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Photochemical "Triode" Molecular Signal Transducer

Amy E. Keirstead,† James W. Bridgewater, Yuichi Terazono, Gerdenis Kodis, Stephen Straight, Paul A. Liddell, Ana L. Moore,* Thomas A. Moore,* and Devens Gust*

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

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Abstract: A molecular "hexad" in which five bis(phenylethynyl)anthracene (BPEA) fluorophores and a dithienylethene photochrome are organized by a central hexaphenylbenzene unit has been prepared. Singlet−singlet energy transfer among the BPEA units occurs on the 0.4 and 60 ps time scales, and when the dithienylethene is in the open form, the BPEA units fluoresce in the 515 nm region with a quantum yield near unity. When the dithienylethene is photoisomerized by UV light to the closed form, which absorbs in the 500−700 nm region, the closed isomer strongly quenches all of the excited singlet states of BPEA via energy transfer, causing the fluorescence quantum yield to drop to near zero. This photochemical behavior permits the hexad to function in a manner analogous to a triode vacuum tube or transistor. When a solution of the hexad is irradiated with steady-state light at 350 nm and with red light (>610 nm) of modulated intensity, the BPEA fluorescence excited by the 350 nm light is modulated accordingly. The fluorescence corresponds to the output of a triode tube or transistor and the modulated red light to the grid signal of the tube or gate voltage of the transistor. Frequency modulation, amplitude modulation, and phase modulation are all observed. The unusual ability to modulate intense, shorter-wavelength fluorescence with longer-wavelength light could be useful for the detection of fluorescence from probe molecules without interference from other emitters in biomolecular or nanotechnological applications.

Introduction

Many molecules can be converted to other forms quickly, easily, and reversibly by addition of chemicals or exposure to light, and this basic property has been used in the construction of multistate molecular switches that employ chemicals and/or light as inputs and outputs.[1−33] Such molecules may act as simple switches, Boolean logic gates, or more complex devices such as half-adders,[3,14,15,25,26,29,34−36] multiplexers and demultiplexers,[4,5,11] encoder−decoders,[6] and keypad locks.[7,28,37] Fluo-

† Present address: Department of Chemistry and Physics, University of New England, 11 Hills Beach Road, Biddeford, ME 04005.

(1) Andréasson, J.; Pischel, U. *Chem. Soc. Rev.* **2010**, *39*, 174–188.
(2) Gust, D.; Moore, T. A.; Moore, A. L. *Chem. Commun.* **2006**, 1169–1178.
(3) Andréasson, J.; Straight, S. D.; Kodis, G.; Park, C.-D.; Hambourger, M.; Gervaldo, M.; Albinsson, B.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2006**, *128*, 16259–16265.
(4) Andréasson, J.; Straight, S. D.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 958–961.
(5) Andréasson, J.; Straight, S. D.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Phys. Chem. C* **2007**, *111*, 14274–14278.
(6) Andréasson, J.; Straight, S. D.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2008**, *130*, 11122–11128.
(7) Andréasson, J.; Straight, S. D.; Moore, T. A.; Moore, A. L.; Gust, D. *Chem.−Eur. J.* **2009**, *15*, 3936–3939.
(8) Pina, F.; Melo, M. J.; Maestri, M.; Passaniti, P.; Balzani, V. *J. Am. Chem. Soc.* **2000**, *122*, 4496–4498.
(9) Balzani, V.; Credi, A.; Venturi, M. *ChemPhysChem* **2003**, *4*, 49–59.
(10) de Silva, A. P.; McClenaghan, N. D. *Chem.−Eur. J.* **2004**, *10*, 574–586.
(11) Perez-Inestrosa, E.; Montenegro, J. M.; Collado, D.; Suau, R. *Chem. Commun.* **2008**, 1085–1087.
(12) Pischel, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 4026–4040.
(13) Pischel, U.; Heller, B. *New J. Chem.* **2008**, *32*, 395–400.
(14) Qu, D. H.; Wang, Q. C.; Tian, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5296–5299.
(15) Remacle, F.; Weinkauf, R.; Levine, R. D. *J. Phys. Chem. A* **2006**, *110*, 177–184.
(16) Langford, S. J.; Yann, T. *J. Am. Chem. Soc.* **2003**, *125*, 11198–11199.
(17) Gunnlaugsson, T.; Mac Donaill, D. A.; Parker, D. *J. Am. Chem. Soc.* **2001**, *123*, 12866–12876.
(18) Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh, S. *J. Am. Chem. Soc.* **1996**, *118*, 1553–1554.
(19) de Silva, A. P.; McClenaghan, N. D. *Chem.−Eur. J.* **2002**, *8*, 4935–4945.
(20) Xu, H.; Xu, X.; Dabestani, R.; Brown, G. M.; Fan, L.; Patton, S.; Ji, H.-F. *J. Chem. Soc., Perkin Trans. 2* **2002**, 636–643.
(21) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2002**, *124*, 2004–2007.
(22) Raymo, F. M.; Giordani, S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941–4944.
(23) Saghatelian, A.; Volcker, N. H.; Guckian, K. M.; Lin, V. S. Y.; Ghadiri, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 346–347.
(24) Kompa, K. L.; Levine, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 410–414.
(25) Guo, X.; Zhang, D.; Zhang, G.; Zhu, D. *J. Phys. Chem. B* **2004**, *108*, 11942–11945.
(26) Margulies, D.; Melman, G.; Felder, C. E.; Arad-Yellin, R.; Shanzer, A. *J. Am. Chem. Soc.* **2004**, *126*, 15400–15401.
(27) Margulies, D.; Melman, G.; Shanzer, A. *Nat. Mater.* **2005**, *4*, 768–771.
(28) Margulies, D.; Felder, C. E.; Melman, G.; Shanzer, A. *J. Am. Chem. Soc.* **2007**, *129*, 347–354.
(29) Zhou, Y.; Wu, H.; Qu, L.; Zhang, D.; Zhu, D. *J. Phys. Chem. B* **2006**, *110*, 15676–15679.
(30) Niazov, T.; Baron, R.; Katz, E.; Lioubashevski, O.; Willner, I. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17160–17163.
(31) Suresh, M.; Jose, D. A.; Das, A. *Org. Lett.* **2007**, *9*, 441–444.
(32) Liu, Y.; Jiang, W.; Zhang, H. Y.; Li, C. J. *J. Phys. Chem. B* **2006**, *110*, 14231–14235.
(33) Szacilowski, K. *Chem.−Eur. J.* **2004**, *10*, 2520–2528.

