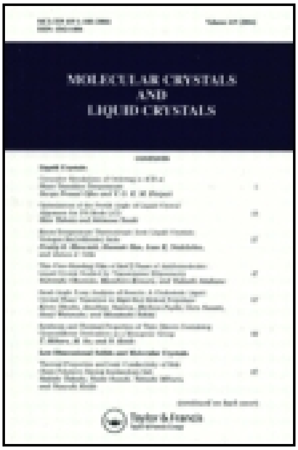


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Ultrafast Responses of Doubly N-Confused Hexaphyrin Derivatives

Jang-Hyun Ryu [a], Toshihiko Nagamura [a], Yasuyuki Nagai [a], Ryuji Matsumoto [a], Hiroyuki Furuta [a] & Kiyohisa Nakamura [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Version of record first published: 23 Aug 2006

To cite this article: Jang-Hyun Ryu, Toshihiko Nagamura, Yasuyuki Nagai, Ryuji Matsumoto, Hiroyuki Furuta & Kiyohisa Nakamura (2006): Ultrafast Responses of Doubly N-Confused Hexaphyrin Derivatives, Molecular Crystals and Liquid Crystals, 445:1, 249/[539]-257/[547]

To link to this article: http://dx.doi.org/10.1080/15421400500366589

Mol. Cryst. Liq. Cryst., Vol. 445, pp. 249/[539]–257/[547], 2006
Copyright © Taylor & Francis LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500366589

Ultrafast Responses of Doubly *N*-Confused Hexaphyrin Derivatives

Jang-Hyun Ryu
Toshihiko Nagamura
Yasuyuki Nagai
Ryuji Matsumoto
Hiroyuki Furuta
Kiyohisa Nakamura
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka, Japan

Confused hexaphyrin derivatives, which are remarkable as the organic optical materials for information processing technology, have been synthesized. Hexaphyrin derivatives, free base type, substituted one and metal complex were studied in view of photophysical properties. The effects of π-conjugation have been studied by measuring of absorption and fluorescence spectra. They were excited by femtosecond pulsed laser to see the photoresponsibility and dynamics. Instantaneous changes, transient bleaching or transient absorption, will be discussed in the visible region.

Keywords: femtosecond photolysis; hexaphyrin derivatives; transient spectra; ultrafast optical responses

INTRODUCTION

There have been increasing demands for much faster speed and larger capacity in the information processing technology. From this point of view, we have been making use of photoinduced complex refractive index changes with the excitation of guided wave mode thin films which were composed of polymer films, containing various functional dyes and metal films [1]. We proposed and achieved new all optical spatial light modulation for ultrafast information processing technology [1–4]. With such devices, we are able to control reflected light

Address correspondence to Jang-Hyun Ryu, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashiku, Fukuoka, 812-8581, Japan. E-mail: jh-ryu@cstf.kyushu-u.ac.jp

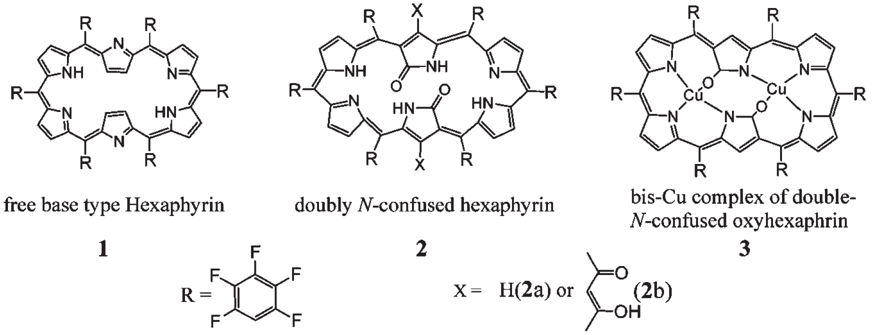


FIGURE 1 The structure of hexaphyrin derivatives.

