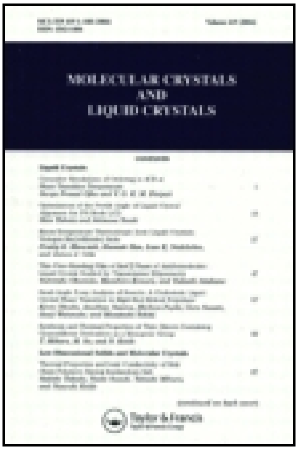

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# Ultrafast Photochromic Reactions of Fulgide Photoswitches

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# Ultrafast Photochromic Reactions of Fulgide Photoswitches

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*The dynamics of fulgide photoswitches has been investigated applying femtosecond transient absorption spectroscopy. The switching performance of differently substituted fulgides is equally improved in polymer (PMMA) environment as compared to liquid solution (toluene). In the polymer a single pathway for the ring-closure reaction, i.e., without the intermediate observed in toluene, allows for sub-picosecond reaction times. The ring-opening (on-switching) reaction in the donor-acceptor substituted energy-transfer system occurs on ps time scale.*

**Keywords:** femtosecond spectroscopy; fulgides; photochromic switches

## INTRODUCTION

In an approach to molecular-scale devices we have intensively studied photoinduced transfer processes in bridged donor-acceptor (D-B-A) supermolecular systems [1–3]. Thus we have already developed D-B-A systems with on/off photoswitchable intramolecular energy as well as electron transfer by incorporation of a photochromic fulgide or dithienylethene switching unit, respectively [4–7]. Although being of crucial importance for the qualification of the optical switches in such functions and in optical storage devices [8–14], details about the reaction dynamics and the reaction mechanisms are not known.

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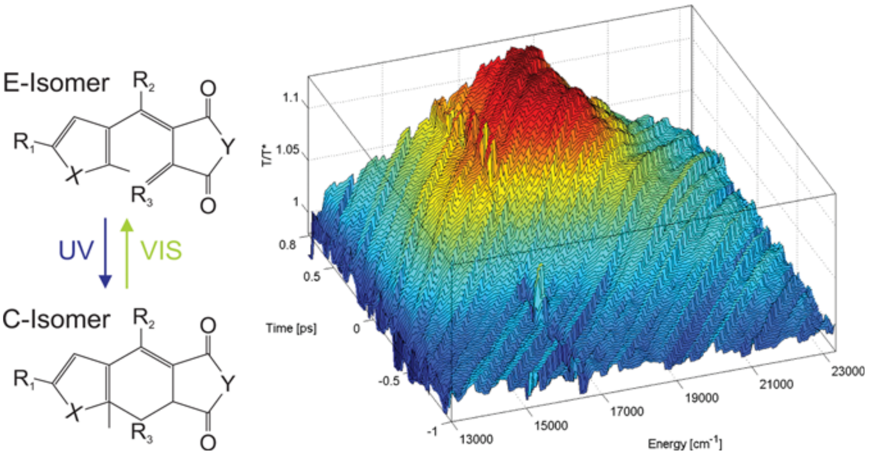

**FIGURE 1** Left: Scheme of molecular structure and photochromic reactions E⇔C. **PH-T-F**: X=S, Y=O, R1=Phenyl, R2=CH3, R3=C(CH3)2; **F-F**: X=O, Y=O, R1=CH3, R2=CH3, R3=C(CH3)2; **F-Ad-F**: X=O, Y=O, R1=CH3, R2=CH3, R3=Adamantylidene. Right: Transient absorption spectra for E⇒C of Ph-T-F in PMMA ($\nu_{\text{ex.}} = 26000\,\text{cm}^{-1}$); time window –1/+1.5 ps, chirp corrected.

The present contribution concentrates on fulgide photoswitches. For these, most reports of the time resolved measurements after pulse excitation suffered from inadequate time resolution [15]. Applying femtosecond transient absorption studies on fulgides in solution we had discovered a two-step process for the ring-closure reaction [16]. It was concluded, that an intermediate state slows down the overall reaction essentially.

We now report on investigations of the photoswitching entity in isolated form (see Fig. 1) and chemically bound in functional units (see Fig. 5). The switching performance is analyzed in liquid and polymer environment. The isomerization reaction of ring-closure/ring-opening and competing energy relaxation pathways are followed up by fs time-resolved pump and probe experiments.