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rescence is often employed as a particularly useful output for these devices,[38] and fluorescence switching has even been observed at the single-molecule level.[39] The use of light as the only inputs for molecular switching is especially attractive, as it does not rely on molecular diffusion for transport, can be used in rigid media, requires no physical access for addition of chemicals or wires, and does not produce byproducts that limit the cycling ability of the system. For these reasons, many of the molecular switches cited above employ photochromic compounds (photochromes) that can be photoisomerized between two metastable species. The photochromes may be used to control the photochemistry and photophysics of chemically attached chromophores. Photochromes can quench excited states via energy transfer or photoinduced electron transfer, act as relays to mediate energy transfer between chromophores, or modify the electronic coupling between chromophores, donors, and acceptors where the coupling occurs either through the linkage bonds or directly. These systems are usually studied as binary "on−off" devices, in analogy with digital computers. Although single molecules may exist only in discrete states, ensembles of molecules may show analog properties that are variable over a range of values. This suggests that molecular systems incorporating photochromic switches should be capable of acting as analog devices for controlling the properties of molecular ensembles. This effect was recently demonstrated by a self-regulating molecule[40] that functionally mimics the nonphotochemical quenching mechanism by which plants downregulate photosynthesis in the presence of bright sunlight. The molecule uses a photochrome to control the quantum yield of photoinduced electron transfer by quenching the singlet excited state of a porphyrin electron donor.

These results encouraged us to investigate new ways in which photochrome-containing molecules can perform functions inspired by those of analog electronic devices. In a triode vacuum tube, for example, the current flowing between a cathode and an anode (device output) is modulated by a voltage applied to a grid between the two electrodes. When a voltage waveform (e.g., a sine wave) is applied to the grid voltage, the current flowing between the cathode and anode is similarly modulated. A transistor is a more modern implementation of this principle: current flowing between the source and the drain is modulated by a voltage applied to the gate.

Here we report a molecular photochemical functional analogue of a triode tube or transistor, molecular hexad **1** (Figure 1). The hexad features five bis(phenylethynyl)anthracene (BPEA) fluorophores and a dithienylethene (DTE) photochromic switch organized by a central hexaphenylbenzene core. The hexaphenylbenzene is a relatively rigid structure that constrains the interchromophore distances and orientations. Hexad **1** may exist either as **1o** with the DTE in the open form, which absorbs light only at short wavelengths, or as **1c** with the DTE in the cyclic, closed form, which absorbs in the 500−700 nm region. Excitation of **1c** at 350 nm generates first excited singlet states of the BPEA moieties, which exchange excitation energy rapidly by singlet−singlet energy transfer. The 350 nm light also photoisomerizes to **1c** any **1o** that may be present. Although BPEA fluoresces in the 520 nm region, the fluorescence from all of the BPEA moieties in **1c** is strongly quenched by energy transfer to the closed DTE moiety. When the sample is concurrently irradiated with >610 nm light, some of the sample is photoisomerized to **1o**. The open DTE moiety in **1o** has no effect on the BPEA excited states, and strong fluorescence is observed from BPEA. Under steady-state illumination, the photostationary distribution of [**1o**] and [**1c**] (and therefore the BPEA fluorescence intensity) is a function of the relative intensities of the 350 nm and >610 nm illumination. Figure 2 shows the BPEA fluorescence intensity at 520 nm under conditions where the intensity of 350 nm light was held constant and the intensity of >610 nm light was sinusoidally modulated. The fluorescence at 520 nm was modulated in concert with the >610 nm light fluctuation. The molecule performed as a photochemical triode (transistor), where the >610 nm light played the role of the "grid" potential in a vacuum tube or the gate voltage in a transistor and the 520 nm fluorescence acted as the device output. The hexad is photochemically very unusual in that the intensity of short-wavelength fluorescence (520 nm) is modulated by irradiation into a transition at longer wavelength (>610 nm). This behavior, which is impossible to realize with a single chromophore, could be useful for signal discrimination

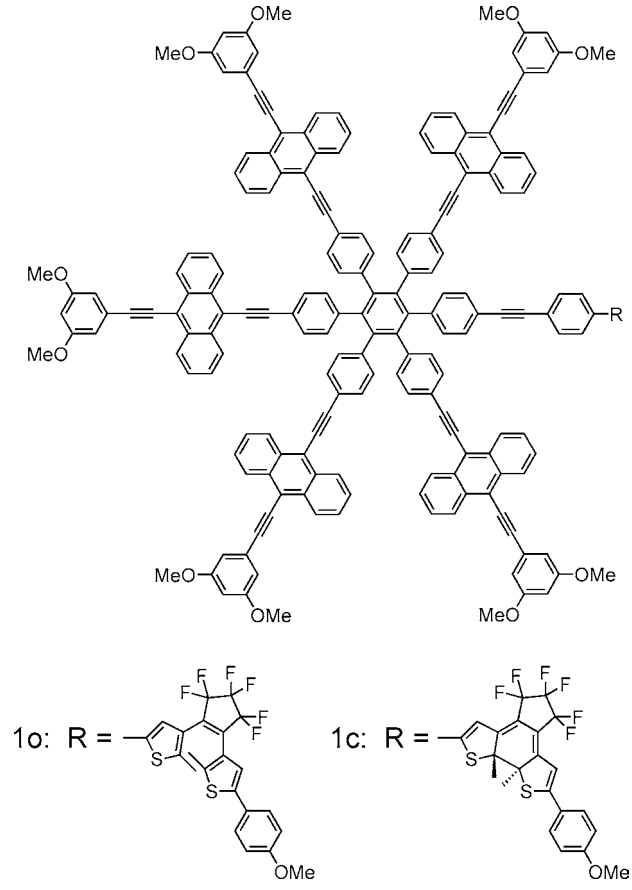

Figure 1. Structures of hexad **1o**, in which the DTE moiety is in the open form that does not absorb visible light, and **1c**, wherein the DTE is in the closed, cyclic form that absorbs in the 600 nm region.

