TERMINALLY SUBSTITUTED CONJUGATED POLYENES: SYNTHESIS AND ENERGY TRANSFER PROPERTIES

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ABSTRACT. — The present publication summarizes the results of our investigations on conjugated polyenes with different end groups. The spectroscopic data reveal the possibility of a selective electronic end group excitation in the conjugated systems influenced by steric factors between the end groups and polyene chains. An intramolecular energy transfer from one excited terminal substituent to the other via the polyene chain is likely. The interruption of the conjugation in the polyenes by a bicycloalkane unit results in a separation of the molecules' spectroscopic behavior. Energy transfer is modified, but still present.

In recent years investigations on energy transfer processes in molecular systems have become more important [1]. Besides basic work on electron transfer in biological systems, in particular on the mechanism of photosynthesis [2], increasing interest exists in the synthesis of organic compounds useful for information transport and storage on the molecular level [3, 4].

In this review we report the synthesis and spectroscopic investigations of terminally substituted polyenes with various chain lengths. The substituents and polyene chains were selected for their distinct excitation energies when considered as independent units. Supposing selective electronic excitation of the end groups, these compounds should be good models to prove an intramolecular energy transfer between the end groups via polyene chains.

Synthesis of terminally substituted conjugated polyenes

At the begining of our investigations, polyenes of this type were not known however, the synthesis of several donor acceptor substituted conjugated polyenes have been published in the meantime [4, 5]. In the present publication only the synthesis of compounds relevant to the investigations and discussion on energy transfer is described.

We previously reported the synthesis of terminally substituted conjugated polyenes in a short communication [6]. A detailed publication [7] contains all aspects concerning the synthesis of these compounds, especially the accurate *E/Z* isomer ratios. For the syntheses we used exclusively segments of naturally occurring carotinoids, for example 2, 7-dimethyl-octatrienedial (**1**) and (7-formyl-2-methyl-2, 4, 6-octatrienyl)-

triphenylphosphonium chloride (**2**), which is easily accessible from **1**. These segments were connected via Wittig reactions to the desired terminal groups, as shown in many published examples using the compounds **1** and **2** to synthesize carotinoids [8, 9]. The presence of methyl side groups increases the stability of the conjugated polyenes against oxygen, light and heat compared to the corresponding nonsubstituted compounds.

Figure 1 summarizes the synthesis of the compounds **6a**, **b**, **c** and **7a**, **b**, **c** which are important for the spectroscopic investigations on intramolecular energy transfer.

The Wittig olefinations with the easily accessible tetraphenylporphyrine aldehyde (TPP-CHO) were conducted with the acetal **2a**, generated *in situ* from the phosphonium salt **2** [9], to avoid expected side reactions. The polyene aldehydes **3** and **4** occur as isomeric mixtures with ca. 70% all-*E* portion. The pure all-*E* compounds of **3** and **4** were obtained in total yields of 50% by recrystallization of the isomeric mixtures [7]. The Wittig olefinations of **3** with the anthrylmethyl phosphonium salts **5a-c** yielded the pentaenes **6a-c**, whose *E/Z* isomers were easily separated and distinguished by HPLC and UV/VIS spectroscopy. By chromatographic purification and several recrystallizations, the pure all-*E* isomers of the compounds **6a-c** were obtained [7]. In the case of the nonaenes **7a-c** synthesized from **4** and **5a-c**, separation of the *E/Z* isomers was not successful and recrystallization of **7a-c** yielded all-*E* portions of only 83-87% [7].

