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Macrocyclic functional dyes: Applications to optical disk media, photochemical hole burning and non-linear optics

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Our recent research activities on macrocyclic functional dyes such as phthalocyanines and porphyrins are reviewed. For optical data storage, we have established tetrabenzoporphine derivatives are suitable for shorter wavelength recording. we have proposed new photon-mode superresolution. The playback of double density EFM signals was achieved using a naphthalocyanine derivative. For future ultrahigh density optical recording, tetraphenylporphine derivatives are found to be a promising class of photochemical hole burning materials. The potential recording density is expected to be enhanced by two or three orders of magnitude compared to conventional optical-data storage. Fundamental computational research is going on to develop new materials with high nonlinear optical properties. We have predicted the hyperpolarizabilities of a series of metallo-porphyrins. These theoretical calculations enabled us to quantitatively design materials.

INTRODUCTION

Macrocyclic compounds such as phthalocyanines and porphyrins are an important class of organic dyes for device applications due to their photophysical/chemical, electrochemical and biological functions. These compounds have two characteristic absorption bands, Soret band (S_0-S_2) and Q band (S_0-S_1), and also have a high triplet quantum yield. Therefore, various type of photophysical and photochemical processes can be investigated in a single molecule. Macrocyclic compounds are suitable model systems for developing the state-to-state manipulated device applications. In the present paper, our recent research activities aiming at applications to high density optical data storage and nonlinear optics are reviewed.

OPTICAL DATA STORAGE

Although many types of optical media, such as CD, MD, CD-R, MO and phase-change disks, are now available, the increasing use of the computer by our information society requires new high-density recording media. The areal density of optical recording is principally determined by the diffraction limit of light. The critical diameter is expressed as a function of λ/NA, where λ is the wavelength and NA is the numerical aperture of the lens, so a shortening of the wavelength and an increase in the NA value raises the recording density. We will report here pit formation with blue laser irradiation on the Soret band of tetrabenzoporphine derivatives. We also report a new mode of superresolution called the photon-mode, which uses a naphthalocyanine derivative to raise the NA value. We employed optically induced depletion of the ground-state absorption of naphthalocyanine derivatives. In addition, we discuss multiplex wavelength recording as an alternate technology for ultra-high-density optical-data storage. We also discuss our recent work on photochemical hole burning (PHB) materials.

Short Wavelength Recording

Laser diodes lasing in the near IR region are utilized in conventional optical-disk systems. Short wavelength laser diodes lasing at 630-680 nm are already available and the frontier of research is focused on blue laser diodes. Phthalocyanine and cyanine dyes are utilized in commercialized WO (write-once) media. In optical data storage, recording materials with sensitivity in the blue region of the spectrum are required to increase recording density. In the short wavelength recording, new recording materials with high sensitivity are required.

Porphyrins have intense Soret absorption bands in the near-UV region. We have found that tetrabenzoporphine derivatives have intense Soret absorption bands in the blue region. The absorption spectrum of zinc tetrabenzoporphine (ZnTBP) dispersed in cellulose acetate phthalate (CAP) is shown in Fig. 1. The weight ratio of ZnTBP/CAP is 1/1. The samples were prepared on glass substrates by spin coating. The film thickness was about 300 nm. The absorption maximum of the Soret absorption band appears around 430 nm. Recording experiments were performed by using a microscope spectrometer. The focused beam of an argon ion laser lasing at 476.5 nm was irradiated. The laser intensity was 8 mW. Exposure times were controlled using an AO modulator. Pit formation was observed with 100 ns of laser irradiation and the pit diameter was about 0.25 μm, as is shown in Fig. 2. The pit size is smaller than the recording wavelength, which indicates that the pit formation has a threshold energy and occurs at the center of the laser beam. Therefore, the main mechanism of the pit formation is the thermal effect. The diameter increases with an increase in the irradiation time: 0.5 μm for 200 ns and 0.7 μm for 500 ns.

