Photochromic Polymer Composites for Two-Photon 3D Optical Data Storage

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In this paper we demonstrate 3D two-photon recording and two-photon readout in photochromic polymer composites containing a mixture of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (diarylethene **1**) and fluorene derivatives 2,2′-(9,9-didecyl-9*H*-fluorene-2,7-diyl)bis(ethene-2,1-diyl)bis-(4,1-phenylene)) dibenzo[d]thiazole (**2**) or poly(9,9-didecyl-2,7-dipheylaminofluorene) (**3**). The recording mechanism in this system is based on two-photon excitation of the closed form of diarylethene **1** at 800 nm. The readout mechanism is based on the modulation of the emission intensity of fluorene derivatives **2** or **3** by the closed form of diarylethene **1** through Resonance Energy Transfer (RET). Föster distances (R_0) and critical concentrations (A_0) were calculated from the spectral overlap of the donor's emission (fluorene derivatives) and the acceptor's absorption (closed form of diarylethene **1**) in solution and in polymer films of PMMA-*co*-VBP. This system was demonstrated to be suitable for recording data by two-photon excitation in thick storage media. The RET-based readout method proved to be essentially nondestructive (exhibiting a loss of the initial fluorescence emission less than 20% of the initial emission after 10 000 readout cycles), providing a solution to a long-standing challenge in photochromic optical data storage.

Introduction

The main motivation for the development of digital data storage (CD-R, CD-RW) has been the improvement in playback quality and increased storage capacity. Two approaches to increase storage capacity are the arrangement of several layers in a DVD (such as the DVD 18 format with 4 layers) and the reduction of the bit size by using laser diodes with emission wavelengths in blue (such in the case of the Blue-Ray disc, the new optical disc format developed by the Bluray Disc Association). The use of blue laser diodes is based on the observation that, with conventional optics, a laser beam spot size is limited by the diffraction limit and dependent on the wavelength (λ) and the numerical aperture (NA).[1,2] However, both approaches have their limitations. In the first approach, the construction of several layers requires the arrangement of bubble-free bonding layers that are difficult to produce, and the penetration depth of the light is limited.[1] In the second approach, the high optical excitation energy and small optical focus size characteristic of blue laser data storage formats lead to significant hot carrier diffusion (HCD) prior to the energy transfer to the Ge−Sb−Te crystal lattice. Therefore, the fundamental limit of resolution for rewritable optical storage systems is determined not only by the laser focus size alone but also by additional nonequilibrium HCD effects.[3]

One of the most attractive alternatives is to store bits throughout all three dimensions of the storage material (multilayer storage). Multilayer data storage can be achieved by the use of two-photon absorbing optical materials.[4−9] Two-photon 3D memories offer increased storage capacity by using volume storage, in a manner similar to the multilayer optical disk systems but with the advantages of simpler media fabrication, many more layers, and potentially lower raw bit error rates (BER).[7] Two-photon optical materials nonlinearly absorb the incident light, confining the absorption at the focus to a volume of order λ^3 (where λ is the laser wavelength), thus affording immense information storage capacity (up to 10^{12} bits/cm^3).[4−9]

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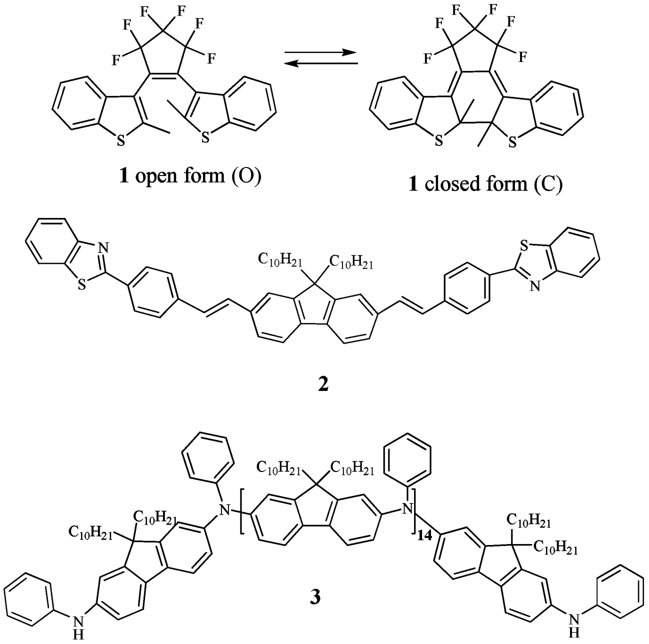
Scheme 1. Molecular Structures of the Open and Closed Forms of Diarylethene 1 and Fluorene Derivatives (2) and (3)



Multilayer two-photon data storage has been demonstrated by using photochromic compounds.[4,7−9] Photochromic materials such diarylethenes (developed by Irie et al. and Lehn et. al.) are promising candidates for applications because of their excellent fatigue resistance, picosecond switching time, high photoisomerization quantum yields, and absence of thermal isomerization.[10−16] One of the most studied diarylethene derivatives is 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (diarylethene **1**, Scheme 1).[17−19]

Upon irradiation with UV light (<360 nm), colorless solutions of **1** (open form) become red (closed form), with new absorption bands appearing at 350 and 517 nm (Figure 1). The open and closed forms of diarylethene **1** codify the binary information. Two-photon excitation can be used to induce photoisomerization in diarylethenes, such as the one depicted in Figure 1.[20−24] For any practical application of diarylethenes in 3D optical data storage, the readout method of the stored information (O or C isomers) should be nondestructive. Various optical systems for reading 3D memories using diarylethene derivatives as storage media have been reported.[14] In particular, Jares-Erijman and Irie used Lucifer Yellow I as the donor and bis(thienyl)ethane as the acceptor to build fluorescent molecules and developed a general conceptual reading/writing system based on RET, where they found that the one-photon fluorescence emission of the donor is reversibly modulated by cyclical transformations of the photochromic acceptor upon irradiation of appropriate UV and visible light, respectively.[25]

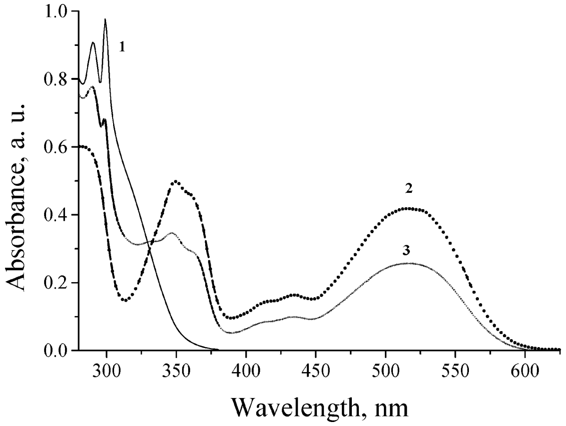


Figure 1. Absorption spectra of the (1) open form (O) (extinction coefficient at λ_{max} (258 nm): 1.5×10^4 M^{-1} cm^{-1}), (2) closed form (C) (extinction coefficient at 517 nm: 9.9×10^3 M^{-1} cm^{-1}), and (3) photostationary state of diarylethene **1** in hexane (λ_{exc}: 254 nm).