Our next goal was to synthesize compounds with structure comparable to **6** resp. **7**, in which a saturated carbon hydrogen spacer is built in the conjugated polyene chain [1]. In terms of molecular electronics, these compounds should serve as
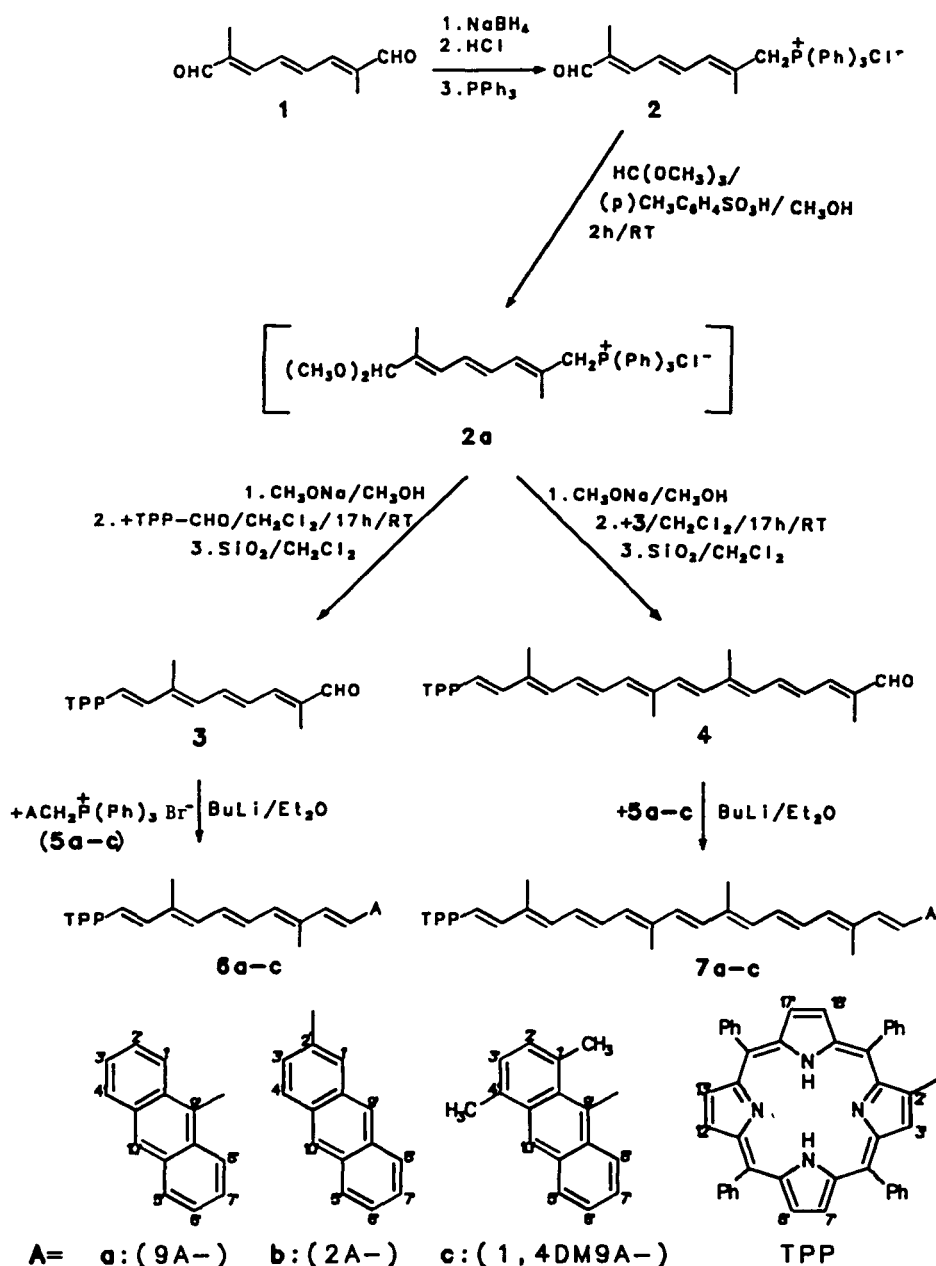
Figure 1

models for a reduction or complete interruption of an energy transfer via a conjugated polyene chain. Bicyclo[2.2.2]-octane, used in many other cases as a spacer unit in electron transfer molecules [10], was chosen as saturated unit to be built in the polyene chains. Figure 2 shows the synthesis of the model compounds 13 a und 15 a obtained so far.

In these cases pure all-E isomers were not obtained; 13 a contains a 12 % and 15 a a 31% portion of Z-isomers.

In order to interpret the spectroscopic behavior of the donor acceptor substituted polyenes 6 a-c, 7 a-c, 13 a and 15 a, it was necessary to synthesize the polyenes 6 d, 7 d and 7 e, shown in Figure 3, via Wittig olefinations likewise [7, 11].

Spectroscopic energy transfer investigations

The absorption, emission and excitation spectra of 6 and 7 were measured in order to investigate if, and to what extent

the electronic levels of the polyene chains and terminal groups are amalgamated into common levels of the whole molecule, and how this amalgamation is influenced by steric factors.

