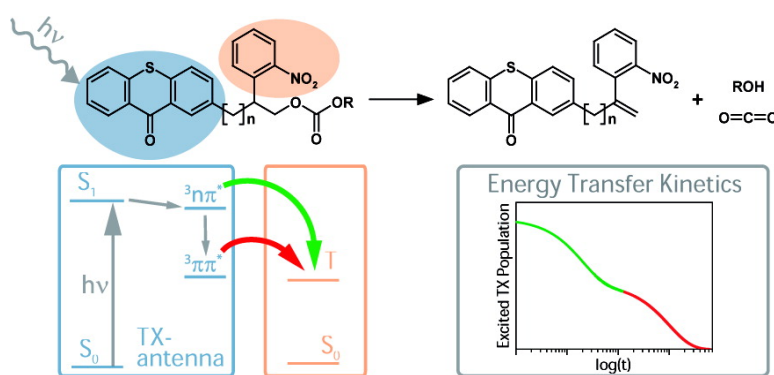Article

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On the Mechanism of Intramolecular Sensitization of Photocleavage of the 2-(2-Nitrophenyl)propoxycarbonyl (NPPOC) Protecting Group

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Abstract: A spectroscopic study of a variety of covalently linked thioxanthone(TX)−linker−2-(2-nitrophenyl)-propoxycarbonyl(NPPOC)−substrate conjugates is presented. Herein, the TX chromophore functions as an intramolecular sensitizer to the NPPOC moiety, a photolabile protecting group used in photolithographic DNA chip synthesis. The rate of electronic energy transfer between TX and NPPOC was quantified by means of stationary fluorescence as well as nanosecond and femtosecond time-resolved laser spectroscopy. A dual mechanism of triplet−triplet energy transfer has been observed comprising a slower mechanism involving the $T_1(\pi\pi^*)$ state of TX with linker-length-dependent time constants longer than 20 ns and a fast mechanism with linker-length-dependent time constants shorter than 3 ns. Evidence is provided that the latter mechanism is due to energy transfer from the $T_2(n\pi^*)$ state which is in fast equilibrium with the fluorescent $S_1(\pi\pi^*)$ state. In the case of direct linkage between the aromatic rings of TX and NPPOC, the spectroscopic properties are indicative of one united chromophore which, however, still shows the typical NPPOC cleavage reaction triggered by intramolecular hydrogen atom transfer to the nitro group.

1. Introduction

Recently it was shown that the light-sensitivity of photolabile protecting groups (ppg's) of the 2-(2-nitrophenyl)propoxycarbonyl (NPPOC) type[1−3] used in photolithographic DNA chip synthesis[4] can be considerably enhanced by spectral sensitization with triplet sensitizers.[5] In the case of NPPOC as a ppg, thioxanthone turned out to be a particularly good choice[6] because it showed the least extent of side reactions. In a further attempt to enhance the efficiency of the sensitizer, we synthesized a series of ppg's wherein the NPPOC moiety is covalently linked to thioxanthone which thus adopts the function of an intramolecular antenna (cf. Scheme 1).[7,8]

Several of these compounds showed excellent performance as ppg's with enhancements of the light sensitivity (expressed as the value of the product $\epsilon \times \phi$ of molar absorption coefficient ϵ and photochemical quantum yield ϕ) by up to a factor of 20 at 366 nm and of 140 at 405 nm. Recently, the concept of using intramolecular antennae to enhance the efficiency of photoreactions was also applied by Corrie and co-workers,[9,10] who studied triplet-sensitizer/1-acyl-7-nitroindoline conjugates and by Dietliker and co-workers[11] who reported on covalently linked triplet-sensitizer/photoinitiator conjugates.

Intramolecular energy transfer in general represents a research field of high current interest. Numerous examples and applications, some of which are reviewed by Speiser,[12] have been published. A major line of such research is driven by the motivation to develop artificial photosynthetic systems.[13,14] Other areas concern photonic devices for molecular electronics[15−18]

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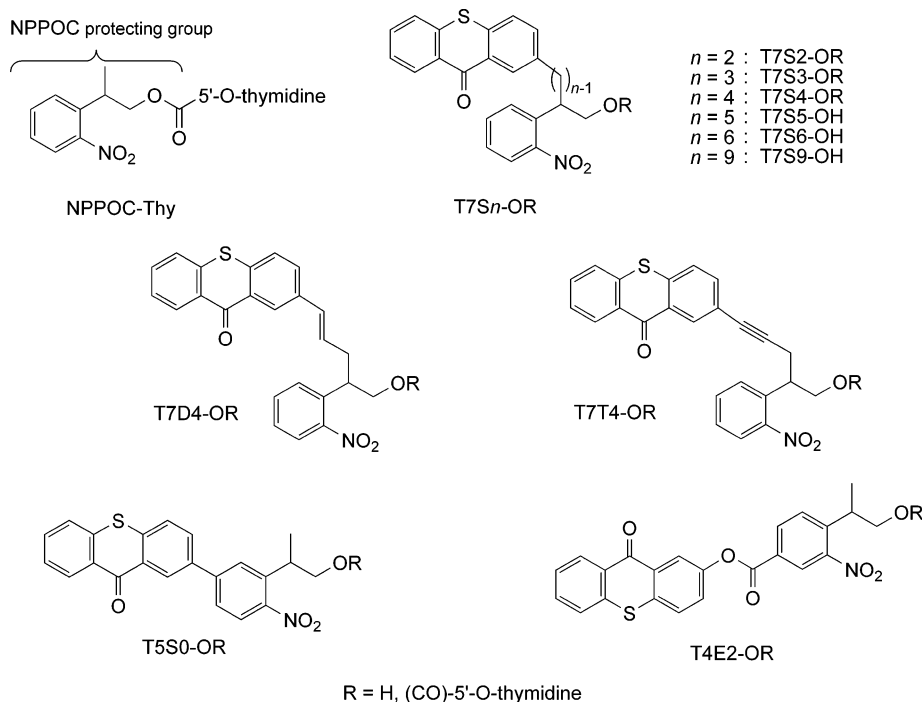
Figure 1. NPPOC conjugates investigated in this work.

Scheme 1. Intramolecular Sensitized Photocleavage of a Protecting Group of the NPPOC Type[a]
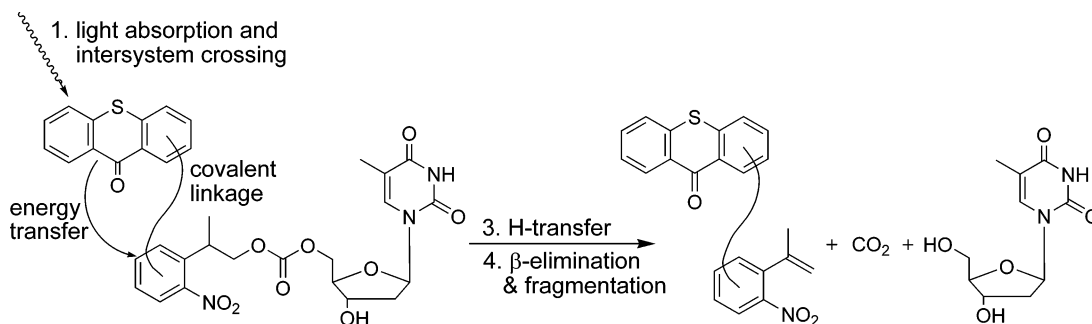
[a] Reproduced, with the publisher's permission, from ref 8.

or bioanalytical applications like fluorescence resonance energy transfer (FRET).[19−22] While in most of these reports the effects of intramolecular energy transfer are reversible, the number of case studies with irreversible chemical change as a consequence of the energy transfer are less numerous. The work of Morrison and colleagues,[23] who showed that Z/E photoisomerizations,[24−26] Norrish type II cleavages,[27] and photoreductions[28] can be brought about by intramolecular energy transfer in nonconjugated aryl olefins and keto olefins, has figured prominently in this respect.

In this paper we present a detailed account of the mechanism of intramolecular energy transfer in a series of thioxanthone/NPPOC conjugates as revealed by stationary and time-resolved spectroscopic investigations. Our study not only contributes to the general aspects of intramolecular energy transfer but also sheds new light on the photophysics of the established sensitizer thioxanthone.

