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Ultrafast kinetics of 9-decylanthracene photodimers and their application to 3D optical storage

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The intermediate states and final product of the photoreaction of 9-decylanthracene monomer and photodimer have been identified and their formation and relaxation pathways and rates determined. In addition, these molecules have been used as media for high density 3D optical storage devices.

Introduction

The extremely large amounts of data that need to be stored and accessed at very fast rates are being limited by the memory capabilities as much as by interconnects and processors. Because of the huge data storage requirements, which continuously increase, and the rather mandatory need for parallel accessing, the need for compact, very high capacity parallel accessing, low cost memory devices is becoming very acute.

One means for satisfying most of these requirements is provided by three-dimensional storage. The main research methods, which are pursued now, that may lead to practical 3D-storage memory devices, are phase holograms[1,2] and two photon optical 3D memories. These devices utilize inorganic photorefractive crystals and photopolymers in the case of holography[1,2] and organic[3–7] or biological molecules such as bacteriorhodopsin[8–11] dispersed in polymer matrices.

In this paper we will be concerned with the photoreaction kinetics of 9-decylanthracene photodimers and the application of this data to 3D memory devices by means of two photon absorption. In previous papers we have presented the basic theory of two photon excitation and the means for utilizing such nonlinear processes for storing information within the volume of a 3D memory device.[3–5] Briefly, the two photon absorption process shown in Fig. 1(a) causes a ground-state molecule, in the unwritten form, to be promoted to the first excited electronic state by the simultaneous absorption of two photons. The energy required to reach the excited state is greater than the energy of either photon alone, therefore each beam propagates through the memory volume without being absorbed. When the sum of the energies of these photons is equal to or greater than the energy gap between the ground and first electronic excited states of the molecule (see Fig. 1(a)) at the point of the intersection of the beams, within the volume, the two photons may be absorbed simultaneously. The excited molecule decays and is transformed into a different ground-state molecular structure, which becomes the written form of the 3D molecular memory device. This new molecular structure absorbs at longer wavelengths than the original ground-state molecules, and therefore it may be excited by one or two photons of lower energy than those absorbed by the original, unwritten form molecules. The written excited state molecules fluoresce and detection of the induced fluorescence is used for accessing the stored information. It is, therefore, possible to access any bit of information within the volume by simply intersecting two beams at the place where the information bit to be retrieved is located. This process is shown schematically in Fig. 1(b). For fast parallel information transfer of an entire 2D plane, located within the volume of the 3D device, a single photon process is used to illuminate this plane, see Fig. 1. To achieve a high density storage and be suitable for use in 3D storage devices the photochromic materials used should fulfil several requirements, including: high nonlinear absorption cross-section; stability in both write and read states; high solubility in the polymer matrix; the written form should have a high fluorescence quantum efficiency and fluorescence in an easily detected region.

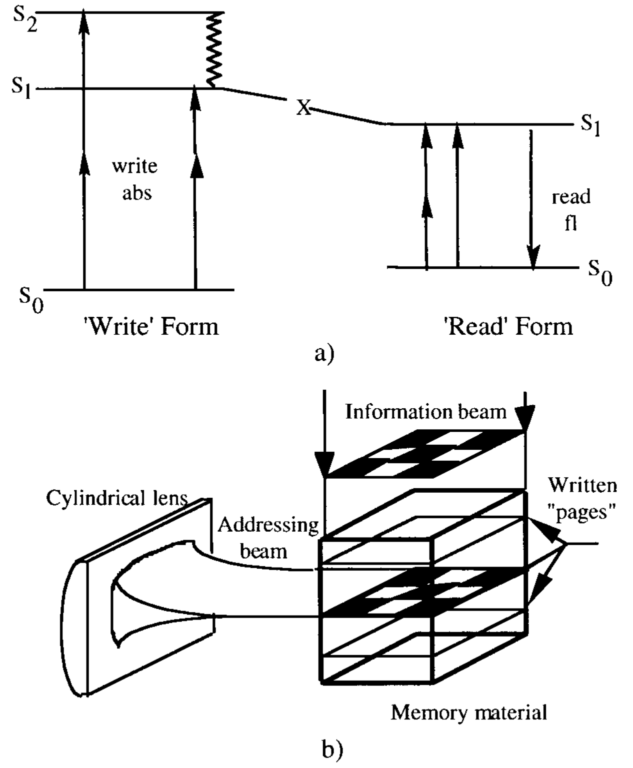


Fig. 1 a) Energy level diagram; b) writing of information in 3D by two-photon absorption.

