All-optical polymeric interferometeric wavelength converter comprising an excited state intramolecular proton transfer dye

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We designed and demonstrated an all-optical wavelength converter using a polymeric Mach–Zehnder interferometer (MZI) comprised of an excited state intramolecular proton transfer (ESIPT) dye, 2,2′-{oxybis[4-(4-methoxyphenyl)quinoline-6,2-diyl]}bis(5-methoxyphenol) (MQ). This MZI wavelength converter is composed of the MQ dye-doped polymeric waveguide and a thick light blocking metal film. A feature of this device is that one arm of the MZI can be irradiated by 355 nm pulses (signal beam), while the other arm was not, thus allowing a differential phase shift in the submicrosecond time scale. Because of the refractive index change of the ESIPT dye in one arm of interferometer upon irradiation with the signal beam, phase modulation of the continuous-wave probe light propagating in the irradiated arm of the MZI takes place, leading to the intensity modulation at the output defined by the signal beam, resulting in an all-optical wavelength converter, that is, the conversion of the signal modulation to output signal modulation of the probe light of the MZI. The characteristics of the wavelength converter are well described by a simple kinetic model. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1755839]

Wavelength division multiplexed (WDM) networks provide a solution to the dramatic increase in demand on communication services. Wavelength conversion is widely recognized as a key function in future all-optical WDM networks. It allows for wavelength reuse, as well as increases the capacity and flexibility of the network. Recently, several techniques have been proposed to achieve all-optical wavelength conversion, such as cross-gain modulation in semiconductor optical amplifiers (SOAs), cross-phase modulation in SOA, four-wave-mixing in SOAs and difference-frequency generation in $LiNbO_3$ or AlGaAs waveguides.[1–4] The majority of wavelength conversion techniques using SOAs require complex processing, steps such as the growth of multiple quantum well active layers on top of a passive InGaAsP waveguide core using standard metalorganic vapor phase epitaxy.[3]

In this letter, we designed and demonstrated an all-optical polymeric wavelength converter using a Mach-Zehnder interferometer (MZI) with a special kind of fluorescent dye showing excited-state intramolecular proton transfer (ESIPT), 2,2′-{oxybis[4-(4-methoxyphenyl)quinoline-6,2-diyl]}bis(5-methoxyphenol) (MQ). The ESIPT dye has a four-level photocycle scheme implemented by the enol (E)-keto (K) phototautomerization ($E \rightarrow E^* \rightarrow K^* \rightarrow K \rightarrow E$) as shown in Fig. 1.[5] ESIPT-exhibiting molecules exist as enol form (E) tautomers in the ground state, but once excited, they are transformed into the excited-state keto form (K^*) tautomers via an extremely fast (subpicosecond order) and irreversible ESIPT process. After K^* decays radiatively to the ground-state keto form (K), the reverse proton transfer from K to E occurs on a submicrosecond time scale. Therefore, the different species in the ground-state enol form (E) and keto form (K) give rise to a change in the refractive index. A reversible change of refractive index between the E and K form with a submicrosecond switching time can be used in applications, such as all-optical switch, modulator, and wavelength converter.

Figure 2 shows the schematic diagram of the MZI wavelength converter. This MZI wavelength converter is composed of a MQ dye-doped polymeric waveguide and a thick light blocking metal film on one arm. The metal film is patterned as a heater to bias the initial state of the MZI to the off state, as well as acting as the blocking layer of the pumping light pulse. Continuous-wave (cw) light (cw probe) is coupled into the input port. Upon irradiation of one arm by the signal pulse at the absorption wavelength of the MQ dye, the enol form changes to the keto form within picoseconds (transition time to the keto form) and the keto form is maintained for submicrosecond time scales (lifetime of the keto form). Since the refractive index of the keto form is different from the enol form, the phase of the cw probe in the signal arm is modulated by the exposure to the signal. As a result, the output intensity from the MZI is modulated by the signal.