Experimental section

Absorption spectra were measured using a conventional spectrophotometer (Sp 8-20, Pye-Unicam) at room temperature in dichloromethane solutions with concentrations between 10^{-7} and 10^{-5} mol/L to obtain concentration independent results in all cases. Fluorescence spectra were obtained using the continuum of a xenon high pressure lamp connected to a monochromator or an argon ion laser for selective excitation at 514 and 257 nm, and were measured in n-hexane solutions at 180 K to exclude photochemical decomposition, which occurs under strong irradiation at room temperature. The fluorescence spectra were recorded by using a Jarell-Ash
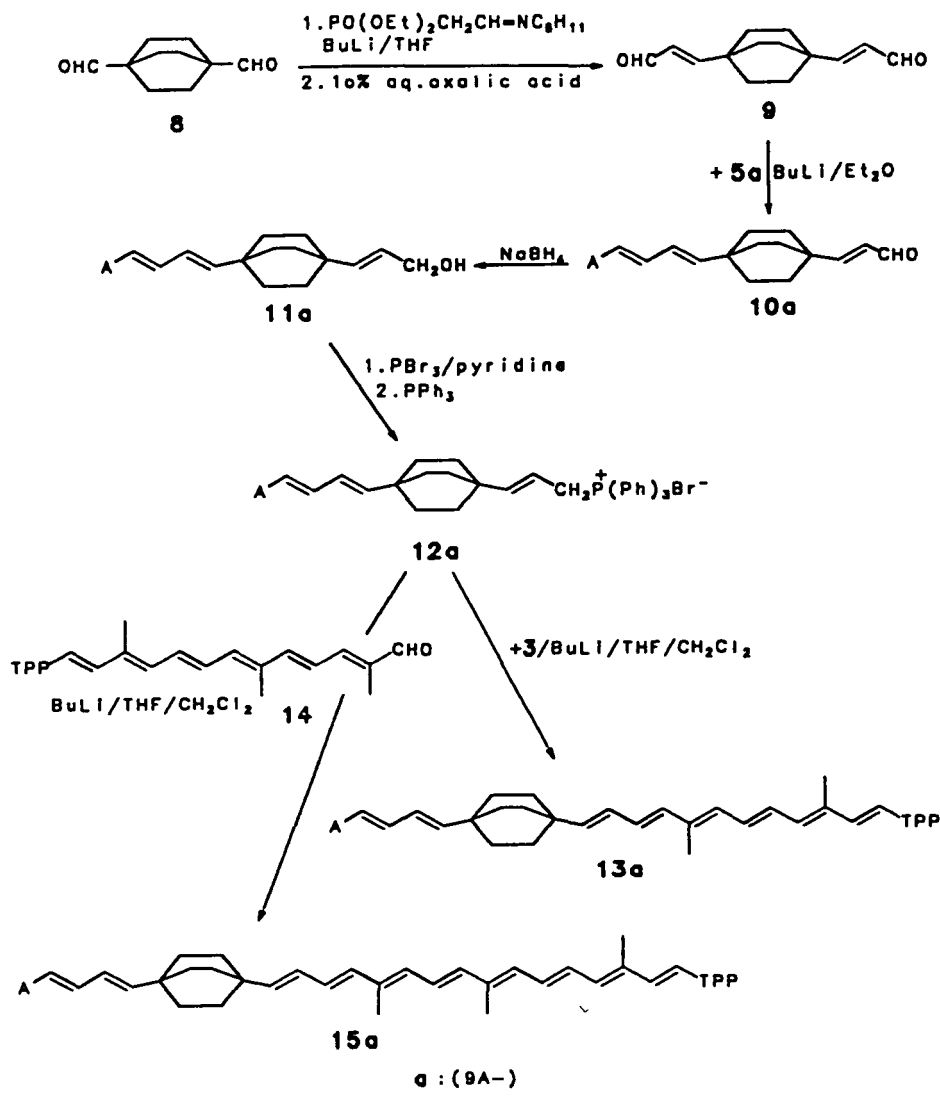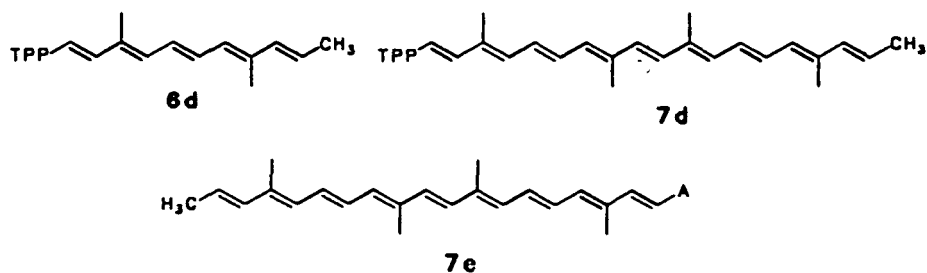
a : (9A-)

Figure 2

Figure 3

double monochromator and an EMI 9658 photomultiplier and were corrected with regard to their spectral sensitivity. The quantum yields reported are data relative to the usual standards anthracene in n-hexane, perylene in cyclohexane and tetraphenylporphyrine.

