Ultrafast Optical Responses of Doubly *N*-Confused Hexaphyrin Derivatives with Femtosecond Laser Excitation

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Confused hexaphyrin derivatives were excited by femtosecond pulsed laser to study transient responses. An extended π -conjugated system showed characteristic absorption changes with relatively weak power of laser irradiation. Recovery of transient bleaching was observed with time constants less than 100ps by both 400nm and 800nm excitation. Copper complex derivative showed the fastest response of 21 ps. Optical responses in the visible region and its mechanism are discussed.

Keywords: Transient spectra, Photoexcitation, Photoresponsiveness, Confused hexaphyrin

1. Introduction

Much faster processing speed and larger capacity are needed in the information technology. From this point of view, we have been making use of photoinduced complex refractive index changes in guided wave mode (GWM) thin films which were composed of metal films and polymer films containing various functional dyes[1-7]. We achieved all optical spatial light modulation by this GWM geometry for ultrafast information processing technology[1-7]. With such devices, we can control reflected light with changes of imaginary and/or real parts of complex refractive index caused by photoexcitation of dyes. We demonstrated ultrafast persistent optical property changes in the near infrared region by ion pair charge transfer complexes, phthalocyanines and photochromic compounds[1-10]. Many other organic materials have been synthesized for application to the optical data processing technology including telecommunication[1-19]. Among of them, extended porphyrin derivatives which have good optical and electrochemical properties based on their rigid planar structure attracted much attention[10, 15-19]. Various types of fused and confused porphyrin derivatives have recently been synthesized[15-

17]. They show strong absorption in the visible and near infrared region[15-17]. In this study, we report optical properties and ultrafast dynamics in solution of normal and confused hexaphyrin derivatives.

2. Materials and Experimental

2.1. Preparation of hexaphyrin derivatives

meso-hexakis(pentafluorophenyl) hexaphyrin, compound **1**, bis-acetylacetonate *meso*-hexakis(pentafluorophenyl) doubly *N*-confused dioxohexaphyrin, compound **2b** and bis-Cu(II) *meso*-hexakis(pentafluorophenyl) doubly *N*-confused dioxohexaphyrin, compound **3** were prepared according to the method reported previously[15-17, 20, 21]. The structures of these compounds are shown in Fig. 1. The purity of the compounds was confirmed by TLC and ¹H NMR.

2.2. Measurements

The absorption spectra of hexaphyrin derivatives were recorded at room temperature on a Hitachi U-4100 spectrometer in 10 mm cell of toluene. Fluorescence spectra are measured on Fluorolog spectrometer, Jobin Yvon, for Free base type compound **1** and confused type compound **2b** dissolved in dichloromethane with a 10 mm cell at room temperature.

Figure 1 The structures of hexaphyrin derivatives

Femtosecond laser photolysis system was reported in details previously[8, 10, 21, 22]. Figure 3 shows the block diagram of the femtosecond laser photolysis system. Sample solutions in a 4 mm cell, were excited by femtosecond Ti:sapphire laser at room temperature. A dual beam femtosecond time-resolved transient absorption spectrometer was consisted of an optical detection system (PMA 50), a pulse stretcher & compressor, a Ti:sapphire regenerative amplifier which was pumped by a Q-switched Nd:YAG laser (Quanta Ray) and a mode-locked femtosecond Ti:sapphire laser (Spectra-Physics, TSUNAMI).

An amplified Ti:sapphire laser has 3 mJ/pulse at 800 nm and the repetition is 10 Hz. 800 nm pulse from the amplified Ti:sapphire laser shows about 250 fs of a full width at half maximum. 400 nm pulse was generated from the amplified output beam by passing through a BBO crystal. For 800 nm excitation, output from Ti:sapphire regenerative amplifier was divided by a 800 nm beam splitter. Then the residual 800 nm light was focused into a 10 mm cell filled with $\text{D}_2\text{O}:\text{H}_2\text{O}$ (2:1) mixture to obtain a fs white probe light. The pump and probe beams were focused on a 4 mm sample cell to about 1 mm diameter. The power of pump beam was adjusted by using a variable neutral-density (ND) filter to avoid damage of samples. Laser excitation was performed by overlapping of pump and probe beams in the sample cell. Transient spectra were measured by using an optical delay stage with 30 fs/step time resolution. Additionally, a probe beam was divided to two beams by beam splitter. One was introduced into a sample cell with a pump beam and another was used as a reference beam. Two probe beams

were detected by a dual photodiode array system (Hamamatsu Photonics, C6140-PMA) through optical fibers. In this experiment, probe light was accumulated for 20 ~ 24 times.