(34) Andréasson, J.; Kodis, G.; Terazono, Y.; Liddell, P. A.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2004**, *126*, 15926–15927.
(35) de Silva, A. P.; McClenaghan, N. D. *J. Am. Chem. Soc.* **2000**, *122*, 3965–3966.
(36) Stojanovic, M. N.; Stefanovic, D. *J. Am. Chem. Soc.* **2003**, *125*, 6673–6676.
(37) Strack, G.; Ornatska, M.; Pita, M.; Katz, E. *J. Am. Chem. Soc.* **2008**, *130*, 4234–4235.
(38) Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327–336.
(39) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849.
(40) Straight, S. D.; Kodis, G.; Terazono, Y.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D. *Nat. Nanotechnol.* **2008**, *3*, 280–283.

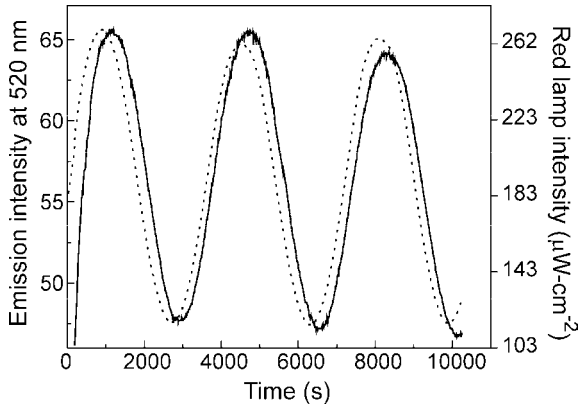

Figure 2. Fluorescence emission (arbitrary units) at 520 nm (solid line) from the BPEA moieties of **1** in 2-methyltetrahydrofuran solution ($\sim 3 \times 10^{-6}$ M). The fluorescence was excited by a steady-state light beam at 350 nm (6.0 μW cm^{-2}), which also drives photoisomerization of **1** toward a photostationary distribution enriched in **1c**. The sample was also irradiated with a beam at >610 nm (dotted line) that was modulated as a sine wave with a period of 3600 s.

in fluorescence detection for applications such as biomedical imaging or long-distance detection.

Results and Discussion

Synthesis. Hexad **1** was prepared by functionalization of hexakis(4-iodophenyl)benzene.[41] First, a single DTE was attached by palladium-catalyzed coupling of a suitable precursor.[42] The five BPEA moieties were then linked via palladium-catalyzed coupling of the DTE-bearing hexaphenylbenzene with 9-(3,5-dimethoxyphenyl)ethynyl-10-ethynylanthracene.[43] Model compounds were prepared using related methods. All of the new compounds were characterized by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. The details are given in the Supporting Information.

Absorption and Emission Spectra. Figure 3a shows the absorption and emission spectra of model BPEA **2** (Figure 4) in 2-methyltetrahydrofuran solution. The absorption spectrum features maxima at 309, 319, 445, and 469 nm, whereas the emission maxima are at 483, 515, and ~547 (sh) nm. The fluorescence quantum yield is 0.94.[44] Figure 3b shows the absorption spectra of model DTE **3** (Figure 4) in the same solvent. The open form of the molecule, **3o**, shows a maximum at 305 nm with no absorption in the visible. Irradiation of the solution of **3o** with UV light leads to photoisomerization, resulting in a solution with a photostationary distribution rich in the closed form **3c**, which features absorption in the visible with λ_{max} at 602 nm. Irradiation into the visible band converts **3c** back to **3o**.

Figure 5a shows absorption spectra of hexad **1** in 2-methyltetrahydrofuran. The spectrum of **1o** looks very much like that of model BPEA **2**, with maxima at 311, 320, 446, and 469 nm. The bands of **1o** in the 310−320 nm region have slightly different shapes than those of **2** because of the underlying absorption by the open DTE (see Figure 3a). After irradiation of the solution at 365 nm to convert the sample to a photostationary distribution containing mostly **1c**, the absorption spec-

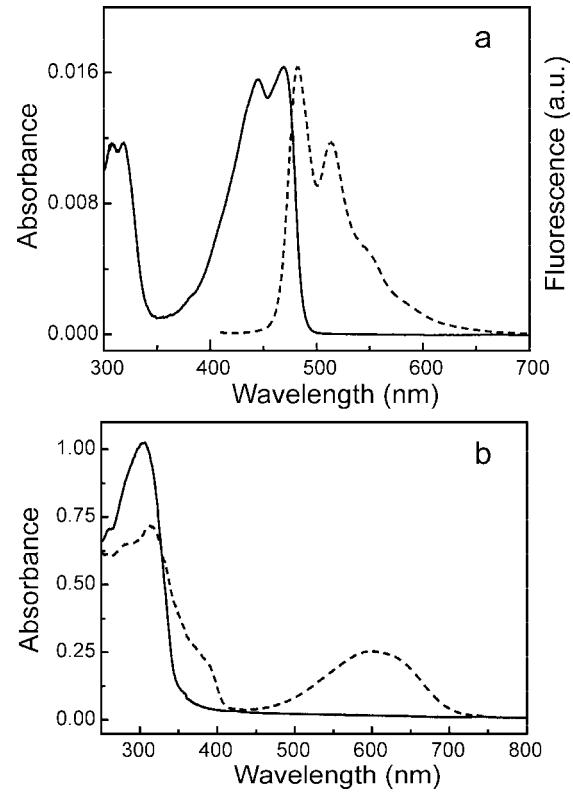

Figure 3. (a) Absorption (solid line) and emission (λ_{ex} = 400 nm, dashed line) spectra of a 2-methyltetrahydrofuran solution of model BPEA chromophore **2**. (b) Absorption spectra of a 2-methyltetrahydrofuran solution of model DTE chromophore **3** in the open (**3o**, solid line) and closed (**3c**, dashed line) isomeric forms.