We have shown previously[5] that photo-induced reversible photodimerization of anthracene and 9-methylanthracene fulfil quite well most of these requirements except that they do not dissolve sufficiently well in PMMA [poly(methyl methacrylate] and other polymer matrices. This difficulty has been eliminated because we have been able to synthesize 9-*n*-decylanthracene which, as we anticipated, exhibits photochromism and in addition is quite soluble in polymer matrices, thus being a promising material for optical switching and 3D memory devices.

Here we present the ultrafast kinetics of this new photochromic material, which is based on the reversible photodimerization of 9-*n*-decylanthracene dispersed in PMMA. In addition to the basic science information regarding the mechanism of the photo-transformation of this material, we found that the photo-induced dimers of this substituted anthracene fulfil most of the requirements for use as a 3D computer memory material.

Experimental

A double beam Shimadzu UV160U spectrophotometer and a Shimadzu RF 5000U spectrofluorophotometer recorded the ground state absorption and fluorescence spectra respectively. A 'Quantel' Nd/YAG laser generated 30 ps, 1064 nm pulses, which were converted to 532 nm pulses and used for two-photon excitation. The ultrafast kinetics, transient absorption spectra and mechanism, presented here, were studied by the ultrafast experimental system described previously.[5]

The materials used for the synthesis of the photodimer and all solvents were Aldrich spectroscopic purity grade. 9-Decylanthracene (white crystals with a blue fluorescence, mp 44 °C) was synthesized using the method described in ref. 12 and purified by column chromatography (silica gel; eluent: pentane). ^{1}H NMR δ (CCl_4): 0.85–0.95 (t, 3H, A-$(CH_2)_9$-CH_3), 1.25–1.5 (m, 2H), 1.5–1.65 (m, 2H), 1.7–1.85 (m, 14H), 3.5–3.6 (m, 2H, benzylic: A-CH_2-$(CH_2)_8$-CH_3), 7.35–7.45 (m, $4H_{Ar}$), 7.85–7.95 (m, $2H_{Ar}$), 8.15–8.25 (m, $3H_{Ar}$). ^{13}C NMR δ ($CDCl_3$): 14.3(CH_3), 22.9, 28.3, 29.6, 29.8, 29.9, 30.6, 31.6, 32.1 (-$(CH_2)_9$-), 124.6, 124.9, 125.4, 125.6, 129.4 (CAr-H), 129.7, 131.8, 135.6 (quaternary C). HRMS: (AutoSpec EQ FAB$^+$) $C_{24}H_{30}$ calc: 318.234751, found: 318.234305.

The anthracene photodimer was generated by irradiation with $\lambda > 320$ nm light emitted by a 150 W arc Xenon lamp, for 48 h, of a deaerated saturated hexane solution of 9-decylanthracene (≈ 25 mg cm^{-3}). The white solid precipitate was collected, washed with fresh solvent and dried. It was shown by NMR that the head-to-tail photodimer was the sole photoproduct formed.[13,14]

Thin polymer films of 9-decylanthracene photodimers dispersed in PMMA were prepared by pouring a solution of the photodimers and PMMA in 1,2-dichloroethane on the surface of a microscope slide. The slide was then spin-coated, resulting in a 20 µm thickness uniformly distributed polymer film.