2. Results

The compounds investigated in this work are shown in Figure 1. Normally, thymidine, protected at the 5′-OH position and connected to the 2-(2-nitrophenyl)propyl moiety through a carbonate linkage, was used as a test substrate. The sensitizer antenna was connected to the 2-nitrophenyl chromophore at various positions and through various types of linkers. The letter/number code for these compounds is of the general structure TmLn-OH for the free alcohols and TmLn-O(CO)Thy for the protected thymidines. The first letter codes for the antenna moiety (T for thioxanthone), and the number m gives the position at the NPPOC moiety to which the linker is attached (1−6 aromatic positions, 7 benzylic position). The letter L characterizes the type of chain linking NPPOC and the sensitizer (S, saturated carbon chain; D, single bond carbon chain including

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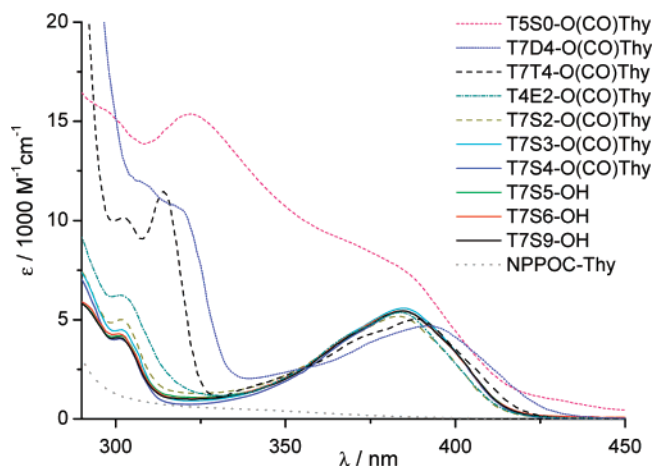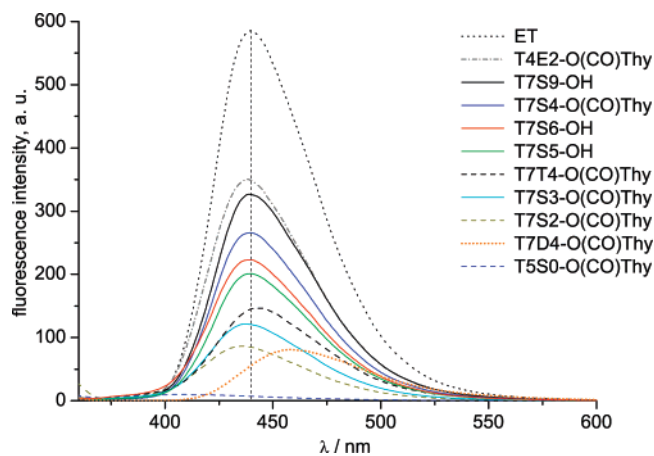
Figure 2. Absorption spectra of the thioxanthone/NPPOC conjugates. For better recognition, the labels to the various spectra are ordered in parallel to the absorbance values at 320 nm.

one double bond; T, single bond carbon chain including one triple bond; E, ester bridge). The number n is the length of the chain connecting the aromatic rings of NPPOC and thioxanthone.

The synthesis of most of the protected thymidines is described in ref 29. In order to study the length effect of the linker more systematically, the protected thymidine T7S2-O(CO)Thy and the alcohols T7Sn-OH ($n = 5, 6, 9$) have also been synthesized. Their syntheses are described in the Supporting Information. All spectroscopic experiments were carried out in MeOH as solvent.

2.1. Absorption and Fluorescence Spectra. Figure 2 shows the absorption spectra of the new protecting groups in comparison to the unmodified NPPOC chromophore. Since thymidines have negligible absorption above 300 nm, the thioxanthone chromophore dominates the picture of the conjugates in this region of wavelengths. If thioxanthone is linked to NPPOC through an aliphatic chain with more than two carbon atoms, the spectrum is essentially identical to a superposition of the spectra of 2-alkyl-thioxanthone and NPPOC (T7S3-O(CO)Thy to T7S9-OH). In the case of a very short aliphatic linker (T7S2-O(CO)Thy), small deviations from additivity are noticeable, indicating a weak interaction of the chromophores in the ground state.[30]

A weak spectral change is also observed for the ester-group-linked T4E2-O(CO)Thy, which is probably due to the effect of the benzoyloxy substituent at ring position 2 in thioxanthone. More pronounced spectral effects are associated with a double or triple bond in the linker in conjugation with the thioxanthone chromophore (T7D4-O(CO)Thy and T7T4-O(CO)Thy). These compounds exhibit a bathochromic shift of the first thioxanthone absorption band and the appearance of a new strong UV absorption band around 340 nm. Both of these effects can be attributed to the extension of the π-system of thioxanthone. Here a double bond has a stronger effect than a triple bond. The largest spectral change is observed for T5S0-O(CO)Thy where the aromatic systems of thioxanthone and NPPOC are directly linked. Obviously, the interaction is very strong, so that the

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Figure 3. Fluorescence spectra of investigated NPPOC conjugates excited at 355 nm. Line labels are ordered in parallel to the fluorescence intensities at 440 nm. The concentrations were adjusted such as to yield an absorbance of 0.05 at 355 nm for each sample.

Table 1. Fluorescence Quantum Yields ϕ_f and Wavelengths λ_{max} of Fluorescence Maxima

| compound	ϕ_f	λ_{max} (nm)
ET[a]	0.22	440
T4E2-O(CO)Thy	0.13	438
T7S9-OH	0.12	440
T7S4-O(CO)Thy	0.10	440
T7S6-OH	0.09	440
T7S5-OH	0.08	440
T7T4-O(CO)Thy	0.06	444
T7S3-O(CO)Thy	0.05	438
T7S2-O(CO)Thy	0.04	436
T7D4-O(CO)Thy	0.04	458
T5S0-O(CO)Thy	0.01	406

[a] 2-Ethylthioxanthone.

linked moieties essentially form a joint chromophore with a strong absorption maximum at 325 nm and a pronounced shoulder around 380 nm, the position of the absorption maximum of the parent thioxanthone chromophore. It should be noted that relative to the unmodified NPPOC group, the absorbances of the new protecting groups are increased by a factor of 12 to 33 at 366 nm and by a factor of 100 to 190 at 405 nm, to mention two convenient mercury lines. No significant differences between the free alcohols of the protecting groups and the protected thymidines were observed above 300 nm.

The fluorescence spectra are shown in Figure 3. Fluorescence quantum yields and wavelengths of fluorescence maxima are listed in Table 1. The spectral shapes and positions are in agreement with Kasha's mirror image rule.[31] The fluorescence maxima are centered at about 440 nm. In accordance with the bathochromic shifts of the absorption spectra of compounds T7D4-O(CO)Thy and T7T4-O(CO)Thy, there is also a corresponding shift of their fluorescence spectra. The fluorescence maximum of the unified chromophore of T5S0-O(CO)Thy appears at the shortest wavelength. In all cases, the fluorescence quantum yields are lower than that in the reference compound 2-ethylthioxanthone. Within the series T7S*n* of compounds with an aliphatic linker of variable length between the two chromophores, there is a systematic decrease of the fluorescence quantum yield with decreasing length n of the linker. In this
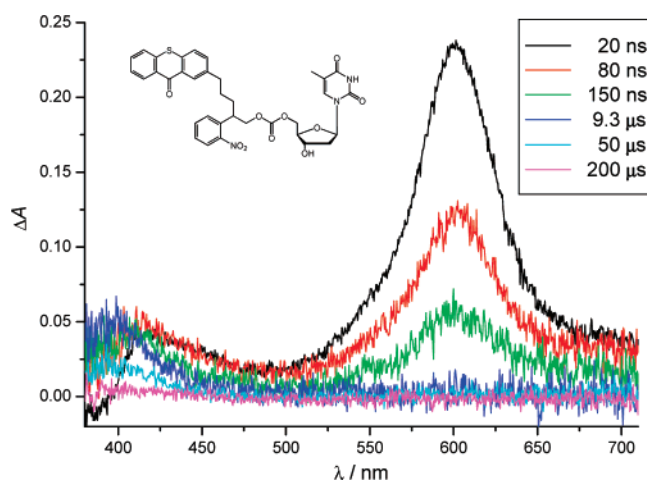
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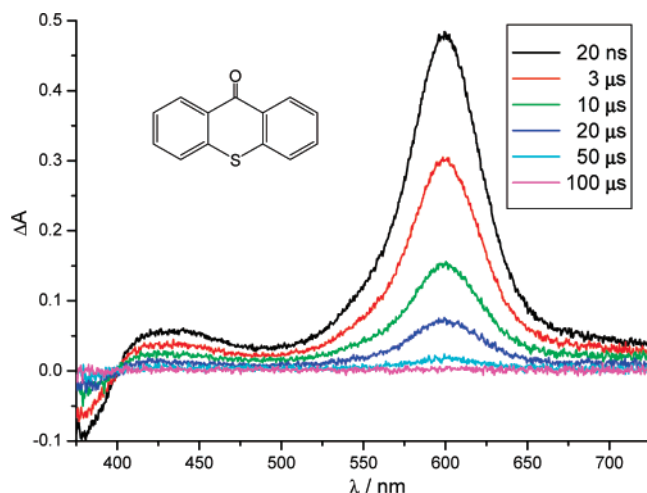
Figure 4. Transient absorption spectra of thioxanthone in deaerated MeOH after excitation with a 355 nm nanosecond laser pulse.