3. Results and Discussion

Four types of hexaphyrin derivatives were prepared as shown in Fig. 1. Compound **2b** was prepared to improve its durability against laser irradiation by substituting two hydrogen atoms in **2a** with acetylacetonate groups. After laser excitation, compound **2a** showed new absorption peak around 1150 nm. This new peak was possibly due to oxidation or subtraction of hydrogens in **2a**.

Figure 2 The absorption spectra and fluorescence spectra of hexaphyrin derivatives in solutions. Inset shows enlarged absorption spectra of Q-bands at NIR region. (Abs.: in toluene, FL.: in CH_2Cl_2 ; **1** was excited at 566nm, **2b** was excited at 583nm for fluorescence spectra).

Figure 3 The block diagram of a femtosecond laser photolysis system. (detector : Hamamatsu Photonics, C6140 PMA)

By introducing of acetylacetonate groups, hexaphyrin derivative **2b** showed no such new peaks after laser excitation. In Fig. 2, hexaphyrin derivatives showed absorption in the visible and near IR region by extended π -conjugation. The characteristic and sharp Soret bands were detected at 570 nm for **1**, 588 nm for **2** and 615 nm for **3**, respectively. And comparatively weak and broad Q-bands were shown in the near IR region. The absorption peaks were slightly shifted to the longer wavelength according to the conjugation in their structures. The fluorescence peaks were detected at 1028 and 1200 nm for **1**, and at 1079 and 1257 nm for **2b** as shown in Fig. 2. Observed fluorescence spectra are mirror images of the Q band in the absorption spectra. On the other hand, fluorescence of **3** containing copper could not be detected, which was attributed to very fast intersystem crossing due to paramagnetic Cu(II).

Samples in toluene were irradiated at 400 nm and 800 nm by the femtosecond laser to study their transient absorption behavior. All sample solutions showed largest absorption change at their Soret band. Excitation at 400 nm will generate the S_2 or higher excited singlet state. In the case of 800 nm excitation, the lowest excited state S_1 is generated. Observed absorption changes are divided into two phenomena. One is transient bleaching, and another is transient absorption. The transient bleaching is due to the fact electrons excited to S_1 or higher S_n state by pump energy do not return back transiently to the ground state. Certain decreased absorbance appears momentary at the

ground state absorption band. In the mean time, transient absorption is caused by transition from S_1 to higher S_n state.

Figure 4 shows the results of time-resolved spectra in the visible region and a time profile for **3** at 617 nm upon 400 nm fs laser excitation. Transient bleaching was observed at 570 nm for **1**, 592 nm for **2** and 617 nm for **3** corresponding to their own Soret bands. Time profiles were composed of two components, slow (τ_1) and fast one (τ_2). They were analyzed by following double exponential equation:

$$\Delta A(t) = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

Values of time constants observed at 400 nm excitation were 105 and 12 ps for **1**, 95 and 21 ps for **2b**, 18.2 and 4.8 ps for **3**, respectively. On the other hand, the transient spectra by 800 nm excitation showed bleaching recovery with time constants of 97 ps for **1**, 91 and 29 ps for **2b** and 21 ps for **3**. Figure 5 shows transient spectra and time profile by 800 nm excitation for **3**. Time constants of bleaching recovery after 400 nm and 800 nm ex-

Figure 4 (a) Time-resolved transient bleaching spectra in the visible region for **3** in toluene solution, excited with a 400 nm femtosecond laser pulse, 29 μ J/pulse. (b) Time profile of absorbance at 617 nm.

Figure 5 (a) Time-resolved transient bleaching spectra in the visible region for **3** in toluene solution, excited with a 800 nm femtosecond laser pulse, 28 $\mu\text{J}/\text{pulse}$. (b) Time profile of absorbance at 617 nm.

citation, are almost the same within less than 7 ps. Ahn *et al.* have reported that the deactivation of excited state for the free base type hexaphyrin **1** is the S_1 to S_0 internal conversion by measurements of fluorescence lifetime[23]. The present result for **1** supported their assignment. It will also be the case for **2** judging from the time constants of bleaching recovery. The fluorescence lifetime measurement by up-conversion system is underway to elucidate the mechanism. According to similar time constants observed by 400 nm and 800 nm excitation, the internal conversion from S_2 to S_1 state is assured to be extremely rapid within the time resolution of our fs photolysis system.