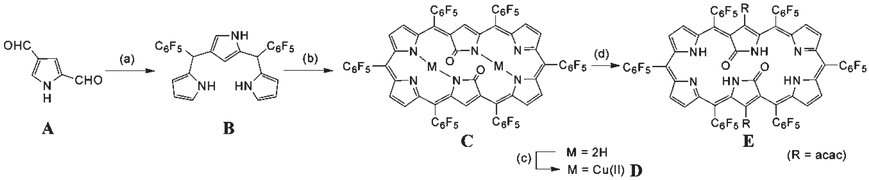
with marvelous changes of imaginary and real parts of complex index carried by Δabsorbance of thin films. It has been reported that ultrafast change of absorbance was revealed in the near infrared region in such materials, carbon nanotube, fused porphyrin and ion pair complexes [1–6]. Many organic materials have been synthesized for application to the optical data processing including telecommunication recently [1]. Among of them, expanded porphyrin derivatives which have good optical and electrochemical properties are expected for the optical applications due to their desirable characteristics such as rigid planar geometry, high stability, intense electronic absorption, and small HOMO-LUMO energy gap [6–9,11].

Various types of fused and confused porphyrin structures have recently been synthesized [7–9]. They show unique properties of strong absorption in the visible and optical telecommunication wavelength [7–9]. In this paper, we report on photophysical properties and ultrafast dynamics in solutions of normal and confused hexaphyrin derivatives (Fig. 1).

EXPERIMENT

Synthesis of Doubly *N*-Confused Hexaphyrin

2,4-diformylpyrrole was converted into *N*-confused tripyrrane in 44% yield by Grignard reaction, followed by acid-catalyzed condensation with pyrrole. When N-confused tripyrrane was treated with pentafluorobenzaldehyde in the presence of *p*-toluenesulfonic acid, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), meso-hexakis(pentafluorophenyl)-substituted doubly *N*-confused dioxo-hexaphyrin was obtained in 10% yield. Though a type without dioxo group was obtained by changing oxidizing agent from DDQ to



SCHEME 1 Synthesis of *N*-confused hexaphyrin derivatives. Reagents and conditions: (a) (i) Mg, C_6F_5, THF, 0°C (ii) pyrrole, TFA, r.t., 44% (2 steps); (b) (i) C_6F_5-CHO, p-TsOH, CH_2Cl_2, r.t.; (ii) DDQ, r.t., 10% (2 steps); (c) $Cu(OAc)_2$, CH_2Cl_2, r.t., 99%; (d) Mn(acetylacetonate)$_3$, toluene, reflux, 52%.

p-chloranil, the compound was gradually oxidized into dioxo type. Then, a solution of doubly *N*-confused dioxohexaphyrin in CH_2Cl_2 was stirred in the presence of Cu(II)(OAc)$_2$ at room temperature. After work-up, binuclear copper(II) complex was isolated in 99% yield. Bis-(acetylacetonate) dioxohexaphyrin was obtained in 52% yield by refluxing in toluene in the presence of Mn(acetylacetonate)$_3$. In other hands, *meso*-tetra(pentafluorophenyl)hexaphyrin, **1**, was synthesized by the modified Rothemund-Lindsey reaction of pyrrole with 2,6-disubstituted electron-deficient aryl aldehydes as 20% of yield. In the ^{1}H NMR spectrum of **1**, the NH protons appears as broad peak at –1.98 ppm, the inner pyrrolic CH-protons appear as sharp doublet at –2.43 ppm, and the outer pyrrolic CH protons appear as two sharp doublet at 9.11 and 9.44 ppm [12,13].

5, 10, 15, 20, 25, 30-Hexakis(pentafluorophen-yl) [26] Doubly N*-Confused Dioxohexaphyrin (1.1.1.1.1.1) (C) [7,8]*