Thus, while other groups have previously demonstrated fluorescence readout using intramolecular RET with relatively complex and difficult to synthesize compounds, herein we demonstrate intermolecular RET from highly efficient two-photon absorbing fluorene derivatives to the closed isomer of a photochromic diarylethene as an efficient readout method in a two-photon optical data storage system. This is particularly attractive since covalent derivatization of the photochrome often leads to reduction or elimination of photochromic activity due to formation of a conformer that does not undergo electrocyclic ring closure. The storage medium consists of a commercial available photochromic molecule diarylethene **1** and specifically designed two-photon absorbing fluorene derivatives **2** or **3** (Scheme 1) in a polymeric matrix of poly[methylmethacrylate-*co*-(diethylvinylbenzylphosphonate)] (PMMA-*co*-VBP). Data recording in this system was achieved by single-photon excitation of the closed form of diarylethene **1** and by two-photon excitation of the closed form of **1** at 800 nm (where its two-photon absorption cross-section (δ_{2PA}) is relatively high). Data readout was also achieved by two-photon excitation of the fluorene derivative at 800 nm using much lower intensities than the ones required for recording. Differences (close to an order of magnitude) in the nonlinear absorption of the two components in this system allowed recording and readout using the same excitation wavelength at different laser intensities. This system is suitable for recording data in thick storage media providing a virtually "nondestructive"

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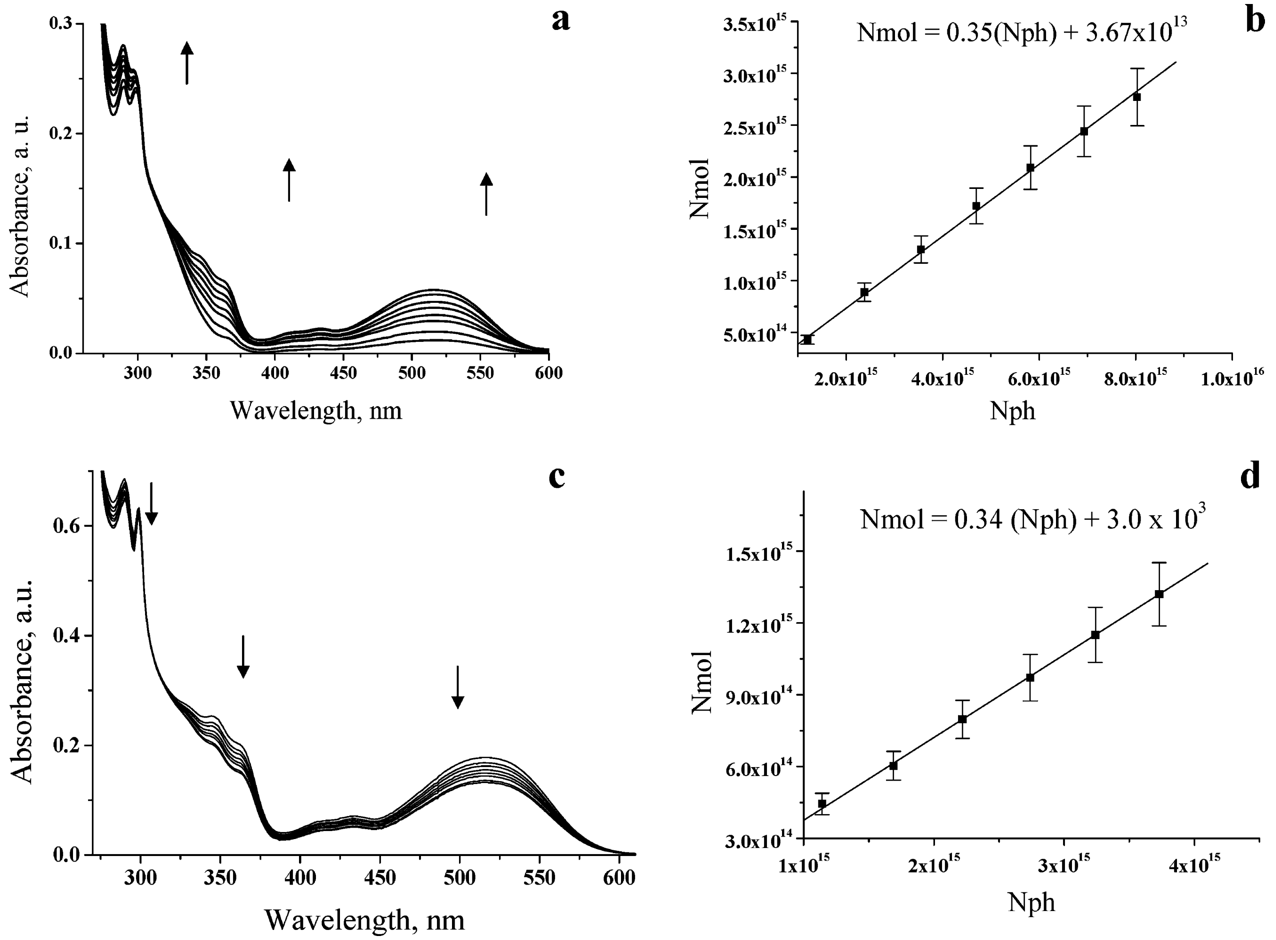

Figure 2. Kinetic changes in the absorption spectra of **1** in hexane ($C \approx 4.0 \times 10^{-5}$ M): (a) initial spectrum corresponds to the open form and subsequent spectra show changes in absorption under irradiation at $\lambda_{exc} = 313$ nm, (b) N_{mol} vs N_{ph} plot for determination of $\Phi_{O\to C}$ at 313 nm, (c) initial spectrum corresponds to the photostationary state and subsequent spectra show changes in absorption under irradiation at $\lambda_{exc} = 517$ nm, and (d) N_{mol} vs N_{ph} plot for determination of $\Phi_{C\to O}$ at 517 nm.

readout method (without exhibiting loss of the initial fluorescence intensity greater than 20% after 10 000 readout cycles). Finally, multilayer bit-by-bit two-photon recording and two-photon readout was demonstrated in this optical storage medium.

