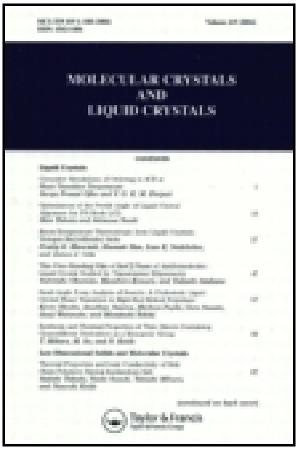

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FULGIDES AS LIGHT SWITCHES FOR INTRA-SUPERMOLECULAR ENERGY TRANSFER

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Abstract Photochromic fulgides undergo reversible color change upon irradiation with UV/VIS light. This is due to electrocyclic ring closure/ring opening. On addition of substituents, the fulgides examined retain their photochromic behavior; however, their photophysical properties, i.e. reaction quantum yields and fluorescence properties, are altered. The photoswitching has been analyzed in solid polymer matrix and in vapor deposited thin films. In addition to UV/VIS spectroscopy, IR absorption was used to examine the isomerization reactions. The photochromism of a donor-acceptor substituted thienyl-fulgimide can be used for optical switching of intramolecular energy transfer.

INTRODUCTION

The search for molecular functional units or supermolecular systems which can be used as building blocks in photonic or electronic devices is of high current interest [1][2]. One of the callenging problems is to find systems existing in two different, thermally stable states which can be transformed into each other by optical irradiation and which determine significantly different functions of the supermolecule.

FULGIDES AS PHOTOSWITCHES FOR TRANSFER OF EXCITATION ENERGY

We used the photochromism of fulgides to switch on and off intramolecular energy transfer. Fulgides are well known photochromic compounds [3]. The light-induced ring closure / ring opening reaction $E \rightleftharpoons C$ of the thienyl fulgide shown in fig. 1 has rather high quantum yields (e.g. $\phi_{EC} = 60\ \%$; $\phi_{CE} = 14\ \%$ at $\lambda = 366$ nm at 295 K), and the isomers are thermally stable at ambient temperatures. The process is reversible and can hence be repeated many times without loss of performance if E/Z isomerization, i.e. rotation around the exocyclic double bond, does not occur. This undesired side reaction, which lowers the quantum efficiency of $E \rightarrow C$, can be suppressed by introduction of an isopropyl substituent, cf. fig. 1 [4][5].

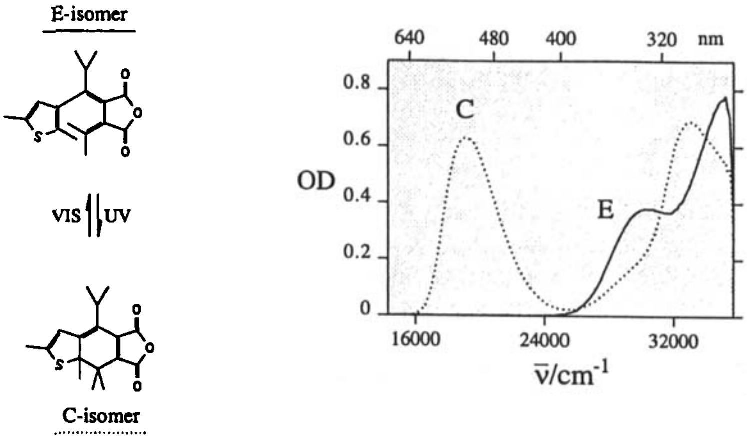

Fig. 1: Structure and absorption spectra of isopropyl-thienyl fulgide T-iF; reversible switching is possible using UV (E→C) or visible light (C→E).

The switchable supermolecule [6], which is a donor-acceptor substituted thienyl-fulgimide, is shown in fig. 2. The anthryl group is excited by light at 393 nm and acts as a donor, transferring its excitation energy to the coumarin group which acts as an acceptor when the central fulgimide is in the state E. The energy transfer is detected by the coumarin-type fluorescence at 453 nm. When the fulgimide is transformed to its C-conformation by light of 336 nm, it traps the excitation energy because its S_1 state is lower than those of anthryl

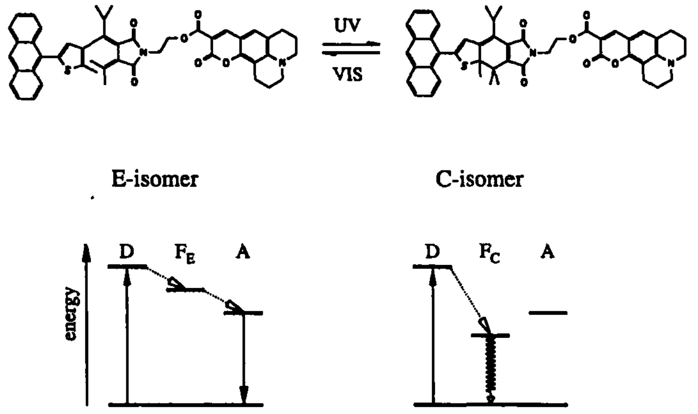

Fig. 2: Anthryl- and coumarin-substituted isopropyl-thienyl fulgimide 9A-T-iFm-Cou; model for the switching of intramolecular energy transfer from anthryl-donor to coumarin-acceptor [6].