Figure 5. Transient absorption spectra of T7S4-O(CO)Thy in deaerated MeOH after excitation with a 355 nm nanosecond laser pulse.

respect it does not seem to matter whether free alcohols T7S*n*-OH or protected thymidines T7S*n*-O(CO)Thy are considered. The only irregular case in the series is T7S4-O(CO)Thy which ranges between T7S9-OH and T7S6-OH. Introducing a double or triple bond in conjugation with the thioxanthone chromophore in a chain of four carbon atoms (T7D4-O(CO)Thy and T7T4-O(CO)Thy) further decreases the fluorescence quantum yield, whereby the effect of the double bond is more pronounced. By far the lowest fluorescence quantum yield is found for the directly linked conjugate T5S0-O(CO)Thy, a fact which, together with the relatively large hypsochromic shift, emphasizes the special role of the unified chromophore.

2.2. Nanosecond Laser Flash Photolysis. The new compounds were systematically examined by nanosecond laser flash spectroscopy measuring their transient absorption spectra at variable delay times with a CCD camera and recording kinetic decay curves at selected wavelengths.

2.2.1. Compounds with an Oligomethylene Chain Linker (T7S*n*-OR). For comparison, the transient spectra of the parent thioxanthone and compound T7S4-O(CO)Thy as a typical representative of this class of conjugates are shown in Figures 4 and 5. The triplet–triplet absorption spectrum of thioxanthone is characterized by a strong band at 600 nm and a weaker band somewhat below 450 nm, the maximum of which cannot be

Table 2. Triplet Lifetimes τ and Rate Constants k_{q,O_2} of Quenching of Thioxanthone Triplet in the Investigated Thioxanthone/NPPOC Conjugates by Molecular Oxygen[a]

| | τ / ns | | | | k_{q,O_2}/ 10^9 M^{-1} s^{-1} | |
| | N$_2$-saturated MeOH | | aerated MeOH | | | |
compound	R = H	R = (CO)Thy	R = H	R = (CO)Thy	R = H	R = (CO)Thy
T7S2-OR	19	23	19	23	---	---
T7S3-OR	38	36	32	30	2.35	2.65
T7S4-OR	109	102	64	68	3.07	2.33
T7S5-OR	110		72		2.28	
T7S6-OR	66		58		1.00	
T7S9-OR	242		195		0.47	
T7T4-OR	914	1020	185	245	1.92	1.48
T5S0-OR	---	134	---	117	---	0.52
T4E2-OR	3070	3640	215	217	2.06	2.06

[a] A concentration of 2.1×10^{-3} M for oxygen in air-saturated methanol was used (cf. p. 291 in ref 35).

accurately determined because this band is superimposed by the bleaching of the ground state absorption band.[32] Immediately after the laser flash, the shapes of the transient spectra of thioxanthone and T7S4-O(CO)Thy are practically identical, although the magnitude of the latter is only about half of the former. A second characteristic difference is the decay time of the transients. At 600 nm, the decay kinetics of the free thioxanthone triplet had to be fitted with a mixed first- and second-order kinetic model taking triplet–triplet annihilation (second-order rate constant k_{TT}) into account. This yielded a first-order rate constant of 3.8×10^4 s^{-1} and a second-order rate constant of 4×10^9 M^{-1} s^{-1}. The decay of the thioxanthone/NPPOC conjugate was single exponential with a decay constant of 9.8×10^7 s^{-1}. This indicates a very efficient triplet energy transfer in the conjugate. For T7S4-O(CO)Thy, the transient absorption below 450 nm undergoes a weak bathochromic shift, the negative absorption due to the ground state bleaching is compensated by a stronger absorption with a maximum at about 410 nm and a decay constant of 1.4×10^4 s^{-1}. This transient can be assigned to the *aci*-nitro form of NPPOC,[33] indicating that energy transfer from the thioxanthone triplet to NPPOC is followed by the well-known intramolecular hydrogen atom transfer from the benzylic position to the nitro group which is characteristic for 2-nitrobenzyl compounds.[34] Corresponding transient absorption spectra and decay curves for the other compounds in this class can be found in the Supporting Information. As far as lifetimes (cf. Table 2) and initial intensities of the transient spectra of the triplet moieties are concerned, there is little difference between the protected thymidines T7S*n*-O(CO)Thy and the free alcohols T7S*n*-OH. However, as is borne out by Figure 6, both of these parameters are significantly affected by the length *n* of the linker. In general, the initial transient absorption, i.e., the yield of detected thioxanthone triplet, decreases as the chain length of the linker is decreased. The same applies to the triplet lifetime (for a compilation of the triplet lifetimes, cf. Table 2). Exceptions to the general trend are compound T7S4-O(CO)Thy with a relatively high triplet yield and compound T7S6-O(CO)Thy with a relatively short triplet decay time.

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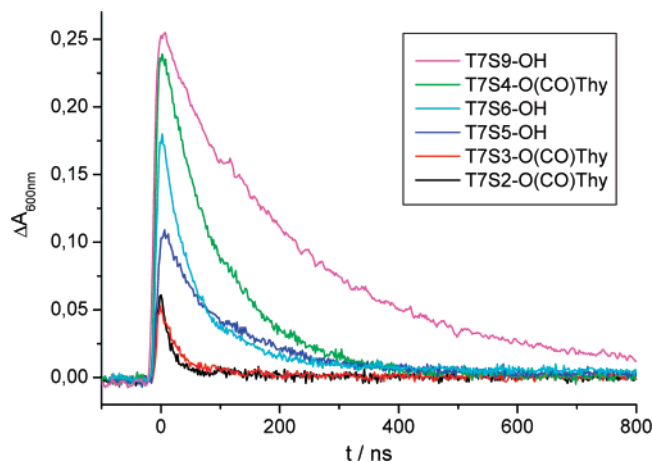
Figure 6. Triplet decay curves of compounds T7S*n* observed at 600 nm in deaerated MeOH after excitation with a 355 nm nanosecond laser pulse.

Table 3. Decay Times τ of *aci*-Nitro Species in the Investigated Thioxanthone/NPPOC Conjugates

| | $\tau / \mu s$ | | | |
| | N$_2$-saturated MeOH | | aerated MeOH | |
compound	R = H	R = (CO)Thy	R = H	R = (CO)Thy
T7S2-OR	38	99	39	101
T7S3-OR	39	118	40	99
T7S4-OR	32	71	32	63
T7S5-OR	26		16	
T7S6-OR	23		23	
T7S9-OR	25		27	
T7T4-OR	30	123	36	123
T5S0-OR	68	129	84	122
T4E2-OR	78	85	60	64

It is remarkable that, although the initial triplet yield detected after the laser flash in the T7S*n*-O(CO)Thy series is strongly dependent on the chain length of the linker, the observed initial intensity of the *aci*-nitro band in all these compounds is fairly independent of the linker length (cf. Discussion). The decay time of the *aci*-nitro band does show some, but not a very pronounced, dependence on the linker length (cf. Table 3). However, it is significantly shorter for the free alcohols than for the protected thymidines.