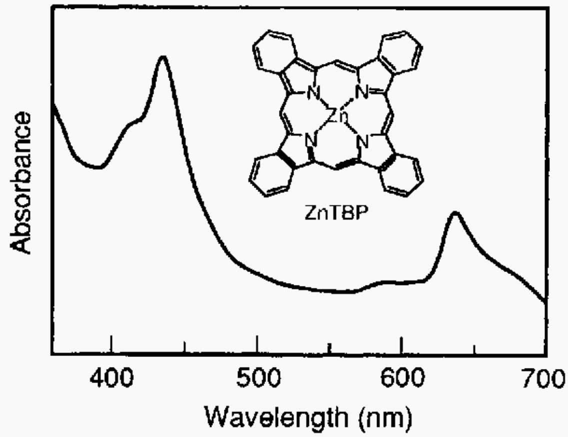

Fig. 1 Absorption spectrum of ZnTBP in cellulose acetate phthalate.

a)
b)
c)

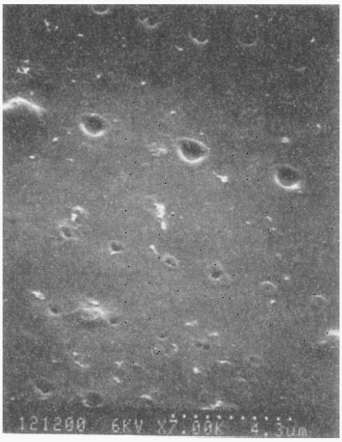

Fig. 2 Pit formation in a ZnTBP/CAP sample. a) 200 ns, b)500 ns and c) 100 ns of the irradiation time.

Present preliminary experiments show that tetrabenzoporphine derivatives are promising as recording materials in the blue region of light. We also investigated the photodegradation mechanism of the dye. We have carried out quenching experiments by flash photolysis and found out that the reaction proceeds by way of the lowest triplet state and that triplet quenchers are effective for improving durability. Work is going on to develop stable material systems.

Superresolution Read-out

Recently, superresolution has been attracting attention as a promising method for improving recording density. In optical microscopy, the resolving power is known to increase beyond the diffraction limit of light when an optical stop with a pinhole smaller than the spot size is placed close to the object (1). Recently, IRISTER (IRIS thermal eclipse reading) was proposed as a superresolution read-out method for optical data storage (2). Signals from minute area in a focused laser spot can be read out by generating a transient aperture with laser light irradiation. High carrier-to-noise ratios of 42-51 dB were achieved for a mark length of 0.3 μm. In these cases, a transient optical aperture is generated by a thermal effect (the heat-mode) induced by laser light. We have invented a new type of superresolution, in which a transient aperture is generated in a the photon-mode (3).

When the number of molecules promoted to the excited state is larger than the number of molecules relaxing to the ground state, depletion of the ground state absorption occurs. The number of molecules going up to the excited state with laser irradiation is linearly proportional to the number of photons absorbed according to Lambert-Beer's law. At the same time, the transmittance, T, is proportional to 10^{-A}, where A is the absorbance and is proportional to the number of molecules in the ground state. Therefore, the transmittance increases nonlinearly with decreasing absorbance. So, a minute aperture is formed around the center of the incident Gaussian laser beam. We must determine which organic dyes are suitable for this purpose. A saturable dye is required to have a large absorption coefficient at the laser wavelength and a long relaxation time from the excited state to the ground state. We have found out that a silicon naphthalocyanine derivative (SiNPC) is suitable as a saturable absorber. The chemical structure and the absorption spectrum of SiNPC are shown in Fig. 3. An absorption maximum appears at around 780 nm and the absorption coefficient is 5 x 10^5 /mol•cm at 780 nm. The relaxation time is about 2 ns. We have simulated the size of the minute aperture as a function of the laser intensity and the transport speed of the recording medium. Figure 4 shows the case with 1.4 m/s of disk velocity. The diameter of the laser spot can be minimized to 1/2 of the incident beam and the recording density potentially enhanced by four times.

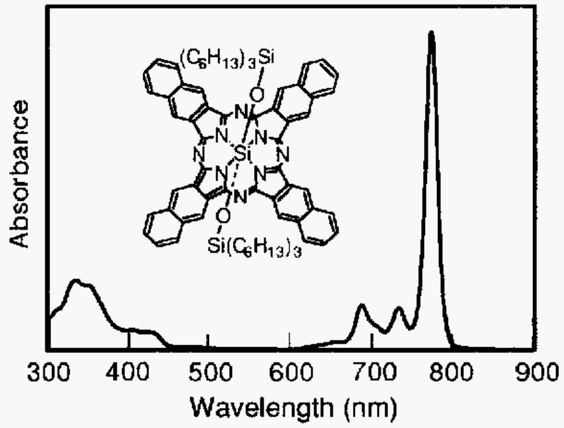

Fig. 3 Absorption spectrum of a SiNPC derivative.