B(0.90 mmol, 500 mg) and penta-fluorobenzaldehyde (0.90 mmol, 0.11 mL) in CH_2Cl_2 (250 mL) were stirred under atmosphere for 15 min at room temperature. *p*-TsOH·H_2O (0.09 mmol, 15 mg) was added to the above mixture. The solution was stirred for further 1 h under the dark condition. The solution was stored in the air and DDQ (2.69 mmol, 0.61 g) was added. The mixture was stirred at room temperature for 3 h. After removal of solvent, the crude product was purified by column chromatography using basic alumina followed by silica gel column. A pink fraction eluted with CH_2Cl_2/n-hexane (3:7) gave 66 mg (10% of yield from **B**) of 5, 10, 15, 20, 25, 30-hexakis(pentafluorophenyl) [26] doubly *N*-confused dioxohexaphyrin (1.1.1.1.1.1) (**C**): green solid ; ^{1}H NMR (300 MHz, $CDCl_3$, r.t.)δ10.75 (s, 2H, outer −CH) 9.50 (d, $J = 4.8$ Hz, 2H) 9.43 (d, J = 5.1 Hz, 2H) 9.22 (d, J = 4.8 Hz, 2H) 9.18 (d, J = 4.8 Hz, 2H) –0.76 (s, 1H); MALDI TOF-MS (dithranol) m/z: 1493 ($M + H^+$, $C_{66}H_{14}F_{30}N_6O_2$ requires

1492.07); UV/vis (CH_2Cl_2): □λ_{max} [nm] ($\varepsilon \times 10^{-5}$) = 1049 (0.092), 907 (0.075), 793 (0.38), 722 (0.23), 664 (0.13), 589 (1.96), 566 (4.05), 382 (0.38), 335 (0.30).

Bis-Cu(II) N_2CO_2H Complex (D) [7–8]

A solution of anhydrous Cu(II)$(OAc)_2$ was added to a solution of **C** in CH_2Cl_2. After stirring at room temperature for 2 h, the solvent was removed. bis-Cu(II) complex was given by the purification with silica gel column chromatography (Wakogel-C200, CH_2Cl_2/*n*-hexanes, 3:7): blue greenish solid; MALDI TOF-MS (dithranol) m/z: 1616 ($M + 2H^+$, $C_{66}H_{14}F_{30}N_6O_2$ requires 1613.9); UV/vis (CH_2Cl_2)□λ_{max} [nm] = 1050, 911, 786, 616, 461, 403, 362.

Bis(acetylacetonate)-N_2CO_2H (E) [7-8]

A solution of Mn(acetylacetonate)$_3$ in MeOH was added to a solution of **C** in toluene. After refluxing the mixture for 12 h, the solvent was removed. Residue was separated by column chromatography using silica gel with CH_2Cl_2/*n*-hexanes (1:1). Further purification by recrystallization from CH_2Cl_2/hexanes, gave **E** in 52% yield: blue solid; MALDI TOF-MS (dithranol) m/z: 1689 ($M + H^+$, $C_{76}H_{26}F_{30}N_6O_6$ requires 1688.14); UV/vis (CH_2Cl_2)□λ_{max} [nm] ($\varepsilon \times 10^{-5}$) = 1067 (0.027), 926 (0.033), 824 (0.13), 745 (0.082), 687 (0.051), 584 (1.38), 393 (0.17).

MEASUREMENTS

Absorption and Fluorescence Spectra

The absorption spectra of hexaphyrin derivatives were observed by Hitachi U-4100 spectrometer. Samples in a 10 mm cell were dissolved in toluene solution for absorption spectra. Fluorolog spectrometer, Jobin Yvon, was used for the measurement of fluorescence spectra with a 10 mm cell in dichloromethane solutions. All measurements were performed at room temperature.

Femtosecond Laser Photolysis Experiment

Figure 2 shows a schematic representation of the femtosecond laser photolysis system[5,6,10]. The sample solutions in 4 mm cells were excited by femtosecond Ti:sapphire laser at room temperature. The dual beam femtosecond time-resolved transient absorption spectrometer consisted of a mode-locked femtosecond Ti:sapphire laser (Spectra-Physics, Tsunami), a Ti:sapphire regenerative amplifier (TSA) pumped by a Q-switched Nd:YAG laser (Quanta-Ray), a pulse

