

Photostability of High $\mu\beta$ Electro-Optic Chromophores at 1550 nm[†]

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We present the photostability results of seven novel electro-optic chromophores made to be used in high-speed fiber optic signal modulators. We measured the photobleaching rate of the chromophores at room temperature by using a fiber optic pump–probe technique. Thin polymer film guest–host samples were deposited on the end of SMF-28 fiber pigtails and bleached by using 100 mW of 1550 nm radiation as the pump. The bleaching rate was measured by monitoring the main absorption band of the chromophores by using a 660 nm probe beam that was multiplexed into the fiber pigtail. The relative photostability was reported as a figure of merit which is proportional to the 1/e bleaching lifetime of the chromophore. We found the bleaching rate to increase linearly with incident 1550 nm power at the end of the single-mode fiber up to at least 100 mW. Our results show that the photobleaching rate is reduced dramatically when the test is conducted in an inert atmosphere. We also show that the presence of the singlet oxygen quencher DABCO can be used to increase the lifetime of the chromophore. The effect that chromophore structure and polymer host type have on photostability are also discussed.

Introduction

Many research groups have demonstrated the feasibility of using electro-optic (EO) polymers in high-speed optical communication modulators.^{1–3} Recently we reported the synthesis and characterization of a new class of EO chromophores with very high $\mu\beta$ EO coefficients.^{4–6} Though high EO coefficients are necessary for making modulators that are very efficient with low drive voltage, there are other properties that the active material must possess in order to be successfully implemented in a reliable device. One of the most important of these properties is long-term photostability.

Several research groups have done extensive work examining the photostability of EO polymers. These studies have shown that the photostability of the chromophore is affected by factors such as wavelength and intensity,^{7–9} chromophore structure,^{10,11} and the presence of oxygen.^{3,11} Though much work has been done in this area, these studies have been performed at wavelengths up to approximately 1300 nm. Very few results have been reported using the telecommunication C-band wavelengths (1525–1575 nm) which are used for most WDM (wavelength division multiplexing) and DWDM (dense wavelength division multiplexing) applications.^{3,12} The objective of this paper is to report the photostability of several novel chromophores at 1550 nm using a fiber optic pump–probe photobleaching test setup. We examine how factors such as atmosphere, optical intensity, and chemical structure affect the rate of photobleaching.

Experimental Section

Materials. The structures of the chromophores used in our study are shown in Table 1.

The synthesis of IPC-E and DPC-T was reported earlier.^{4,5} The synthesis of the other chromophores is reported by He et al.¹³

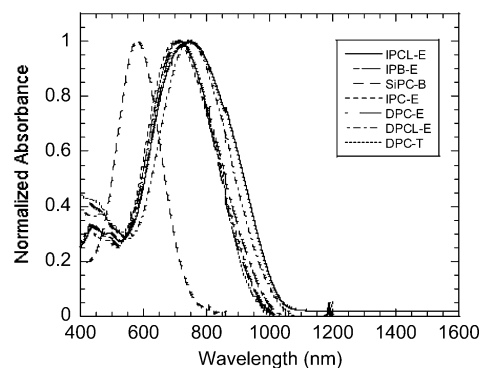


Figure 1. Normalized UV–vis–NIR spectra of EO chromophores in Udel host.

We made guest–host films by preparing solutions of each chromophore in polycarbonate (PC) or a polyether sulfone (Udel, Amoco) using dichloroethane (DCE) as a solvent. The concentration of chromophore in the polymer host was 2.8×10^{-4} (moles chromophore/grams host) for all materials. Typical solid loading of the solutions before spin casting was 11 wt %.

After each solution was prepared, we spin-coated glass slides with films of each material. The films were 1.3 μm thick. The absorption spectra of the films were then measured by UV–vis–NIR spectroscopy (Perkin-Elmer Lambda 900). The spectra are shown in Figure 1.

We also prepared some solutions using a singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO) to observe the effect of this material on the photobleaching rate. We made films of IPC-E in PC with 2 wt % DABCO. The molar ratio of DABCO to IPC-E was 0.32.

