A Family of Multiaddressable, Multicolored Photoresponsive Copolymers Prepared by Ring-Opening Metathesis Polymerization

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Received June 9, 2005. Revised Manuscript Received August 18, 2005

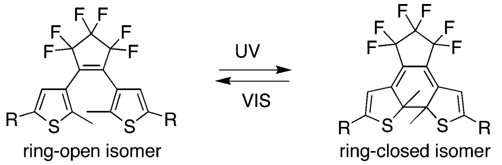
A series of homo- and copolymers containing different photochromic dithienylethene (DTE) architectures was prepared by ring-opening metathesis polymerization (ROMP) techniques. Each DTE structure can be uniquely addressed in the two- and three-component copolymers, providing a means to generate a wide range of colors when the compounds are selectively photocyclized to their ring-closed forms. Multicomponent, multiaddressable materials of this type are beneficial for applications such as multistate photochromic recording, displays, inks, and barcodes.

Introduction

Molecules that undergo reversible transformations between two distinct isomers in response to external stimuli have the potential to significantly influence the development of many important materials science technologies.[1] This is because the isomerization reactions are accompanied by striking changes in the molecules' geometric and electronic characteristics. The implications are that such compounds can act as switching elements in numerous optoelectronic devices and as dynamic functional materials by providing the user with a convenient way to regulate the function of a device by stimulating it with light, electricity, or chemical reagents.[1]

Photons are especially practical stimuli because modern lasers can be easily tuned and focused to trigger a switching event in localized areas or volumes, while affecting the surrounding environment to a minimal extent. Molecules that undergo reversible photoreactions between two isomers that have different UV−vis absorption characteristics are termed photochromic and the process is referred to as photochromism.[2] Photochromic dithienylethene (DTE) derivatives undergo reversible photocyclization reactions between colorless ring-open and colored ring-closed isomers when irradiated with the appropriate wavelengths of light (Scheme 1).[3] They are some of the most promising candidates for use in practical materials science applications due to their fast response times, to the thermal stability of both isomers, and to the fatigue resistance that is often associated with their photoreactions. The less often discussed but perhaps most useful characteristic of DTE derivatives is the ease with which their structures can be synthetically modified and the tolerance of the photoreactions to the structural diversity of functionalized versions of the hexatriene skeleton. The optical and electronic properties of each isomer can be fine-tuned by strategically decorating the DTE backbone with appropriate substituents (most commonly at the positions labeled R in Scheme 1). The most immediately striking property that can be photoregulated by use of the DTE hexatriene is the color of the ring-closed form, which is easily adjusted by varying the length of the linearly π-conjugated pathway extending along the molecular backbone. The differences in the molecular structure that account for the changes in color are also responsible for variations in other useful properties such as refractive index,[4] luminescence,[5] viscosity,[6] electronic conductance,[7] optical rotation,[8] and redox chemistry.[9] The photoregulation of these properties has been applied to several optoelectronic technologies such as optical data storage,[5a,7b,10] waveguides,[11] and actuators.[12]

Scheme 1. Reversible Photocyclization Reactions of DTEs



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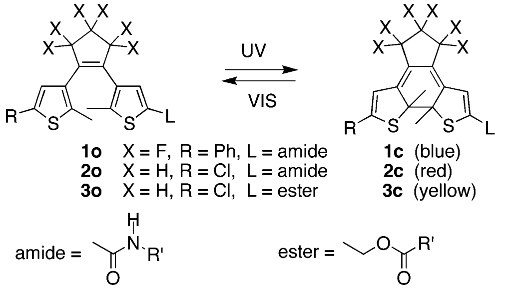
10.1021/cm051231d CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/06/2005

The development of polymeric versions of these versatile compounds is a key step if DTEs are to be used in optoelectronic applications. The major considerations when designing photoresponsive polymers for general use in materials science applications are as follows: (1) the polymer must contain a high content of the DTE component, (2) it should be soluble in a variety of solvents, (3) it must be based on a molecular architecture that does not limit the ability to fine-tune the optoelectronic properties by sacrificing the functional sites labeled R in Scheme 1, and (4) it must maintain its photochromic activity under a wide range of conditions.[13] If these requirements are met, the photoresponsive material can be fine-tuned for a series of specific applications and easily processed into useful forms such as photoactive optically homogeneous thin films.

Several approaches have been explored to construct DTE polymers including radical polymerization,[4c,14] oxidation polymerization,[15] silesquinoxane and siloxane chemistry,[16] and Wittig polycondensation reactions.[14a,17] These systems suffer, however, from serious limitations such as low content of the DTE component,[4c,14] low photochromic conversions in the solid state,[14b] and loss of the ring positions labeled R during the polymerization process.[14a,17] Another limitation is that these approaches tend to require synthetic conditions that are not always compatible with the wide range of functional groups needed to fully exploit the ability to tune the properties of the DTE backbone.[14−17] The polymerization processes can also render the resulting materials highly insoluble in common solvents, demanding that films are directly prepared in conjunction with the polymerization reaction.[15,16] We have taken advantage of the mild ring-opening metathesis polymerization (ROMP) process, which can be used to polymerize highly functionalized substrates under a variety of conditions,[18] to synthesize high-content (63−93 wt %) pendant and main-chain DTE-based homopolymers.[19] Our examples include both hydrophobic and water-soluble versions that display photochromic properties that can be easily adjusted in solution and in thin films.