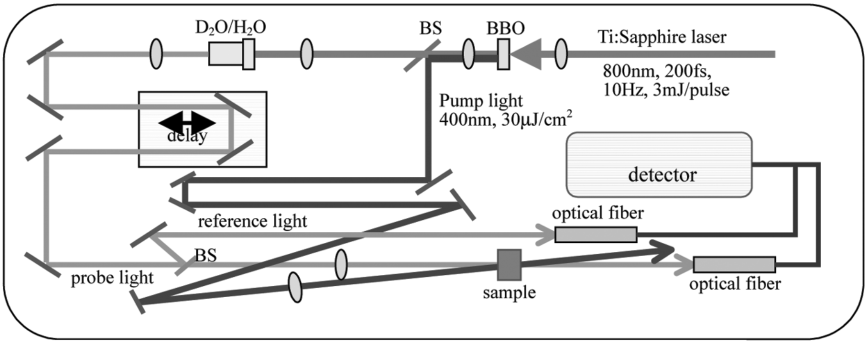


FIGURE 2 The block diagram of a femtosecond laser photolysis system. (BS: beam splitter, detector: Hamamatsu photonics, C6140 PMA).

stretcher/compressor, and an optical detection system (PMA11/50). An amplified Ti:sapphire laser produced pulses at 800 nm with a full width at half maximum (FWHM) of 250 fs, an averaged power of 3 mJ/pulse at 800 nm, and 10 Hz repetition. The amplified output beam was converted by a BBO crystal into second harmonic 400 nm pulse. Probe white light was generated by focusing the residual 800 nm light into a 10 mm cell containing D_2O:H_2O (2:1) mixture after passing through a BBO crystal. The pump and probe beams were focused to about 1 mm diameter spot on a 4 mm cell. The laser fluence was adjusted to avoid the damage of samples by using a variable neutral-density (ND) filter. The one part of the white-light probe beam was overlapped with the pump beam at the sample to probe the transient spectrum. The other part of the beam was detected without passing the sample solution. The time delay between pump and probe beam was controlled by making probe beam travel along a variable optical delay stage, 10 μm/step. Probe beams were detected by a dual photodiode array system (Hamamatsu Photonics, C6140-PMA). The probe light was accumulated for 20 ∼ 24 times.

RESULTS AND DISCUSSION

Three hexaphyrin derivatives as shown in Figure 2 were studied. Due to extended π-conjugation they showed absorption peaks in the visible to near IR region. Figure 3(a) shows the absorption spectra in toluene. There are Soret bands at 570 nm for **1**, 588 nm for **2b** and 615 nm for **3**, respectively. The Q bands were observed in near IR region. It was observed that the peaks shifted to longer wavelength in the order from **1** to **3**. Fluorescence spectra were observed with samples **1** and **2b** in

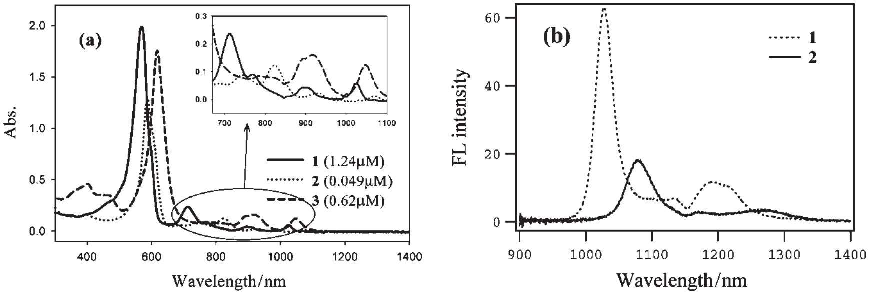


FIGURE 3 (a) The absorption spectra of hexaphyrin derivatives in toluene solutions. (b) Fluorescence spectra of hexaphyrin derivatives in dichloromethane solutions. 1 was excited at 566 nm, 2b was excited at 583 nm.

dichloromethane in the near IR region as shown in Figure 3(b). Samples **1** and **2b** were excited at the wavelength of their Soret band. Peaks appeared at 1028 and 1200 nm for **1** and 1079 and 1257 nm for **2b**, respectively. There was no fluorescence from **3** which included copper in the structure. Sample solutions were excited at 400 and 800 nm with femtosecond laser to observe transient responses. All sample solutions showed transient bleaching at their Soret band. Additionally there are two acetylacetonate groups in the structure of **2b** only. First, we have tried to approach the transient change with **2a** which was not substituted by acetylacetonate group. There was a problem in the durability of structure after laser excitation in the sample **2a** as shown in Figure 4. Around 1150 nm, a strange absorption peak was observed after laser excitation. It was suggested that it was broken by the oxidation of hydrogen atom located on the R position of **2a** probably after laser irradiation. So the hydrogen of **2a** was substituted by acetylacetonate group for the structural durability of sample **2**.