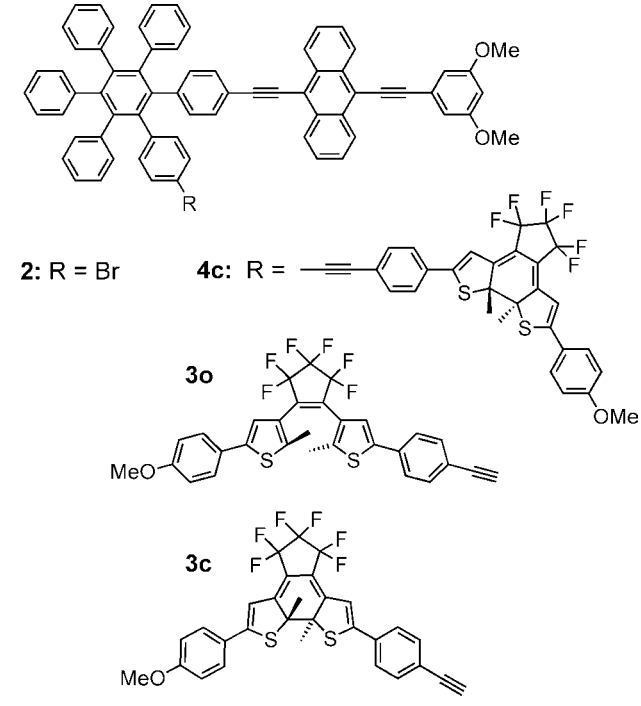

Figure 4. Structures of model BPEA **2**, model DTE **3** in the open (**3o**) and cyclic, closed (**3c**) isomeric forms, and BPEA−DTE dyad **4** with the DTE portion in the closed form (**4c**).

(41) Kobayashi, K.; Kobayashi, N.; Ikuta, M.; Therrien, B.; Sakamoto, S.; Yamaguchi, K. *J. Org. Chem.* **2005**, *70*, 749–752.
(42) Liddell, P. A.; Kodis, G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2002**, *124*, 7668–7669.
(43) Terazono, Y.; Liddell, P. A.; Garg, V.; Kodis, G.; Brune, A.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Porphyrins Phthalocyanines* **2005**, *9*, 706–723.
(44) Kodis, G.; Terazono, Y.; Liddell, P. A.; Andréasson, J.; Garg, V.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2006**, *128*, 1818–1827.

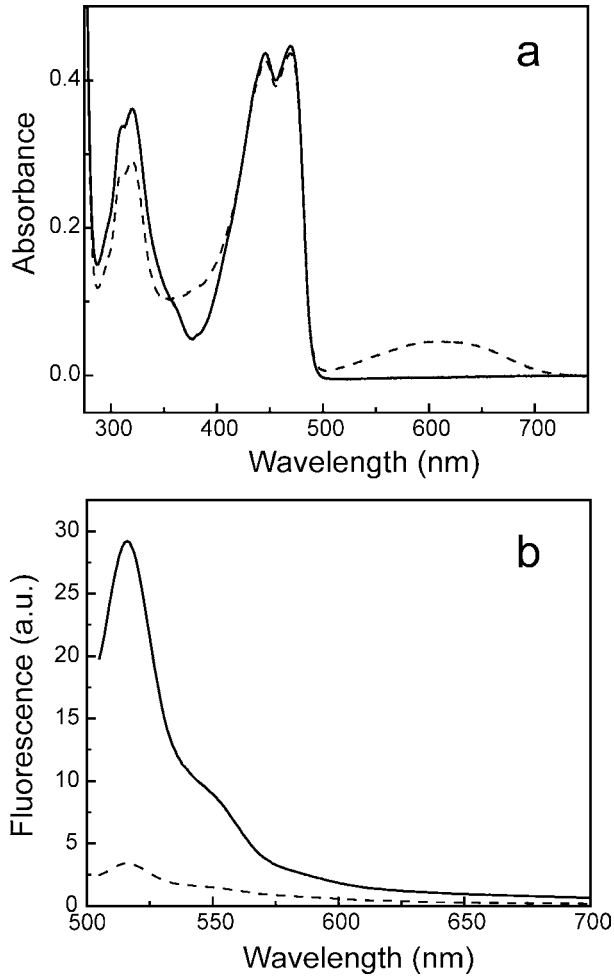

Figure 5. (a) Absorption and (b) fluorescence emission (λ_{ex} = 440 nm) of a 2-methyltetrahydrofuran solution of hexad **1** in the open form **1o** recorded after >610 nm irradiation to achieve a photostationary distribution (solid lines) and in a photostationary distribution highly enriched in the closed form **1c** (dashed lines).

trum shows some decrease in absorption in the 310−320 nm region and an increase around 375 nm. Most striking is the appearance of a broad new absorption band centered around 610 nm. These changes are all consistent with isomerization of the DTE moiety from open to closed (see Figure 3). Irradiation of the sample with visible (>610 nm) light causes the spectrum to revert to that of **1o**.

Figure 5b shows the fluorescence spectra in the 500−700 nm region for the solutions of **1** whose absorption spectra are shown in Figure 5a. The emission of **1o**, with a maximum at 514 nm and a shoulder around 547 nm, is essentially identical in shape to the 500−700 nm portion of the emission spectrum of model BPEA **2** shown in Figure 3a. After conversion of **1o** to a solution containing mainly **1c** by irradiation at 365 nm, the emission spectral shape did not change, but the intensity decreased by a factor of 8.5. This decrease is ascribed to quenching of the BPEA emission by the closed DTE moiety. Clearly, this large decrease indicates that the closed DTE quenches the emission from not only the two adjacent BPEA moieties but also the more distant BPEA groups. This is consistent with the occurrence of singlet−singlet energy transfer among the BPEA chromophores.

Time-Resolved Spectroscopic Investigations. In order to learn more about the interactions among the chromophores of **1**, time-

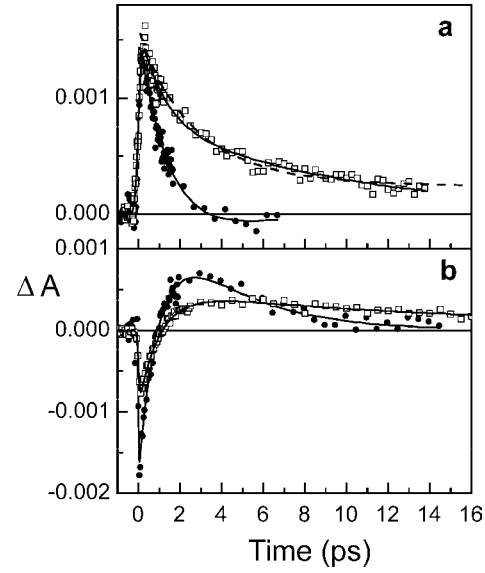

Figure 6. Transient absorption kinetics for hexad **1** and dyad **4** in 2-methyltetrahydrofuran solution. Samples were excited at 460 nm with ~100 fs laser pulses and irradiated continuously at 365 nm in order to maintain the samples in the closed forms (**1c** and **4c**). (a) Transients for **1c** (□) and **4c** (●) monitored at 630 nm. (b) Transients for **1c** (□) and **4c** (●) monitored at 515 nm. The solid lines show best fits of exponential processes to the data, and the dashed line in (a) shows the results of a simulation using a kinetic model (see the text).

