl-BODIPY complex in ethanol exhibited laser action at 546 nm and lased about three times more efficiently than Coumarin 545 and about 10 percent less efficient than Rhodamine 6G. The 1,3,5,7,8-pentamethyl-2,6-diethyl-BODIPY (**37**) complex commercially known as Pyromethene-567 lases at 567 nm and has an output about three times higher than that of Rhodamine 560. Other BODIFYs show similar efficiencies. Another typical BODIPY complex is (**36**).

This dye (**36**) ranks among the more efficient BODIPY dyes. The molecular structures of three of the most important commercial BODIPY dyes are shown in *Table* 4.

New BODIPY dyes with two 4-formyl-phenyl,4-(2,2-dimethoxycarbonyl-vinyl) phenyl and 4-(2,2-dicyano-vinyl)phenyl groups at the 3- and 5-positions are listed

Table 5. Continued...



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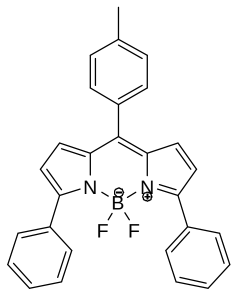

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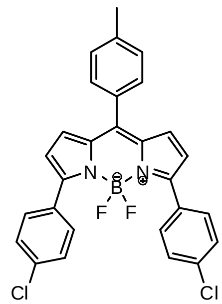

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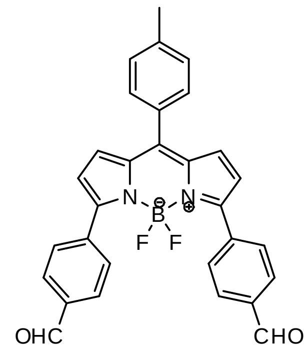

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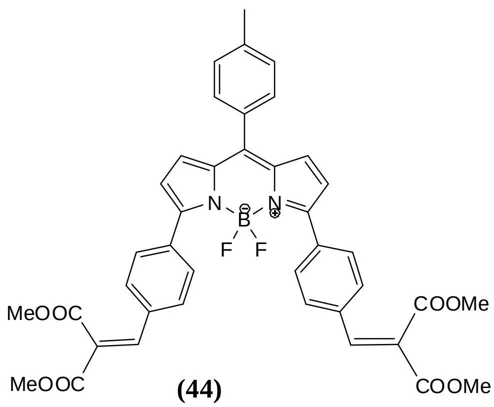

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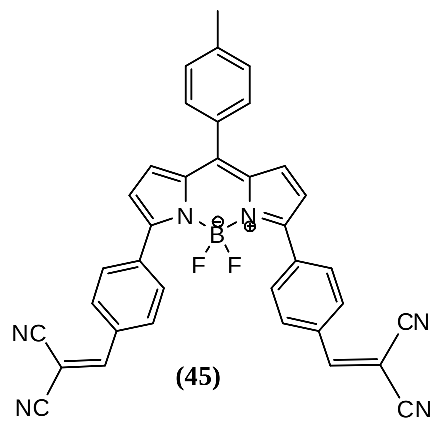
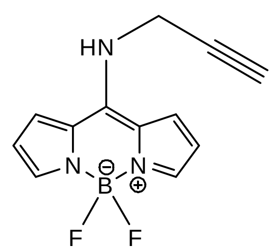


(45)

Table 5. BODIPY laser dyes.

in *Table* 5. Recently, the synthesis of 8-propargylamino BODIPY laser dye (**46**) with emission in the blue spectral region has been reported.

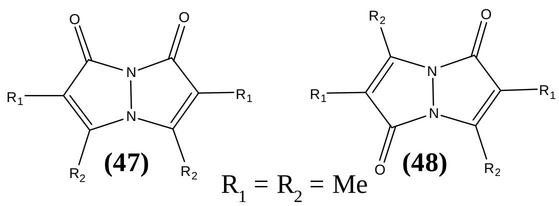


(46) 8-propargylamino BODIPY

Apart from these classes, a number of other laser dyes are described by Brackman in the book *Lambdachrome Laser Dyes*.

5. Designing a Laser Dye

In recent years, molecular engineering and suitable additives have led to superior laser dyes with increased photostabilities. For instance, replacement of 4-methyl group in Coumarin 125 (**3**) by more stable trifluoromethyl group resulted in a thermally more stable compound Coumarin 152. The compounds (**47**) and (**48**)



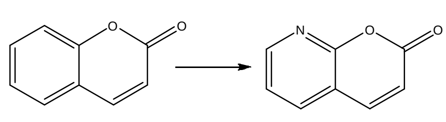
(47) (48) $R_1 = R_2 = Me$

are an interesting class of fluorescent compounds. The compound (**47**) is known as syn-biamine which gives rise to very high fluorescent quantum yield of 0.7 to 0.9, whereas the corresponding 'anti' isomer (**48**) is however, only weakly fluorescent.

