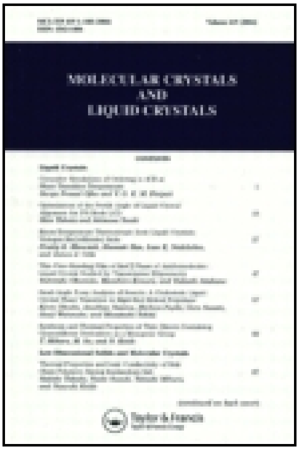

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Dyes for Optical Recording

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Dyes for Optical Recording

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Dyes for optical recording systems such as laser optical recording systems, laser printing systems, cycolor and related systems, xerography and so on are reviewed. Infrared absorbing (IR) dyes are newly designed for laser optical recording systems such as DRAW and erasable type recording systems. The chemistry of IR dyes developed the new fields in dye chemistry. Many of functionalities in dye chromophores are newly developed for optical recording systems such as PHB and cycolor systems. New technology has developed new dye chemistry and new characteristics of dye chromophores advanced the technology for new optical recording systems.

Keywords: optical recording, information recording, PPP MO method, molecular design, dye media

1. INTRODUCTION

According with the advances in high technology for information recording systems, the electro-magnetic recording systems are being replaced with the optical recording systems which have recording capacity of more than several hundred times compared with the electro-magnetic counterpart in which inorganic recording media are used. The full color hard copy systems required the development of new coloring matters such as leuco dyes, color toners, new charge generating materials (CGM) for OPC and so on.

New laser technology has developed new dye chemistry. It is the chemistry of infrared absorbing (IR) dyes.[1] Development of diode lasers which emit laser light at 780–830 nm has enabled the development of new opto-electronic systems including laser optical recording systems, laser printing systems, and so on.[2] In the systems, IR dyes can be used as a photoreceiver for diode lasers as a light source. Laser light can be highly monochromatic, very well collimated, coherent, and in some cases, extremely powerful. These characteristics made diode lasers a very cheap, convenient, and useful light source for a variety of applications in science and technology.

On the other hand, the idea of erasable optical recording systems developed new photochromic dye systems. Photochromic properties of dye chromophores have been well known[3] but their durability as recording media and absorption maxima in both states should be designed carefully for erasable optical recording media.

The photochemical hole burning (PHB) optical recording system has been developed as one of high density optical recording systems in a future. The dye media having special characteristics can be applied for these systems. New technologies such as cycolor system for one shot color copy, decolorizable toner for the recycle of copying paper, leuco IR dyes for bar-code systems, and new charge-generation materials for OPC in laser printer systems are currently investigated for the applications of dye materials for high performance optical recording systems. In this paper, dyes for optical recording systems are reviewed.

2. INFRARED ABSORBING DYES FOR OPTICAL RECORDING SYSTEMS

2.1. Molecular Design of IR Dyes

The color-structure relationship is the most important factor for the molecular design of IR dyes. IR dyes do not have any color in principle but comprise a very new category of dyes, and their synthetic design should be based on the new ideas and methodology. The absorption spectra of IR dyes must be predicted correctly in order to apply dye materials for diode lasers, which emit single-wavelength laser light at 780–830 nm. The PPP MO method can be used to design IR dyes, and it analyzes chromophoric systems of dyes and then the substituent effect on the absorption spectra can be evaluated quantitatively. Some sets of PPP MO programs that can be run on personal computer are now available for design of dye chromophores. They are set up automatically by including structure drawing and parameter setting, and then parts of desirable results such as energy levels of the frontier orbitals, π-electron densities and their changes accompanying the first excitation can be printed. Several minutes are required for the calculation of a medium-sized dye molecule. The applications of the PPP MO method for dye chromophores have been summarized by Griffiths,[4] Fabian and Hartmann.[5] Recently we published a book in Japanese entitled Molecular Design of Functional Dyes by the PPP MO Method.[6] It summarizes the parameters for calculations and deals with practical examples to design IR and some other dyes. In case of the molecular design of indonaphthol type IR dye, for example, the π-electron density changes accompanying the first transition of the parent chromophore **1** are shown in Figure 1.