## EXPERIMENTAL

Time resolved transient absorption (TA) measurements were carried out with a pump and probe technique at T = 295 K. The experimental setup is described in detail elsewhere [1,7]. Frequency doubled pulses of the Ti:Sa laser were used for excitation in the ultraviolet

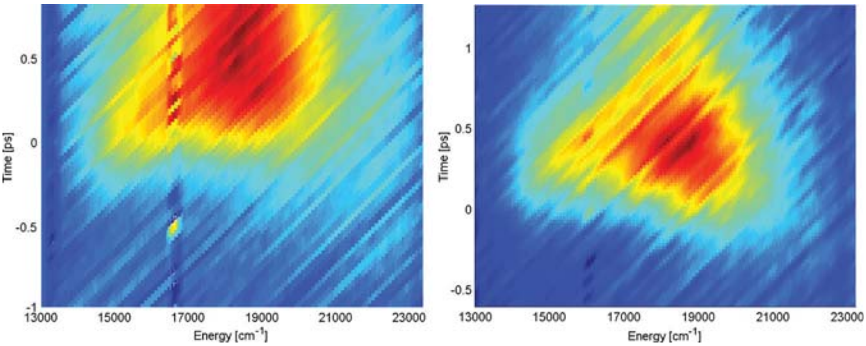

**FIGURE 2** Contour plots of transient absorption spectra for E⇒C. Left: F-F, right: F-Ad-F in PMMA, resp. $\nu_{\text{exc.}} = 26000\,\text{cm}^{-1}$. Time Window –1/+ 0.8 ps and –0.6/1.2 ps, resp.

($\nu_{\text{exc.}} = 26000\,\text{cm}^{-1}$). For excitation in the visible ($\nu_{\text{exc.}} = 20000\,\text{cm}^{-1}$) pump pulses were generated by an optical parametrical amplifier. After excitation the transient absorption spectra were measured by using a white light continuum ($\nu_{\text{probe}} = 10000\,\text{cm}^{-1} - 30000\,\text{cm}^{-1}$), which is delayed stepwise with respect to the excitation pulse. The measured spectra were calculated as $T/T^*$ with the transmission of the white light pulse, $T^*$ through the sample after excitation and the transmission T without the excitation. The setup allows a time resolution of about 150 fs.

The spectra at early delay times in Figures 1 and 2 are corrected for the chirp effect caused by temporal dispersion of the probe pulse.

In Figure 1 (left) the molecular structure of the investigated fulgides is shown, which changes in the photochromic reaction between E- and C-isomer upon excitation with UV-light and visible light, respectively. Both isomers are stable at room temperature.

## Ring-Closure Reaction E⇒C

In Figure 1 (right) the time evolution for the transient absorption spectra of Ph-T-F in PMMA is shown. Immediately after excitation of the E-isomer at $\nu_{\text{exc.}} = 26000\,\text{cm}^{-1}$ a broad absorption band around $\nu = 18000\,\text{cm}^{-1}$ appears. The rise of this signal is limited by the system response function. It's blue shift by about $1000\,\text{cm}^{-1}$ also occurs on ultrafast timescale. For the signal decay towards the narrower band (B) a time scale of about 500 fs is observed.

For the furyl-fulgide derivatives F-F and F-Ad-F in PMMA, the short time behaviour is presented in contour plots, Figure 2 (with comparable colour scale as in fig. 1). Whereas the absorption band A of F-F similarly to PH-T-F shifts to the blue, the corresponding band of F-Ad-F broadens and shifts to the red. On the other hand, the signal decay is comparably fast (0.5 ps) for F-Ad-F but essentially slower (0.9 ps) for F-F.

## Reaction Dynamics of E⇒C

For Ph-T-F in PMMA the time evolution of the absorption intensity at $\nu = 18400\,\mathrm{cm}^{-1}$ can be seen in Figure 3 (left), measured in an extended time range up to 200 ps. The qualitative features described here are common for all three compounds. The first intensity peak can be attributed to the band A which is due to excited state absorption of the E-isomer. Instead, the signal for long times is due to band B, which can be identified as the ground state absorption of the closed isomer. The center wavenumber and spectral shape of band B agree with those of the steady-state absorption of the C-isomer. As the ground state $C_0$ is the final state of the reaction process, band B is indicative for the photoreaction E⇒C.