2.2.2. Compounds with Unsaturated Alkyl Linker (T7T4-OR, T7D4-OR). The triplet–triplet absorption of compounds T7T4-OR is centered at 630 nm (cf. Figure S7 in the Supporting Information). Compared to the compounds with saturated linker, this corresponds to a bathochromic shift by 30 nm. The band is also slightly broader. These changes are likely due to the extension of the thioxanthone chromophore by the conjugated triple bond. The ground state bleaching around 400 nm observed with the saturated linkers can also be observed in the transient spectra of T7T4-OR. In this compound, the thioxanthone triplet decays relatively slowly with a lifetime of 1.02 μs. Its decay is concomitant with the appearance of an absorption band at 400 nm that can be associated with the corresponding *aci*-nitro form. It has a lifetime of 123 μs. However, the yield of this intermediate is only half the yield of the compounds with a saturated linker. This fits with the observation of a competing photochemical reaction which does not result in the formation of the *aci*-nitro intermediate.[8]

For the compounds T7D4-OR, it was not possible to detect any transient signal, although a weak fluorescence, comparable
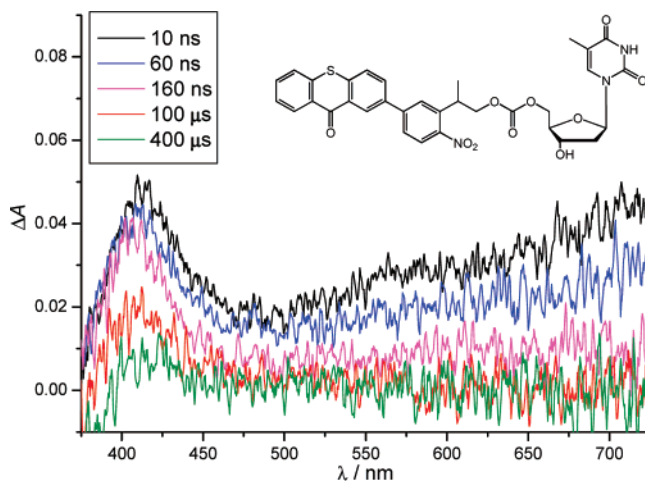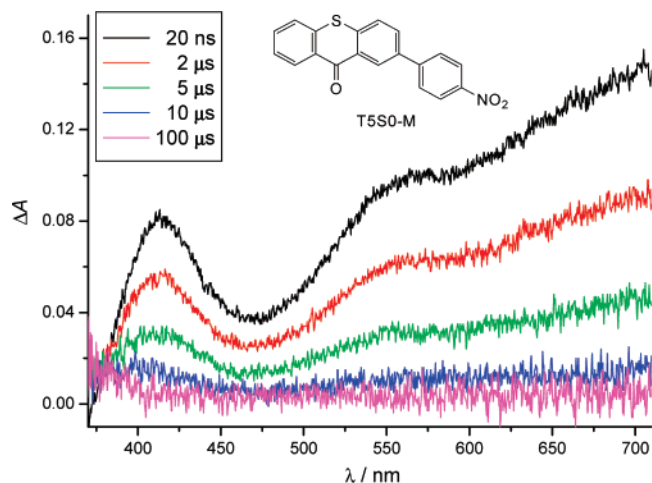
Figure 7. Transient absorption spectra of T5S0-O(CO)Thy in deaerated MeOH after excitation with a 355 nm nanosecond laser pulse.

to the case of T7S2-OR, is still observable (cf. Figure 3). Very likely, in this case a photochemical *trans*/*cis*-isomerization of the vinyl thioxanthone triplet impedes the observation of a transient on the nanosecond time scale.

2.2.3. Compounds with an Ester Linkage (T4E2-OR). The transient spectra of these compounds show a triplet–triplet absorption maximum at 600 nm. The triplet lifetime of 3.6 μs is the longest of all thioxanthone/NPPOC conjugates investigated here, but it is still by almost 1 order of magnitude shorter than that for the parent thioxanthone. Thus energy transfer takes place, and the *aci*-nitro product is formed as can be seen from a long-lived transient absorption with a maximum at about 420 nm and a lifetime of about 80 μs.

2.2.4. Compounds with a Direct Connection of the Chromophores (T5S0-OR). The transient spectrum of T5S0-O(CO)-Thy differs significantly from the spectra of the other protecting groups (cf. Figure 7). It shows an absorption peak at about 420 nm and a broad absorption increasing from 470 to 700 nm without reaching a maximum. The broad absorption has a decay time of 134 ns, and the peak at 420 nm decays in about 130 μs. In an aerated solution, the former is quenched to a value of 117 ns whereas the latter is not affected. Therefore, we assume that the unstructured, broad absorption can be attributed to a triplet state of the conjugated thioxanthone/nitrophenyl chromophore and the absorption at 420 nm is due to both the triplet state and the *aci*-nitro form that is formed during the decay of the triplet. A slight hypsochromic shift of the band maximum observed while the triplet is decaying indicates the transformation of the triplet to the *aci*-nitro form.

In order to study the isolated T5S0 chromophore, the model compound T5S0-M was synthesized, which yielded the transient absorption spectrum shown in Figure 8. It is very similar in shape, although about 3 times higher in intensity to the initial spectrum observed with T5S0-O(CO)Thy, but its decay is spectrally uniform; i.e., it does not show the band due to the *aci*-nitro form, which cannot be formed in such a compound. The whole spectrum decays with a lifetime of 4 μs. Its assignment to a triplet–triplet absorption is supported by quenching experiments with oxygen, yielding a quenching constant of 3.5×10^8 M^{-1} s^{-1}. Comparing Figures 7 and 8, we may thus conclude that the triplet of the T5S0-chromophore, even if the excitation encompasses a much larger electronic

Figure 8. Transient absorption spectra of T5S0-M in deaerated MeOH after excitation with a 355 nm nanosecond laser pulse.

system, shows a similar reactivity toward benzylic hydrogen as that of NPPOC.

2.2.5. Quenching of Thioxanthone Triplet in the Thioxanthone/NPPOC Conjugates by Molecular Oxygen. The triplet lifetime of the thioxanthone chromophore in the thioxanthone/NPPOC conjugates is reduced in the presence of oxygen. However, in comparison to free thioxanthone, this sensitivity of the triplet lifetime to oxygen is greatly reduced because of the competing intramolecular energy transfer process that shortens the triplet lifetime of the thioxanthone chromophore. Denoting the triplet decay constants in aerated and deaerated solutions by k_{air} and $k_{nitrogen}$, respectively, the quenching rate constant is given by

$$k_{q,O_2} = \frac{k_{air} - k_{nitrogen}}{[O_2]} \tag{1}$$

The values of k_{q,O_2} determined for the investigated compounds are listed in Table 2. In general, the observed values are in the expected order of magnitude, that is about one-ninth of the diffusion controlled rate constant.[36,37] Quenching of the T5S0-O(CO)Thy triplet by oxygen ($k_{q,O_2} = 0.52 \times 10^9$ M^{-1} s^{-1}) is relatively slow. Similar (unexplained) deviations from the rule have been reported, e.g., for the coronene triplet.[36]

2.3. Femtosecond Transient Absorption. In order to clarify the mechanism of energy transfer in further detail, compound T7S2-OH showing the shortest triplet decay time and the strongest intramolecular fluorescence quenching was investigated by femtosecond (fs) laser spectroscopy. As a suitable reference, not linked to the NPPOC chromophore, 2-ethylthioxanthone was chosen.