The time-resolved bleaching spectra in the visible region of hexaphyrin **1** in toluene solution by excitation at 400 nm are shown in Figure 5(a). Instantaneously, after excitation, transient bleaching in the visible region with a peak at 570, 592 and 617 nm were observed. The time profile of transient bleaching at 570 nm for **1** is shown in Figure 5(b). Time decays were consisted of two components, slow (τ_1) and fast one (τ_2).

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

The values of τ_1 and τ_2 are 105 and 12 ps for **1**, 95 and 21 ps for **2b** and 18.2 and 4.8 ps for **3**, respectively. At 400 nm excitation, the S_2 or higher states will be formed, while the S_1 state will be generated by

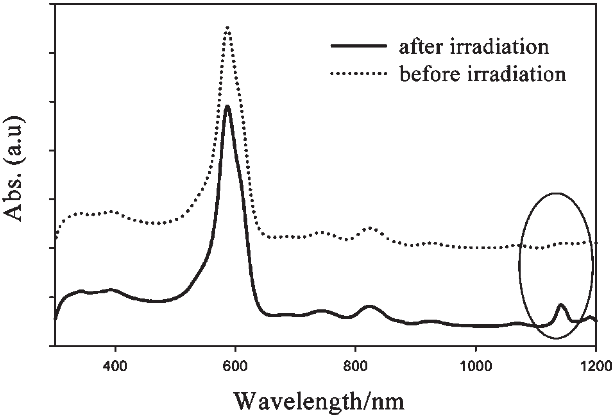


FIGURE 4 Comparison of absorption spectra of **2a** before irradiation and after.

800 nm excitation. Transient absorption and bleaching spectra upon 800 nm excitation are shown in Figure 6 together with the time profile at 572 nm. The time constant for the ground state bleaching recovery by 800 nm excitation were 96 ps for **1**, 55 ps for **2b**, 21 ps for **3**. These data are almost the same as those observed by 400 nm excitation, respectively. As an expectation, it was observed that the recovery became faster in the order from **1** to **3**. In the case of **2b**, hydrogen bonds which are located in both sides of amide group in hexaphyrin

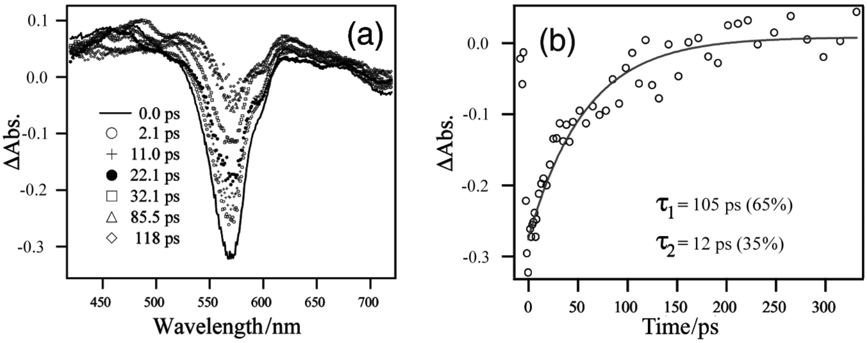


FIGURE 5 (a) Time-resolved transient bleaching spectra in the visible range of 1 in toluene solution, excited with a 400 nm femtosecond laser pulse. (b) Time profile of absorbance at 570 nm.; YAG laser, 141 mJ/pulse; seed pulse, 0.365 W; pump beam, 32 μJ/pulse; accumulation, 20 times; 2200 laser shots.