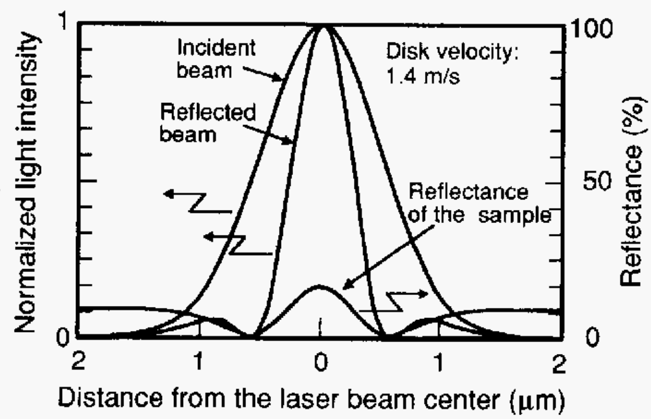

Fig. 4 Minimization of the beam diameter in the photon-mode superresolution.

3 μm-thick films of SiNPC dispersed in polyvinylcarbazole were coated on premastered disk substrates. An important issue in photon-mode superresolution is the temperature elevation of the film caused by relaxation from the excited states. Therefore, we suppress the temperature elevation by expanding the volume irradiated by the laser beam. Playback signals were detected using a 780 nm laser diode and a focusing lens of NA 0.5. The cut-off frequency of the optical system is 1282 cm^{-1} and pits shorter than 0.39 μm cannot be detected under normal conditions. 0.3 μm length pits were detected at 0.5 mW, which indicates that the photon-mode superresolution has no threshold energy. We have achieved readout of a linear double-density EFM(8-14 modulation) signals. The rotating speed of the sample disk was 1m/s in a constant linear velocity mode. An eye-pattern appears at 5mW of laser power and is clearly detected with 10 mW , as is shown in Fig. 5. This is the first readout in photon-mode superresolution.

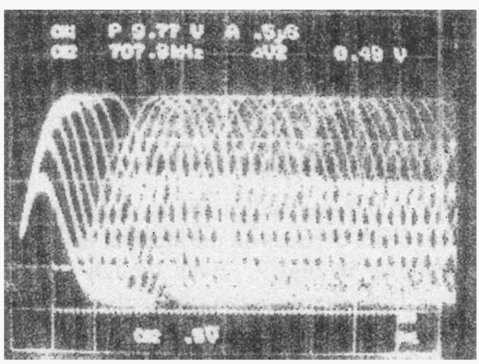

Fig. 5 Retrieved eye-pattern of double density EFM signals.

Photochemical Hole Burning

Recording densities are expected to be enhanced about ten times by combining short wavelength recording, superresolution and land-groove recording even in the framework of the conventional optical disk technology. Photochemical hole burning has the potential of improving recording density by two or three orders of magnitude (4). Development of new recording material systems with high sensitivity and wavelength multiplicity is essential for practical frequency-domain optical-data storage. In the first part of this section, we will report on multiple hole formation in the frequency domain. Next, we will present new photon-gated recording materials.

Tetraphenylporphine (TPP) derivatives used are shown in Fig. 6. Each compound was dispersed in polymethlymethacrylate (PMMA, MW. 9.0 x 10^4) at a concentration of 1 x 10^{-4} mol/kg. Single-mode tunable dye lasers with a 500 kHz bandwidth were used as burning sources. Produced holes were observed mainly by using a 1 m double monochromator for the loosely focused cases, meanwhile holes were detected by scanning the dye laser wavelengths in the case of PHB recording with a 10 μmϕ laser spot.

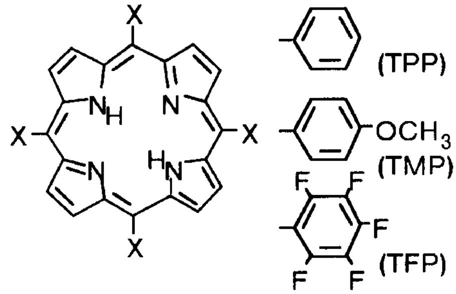

Fig. 6 Tetraphenylporphine derivatives used in PHB experiments.

