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In order to realize an organic distributed feedback (DFB) laser based on photoinduced surface relief grating (SRG) on azobenzene polymer, fluorescence quench of dye doped in azobenzene polymer is large obstacle. In order to elucidate the mechanism, time-resolved fluorescence and pump-probe transient absorption were measured, and the quench mechanism was suggested to be oxidative electron transfer from azobenzene to the dye. Some solutions to the quenching problem were proposed in terms of device and material designs, and a double-layer design was actually employed to fabricate an organic DFB laser based on SRG, resulting in successful lasing and demonstration of wavelength programmability.

Keywords: azobenzene polymer; electron transfer; femtosecond transient absorption spectroscopy; fluorescence quench; organic distributed feedback laser

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Organic distributed feedback (DFB) lasers are attracting increasing interests as low-cost, high-performance, and low environmental-load light sources. We have proposed and demonstrated wavelength-programmable organic DFB lasers based on photoinduced surface relief grating (SRG) on azobenzene polymer, so that the lasing wavelength is reprogrammable by erasing and rewriting the SRG [1]. During the research, a single-layer structure was employed at first, in which a laser dye was doped in azobenzene polymer so that the layer should provide both optical gain and distributed feedback with SRG. However, it was found that fluorescence of organic laser dyes was significantly quenched when doped in azobenzene polymer. In this work the mechanism of quench was investigated through time-resolved fluorescence and transient absorption spectroscopy, in order to find solutions to this problem. According to the understandings obtained in this work, the problem has been overcome by employing a double-layer structure separating the dye from the azobenzene polymer, and lasing and wavelength-programmability was successfully demonstrated [1].

In the experiment, film samples were prepared by spincoating a chroloform solution of a dye doped in a polymer on a quartz substrate. Three laser dyes, i.e., rhodamine 101, HIDCI, and Oxazine 1, and two polymers, an azobenzene polymer (pDR1M) and poly(methyl methacrylate) (PMMA), were used (Fig. 1), and thus totally 6 films were prepared as combinations of dye and polymer. The thickness was ca. 270 nm and 460 nm for dye/pDR1M and dye/PMMA films, respectively. The dyes were selected in terms of absorption bands to be located at around 600 nm and not overlapped with that of pDR1M, so that only the dyes can be photoexcited without excitation of pDR1M. All laser dyes were purchased from Exciton Inc. and used without further purification. pDR1M was synthesized through the procedure written in literature [2]. PMMA was purchased from Scientific Polymer Products, Inc. and used without further purification.

Absorption and fluorescence spectra were measured using a UV-visible spectrophotometer (UV3100, Shimadzu Co.) and a fluorescence spectrometer (F6500, JASCO Co.). Dye/PMMA films presented absorption bands originating in the dyes, and showed strong fluorescence at each fluorescence band. Dye/pDR1M films presented absorption spectra composed of absorption bands of the dye and of pDR1M. However, fluorescence of dye/pDR1M films were significantly quenched by factors of twenty or more.

Picosecond time-resolved fluorescence and subpicosecond transient absorption measurements of the films were performed using a setup shown in Figure 2. An optical parametric amplifier (OPA) (OPA9400, Coherent Inc.) pumped by a Ti-sapphire regenerative amplifier