Scheme 2. Reversible Photoreactions of DTE Derivatives 1−3 Providing the Three Primary Colors



We recently focused our efforts on developing DTE copolymers for use in multifrequency photochromic memory media, multicolor displays, inks, barcodes, and other applications that would benefit from the control offered by a single material that can be interconverted between several unique states. (A three-component copolymer, for example, could be switched between 2^3 or 8 possible states.) This approach is more practical than doping several of the photoactive components in polymer matrixes[20,21] or relying on the challenge of obtaining multicomponent single crystals.[22] Another appeal to this approach is that the desired property (color in this study) of the final material can be fine-tuned by strategically blending the amount of each DTE component to produce “made-to-order” copolymers. Combinatorial color mixing has been applied to electrochromic devices, where a wide range of colors can be generated by use of an electroactive polythiophene material.[23] To the best of our knowledge, this has not been paralleled with photochromic DTE polymers, and it has been used only to a limited extent with single molecules cast from solution.[24]

In this article we describe the synthesis and photochromic properties of a series of copolymers where the color of each material is programmed by the appropriate blending of three DTE derivatives. The most appropriate monomeric precursors are based on the DTE architectures **1−3** (Scheme 2). These particular structures are fitting for use in multicolormaterials

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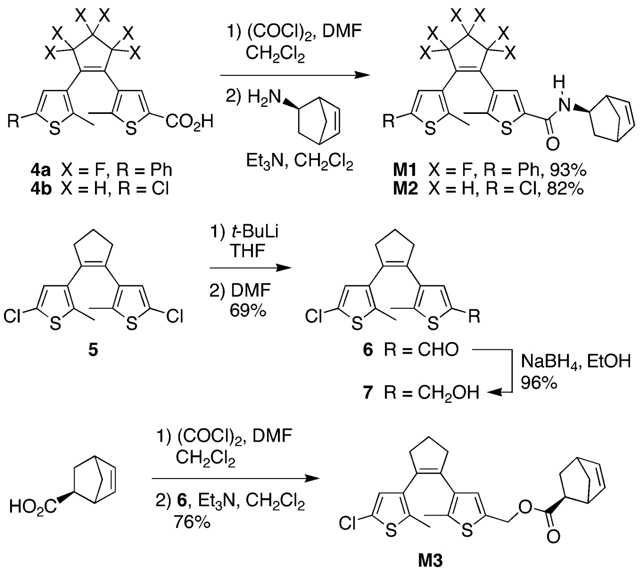
Scheme 3. Synthesis of Monomers M1−M3



technology because their ring-closed isomers provide the primary colors (blue, red, and yellow) necessary to prepare the blended polymers, as will be described further in this report.

Synthesis of Monomers. The synthetic routes used to prepare the three photoresponsive DTE monomers (**M1**−**M3**) are shown in Scheme 3. All three monomers possess the strained bicyclic 5-*exo*-norbornene, an alkene that is frequently used with great success in ROMP technology, and the appropriate DTE architectures (**1o** for monomer **M1**, **2o** for monomer **M2**, and **3o** for monomer **M3**). By attaching the norbornene to the DTE backbone through an ester or amide linkage, the two components (i.e., photoactive and ROMP-reactive) are separated and insulated from each other to maximize the chances of all three monomers reacting identically. This is essential to minimize incomplete polymerization of certain monomers and prevent the production of tapered block copolymers.[25] The amide versions (**M1** and **M2**) are prepared by coupling the appropriate acid chloride (**4a** and **4b**)[19b] with *exo*-2-aminobicyclo[2.2.1]hept-5-ene.[26] Ester **M3** is prepared in three steps from 1,2-bis[3-(5-chloro-2-methylthienyl)]cyclopentene (**5**)[27] by first converting **5** into aldehyde **6**, reducing the aldehyde to the primary alcohol **7**, and finally coupling the alcohol to the acid chloride of *exo*-bicyclo[2.1.1]hept-5-ene-2-carboxylic acid.[28] All syntheses can be carried out on a large scale and in good yield, and all new compounds show appropriate characterizations (NMR, UV−vis spectroscopy, mass spectrometry, and elemental analysis) consistent with the structures illustrated in the schemes and figures.

Synthesis and Photochromic Reactions of Homopolymers. The homopolymers (**P1**−**P3**) are prepared by treating tetrahydrofuran (THF) solutions of the appropriate DTE monomer (**M1**−**M3**) with 2 mol % of Grubb's reagent bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride to initiate and propagate the living metathesis polymerization (Scheme 4). Typically, the living polymerization reaction is completed after 16 h, at which time it is quenched with ethyl vinyl ether. The homopolymers are isolated in high purity by precipitating them directly from the THF solutions and collecting them by vacuum filtration.

Analysis of the polymers by gel-permeation chromatography (GPC) (CH_2Cl_2 solutions calibrated with polystyrene) reveals that they all have monomodal molecular weight distributions and polydispersity indices (M_w/M_n) close to unity, which reflect the similar reactivity of each monomer (Table 1). Glass transition temperatures (T_g), measured by differential scanning calorimetry (DSC), are all below 10 °C, and are minimally affected by subtle changes in the pendant DTE units within the polymers. Low values of T_g such as these are beneficial for photochromic polymers because they imply there is adequate flexibility of the side chains within the matrix for the conformation freedom that is needed during the cyclization reactions.[29] Thermal gravimetric analysis (TGA) of the polymers shows that they are stable until ∼250 °C and do not decompose until the polymers are heated above 300 °C.

The photochromic reactions of all monomers and their corresponding polymers are best evaluated by alternately irradiating solutions of the compounds with UV and visible light while monitoring the changes in their UV−vis absorption spectra. Representative examples are shown in Figure 1 for solutions of monomer **M1** and its corresponding polymer **P1**.[30] In both cases, irradiation with 295-nm light induces immediate decreases in the high-energy absorptions and corresponding appearances of absorptions in the near-UV and visible regions of the spectra as the ring-open DTE isomers are converted to their blue ring-closed forms. These trends are typical for all compounds used in this study, and the spectral characterizations are summarized in Table 2, which also shows that the colors of the irradiated solutions of monomer **M2** and polymer **P2** are red while **M3** and **P3** are yellow. As previously mentioned, the particular DTE structures (**1**−**3**) were designed with the prediction that their ring-closed forms would offer these primary colors, which can be used to complete a full "color wheel".[31] As anticipated for these side-chain polymers, the monomers and their corresponding polymers exhibit similar spectral characteristics, indicating that the photochromic properties are not adversely affected by polymerization.[32] The corresponding ring-closed forms of all compounds can be converted back

