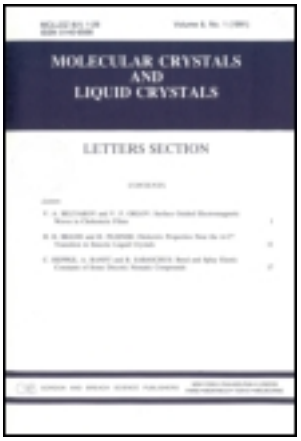

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Fabrication of Multilayer Film Type Laser Devices Containing Azobenzene Polymer and Control of Polarized Laser Emission

Ryohei Yagi [a], Yutaka Kuwahara [a c], Tomonari Ogata [b], Sunnam Kim [a] & Seiji Kurihara [a c d]

[a] Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami, Kumamoto, 860-8555, Japan

[b] Innovative Collaboration Organization, Kumamoto University

[c] JST-CREST, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo, 102-0076, Japan

[d] Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Higashi-ku, Kumamoto, 862-0901, Japan

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Fabrication of Multilayer Film Type Laser Devices Containing Azobenzene Polymer and Control of Polarized Laser Emission

RYOHEI YAGI,[1] YUTAKA KUWAHARA,[1,3] TOMONARI OGATA,[2] SUNNAM KIM,[1] AND SEIJI KURIHARA[1,3,4,*]

[1]Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555, Japan
[2]Innovative Collaboration Organization, Kumamoto University
[3]JST-CREST, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan
[4]Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Higashi-ku, Kumamoto 862-0901, Japan

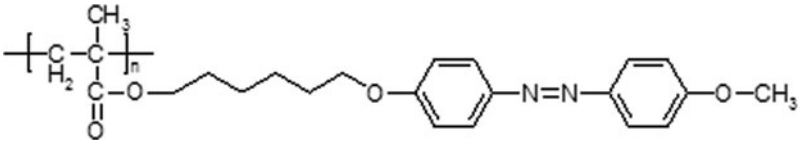
We prepared multi-bilayered films consisting of methacrylate polymer having azobenzene side chain groups (PMAz6Mc), polyvinyl alcohol and lasing dye. We investigated effects of molecular orientation of azobenzene moieties on the lasing behavior by measuring laser emission of the multi-bilayered films with/without polarized visible light irradiation to cause trans-cis-trans photoisomerization of azobenzene moieties. After irradiation of the polarized visible light, significant dependence of polarization direction of the laser emission intensity was observed, corresponding to the change in the molecular orientation of azobenzene moieties.

Keywords azobenzene polymers; photonic crystals; laser emission

Introduction

Photonic crystals (PC) consisting of a periodic lattice in the range of optical wavelengths is being actively investigated due to showing photonic band gap (PBG) in which the existence of a certain energy range of photon is forbidden. Multi-bilayered films are known as one dimensional photonic crystals (1DPC), as the specific wavelength of light is reflected according to bragg diffraction equation. In the photonic band edge of 1DPC, group velocity of photon decreases remarkably, so that the population inversion is easily caused when the medium in PC is excited. Therefore, the low threshold laser emission is induced and there are some reports on laser emission of 1DPC devices [1, 2]. On the other hands, in our previous study, we reported on–off switching of the reflection of the multi-bilayered film consisting of an azobenzene containing polymer layer and a polyvinyl alcohol (PVA) layer by control of molecular orientation via photoisomerization of the azobenzene group

*Address correspondence to Prof. Seiji Kurihara, Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan. Tel.: +8196-342-3677; Fax: +8196-342-3679. E-mail: kurihara@gpo.kumamoto-u.ac.jp



Scheme 1. Structure of PMAz6Mc.

to induce the difference in the refractive index of the multi-bilayered film [3]. According to Weigert effect, azobenzene groups in the multi-bilayered films are oriented perpendicular to the polarization direction of linearly polarized light [4]. Selective reflection of polarized light for the multi-bilayered films can be achieved. Several papers reported about laser emission of PC that tuned photonic band gap to shift the laser emission wavelength [5,6]. However, there have been *few* reports on the control of polarized laser emission [7]. In this study, we fabricated the dye-doped multi-bilayered film containing azobenzene polymer, and we discussed 1DPC laser devices that can control the polarized laser emission by the change in the molecular orientation of the azobenzene groups.