Remarkably, this time evolution in PMMA environment drastically differs from the one observed for Ph-T-F in toluene, Figure 3 (right). There, after fast decay of band A a slow signal recovery takes place towards constant intensity of band B above about 80 ps. The same observation has been made previously also for F-F and F-Ad-F in toluene [16]. It could be interpreted quantitatively in a kinetic model, which distinguishes two parallel reaction pathways, one of them

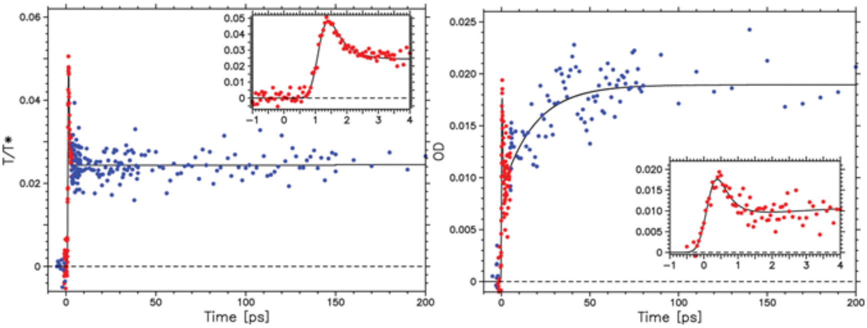

**FIGURE 3** Time evolution of the transient absorption E⇒C at $\nu = 18400\,\mathrm{cm}^{-1}$ after pulse excitation of PH-T-F E-isomer, left: in PMMA, right: in toluene. Experimental Data (dots) and fitted model curve (line) are shown; notice stretched abscissa in insert.

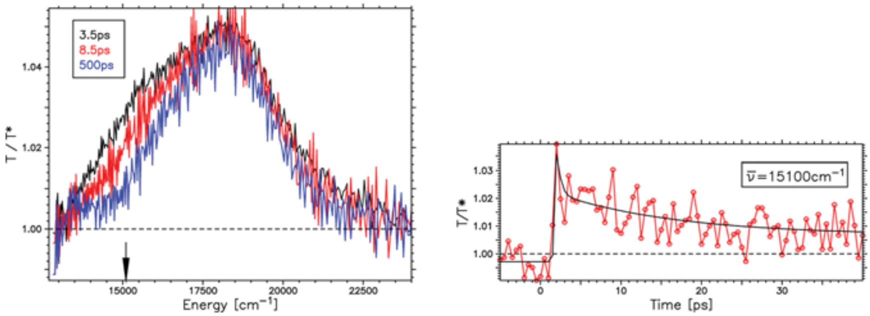

**FIGURE 4** Ph-T-F in PMMA: Left: transient absorption spectra for E⇒C 3.5 ps, 8.5 ps and 500 ps after pulse excitation at $\nu_{\mathrm{ex.}} = 26000\,\mathrm{cm}^{-1}$ of E-isomer. Right: Time Evolution at $\nu = 15100\,\mathrm{cm}^{-1}$.

including an intermediate state. Based on this model the fitting lines in Figure 3 (right) are obtained. Instead, the fitting curves in Figure 3 (left) are neglecting this intermediate. There is merely one reaction pathway in polymer environment, and as a result, the reaction E⇒C is speeded-up essentially.

Upon closer inspection of the low energy tail of band B at intermediate times, Figure 4, it turns out that band B of Ph-T-F in PMMA contains a slower decaying ($\tau = 15\,\mathrm{ps}$) spectral component at about $\nu = 15100\,\mathrm{cm}^{-1}$. The nature of this absorption cannot be explained definitely, vibrational energy redistribution in the $C_0$ ground state seems to play a role.

## Ring-Opening Reaction C⇒E

The switchable energy-transfer system 9A-TiFm-Cou (for the molecular structure see Fig. 5) uses the thienyl-fulgimide as switching entity [4]. Upon optical excitation with visible light the C-isomer of the switch can be addressed selectively, and the ring-opening photoreaction C⇒E (initiating off/on-switching of energy transfer) is analyzed separately.

In Figure 5 a sequence of transient absorption spectra for 9A-Ti-Fm-Cou in PMMA measured after pulse excitation at $\nu_{\mathrm{exc.}} = 20000\,\mathrm{cm}^{-1}$ is given. Clearly, the spectra contain different, positive and negative signal contributions. At $\nu = 15500\,\mathrm{cm}^{-1}$ the instantaneous signal rise is followed by a decay with 1.3 ps. Instead, at $\nu = 18500\,\mathrm{cm}^{-1}$ the decay of the negative signal is slower with time constant of 3.4 ps. The positive and negative signal contributions are