Multiple photochemical hole burning was carried out for the TMP/PMMA and TFP/PMMA systems in a 10 mm laser spot (5). Figure 7 shows the multiple holes produced in TFP/PMMA. Each hole was produced with 4.4 mW/cm^2 of laser power for 30 s. As many as 114 holes were produced at 2.4 cm^{-1} intervals in a 272 cm^{-1} range from 15174 to 15446 cm^{-1}. In the case of TMP/PMMA, 100 multiple holes were produced in a 330 cm^{-1} range. We also proved that two holes produced in TFP at 0.3 cm^{-1} intervals were well distinguished by detecting the holes by scanning the dye laser wavelengths. Therefore, the potential recording density can be estimated to be more than 1000 in a single Q absorption band. For practical applications, it is very important to produce multiple holes in a focused laser spot in order to achieve high areal densities. Figure 8 shows the transmittance spectrum of 11 holes produced in a 10 μmϕ laser spot. Each hole was produced with irradiation of a 5.6 mW/cm^2 power for 300 s. (8). Two holes separated by 1.5 cm^{-1} are distinguishable. Therefore, the frequency multiplicity is estimated to be more than 200, and the areal recording density approaches 2 x 10^8 bit/cm^2. This value is 2 or 3 times larger that in conventional optical storage, even though the spot diameter is about 10 times larger.

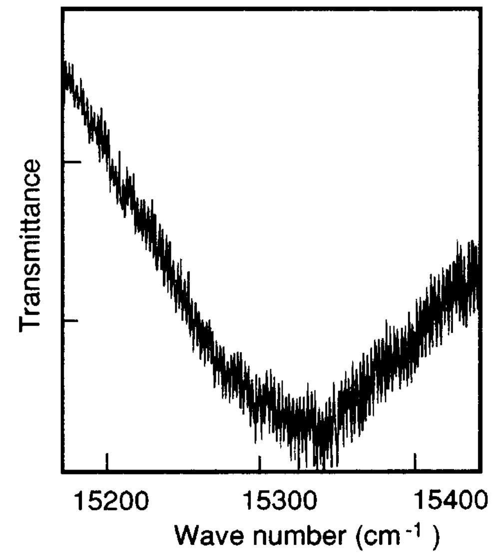

Fig.7 114 mutiple holes produced in the TFP/PMMA system.

In the course of these studies, we have found that the hole depth depends on the incident laser power, as shown in Fig. 9. Even though the total incident laser energy is the same, the hole depth decreases with increasing laser power. Similar phenomenon have been reported from the bottleneck effect in the phthalocyanine/polyethylene case (6). This behavior is interpreted as the depletion of the population in the ground state due to the remaining excited state molecules in the lowest triplet state. Among the TPP derivatives studied, we found that TMP has a high PHB quantum yield. However, in order to form a deep hole in a shorter burning time, it is necessary to activate the molecules remaining in the triplet state during the irradiation time. Thus, pumping the triplet molecules up to the higher excited reaction state by irradiating a second laser light (gating light) is effective. A spectral hole is produced by way of step-wise

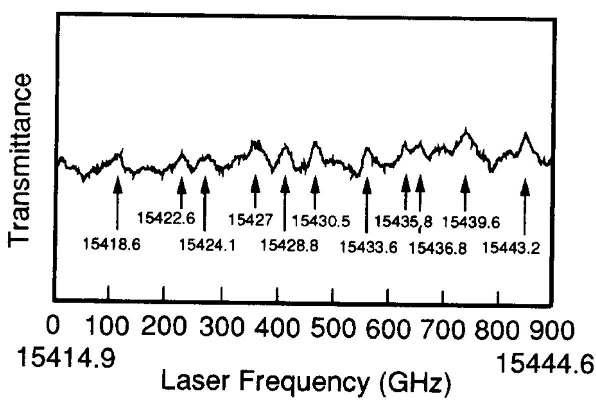

Fig. 8 11 mutiple holes produced in a 10 μmϕ laser spot.

two photon excitation The mechanism is called as photon-gated PHB, which has been investigated so far for nondestructive reading.

We have reported photon-gated PHB caused by the electron transfer reaction from the higher excited triplet state of ZnTPP to various electron acceptor molecules (9). The hole formation reaction needs to proceed during the short lifetime of the higher excited states. Therefore, chemically bridged electron donor-electron acceptor dyad molecules have advantages in reactivity compared to systems in which each molecule is individually dispersed. We have synthesized carboxyl-group bridged ZnTPP-ethylbromide (ZnTBEP) and ZnTPP-propylbromide (ZnTPBP) molecules (10). Figure 10 shows the effect of the gating light intensity on hole formation in the ZnTBEP/PMMA system. The irradiation time was 30 min when no gating light was applied and 10 min in other cases. The power of the wavelength selective light was fixed at 1 mW/cm2. Hole depth increases as the gating light intensity increases, which indicates that the hole formation proceeds by way of the photon-gated mechanism. We conclude that the hole formation proceeds via. the higher excited triplet state, since the action spectrum of hole formation was in good accordance with the triplet-triplet (T-T) absorption spectrum.