resolved studies were performed. As reported previously,[44] the lifetime of the first excited singlet state of the model BPEA chromophore **2** is 2.80 ns, as determined by time-resolved fluorescence studies. The energy of the excited state, as estimated from the wavenumber average of the longest-wavelength absorption maximum and shortest-wavelength emission maximum, is 2.61 eV. The lifetime of the first excited singlet state of the closed form of the DTE model compound, **3c**, was previously reported to be 2.9 ps.[42]

Model BPEA−DTE dyad **4** (Figure 4) was investigated by transient absorption spectroscopy in 2-methyltetrahydrofuran solution. Figure 6 shows the transient absorption traces for hexad **1** and dyad model **4** in 2-methyltetrahydrofuran after excitation with a 460 nm, ~100 fs laser pulse. During these studies, the sample was continuously irradiated at ~365 nm in order to force most of the sample into the **4c** form. The data in Figure 6a were obtained at 630 nm. The transient for dyad **4c** shows prompt formation of the BPEA excited state and then rapidly decays to a negative value representing ground-state bleaching of the closed-form DTE (DTEc) moiety. The kinetics for **4c** at 515 nm show a prompt stimulated emission of BPEA (see Figure 6b) that decays to an induced absorption attributed to ^{1}DTEc. These data could be fitted to two exponential lifetimes of 1 and 3 ps. Similar studies on **4o** (and **1o**) obtained by irradiation of the sample at $\lambda > 610$ nm simply yielded transients that did not decay on the 16 ps time scale, which is consistent with the 2.80 ns lifetime of unperturbed ^{1}BPEA. The results for **4c** indicate prompt formation of ^{1}BPEA, which rapidly (1 ps) decays by singlet−singlet energy transfer to DTEc to yield ^{1}DTEc, which in turn decays with τ = 3 ps. This lifetime for ^{1}DTEc is consistent with that of model **3c**. The extremely short lifetime of ^{1}BPEA in comparison with that of **4o** shows that the quantum yield of energy transfer is essentially unity.

We now turn to the results for hexad **1c**, with the DTE moiety held in the closed form by UV irradiation as described above (Figure 6). The transients at 630 and 515 nm were in this case

fitted by three exponential components with lifetimes of 1, 3 (fixed in the fitting process), and 13 ps. The transient in Figure 6a corresponds mainly to decay of ^{1}BPEA with time constants of 1 ps (70% of the decay) and 13 ps (30% of the decay). We previously reported studies of the stimulated emission anisotropy decay of BPEA in a model BPEA dyad whose structure was similar to that of **2** but had the bromine atom replaced by a second BPEA unit.[44] We found that for 80% of the molecules, singlet−singlet energy transfer between BPEA units occurred with a time constant of 0.4 ps, whereas for 20% of the sample, the energy-transfer time constant was ∼60 ps. The minor 60 ps component was attributed to molecules in which the BPEA units were in conformations that were not favorable for energy transfer.

Given the results for the model compounds, we can interpret the data for **1c**. The majority of the BPEA excited states rapidly exchange excitation energy by singlet−singlet energy transfer on the subpicosecond time scale and then transfer the excitation energy to the DTEc moiety with a time constant of 1 ps. The DTEc excited state decays with a time constant of 3 ps. With a minority of the BPEA excited states, exchange of excitation energy is slower (∼60 ps) because of unfavorable orientations. The 13 ps lifetime observed for **1c** is attributed to decay of the BPEA excited states by this exchange process followed by a 1 ps transfer to an ortho DTEc, and perhaps by direct energy transfer to DTEc moieties meta or para to BPEA. This analysis is likely oversimplified in that the observed lifetimes actually represent data for a range of conformations and transfer time constants that are satisfactorily fitted by the three decay times. The dashed line in Figure 6a is the result of simulating the decay of the excited states of the BPEA units in **1c** with a kinetic model in which the time constants are drawn from studies of the model compounds: 0.4 ps for 70% of the BPEA exchange excitation energy, 60 ps for 30% of the BPEA exchange excitation energy, and 1 ps for transfer of singlet excitation to DTEc from the two BPEA moieties ortho to DTEc. The fit is well within the noise limits of the data. Thus, for hexad **1c**, all of the BPEA excited states decay by singlet−singlet energy transfer to DTEc, and the quantum yield of this energy transfer is essentially unity.

The results for **1c** obtained at 515 nm (Figure 6b) are consistent with the above interpretation. The majority of the BPEA stimulated emission decays with, and the DTE induced absorption appears to rise with, time constants of 1 and 3 ps. However, some of the DTE induced absorption appears to decay with a time constant of 13 ps. This unusual spectral behavior is an example of inverted kinetics, where a fraction of the DTE excited states decay more rapidly (3 ps) than they are formed (13 ps). In summary, the transient spectroscopy shows that hexad **1o** exhibits strong BPEA fluorescence with normal excited state lifetimes but that BPEA singlet excitation energy in hexad **1c** migrates from BPEA to adjacent BPEA chromophores and is ultimately quenched within a few picoseconds by singlet energy transfer to DTEc. The BPEA fluorescence is thus very strongly quenched in **1c**, as observed by steady-state fluorescence spectroscopy.

Photoisomerization. Photoisomerization of **1** due to the DTE moiety was investigated in order to determine suitable time scales for the photomodulation experiments. Thermal isomerization of **3o** and **3c** (or **1o** and **1c**) does not occur on the time scales of the experiments described here. The quantum yields for photochemical cyclization and ring opening of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, a model compound for **3**, are 0.68 and 0.013, respectively, in organic solvents.[45] The time constants for cyclization and ring opening of course depend on the irradiation wavelength and lamp intensity, and in the experiments reported here, the rate of stirring of the sample, which determines the percentage of time that a given molecule is exposed to the excitation beam. Under the experimental conditions employed in these studies, the BPEA fluorescence at 520 nm of a sample of **1o** in 2-methyltetrahydrofuran irradiated at 350 nm (6.0 μW cm^{-2}) decayed exponentially with a time constant of 328 s (Figure 7a). This decay represents the approach to a photostationary distribution of **1o** and **1c** via photochemical cyclization of **1o**. The BPEA fluorescence is quenched by energy transfer in **1c**, as discussed above. When a similar solution enriched in **1c** was irradiated at both 350 and >610 nm (117 μW cm^{-2}), a photostationary distribution enriched in **1o** was reached with $\tau = 247$ s (Figure 7b). Thus, for the experiments performed below, the time scale for photoisomerization to a photostationary distribution from either **1o** or **1c** was ∼5 min.