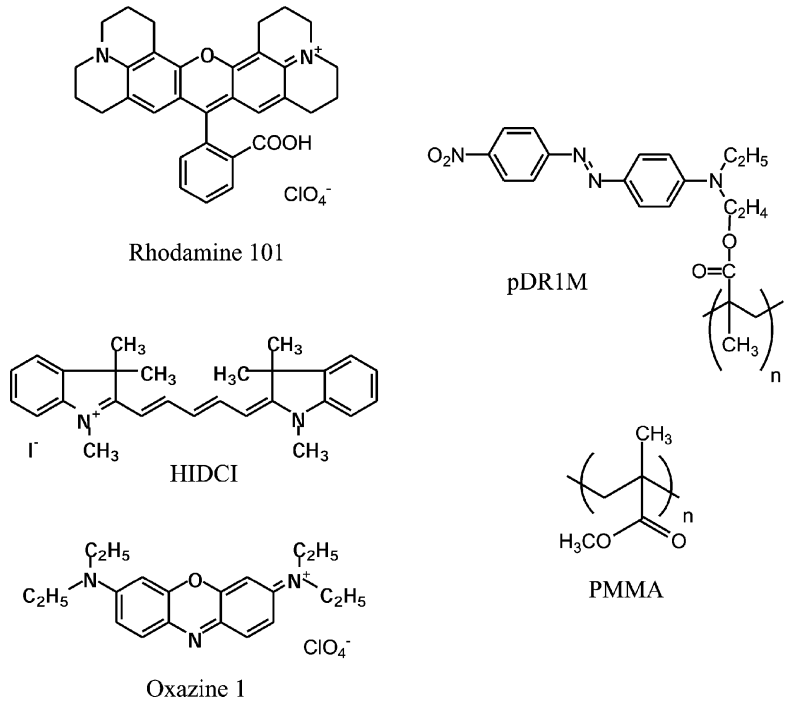

FIGURE 1 Laser dyes and polymers used in this work.

(TSA-1000, Spectra Physics Co.) and a mode-locked Ti-sapphire laser (MIRA900, Coherent Inc.) was used as the excitation and pump light source. In time-resolved fluorescence measurements, the samples were

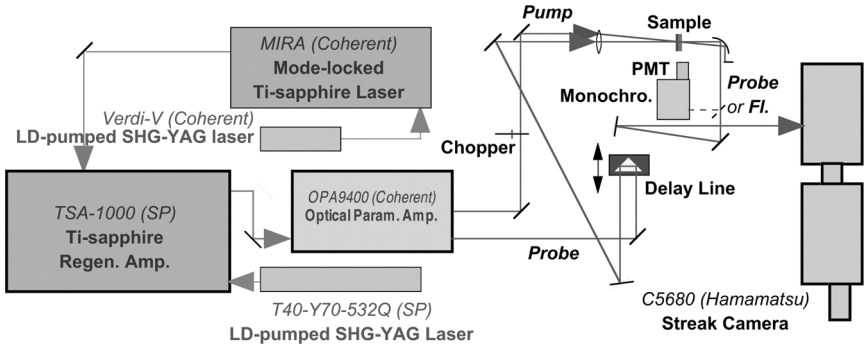

FIGURE 2 Schematic diagram of time-resolved measurement setups.

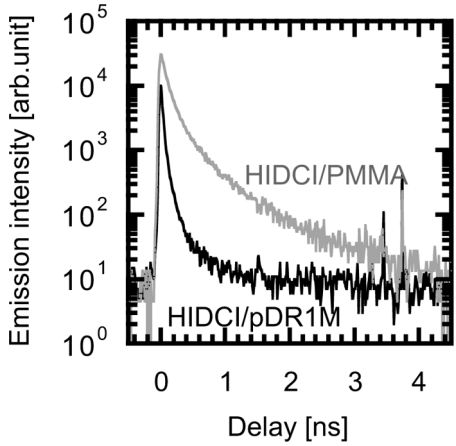

FIGURE 3 Time-resolved fluorescence of HIDCI/PMMA film (gray dots) and HIDCI/pDR1M film (black dots). Excitation wavelength is 605 nm.

excited at 605 nm and fluorescence was detected with a picosecond streak camera (C5680, Hamamatsu Photonics Co.). At this excitation wavelength, only the dyes were excited but not pDR1M. Figure 3 shows time-resolved fluorescence which presented significant reduction of fluorescence lifetime in the HIDCI/pDR1M film compared with that in the HIDCI/PMMA film. Similar reduction in fluorescence lifetime was observed also in Rhodamine101/pDR1M and Oxazine1/pDR1M films, suggesting that the quenching was induced by energy and/or electron transfer from the dye to pDR1M. The decay time constants in dye/pDR1M were ca. 12 ps, possibly limited by the temporal resolution of the streak camera. It should be noted that the fluorescence decay profile of HIDCI/pDR1M shown in Figure 3 presented small tail with rather long decay time constant, similar to that of HIDCI/PMMA. Oxazine1/pDR1M also presented a similar slow tail, while Rhodamine101/pDR1M did not. This will be discussed later.