Results and Discussion

Diarylethene 1. Individual absorption spectra of the open and closed forms of diarylethene derivative **1** in hexane are shown in Figure 1. The absorption spectrum of **1** in the photostationary state in hexane is shown in Figure 1 (3). Diarylethene **1** is especially well suited for data storage due to its high cyclization ($\Phi_{O\to C}$) and cycloreversion ($\Phi_{C\to O}$) photoisomerization reaction quantum yields ($\Phi_{O\to C}$: 0.34 at 313 nm and $\Phi_{C\to O}$: 0.34 at 517 nm in hexane). Neither the open nor the closed forms display significant fluorescence (fluorescence quantum yield: open form ~ 0.02 and closed form <0.02).

Kinetic changes in the absorption spectra of the hexane solutions of **1** under steady-state irradiation at $\lambda_{exc} = 313$ and 517 nm are shown in parts a and c, respectively, of Figure 2. The initial slopes of the dependences $N_{mol} = f(N_{ph})$ (where N_{mol} and N_{ph} are the number of reacted molecules and the number of absorbed photons, respectively) are shown in Figure 2b,d.

The temporal step between two adjacent spectra in Figure 2a,c is 15 s (excitation irradiance = 0.167 mW/cm^2 in Figure 2a and = 0.10 mW/cm^2 in Figure 2c). These measurements were performed for different λ_{exc} in the main absorption band of **1**, resulting in determination of the spectral dependences of the cyclization and cycloreversion reaction quantum yields. The values of $\Phi_{O\to C}$ were in the range 0.24−0.37. The calculated value of $\Phi_{O\to C}$ at 313 nm (0.34) was in good agreement with the value reported by Uchida et al.[17] The values of $\Phi_{C\to O}$ were in the range 0.34−0.43. The calculated value of $\Phi_{O\to C}$ at 517 nm (0.34) was also in agreement with the reported value.[17] Only a very weak spectral dependence of $\Phi_{O\to C}$ and $\Phi_{C\to O}$ was observed.

To ascertain the optimized experimental conditions for two-photon recording and readout, two-photon absorption cross-sections (δ_{2PA}) of the open and closed forms of diarylethene **1** in ethyl acetate were determined by an open aperture Z-scan method, using a picosecond laser excitation source.[26] The δ_{2PA} of the open form at 520 nm (corresponding to 260 nm of single photon excitation) was 85 GM (1 GM = 1×10^{-50} cm^4 s/photon molecule), comparable to δ_{2PA} reported for structurally related diarylethenes.[23,27,28] The δ_{2PA}

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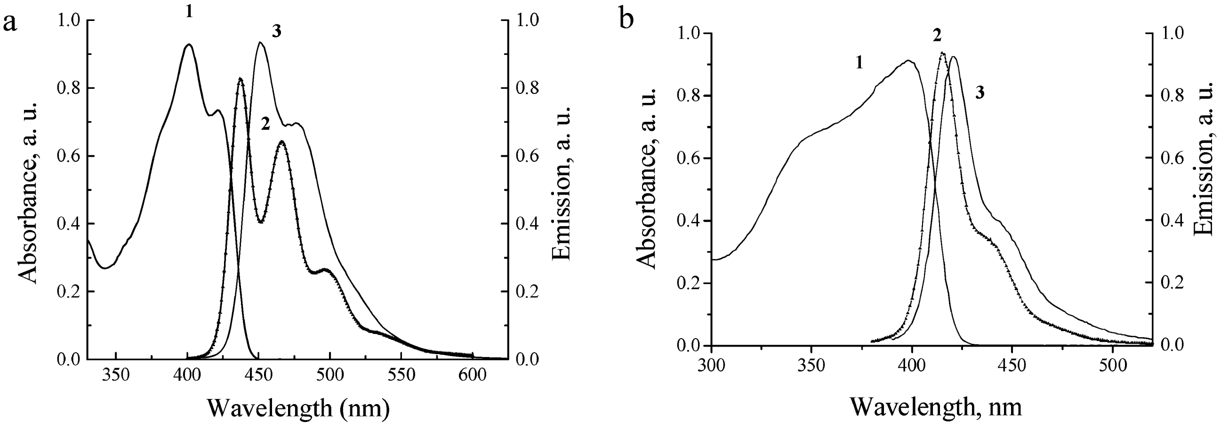

Figure 3. a.1. Absorption spectrum of fluorene derivative **2** in THF; a.2. emission spectrum of fluorene derivative **2** in THF; a.3. emission spectrum of fluorene derivative **2** in polymer film; b.1. absorption spectrum of fluorene derivative **3** in THF; b.2. emission spectrum of fluorene derivative **3** in THF; and b.3. emission spectrum of fluorene derivative **3** in polymer film of PMMA-*co*-VBP, respectively.

of the closed form of diarylethene **1** at 680, 750, and 800 nm was 150, 145, and 120 GM, respectively.

Fluorene Derivatives 2 and 3. Fluorene derivatives **2** and **3** were introduced in order to provide a signal output used for readout (two-photon up-converted fluorescence/RET). These fluorene derivatives were selected from a group of efficient two-photon absorbing (2PA) fluorescent probes synthesized in our laboratory,[29−31] since they exhibit high fluorescence quantum yields, large 2PA cross-sections, an emission spectrum largely overlapping the absorption spectrum of the closed form of diarylethene **1**, and high photostability.[32,33] Absorption and single-photon induced emission spectra of fluorenes **2** and **3** in THF and in a thin film of PMMA-*co*-VBP are shown in Figure 3. Fluorescence quantum yields (Φ_f) of **2** were 1.0 in hexane and 0.98 in THF.[34] The Φ_f of **3** were also near unity in hexane and cyclohexane.[35] One paradigm for a chromophore to exhibit high δ_{2PA} is an extended π-conjugation system with various electron acceptor (A) or donor (D) groups attached in specific locations of a molecule in either symmetrical (D-π-D, A-π-A, D-π-A-π-D, A-π-D-π-A) or unsymmetrical (D-π-A) architectures.[29−37] The acceptor or donor groups facilitate photoinduced charge transfer along the conjugation path upon excitation, resulting in large optical nonlinearity.