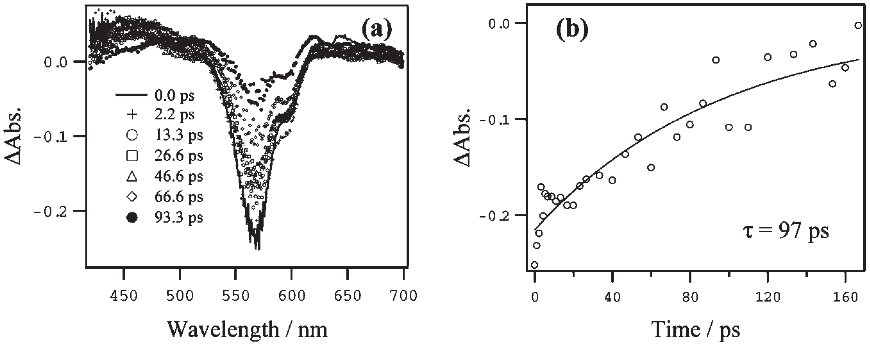


FIGURE 6 (a) Time-resolved transient bleaching spectra in the visible range of 1 in toluene solution, excited with a 800 nm femtosecond laser pulse. (b) Time profile of absorbance at 572 nm. YAG laser, 143 mJ/pulse; seed pulse, 0.350 W; pump beam, 30 μJ/pulse; accumulation, 24 times; 1920 laser shots.

ring will cause the extension of π-bonding more than **1**. According to these results, the internal conversion from S_2 to S_1 is concluded to be extremely rapid within the time resolution of our system. The sample **3** having Cu^{2+} in molecules gave faster recovery than sample **2b**. Copper ion, Cu^{2+} has a paramagnetic nature, which contributes to the rapid intersystem crossing of excited electrons from S_1 to T_1 or T_1 to S_0 by a spin orbital coupling as reported for excited triplet states in some metal phthalocyanines including Cu^{2+} complex [2].

CONCLUSION

The purpose of the present research is to find new organic photoresponsible materials for the information processing technology such as optical telecommunication. We obtained useful results with normal and *N*-confused hexaphyrin derivatives for such purpose. They have almost planar structure and also durability against repeated laser excitation by introducing acetylacetonate structures. They show absorbance in near IR region which can be used for ultrafast responses of appropriate devices are developed.

REFERENCES

[1] Nagamura, T. (2002). *Development of Molecular Photonics Materials and Devices*, *76*, 353.
[2] Nagamura, T., Naito, A., & Yoshida, I. (2002). *J. Nonlinear Opt. Phys. & Mat.*, *11*(3), 205.

[3] Nagamura, T. & Yoshida, I. (2003). *Mol. Cryst. Liq. Cryst.*, *406*, 19.

[4] Nagamura, T., Sasaki, K., Iizuka, F., Adachi, T., & Yoshida, I. (2002). *Opt. Comm.*, *205*, 107.

[5] Nagamura, T., Sakaguchi, H., & Muta, S. (1995). *Proc. SPIE*, *241*, 2514.

[6] Inoue, H., Sakaguchi, H., & Nagamura, T. (1998). *Appl. Phys. Lett.*, *73*(1), 10.

[7] Srinivasan, A., Ishizuka, T., Osuka, A., & Furuta, H. (2003). *J. Am. Chem. Soc.*, *125*, 878.

[8] Suzuki, M. & Osuka, A. (2003). *Org. Lett.*, *21*(5), 3943.

[9] Cho, H. S., Jeong, D. H., Cho, S. , Kim, D., Matsuzaki, Y., Tanaka, K., Tsuda, A., & Osuka, A. (2002). *J. Am. Chem. Soc.*, *124*, 14642.

[10] Kawai, H. & Nagamura, T. (1998). *J. Chem. Soc., Faraday Trans.*, *94*, 3581.

[11] Yoon, M. C., Jeong, D. H., Cho, S., & Kim, D. H. (2003). *J. Chem. Phys.*, *118*, 164.

[12] Neves, M. S., Martins, R. M., Tome, A. C., Silvestre, A. D., Silvia, A. S., Felix, V., Drew, M. B., & Cavaleiro, J. S. (1999). *Chem. Commun.*, *385*.

[13] Shin, J. Y., Furuta, H., Yoza, K., Igarashi, S., & Osuka, A. (2001). *J. Am. Chem. Soc.*, *123*, 7190.