Experimental

Synthesis

We synthesized methacrylate polymer having azobenzene side chain groups through hexamethylene spacer (PMAz6Mc, Scheme 1) by a method similar to the synthetic route reported earlier [3].

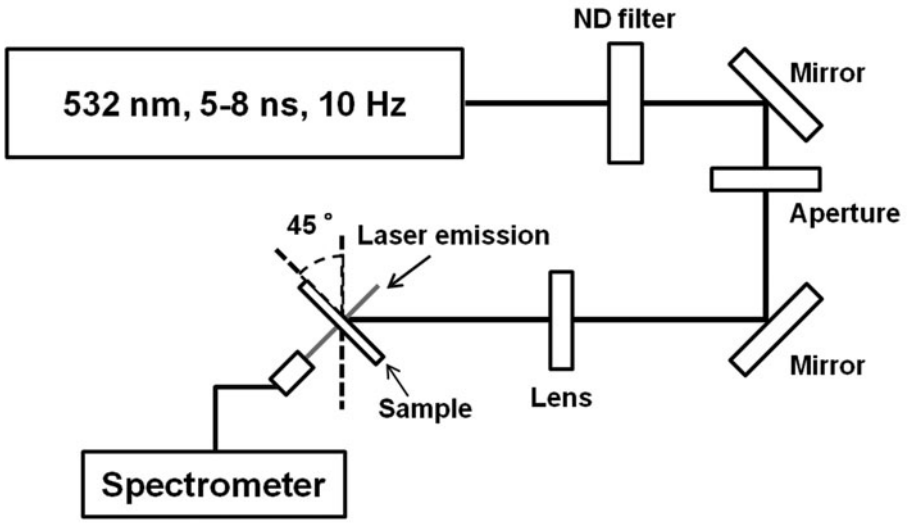


Figure 1. Experimental set up for measurement of laser emission.

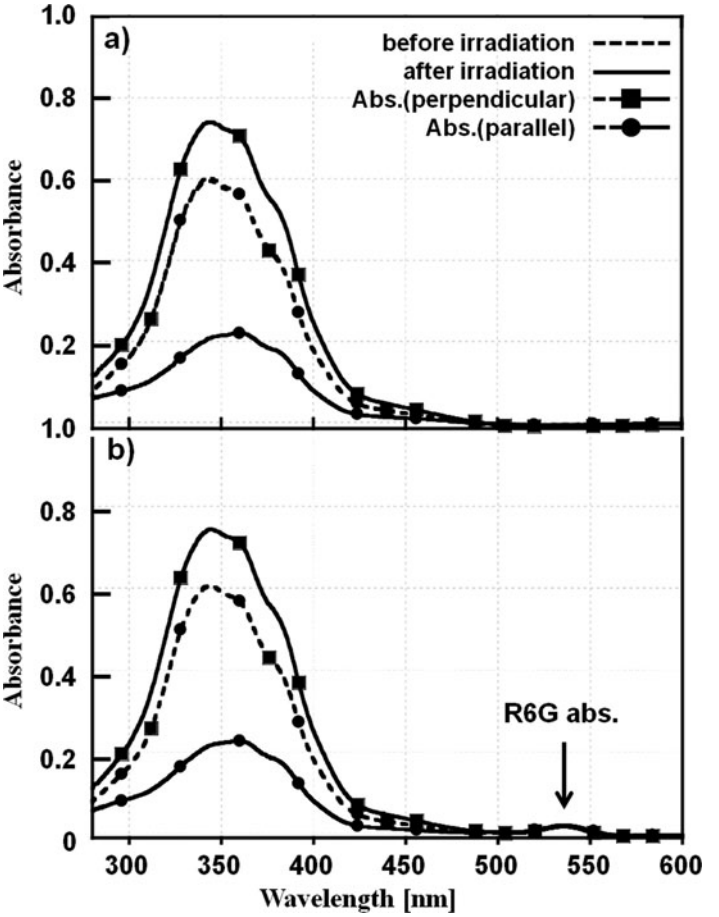


Figure 2. Change in polarized absorption spectra of R6G doped (b) or undoped (a) PVA/PMAz6Mc film before (dotted line) and after (solid line) LPL ($\lambda = 436$ nm, 195 mW/cm^2) irradiation. Polarized absorbance was monitored with perpendicular (square) or parallel (circle) polarized light to polarization direction of LPL.