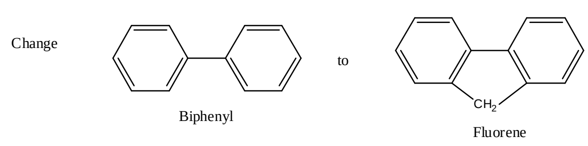
T G Pavlopoulos in his overview on laser dyes titled *Laser dyes: structure and spectroscopic properties* [4], has discussed various approaches to design laser dyes by molecular engineering and spectroscopic studies.

Following are a few approaches to design better laser dyes.

- Following the classical methods of organic dyes, one can keep the chromophore constant and change the auxochrome groups to improve properties of the laser dye. For example, replacing one or more carbons by a hetero-atom improves the laser effect as shown below in coumarins (**49**) and azacoumarins (**50**).
- Enhancing molecular rigidity of the dye to improve its quantum yield and laser action efficiency. Example Biphenyl **(51)** with $Q_F = 0.18$, whereas the $>CH_2$ bridged fluorene (**52**) which has a $Q_F = 0.80$ in cyclohexane.
- The photostability of dyes (e.g., coumarin) may be improved by switching a $-CH_3$ group to a $-CF_3$ group.
- Planar molecules exhibit strong fluorescence because the motion of electrons is not restricted in them. However, in case of non-planar molecules, resonance is reduced or even lost due to steric crowding. For example, to keep the amino group



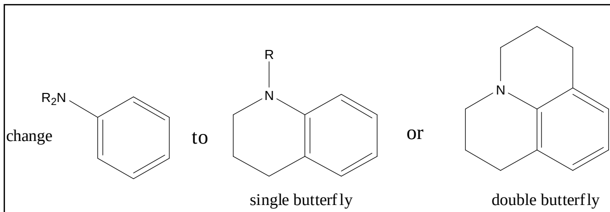
(49) Coumarin **(50)** Aza-coumarin



(51) **(52)**

coplanar, it has been replaced by the single butterfly or double butterfly system as shown in (**53–55**).

By adopting the molecular design theory, about 125 new coumarin derivatives have been reported over the last 40 years.



(53) **(54)** **(55)**

Methods for rendering atoms and groups planar to molecular plane.

6. Applications

Industrial applications of laser dyes include separation of isotopes of important radioactive elements such as Uranium. Uranium is used as fuel in the nuclear power reactors to generate electricity. In nature, uranium exists as several isotopes: primarily uranium-238, uranium-235, and a very small amount of uranium-234. The medical applications of laser dyes include skin treatments, including port-wine stain and tattoo removal, diagnostic measurements, lithotripsy, activation of photosensitive drugs for photodynamic therapy, etc.

In the field of medical applications, dye lasers have potential advantages over other lasers. Dye lasers are unique sources of tunable coherent radiation, from the ultraviolet to the near infrared, using hundreds of dye molecular species. Broadly tunable lasers have a tremendous impact in diverse fields of science and technology. A Costela and coworkers have reviewed the medical applications of dye lasers [8]. Some of the most important clinical applications of dye lasers are presented here.

6.1 *Laser Treatment of Port-Wine Stains*

Port-wine stains (PWS) were one of the first vascular malformations to be treated with laser radiation. They are congenital malformations consisting of superficial and deep dilated capillaries in the skin. The swollen blood vessels cause a reddish discoloration of the skin. Although PWS can appear in any part of the body, they occur more often on the face and persist throughout life.

In the field of medical applications, dye lasers have potential advantages over other lasers.

After successful treatment, no textural changes or damage to the surrounding dermis is seen in treated skin.

Optical fibers conduct light from the laser head to the malformed area, and convex lenses focus the laser beam directly onto the skin to a spot of at most 1cm diameter, to reach energy fluencies (radiant exposure) in the range 4–10 J/cm^2, depending on the age of the patient and the region irradiated. Children, with smaller overall lesions and more superficial vessels with smaller diameters, require lower energy fluence than adults. Sensitive areas, such as eyelids and hands, also require reduced energy fluence. After successful treatment, no textural changes or damage to the surrounding dermis is seen in treated skin.

6.2 *Lithotripsy*

Lithotripsy is a medical procedure that uses shock waves to break up stones that form in the kidney, bladder, and gallbladder. There are several forms of lithotripsy. The most common is extracorporal shock wave lithotripsy; however, for typical stone types and restricted access, laser lithotripsy acts as a complementary technique.

In the usual extracorporal shock wave lithotripsy (ESWL) technique, an externally applied, focused, high-intensity acoustic pulse passes through the body to the area on the stones. The successive shock wave pressure pulses break the stones into tiny pieces that then can pass easily through the ureters or the cystic duct.

When a laser is used, a train of laser pulses is guided by a fiber to the application site which ignites plasma at the surface of the stone. The breakdown of the plasma creates a shock wave, which detaches some fragments. After many repetitions, the stone will be fragmented into smaller pieces, which then can pass spontaneously.

Lithotripsy is a medical procedure that uses shock waves to break up stones that form in the kidney, bladder, and gallbladder.