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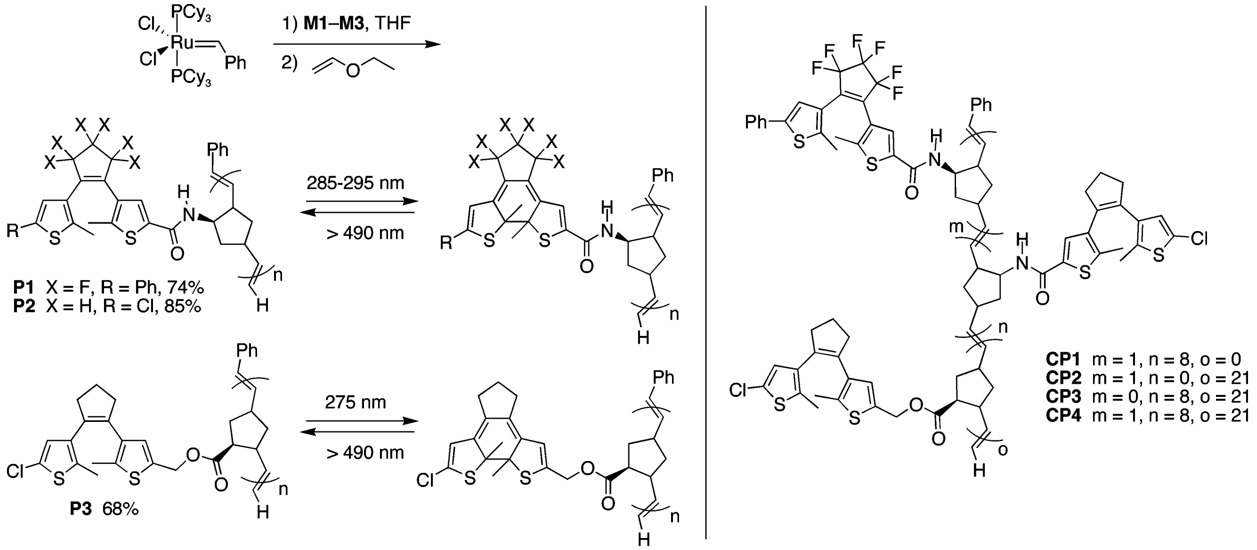
(30) See Supporting Information for more details.

(31) A color wheel is a radial diagram that displays the spectrum of visible colors. The primary colors red, yellow, and blue overlap, creating different colors, and in the middle they form gray or black. It provides a graphic representation of the relationship between primary and secondary colors and is a visualization of the theory of how different colors relate to each other when mixed.

(32) For a discussion on this concept, see ref 19b.

(33) The CIE (Commission International de L'Eclairage) color model is a method for systematically measuring color in relation to the wavelengths they contain based on the tristimulus theory of color perception.

Scheme 4. Synthesis and Photoreactions of Homopolymers P1−P3 and the Structures of Copolymers CP1−CP4[a]



[a] The stereochemistry, regiochemistry, and distribution within each polymer are arbitrary.

Table 1. Yields and Characterizations of All Polymers Described in This Report

polymer	ratio[a] M1:M2:M3	yield (%)	M_w	M_n	PDI[b] (M_w/M_n)	T_g[c] (°C)
P1	1:0:0	74	27 200	25 200	1.07	7
P2	0:1:0	85	30 000	29 400	1.02	3
P3	0:0:1	68	26 300	23 800	1.11	7
CP1	1:8:0	94	44 300	43 000	1.03	4
CP2	1:0:21	88	53 700	48 100	1.12	6
CP3	0:8:21	54	46 100	44 400	1.04	6
CP4	1:8:21	92	40 600	36 900	1.10	7

[a] Represents the molar ratio of the monomers prior to polymerization. [b] CH_2Cl_2 as eluent, 0.3 mL/min, calibrated with polystyrene. [c] Reported for the second heating cycle, heating rate 10 °C/min.

to their ring-open counterparts by exposing the solutions to visible light (>490 nm), which regenerates the original absorption spectra. These ring-closing/ring-opening cycles can be carried out several times with minimal observable degradation.

The range of absorbance frequencies listed in Table 1 illustrates how the colors of the ring-closed forms can be fine-tuned by synthetically tailoring the photoresponsive backbone and attests to the versatility of the DTE structure when materials possessing made-to-order properties are desired. To obtain a wide range of colors for applications such as display technologies, inks, and bar codes, monomers **M1−M3** can be copolymerized in different ratios to produce a series of designer copolymers. These ratios can be easily determined by visually screening a series of two- and three-component blends prepared by varying the amount of the ring-closed form of polymers **P1−P3**. The widest range of colors is obtained by using optimized 1:8:21 mixtures containing a combination of the polymers **P1**:**P2**:**P3**. This is shown in Figure 2a, where the vials, from left to right, contain [**P1** + **P2** + **P3**], [**P1**], [**P1** + **P3**], [**P1** + **P2**], [**P2**], [**P2** + **P3**], and [**P3**].

Synthesis and Photochromic Reactions of Copolymers. By use of the optimized 1:8:21 ratio of homopolymers **P1**:**P2**:**P3**, copolymers **CP1−CP4** can be prepared by treating the monomer blends listed in Table 1 with the identical

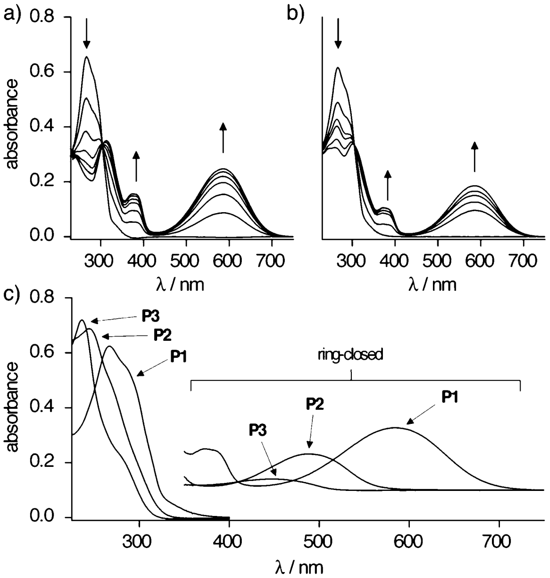


Figure 1. Changes in the UV−vis absorption spectra of THF solutions of (a) monomer **M1** and (b) homopolymer **P1**. The concentration of the photochromic units is 2×10^{-5} M in both cases. The irradiation was carried out for 30-s intervals until a period of 2.5 min was reached. (c) UV−vis spectra of the ring-open forms of polymers **P1−P3** and the corresponding photostationary states (inset) generated by irradiating the solutions with 295-nm (**P1**), 285-nm (**P2**), and 275-nm light (**P3**). The concentrations of the photochromic units are 2×10^{-5} M for **P1** and 3×10^{-5} M for **P2** and **P3**.