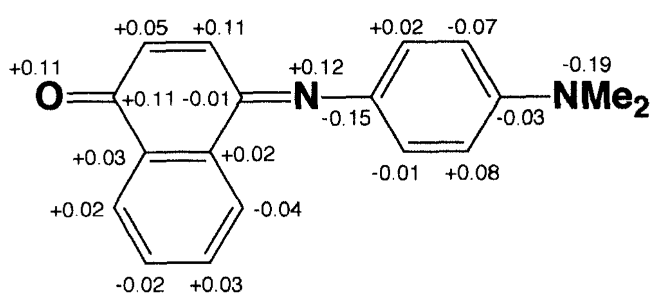

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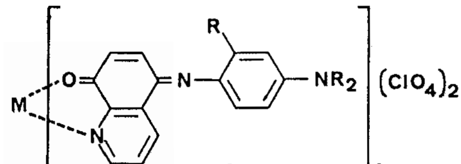
FIGURE 1 π-electron density changes accompanying the first excitation of dye **1**.

The values indicate the intramolecular charge-transfer (CT) character of chromophoric system in dye **1**; that is, the aniline moiety acts as a donor and the naphthoquinoneimine moiety acts as an acceptor. From these results, substitution of an acceptor at the 2- and/or 3-positions, or substitution of a carbonyl group by a much stronger acceptor such as a dicyanomethylene group causes a large bathochromic shift of λ_{max}. The practical effect of a bathochromic shift was observed in dyes **2** and **3**.



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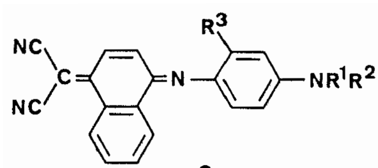

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The other IR dye chromophores can be designed in the same way from the point of their absorption properties. The ε values of dye chromophores can be also calculated by the PPP MO method as *f* value of oscillator strength. The solubility of dyes, which is an important factor for their application by the wet-coating method, is mentioned in the later section.

2.2. IR Dyes for DRAW System

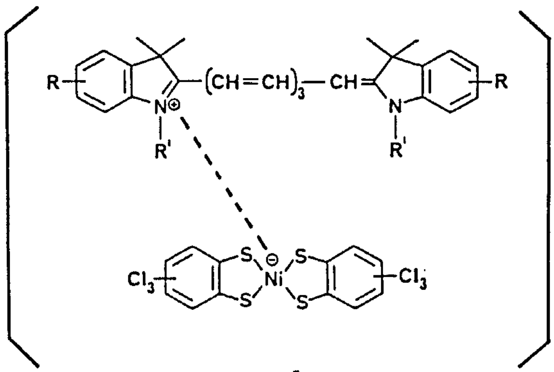
An optical recording system allows a user to record and reproduce the information which can be converted into electrical signals and then into optically modulated signals. The user can record the information onto the optical memory disk, and it can be optically reproduced by reading the difference of the reflectance on light irradiation. The optical disk drive and its recording/reproducing system are designed to record and read the information by light irradiation onto the recording medium.[7]

By function, optical disks are classified into two types; the erasable type, which allows overwriting of the information many times, and the write-once or direct read after write (DRAW) type, which allows a user to record the information only once onto the recording media. By recording principle, optical disks can be classified into two functional modes; the heat mode, which causes the structural alternation on the media by heat on light absorption such as the case of DRAW media, and the photon mode, which causes the reversible structural changes by means of photoenergy in case of photochromic media. Many types of IR dyes have been developed and evaluated for DRAW type recording media. The general requirements for dye media are as follows:

1. Strong absorption at around 800 nm.
2. High reflectance over 15% at 800 nm for reproducing.

3. High recording sensitivity; large ε, low thermal conductivity, and large optical difference after writing.
4. Light stability against reproducing light; thermal stability.
5. Durability for storage, nontoxicity.
6. Homogeneity of recording layer by wet coating method.