When a solution of 2-ethylthioxanthone is photoexcited by femtosecond laser pulses, at delay times of 2 ns (approximately the longest time accessible with our femtosecond equipment), one observes a transient spectrum as shown in Figure 9A with an intense band at 600 nm and a weaker band at about 420 nm. These features are in good agreement with those observed in

the nanosecond LFP experiments with thioxanthone (cf. Figure 4). They have been assigned to the lowest triplet state of the latter chromophore. The deviations between the spectrum at 2 ns in Figure 9A and the spectrum at 20 ns in Figure 4 are mainly due to the fact that the population of the triplet state, that grows in with a time constant of about 2 ns, is not yet completed at 2 ns but fully completed at 20 ns (cf. Discussion). At earlier delay times, a strong, negative transient "absorption" (marked in blue in Figure 9A) is observed. This negative spectral contribution is due to stimulated emission and results from the excited singlet state. It decays with a time constant of ~2 ns, matching the reported fluorescence lifetime.[38]

The effect of a potential triplet energy acceptor on the observed excited states of 2-ethylthioxanthone was studied by adding 1-methylnaphthalene at high concentrations (1.0 M) (cf. Figure 9B). Under such conditions, the lifetime of the stimulated emission and the transient absorption around >600 nm is reduced. This reduction cannot be described by simple exponential kinetics since dynamic and static components contribute to the quenching (see discussion in ref 39). A biexponential approximation yields time constants of ~50 ps and ~1.5 ns. It has to be stressed that either constant is shorter than the fluorescence lifetime of 2.6 ns.[38] In addition to the decay of the stimulated emission and the transient absorption at >600 nm, a sharp absorption band at 415 nm is seen to grow in. This band can be assigned to the triplet state of 1-methylnaphthalene.[39]

Finally, femtosecond photoexcitation of the thioxanthone moiety linked to NPPOC in T7S2-OH results in a transient absorption pattern (Figure 9C) which, at early delay times, is identical to that of 2-ethylthioxanthone. Later on, a quenching of the stimulated emission and the induced absorption around 600−650 nm is observed. The decay time of the stimulated emission is ~500 ps as compared to 2 ns for 2-ethylthioxanthone. The decay time of the absorption peak at 600 nm cannot be determined precisely but may be extrapolated to some 10 ns.

3. Discussion

The energetic requirements for fast energy transfer demand that the energy of the excited donor state be higher than that of the excited acceptor state. For NPPOC, the exact energy of the lowest triplet state is not known, but the value of $E_T = 252$ kJ/mol for nitrobenzene in polar solvents[35] may be a good estimate. Since it lies by 13 kJ/mol below the triplet energy of thioxanthone ($E_T = 265$ kJ/mol),[35] electronic energy transfer should proceed at a considerable rate. This expectation is in accord with data for energy transfer between unlinked thioxanthone triplet and NPPOC-protected substrates.[5] Here the rate constants were found in a range between 10^9 M^{-1} s^{-1} and 4×10^9 M^{-1} s^{-1}, showing some variation with solvent and substrate linked to NPPOC. This range of values is close to, but yet below, the diffusion controlled limit. Wirz and co-workers[40] studied intramolecular triplet energy transfer between thioxanthone and naphthalene ($E_T = 253$ kJ/mol). In these systems, establishment

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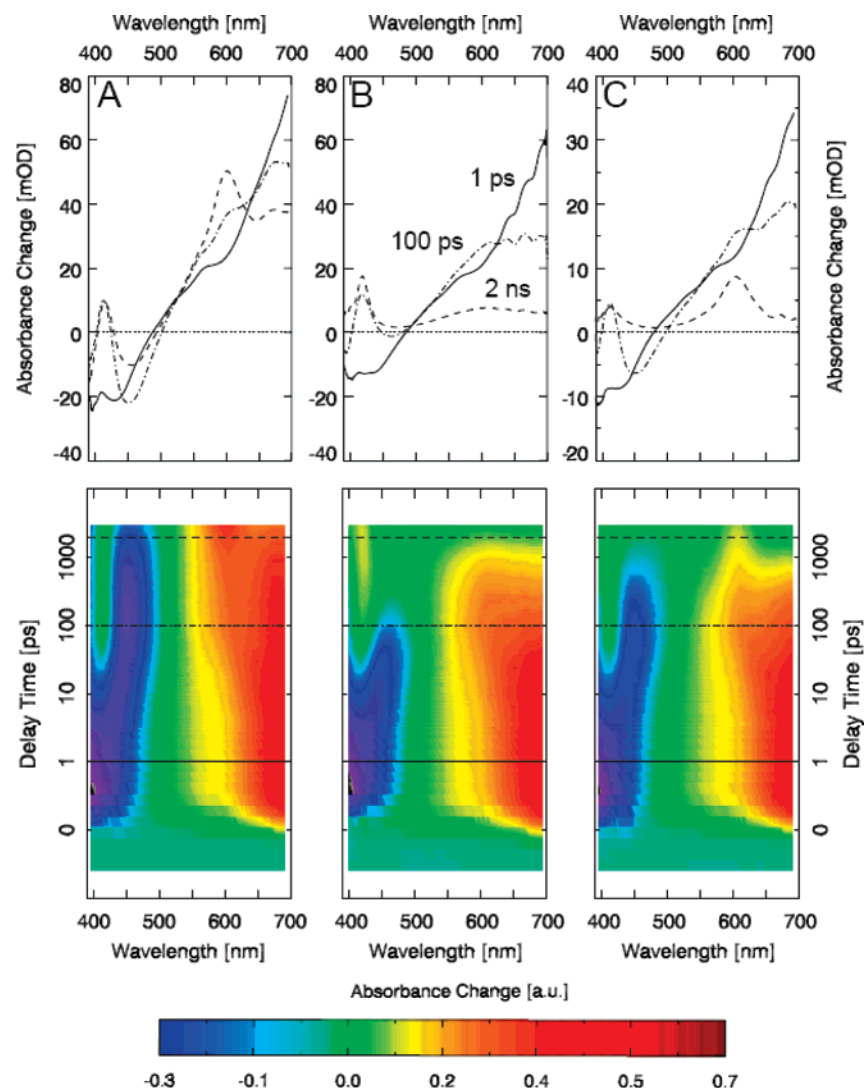
Figure 9. Femtosecond transient absorption spectra of (A) 2-ethylthioxanthone, (B) 2-ethylthioxanthone in the presence of 1-methylnaphthalene (1.0 M), and (C) T7S2OH. The smaller signal magnitude here is due to a lower concentration of T7S2-OH. The samples were excited with laser pulses at 388 nm, and absorption changes were probed by a white light continuum in multichannel fashion. Lower panels: contour representation of the time dependence of the transient absorption spectra. The color code for the absorbance change is indicated at the bottom. The time axis is linear until 1 ps and logarithmic thereafter. Upper panels: transient absorption spectra at representative delay times of 1 ps (solid line), 100 ps (dash-dotted), and 2 ns (dashed). For comparison, these delay times are also marked in the lower panels.

of an equilibrium between the two triplets is observed, demonstrating that in polar solvents the triplet energy of thioxanthone is only slightly above the value of naphthalene which is close to that of nitrobenzene.

As was found here, triplet energy transfer from the thioxanthone chromophore to NPPOC leads to a strongly reduced triplet lifetime of the thioxanthone moiety (cf. Table 2) as compared to free 2-ethylthioxanthone ($\tau = 26$ μs in deaerated MeOH). Even in the slowest case (T4E2-O(CO)Thy), it is 7 times shorter, which means that the triplet lifetime is essentially determined by the energy transfer process. Values of the pertinent rate constant k_T are obtained by the equation

$$k_T = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (2)$$

where τ is the triplet lifetime of the NPPOC-linked thioxanthone and τ_0 is the triplet lifetime of 2-ethylthioxanthone.
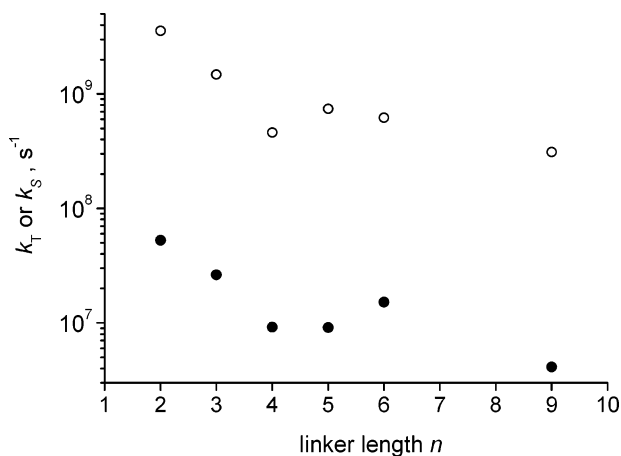
3.1. Energy Transfer in the Series T7S*n*-OR. In the series of thioxanthone/NPPOC conjugates where the energy donor and

acceptor are linked by a linear aliphatic chain, trends of k_T are particularly interesting to analyze. Figure 10 shows how k_T varies as a function of the chain length parameter *n*. The k_T values range from 5.3×10^7 s^{-1} for the shortest linker ($n = 2$) to 4.1×10^6 s^{-1} for the longest ($n = 9$).