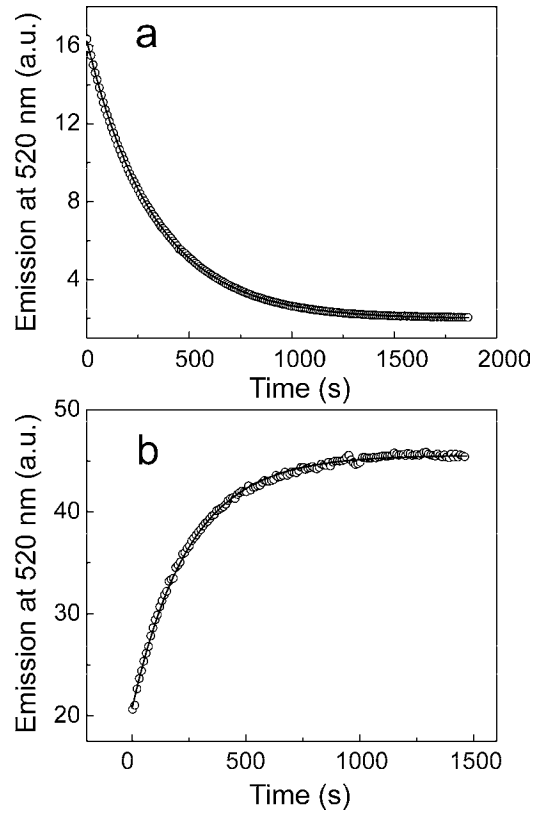

Figure 7. (a) BPEA fluorescence at 520 nm (○) of a sample of **1o** in 2-methyltetrahydrofuran (∼3 × 10^{-6} M) as a function of time during irradiation at 350 nm (6.0 μW cm^{-2}). The data were fitted to an exponential decay (solid curve) having a time constant of 328 s ($R = 0.999$). (b) Fluorescence at 520 nm (○) of a sample of **1** (∼3 × 10^{-6} M) highly enriched in **1c** in 2-methyltetrahydrofuran as a function of time during irradiation at 350 nm (6.0 μW cm^{-2}) and >610 nm (117 μW cm^{-2}). The data were fitted to an exponential rise (solid curve) having a time constant of 247 s ($R = 0.999$). In each case, a photostationary distribution of **1o** and **1c** was nearly achieved at the end of the irradiation period shown.

Modulation Experiments. The experimental setup included a cuvette containing a solution of **1** in 2-methyltetrahydrofuran that had been degassed by at least five freeze−pump−thaw cycles to remove oxygen and then sealed. The presence of

(45) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun.* **1999**, 747–748.

oxygen greatly accelerated sample photodecomposition. The sample was continuously illuminated with UV light at 350 nm from a fluorimeter in order to both induce fluorescence from BPEA and photoisomerize **1o** to **1c**. Photoisomerization is much more rapid with excitation in the 300 nm region (see Figure 3b), but photodecomposition[45] is also more rapid in this wavelength region. The sample was also illuminated at right angles to the 350 nm light beam with visible light >610 nm in order to induce photoisomerization of **1c** to **1o**. This light was generated by a quartz−halogen bulb and focused through a 610 nm long-pass filter into a fiber-optic cable. The variable intensity of this beam was computer-controlled via a custom-built feedback circuit that utilized a linear response photodiode to monitor the lamp intensity. This circuit ensured that the lamp intensity was proportional to a computer-supplied voltage (see the Supporting Information). The BPEA fluorescence was monitored at right angles to the two excitation beams using the fluorimeter monochromator at 520 nm and a 10 nm bandpass filter at 520 nm to further exclude stray light. Sample concentrations were $\sim 3 \times 10^{-6}$ M. For each experiment, the intensities of the 350 nm light and >610 nm light were adjusted to ensure that a significant amount of **1o** and **1c** were both present in the photostationary distribution.

Sine Wave: Frequency and Phase Modulation. One of the ways that information can be transmitted using radio-frequency radiation is via frequency modulation, in which information is carried by changes in the frequency of the wave. Figure 2 shows the BPEA fluorescence intensity at 520 nm as a function of time obtained when the >610 nm light was modulated as a sine wave with a period of 3600 s. The 350 nm light intensity was 6.0 μW cm^2, and the >610 nm light was modulated between 117 and 269 μW cm^{-2}. Emission and >610 nm irradiation data were collected every 10 s. The fluorescence output is a sine wave having the same period as the modulating beam. The intensity variations of the maxima and minima were mainly due to changes in the intensity of the 350 nm beam during the long irradiation period. It should be noted that there is a small (22°) phase shift between the modulation waveform and the emission waveform. If the period of the sine wave had been long enough that photoisomerization to a photostationary distribution had been rapid relative to the modulation period, then this phase shift would not have occurred. It is due to the fact that after each change in >610 nm lamp intensity, the photoisomerization to a new photostationary distribution does not quite "catch up" with the new lamp intensity before the intensity is changed again. This effect was more pronounced when the period of the modulation was decreased relative to the time required for photoisomerization to a photostationary distribution. Figure 8a shows a sine wave with modulation having a period of 960 s (350 nm irradiation at 5.6 μW cm^{-2}), for which the phase shift was 60°. Figure 8b shows a similar experiment using modulation with a period of 480 s; the phase shift increased to 258°. When the modulation period is short relative to the time required to reach a photostationary distribution, changes in the intensities at 350 or >610 nm can result in changes in the shape of the fluorescence output waveform as well as a phase shift. In communications, phase modulation is often used in remote-control units, for example.