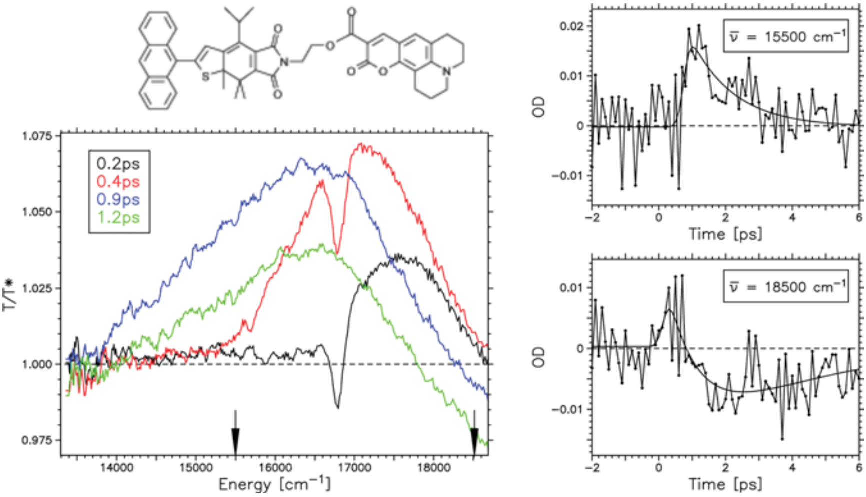

**FIGURE 5** C$\Rightarrow$E ring opening reaction of 9A-TiFm-Cou Left: Transient absorption spectra at 0.2 ps, 0.4 ps, 0.9 ps and 1.2 ps after pulse excitation ($\nu_{ex.} = 20000\,cm^{-1}$) of C-isomer (Raman line at 16800 cm$^{-1}$). Right: Time evolution at $\nu = 15500\,cm^{-1}$ and $\nu = 18500\,cm^{-1}$.

attributed to excited state absorption and transient bleaching of the C-isomer, respectively.

## CONCLUSION

By changing the environment from toluene liquid to solid phase polymer, the influence of the intermediate state as a delay factor in the ring-closure reaction can be avoided. This leads to an overall accelerated photoreaction and reaction times in the ps range for both switching directions. It supports the application of fulgides as ultrafast molecular photoswitches.

For to achieve an understanding of the photoreactions at early times, which obviously (see Figs. 1 and 2) depend on the composition of the photoswitch, pump and probe measurements with higher time resolution are in progress.

## REFERENCES

[1] Hirsch, T., Port, H., Wolf, H. C., Miehlich, B., & Effenberger, F. (1997). *J. Phys. Chem. B*, *101*, 4525.

[2] Vollmer, M. S., Würthner, F., Effenberger, F., Emele, P., Meyer, D. U., Stümpfig, T., Port, H., & Wolf, H. C. (1998). *Chem. European Journal*, *4*, 260.

[3] Hartschuh, A., Ramsteiner, I. B., Port, H., Endtner, J. M., & Effenberger, F. (2004). *J. Lumin., 108*, 1.

[4] Walz, J., Ulrich, K., Port, H., Wolf, H. C., Wonner, J., & Effenberger, F. (1993). *Chem. Phys. Lett.*, *213*, 321.

[5] Port, H., Hartschuh, A., Hennrich, M., Wolf, H. C., Endtner, J., & Effenberger, F. (2000). *Mol. Cryst. Liq. Cryst.*, *344*, 145.

[6] Endtner, J., Effenberger, F., Hartschuh, A., & Port, H. (2000). *J. Am. Chem. Soc.*, *122*, 3037.

[7] Ramsteiner, I. B., Hartschuh, A., & Port, H. (2001). *Chem. Phys. Lett.*, *343*, 83.

[8] Heller, H. G. (1991). In: "*Electronic Materials. From Silicon to Organics*", Miller L. S. & Mullin, J. B. (Eds.), Plenum: New York, 471.

[9] Yokohama, Y. (2000). *Chem. Rev.*, *100*, 1717.

[10] Irie, M. (2000). *Chem. Rev.*, *100*, 1685.

[11] Rath, S., Mager, O., Klingler, T., & Port, H. (2001). *Journal of Microscopy*, *203*, 182.

[12] Rath, S., Mager, O., Heilig, M., Strauß, M., Mack, O., & Port, H. (2001). *J. Lumin., 157*, 94–95.

[13] Belefield, K. D., Lin, Y., Negres, R. A., Fan, M., Pan, G., Hagan, D. J., & Hernandez, F. E. (2002). *Chem. Mater.*, *14*, 3663.

[14] Liang, Y. C., Dvornikov, A. S., & Rentzepis, P. M. (2003). *PNAS 100*, *14*, 8109.

[15] Tamai, N. & Miyasaka, H. (2000). *Chem. Rev.*, *100*, 1875.

[16] Handschuh, M., Seibold, M., Port, H., & Wolf, H. C. (1997). *J. Phys. Chem.*, *101*, 502.