Meanwhile the recovery time for hexaphyrin derivatives became faster in the order of **3** < **2b** < **1**. In the case of confused type hexaphyrin **2b**, more extended π -conjugation than **1** can be expected, because of hydrogen bonding which is located in both sides of amide groups in the hexaphyrin ring. Copper complex type derivative **3** showed much faster bleaching recovery than **1** and **2b**. Copper

ions in **3** have a paramagnetic nature. That contributes to faster intersystem crossing of excited electrons from S_1 to T_1 state or T_1 to S_0 state by a spin-orbital coupling as reported for excited triplet states in some metal phthalocyanines including Cu^{2+} [2, 4].

4. Conclusion

To find new organic photoresponsive materials for the information processing technology such as optical telecommunication, three types of hexaphyrin derivatives were synthesized and measured by femtosecond laser. Transient absorption changes were observed by laser excitation with normal, metal complex and *N*-confused hexaphyrin derivatives. The structures of compounds are almost planar. Durability against repeated laser excitation, was improved by introducing acetylacetonate groups in the structure. Copper complex type hexaphyrin showed the fastest time recovery caused by the rapid intersystem crossing of excited electron by spin-orbital coupling. The present compounds show absorbance also in the near IR region which can be used for ultrafast responsive materials if appropriate devices are developed.

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References

1. T. Nagamura, in *Nanotechnology and NICE Devices*, edited by M. Iwamoto, K. Kaneto and S. Mashiko (Elsevier Science, New York, 2003), Chap. 8, p. 105-131
2. T. Nagamura, A. Naito, I. Yoshida. *J. Nonlinear Opt. Phys. & Mat.*, **11**, 3 (2002) 205
3. T. Nagamura, I. Yoshida. *Mol. Cryst. Liq. Cryst.*, **406** (2003) 19
4. T. Nagamura, K. Sasaki, F. Iizuka, T. Adachi, I. Yoshida. *Opt. Comm.*, **205** (2002) 107
5. T. Nagamura and K. Sasaki, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **344** (2000) 204
6. T. Nagamura, T. Adachi, I. Yoshida, H. Inoue, H. Heckmann, and M. Hanack, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **370** (2001) 97
7. T. Nagamura, R. Matsumoto, A. Naito, Y. Nagai, *Appl. Phys. Lett.*, **87** (2005) 041107

8. T. Nagamura, H. Sakaguchi, S. Muta. *Proc. SPIE*, **241** (1995) 2514
9. T. Nagamura, Y. Nagai, A. Furube, S. Murata, *Appl. Phys. Lett.*, **85** (2004) 3444
10. H. Inoue, H. Sakaguchi, T. Nagamura. *Appl. Phys. Lett.*, **73**, 1 (1998) 10
11. S. Tatsuura, M. Tian, M. Furuki, Y. Sato, I. Iwasa, and H. Mitsu, *Appl. Phys. Lett.* **84** (2004) 1450
12. Y.-C. Chen, N. R. Raravikar, L. S. Schadler, P. M. Ajayan, Y.-P. Zhao, T.-M. Lu, G.-C. Wang, and X.-C. Zhang, *Appl. Phys. Lett.* **81** (2002) 975
13. M. Ichida, Y. Hamanaka, H. Kataura, Y. Achiba, and A. Nakamura, *Physica B* **323** (2002) 237
14. S. Tatsuura, M. Furuki, Y. Sato, I. Iwasa, M. Tian, and H. Mitsu, *Adv. Mater. (Weinheim, Ger.)* **15** (2003) 534
15. A. Srinivasan, T. Ishizuka, A. Osuka, H. Furuta. *J. Am. Chem. Soc.* **125** (2003) 878
16. M. Suzuki, A. Osuka. *Org. Lett.*, **21** (2003) 3943
17. H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, A. Osuka. *J. Am. Chem. Soc.* **124** (2002) 14642
18. M. C. Yoon, D. H. Jeong, S. Cho, D. H. Kim. *J. Chem. Phys.*, **118** (2003) 164
19. M. Suzuki, M. -C. Yoon, D. Y. Kim, J. H. Kwon, H. Furuta, D. H. Kim, A. Osuka, *Chem. Eur. J.*, **12** (2006) 1754
20. M. S. Neves, R. M. Martins, A. C. Tome, A. D. Silvestre, A. S. Silvia, V. Felix, M. B. Drew, J. S. Cavaleiro. *Chem. Commun.*, **4** (1999) 385
21. J. H. Ryu, T. Nagamura, Y. Nagai, R. Matsumoto, H. Furuta, K. Nakamura, *Mol. Cryst. Liq. Cryst.*, **445** (2006) 249
22. H. Kawai, T. Nagamura. *J. Chem. Soc., Faraday Trans.*, **94** (1998) 3581
23. T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. K. Kim, M. Suzuki, S. Shimizu, A. Osuka and D. H. Kim, *J. Am. Chem. Soc.*, **127**, 37 (2005) 12856