Results and discussion

1. Ultrafast kinetics

The process of reversible photodimerization and photodissociation of polycyclic aromatic hydrocarbons such as anthracenes may be used for developing photochromic materials,[13–15] which may also prove to be suitable for optical switching and as 3D optical storage memory media.[3,5] The photodimers were formed by excitation of the corresponding monomer with 355 nm laser light.

The reverse process occurs when the photodimers are exposed to 266 nm UV radiation. Reversibility is a very desirable property, because it makes this molecular system suitable for application to re-writable memory disks and photonic switching. We have also studied the dissociation kinetics and intermediates of this 9-anthracene derivative dimer photoreaction. The solubility of the photodimer in MMA was measured to be about 30 mg cm^{-3} ($\sim 5 \times 10^{-2}$ M). This high solubility in MMA makes possible the fabrication of solid PMMA blocks with homogeneously dispersed dimer molecules at the concentrations which are required to store high density of information in 3D volume.

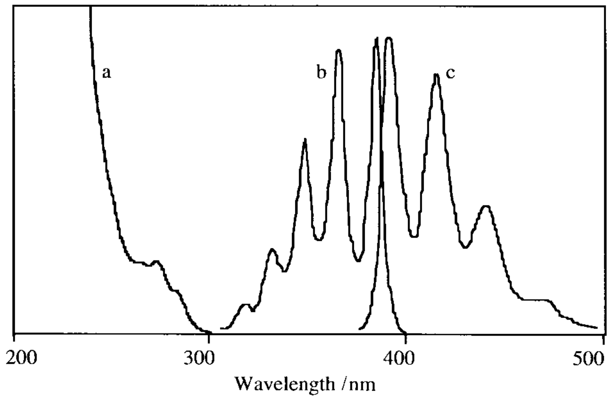


Fig. 2 Absorption spectra of a) photodimer, b) long wavelength contribution of monomer and c) fluorescence spectrum of 9-decylanthracene (monomer) in 1,2-dichloroethane solution, at room temperature, conc. $\approx 10^{-4}$ M.

The absorption spectra of the monomer and photodimer are shown in Fig. 2. The monomer has its long wavelength absorption band in the 300–400 nm region, while the photodimer is blue shifted and has practically no absorption at wavelengths longer than 300 nm. The photodissociation of this product results in the regeneration of the monomer, which is a conjugated double bond system and therefore exhibits a red shifted absorption band. The monomer of 9-decylanthracene was found to fluoresce in the 380 to 450 nm region, see Fig. 2. The fluorescence quantum yields of the monomer in ethyl acetate and 1,2-dichloroethane solutions were measured to be $\phi_F = 0.35$ and $\phi_F = 0.70$ respectively; the standard used for the calibration of the quantum yield was a solution of dimethyl POPOP in cyclohexane, which is known to emit with a quantum efficiency of 0.93.[16] The photodimer does not fluoresce at room temperature.

The formation and photodissociation mechanism of anthracene photodimers and related compounds has been extensively investigated previously.[14,17–26] Anthracene and its derivatives may form the corresponding photodimers after excitation of the monomer to its first singlet excited state[14] and the subsequent interaction of two monomers. When the photodimers are excited to the first allowed electronic state it may be shown that some of them may dissociate adiabatically *via* intermediate excimer formation.[5,17–19,22] It has also been reported that at low temperature (77 K) the first excited triplet state becomes the dominant channel for the photodimer dissociation.[22]

Studies of 9-decylanthracene–1,2-dichloroethane solutions, by means of ultrafast absorption spectroscopy, show that after excitation with a 355 nm, 30 ps laser pulse, short lived intermediates are formed which are characterized by the absorption spectra, shown in Fig. 3. Three new absorption bands with maxima at 560, 600 and 700 nm appear immediately after excitation. Comparison of this transient spectrum with the spectrum observed for anthracene and 9-methylanthracene[5,27] strongly suggests that this transient spectrum detected may well be the first excited singlet state of 9-decylanthracene. This transient singlet state decays with a lifetime of about 7 ns, while the new absorption band at $\lambda = 430$ nm is formed with the same rate; this process is shown in Fig. 3. It is known[28] that the triplet–triplet absorption spectrum of anthracene has a band at 430 nm and it seems reasonable therefore to assume, that the observed absorption band belongs to the triplet excited state, formed by relaxation of the excited singlet state *via* the intersystem crossing. A transient with absorption at 430 nm