Subpicosecond transient absorption change was measured using pump-probe configuration shown in Figure 2. White spectral continuum generated in the OPA was used as the probe pulse. After optical delay to control relative timing of the probe to the pump pulses, the probe pulse went through the sample, monochromated, and detected by a photomultiplier tube. The pump pulse train was chopped by an optical chopper, and the change in probe intensity by chopping was detected using a lock-in amplifier. Pump wavelength was 660 nm for HIDCI and Oxazine 1, and 605 nm for Rhodamine101, at which

wavelengths pDR1M was not excited. Probe wavelengths were 460–700 nm, and pump-to-probe delay was scanned up to 500 ps. Figure 4 shows transient transmission change at a probe wavelength of 480 nm. HIDCI/pDR1M presented fast excited-state absorption with decay time constant of ca. 3 ps followed by slow absorption saturation with decay time constant much longer than 500 ps, while HIDCI/PMMA presented only rather slow excited-state absorption.

Considering the fact that HIDCI/PMMA has no absorption at this probe wavelength, the slow absorption saturation originates from pDR1M which has no absorption at the pump wavelength. On the other hand, semiempirical molecular orbital calculations confirmed that the highest occupied molecular orbital (HOMO) of an azobenzene group is located at higher energy by 2–3 eV compared with the laser dyes. Thus, it is suggested that the photoexcitation of a dye molecule induced absorption saturation of pDR1M through oxidative electron transfer from azobenzene to the dye [3,4] in ca. 3 ps. Thus fluorescent transition of the dye was forbidden by occupation of HOMO level.

We have also performed polarization-dependent transient absorption measurements, which presented ultrafast (ca. 200 fs) depolarization in the dye responses. This ultrafast depolarization is not originated in molecular orientational relaxation which is in the order of 10 to 100 ps even in a solution and much slower than that in a

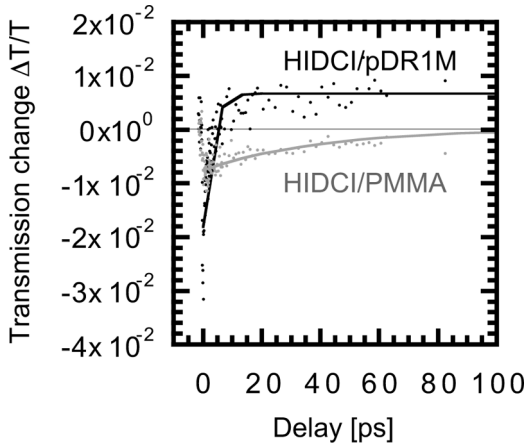

FIGURE 4 Transient transmission change of HIDCI/PMMA film (gray dots and line) and HIDCI/pDR1M film (black dots and line). Pump and probe wavelengths are 660 nm and 480 nm, respectively. Positive transmission change corresponds to absorption saturation and negative change to excited-state absorptions.

polymer. Therefore it is strongly suggested that the depolarization is originated in fast excitation migration among dye molecules possibly due to aggregation. This hypothesis is also consistent with the small slow tails in time-resolved fluorescence: the aggregation suppresses electron transfer from the dye located at the center of an aggregate and thus such a dye molecule presents fluorescence dynamics similar to that of the dye in PMMA.

Considering these results, there are some ways to avoid fluorescence quench. In terms of device design, interaction of the laser dye and pDR1M can be avoided by separating them into different layers. In terms of material design, molecular encapsulation of the dye will avoid electron transfer. Embed into some caged compounds such as a dendrimer, or molecular wrapping by surface sol-gel method can be utilized.

According to the guideline described above, a double-layered device structure has been designed: an active layer of dye-doped poly (vinyl alcohol) (PVA) is formed on a quartz substrate, and then pDR1M layer is formed by spincoating and SRG was formed by interference exposure. With this device structure, photopumped DFB lasing has been successfully observed, and wavelength programmability has been demonstrated through erase-and-rewriting of SRG. The detail will be described elsewhere [1].

In conclusion, fluorescence quench in dye/azopolymer films was investigated. Time-resolved fluorescence spectroscopy and pump-probe transient absorption spectroscopy were used, and the quench mechanism was suggested to be oxidative electron transfer from HOMO level of azobenzene to that of the dye. Some solutions to the quenching problem were proposed in terms of device and material designs, and a double-layer design was actually employed to fabricate an organic DFB laser based on SRG, resulting in successful lasing and demonstration of wavelength programmability.

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