Sine Wave: Amplitude Modulation. Information can also be transmitted via radio-frequency radiation by amplitude modulation of a sine wave. In hexad **1**, the fluorescence amplitude can be modulated by a unique mechanism: modulation of the >610 nm irradiation, which changes the average and waveform-driven

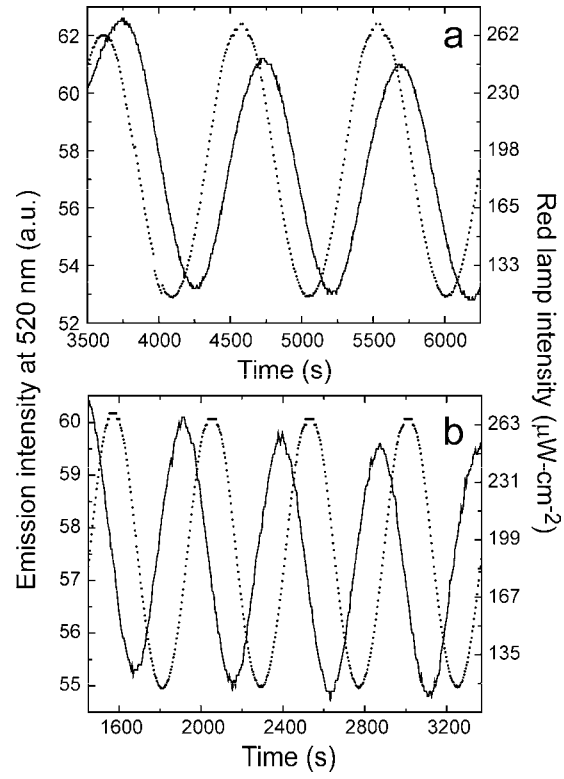

Figure 8. Frequency modulation. The fluorescence emission intensity (solid line) at 520 nm of a solution of hexad **1** in 2-methyltetrahydrofuran ($\sim 3 \times 10^{-6}$ M) is shown. The sample was excited by continuous irradiation at 350 nm (5.6 μW cm^{-2}). The sample was also irradiated by a light beam with $\lambda > 610$ nm whose intensity (dotted line) was modulated between 117 and 269 μW cm^{-2} by sine waves with periods of (a) 960 and (b) 480 s.

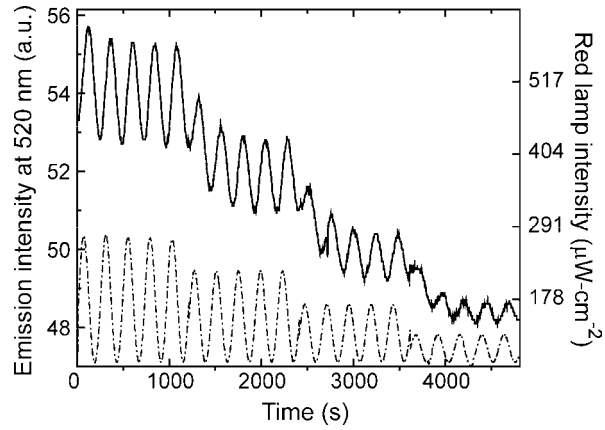

Figure 9. Amplitude modulation. The fluorescence emission intensity (solid line) at 520 nm of a solution of hexad **1** in 2-methyltetrahydrofuran ($\sim 3 \times 10^{-6}$ M) is shown. Fluorescence was excited by continuous irradiation at 350 nm (5.6 μW cm^{-2}). The sample was also irradiated by a light beam with $\lambda > 610$ nm whose intensity (dot-dashed line) was modulated with a sine wave having a period of 240 s. The intensity range of the modulating light was changed every five cycles to show the results of amplitude modulation.

population of **1c** and thus the emission intensity for a given intensity of 350 nm steady-state irradiation. An example is shown in Figure 9. In this experiment, the intensity of the 350 nm radiation was fixed at 5.6 μW cm^{-2}, and the >610 nm light was frequency-modulated with a period of 240 s. For the first five cycles, the >610 nm light was amplitude-modulated between 82 and 269 μW cm^{-2}, and then the modulation was changed to 82−223 μW cm^{-2} for five cycles, 82−166 μW cm^{-2} for five

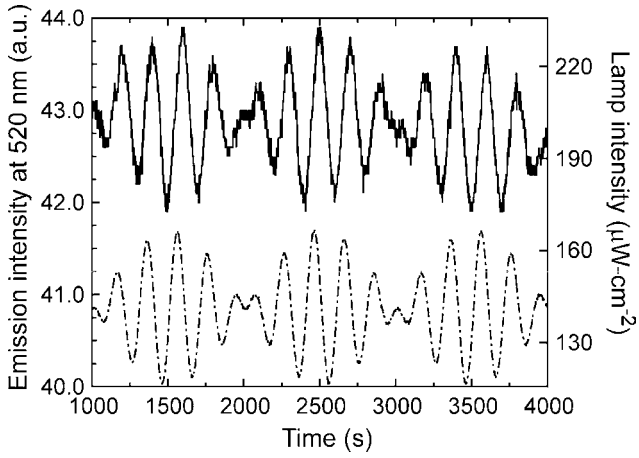

Figure 10. Amplitude modulation. The fluorescence emission intensity (solid line) at 520 nm of a solution of hexad **1** in 2-methyltetrahydrofuran ($\sim 3 \times 10^{-6}$ M) is shown. Fluorescence was excited by continuous irradiation at 350 nm (5.6 μW cm^{-2}). The sample was also irradiated by a light beam at >610 nm whose intensity (dot-dashed line) was modulated with the product of two sine waves, one having a period of 200 s and the other having a period of 2000 s.

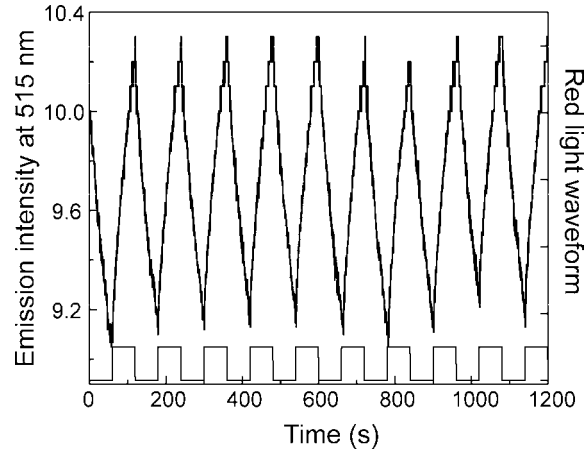

Figure 11. Square-wave modulation. The fluorescence emission intensity (upper line) at 515 nm of a solution of hexad **1** in 2-methyltetrahydrofuran ($\sim 3 \times 10^{-6}$ M) is shown. The solution was illuminated with steady-state 350 nm excitation at 6.0 μW cm^{-2} and with >610 nm light whose intensity was modulated between 0 and a high intensity ($\sim$300 μW cm^{-2}) with a period of 1 min on followed by 1 min off (lower line).

cycles, and finally 82−117 μW cm^{-2} for 5 cycles. With each change in average modulated lamp intensity, the average emission intensity decreased accordingly because of the decrease in the amount of **1o** present at and near the photostationary distribution. In addition, the degree of amplitude modulation of the emission sine wave decreased because the smaller variation in intensity of the modulating light gave rise to a smaller change in the isomer ratio in the photostationary distribution.