Absorption and fluorescence spectra; selective excitation of polyene terminal groups

Figure 4 shows the electronic absorption spectra of the bisubstituted nonaene $9A-P_9-TPP$ (7a), the methyl substi-

tuted nonaenes $TPP-P_9-CH_3$ (7d) and $9A-P_9-CH_3$ (7e) as well as the spectra of anthracene and tetraphenylpor-phyrine. In the spectrum of 7a the three molecule components can be identified individually: the S_3-absorption of the anthryl group at 250 nm, the absorption of TPP around 400 and 600 nm and the absorption of the polyene chain between 450 and 550 nm. The absorption areas of these three molecule components are modified when compared with those of anthracene, tetraphenylporphyrine and the nonaenes 7d and 7e which bear a terminal methyl substituent. The absorption coefficients of 7a are reduced, the bands are generally broadened and slightly shifted in their positions.
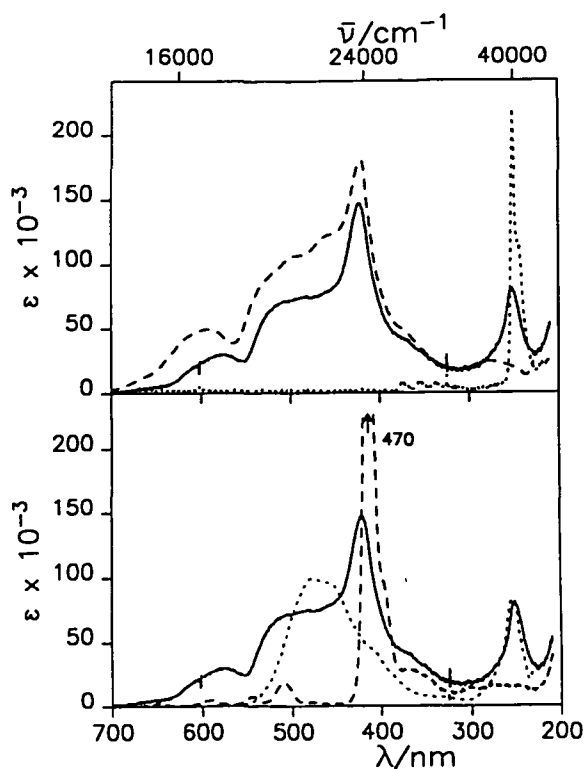
Figure 4. – Absorption spectra (in *n*-hexane, *T*=295 K). Top: —— 9 A – P₉ – TPP (7 a), —— TPP – P₉ – CH₃ (7 d) solvent chloroform ... anthracene. Bottom: —— 9 A – P₉ – TPP (7 a), ... 9 A – P₉-CH₃ (7 e), —— tetraphenylporphyrine P₉ = polyene chain corresponding to 7.

Figure 5. – Excitation and absorption spectra (in *n*-hexane, *T* = 180 K). (*a*) —— excitation of 1,4 – DM 9 A – P₅ – TPP (6 c) (λ_d = 730 nm). --- absorption of 6 c. ... excitation of TPP – P₉ – CH₃ (6 d) (λ_d = 730 nm). (*b*) —— excitation of 1,4 – DM 9 A – P₉ – TPP (7 c) (λ_d = 730 nm). --- absorption of 7 c. P₅ = polyene chain corresponding to 6.

As shown in Figure 5, the absorption areas of the individual molecule parts can also be recognized in the absorption spectra of the 1, 4-DM 9 A and TPP substituted molecules 6 c and 7 c, as well as the red shift of the polyene absorption with increasing chain length.

The 2-anthryl substituted polyenes 6 b and 7 b show characteristic differences to anthracene in their absorption between 220 and 300 nm. These differences are less evident in the case of the nonaene 7 b with longer polyene chain than in the case of the pentaene 6 b.

Figure 6 shows the emission spectra of the compounds 7 a, 7 d and 7 e after the excitation at 256 nm and normalization to the same maximum intensity. The 9-anthryl and TPP substituted molecule 7 a has a dual fluorescence, in which the emission between 400 and 500 nm can be coordinated to the anthryl group, and the 650 to 800 nm emission correlates to the TPP substituent. In 7 d and 7 e only one emission band, characteristic of the corresponding emitting polyene terminal group, occurs.