and coumarin, leading to radiationless deactivation of the energy in the fulgimide unit. Consequently, only weak emission is observed. The coumarin fluorescence reappears upon conversion of the C-isomer to the E-isomer by light of 530 nm, fig. 3. This cycle can be repeated many times.

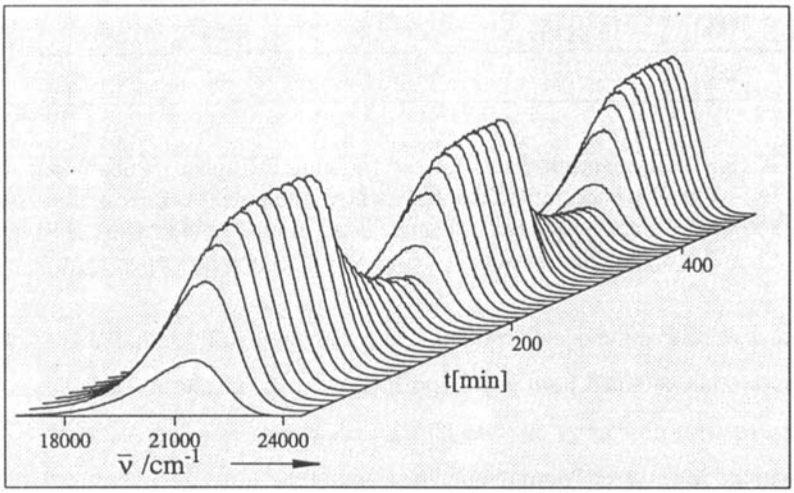

Fig. 3: Experimental verificaton of the switching of intramolecular energy transfer in 9A-T-iFm-Cou (PMMA; T=295K): coumarin-type fluorescence (λ_{exc}=393nm) rises after each irradiation interval at 530 nm (photoreaction C→E) and almost disappears after irradiation at 336 nm (E→C); irradiation intervals 10 min.

PHOTOSWITCHING IN MATRIX AND SOLID STATE

In order to make use of this switching process in photonic or electronic devices it is important to incorporate the supermolecule into a solid matrix or into an ultrathin layer on a surface [7]. We have been able to show that the photochromic processes of different heterocyclic fulgides with and without substituents are possible in polymer matrices as well as in thin vapor deposited layers. The isomerization reactions of the supermolecule shown in fig. 3 have high quantum yields in polymer matrix (ϕ_{EC} = 7 % at λ = 366 nm; ϕ_{CE} = 8 % at λ = 546 nm in both polystyrene PS and poly(methyl-methacrylate) PMMA at 295 K).

For a systematic study of matrix and temperature effects on the efficiency of the photoswitching we investigated unsubstituted furyl and thienyl fulgides as well as a phenyl substituted thienyl fulgide [8]. Due to the fact that the relatively rigid and planar C-isomer has steric requirements different from the more flexible non-planar E-configuration, a certain reaction volume is needed for the photoreaction to take place. Thus, reaction quantum yields are determined not only by intramolecular steric effects, but also by intermolecular interaction with the polymer matrix, tab. 1.

	F-F	Ph-T-F	9A-T-iF	9A-T-iFm-Cou
$\phi_{EC,366}$ [%]	18 (15)	22 (29)	58 (56)	7 (7)
$\phi_{CE,546}$ [%]	6 (7)	3 (5)	10 (15)	8 (8)

Tab. 1: Reaction quantum yields for furyl fulgide F-F; phenyl-substituted thienyl fulgide Ph-T-F; anthryl-substituted isopropyl-thienyl fulgide 9A-T-iF; anthryl- and coumarin-substituted isopropyl-thienyl fulgimide 9A-T-iFm-Cou in PMMA (PS) polymer matrix (T = 295 K) for ring closure E→ C (λ=366nm) and ring opening C→E (λ=546nm).

In polymer matrix, the quantum yields are comparable to those in toluene solution. For all compounds examined both in PS and PMMA, ring opening C→E is thermally activated with an activation energy of 50 to 80 cm^{-1}, which causes a decrease of ϕ_{CE} by two orders of magnitude between room temperature and 10 K.

