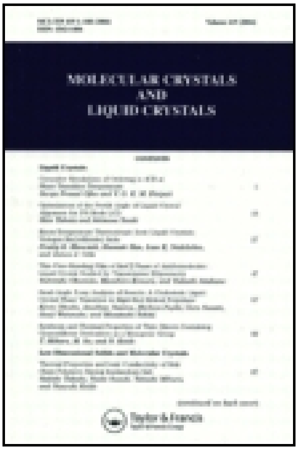

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Diarylethenes with Electro-active Substituents for Optical Memories: A Theoretical Study and the Realization of a Memory with a Readout in the Mid Infrared

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Diarylethenes with Electro-active Substituents for Optical Memories: A Theoretical Study and the Realization of a Memory with a Readout in the Mid Infrared

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Since photochromic molecules occur as two stable forms, they can be used to make optical memories. The readout process must preserve the information stored and can be carried on by using mid-IR light and exploiting the differences in the IR spectrum between the two forms. Three diarylethenes with different electroactive lateral substituents have been studied theoretically (B3LYP 6-31G**) to understand the effect of the substituent on the difference in absorbtion intensities of the vibrational spectrum. Calculations show that the presence of a donor group in the molecule enhances the absorbtion intensity of some normal modes of the molecule in the closed form. The molecule with a donor side group has been synthesized, a film was deposited on a substrate, a simple setup with a multibolometer camera has been built and patterns written on the film were read.

Keywords: DFT; diarylethenes; infrared spectroscopy; optical memories

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INTRODUCTION

The field of information storage is becoming more and more important because the quantity of data to be stored is increasing due to large use of computers and the development of information technology. In this field, optical memories become important devices and their storage capacity has been increased enormously in last ten years. Optical memories which use molecules with peculiar properties overcome some of the problems which affect the standard memories (thermal threshold, resolution). In this case, the single molecule carries the information, then, theoretically, the density and precision can substantially increase.

Photochromic molecules are good candidates for this purpose. Based on the fact that the two stable forms have different colors, it is possible to use visible light to write the information and the UV light to erase them. The problem is the readout process since any erasing of the information must be prevented during this process. Different approaches have been proposed to solve this problem, such as the use of gated photochromism [1], photocurrent detection [2] or low power reading laser using photochromic molecules with very low ring opening quantum yield. As alternative a mid-infrared readout method can be used [3–5], where IR photons can be used to read the information stored, without causing any molecular rearrangement because of their low energy.

Considering the last case, we studied some diarylethene molecules bearing electroactive lateral substituents in their two isomer form to evaluate the effect on the physico-chemical properties and in particular on the absorption intensity in the infrared. The structure of the three dithienylethenes bearing different substituents in 5,5′-position is reported in Figure 1. They are characterized by a good cyclization quantum yield and a high conversion rate [6].

The side groups in para position of the benzene ring are: −H (daeph), a −O−CH3 donor group (daeome) and a −CN withdrawing group (daecn).

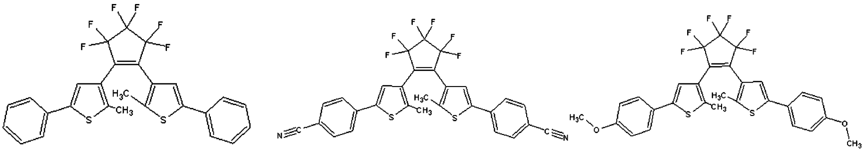

FIGURE 1 Chemical structure of the three molecules: daeph, daecn and daeome.

As for the infrared absorption intensity for conjugated molecules, becomes important the contribution of the charge flux especially if electron donating and electron withdrawing groups are present at the same time in the molecule structure [7].

To choose the best of the three diarylethenes for applying the mid-IR readout method, a theoretical study was carried out.

THEORETICAL RESULTS

The calculations were DFT B3LYP with a basis set 6–31G** and they were performed with Gaussian98 software [8]. The geometry optimization and the vibrational properties were computed for all the molecules in the two different photochromic structures. Moreover, the geometry optimization was carried out without symmetry constrains.

As an example in Figure 2 we report the calculated and experimental infrared spectra of the daeome molecule to show the differences in the spectra between the two forms.