ROMP conditions as previously described. After quenching with ethyl vinyl ether, copolymers **CP1−CP4** can be isolated as white powders after precipitating them from the crude THF reaction mixture by adding cold CH_3CN or Et_2O. All polymers are produced and isolated in good yields with the exception of **CP3**, which is more difficult to isolate due to the repeated precipitations (THF/CH_3CN) necessary to convert the initially isolated viscous oil to a white powder. We attribute the lower yield of **CP3** to small losses in each purification step because the TLC of the crude reaction mixture shows that both monomers were consumed in the polymerization reaction. We assume that the different photochromic DTE units are randomly distributed throughout the copolymers. Table 1 also lists the characteristics of the

Table 2. Optical Characterization of Monomers M1−M3 and Polymers P1−P3

compound	λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) ring-open	ring-closed[a]	color (ring-closed)
M1	267 (33 100)	585 (14 300)	blue
P1	267 (29 300)	585 (9800)	blue
M2	245 (24 900)	486 (8500)	red
P2	246 (24 700)	489 (6800)	red
M3[b]	235 (26 700)	448 (10 600)	yellow
P3	236 (24 700)	445 (5500)	yellow

[a] Measured on the photostationary states prepared by irradiating with 275-nm (**M3** and **P3**), 285-nm (**M2** and **P2**), or 295-nm light (**M1** and **P1**) until no spectral changes occurred. The photostationary states are 90% for **M1**, 50% for **M2**, and 25% for **M3**. [b] Isolated as an oil.

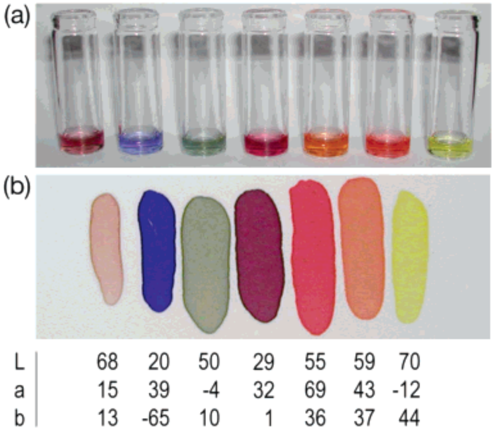


Figure 2. (a) Color mixing of DTE homopolymers **P1**−**P3** after THF solutions are irradiated with 313-nm light. The solutions contain (from left to right) [**P1** + **P2** + **P3**], [**P1**], [**P1** + **P3**], [**P1** + **P2**], [**P2**], [**P2** + **P3**], and [**P3**]. (b) Samples of homo- and copolymers (from left to right) **CP4**, **P1**, **CP2**, **CP1**, **P2**, **CP3**, and **P3** painted onto a silica plate followed by irradiation with 313-nm light. *L*, *a*, and *b* values refer to those of the CIE color model,[33] which were estimated directly from the electronic images.

polymers (PDI, T_g), which are consistent with the homopolymers.

The amount of each photochromic DTE in the random copolymers can be assessed by UV−vis absorption spectroscopy by comparing the properties of equivalent mixtures of homopolymers to those of each copolymer before and after irradiation with UV light. In all cases, the absorption spectrum for each pure copolymer is identical in both its ring-open and ring-closed forms to the sum of the individual homopolymers when blended in the appropriate ratio.[30] These comparisons reveal three important features: (1) the molar equivalents of each DTE structure are identical in the mixture of monomers prior to polymerization and in the final copolymer, implying that all monomers are included in the polymer backbone; (2) the ground-state properties of each DTE are not affected when the compounds are incorporated into either homo- or copolymers; and (3) the photostationary states are the same for each copolymer and its corresponding blend of homopolymers. Figure 2b shows irradiated samples of each homo- and copolymer painted onto a silica plate. The similarity of the colors for the copolymers to the equivalent blend of homopolymers in solution supports the conclusions from the UV−vis spectroscopy studies and attests to the success in tuning the color of DTE copolymers by use of ROMP technology.[30]

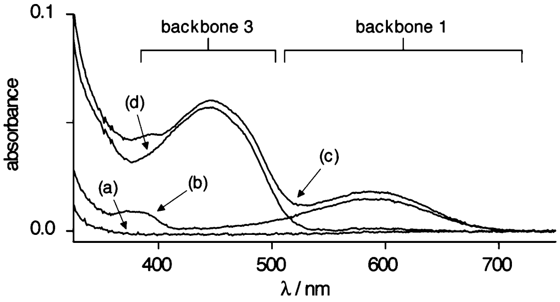


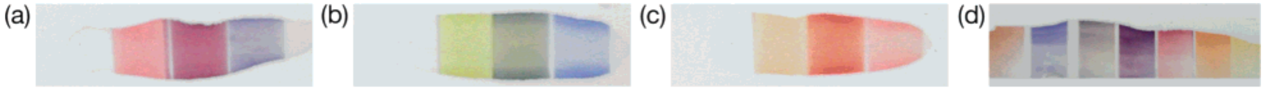
Figure 3. UV−vis spectra of a THF solution (3×10^{-5} M) of **CP2** (a) in its all-ring-open state, (b) after irradiation with 340-nm light for 120 s, (c) after irradiation with 275-nm light for 150 s, and (d) after irradiation with >557-nm light for 30 s.