In addition to the strength of the donor or acceptor groups, another major factor affecting 2PA is the number of π-electrons (or extent of conjugation or excited-state charge separation). In our molecules, we have incorporated a donor (phenylamine) and an acceptor (benzothiazole) and increased the conjugation length (via the incorporation of a styryl group). Compound **2** belongs to the A-π−π-π-A molecular structure. The δ_{2PA} of fluorene **2** was 6000 GM at 600 nm and ≈ 1200 GM at 800 nm.[34] Compound **3** belongs to the D-π-D type of two-photon chromophores, having high thermal and photostability. The δ_{2PA} of fluorene **3** (containing 16 chromophore units) was 16 500 GM at 660 nm and 2000 GM at 720 nm.[35]

Resonance Energy Transfer Experiments. One method to develop more efficient 2PA diarylethenes (for efficient photochromism induced by two-photon excitation, the diarylethene isomer should have a relatively high 2PA cross-section (δ_{2PA}) at the excitation wavelength) is to covalently attach an efficient 2PA chromophore to a photochromic molecule.[27,28] A major problem encountered using this approach is that covalent attachment of the 2PA chromophore often perturbs the electronic distribution and conformation of the photochrome, resulting in the loss of desirable photochromic properties.[27,28] Instead of chemical modification, the use of other mechanisms have been suggested to enhance the nonlinear optical performance of organic materials, such as the use of RET.[38−40] An intriguing alternative is to employ a mixture of 2PA dyes and photochromic molecules. The 2PA dye serves as a donor (**D**) and the photochromic compound as an acceptor (**A**), combining efficient two-photon excitation with intermolecular RET. The transfer rate constant of RET, $k_{RET}(r)$, can be expressed as[41]

$$k_{RET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 = \frac{k^2 \cdot \Phi_{FL}}{\tau_D \cdot r^6} \cdot \left(\frac{9000\ln(10)}{128\pi^5 n^4 N_A}\right) \cdot J$$

where R_0 is the Förster distance and r is the distance between **D** and **A** molecules; τ_D and Φ_{FL} are the lifetime and

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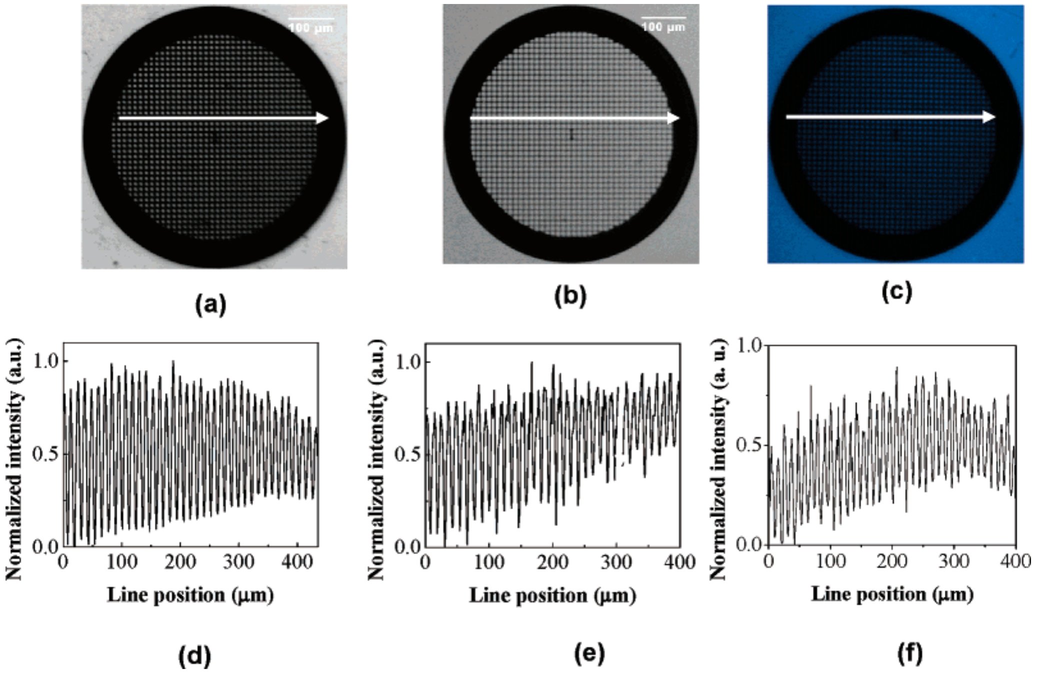

Figure 4. TEM mask (a) and storage medium (b) after single-photon data recording. (a) and (b) correspond to brightfield images and (c) corresponds to fluorescence readout (using 10× objective). (d)−(f) are the intensity profiles (whose direction is shown by the arrows) of the corresponding patterns in (a)−(c), respectively. The scale bars correspond to 100 μm.

fluorescence quantum yield of the **D** in the absence of **A**, correspondingly; k is the orientation factor depending on the relative space orientation of the transition dipoles of **D** and **A**; N_A is Avogadro's number; n is the refractive index of the medium; and J is the overlapping integral expressed as the degree of spectral overlap between the **D** emission and **A** absorption. Virgili et al.[40] demonstrated efficient Förster transfer from poly(9,9-dioctylfluorene), PFO, to the fluorescent red dye tetraphenylporphyrin (TPP) in films of PMMA. From the spectral overlap of the donor emission and acceptor absorption spectra, they calculated an R_0 value of 48 Å. A Förster radius of 42 Å was determined by a femtosecond pump−probe spectroscopy method in a series of PFO/TTP blends with different TPP concentrations.[42]

Belfield et al. investigated RET from two-photon absorbing fluorene derivatives to the open isomer of the photochromic diarylethene 3,4-bis(2,4,5-trimethylthiophen-3-yl)furan-2,5-dione in hexane under one- and two-photon excitation.[43] Herein, a novel approach was demonstrated, consisting of the use of RET from fluorene derivatives to the closed isomer of the diarylethene, rather than its open isomer, facilitating nondestructive RET-based readout. The selection of diarylethene-fluorene derivative pairs in this case was based on good spectral overlap of the emission of fluorene derivatives and the absorption of the closed form of the diarylethene.