The results of the absorption and fluorescence measurements can be summarized as follows: the partners connected to one common molecule retain the identity of their electronic levels with their vibronic structures to a great extent. A selective excitation of anthryl terminal groups is possible. Thus a complete amalgamation of the molecule part's energy levels into new levels of the whole molecule does not occur. Changes in the molecular levels of the different partners connected to a common molecule can be seen on the other hand:
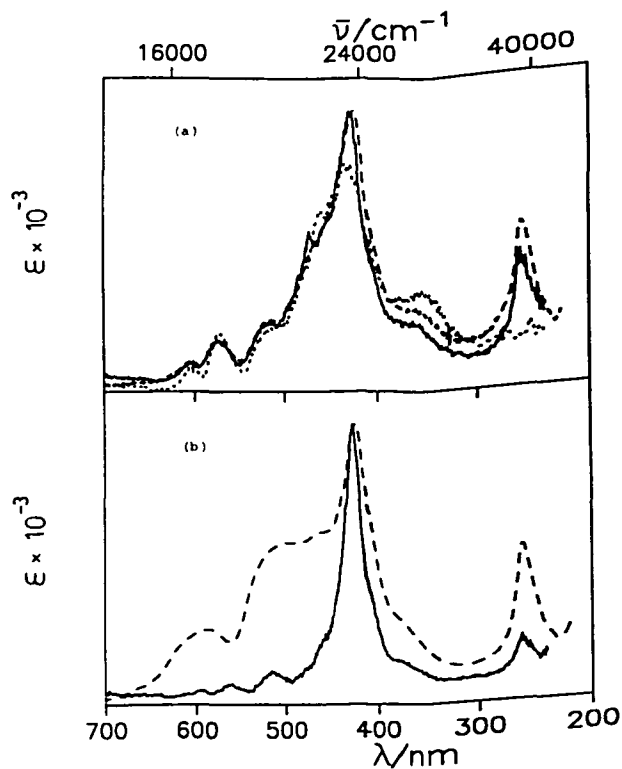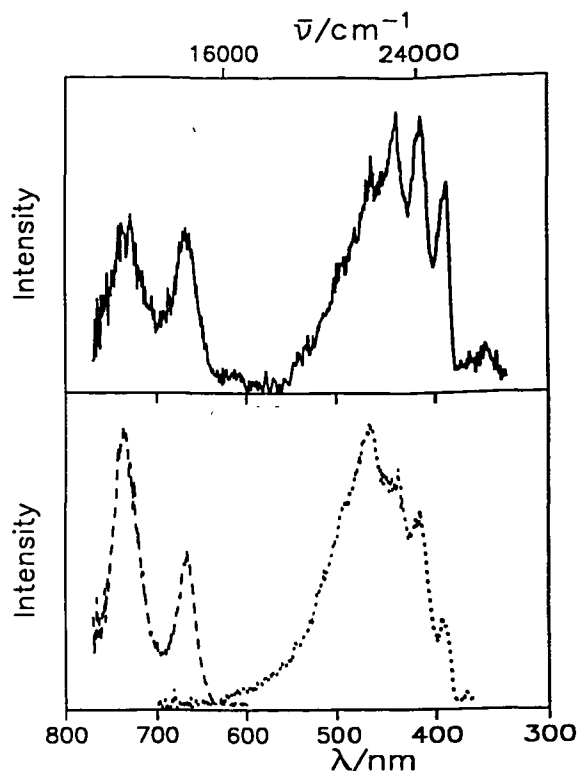

Figure 6. – Emission spectra (in *n*-hexane, at 180 K, excitation at 256 nm). Top: —— 9 A – P₉ – TPP (7 a). Bottom: --- TPP – P₉ – CH₃ (7d), ... 9 A – P₉-CH₃ (7 e). The three emission spectra are each normalized to the same maximum intensity.

— energy shift and loss of vibronic structure in the polyene absorption.

— decreasing absorption coefficients, line broadening and a slight energy shift in the area of the anthryl S_3-band.

— changes in the structure and energies of absorption spectra at wavelengths between 220 and 400 nm which are not yet understood in detail in the case of the 2-anthryl substituted polyenes.

The amalgamation between the electronic levels of the terminal substituents and the polyene chain is obviously strongest if the chain is short and a coplanar arrangement of the polyene chain and aromatic substituent is possible such as in the case of the 2-anthryl substituted compounds 6b and 7b. A coplanar arrangement of the anthryl substitutent and polyene chain is energetically unfavorable in the 9-anthryl substituted polyenes 6a, c and 7a, c based on steric hindrance. This was confirmed theoretically by Hückel calculations and group theoretical considerations [12].