Figure 10 shows another amplitude modulation experiment that employed a waveform with a period of 2000 s modulating a "carrier" waveform with a period of 200 s. The 350 nm steady-state irradiation was at 5.6 μW cm^{-2}, and the modulated waveform at >610 nm varied from 117−166 μW cm^{-2}. The overall shape is reminiscent of an amplitude-modulated radio transmission in which the information is carried by the amplitude modulation of the fixed-frequency carrier wave.

Square-Wave Modulation. Square-wave modulation of the >610 nm light beam featured "instantaneous" switching of the intensity of this beam, and thus, the photoisomerization to a photostationary distribution did not occur rapidly enough to track the change in long-wavelength light intensity. Figure 11 shows the results of an experiment in which the sample was irradiated with steady-state 350 nm light at 6.0 μW cm^{-2} and with >610 nm light whose intensity was modulated between 0 and a high intensity ($\sim$300 μW cm^{-2}) with a period of 1 min on followed by 1 min off. When the >610 nm light was turned on, only **1c** absorbed, resulting in a net photoisomerization to increase the concentration of **1o** and therefore the fluorescence intensity at 515 nm. When the >610 nm light was then turned off, the steady-state 350 nm radiation drove the system to an increased concentration of **1c**, with consequent quenching of fluorescence at 515 nm. Changing the intensity of one of the irradiation beams could alter the waveform to yield a variety of triangular or sawtooth forms.

Unique Features, Limitations, and Possible Applications. It is clear from the above results that hexad **1** can operate as a kind of molecular photochemical "triode tube" or transistor wherein modulation of one input (red light) modulates the fluorescence output excited by a second, steady-state input (blue light). Although it might at first seem that a similar result could be easily accomplished by simply modulating the light beam that excites fluorescence, the hexad operates in a fundamentally different way. In **1**, fluorescence excited through light absorption by a shorter-wavelength electronic transition is modulated by light absorbed by a second, longer-wavelength transition. Such a result is thermodynamically precluded in a single-chromophore system or a multichromophoric system in which energy is simply transferred from one moiety to another. It can occur in **1** because the long-wavelength transition modulates the population ratio of the two isomeric forms of the DTE, only one of which quenches BPEA fluorescence. This unique mode of operation also allows the generation of an output waveform that is phase-shifted relative to the modulating waveform or even has a different shape. Simple modulation of the light exciting a fluorophore cannot accomplish these things.

The phenomena described here might be useful in a variety of detection and labeling applications. In biomedical imaging, for example, fluorescence detection of a labeling chromophore can be very sensitive, but interference and noise are often introduced by extraneous background light at the emission frequency or by emission (fluorescence, phosphorescence) from materials other than the label that are excited by the probe light (sometimes called "autofluorescence"). Although interference from background light may be reduced by detecting fluorescence in-phase with a modulated probe light, this does not discriminate against emission from materials in the sample other than the label. The fluorescence of a label having the properties of **1**, however, would be modulated by light of a wavelength longer than that of the steady-state probe beam that excites fluorescence. Thus, the modulation and phase-sensitive detection would discriminate not only against steady-state background light but also against all fluorescence by interfering materials, because any such materials would necessarily emit at wavelengths longer than that of the modulating beam that excites them. (Two-photon excitation of a fluorophore could partially discriminate against interfering fluorescence to the extent that the interfering materials had small cross sections for two-photon absorption.) Similar advantages could be gained by using this approach for fluorescence detection of labeled micro- or nanoparticles or for fluorescence detection at large distances in the presence of a

variety of interferences. Although the experiments reported above featured only modulation of the long-wavelength light beam, various other combinations of frequency and amplitude modulation could be achieved by modulating both the shorter- and longer-wavelength input beams. For example, in an amplitude modulation experiment, one beam could provide carrier modulation and a second beam the signal modulation. Also, in the experiments described here, the short-wavelength (350 nm) input served to both photoisomerize the photochrome and excite fluorescence of the BPEA moieties. This was done only for convenience, and in the more general case, two inputs would drive photoisomerization and a third would excite fluorescence. Any combination of these could be modulated to achieve complex data manipulation and transmission.

Although **1** illustrates possibilities for practical application of the phenomena described, the hexad has several properties that make it less than ideal. One of these is the time scale for photoisomerization to a photostationary distribution, which determines the upper limit to the modulation frequency. The rate of approach to a photostationary distribution is a function of the quantum yield of each photoisomerization, the extinction coefficient of each isomer at the irradiation wavelength, and the intensity of the two irradiation beams. In principle, the irradiation beams could be made arbitrarily intense, in order to drive the approach to a photostationary distribution arbitrarily rapidly. In practice, this would require not only potentially very intense irradiation but also very high photostability. The DTE photochrome in **1** degrades relatively rapidly under UV irradiation in the presence of oxygen. This can be minimized by deoxygenation, but there is residual degradation by the UV light due to photoisomerization that leads to an inert byproduct.[45] This is not apparent in the data shown here but comes into play when the modulation experiment is extended significantly. There are other DTE chromophores that are much more resistant to photodegradation than the one used in **1**.[46] In most photochromes, UV light is much more likely to lead to photodegradation than longer-wavelength irradiation. Thus, another solution to the degradation problem would be to use a photochrome that is thermally stable in and rapidly thermally isomerized to the long-wavelength absorbing form. For such a system designed with a fluorophore that is excited by visible irradiation, UV irradiation could be avoided completely.

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Supporting Information Available: Experimental details of the synthesis and spectroscopic investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.