Buried ridge waveguides were fabricated by conventional photolithography and dry etching techniques.[6,7] First, 11 μm thick benzocyclobutene ($n^{TE} = 1.548$ at 1.55 μm) was spincoated on a silicon substrate as the cladding material. A polycarbonate layer doped with MQ (24.6 wt %, $n^{TE} = 1.586$ at 1.55 μm) was then spincoated on the cladding layer and baked on a hot plate at 150 °C for 1 h. The MQ content of 24.6% was just below the upper limit for ensuring optical clarity. Even with the high dye content, no agglomeration was observed. The dimensions of the core layer are controlled to satisfy the single-mode condition at 1.55 μm. The width and height of the core waveguide are 4 and 5 μm,

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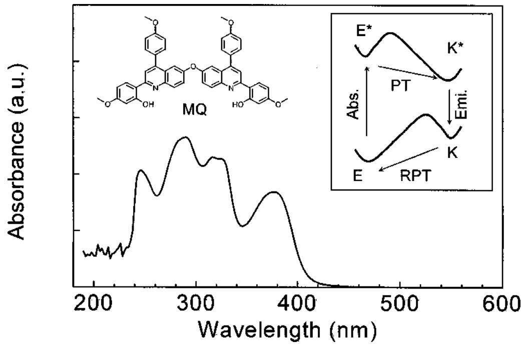

FIG. 1. Molecular structure, absorption spectrum, and schematic diagram of proton-transfer reaction path of MQ: Absorption (Abs.), emission (Emi.), proton transfer (PT), and reverse proton transfer (RPT).

respectively, and the ridge is etched to a depth of 2 μm using O_2 reactive ion etching. As the upper cladding layer, 11 μm-thick benzocyclobutene was spin-coated on the core layer. Finally, a 200 nm thick Au layer was thermally evaporated and patterned by a wet etching process. Figure 2 shows top views of the MZI wavelength converters and a microphotograph of the fabricated device.

Nd–YAG pulsed laser light at 355 nm (pulse width of 7 ns with a 10 Hz repetition rate, B.M. Industries™) was used to irradiate the open arm of the MZI through a beam expander and served as the signal. cw laser light (Lasermax LAS-300-1550-6) at 1.55 μm was launched into the MZI wavelength converter from a single-mode fiber and was used as the cw probe. Modulated probe from the output of the converter was directed to a photodetector (Newport 818-IR) through a single-mode fiber and observed on a computer through a sampling scope (Tektronix, TDS 520B).

A signal modulated probe light is shown in Fig. 3 for different signal intensities. The initial state of the MZI is controlled to the off state by the heater on one arm through the thermo-optic effect. Figure 3 clearly shows that the input cw probe light is modulated by the signal light to convert the 355 nm signal to the 1.55 μm wavelength. Higher signal intensity resulted in larger modulation of the probe light. This is an expected result since high signal intensities will

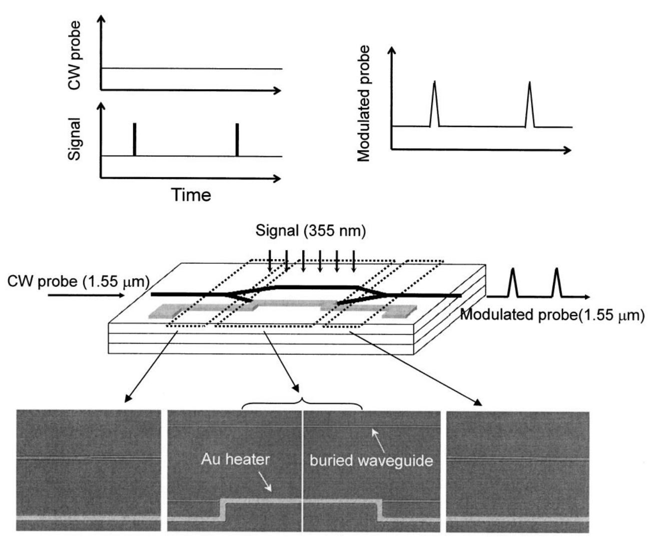

FIG. 2. Schematic diagram of the MZI wavelength converter, illustration of device operation, and microphotograph of the fabricated device.