Photobleaching Test. Photobleaching measurements were made by using the fiber optic pump–probe test setup shown in Figure 2. Fiber samples were prepared by cleaving a 1 m segment of SMF-28 single-mode fiber. The cleaved end was dipped into the EO chromophore solution and was vacuum

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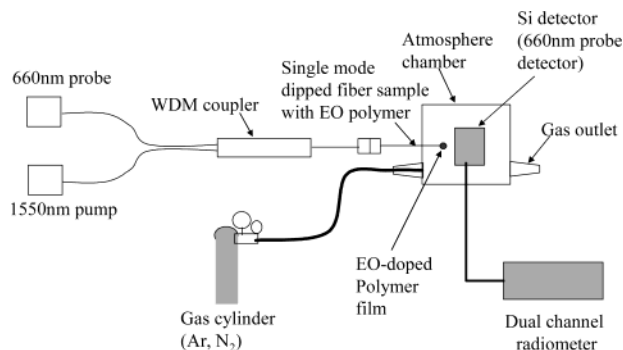


Figure 2. Fiber optic pump–probe EO polymer photobleaching test setup.

TABLE 1: EO Chromophore Structures

Chromophore	Structure
IPC-E	
IPC1-E	
IPB-E	
SIPC-B	
DPC-E	
DPCL-E	
DPC-T	

stripped at room temperature for 8 h to remove the DCE solvent. The film deposited on the end of the fiber was approximately 5–10 μm thick. Samples were covered with aluminum foil until used to prevent them from premature bleaching caused by

ambient room light. In all fiber samples the films were unpoled with the chromophores randomly aligned.

The fiber samples were fusion spliced into the photobleaching test setup shown in Figure 2. With this setup we conducted accelerated bleaching tests by exposing the film to 100 mW of 1550 nm pump beam to induce photobleaching and intermittently monitored the decrease in the magnitude of the main absorption band of the chromophore by using a low-power 660 nm probe beam. We used a tunable erbium fiber laser model ELT-4AM (IRE Polus Group) for the 1550 nm source. The 660 nm diode laser probe beam was launched into the sample fiber by means of a 980/1550 nm WDM coupler. Though the coupler is optimized to multiplex 980 and 1550 nm light into the same fiber, it does allow the transmission of a small amount of 660 nm signal. In our study we used 0.27 μW of 660 nm light measured at the location of the EO film to monitor the change in film absorption. The single-mode field diameter of the beam at 1550 nm is 10.0 μm with a dominant central peak. This is predominantly in a single but unidentified polarization state. The multimode 660 nm probe, however, offered a relatively uniform unpolarized illumination of the area incident by the pump power. In this way, any specific chromophore affected by the pump power would be monitored.

After the fiber sample was spliced into the setup, the coated end of the fiber was placed into a fiber holder and placed within 5 mm of the face of a silicon detector (model 818-UV, Newport Corp.). The Si photodetector is used to measure the intensity of the probe beam at 660 nm and can measure down to -83 dBm (0.005 nW). The fiber sample endface is placed close to the detector face so that all the power from the probe beam is captured by the detector. This way, any lensing or forward scattering that occurs at the end of the fiber as a result of film imperfections or testing will be captured and recorded by the detector. The Si photodetector was unaffected by the incident high-power pump beam at 1550 nm. The entire detector and fiber sample were enclosed in a chamber (19 cm long \times 16 cm wide \times 10 cm tall) which could be flushed with inert gas for some experiments. The chamber also acted to shield the chromophore from ambient UV light that could degrade the chromophore during the measurement.

The test was carried out by first measuring the initial probe beam power (dBm) with no sample. This is taken as the input power. We then measured the initial probe beam power of a fiber-dipped film sample at time equal to zero minutes of pump beam exposure. The difference between the initial probe beam power transmitted through the fiber with a film sample and the fiber without a film sample provides the initial absorbance of the film (IL_0) in dB. The probe beam is only turned on for 2–3 s to measure the absorbance of the film at the end of the fiber. We used this short probe beam exposure time to ensure that we did not bleach the chromophore and that any degradation recorded was due to the pump beam only. After the initial probe beam absorbance is measured, we turned on the 1550 nm laser. Every 15 min we turned the pump laser off and turned on the probe beam for 2–3 s to measure the absorbance. We did this for one to several hours to monitor the rate of photobleaching of the fiber film sample.