Intramolecular energy transfer

In order to prove an intramolecular energy transfer via polyenes, the excitation spectra of the compounds 6 and 7 were investigated, see ref. [13]. Figure 5 shows that an excitation of TPP emission is possible over the whole area of the absorption spectra. The excitation at 250 nm, where the S_3-absorption of the anthryl group is located, corresponds to an energy transfer from the anthryl substituent to TPP. The following difference between Figure 5a and 5b is noticed furthermore: the excitation spectrum of the pentaene 6c covers the absorption spectrum largely, representing an energy transfer to the TPP terminal group in spectral areas having mainly polyene absorption. On the other hand, the broad maximum at 500 nm belonging to the polyene absorption does not appear in the excitation spectrum of the nonaene 7c with a longer polyene chain, indicating that no energy transfer from the polyene to the TPP group occurs.

In order to prove an intramolecular energy transfer, intermolecular mechanisms must be excluded. The concentration independence of the spectroscopic results show that a reabsorption mechanism does not occur. The Förster mechanism for nonradiative energy transfer between the molecules seems to be insufficient to explain all experimental data either: the expected concentration dependence was observed just as little as a shortening of the donor emission's decay time constant and a corresponding delay of the start of the acceptor emission. Because of the low quantum yields further experiments will be necessary to support and confirm these statements.

Altogether, our measurements point at an energy transfer between the anthryl and TPP terminal group in the present molecules. We suppose a partial relaxation of the energy absorbed by the anthryl substituent into an electronic level belonging to the whole molecule and resulting from an amalgamation of electronic levels of the three partners. The emission from the TPP acceptor takes place after further relaxation into its lowest excited S-level.

Quantum yields

For further investigations on the energy transfer, the fluorescence quantum yields of the blue and red emission of the polyenes and the comparison compounds anthracene, 1, 4-dimethylanthracene and tetraphenylporphyrine, summarized in Table I, were measured. Since the quantum yields are very low and therefore not determined with high accuracy, a quantitative evaluation of these measurements to register the complete quantum flow in a molecule and its parts cannot yet be made with reliability. Furthermore, the partly strong overlay of the absorption areas of the molecule segments creates large uncertainties for dividing up the absorbed quantum to different parts of a molecule.

Table I. — Quantum yields in % measured at $\lambda_{exc} = 250$ nm [*].

Molecule	Red emission	Blue emission
Anthracene	---	45
1,4-dimethylanthracene	---	31
5,10,15,20-tetraphenylporphyrine	1.6	---
TPP−P$_5$−CH$_3$(6d)	0.9	---
9A−P$_5$−TPP(6a)	0.1	0.4
1,4−DM9A−P$_5$−TPP (6c)	0.2	0.2
TPP−P$_9$−CH$_3$(7d)	0.2	---
9A−P$_9$−TPP(7a)	0.03	1.7
1,4−DM9A−P$_9$−TPP (7c)	0.2	0.4
9A−P$_2$−Bic−P$_1$−CHO(12f)	---	49
TPP−P$_6$−CHO(14)	0.4	---
9A−P$_2$−Bic−P$_6$−TPP(13a)	1.7	9
TPP−P$_8$−CHO(4)	0.2	---
9A−P$_2$−Bic−P$_8$−TPP(15a)	0.1	3

[*] experimental range of error ±20%

Spectra, quantum yields and energy transfer in molecules with spacer

The comparison between the absorption spectra of the polyenes with spacer, 10a, 13a and 15a, and the polyenes without spacer, 4 and 14 (Fig. 7) reveals no appearance of the spacer in the range of 200 to 700 nm. The absorption spectra of the polyenes 13a and 15a are to a first approximation additive overlays of the spectra of the molecules 4 resp. 14 and 10a. The areas characterizing the absorption of TPP, the polyene chains and the anthryl groups are also recognizable here. Further bands appear between 200 and 300 nm besides the intense S_3-band of the anthryl terminal group. The band at 220 nm can be related to the diene part of the molecule, whereas the weak bands between 260 and 300 nm obviously result from overlay levels of the diene and anthryl group. Since the absorption spectra reveal no indication of coupling between the polyene chains to both sides of the spacer, obviously a noticeable separation of their electronic levels takes place by the spacer.

Like in the case of 6a, c and 7a, c, the fluorescence spectra of the anthryl TPP molecules with spacer 13a and 15a show a dual emission (Fig. 8). The short wavelengths (blue) component at 500 nm is slightly redshifted relative to the emissions known from the anthryl group (see Fig. 6) and shows no vibronic structure. Furthermore, a decrease of the relative intensity between the emissions at short and long wavelengths occurs with increasing polyene chain length.