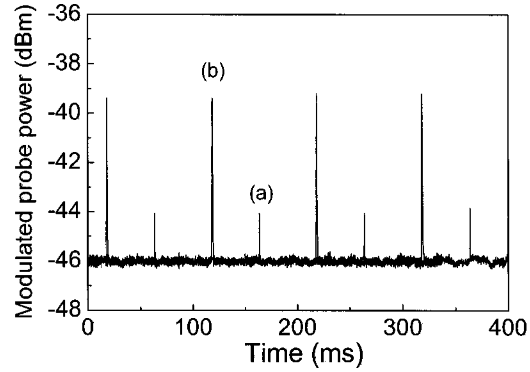

FIG. 3. Modulated probe intensities of the MZI wavelength converter measured by a photodetector for various signal intensities of (a) 2.6 and (b) 11 pJ/cm^2/pulse at a wavelength of 355 nm.

result in large refractive index differences. The phase shift $\Delta\Phi$ which induces the wavelength conversion can be calculated from the following equation:[7]

$$\Delta\Phi = (2\pi\Delta n_{eff}L)/\lambda, \tag{1}$$

where L is the length of the Mach–Zehnder arm, Δn_{eff} is the effective index change of the arm, and λ is the wavelength of the laser. The value of Δn_{eff}, the difference of refractive index between enol (E) and keto (K) form states, required for a π phase shift is 0.000 042, based on Eq. (1). The analysis of the wavelength converter can be performed by relating the phototautomerization process to the refractive index change of one arm of the MZI, and relating the induced refractive index change to the resulting phase shift in that arm.

Consider the amplitude of the two waves in the separate arms of MZI equal (i.e., $E_1 = E_2$). The total intensity of optical interference with two-wave interference is described by

$$I/I_0 = (1 + \cos[\Delta\Phi + \pi])/2, \tag{2}$$

where I_0 is the incident light intensity. A phase shift of π is introduced in the above equation because the initial state of the MZI is controlled to the off state by the heater on one arm using the thermo-optic effect. Assuming that the value of Δn_{eff}, the difference of refractive index between enol (E) and keto (K) states, is proportional to the number density of the keto (K) form, N_k, which is in turn related to signal intensity and lifetime of the keto (K) form, Δn_{eff} as a function of time (t) is described by

$$\Delta n_{eff} = C I_{signal} \exp(-t/\tau), \tag{3}$$

where C is constant, I_{signal} is the signal intensity, and τ is the lifetime of the keto form. In Eq. (3) the total number of keto form molecules formed by irradiation is assumed to be proportion to the number of photons irradiating the film and the decay of the keto form to enol form is assumed to follow first-order kinetics. The intensity variation of the modulated (i.e., wavelength converted) light from the MZI with the signal intensity and time is obtained by combining the Eqs. (1)–(3).

$$I/I_0 = (1 + \cos(A\exp(-t/\tau) + \pi))/2, \tag{4}$$

where A is a constant described by $A = 2\pi C\, L I_{signal}/\lambda$. In the case of a double exponential lifetime for the conversion from the keto to enol form, the Eq. (4) is modified to

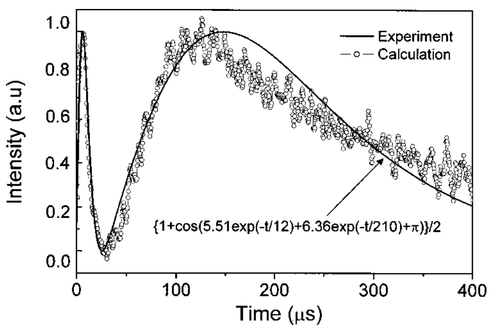

FIG. 4. Wavelength conversion performance of the MZI measured by a sampling oscilloscope and fitted by using simple Eq. (5) for a signal intensity of 69 pJ/cm^2/pulse.

$$I/I_0=(1+\cos(A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+\pi))/2, \quad (5)$$