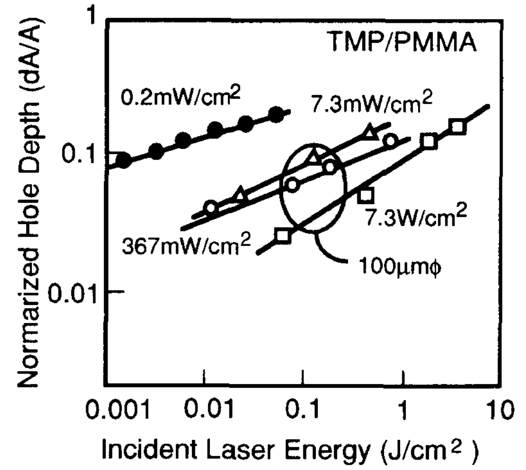

Fig. 9 Normalized hole depth in absorbance as a function of the incident laser powers.

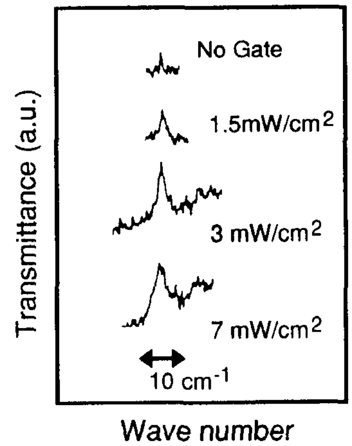

Fig. 10 Effects of the gating-light intensity on the depth of spectral holes produced in ZnTBEP.

NONLINEAR OPTICAL PROPERTIES

For applications to electro-optic devices, new materials with high nonlinear properties are required. Organometallic macrocyclic compounds are of significant interest in this field, as the presence of metal-ligand bond leads to large molecular hyperpolarizability due to the transfer of electrons between a metal atom and a conjugated ligand system. The diversity of central metal atoms, oxidation states, and the nature of ligands helps tailoring materials to optimize the charge transfer interactions (11).

We have calculated second-order hyperpolarizabilities (γ) of a series of metalloporphyrins (12) by applying the density functional theory (13) at the nonlocal level (14) using the program system DMol (BIOSYM Technologies, San Diego). We have applied this method for systems of benzene derivatives, and have found that this method can be used for quantitative prediction of the nonlinear properties (15). γ of Fe-, Ni-, Zn-, Ru-, Pd- and Cd-porphines were calculated and plotted in Fig. 11 together with the calculated charge on the metal. The values of γ clearly correlate with the charge, which is dominated by the number of d electrons (nd). The charge transfer between the metal and the ligand

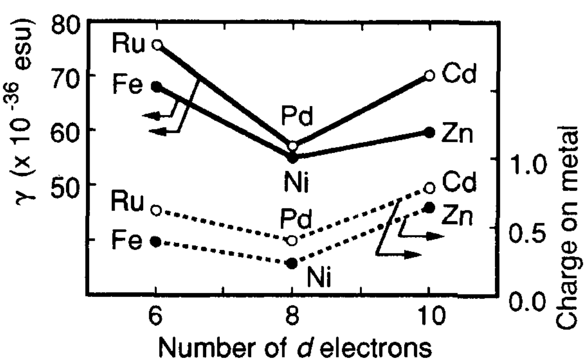

Fig.11 Second-order hyperpolarizabilities calculated for a series metalloporphyrins.

is minimized if nd = 8, consequently, larger γ values are predicted for the case of nd = 6 and 10 as compared to those at nd = 8. This result demonstrates that the perturbation of the π potential of macrocyclic compounds in a centrosymmetric fashion leads to the enhancement of γ.

SUMMARY

We have reported our recent research activities on applications of macrocyclic functional dyes to high density optical data storage including short wavelength recording, new photon-mode superresolution and photochemical hole burning. Computational studies can predict new material functions. We also show some preliminary activities on nonlinear optical properties. Various functions of macrocyclic compounds are evolving into new device application fields.

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