In order to monitor the amount of degradation caused by the probe beam alone, we performed a control experiment with a continuous exposure of a material using only the 660 nm probe beam. Figure 3 shows the degradation of IPC-E in PC in air under continuous exposure at 0.5 μW which is twice the intensity used to probe our samples during typical photobleaching tests. After 5 min of continuous exposure to 660 nm, 1.7%

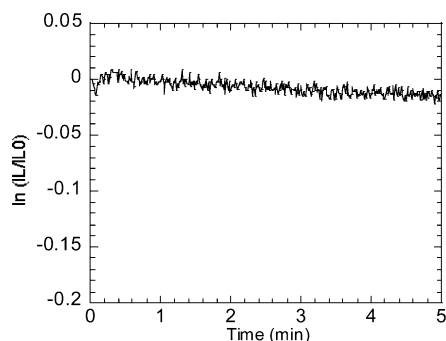


Figure 3. Effect of probe beam alone on the photobleaching rate of IPC-E in polycarbonate in air.

of the chromophore was bleached. However, during a typical photobleaching measurement, our samples were exposed to half the intensity for approximately 3 s every 10–15 min. Therefore, we exposed the chromophore to the probe beam for a total time of less than 30 s during a 2 h pump–probe test. This small amount of probe beam exposure causes negligible bleaching, and therefore the bleaching we measured is due almost entirely to the 1550 nm pump.

We also conducted photobleaching tests in an inert atmosphere using nitrogen or argon. We compared these results to those measured in air to see the effect oxygen had on the photobleaching rate. We performed the inert atmosphere tests by using a continuous flow of nitrogen or argon through the sample chamber. Before inert atmosphere tests were started we continuously flushed the chamber with nitrogen at a flow rate 10 ft³/h for 1 h.

Results and Discussion

Photodegradation Technique. We analyzed the photobleaching data assuming a simple three-level degradation kinetic process which has been reported by others.^{14,15} If the degradation rate is proportional to the initial concentration of chromophore species in state 1, then the depletion of molecular species in this state for a single-photon process is given by^{14–16}

$$\frac{dN_1}{dt} = -\frac{\sigma(\lambda)}{B(\lambda)}n(t)N_1(t) \quad (1)$$

where $\sigma(\lambda)$ is the absorption cross-section at wavelength λ , B^{-1} is the photodegradation quantum efficiency, $n(t)$ is photon flux given by the number of photons per second per unit area, and $N_1(t)$ is the concentration of chromophores in state 1. Rearranging and integrating eq 1 from time 0 to t we get

$$\ln\left(\frac{N_t}{N_0}\right) = -\frac{\sigma}{B}nt \quad (2)$$

Equation 2 yields the 1/e lifetime (τ) of the chromophore as

$$\tau = \frac{B}{\sigma n} \quad (3)$$

Since the parameter B/σ is directly proportional to the 1/e lifetime of the chromophore, it can be used as a figure of merit for photostability where larger values of B/σ represent a more stable molecule.^{10,17}

In our fiber optic pump–probe technique, we monitored the insertion loss (IL) of the fiber tip sample as a function of time. Since the chromophore concentration N is proportional to absorbance (A) by Beers law, and $\text{IL}(\text{dB}) = 10A$, a plot of $\ln(\text{IL}/\text{IL}_0)$ versus time will yield a linear function with a slope, from

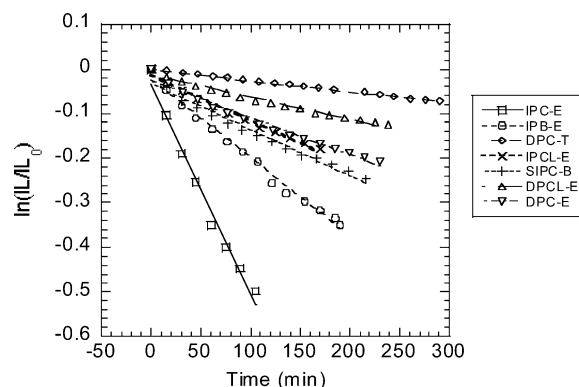


Figure 4. Photobleaching rates of thin films of EO chromophores in Udel host deposited on the end of SMF-28 fiber. Samples are exposed to 100 mW of 1550 nm radiation in air.