Based on the spectral data, and taking into account that $\epsilon_A(\lambda^{max}) \approx 9.9 \times 10^3$ $M^{-1}\cdot cm^{-1}$ for the closed form of diarylethene **1** in THF, the efficiency of RET was estimated, using the methodology described previously.[43] The fluorescence quantum yields, Φ_{FL}, calculated overlapping integrals, J, Förster radius, R_0, and critical concentrations, A_0, for fluorenes **2** and **3** in THF and in polymer films are presented in Table 1 (n^{20}_D of PMMA-*co*-VBP film was 1.44 ± 0.01).

Table 1. Quantum Yields, Φ_{FL}, Calculated Overlapping Integrals, J, Förster Radius, R_0, and Critical Concentrations, A_0, for Fluorenes 2 and 3 in THF and in Polymer Films of PMMA-*co*-VBP

fluorene	**2** (THF)	**2** (film)[a]	**3** (THF)	**3** (film)[a]
$\Phi_{FL} \times 10^2$	98 ± 5	97 ± 5	98 ± 5	96 ± 5
$J \times 10^{15}$, $M^{-1}\cdot cm^3$	29.5	33.8	12.4	15.3
R_0, Å	40.3 ± 2.3	40.5 ± 2.3	34.9 ± 2.0	35.5 ± 2.0
$A_0 \times 10^3$, M	6.8 ± 0.4	6.7 ± 0.4	10.5 ± 0.6	10.0 ± 0.6

[a] 30 μm polymer films.

From these data, it can be seen that fluorene **2** exhibits the higher potential efficiency of Förster's RET, relative to fluorene **3**. The J value for fluorene derivatives **2** and **3** to the closed form of diarylethene **1** was found to be greater than the ones calculated for related fluorene derivatives to the open form of the diarylethene (for some of them an order of magnitude greater).[43]

Single-Photon Recording /Single-Photon Readout. Results from preliminary studies in solution provided the basis for subsequent studies in solid thin films. The principles of the device were demonstrated by recording data by single-photon excitation in 2-D polymeric films. For the solid film studies, PMMA-*co*-VBP was used as the host polymer.[44] This polymer was chosen due to its excellent solubility in acetonitrile and its ability to solubilize diarylethene **1** and fluorene **2** at high concentrations without aggregation. Solutions containing approximately 0.01 M of the closed

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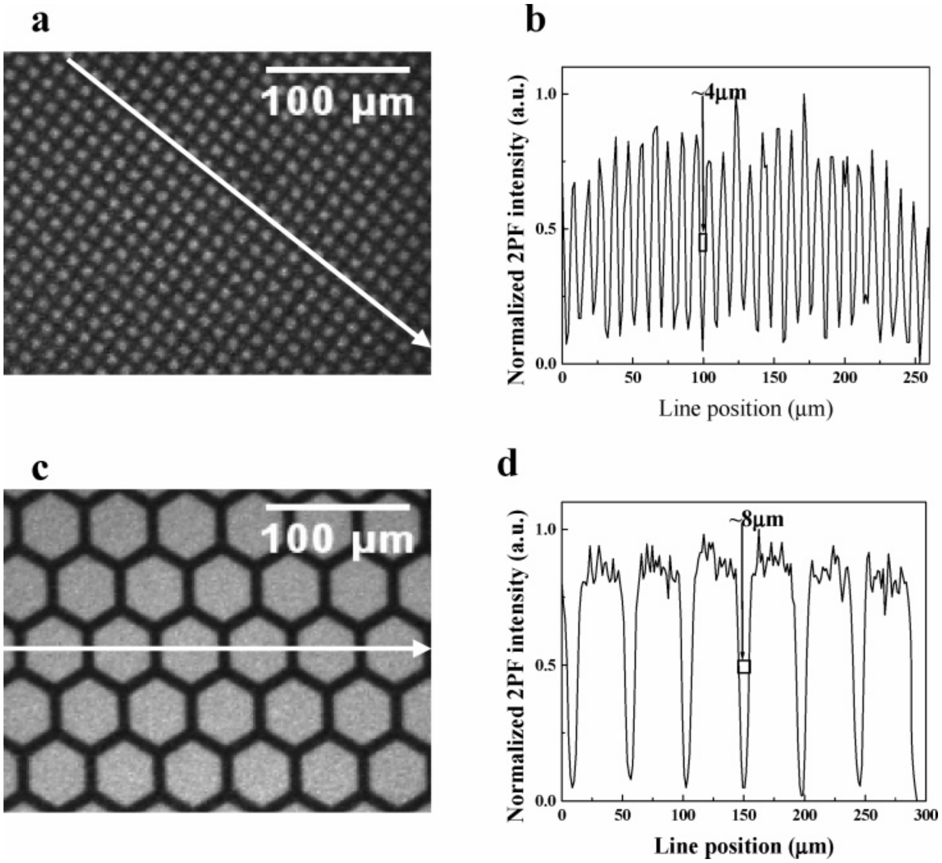

Figure 5. Upconverted two-photon fluorescence readout of data recorded by single-photon excitation in a photochromic polymer composite containing diarylethene **1** and fluorene derivative **2**: (a) pattern from a 400 mesh TEM mask; (b) intensity profile (direction is shown by the arrows) of the recorded data in (a); (c) pattern from a 100 mesh TEM mask; and (d) intensity profile (direction is shown by the arrows) of the recorded data in (c).

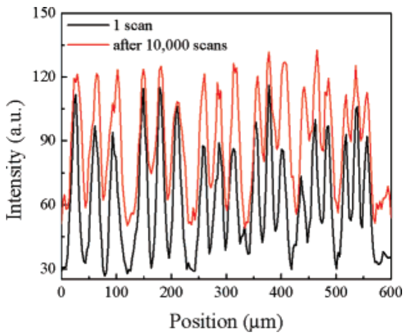

Figure 6. Comparison of the intensity profiles of a two-photon fluorescence readout after 1 scan vs 10 000 scans.

form of diarylethene **1** and 2 wt % fluorene derivative **2** or **3** (relative to the polymer) were irradiated in a Rayonet photoreactor (254 nm), until the photostationary state of diarylethene **1** was reached. Red solutions were obtained before coating. Films of ca. 40 μm were coated on glass slides using the photostationary state mixture.