In between, the decrease is monotonic except for a "hump" at $n = 6$. For this length of the linker, the rate constant is found between those of $n = 3$ and 4. Such irregularities are not unusual in the study of the interactions of reactive ends of aliphatic chains (for examples, cf. the references given by Wagner and co-workers[41] for electron-transfer reactions, exciplex formation, as well as spin−orbit and exchange interaction effects in biradicals). It must be assumed that they reflect the ease at which specific conformations of the linker chain bring the reactive ends into a relative position suitable for reaction. In experiments on triplet energy transfer in alkane linked benzoyl/aryloxy moieties, a second relative maximum in the chain length

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Figure 10. Decay constants of thioxanthone triplet (k_T, ●) and singlet (k_S, ○) as a function of linker length in the series T7Sn-OH.

dependence of the triplet energy transfer rate from the benzoyl to the aryloxy chromophore has been observed. The maximum was located at linker lengths between 7 and 10 atoms and was sensitive to the position at which the linkers were connected to the chromophores.[42,43] These findings have been rationalized by means of molecular modeling.[41] For excimer formation in 1,n-bis(1-pyrenylcarboxy)alkanes, a pronounced peak at $n = 5$ was found, whereas a pronounced minimum appeared at $n = 7$ in corresponding 1,n-bis(1-pyrenyl)alkanes.[44,45] Altogether, these examples demonstrate that the exact length at which intermediate maxima or minima occur in the chain-length dependence of the rate of an end-to-end interaction differ with the structure of the reactive ends and with the position to which the linker ends are attached.

In principle, the rate constant of energy transfer is a function of distance and the relative orientation of the energy donor and acceptor. It depends on an overlap integral of the respective wavefunctions (where through space and through bond contributions have to be distinguished) and a Franck−Condon (FC) factor. Depending on the particular coupling mechanism, the overlap integral will decay exponentially with distance whereby the length parameter of this decay is shorter for the through-space than for the through-bond mechanism. The FC factor is a function of the free energy difference ΔG between the excited donor and excited acceptor and a reorganization energy λ. In general, these latter two parameters are only slightly dependent on the distance. On excitation of the donor, the conformation of the linker chain will be represented by a statistical distribution. Since the rate constant of energy transfer is faster at close distances of donor and acceptor moiety, the triplet population in such close-to-contact conformations will decrease more rapidly and part of the energy transfer kinetics will involve repopulation of such favorable conformations through the dynamics of the linker chain (chain diffusion). Depending on which of the two processes is faster, the rate constant of energy transfer will be closer to one of the two limiting kinetic cases: (i) "static" energy transfer control or (ii) chain diffusion control.
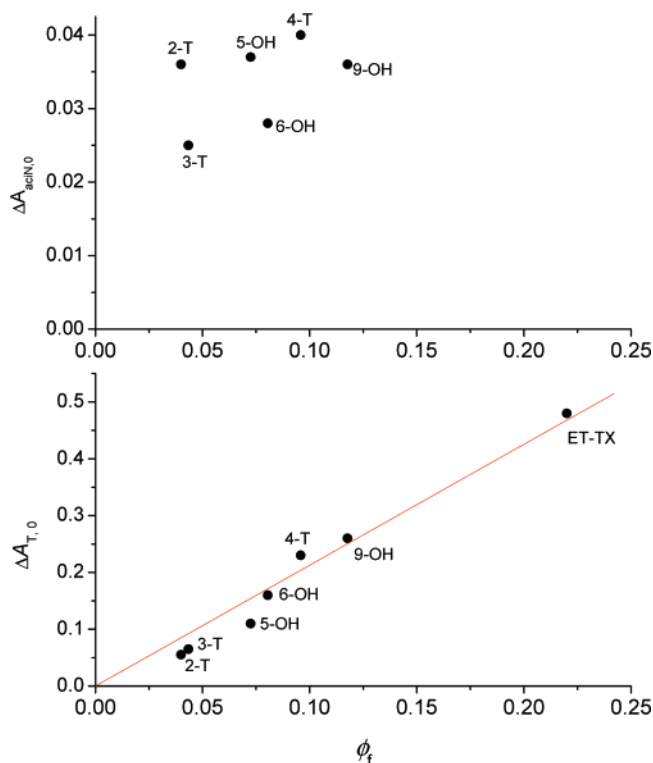
Figure 11. Correlation of initial triplet absorbance ($\Delta A_{T,0}$) and initial absorbance of *aci*-nitro form ($\Delta A_{aci-N,0}$) with fluorescence quantum yield ϕ_f (the symbols n-OH and n-T represent the compounds T7n-OH and T7n-O(CO)Thy, respectively, and ET-TX represents 2-ethylthioxanthone).

We note that, for the corresponding linker length, the rate constants observed by us are by about 2 orders of magnitude smaller than those found for triplet−triplet energy transfer in linked benzoyloxy/aryloxy conjugates[42,43] or for electron transfer in 1-pyrenyl-n-dimethylaniline alkanes.[46] Thus it should be clear that triplet−triplet energy transfer in our case is not controlled by chain diffusion dynamics but that it is limited by the rate of the "static" triplet energy process itself. It is noteworthy that triplet energy transfer in polypeptide linked thioxanthone/naphthalene pairs[40] occurs at about the same rate as those in our systems which supports the authors' conclusion that the observed time constant of 20 ns represents the slowest temporal component of the folding kinetics of a short oligopeptide with as little as three peptide bonds.[47]

When investigating the triplet decay curves for the various thioxanthone/NPPOC conjugates we noticed that the initial amplitude of the triplet signal showed a systematic correlation with the length of the linker and, hence, with the triplet decay time (cf. Figure 6). We also found a significant dependence of the fluorescence quantum yield on the linker length. A plot of the initial triplet absorbance $\Delta A_{T,0}$ versus the fluorescence quantum yield ϕ_f shown in Figure 11 reveals that both quantities are linearly correlated. This means that the quenching of S_1 of the thioxanthone chromophore prevents formation of the triplet

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(47) Recently, using intramolecular triplet−triplet energy transfer between the xanthone triplet and naphthalene, it has been confirmed that time constants of about 20 ns do indeed represent the slowest temporal components of the folding kinetics which otherwise extend to the 50−500 ps regime. Cf. Fierz, B.; Satzger, H.; Root, C.; Gilch, P.; Zinth, W.; Kiefhaber, T. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 2163−2168.

state normally formed at yields above 50%.[48] The apparent rate constant k_S of intramolecular singlet quenching can be evaluated as

$$k_S = \frac{1}{\tau_{S,0}}\left(\frac{\phi_{f,0}}{\phi_f} - 1\right) \qquad (3)$$

which follows from the usual Stern–Volmer equation. Here ϕ_f and $\phi_{f,0}$ are the fluorescence quantum yields of the thioxanthone/NPPOC conjugate and of free ethyl thioxanthone, respectively, and $\tau_{S,0}$ is the fluorescence lifetime of the thioxanthone chromophore, for which a value of 2.6 ns in MeOH[38] was used. In Figure 10, the values obtained for k_S are plotted versus the linker length n together with the values of k_T. Both rate constants exhibit a similar dependence on n, but the absolute values of k_S are larger than those of k_T by almost 2 orders of magnitude.