TABLE 2: Figure of Merit for EO Chromophores in Udel Host at 100 mW at 1550 nm in Air

chromophore	$B/\sigma \times 10^{32} (\text{m}^{-2})$
IPC-E	1.3
IPC-E	5.9
IPB-E	3.4
SIPC-B	5.8
DPC-E	7.1
DPC-E	12.2
DPC-T	23.9

TABLE 3: Figure of Merit of EO Chromophores in Polycarbonate Host at 100 mW at 1550 nm in Air

chromophore	$B/\sigma \times 10^{32} (\text{m}^{-2})$
IPC-E	0.8
DPC-T	6.6

eq 2, that gives the figure of merit B/σ at photon flux n . Figure 4 shows a plot of all EO chromophores in a Udel host at 100 mW of 1550 nm radiation in air.

The figure of merit results for all the chromophores in a Udel host at a constant pump power of 100 mW, which is an intensity of 127 kW/cm², at 1550 nm are given in Table 2. Figure of merit values for IPC-E and DPC-T in a polycarbonate host are given in Table 3.

In all of our tests we found that the photobleaching rate was linear with intensity. In the case of IPC-E in polycarbonate in air the bleaching rate was linear with intensity even up to 100 mW at 1550 nm where the intensity at the end of the fiber was 127 kW/cm². This intensity is at least 2–3 times higher than would be expected at the input of a typical signal-modulating device. The linear behavior indicates that the photobleaching process in these chromophores was due to a single-photon process.⁸

Effect of Chromophore Structure. The results given in Table 2 provide information on how photostability is related to the chemical structure of the acceptor group, donor group, and bridge. The photostability based on the acceptor group for three of the chromophores with the isophorone bridge and diethyl amino donors are in the order of IPC-E > IPB-E > IPC-E. All three chromophores have the same donor and bridge system but different acceptor groups. The photostability could be related to acceptor structures. The acceptor group on IPC-E has a benzylic tert-carbon which is in a location that can most easily form a free radical by losing a proton. IPB-E has a benzylic secondary carbon in the acceptor group which is the next easiest type of carbon to form a free radical in this series. IPC-E has no alkyl group on the acceptor phenyl ring so it is the most stable chromophore in the series of these three acceptors. This

TABLE 4: Figure of Merit in Air and Inert Atmosphere at 100 mW at 1550 nm

sample	air $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$	inert atmosphere $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$
IPC-E/polycarbonate	0.83	42.3 ^a
DPC-T/Udel	23.9	3467 ^b

^a Argon atmosphere. ^b Nitrogen atmosphere.

trend in photostability also holds for the same acceptors found in DPC-E and DPCL-E chromophores with the same diethyl amino donor and thiophene bridge. Again, DPCL-E is more stable than DPC-E which is consistent with the trend found for acceptor structure as the isophorone bridge molecules.

We also examined the photostability of chromophores when they have different size donor groups or different donors. Chromophores DPC-E and DPC-T have the same acceptor and thiophene bridge system, but the DPC-T molecule is more stable. DPC-T has a bulky TBDMS (*tert*-butyldimethylsilane) group which may serve to protect the amino group from being oxidized. In the case of the chromophores with isophorone bridge structures, SIPC-B has the same acceptor as IPC-E but SIPC-B has a sulfur donor structure instead of the diethyl amino donor which is on IPC-E. By changing amino to sulfur the λ_{max} of the chromophore is blue shifted by more than 100 nm. This resulted in a much lower EO coefficient, but the photostability increased by 4.5 times. We found the EO coefficient of SIPC-B in polycarbonate at 1.06 μm to be 20.2 pm/V compared to 54 pm/V for IPC-E in the same host, as measured by the ATR method described by Garner et al.⁶

Finally, we observed an impact on the photostability due to the structure of the bridge. DPC-E, which has a thiophene bridge, is much more stable than IPC-E which has an isophorone bridge. Both have the same acceptor and donor group structures. It is clear that the aromatic ring bridge is much more stable than a double-bond bridge even though the double bond is locked within a ring such as in isophorone.