Selectively Addressing Each DTE Structure in Copolymers CP1−CP4. Because each photochromic DTE structure has unique absorption characteristics in both its ring-open and ring-closed states, the copolymers made up of them are multiaddressable. Copolymers **CP1**, **CP2**, and **CP3** contain two DTEs and can display four unique states. Copolymer **CP4** contains three DTEs and can exhibit up to eight possible states in a single polymer. Materials of this type have potential applications in multifrequency optical data storage, if one assumes that each molecular state (color in our case) represents one bit of data,[20,21] and in ink and display technologies.

Although the colorless ring-open forms of homopolymers **P1**−**P3** have overlap in the UV region of their absorption spectra (see Figure 1c), the low-energy shoulder for polymer **P1** allows it to be selectively photoisomerized by greater than 340-nm light. The absorptions for the colored ring-closed forms are better resolved in the visible region of the spectrum, providing the means to selectively bleach each DTE component in a copolymer by use of the appropriate cutoff filter. This is illustrated in Figure 3 for copolymer **CP2**, where an irradiation algorithm can be used to generate four unique optical outputs (colorless, blue, green, and yellow).[30] The DTE component **1c** (see Scheme 2 for the molecular structure) can be selectively generated by irradiating a colorless THF solution of the copolymer with 340-nm light to generate a blue color. Irradiation of the original colorless solution with 275-nm light converts both DTE components to their colored ring-closed forms (blue for **1c** and yellow for **3c**), producing the green state. The yellow state cannot be obtained directly from the colorless solution owing to the spectral overlap of both DTE components in the UV region of the spectrum. However, the longer wavelength blue component (**1c**) in the green solution (generated with 275-nm light) can be selectively photobleached with light greater than 557 nm to produce the yellow state.

This irradiation sequence can be used to produce a multicolor barcode from the single copolymer as shown in Figure 4b. The sample was prepared by painting a THF solution of copolymer **CP2** onto a silica plate, selectively masking a portion of it, and irradiating the exposed areas of the plate with the appropriate wavelengths of light. Each of the unique states in **CP2** can be easily seen by its obvious color. The barcodes remain in their colored state when left in the dark for over 30 days and can be erased by irradiating the entire plate with greater than 434-nm light.

In a similar manner, the other copolymers can be selectively addressed, and the resulting barcodes are illustrated



	(a)				(b)				(c)				(d)						
L		64	47	60		72	60	62		71	62	67	54	51	51	34	50	55	63
a		28	31	3		-9	-4	4		7	37	24	11	4	2	17	26	21	-1
b		14	0	-7		25	10	-11		18	35	15	16	-12	0	-7	7	30	15
1	o	o	c	c	o	o	c	c					c	c	c	c	o	o	o
2	o	c	c	o					o	o	c	c	c	o	o	c	c	c	o
3					o	c	c	o	o	c	c	o	c	o	c	o	o	c	c

Figure 4. Barcodes generated by painting samples of copolymers **CP1**−**CP4** onto silica plates, masking them, and irradiating them with the appropriate wavelengths of light. In each case, the irradiation sequence corresponds to the colors from left to right. (a) **CP1**: 313 nm (45 s) then >557 nm (60 s); 313 nm (45 s); 365 nm (30 s). (b) **CP2**: 313 nm (60 s) then >557 nm (60 s); 313 nm (60 s); 365 nm (45 s). (c) **CP3**: 313 nm (45 s) then >490 nm (60 s); 313 nm (45 s); 365 nm (45 s). (d) **CP4**: 275 nm (90 s); 370 nm (60 s); 265 nm (90 s) then >490 nm (60 s) then 265 nm (45 s) then > 490 nm (30 s) then 370 nm (60 s); 340 nm (45 s); 340 nm (45 s) then >557 nm (60 s); 275 nm (90 s) then >557 nm (30 s); 265 nm (90 s) then >490 nm (60 s) then 265 nm (60 s) then >490 nm (45 s). *L*, *a*, and *b* values refer to those of the CIE color model, which were estimated directly from the electronic images. The o and c labels describe the state of each photoactive structure (**1**−**3**), where o refers to the ring-open form of the DTE backbone and c refers to the ring-closed form.

in Figure 4.[30] In the case of **CP1**, 365-nm light produces a blue color by triggering the ring-closing reaction of only the **1o** component. Higher energy light stimulates both red (**2o**) and blue (**1o**) components and a purple color is produced. The red color can be obtained by selectively bleaching the blue color with greater than 557-nm light. In the case of **CP3**, 365-nm light produces a red solution by triggering the ring-closing reaction of only the **2o** component. Higher energy light stimulates both red (**2o**) and yellow (**3o**) components and an orange color is produced. The yellow color can be obtained by selectively bleaching the red color with greater than 490-nm light. The most challenging barcode to address is the one prepared from copolymer **CP4**, as would be expected considering all three DTE structures are present. Figure 4d shows the results using an irradiation algorithm of several wavelengths of light to produce a range of colors.

Conclusions

In this article we have shown that a series of multiaddressable homo- and copolymers, which exhibit a full spectrum of colors in their ring-closed states, can be conveniently prepared by ROMP techniques. This polymerization process is ideal for this purpose because of its tolerance to a wide range of functional groups. It produces polymers that have narrow PDIs, good thermal stability, and low T_g values.

We have also demonstrated that the ring-closed forms of these copolymers have the same optical properties as mixtures of the appropriate homopolymers. These materials offer a new approach to DTE color tuning for display technology and have potential applications in high-density optical data storage. This approach to blending the electronic properties in DTEs is advantageous because it provides the user with a single off-the-shelf material that can be easily processed into optically homogeneous materials. To fully exploit these materials in data-storage applications, it is desirable to have a multistate material where each state can be directly addressed. This can be achieved by further modifying the DTE framework to separate the absorption profiles of the ring-open form of each component and will be the subject of future studies.