The observations regarding the linker-length dependence of fluorescence quantum yield and initial triplet yield indicate that intramolecular quenching of the singlet excited thioxanthone chromophore by the NPPOC moiety precludes the formation of observable thioxanthone triplets on the nanosecond time scale. However, it is important to note that the yield of the *aci*-nitro intermediate generated through this quenching process is rather independent of the linker length (cf. Figure 11). The same applies to the overall photochemical quantum yield.[8] In search of a quenching mechanism that can account for all these observations, singlet–singlet energy transfer from thioxanthone ($E_{S1} \approx 285$ kJ/mol)[49] to NPPOC ($E_{S1} \approx 314$ kJ/mol)[49] can be discarded, since it is too strongly endothermic to occur at such a fast rate. Singlet quenching through a charge transfer intermediate might be invoked since electron transfer from singlet excited thioxanthone to nitrobenzene is estimated to be exergonic by about -38 kJ/mol (cf. Supporting Information). However, the femtosecond experiments provide conclusive evidence that a different quenching pathway is followed in the linked thioxanthone/NPPOC conjugates. Recently, for xanthone in water, it was shown that its first excited singlet state undergoes an ultrafast intersystem crossing in the picosecond domain but that the fluorescence decay time is 700 ps.[39,50] This "delayed" fluorescence is due to a rapidly established equilibrium between the $^1\pi\pi^*$ state and the $^3n\pi^*$ state which are nearly isoenergetic. The observed "delayed" fluorescence decay reflects the relatively slow internal conversion process between the $^3n\pi^*$ state and the $^3\pi\pi^*$ state. The $^3n\pi^*$ state can be quenched by high concentrations of 1-methylnaphthalene with concomitant formation of the triplet state of the quencher. As documented by the results of the femtosecond time-resolved experiments with 2-ethylthioxanthone and T7S2-OH presented in Figure 9, this scenario is also fully applicable to thioxanthone.

According to Figure 9A, the growing-in time of about 2 ns of the transient absorption of the $^3\pi\pi^*$ state matches the decay time of the stimulated emission from the fluorescing $^1\pi\pi^*$ state. This seems to imply that intersystem crossing takes place in $\sim$2 ns. However, as can be learned from the example of the xanthone case,[50] such a conclusion may be premature. In our

case, too, the experiment with the addition of the triplet energy acceptor 1-methylnaphthalene (Figure 9B) gives clear evidence that triplet energy transfer between the photoexcited 2-ethylthioxanthone and the triplet energy acceptor takes place. This requires that at least partially a triplet state, which is not the lowest $^3\pi\pi^*$ state, is populated well before 2 ns. As in the case of xanthone,[50] the establishment of an equilibrium between the primarily excited $^1\pi\pi^*$ singlet state and an upper $^3n\pi^*$ triplet state must be invoked. Within this mechanism, the time constant of 2 ns is assigned to the simultaneous decay of the equilibrated $^1\pi\pi^*$ and $^3n\pi^*$ states. This decay populates the lowest $^3\pi\pi^*$ state. During the first 20–30 ps, the stimulated emission slightly decays in magnitude and experiences a red shift. A global analysis yields a time constant of $\sim$10 ps for this process (for all three samples). This constant represents the characteristic time of the equilibration between the $^1\pi\pi^*$ and the $^3n\pi^*$ states.

The femtosecond time-resolved experiment with the thioxanthone/NPPOC conjugate T7S2-OH (cf. Figure 9C) shows that the behavior of this system is essentially similar to that of the combination of the free thioxanthone chromophore and a triplet energy acceptor in high concentration. The observed shortening of the excited singlet decay time of T7S2-OH must be assigned to an intramolecular triplet energy transfer from the upper ($^3n\pi^*$) state of the thioxanthone moiety to the NPPOC group. The $^3n\pi^*$ state ($E_T \approx 295$ kJ/mol)[51] is close in energy to the $^1\pi\pi^*$ state, and therefore, a fast and reversible intersystem crossing between these states occurs. Hence, when this higher triplet state is quenched by the attached NPPOC group, the fluorescence of thioxanthone will be also quenched. Thus, fluorescence quenching occurs through triplet–triplet energy transfer from the $^3n\pi^*$ state. This process is by 2 orders of magnitude faster than the energy transfer from the lower $^3\pi\pi^*$ state. The increase can be related to the Gibbs free energy ΔG released in either process. The $^3n\pi^*$ state is expected to lie higher in energy by $\sim$30 kJ/mol.[51] This value matches those derived for the closely related compounds xanthone (35 kJ/mol)[50] and benzophenone (25 kJ/mol).[52] Therefore, the free energy release ΔG for energy transfer to the NPPOC group is expected to be more negative by 25–35 kJ/mol for the transfer from the $^3n\pi^*$ than that from the $^3\pi\pi^*$ state. Provided that the process shows normal behavior in a Marcus theory sense, this should result in an increased rate, as observed. The transfer from the $^3n\pi^*$ state leads to direct formation of the NPPOC triplet, which reacts further to the *aci*-nitro compound. No intermediate formation of the $^3\pi\pi^*$ state of thioxanthone is observable for this energy transfer channel. Hence the amplitude of the $^3\pi\pi^*$ absorption in the nanosecond time-resolved experiment is decreased. The mechanism is summarized in Scheme 2.

The present findings on the decay mechanism of the first excited singlet state and the two lowest triplet states of thioxanthone reveal a remarkable parallelism to the behavior of xanthone: namely, the detectability of a fast $S_1(\pi\pi^*) \rightleftarrows T_2$-$(n\pi^*)$ equilibrium and the fairly slow internal conversion from $T_2(n\pi^*)$ to $T_1(\pi\pi^*)$. In a previous investigation by Ley et al.[38] employing laser spectroscopy with about 30 ps time resolution, a fast ($\sim$10^{11} s^{-1}) and slow component of intersystem crossing were observed. The latter was closely correlated with the solvent-dependent singlet lifetime. Based on the experimental

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(49) These singlet energies were estimated from the onsets of the first absorption bands in MeOH yielding 420 nm for thioxanthone and 380 nm for NPPOC.

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Scheme 2. Deactivation Pathways of Photoexcited Thioxanthone Linked to NPPOC as Energy Acceptor Group
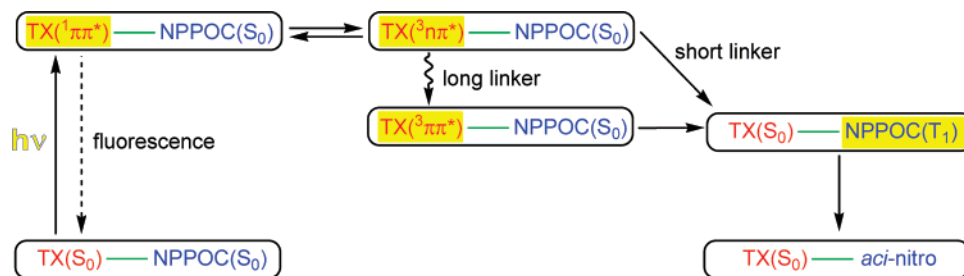
findings at that time these processes have been assigned to the $S_2(n\pi*)$ to $T_1(\pi\pi*)$ and the $S_1(\pi\pi*)$ to $T_2(n\pi*)$ intersystem crossing, respectively. In light of the new results reported here, this interpretation ought to be reconsidered.

3.2. Other Linkers. 3.2.1. T4E2-OR. Although the oxycarbonyl group in this compound represents a very short linker between the two chromophores, energy transfer is very slow. Nevertheless, it should be noted that, for the observed triplet lifetime of the thioxanthone chromophore of 3 μs, the efficiency of energy transfer is still close to 90%. One reason for the slow energy transfer might be a possible unfavorable shift of the triplet energy of thioxanthone by the substitution with a 2-benzoyl function. In order to check this possibility, we performed triplet quenching experiments with the unlinked chromophore, viz. the benzoic acid ester TOBz using NPPOC-Thy as a quencher. The triplet quenching constant was found

TOBz
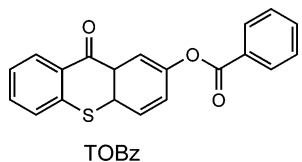
to be 6.4×10^8 M^{-1} s^{-1}, whereas for unsubstituted thioxanthone it was 1.0×10^9 M^{-1} s^{-1}. This difference is not so pronounced as to explain why intramolecular energy transfer should be so much slower in T4E2-OR than in the compounds T7Sn-OR.