Fabrication of Multi-Bilayered Film Type Laser Devices

Multi-bilayered films were fabricated by alternately coating of PVA containing Rhodamine 6G (R6G) film and PMAz6Mc film on a glass substrate. Each film was coated by spin-coating method from 2.25 wt% PVA (0.5 wt% R6G added to PVA) aqueous solution or 4 wt% PMA6Mc cyclohexanone solution.

Irradiation of Polarized Visible Light

Linearly polarized visible light (LPL, $\lambda = 436$ nm, 195 mW/cm^2) was irradiated on the PVA/PMAz6Mc multi-bilayered film to introduce molecular orientation of azobenzene groups.

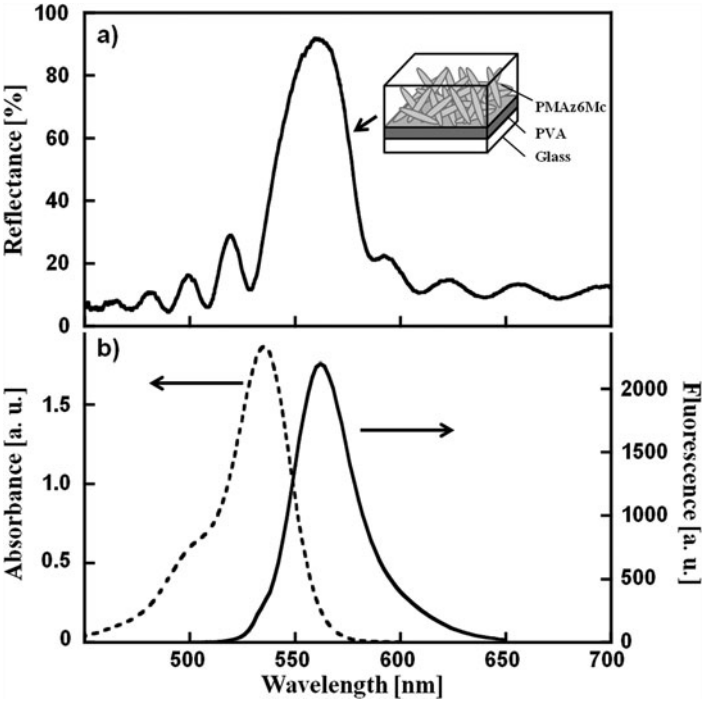


Figure 3. (a) Reflectance spectra of PMAz6Mc/PVA 20-bilayered film and (b) absorbance (dotted line) and fluorescence (solid line) spectra of PVA (0.5 wt% R6G added to PVA) thin film.

Measurements

The reflection spectra of the multi-bilayered films were measured with a spectrometer (Ocean optics USB2000). To measure the laser emission, dye doped multi-bilayered films were photo-pumped by the second harmonic pulse (532 nm) of a neodymium yttrium aluminium garnet (Nd:YAG) laser, which had a 5–8 ns pulse duration and a repetition rate of 10 Hz (Fig. 1). Laser emission spectra were measured before and after LPL irradiation, and polarized laser emission spectra were measured with a polarizer parallel or perpendicular to the polarization direction of LPL irradiatied on the multi-bilayered films.

Results and Discussion

Figure 2 shows change in polarized absorption spectra of R6G doped or undoped PVA/PMAz6Mc film by LPL ($\lambda = 436$ nm, 195 mW/cm^2) irradiation. Before LPL irradiation, no difference was observed for absorbance monitored with perpendicular and parallel polarized light to polarization direction of LPL. After LPL irradiation, absorbance monitored with perpendicular was increased and parallel was decreased (Fig. 2(a)). It is assumed that azobenzene groups in PVA/PMAz6Mc films are oriented perpendicular to the polarization direction of LPL, and the molecular orientation behavior was not changed by lasing dye (Fig. 2(b)).