where A_1 and A_2 are constants described by $A_1=2\pi C_1 L I_{\mathrm{signal}}/\lambda$ and $A_2=2\pi C_2 L I_{\mathrm{signal}}/\lambda$. The constant A_1, A_2, and lifetime τ_1, τ_2 are simultaneously determined as the values that provide the best fit to the experimental results as shown in Fig. 4. The wavelength conversion of the MZI shows two on–off–on cycles with the pulsed Nd–YAG laser, indicating that the total phase shift of the light through one arm is about $2\times 2\pi$ resulting in the values of $\Delta n_{\mathrm{eff}}\sim 2\times 10^{-4}$. We also obtain the following values fitted: $A_1=5.51$, $A_2=6.36$, $\tau_1=12\ \mu$s, and $\tau_2=210\ \mu$s. Recently, Jang *et al.*[8] investigated the dynamics of a structurally related polymer (PQH) possessing MQ as a repeating unit by using transient absorption spectroscopy and assigned the lifetime (τ_1) of the ground-state keto form as 10 μs. Our experimental data of $\tau_1=12\ \mu$s is consistent with the dynamics data of $\tau_1=10\ \mu$s, thus confirming our simple model. The origin of the slow decay component is not clear yet. One plausible origin is the thermal effect coming from the absorption of the signal light by the waveguides and the substrate. The decay time constant of submillisecond and the proportionality of the amplitude with the signal intensity as described below support the possibility.

Using the simple model, we estimated the dependence of wavelength conversion on the signal intensity by varying the constant A_1 and A_2 proportional to I_{signal}. The calculated results are displayed in Fig. 5(b) and compared with the experimental results in Fig. 5(a). These results also confirm that the phototautomerization process and the characteristics of the wavelength converter are described very well by our simple model.

In conclusion, we designed and demonstrated an all-optical wavelength converter using a polymeric MZI comprising an ESIPT dye. This MZI wavelength converter is composed of an ESIPT dye-doped waveguide and a thick thermo-optic and light blocking metal film. A unique feature of this device is that one arm of the MZI can be irradiated by 355 nm pulses, while the other arm was not, thus allowing a differential phase shift in microsecond time scale. This structure allows phase modulation of the cw light propagating in the MZI using the pulse repetition of the signal beam, resulting in wavelength conversion from the signal beam to the guided light of the MZI. Because of the refractive index change in one arm of the interferometer, the modulated cw light is observed at the output and thus controlled by the pulsed signal beam. We calculated the dependence of the wavelength conversion on pumping intensity using a simple model, which describes the experimental results very well. This idea can be extended to other molecules with different excitation wavelengths so that the conversion wavelength can be changed. If a dye has absorption at 650 nm, the device must have utility for plastic optical fiber network at home.

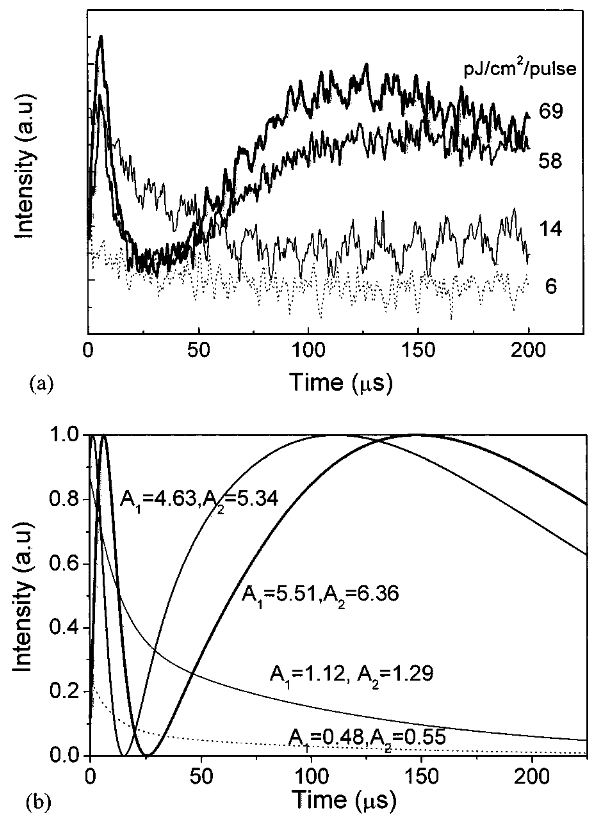

FIG. 5. (a) Dependence of wavelength conversion of the MZI on signal beam intensity of 6, 14, 58, and 69 pJ/cm^2/pulse and (b) calculated wavelength conversion on signal intensity parameter of A_1 ($A_1=2\pi C_1 L I_{\mathrm{pump}}/\lambda$) and A_2 ($A_2=2\pi C_2 L I_{\mathrm{pump}}/\lambda$). The experimental wavelength conversion results are consistent with those calculated at a various light intensities.

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