The other practical requirements for dye media were also summarized.[7]



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Synthetic design and structural modification of dyes to shift the λ_{max} into the IR region are studied. In general, the thin layer of dye medium absorbs at longer wavelength by 30–50 nm than that in solution of the same dye, and it shows broader absorption spectra in the solid state. The absorption spectra of 190 IR dye chromophores in solution and on thin film are summarized as a data book.[8] Cyanine IR dye with dithiol nickel complex as a counter anion (dye **4**) was the first example which was practically used as a dye medium for DRAW system. Cyanine dyes generally have poor light stability but the light stability was very much improved by using singlet oxygen quencher (nickel complex) as a counter anion. The absorption spectra, reflectance curve and transmission spectra of dye **4** on wet coating thin film are exemplified in Figure 2.

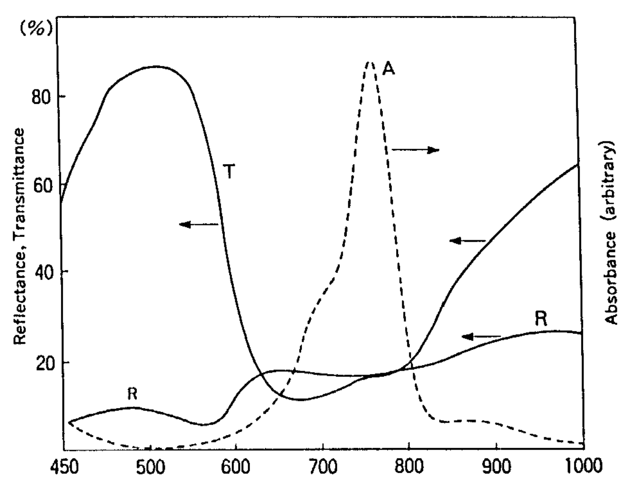
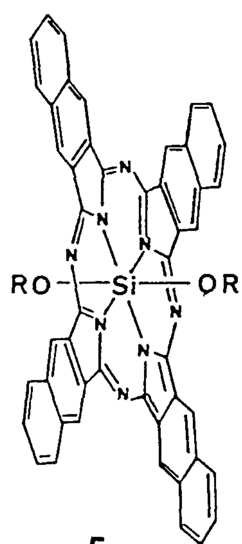


FIGURE 2 Absorption, reflection and transmission spectra of cyanine-metal complex dye **4** on thin film.

Some phthalocyanine metal complexes[9] absorb at the IR region and are evaluated as dye media. But they have poor solubility in organic solvents and then their sensitivity are insufficient. Introductions of phenylthio groups in phthalocyanine nucleus shift the λ_{max} into the IR region and improve largely their solubility in organic solvents by the steric hindrance of the substituents. The intermolecular π-π interaction to form aggregates is sterically restricted and the solubility is improved. Another example to improve solubility by steric hindrances of substituents is well known in naphthalocyanine chromophores. Naphthalocyanine[9] absorbs at the IR region which is produced by the annelation in benzene rings of phthalocyanine. Introduction of long alkyl groups or branched alkyl groups to naphthalene rings of naphthalocyanine improved their solubility in organic solvents. Silicone naphthalocyanine, which can have two substituents from the central silicone to upper and lower sides from the π-plane, prevented their aggregation by steric hindrance of long alkoxyalkyl substituents as shown in dye **5**. Dye **5** has enough solubility for wet coating process to prepare thin film for recording media.