For single-photon recording, films were placed on the stage of an inverted microscope (Olympus IX81) and irradiated through the condenser of the same microscope (N.A. = 0.55). A band-pass filter (IF550, Olympus) with peak transmission at 520 nm and full width at half-maximum equal to 65 nm was placed in front of the light source (a halogen lamp). A TEM grid (400-mesh hexagonal grids from Polysciences, Inc.) was used as masks (Figure 4 (a)). Data were recorded by focusing the excitation light (~10 mW/cm^2) through the mask and then exposing the photochromic film for 20 s. In the exposed areas there is a decrease in the number of closed form molecules, resulting in an increase of fluorescence emission and a modulation of the refractive index. After mask removal, confocal fluorescence microscopy (λ_{ex}: 377/50 nm-DM: 409 nmLP-λ_{em}: 460/50 nm) or brightfield microscopy was used to readout the recorded data, where a 10× (Olympus UplanFLN 10×, N.A. = 0.3) objective lens was used. The readout experiments using brightfield transmission imaging were designed to help optimized experimental conditions for further two-photon recording/readout and for comparison with two-photon readout. The optimal exposure time for our storage medium under single-photon excitation was estimated by identifying the intensity profile and calculating the contrast (signal-to-background ratio). For 40

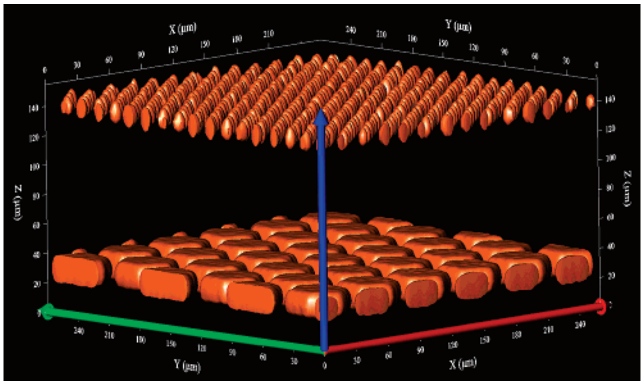

Figure 7. Two-photon fluorescent images of the photosensitive films constructed in a multilayer configuration.

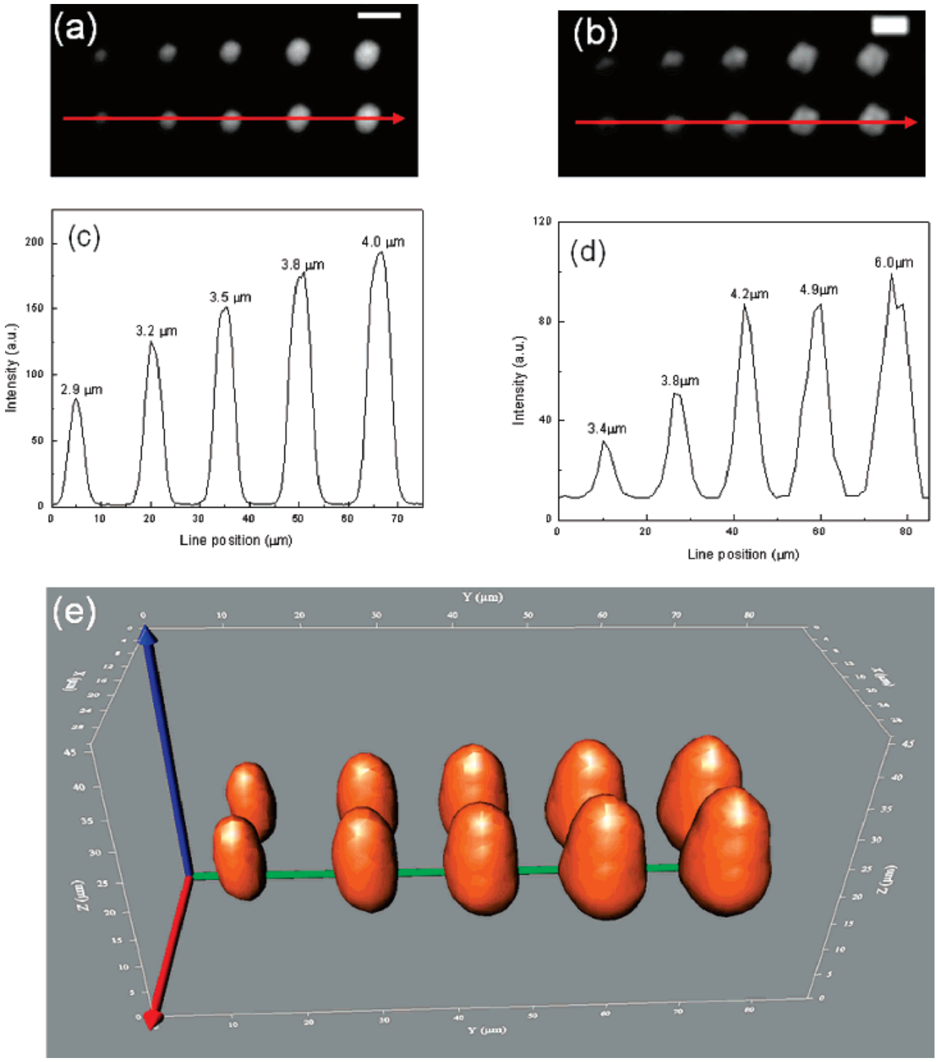

Figure 8. (a) A single-photon and (b) a two-photon readout of data bits recorded by two-photon excitation (recording: obj. 20×/NA = 0.5, $\lambda = 800$ nm, $P = 12.6$ mW, $t = 1, 3, 5, 7, 10$ s (from left to right); readout: $\lambda = 800$ nm, $P = 4$ mW). The scale bar corresponds to 10 μm. The corresponding intensity profiles (the direction is shown by the arrows) (c) represents image (a) and (d) represents image (b), and (e) the 3D image represents 45 consecutive layers (1 μm layer interval).