DFT calculations provide a very acceptable prediction of the spectra of the diarylethene both in the open and in the closed forms. As seen in Figure 2, the changes in intensity occur in the region between 1400 and 1600 cm^{-1}, where the normal modes involve the collective stretching of the conjugated double bonds.

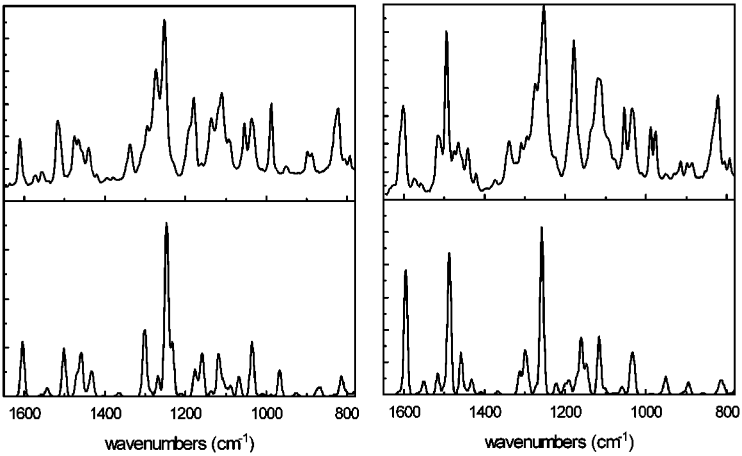

FIGURE 2 Infrared spectra of the open (left) and closed (right) forms of the daeome: experimental (upper panels) and theoretical (lower panels). Two strong bands appear in the closed form.

Considering the infrared intensity, it is originated from the change of molecular electrical dipole moment during a given vibration and the normal mode involved:

$$I_{IR} = \left[\frac{\partial \mu}{\partial R} \times L_R\right]^2$$

where μ is the total molecular dipole moment, R is the "internal coordinate" and L_R the eigenvectors in the R space derived from the calculation.

If we compare (see Fig. 3) the change of $d\mu/dR$ between the open form and the closed form of the CC stretching for the three molecules, we notice that deaome shows the largest increment especially for the bonds of the phenyl ring. On the other hand for the deacn, the changes are very small and even negative for the same bonds.

It means that when the photochromic molecule switches between the open to the closed form, the rearrangement of double bonds allows the perfluorocyclopenthene ring (a withdrawing group) to feel the side group attached to the benzene ring. In the case of deaome, the new structure is a donor-acceptor which turns into an increment of charge flux; in deacn, the structure is acceptor-acceptor, therefore there is a competition that depletes the charge flux. This is one of the reason why the change in intensity is so different between the two molecules. Daeph lies in between because no active substituent is present.

Looking at the normal modes between 1400 and 1650 cm^{-1}, there are differences between the daeome and the other two molecules. In particular, bonds 3 and 4 (see Fig. 3) are coupled with the bond 13 only in the daeome, giving a very intense normal mode (taking also into

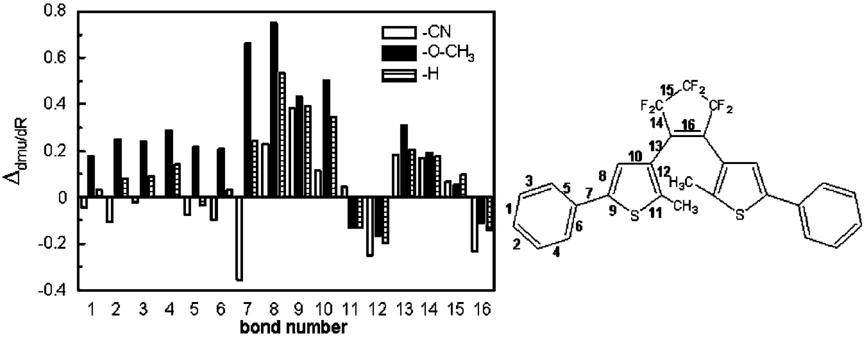

FIGURE 3 Bar plot of the difference between the modulus $d\mu/dR$ (a.u.) in the closed form and open form.

account the increment of dμ/dR). For the deacn the coupling is negligable and the normal mode involving the stretching of bonds 3 and 4 has low IR intensity.

It is, therefore, clear that the presence of a donor-acceptor bridge as in the closed form of the photochromic molecule (daeome) turns into the largest change in the infrared intensity between the two forms. Consequently daeome has been chosen to build a memory layer.