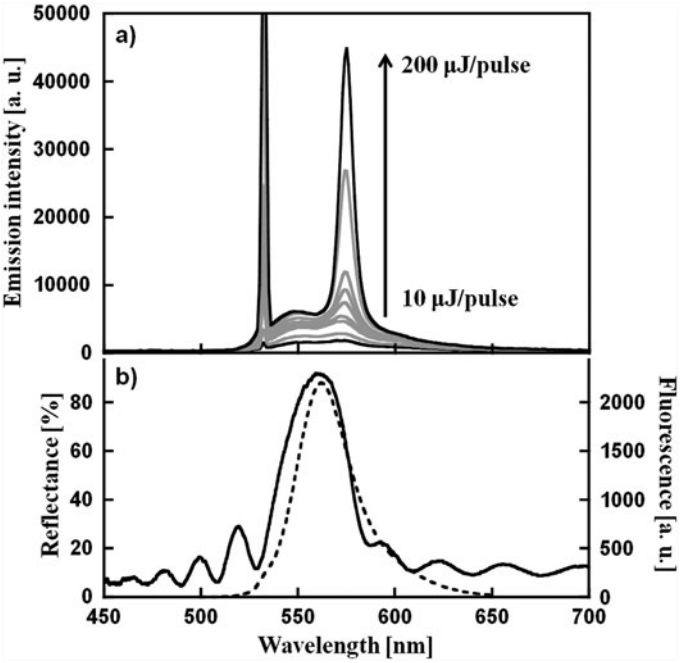


Figure 4. (a) Laser emission spectra of PVA/PMAz6Mc 20-bilayered film as a function of excitation pulse energy and (b) reflectance (solid line) and fluorescence (dotted line) of PVA/PMAz6Mc 20-bilayered film and PVA (0.5 wt% R6G added to PVA) thin film.

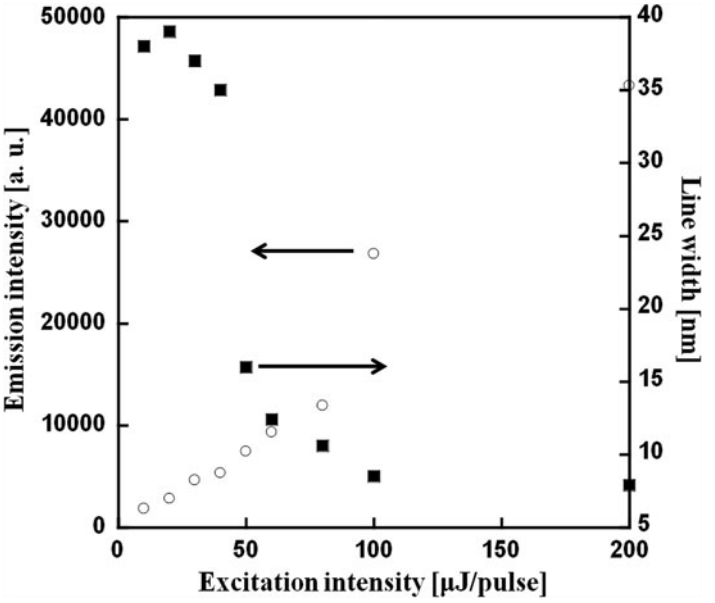


Figure 5. Changes in the laser emission intensity (circle) and linewidth (square) of PVA/PMAz6Mc 20-bilayered films as a function of excitation pulse energy.