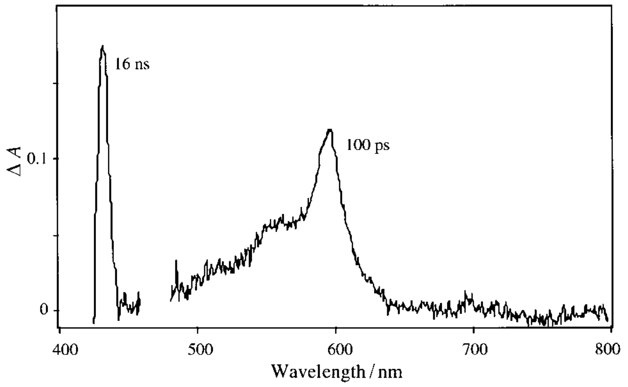


Fig. 3 Transient absorption spectra of intermediates formed by 355 nm, 30 ps excitation of the monomer, measured at 100 ps and 16 ns after excitation pulse; the lifetime of the shorter transient (5–10 ns) was determined by measuring the signal intensity *vs.* time delay (not shown here). The longer transient (430 nm) was assigned to the monomer triplet excited state.

was also observed for anthracene and 9-methylanthracene,[5] which was also formed with the same rate as the rate of 9-decylanthracene. We propose, therefore, that the photoreaction mechanism of 9-decylanthracene in 1,2-dichloroethane solutions follows the $S_0 + h\nu \rightarrow S_1 \rightarrow S_0 + T_1$, $T_1 \rightarrow S_0$ relaxation, which is very similar to the mechanism for anthracene and 9-methylanthracene.

Excitation of the photodimers in 1,2-dichloroethane solution with a 266 nm, 30 ps pulse leads to the formation of a transient with a broad absorption spectrum shown in Fig. 4. This spectrum is also similar to the one observed for anthracene and 9-methylanthracene and assigned to excimer formation.[5] This excimer decays with a lifetime of about 7 ns, while the characteristic absorption band of the monomer triplet excited state at $\lambda_{max} = 430$ nm is formed with the same rate, Fig. 4. The appearance of the monomer triplet–triplet absorption band at 430 nm suggests that the excimer dissociates adiabatically with formation of a monomer molecule in the excited state. It has been shown previously,[17–22] that the dissociation reaction of the photodimer at room temperature proceeds *via* the S_1 excited state. It was also observed, by means of time resolved fluorescence,[17] that monomer molecules were formed in the S_1 state during the photodissociation of the dimer. Based on the very strong similarity of the transient spectra and ultrafast kinetics found in this study for 9-decylanthracene to those of anthracene and 9-methylanthracene studied earlier,[5] we feel confident to propose the mechanism shown in Scheme 1 for the photodissociation process of 9-decylanthracene photodimers.

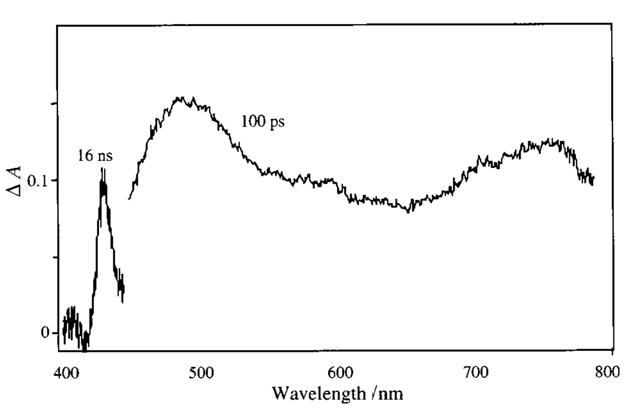
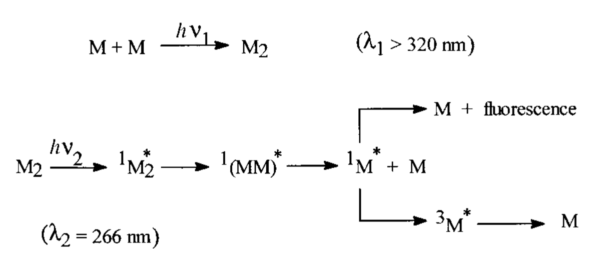