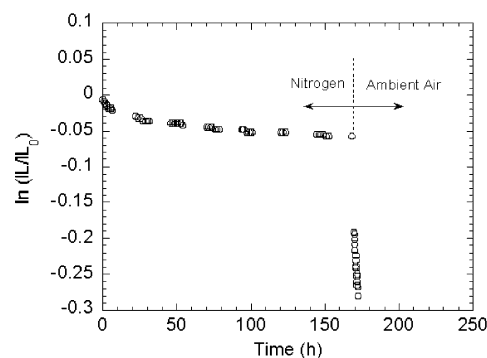
We did notice that there was a difference in photostability based on the host polymer. Tables 2 and 3 show the results of chromophores IPC-E and DPC-T in Udel and polycarbonate, respectively. In Udel, DPC-T is about four times more stable than it is in polycarbonate and IPC-E is about 1.5 times more stable. These results indicate that Udel provides a more photostable environment than polycarbonate. This may be due to the fact that carbonyl groups in polycarbonate form radicals more easily than the sulfonyl groups in Udel.

Effect of Oxygen on Chromophore Lifetime. Previous studies clearly show that the presence of oxygen can greatly increase the rate of degradation of organic chromophores.^{11,17} In our study, we examined the effect of oxygen on the photobleaching rate of two chromophores: IPC-E and DPC-T. We did this by first comparing the rate of photobleaching of the guest–host polymer in air to that in either a nitrogen or argon atmosphere.

We observed that by exposing samples in the inert atmosphere we can dramatically decrease the rate of photobleaching. Table 4 shows the figure of merit of IPC-E in a polycarbonate host in an argon atmosphere and that of DPC-T in a Udel host in a nitrogen atmosphere. Both samples were exposed to 100 mW at 1550 nm.

The results indicate that, by using an inert atmosphere, we were able to increase the lifetime of IPC-E in polycarbonate by a factor of 51, and for DPC-T in Udel we increased the lifetime by a factor of 145.

Our inert atmosphere experiments clearly indicate that the presence of oxygen increases the photobleaching rate of the EO

**Figure 5.** Photobleaching of DPC-T in Udel at 100 mW of 1550 nm radiation going from nitrogen to ambient air atmosphere.

chromophore—a phenomenon which has also been observed by others. The rate at which this occurs appears to be quite rapid. In one experiment we exposed a sample of DPC-T in Udel under a continuous purge of nitrogen for 167 h. We then allowed ambient air to fill the chamber and monitored the insertion loss of the sample. The results shown in Figure 5 indicate that the photobleaching process occurs rapidly with the introduction of oxygen into the chamber. This may have occurred because the polymer film was so thin and directly exposed to the ambient atmosphere. In an actual device the rate of bleaching may be slower if the core is doped with chromophore and sandwiched between cladding layers which would serve to retard diffusion of any oxygen that might leak into the package.

Previous studies have proposed several possible mechanisms of how oxygen plays a role in the photodegradation process of organic chromophores. First, it has been suggested that singlet oxygen can be produced from ground state oxygen by direct absorption of light near 1300 nm.^{18,19} This reactive species of oxygen then goes on to react with EO chromophores¹⁷ to degrade their structure. Second, the chromophore, or some sensitizer, can directly absorb photons to create an excited state. This excited molecule can then either (1) create free radicals that go on to degrade other chromophores or (2) react with oxygen which helps accelerate the degradation process.^{20,21} This mechanism is well-known for ultraviolet light-induced photo-oxidation processes and for wavelengths near the main absorption band of chromophores. In our materials the main absorption band is hundreds of nanometers away from the 1550 nm pump beam, and therefore it would be expected that the lifetime would be increased by several orders of magnitude. Such an observation was reported by Galvan-Gonzalez et al. who found that the photostability lifetime figure of merit (B/σ) of several EO polymers increased exponentially as the pump wavelength was increased beyond the λ_{max} of the chromophore.¹⁰ We are uncertain as to the possibility of or efficiency at which singlet oxygen could be generated by wavelengths in the near infrared communication C-band. Nevertheless, it is quite apparent that any device using such chromophores will have to be packaged to ensure that it is isolated from oxygen to allow longer device lifetimes.