μm thick films a contrast of 5.7 was achieved after 20 s exposure, while a contrast of 3.6 was obtained after 10 s exposure. Improvement of the recorded signal-to-noise ratios minimized the potential hazard of overexposing films and compromising resolution. Figure 4(d)−(f) shows the intensity profiles of the data mask (the TEM target) and our recorded data, readout by brightfield and by fluorescence imaging, respectively.

Linear (one-photon) excitation of fluorene **2** or **3** did not provide a nondestructive readout method, since there is considerable absorption of the closed form of the diarylethene at the excitation wavelength used in the fluorescence readout (377 nm). In contrast, due to the differences in nonlinear absorption (2PA) cross sections of the components of the system at the excitation wavelength, a virtually nondestructive readout method by two-photon excitation was demonstrated, as shown below.

Single-Photon Recording/Two-Photon Readout. Using a modified Olympus Fluoview FV300 two-photon microscope equipped with a tunable femtosecond laser (tuned to 800 nm in this experiment), two-photon readout was demonstrated (Figure 5). In particular, memory (data) readout was achieved by detecting the two-photon up-converted fluorescence of fluorene **2** at 800 nm or fluorene **3** at 720 nm as a function of position. At the readout wavelength, fluorenes **2** and **3** have a δ_{2PA} over an order of magnitude greater than the closed form of diarylethene **1**. So when a weak 720 nm or 800 nm femtosecond laser (<8 mW) was utilized for the readout process, strong two-photon fluorescence from **2** or **3** was observed.

This incident intensity is too weak to cause the closed form of diarylethene **1** to undergo significant photochromic or photochemical reaction (which is related to data erasing). Particularly noteworthy is that 10 000 readout cycles were accomplished with less than 20% decrease in the contrast and fluorescence intensity of the original two-photon image (Figure 6). Since this type of fluorene derivative is highly photostable under the laser irradiation used in this experiment,[32−33] the less than 20% change in upconverted two-photon fluorescence emission after 10 000 cycles can be attributed to the photostability of the closed form of the photochromic diarylethene derivative.[23]

In Figure 7, the ability to read multiple layers of information by the two-photon readout method is demonstrated. A

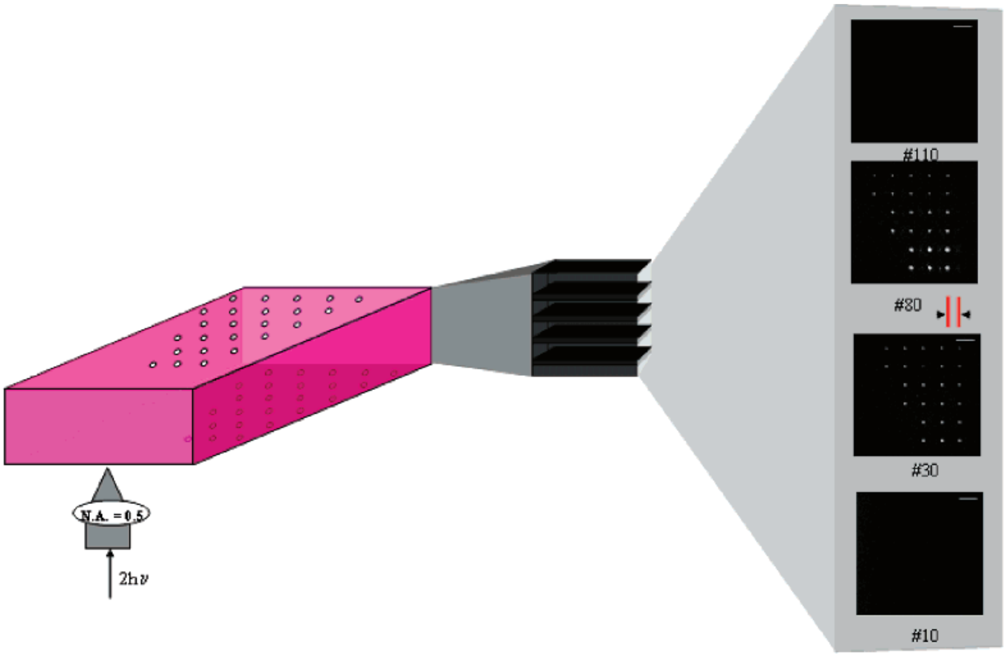

Figure 9. The two-photon readout of 110 consecutive layers (1 μm layer interval) inside the polymer film. Two layers (images #30 and # 80) were recorded by two-photon excitation. The bulk film is illustrated on the left, while actual data layers are shown on the right. The distance between layers was 50 μm, and the distance between neighboring bits in each layer was 50 μm. Bits in each layer were recorded at several exposure times: $t = 200$ ms (for the two top lines), 500 ms (for the next two middle lines), and 1 s (for the two bottom lines). Recording in the second layer was achieved by moving the XY stage 25 μm to the left (offset relative to the first layer, depicted by the red lines in the figure). The scale bar corresponds to 50 μm.

multilayer assembly was constructed by stacking two storage layers (shown in Figure 5). The assembly was translated in the axial (or *z*) direction by a computer-controlled step motor connected to the focusing knob of the microscope. 3D data from this memory stack were read by successively imaging 31 XY data planes along the axial direction (5 μm distance between each image). A 3D image was reconstructed from the real original two-photon fluorescence imaging planes using 3D constructor ver. 5.1 (MediaCybernetics Inc.). An *xy* planar scan of each film (hexagonal grid image on the bottom and square grid image on the top) within the multilayer clearly shows the photopatterned image.

Bit-by-Bit Two-Photon Recording/Two-Photon Readout. In Figure 8, the two-photon bit-by-bit recording ability in this photochromic system is demonstrated. A 20× microscope objective (NA=0.50) was used to focus the femtosecond laser ($\lambda = 800$ nm, $P = 12.6$ mW) into the film, where the exposure time (from 1 to 10 s) was manually controlled, and the distance between two bits (15 μm) was controlled by moving the film position with a manual X−Y linear stage (Model 406, Newport Corp.). Exposure times less than 1 s were not attempted by this manual method. The data bits were readout by the same two-photon fluorescence microscopy method (described above) using a low incident intensity of 4 mW and a 20× objective (Figure 8(a),-(b)). 3D data from these data bits were readout by successively imaging 45 XY data planes along the axial direction (1 μm distance between each image). The 3D image shown in Figure 8(e) was also reconstructed from the real original two-photon fluorescence imaging planes using 3D constructor version 5.1 (MediaCybernetics Inc.) and clearly indicates that the volume of data bits can be controlled by the exposure time.