Experimental Section

Materials. All solvents used for synthesis and spectroscopy were dried and degassed by passing them through steel columns containing activated alumina under nitrogen using an MBraun solvent purification system with the exception of the solvents for NMR analysis (Cambridge Isotope Laboratories), which were used as received. Column chromatography was performed using silica gel 60 (230−400 mesh) from Silicycle Inc. All other reagents and starting materials were purchased from Aldrich with the exception of bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubb’s reagent), which was purchased from Strem, and compounds **4a**,[19b] **4b**,[19b] **5**,[27] *exo*-2-amino-bicyclo-[2.2.1]hept-5-ene,[26] and bicyclo[2.2.1]hept-5-ene-2-exo-carboxylic acid,[28] which were prepared according to literature procedures.

Techniques. ^{1}H and ^{13}C NMR characterizations were performed on a Bruker AMX 400 instrument working at 400.103 MHz for ^{1}H NMR and 100.610 MHz for ^{13}C NMR or a Varian Inova 500 instrument working at 499.77 MHz for ^{1}H NMR and 125.68 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in Hertz. FT-IR measurements were performed using a Nicolet Nexus 670 instrument. UV−vis measurements were performed using a Varian Cary 300 Bio spectrophotometer. Mass spectrometry measurements were performed using a Varian 4000 GC/MS/MS with electron impact operating at 10 mamp as the ionization source. GPC analyses were performed using a Waters 1515 HPLC pump equipped with two polystyrene-packed Styragel columns (HR4 and HR2, 4.6 × 300 mm) connected in series and in-line with a Waters 2487 Absorbance detector, and a Waters 2410 RI detector equipped with a Precision Detectors PD 2010 light-scattering detector. CH_2Cl_2 was used as the eluent at a flow rate of 0.3 mL/min, and the instrument was calibrated with polystyrene standards from Polymer Laboratories. Differential Scanning Calorimetry (DSC) was performed using a Perkin-Elmer DSC7 instrument equipped with a TAC7/DX thermal analysis controller. Thermogravimetric analysis was performed using a Shimadzu TGA-50 thermogravimetric analyzer.

The ring-closing reactions of all compounds were carried out using the light source (75 W xenon lamp) from a PTI QM-2000−4 scanning spectrofluorimeter with a 5 nm slit-width. The ring-opening reactions were carried out using the light of a 150-W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light. Vials and barcodes were irradiated at 313 or 365 nm using standard lamps used for visualizing TLC plates (Spectroline E-series, 470 mW/cm^2) or by using a spectrofluorimeter for monochromatic light.

Synthesis of Phenyl-Substituted Monomer M1. A solution of DTE carboxylic acid **4a** (0.50 g, 1.00 mmol) and anhydrous *N*,*N*-dimethylformamide (DMF) (40 μL, 0.51 mmol) in anhydrous CH_2Cl_2 (40 mL) was treated dropwise over 5 min with a solution of oxalyl chloride (0.46 mL, 5.11 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 °C under an N_2 atmosphere. The cooling bath was removed and the reaction mixture was slowly warmed to room temperature and stirred there for 1.75 h, when it was evaporated to dryness in vacuo and dried under high vacuum (1 mmHg) for 18 h. The resulting acid chloride was dissolved in anhydrous CH_2Cl_2 (40 mL), treated with Et_3N (2 mL) and *exo*-2-aminobicyclo-[2.2.1]hept-5-ene (0.22 g, 2.00 mmol), and stirred for 4 h at room temperature under an N_2 atmosphere. The reaction mixture was diluted to 60 mL with CH_2Cl_2, washed with 5% aqueous HCl (20 mL), dried (Na_2SO_4), filtered, and evaporated to dryness in vacuo. Purification by column chromatography (0.1% Et_3N in CH_2Cl_2) yielded monomer **M1** (0.55 g, 93%) as white crystals after recrystallization (20% CH_2Cl_2/hexanes); mp = 246−248 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, 2H, J = 7.5 Hz), 7.39 (m, 3H), 7.31 (m, 1H), 7.24 (s, 1H), 6.19 (dd, 1H, J = 5.5 and 2.5 Hz), 6.12 (dd, 1H, J = 5.5 and 2.5 Hz), 5.87 (d, 1H, J = 7.0 Hz), 3.90 (dt, 1H, J = 7.0 and 2.0 Hz), 2.91 (s, 2H), 1.98 (s, 3H), 1.93 (s, 3H), 1.84−1.76 (m, 1H), 1.61 (d, 1H, J = 9.0 Hz), 1.45 (d, 1H, J = 9.0 Hz), 1.31 (dt, 1H, J = 12.5 and 3.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.8, 146.7, 142.8, 141.5, 139.1, 137.7, 134.8, 133.3, 129.3, 128.3, 127.1, 125.8, 125.7, 125.6, 122.4, 50.9, 48.1, 46.3, 41.3, 35.6, 15.1, 14.8 (22 of 27 carbons found). FT-IR (KBr cast) 3303, 3065, 2975, 2865, 1616, 1558, 1268, 1120, 985, 753 cm^{-1}. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutane] m/z = 580 [M + H]$^+$. Anal. Calcd for $C_{29}H_{23}NOS_2F_6$: C, 60.09; H, 4.00; N, 2.42. Found: C, 60.01; H, 3.92; N, 2.43.