The laser parameters appropriate for lithotripsy have a wide range, depending on fiber diameter, lasing wavelength, location, and composition of stones, which define their absorption bands. Typical operational parameters of flashlamp-pumped dye lasers used in lithotripsy treatment are: emission wavelength of 504 nm and 595 nm, depending on stone composition; pulse energy in the range 50–120mJ/pulse; pulse duration from 1–42.5 μs; and repetition rate of 1–10 Hz. The procedure requires endoscopic control of laser effects and a system for stone recognition. Since the laser light is green, there is minimal tissue absorption and almost negligible tissue damage. Because the energy effects take place on structures with crystalline makeup, soft tissue is basically unaffected. Thus, even if the laser fiber fires repeatedly against the urethral wall, very little tissue damage takes place.

6.3. *Laser Angioplasty*

Arteries can become narrowed or blocked by deposits called plaque. Plaque is made up of fat and cholesterol that builds up on the inside of the artery walls. This condition is called atherosclerosis. Angioplasty is a medical procedure to open arteries that are obstructed by atherosclerotic plaque. It involves different forms of minimally invasive vascular interventions, which can be exemplified by balloon angioplasty, a procedure in which a balloon is used to open a blockage in an artery narrowed by atherosclerosis.

Laser angioplasty is a promising alternative method to open arteries obstructed by atherosclerotic plaque, with potential advantages over surgery, balloon angioplasty, and other forms of vascular interventions. Laser radiation can be introduced into arteries via small optical fibers, thus avoiding major surgery. The radiation can remove plaque rather than displacing it, thus potentially reducing the high rate of restenosis (gradual re-narrowing of the artery during several months following the procedure) that occurs with balloon angioplasty. Laser radiation with the appropriate wavelength is preferentially absorbed by plaque, thereby adding an element of specificity and safety that does not exist with mechanical devices.

6.4 *Laser Treatment of Vascular Lesions*

Most vascular abnormalities can be successfully treated with lasers. A theory of selective photothermolysis predicts that selective destruction of blood vessels is possible by matching the

Suggested Reading

[1] K H Drexhage, Structure and properties of laser dyes, *Laser Focus*, Vol.3, pp.35–36, 1973.

[2] K Drexhage, *Dye Lasers*, Edited by F P Schafer, Springer-Verlag, Berlin, pp.167–173, 1990.

[3] U Brackmann, *Lambdachrome Laser Dyes*, Lambda Physik, Germany, pp.27–213, 1994.

[4] T G Pavlopoulos, *Laser dyes: structure and spectroscopic properties*, Edited by H S Freeman and A T Peters, Elsevier Sciences, pp.275–337, 2000.

[5] M Maeda, *Laser Dyes*, Academic Press, New York, pp.161–167, 1984.

[6] P Gregory, *High Technology Applications of Organic colorants*, Plenum Press, New York, London, pp.27–28, 1991.

[7] D Klick, *Dye laser Principles with applications*, Edited by F J Durarte and L W Hillman, Academic Press, Boston, pp.345–412, 1990.

[8] A Costela, I García-Moreno, and R Sastre, *Tunable Laser Applications*, Edited by F J Duarte, CRC Press, Taylor and Francis Group, 2nd Edition, pp.227–244, 2009.

wavelength of light absorbed by hemoglobin into the vessels. Defining thermal relaxation time as the time required for the target tissue to lose 50% of its heat, they proposed using a pulsed laser with the appropriate wavelength and with a temporal pulse length shorter than the calculated thermal relaxation time for blood vessels. This led to the development of flashlamp-pumped pulsed dye lasers (FPDL) especially designed for treatment of cutaneous vascular lesions. The first FPDL systems used in the treatment of vascular lesions were tuned to yellow, at 577 nm, a wavelength in the region of the third absorption spectral peak of oxyhemoglobin. The pulse duration was in the range 300–500 ms, calculated to match the thermal relaxation time of cutaneous blood vessels.

6.5 *Prospects of Dye Lasers*

A number of research groups are working around the world to develop dye laser technology for a wide range of applications. Nowadays the use of solid matrices containing laser dyes are coming as an attractive alternative to the conventional liquid dye solutions. The future of laser dyes continues to be good. Currently the main challenge in the development of dye lasers is to increase their photostability and to extend the range of output of the dyes.

7. Summary

Dye laser technology has advanced significantly over the last 50 years since the first laser action was from chloro-aluminium-phthalocyanine. The laser dyes find uses in many scientific, industrial, medical and military applications, ranging from spectroscopy to potential countermeasure devices.

The development of a new dye laser is related to the development in terms of easy tunability, wide wavelength coverage and synthetic simplicity. Changing of functional groups within the classes of laser dyes having good laser characteristics has proven to be a useful way of creating new laser dyes.

Address for Correspondence
G S Shankarling and
K J Jarag
Dyestuff Technology
Department
Institute of Chemical
Technology, Matunga
Mumbai 400 019, India
Email:
gsshankarling@gmail.com