Table I also summarizes the quantum yields of the long wavelengths (red) and short wavelengths (blue) emissions of
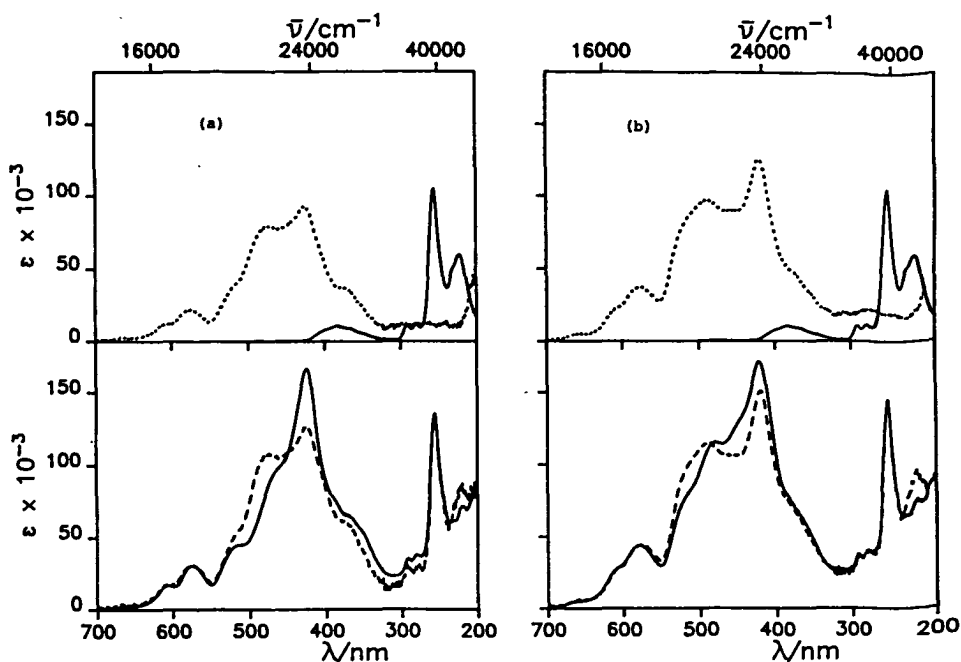
Figure 7. – Absorption spectra of molecules with spacer (in *n*-hexane, *T*=295K). (*a*) Top: —— 9A–P$_2$–Bic–P$_1$–CHO(10a), ... TPP–P$_6$–CHO(14). Bottom: —— 9A–P$_2$–Bic–P$_6$–TPP(13a) measured, — additive overlay of normalized spectra of 10a and 14, *see* ref. [14]. (*b*) Top: —— 9A–P$_2$–Bic–P$_1$–CHO(10a), ... TPP–P$_8$–CHO(4). Bottom: —— 9A–P$_2$–Bic–P$_8$–TPP(15a) measured, — additive overlay of normalized spectra of 10a and 4, *see* ref. [14].
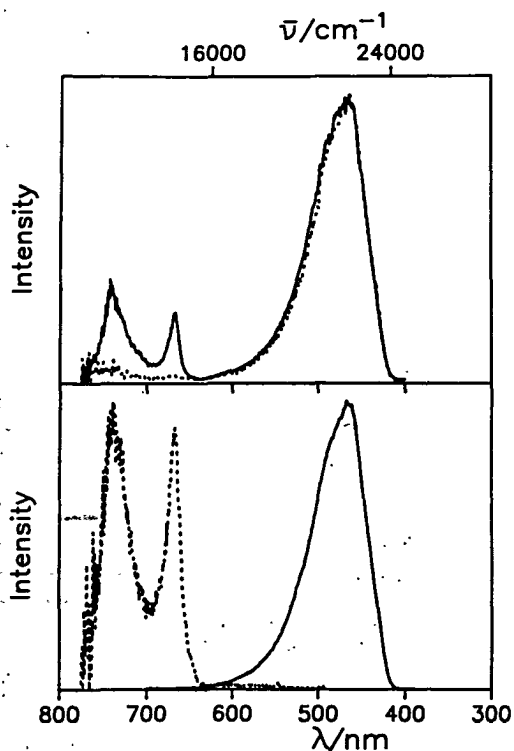
Figure 8. – Emission spectra of molecules with spacer (in *n*-hexane, at 180K, excitation at 256 nm). Top: —— 9A–P$_2$–Bic –P$_6$–TPP(13a), ... 9A–P$_2$–Bic–P$_8$–TPP(15a). Bottom: —— 9A–P$_2$–Bic–P$_1$–CHO(10a), ... TPP–P$_6$–CHO(14).

the molecules with spacer 10a, 13a and 15a. The introduction of a spacer into the polyene chain greatly influences the quantum yield of the blue emission, producing higher values

in the spacer molecules 10a, 13a and 15a than in the anthryl polyenes without spacer 6a, c, 7a and 7c. As already mentioned, a detailed analysis of the quantum yields is difficult and not yet complete.