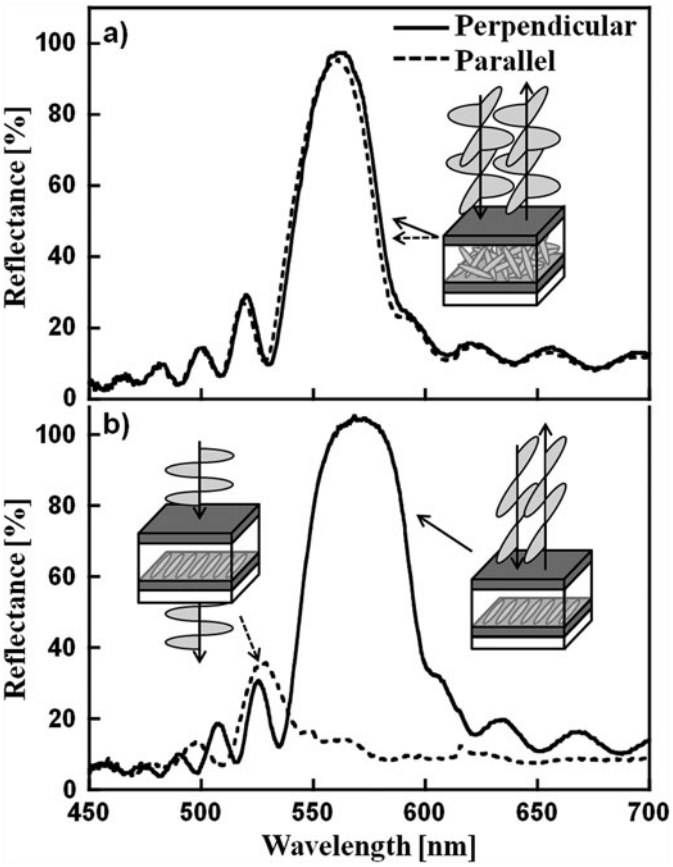


Figure 6. Reflectance spectra of PVA/PMAz6Mc 20-bilayered films (a) before and (b) after uniaxially molecular orientation by irradiation LPL ($\lambda = 436$ nm, 195 mW/cm^2) for 10 min. Reflection and laser emission spectra was measured with a polarizer parallel (dotted line) or perpendicular (solid line) to the polarization direction of LPL.

Multi-bilayered film reflects light of a specific wavelength according to the Bragg diffraction equation as follows, [3]

$$m\lambda = 2a\sqrt{n_1^2\frac{d_1}{a} + n_2^2\frac{d_2}{a}}.$$

where a is the thickness of each bilayer, n_1, n_2 and d_1, d_2 are the refractive indices and the layer thicknesses of both coated materials in bilayer, respectively, and m is the diffraction order integer. For PMAz6Mc/PVA multi-bilayered film, n_1 and n_2 are respectively 1.49 for PVA and 1.60 for PMAz6Mc, various reflection wavelength can be controlled by changing the thickness of layer. The PVA/PMAz6Mc 20-bilayered film was fabricated that the reflection peak was located at 560 nm corresponding to fluorescence emission peak of R6G to enhance the fluorescence emission. Figure 3a shows reflection spectra of PMAz6Mc/PVA 20-bilayered film. Figure 3b shows absorbance and fluorescence spectra of R6G-doped PVA thin film. Absorption and fluorescence peak of R6G was 532 nm and 560 nm, respectively. In addition, reflectance, R of the multi-bilayered film is given by