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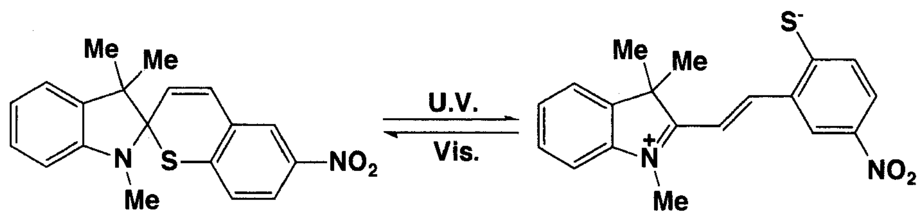
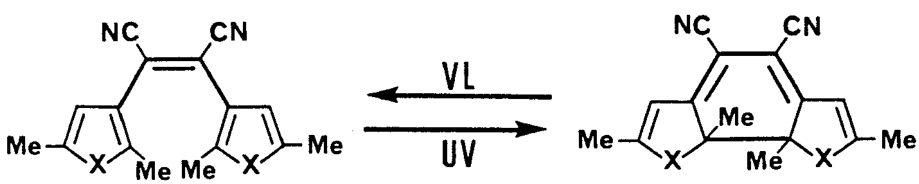
Indonaphthol metal complex IR dyes **2**, which absorb in the IR region and have large ε values corresponding to those of cyanine dyes, are also one of the candidate for dye media.[10] Dicyanomethylene indonaphthols **3** which have good characteristics for dye media are also known.[10] The practical uses of dyes **2**–**5** as dye media for various optical recording systems are under investigation.

2.3. Dyes for Erasable Optical Recording

The dyes that show photochromic properties due to bond alternation or tautomerism are important for use in erasable optical recording media. In the systems two or three different wavelength laser lights should be used for recording and reproducing of information. Spiropyrans and fulgides are well known as photochromic compounds but their colored forms do not have absorption band in the IR region, and their recycle durability is not enough for practical use. Spirothiopyran **6** is colorless but absorbs at 700 nm after u.v. irradiation to give cyanine dye **7** which reverts to dye **6** again on exposure to visible light but the recycle durability of this system is poor.[11] Diarylethene derivatives **8** have superior durability for recycle use (10^4 times) and have irreversibility of cycle by heat energy.[12] But these compounds do not have strong absorption in the IR region and can not be applied as erasable dye media for diode laser optical recording systems. A large bathochromic shift of the colored form of **8** is anticipated, but is difficult from the observation of the PPP MO calculation results. The erasable optical recording disk systems by using photochromic dye media are not commercialized yet.



6 **7**



X = O, S, Se, NR **8**

2.4. Dyes for Multiple Wavelength Recording

Increase of recording capacity in optical recording system is anticipated by using shorter wavelength laser light, and improvement of recording/reproducing method and disk-track shapes. On the other hand, multiple layer dye media composed of different J-aggregate of cyanine dyes are proposed as multiple wavelength recording systems.[13] The J-aggregate of cyanine dye has very sharp absorption curve with strong absorption coefficient. If J-aggregates of LB film with different λ_{max} are duplicated to produce multiple layers of dye film, we can get several times of capacity for recording by using wavelength changeable laser as a light source.

Photochromism and formation of J-aggregate of spiropyrans are shown in Figure 3.[13] The λ_{max} and the performance of LB film of spiropyrans are affected by the substituents. The technology of multiple wavelength optical recording system is now under investigation, and there are many factors to improve the characteristics of dye media.[13] Another high capacity optical recording system is photochemical hole burning (PHB). Some types of tautomeric dye media such as quinizarin, naphthazarin and metal free phthalocyanines are now investigated as dye media

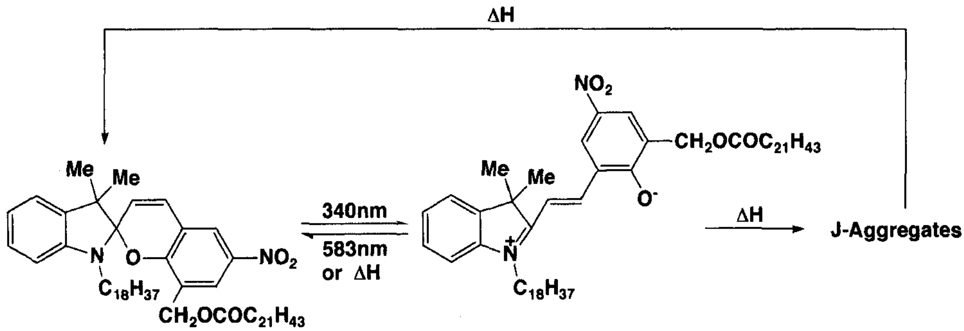


FIGURE 3 Photochromism and formation of J-aggregate of spiropyran.