Synthesis of Chloro-Substituted Monomer M2. A suspension of DTE carboxylic acid **4b** (0.85 g, 2.51 mmol) and anhydrous DMF (97 μL, 1.25 mmol) in anhydrous CH_2Cl_2 (50 mL) was treated dropwise over 5 min with a solution of oxalyl chloride (1.12 mL, 12.5 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 °C under an N_2 atmosphere. The cooling bath was removed and the reaction mixture was slowly warmed to room temperature and stirred there for 1.75 h, when it was evaporated to dryness in vacuo and dried under high vacuum (1 mmHg) for 18 h. The resulting acid chloride was dissolved in anhydrous CH_2Cl_2 (50 mL), treated with Et_3N (3 mL) and exo-2-aminobicyclo[2.2.1]hept-5-ene (0.55 g, 5.02 mmol), and stirred for 4 h at room temperature under an N_2 atmosphere. The resulting crude reaction mixture was diluted to 100 mL with CH_2Cl_2, washed with 5% aqueous HCl (25 mL), dried (Na_2SO_4), filtered, and evaporated to dryness in vacuo. Purification by column chromatography (0.1% Et_3N in CH_2Cl_2) yielded monomer **M2** (0.88 g, 82%) as white crystals after recrystallization (20% CH_2Cl_2/hexanes); mp = 209−210 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.14 (s, 1H), 6.57 (s, 1H), 6.18 (dd, 1H, J = 5.5 and 2.5 Hz), 6.11 (dd, 1H, J = 5.5 and 2.5 Hz), 5.73 (d, 1H, J = 7.5 Hz), 3.89 (dt, 1H, J = 7.5 and 3.0 Hz), 2.91 (s, 1H), 2.89 (s, 1H), 2.79−2.72 (m, 4H), 2.04 (p, 2H, J = 7.5 Hz), 1.99 (s, 3H), 1.85 (s, 3H), 1.83−1.78 (m, 1H), 1.60 (d, 1H, J = 8.5 Hz), 1.44 (d, 1H, J = 8.5 Hz), 1.28 (dt, 1H, J = 12.5 and 3.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.7, 139.9, 139.0, 136.4, 135.1, 134.9, 134.8, 134.6, 133.5, 129.4, 126.9, 125.5, 50.6, 48.2, 46.3, 41.2, 38.6, 38.5, 35.7, 23.1, 15.0, 14.4 (22 of 23 carbons found). FT-IR (KBr cast) 3303, 2959, 2923, 2848, 1609, 1558, 1525, 1114, 663, 618 cm^{-1}. LRMS (CI isobutane) m/z = 430 [M + H]$^+$. Anal. Calcd. for $C_{23}H_{24}NOS_2Cl$: C, 64.24; H, 5.63; N, 3.26. Found: C, 64.04; H, 5.43; N, 3.43.

Synthesis of Aldehyde 6. A solution of dichloride **5** (1.20 g, 3.60 mmol) in anhydrous THF (40 mL) was treated dropwise with *t*-BuLi (2.40 mL, 1.7 M in pentane, 4.01 mmol) at −78 °C under an N_2 atmosphere. The resulting yellow solution was stirred at this temperature for 30 min, when it was treated with anhydrous DMF (0.42 mL, 5.47 mmol) in one portion via a syringe. The cooling bath was removed and the reaction was slowly warmed to room temperature and stirred there for 1.5 h, when it was quenched with saturated NH_4Cl (10 mL). After the mixture was stirred for 10 min, the aqueous layer was removed and extracted with ether (2 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated to dryness in vacuo. Purification by column chromatography (20% ether/hexanes) yielded aldehyde **6** (0.80 g, 69%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.73 (s, 1H), 7.43 (s, 1H), 6.57 (s, 1H), 2.80−2.73 (m, 4H), 2.08−2.02 (m, 5H), 1.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 182.4, 146.5, 139.9, 137.8, 137.4, 135.6, 134.5, 133.8, 133.3, 126.5, 125.6, 38.4, 38.3, 22.8, 15.4, 14.1. FT-IR (KBr): 2952, 2918, 2843, 1668, 1542, 1455, 1252, 1142, 1004, 831, 733, 649 cm^{-1}. LRMS (electron ionization, EI) m/z = 322 [M]$^+$. Anal. Calcd. for $C_{16}H_{15}S_2OCl$: C, 59.52; H, 4.68; N, 0.00. Found: C, 59.10; H, 4.94; N, 0.00.

Synthesis of Alcohol 7. A solution aldehyde **6** (0.78 g, 2.46 mmol) in absolute EtOH was treated with $NaBH_4$ (0.14 g, 3.69 mmol) and stirred for 18 h under an N_2 atmosphere. The crude reaction mixture was evaporated to dryness in vacuo, suspended in Et_2O (20 mL), quenched slowly with 10% aqueous HCl (5 mL), and poured into a mixture of Et_2O (20 mL) and water (10 mL). The aqueous layer was removed and extracted with Et_2O (2 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated to dryness in vacuo. Purification by column chromatography (33% Et_2O/hexanes) yielded alcohol **7** (0.75 g, 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.66 (s, 1H), 6.58 (s, 1H), 4.68 (d, 2H, J = 6.0 Hz), 2.78−2.70 (m, 4H), 2.02 (p, 2H, J = 7.6 Hz), 1.96 (s, 3H), 1.85 (s, 3H), 1.62 (t, 1H, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.8, 135.3, 135.1, 135.1, 135.0, 133.7, 133.1, 126.8, 126.5, 124.9, 60.1, 38.4, 38.3, 22.9, 14.4, 14.1. FT-IR (KBr) 3332, 2948, 2917, 2844, 1550, 1440, 1147, 1005, 832, 734 cm^{-1}. LRMS (EI) m/z = 325 [M + H]$^+$. Anal. Calcd. for $C_{16}H_{17}S_2OCl$:

C, 59.15; H, 5.27; N, 0.00. Found: C, 59.03; H, 5.50; N, 0.00.