EXPERIMENTAL RESULTS AND DISCUSSION

The idea is to write a pattern with UV light onto a photochromic film. Which was prepared embedding daeome in PMMA (M_w 560000). A chloroform solution of PMMA and daeome (14.8 mg daeome +20 mg

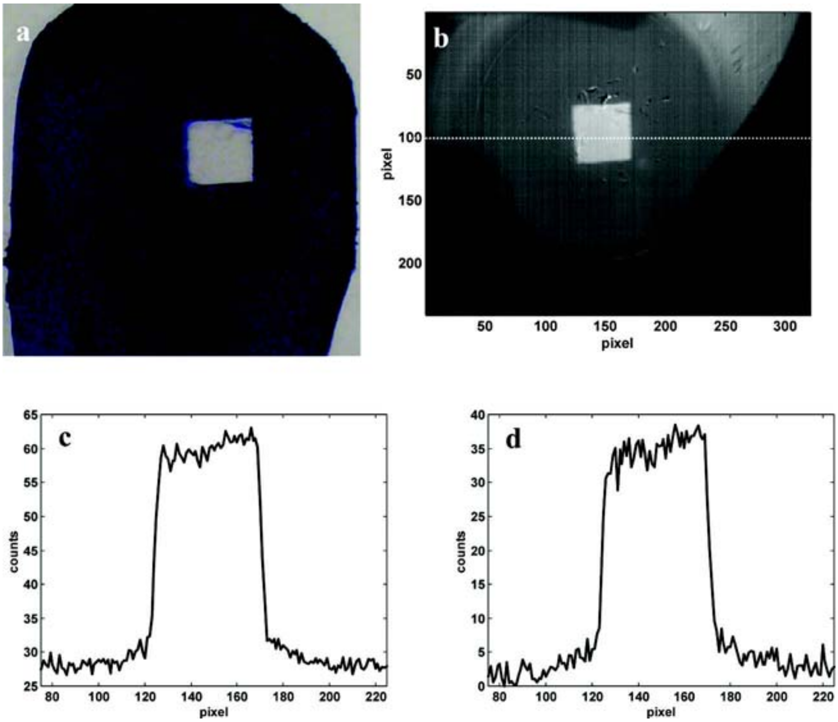

FIGURE 4 Squared pattern written on the memory film in the visible (a) and in the IR (the background is subtracted) (b). Plot of the row 100 of the FPA: average of 50 frames (c), single frame (d).

PMMA in 1 ml of $CHCl_3$) is cast on a PTFE substrate (100 μm thick) by using doctor blade technique thus obtaining a homogeneous film. The thickness of the film was about 12 μm. The choice of PTFE as substrate is justified by the fact that it acts as a filter because of its strong band at 1200 cm^{-1}, which cuts wavenumbers below 1300 cm^{-1}.

The setup we built for the readout is very simple. It consists of an infrared source which is a broadband Globar, an infrared filter (transparent below 2000 cm^{-1}), a sample holder and an infrared camera, we chose a multibolometer (Merlin Camera 12 bit, multi bolometer 320 × 240).

Therefore the transparent window of the setup is 2000–1300 cm^{-1} which contains the range where the intensity changes occur.

The film is illuminated with UV light to photoinduce the switching from the open to the closed form (blue) form; the film is placed in a sample holder and a set of frames is collected (50 frames with 45 ms of integration time and 250 ms delay between each frame). It represents the reference, which is necessary because the light source is not uniform on the focal plane of the camera. After that, without removing the sample a green laser light is used to write the squared pattern on the film (Fig. 4a). Then a new set of frames is collected with the same conditions. This new set of frames is the memory readout which is subtracted from the reference.

The results are shown in Figure 4b. The square is clearly visible in the infrared both on the average of the 50 frames (Fig. 4c) and on a single frame (Fig. 4d) where the signal to noise is lower but still enough to read the information.

In conclusion, we were able to use a readout process in the mid-IR over a quite wide range, without matching the exact band of the photochromic molecule since the differences in intensity between the two forms are very large. By a suitable change of the side groups in the basic diarylethene unit it is possible to increase the difference in the IR spectrum; of practical relevance are the changes obtained by introducing donor side groups.

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