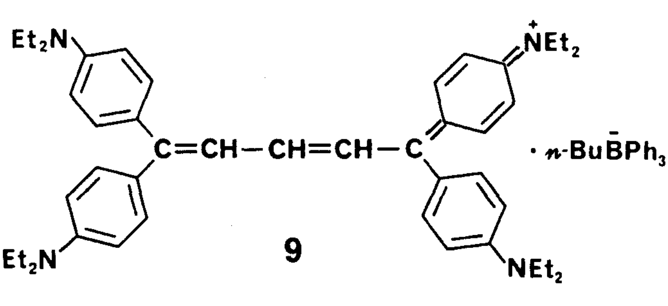
but it may take a long time for their practical application. The basic principle of PHB system using organic dye media has been reported.[14]

3. DYES FOR FULL COLOR HARD COPY SYSTEM

Information recording is very important technology and now full color hard copy becomes available in convenient method. From the point of optical recording systems, following two technologies are important in their chemistry.

3.1. Dyes for Cycolor and Related Systems

Cycolor system is well known to get full color hard copy by one-shot color process. The basic principle of the system has been reported.[15] In the system, cyanine dye triphenylalkyl borate is used as photosensitizer to produce alkyl radical which polymerizes acrylic monomer in microcapsule. The microcapsule contains cyanine photosensitizer, monomer and leuco dye which give color (yellow, magenta, cyane) when the capsule is broken and contacts with acid on the recording paper. The details of full color system are well summarized in the paper.[15] On the other hand, Hosoda *et al.*[16] recently reported the decolorizable toner system using cyanine borate IR dyes. When the mixture of IR dye **9** and excess of triphenylalkyl borate are irradiated with IR light, the dark-green color of dye **9** is disappeared to give leuco dye **10**. The decolored compound was identified as mesophenyl substituted leuco dye of **9**. They reported that this material can be applied as decolorizable toner for xerography and the copying paper can be recycled. Chemistry of this process can be explained by Equation 1. Photoirradiation of cyanine borate excites



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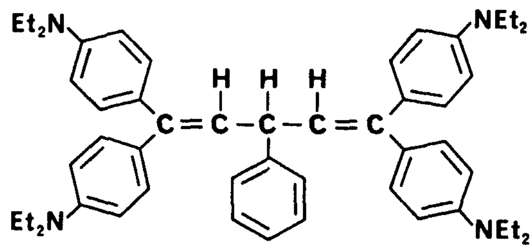

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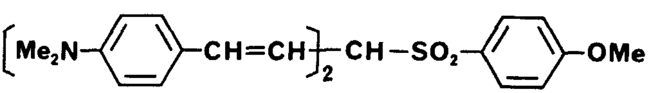
the dye into the singlet state, and subsequent electron transfer from borate to the excited dye gives dye radical, alkyl or phenyl radical and borane. In the cycolor system, alkyl radical initiates the polymerization of monomer but in this case, recombination of dye radical with alkyl or phenyl radical gives colorless leuco dye. Cycolor system has some problems in the stability of leuco dyes in microcapsule for storage in practical use, but cyanine borate can be applied for decolorizable toner. This type of decolorizable process were found in many types of dye chromophores.

$$\mathrm{Dye}^{+}\ \mathrm{Ph_3\bar{B}R} \xrightarrow{h\nu} \mathrm{Dye}^{\bullet}\cdots\mathrm{Ph_3\dot{B}R} \longrightarrow \mathrm{Dye}^{\bullet} + \mathrm{Ph_3B} + \mathrm{R}^{\bullet} \quad \cdots (1)$$

The other types of leuco IR dyes (**11**, **12**) are also known as dye media for information recording process such as bar-code applications. In the systems information can be recorded on the leuco dye media to give colored form, and it can be optically read by using diode laser as a light source.