Fig. 4 Transient absorption spectra of intermediates formed by 266 nm, 30 ps excitation of the photodimer, measured at 100 ps and 16 ns after excitation pulse. The excimer lifetime (100 ps delay spectrum) was found to be 5–10 ns by measuring the signal intensity *vs.* time delay (not shown here). The signal at 430 nm was assigned to the monomer triplet excited state.



Scheme 1

2. Application to 3D storage devices

It has been shown previously[3,29] that by means of two photon virtual absorption it is possible to write several greater than 100 Mbit disks inside a 2 cm^3 volume, with a bit size of ~ 5 μm in diameter. It is possible, however, to store spots less than 0.5 μm. For 0.5 μm spots more than 1 Tbit can be stored in 1 cm^3. Practical devices using the two photon method for writing and one photon for reading have been demonstrated.[29]

We have demonstrated that we can write and read information, in 3D space, using 9-decylanthracene dimer dispersed in a PMMA matrix. To achieve this we have utilized two SHG 532 nm, 30 ps laser pulses, generated by a Nd/YAG picosecond laser, propagating in the optical path shown in Fig. 1. One of the 532 nm beams is passed through a glass slide which contained the information image that was to be stored inside the bulk of the optical memory device, in this case a PMMA cube into which the photodimer is dispersed uniformly. The image on the glass slide was focused into a 5 mm × 5 mm 2D plane inside the 9-decylanthracene dimer–PMMA cube. The 532 nm beam carrying this information is not absorbed because the 9-decylanthracene photodimer does not absorb at this wavelength. However, when it intersects the other 532 nm beam, which propagates orthogonal to the first beam, inside the bulk of the cube, absorption by the 9-decylanthracene photodimer molecules takes place, resulting in the formation of monomers. In computer terminology the zero (dimer) is converted to one (monomer) by two photon absorption. Consequently, the image is stored in the area where the two beams intersected. The entire image contained on the glass slide was written simultaneously. In Fig. 5 we show the image of the USAF resolution target written by two-photon absorption of two 532 nm, 30 ps, 3 mJ cm^{-2} beams. Reading the stored information was achieved by one photon excitation of the monomers of a single 2D plane, within the cube, with a thin plane of light, which illuminates only one written plane, and subsequently detecting the fluorescence of the monomer with a 2D charge coupled device. The readout is not destructive because it is based on monomer fluorescence.

A rather high concentration is desirable in order to increase the two photon absorption. Also a high concentration of the written molecules will result in higher emission intensity and therefore will be more easily detected. We were unable to detect a similar image using 9-methylanthracene photodimers under the same writing conditions, owing to the low solubility, hence concentration, of this molecule in the polymer host. The advantage of the 9-decylanthracene photochromic material is that a high density of information can be stored because of the high concentration of 9-decylanthracene that can be dissolved in the polymer matrix. In addition the information can be stored indefinitely because of the high stability of both photodimer and monomer forms at room temperature.

Fig. 5 USAF Resolution target image written in 9-decylanthracene photodimer–PMMA. Stored by two-photon excitation using 532 nm pulses. Accessing by a single, 370 nm, photon process.

Conclusion

The ultrafast kinetics of the photoreaction of 9-decylanthracene monomer and photodimer have been measured including the rates of decay and formation of the various states and relaxation pathways. The transient spectra of the intermediate states have been recorded and assigned. In addition, these molecules have been used as optical storage media for recording and accessing information in 3D storage devices.

Acknowledgements

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