Multilayer (3D) Bit-by-Bit Two-Photon Recording/Two-Photon Readout. The two-photon 3D recording ability in our system was demonstrated (Figure 9) by recording two layers of bits on thick polymer films (∼120 μm). Films were prepared by casting solutions of PMMA-*co*-VBP containing the closed form of diarylethene **1** and fluorene **2** on glass slides (by using a PI-1210 film coater from Tester Sangyo Co. Ltd.). After coating, films were stored in the dark to avoid any external irradiation exposure. Two layers of bits separated by 50 μm in the *Z* direction (depth) were written in the volume of the polymer film by two-photon excitation. For this bit-by-bit experiment, the same Olympus Fluoview FV300 previously described was used for data recording and data readout. The excitation beam was generated by a mode-locked Ti:Sapphire laser, tuned to 800 nm ($\Delta\lambda = 8$ nm, 150 fs pulse width, 76 MHz repetition rate). The laser beam was focused onto the sample using a 20× objective lens. For two-photon recording, the average beam power (360 mW) was attenuated such that the maximum power measured at the sample was 20 mW. For two-photon readout, the same Ti:sapphire laser was used with a lower average power of 6 mW. High power excitation at the sample was not required due to the increased two-photon photosensitivity afforded by the fluorene derivative. An efficient data writing system was developed by using a motorized MAXY X−Y stage and BSC102 controller, SH05 electronic beam shutter, and SC10 controller (Thorlabs). Recording in the first layer was achieved by using different exposure times: 200 ms (for the first two lines on the top), 500 ms (for the next two lines in the middle), and 1 s (for the two lines on the bottom). The distance between neighboring bits inside one layer was 50 μm. Recording in the second layer was achieved by moving the XY stage 25 μm to the left (offset relative to the first layer) and using the same exposure times and pattern as the first layer. Figure 9 shows representative images of the readout of 110 consecutive layers (1 μm layer interval) inside the polymer film. The bulk film is illustrated on the left, while actual data layers are shown on the right.

Conclusions

Multilayer (3D) two-photon recording and two-photon readout in novel photochromic polymer composites resulted in the realization of a two-photon optical storage system. Recording of the media was based on two-photon excitation of the closed form of diarylethene **1** at 800 nm. The readout mechanism was based on modulation of the fluorescence emission of fluorene derivatives **2** or **3** (D) by the closed form of the diarylethene **1** (A), excited at 800 nm, via RET. Differences in the nonlinear absorption behavior of the two components in this system allowed recording and readout using the same excitation wavelength but different laser intensities, a feature that should have advantageous practical implications. Calculated values of the Förster distances and critical acceptor concentrations for nonbonding D−A pairs strongly suggest that a Förster type RET mechanism was involved in this fluorescence modulation.

Experimental Section

Materials. 1,2-Bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (diarylethene **1**) was purchased from TCI America and used without further purification. 2,7-Bis[4-(9,9-didecylfluoren-2-yl)vinyl] phenyl benzothiazole (fluorene **2**) and poly(9,9-didecyl-2,7-diphenylaminofluorene) (fluorene **3**) were synthesized and characterized as previously described.[34,35] Spectroscopic grade hexane, THF, and ethyl acetate were used as solvents. Preparation of poly[methylmethacrylate-*co*-(diethyl vinyl benzyl phosphonate)] (PMMA-*co*-VBP) was described previously, consisting of a mole ratio of diethyl vinylbenzylphosphonate to MMA of 1:3 in the polymer.[44]

Instrumentation. Absorption spectra were recorded with an UV−visible Agilent 8453 spectrophotometer. The steady-state fluorescence spectra were measured with a PTI Quantamaster spectrofluorimeter in the photon-counting regime of the PMT. 2PA cross-sections of the open form and the closed form of **1** were measured by an open aperture Z-scan method[26] with a picosecond Nd:YAG laser (PL 2143 B Ekspla) coupled to an optical parametric generator (OPG 401/SH) with pulse duration, $\tau_P \approx 35$ ps (fwhm). Two-photon fluorescence images of polymer films were performed on a modified Olympus Fluoview laser scanning confocal microscopy system equipped with a broadband, tunable Coherent Mira Ti:Sapphire laser (tuned to 800 nm, 150 fs pulse width, 76 MHz repetition rate), pumped by a 10 W Coherent Verdi frequency-doubled Nd:YAG laser. Bit-by-bit two-photon recording and two-photon readout of two layers were performed by using the same Olympus Fluoview laser scanning confocal microscopy system previously described, equipped with an automatic XYZ stage and an automatic shutter for control of the exposure times in the ms regime.

General Procedures. The quantum yields of the direct, $\Phi_{O\rightarrow C}$, and reverse, $\Phi_{C\rightarrow O}$, photoisomerization reactions were determined from the temporal changes in the corresponding absorption spectra of **1** under steady-state Xe-lamp irradiation through the excitation monochromator of the PTI Quantamaster spectrofluorimeter.[23]

Polymer films for the two-dimensional recordings were prepared using solutions of 1 wt % of PMMA-co-VBP in THF. Two different films were prepared, by adding diarylethene **1** (0.01 M) and fluorene **2** (1 wt % relative to the polymer) or fluorene **3** (2 wt % relative to the polymer) to the THF solution. The polymeric solution was sonicated, filtered through 0.2 μm pore size filter, and purged with N_2 for 10 min followed by ultrasonic degassing. This solution was irradiated in a Rayonet photoreactor at 254 nm until the photostationary state of diarylethene **1** was reached (as confirmed by comparing the absorption spectrum of the solution with the one of the photostationary state). A red solution was obtained before coating. Solution-cast films of approximately 40 μm were prepared on glass slides by using a PI-1210 film coater from Tester Sangyo Co. Ltd. After coating, films were stored in the dark to avoid any external irradiation exposure. Emission spectra of fluorenes in polymer films were determined in a PTI Quantamaster spectrofluorimeter using front-face illumination and solid-state sample holder at room temperature. Fluorescence quantum yields in solutions and polymer films were determined relative to 9,10-diphenylanthracene in cyclohexane.[41] The refractive index of a transparent PMMA-co-VBP polymer film ($\sim$ 40 μm) was determined on a Abbe refractometer (American Optical Corp.).

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