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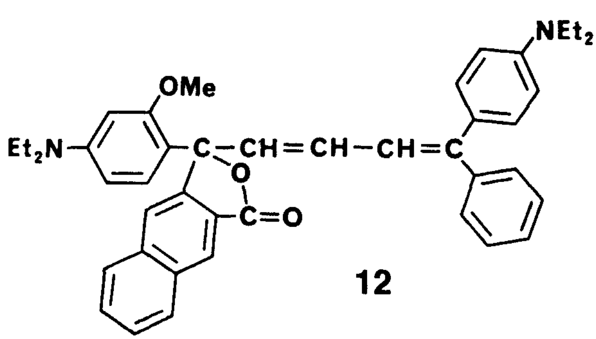

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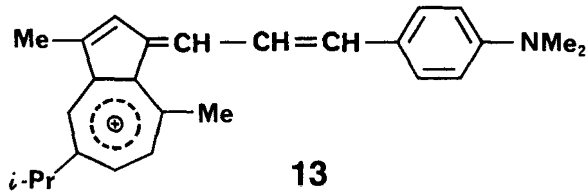
3.2. Dyes for Xerography and Laser Printer

Organic photoconductor (OPC) is used as a key material for xerography and laser printer. An OPC generally consists of two layers, the charge generation layer and the charge transporting layer. Many combinations of the charge generation material (CGM) and the charge transporting material (CTM) have been known. The CGM includes squarylium, phthalocyanine, trisazo and azulenium dyes **13**. The CGM absorbing in the IR region is required for the OPC in laser printers which use diode laser as a light source. Carbazolehydrazones, triarylamines and pyrazolines are known as CTM which must have a small ionization potential to carry the positive hole and have good transfer ability, and be able to absorb in u.v. region. The color toner, which consists of three primary colors of yellow, magenta and cyane, can be used for full color recording. Good transparency of color toner is required to duplicate the color to produce full color. Benzidine dye **14** for yellow, quinacridone or naphtholazo dye **15** for magenta, and phthalocyanine or triphenylmethane dye **16** for cyane are generally used as color toner. The charge controlling agent (cationic dyes or metal complex azo dyes) are generally added in 1–3% to control the charge of toner.



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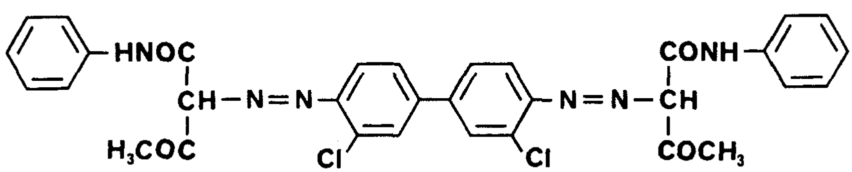

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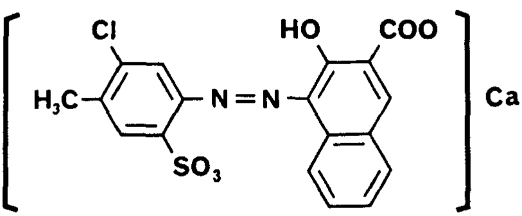

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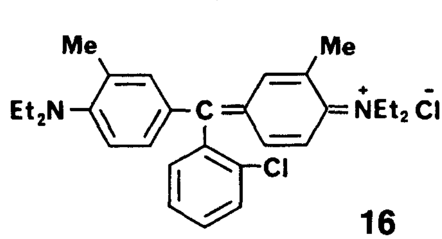

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