Knowing that oxygen plays a key role in the degradation process, we ran another experiment to test the presence of singlet oxygen. Regardless of the specific mechanism of photo-oxidation, if we assume that singlet oxygen is generated by some means, then we should be able to slow the degradation process down by using a singlet oxygen quenching additive. Researchers have long known that quenchers such as DABCO and other antioxidants are effective in slowing the photo-oxidation process when exposing polymer materials to UV or visible wavelengths.^{22–24} However, to our knowledge, no one has reported

TABLE 5: Effect of Argon Atmosphere and DABCO on the Figure of Merit at 100 mW of 1550 nm Radiation

sample	air $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$	air/DABCO $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$	argon $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$	argon + 2% DABCO $B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$
IPC-E/Udel	1.3	2.5	67	700
IPC-E/polycarbonate	0.83	3.4	42.3	335

TABLE 6: Figure of Merit of the IPC-E Chromophore in Polycarbonate as a Function of C-Band Wavelength at 100 mW in Air

wavelength (nm)	$E \text{ (eV)}$	$B/\sigma \times 10^{32} \text{ (m}^{-2}\text{)}$
1533	0.80	0.85
1550	0.79	0.83
1573	0.78	0.85

using singlet oxygen quenching additives to increase the lifetime of EO chromophores exposed to typical communication wavelengths of 1525–1575 nm. However, other researchers have suggested incorporating singlet oxygen quenching species into the chromophore structure itself to improve its photostability.^{17,25}

Table 5 shows the results of the effect of DABCO on the photostability of IPC-E in a Udel and polycarbonate host exposed to 1550 nm. With the Udel host in an air environment, the presence of DABCO increased the lifetime of the chromophore by almost a factor of 2, while in the polycarbonate host the lifetime was increased by almost 4.5 times. Though DABCO did not provide the magnitude of photostability protection of that of an inert atmosphere alone, our results indicate that the combination of inert atmosphere with DABCO can also be used to retard the photobleaching process even further. Table 5 shows that by using both DABCO and an inert atmosphere we can increase the lifetime of IPC-E in polycarbonate by a factor of nearly 8 times that of the case where an inert atmosphere is used alone. This result indicates that even though the sample was flushed with nitrogen for 1 h prior to exposure, this was not sufficient to remove all the residual amount of singlet oxygen species that later caused photobleaching. It may be necessary to either further flush with inert gas or increase the level of singlet oxygen quencher. In our study we did not examine the effect of singlet oxygen quencher concentration on photostability.

Effect of Wavelength on Photostability. The photostabilities of numerous EO chromophores have been reported by Galvan-Gonzalez et al.^{15–17,25} Their studies show that the shortest lifetime of the chromophore occurred at the peak absorption of the charge transfer state at λ_{max} . They observed that as the bleaching wavelength increased, the figure of merit increased by several orders of magnitude. Near 1300 nm the figure of merit decreased sharply. They suggested that the reason for the decrease in stability was the presence of singlet oxygen. Unfortunately they did not report any results with wavelengths longer than 1310 nm.

In our study we did use three wavelengths across the C-band. These results are shown in Table 6 for IPC-E in polycarbonate in air. We found that the photostability was fairly constant across the C-band. This is not surprising considering that the wavelengths are so close in energy and all are far from λ_{max} .

Conclusion

We have measured the rate of photobleaching of seven EO chromophores doped into either a polyethersulfone or polycarbonate host from 1533 to 1573 nm using a novel fiber optic pump–probe test setup. We observed that the chemical structure, the presence of oxygen, and the structure of the host have a significant impact on the photostability of the material. Based on our results we found the most stable chromophores were

ones that contained a bulky donor head, an aromatic bridge, and nonsecondary, tertiary, or benzylic carbon acceptors. The presence of oxygen significantly increased the rate of photobleaching, and we were able to slow this process down by placing the film in an inert atmosphere. The best results were obtained when we combined an inert atmosphere with the singlet oxygen quenching additive DABCO. Sample photostability could possibly be further stabilized by optimizing the additive concentration and structure.

In our study, we have shown that we can measure the rates of photobleaching of these new chromophore structures and have shown what can be done to slow this process down. Currently we are working on a model to show how chromophore lifetime is related to optical device lifetime. In this study we used the 1/e lifetime as measured by bleaching as the figure of merit. However, in reality a device can fall out of the desired performance specifications well before 63% of the chromophore is degraded. Other device parameters, such as half-wave voltage (V_{π}) and waveguiding performance due to refractive index change upon bleaching, ultimately are more direct and sensitive measures of device lifetime and have been used in the past to measure chromophore stability.^{2,3} Nevertheless, the technique we used here does give us valuable insight into the factors that control EO chromophore stability and can ultimately be used in a model to predict device lifetime.

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