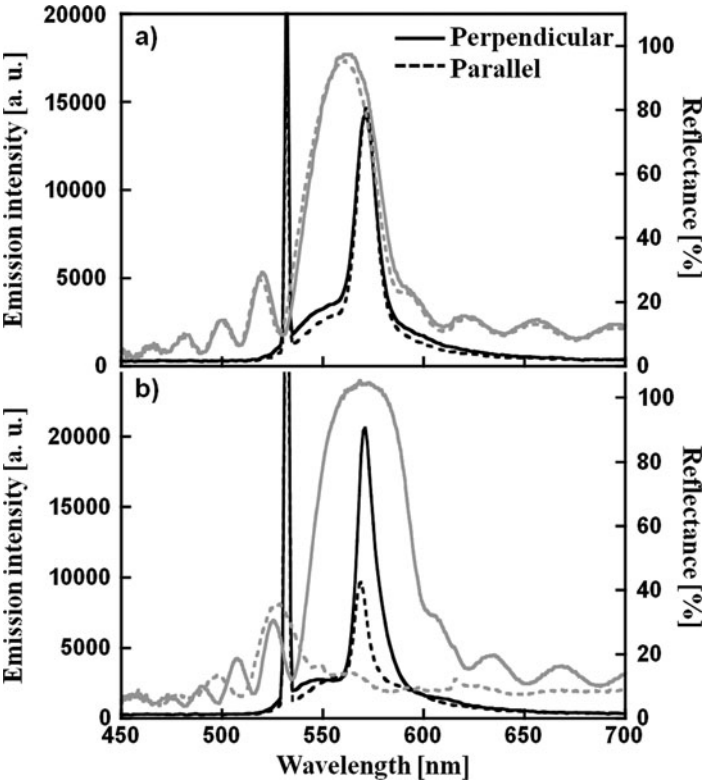


Figure 7. Reflectance (gray line) and laser emission spectra (black line) of PVA/PMAz6Mc 20-bilayered films (a) before and (b) after uniaxially molecular orientation by irradiation LPL (λ = 436 nm, 195 mW/cm^2) for 10 min. Reflection and laser emission spectra was measured with a polarizer parallel (dotted line) or perpendicular (solid line) to the polarization direction of LPL.

following equation, [3]

$$R = \left\{ \frac{1 - \left(\frac{n_H}{n_L}\right)^{2q} \left(\frac{n_H^2}{n_S}\right)}{1 + \left(\frac{n_H}{n_L}\right)^{2q} \left(\frac{n_H^2}{n_S}\right)} \right\}^2 .$$

where n_H and n_L are the high and low refractive indices of both coated materials in bilayer, respectively, n_S is the refractive index of the substrate and q is the number of bilayers. From equation, the reflectance of PMAz6Mc/PVA 20-bilayered film was calculated for 87% as refractive indices of PVA (n_L = 1.49), PMAz6Mc (n_H = 1.60) and glass substrate (n_S = 1.50). The result of calculation corresponded with experimental result. Figure 4 shows laser emission spectra of PVA/PMAz6Mc 20-bilayered film. Laser emission occurred at 570 nm corresponding to the photonic band edge of the 20-bilayered film with increasing excitation intensity from 10 to 200 μJ/pulse [1,2]. The laser emission intensity and full width at half maximum (FWHM) were plotted as a function of imput pumping energy in Fig. 5. When the excitation intensity was 50 μJ/pulse, the FWHM was drastically decreased from 35 to 17 nm with increasing laser emission intensity. Therefore, the threshold of excitation intensity was assumed at about 50 μJ/pulse, and FWHM of PVA/PMAz6Mc

20-bilayered film were and 8.5 nm at 100 μJ/pulse. Figure 6 shows polarized reflection spectra of PVA/PMAz6Mc 20-bilayered film before and after irradiation of LPL (λ = 436 nm, 195 mW/cm^2) for 10 min. Reflection spectra was measured with a polarizer parallel or perpendicular to the polarization direction of LPL irradiatied on the multi-bilayered films. Before irradiation of LPL, no difference was observed for the reflectance intensities measured with parallel and perpendicular polarizers (Fig. 6(a)). On the other hand, after irradiation of LPL, the reflectance and laser emission intensity along perpendicular direction to the polarization direction of LPL became significantly larger than that along parallel (Fig. 6(b)). It was assumed that azobenzene groups in the 20-bilayered film are uniaxially oriented perpendicular to the polarization direction of LPL according to Weigert effect. The 20-bilayered film strongly reflected polarized light of perpendicular to the polarization direction of LPL. Figure 7 shows polarized laser emission spectra of PVA/PMAz6Mc 20-bilayered film before and after irradiation of LPL. Before irradiation of LPL, no difference was observed for the laser emission intensities (Fig. 7(a)). Non-polarized laser emission occurred because the 20-bilayered film as 1DPC reflects and enhanced non-polarized light for laser emission. After irradiation of LPL, the laser emission intensity along perpendicular direction to the polarization direction of LPL became significantly larger than that along parallel (Fig. 7(b)). As a result, the polarized laser emission was achieved corresponding to the strongly reflected polarized light direction.

Conclusion

20-bilayered film type laser emission devices containing azopolymer were fabricated. The threshold and FWHM of PVA/PMAz6Mc 20-bilayered films were found to be about 50 μJ/pulse and 8.5 nm at 100 μJ/pulse, respectively. Azobenzene side chain groups were oriented perpendicular to the polarization direction by irradiation of LPL, resulting in the polarized laser emission. Based on the results, polarization of laser emission would be controlled by irradiation of polarized or non-polarized visible light.

Acknowledgments

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