Synthesis of Chloro-Substituted Monomer M3. A solution of bicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid (0.43 g, 3.09 mmol) and anhydrous DMF (15 μL, 0.19 mmol) in anhydrous CH_2Cl_2 (30 mL) was treated dropwise over 20 min with oxalyl chloride (4.6 mL, 2.0 M in CH_2Cl_2, 9.3 mmol) at 0 °C under an N_2 atmosphere. The cooling bath was removed and the reaction was slowly warmed to room temperature and stirred there for 2 h, when it was evaporated to dryness in vacuo. The resulting acid chloride was dissolved in CH_2Cl_2 (20 mL) and treated with Et_3N (2 mL) and a solution of alcohol **7** (0.67 g, 2.06 mmol) in anhydrous CH_2Cl_2 (10 mL) via a cannula. The resulting solution was stirred for 18 h under an N_2 atmosphere, when it was diluted to 60 mL with CH_2Cl_2, washed with 5% aqueous HCl (20 mL), dried (Na_2SO_4), filtered, and evaporated to dryness in vacuo. Purification by column chromatography (10% Et_2O/hexanes) yielded monomer **M3** (0.70 g, 76%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 6.73 (s, 1H), 6.57 (s, 1H), 6.13 (dd, 1H, $J = 5.5$ and 3.0 Hz), 6.09 (dd, 1H, $J = 5.5$ and 3.0 Hz), 5.14 (d, 1H, $J = 12.5$ Hz), 5.10 (d, 1H, $J = 12.5$ Hz), 3.02 (s, 1H), 2.91 (s, 1H), 2.76−2.70 (m, 4H), 2.44−2.21 (m, 1H), 2.02 (p, 2H, $J = 7.5$ Hz), 1.96 (s, 3H), 1.93−1.89 (m, 1H), 1.81 (s, 3H), 1.50 (d, 1H, $J = 8.0$ Hz), 1.38−1.34 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.8, 138.1, 136.1, 135.7, 135.1, 135.0, 134.1, 133.8, 133.2, 129.0, 126.8, 125.0, 60.7, 46.6, 46.3, 43.1, 41.6, 38.3, 38.3, 30.3, 22.9, 14.3, 14.0 (23 of 24 carbons found). FT-IR (KBr) 3060, 2950, 2844, 1731, 1569, 1550, 1442, 1333, 1004, 842, 756, 720 cm^{-1}. LRMS (EI) $m/z = 445$ $[M + H]^+$. Anal. Calcd. for $C_{24}H_{25}S_2O_2Cl$: C, 64.77; H, 5.66; N, 0.00. Found: C, 64.48; H, 5.89; N, 0.00.

General Polymerization Procedure. A solution of the appropriate monomer(s) **M1**−**M3** in anhydrous THF (1.5 mL) was treated with a solution of bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (0.02 molar equiv) in anhydrous THF (1 mL) in one portion via a cannula. After the cannula was rinsed with anhydrous THF (1 mL), the resulting black solutions were stirred under an N_2 atmosphere for 16 h. The reaction was quenched with excess ethyl vinyl ether (1 mL) and stirred while exposed to the atmosphere for 30 min. The solvent was removed in vacuo and the black residue was redissolved in THF (1 mL) and precipitated with cold Et_2O, hexanes or CH_3CN and collected by vacuum filtration yielding polymers **P1**−**P3** or **CP1**−**CP4** as off-white powders. Polymers precipitated with CH_3CN were cooled for 30 s in a −78 °C dry ice/acetone bath prior to collection by vacuum filtration.

P1. Monomer **M1** (75 mg, 0.13 mmol) was polymerized with Grubb's reagent (2.1 mg, 2.6 μmol), yielding polymer **P1** (56 mg, 74%) after precipitation with cold hexanes. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50 (br s), 7.3 (br s), 5.7−5.0 (br s), 4.3−3.9 (br s), 2.8−1.0 (br m).

P2. Monomer **M2** (75 mg, 0.17 mmol) was polymerized with Grubb's reagent (2.9 mg, 3.5 μmol), yielding polymer **P2** (64 mg, 85%) after precipitation with cold Et_2O. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.5 (br, s), 5.6−5.1 (br m), 4.0 (br s), 2.8−2.5 (br s), 2.3 (br s), 2.1−1.5 (br m), 1.2 (br s).

P3. Monomer **M3** (75 mg, 0.17 mmol) was polymerized with Grubb's reagent (2.8 mg, 3.4 μmol), yielding polymer **P3** (51 mg, 68%) after precipitation with cold CH_3CN. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.7 (s), 6.5 (s), 5.3 (br s), 5.0 (br s), 3.7 (m), 2.8−2.4 (br m), 2.1−1.7 (m), 1.6 (br s), 1.1 (br m).

CP1. Monomers **M1** (10 mg, 0.017 mmol) and **M2** (57 mg, 0.13 mmol) were copolymerized with Grubb's reagent (2.5 mg, 3.0 μmol), yielding copolymer **CP1** (63 mg, 94%) after precipitation with cold Et_2O. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.5 (m), 7.3 (m), 6.5 (br s), 5.5−5.1 (br m), 4.0 (br s), 2.7 (br s), 2.4 (br s), 2.0−1.7 (br m), 1.6 (br s), 1.2 (br s).

CP2. Monomers **M1** (4 mg, 6.5 μmol) and **M2** (61 mg, 0.14 mmol) were copolymerized with Grubb's reagent (2.5 mg, 3.0 μmol), yielding copolymer **CP2** (57 mg, 88%) after precipitation with cold CH_3CN. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.7 (s), 6.5 (s), 5.3 (br s), 5.1 (br s), 3.7 (m), 2.8−2.4 (br m), 2.1−1.7 (br m), 1.1 (br s).

CP3. Monomers **M2** (17 mg, 0.038 mmol) and **M1** (44 mg, 0.099 mmol) were copolymerized with Grubb's reagent (2.5 mg, 3.0 μmol), yielding copolymer **CP3** (33 mg, 54%) after repeated (4 times) precipitation with cold CH_3CN. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.7 (s), 6.5 (s), 5.3 (br s), 5.1 (br s), 2.8−2.4 (br m), 2.1−1.7 (br m), 1.1 (br s).

CP4. Monomers **M1** (9 mg, 0.014 mmol), **M2** (47 mg, 0.11 mmol), and **M3** (128 mg, 0.29 mmol) were copolymerized with Grubb's reagent (6.8 mg, 8.2 μmol), yielding copolymer **CP4** (170 mg, 92%) after precipitation with cold CH_3CN. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.7 (s), 6.5 (s), 5.3 (br s), 5.0 (br s), 3.7 (s), 2.8−2.5 (br m), 2.1−1.8 (m), 1.6 (br s), 1.2 (br m).

Acknowledgment. Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chairs Program, and Simon Fraser University for support of this research. We also thank Nippon Zeon Corp. for supplying the octafluorocyclopentene needed to prepare the appropriate photochromic compounds.

Supporting Information Available: Photochromic characterizations of all compounds described in this report. This information is available free of charge via the Internet at http://pubs.acs.org.

CM051231D