In order to investigate the question of an energy transfer from the 9-anthryl substituent to the TPP terminal group in the spacer molecules 13a and 15a, the excitation spectra of the fluorescence at long and short wavelengths, shown in Figure 9, were measured. The excitation spectra are largely identical to the absorption spectra in the anthryl S$_3$-area when detected at the short wavelength emission (467 nm). In contrast, at the long wavelength emission (668 nm) the intensity in the excitation spectrum in the anthryl S$_3$-area decreases in the case of 13a. This decrease is even larger in the excitation spectrum of the compound 15a with longer polyene chain. The excitation and absorption spectrum of 13a resp. 15a are different also in the area of the long wavelengths polyene absorption at 500 nm. The excitation of TPP depends on the chain length of the polyene, similar to the molecules without spacer 6a, c and 7a, c. The fact that the excitation spectra of 13a and 15a detected at 668 nm reveal a band in the anthryl S$_3$-area leads to the conclusion that an energy transfer from the anthryl to the TPP substituent also occurs in the molecules with spacer. The comparison with the molecules without spacer 6a, c and 7a, c shows indeed that this transfer happens with reduced probability. For more details, *see* ref. [14].

We can summarize that the introduction of a spacer into polyene chains does not completely interrupt but can reduce energy transfer between the terminal groups. Further investigations on quantum yields and especially on rise-time and decay time constants of the emissions are in progress to give a complete explanation of the energy transfer processes.
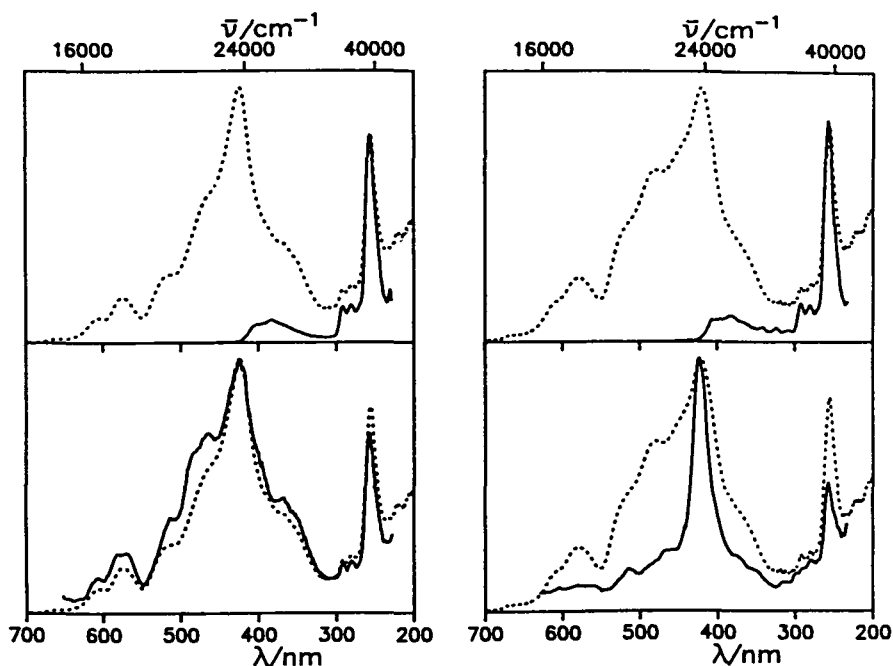
Figure 9. — Excitation spectra of molecules with spacer in comparison to their absorption spectra (in n-hexane, $T=180$ K). (a) $9A-P_2-Bic-P_6-TPP$ (13 a). Top: ... absorption, —— excitation ($\lambda_d = 466.5$ nm). Bottom: ... absorption, —— excitation ($\lambda_d = 667.5$ nm). (b) $9A-P_2-Bic-P_8-TPP$ (15 a) Top: ... absorption, —— excitation ($\lambda_d = 466.5$ nm). Bottom: ... absorption, —— excitation ($\lambda_d = 667.5$ nm).

Acknowledgement

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