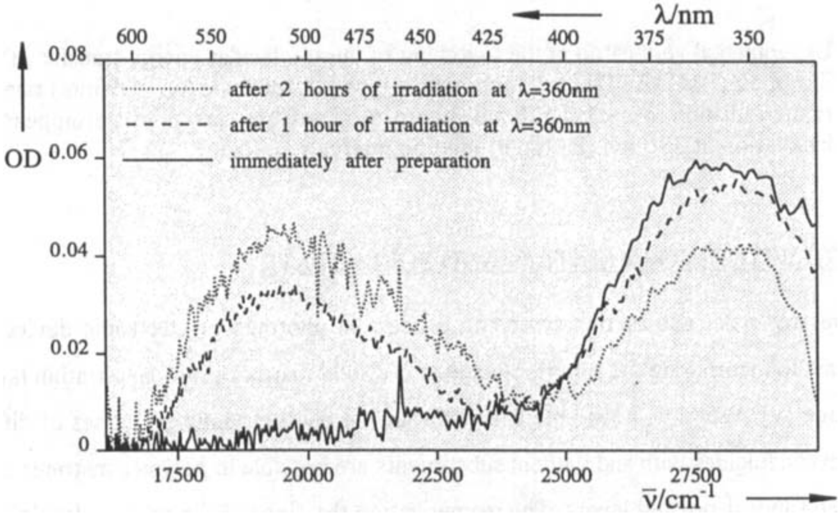

Fig. 4: Absorption spectra of a vapor deposited film (ca. 200 Å) of furyl fulgide F-F on a quartz plate (T=40K): immediately after deposition of the original E-isomer no C-absorption can be observed; upon irradiation at 360 nm, absorption of the C-isomer at 510 nm increases while E-absorption at 360 nm decreases. Several cycles E↔C were performed.

Reversible photoswitching is even possible in thin evaporated layers at low temperature. An example is given in fig. 4.

READING BY INFRARED SPECTROSCOPY

If photochromic compounds are to be used in photonic devices or as media for optical data storage, the capability of non-destructive reading is a crucial requirement. This means that there has to be a method by which the actual isomerization state of the molecule can be recognized without inducing a photoreaction to the other state and thus destroying the information just read [9].

This problem cannot be solved properly if visible light is used for the readout of data, where the absorption of the C-isomer distinguishes between logical states 0 and 1 and the absorbed probe light converts molecules from state C to state E.

Therefore, we suggest to utilize significant features in the infrared absorption spectra for a non-destructive detection method of the isomerization state of fulgides. As shown for isopropyl-thienyl fulgide in fig. 5, the IR spectra of E- and C-isomer are different with two absorption bands at 1298 cm^{-1} and 1507 cm^{-1} existing in the spectrum of the C-form only. As, due to our preliminary experiments, absorption in the mid IR does not induce any photoreaction, molecular vibrations that are characteristic for only one of the two isomers offer a way of non-destructive readout of data while writing and erasing can be done by UV/VIS light.

REACTION DYNAMICS

The microscopic velocity of the isomerisation reaction E→C itself can be measured by detecting the absorption of the C-isomer after pulse irradiation of E. Measurements using furylfulgide in solution at 295 K show that this process is faster than 1 ps.

CONCLUDING REMARKS

This is a preliminary report. More work in all of the fields mentioned above is in progress.

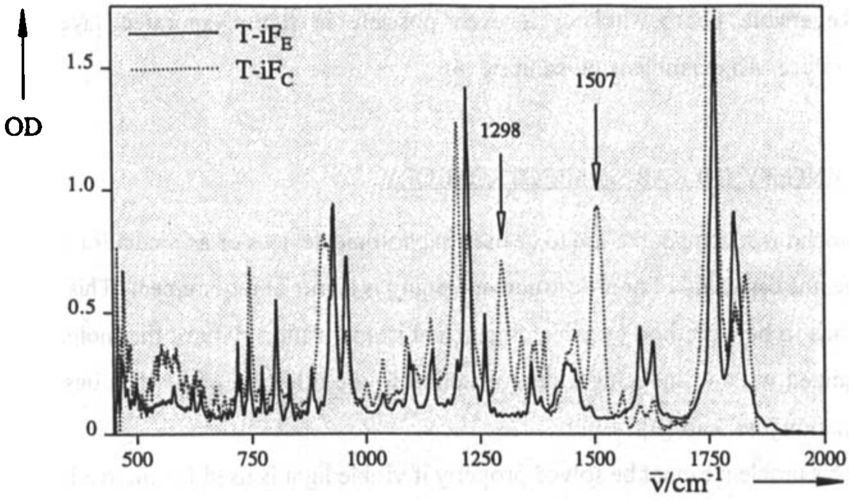

Fig. 5: IR absorption spectra of isopropyl-thienyl fulgide T-iF (E- and C-isomer) in KBr (T=295K).

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