The reason for the slow energy transfer must be probably sought in the rigidity of the ester linkage which only allows free rotation of the two chromophores in a coaxial fashion around the σ-bonds through which they are connected to the $-$O(CO)$-$ bridge. This does not change the distance between them. Obviously, a through-bond mechanism involving this linkage is not effective either.

3.2.2. T7D4-OR. In these compounds, no transient absorption from a $^3\pi\pi*$ state is detectable. However, from the fact that T7D4-O(CO)Thy does show some photodecomposition involving reaction of the NPPOC group,[8] one may conclude that some energy transfer occurs which, according to the reasoning above, should involve the $^3n\pi*$ state. *Trans/cis*-isomerization occurring in either the singlet or triplet state competes with energy transfer.[8] Hence the quantum yield of the NPPOC reaction is low.

3.2.3. T7T4-OR. With a value of 0.9 μs, this compound shows the second longest triplet decay time among the investigated thioxanthone/NPPOC conjugates. This indicates a relatively slow triplet$-$triplet energy transfer, which may be explained by the relatively long, inflexible linear part of the linker chain extending over three C$-$C σ-bonds including the triple bond. It must be pointed out, though, that for T7T4-

O(CO)Thy the yield of photorelease of thymidines is only 33% or less;[8] i.e., other photochemical reaction channels involving the triple bond are dominant. Since these reactions probably compete with electronic energy transfer to the NPPOC group, the triplet lifetime of the thioxanthone moiety as given above is a lower limit to the time constant of the triplet energy transfer process.

3.2.4. T5S0-OR. In this case, the notion of separated chromophores and energy transfer between them is no longer valid. Stationary UV/vis and transient absorption spectra clearly reveal that it is the combined chromophore which is spectroscopically active. In view of this situation, and considering the example of the methylnitropiperonyloxycarbonyl (MeNPOC) group where the methylenedioxy-substituent leads to enhanced absorption but also to a concomitant decrease of the photochemical quantum yield,[5] it is fortuitous that the combined T5S0-chromophore is still very reactive toward benzylic hydrogen to form the *aci*-nitro intermediate. In fact, this process seems to determine the lifetime of the excited triplet state in this chromophore, as can be seen by comparison with the model chromophore T5S0-M that does not have an abstractable benzylic hydrogen.

Conclusions

Intramolecular electronic energy transfer in a novel class of photoremovable protecting groups based on the NPPOC group but enhanced by thioxanthone, covalently linked as an intramolecular antenna, has been studied. Triplet$-$triplet energy transfer has been demonstrated to occur between the thioxanthone and NPPOC chromophores. For long linkers, or for inflexible short linkers forcing the chromophores into relative conformations with weak electronic coupling, energy transfer occurs from the relaxed $^3\pi\pi*$ state of the thioxanthone moiety. From this state, energy transfer is slow enough as to leave it detectable by nanosecond time-resolved laser flash spectroscopy. For short, flexible linkers, fast triplet energy transfer to NPPOC *and* fluorescence quenching is observed. Based on femtosecond time-resolved experiments, evidence has been provided that in this case triplet$-$triplet energy transfer occurs from the higher $^3n\pi*$ state which is in dynamic equilibrium with the $^1\pi\pi*$ state of the thioxanthone moiety. This situation is completely analogous to what was recently reported for xanthone.[39,50] For the acceptor and donor in contact, the rate constant for energy transfer from the $^3n\pi*$ state of thioxanthone is by about 2 orders of magnitude larger than that from the $^3\pi\pi*$ state, a fact which is assigned to the higher energy of the former. However, to what extent each of the two triplet$-$triplet energy transfer channels actually contributes depends on the time it takes to bring the energy donor and acceptor close enough together, that is, on the conformational dynamics of the linker chain. For long linkers,

this time is longer than the time for internal conversion from the $^3n\pi^*$ to the $^3\pi\pi^*$ state, and thus the slower energy transfer process from the $^3\pi\pi^*$ state dominates. For short linkers, contact formation of the energy donor and acceptor is faster than the internal conversion process, and thus energy transfer occurs from the $^3n\pi^*$ state (cf. Scheme 2).

Direct linkage of the aromatic ring systems of donor and acceptor chromophores yields a united chromophore as evidenced by the greatly changed absorption spectra in the ground state and in the triplet state. In this situation, the reactivity of the nitro group toward the benzylic hydrogen atom is by several orders of magnitude slower than that in the case of the locally excited $^3n\pi^*$ state of NPPOC. Nevertheless, it seems that the H-atom transfer still determines the lifetime of the combined chromophore's triplet state since a high yield of photocleavage is observed in this case, too.

4. Experimental Section

4.1. Spectroscopy. 4.1.1. Absorption and Fluorescence Spectra. Absorption spectra were measured on a Cary 50 or a Perkin-Elmer Lambda 18 spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer LS 50 spectrometer. Fluorescence quantum yields were determined for an excitation wavelength of 355 nm using acridone in ethanol as a reference ($\phi_f = 0.98$).[53] The concentrations of all sample solutions were adjusted to an absorbance of 0.05 in order to keep inner filter effects and reabsorption low.

4.1.2. Nanosecond Laser Flash Spectroscopy. Samples were excited by a frequency tripled Nd:YAG-laser (Spectra Physics Quanta Ray GCR 150, 355 nm, repetition rate 5 Hz, pulse width 4−6 ns). The pulse energy of 100 mJ was reduced to about 30 mJ by neutral density filters. The optical detection system for transient absorption involved a xenon lamp (Osram XBO 150), a monochromator (SpectraPro) and a photomultiplier (Hamamatsu R 955) or an intensified gated CCD camera (PI-MAX 1024 HQ-Blue, Princeton Instruments). The photomultiplier signal was recorded by a digital oscilloscope (LeCroy 9354A), and the data were transmitted to a personal computer. The CCD data were processed using the Labview-based program "TOsKaNa" developed in our laboratory. For measurements in oxygen-free media, the solutions were purged with N_2. A flow system was used to exchange the probed sample volume in the cuvette between any two successive laser pulses.

4.1.3. Femtosecond Transient Absorption Spectroscopy. Femtosecond transient absorption spectra were recorded with the setup detailed in ref 54. The setup as described there is used for femtosecond

stimulated Raman spectroscopy, but when blocking the Raman pump beam it can also deliver transient absorption data. The pertinent parameters for the present experiments were the following. Excitation pulses at 388 nm were derived from the output of a CLARK CPA 2001 laser/amplifier (775 nm, 1 kHz) by frequency doubling. The pulse energy at the sample location was ∼300 nJ. The focal spot had a diameter of ∼150 μm there. Excitation induced absorption changes were monitored by a white light continuum generated by focusing the CPA fundamental onto a CaF_2 plate. The relative polarization of excitation and probe light was set to the magic angle. After passing the sample the white light was dispersed and detected with a diode array. The time resolution of the experiment was ∼200 fs. The excitation light was chopped at 500 Hz to yield induced absorption differences. The timing between excitation and probe was adjusted with a delay line. At each delay position, data were accumulated for 2−4 s and the results of two scans of the delay were averaged.

Sample solutions were pumped through fused silica flow cells (path length 1 mm) at a rate sufficient to exchange the sample between subsequent laser shots. The concentration of the thioxanthones dissolved in methanol (Merck UVASOL) was adjusted to 1−3 mM which corresponds to an optical density of ∼1 OD at the excitation wavelength. The volume of the sample solution was 5−10 mL and high enough to avoid signal contributions from photoproducts.

4.1.4. NMR and MS Spectra. NMR Spectra were measured with a JEOL GX 400 FT-NMR or a Bruker DRX 600, respectively. EI and FAB mass spectra were recorded with a Varian MAT 312 mass spectrometer. The FAB ion source was from AMD.

4.2. Materials. The syntheses of most of the protected thymidines are described in ref 29. The alcohols T7Sn-OH ($n =$2, 5, 6, 9), the protected thymidine T7S2-O(CO)Thy, and the reference compounds TOBz and T5S0-M were synthesized as described in the Supporting Information.

Supporting Information Available: 1. Transient spectra and decay curves. 2. Estimation of energy of charge transfer state [TX]$^-$[NPPOC]$^+$. 3. Syntheses. 4. NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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