Steroid-Bridged Anthryloligothienylporphyrins: Synthesis and Study on the Intramolecular Energy Transfer

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The novel steroid-bridged energy transfer system **2** was prepared starting from *epi*-androsterone. The linkage of both the anthrylthienyl and the bithienyl group in the 3- and 17-position of the steroid was achieved by Grignard reaction of the respective carbonyl function of the steroid component. The synthesis was accomplished by linkage of the porphyrin group according to Lindsey's method. This synthetic strategy also enables the approach to molecular subunits required as reference compounds. The photophysical properties were studied using time-resolved fluorescence and fluorescence excitation spectroscopy. Reference donor molecule **6** exhibits—in analogy to other anthryloligothiophenes studied—a dual fluorescence: a blue anthracene-like fluorescence and a dynamically coupled delayed red fluorescence resulting from the relaxed excited state. On the basis of these results, supermolecule **2** was investigated. Besides the typical porphyrin emission, a high energetic fluorescence (blue fluorescence) was detected in **2** which results unambiguously, as stated from spectra of **6**, from the donor part of **2**. The lifetime of this fluorescence is shortened compared with that of **6**. Supermolecule **2** is the first in the series of our energy transfer systems exhibiting donor fluorescence despite a very efficient intramolecular energy transfer (at least 99%).

Introduction

The development of novel multichromophoric molecules which act as light-harvesting and light conversion systems is of great interest with respect to applications in molecular-scale information processing systems[1] as well as synthetic solar energy conversion systems.[2] Inspired by processes of light-harvesting and excitation energy transfer in the photosynthesis, numerous synthetic model compounds have been studied which contain porphyrins as chlorophyll analogues.[3] Understanding the factors that govern intramolecular energy transfer processes in porphyrin systems, for instance, distance, orientation, and electronic communication between the chromophores, is an important prerequisite to the manufacture of molecular photonic devices. All these factors influence the mechanism of energy transfer and determine whether through-bond or through-space interactions between the chromophores are predominant.[3i]

In a recent publication we have described the intramolecular energy transfer properties of the trichromophoric supermolecule **1** bearing the anthracene donor as "input-chromophore", the porphyrin acceptor as "output-chromophore", and a quinquethiophene π-bridge as "mediator unit" (Chart 1).[4] After highly selective excitation of the anthracene end group (about 82% at 254 nm) we could prove a near-quantitative intramolecular singlet−singlet energy transfer to the porphyrin end group via the oligothiophene chain which results in typical porphyrin fluorescence. Neither anthracene-type nor anthrylquinquethienyl-type fluorescence could be detected.[4] The fluorescence signal deduced from time-resolved measurements appears instantaneously (<10 ps) with the pulse response of the apparatus. Consequently, the intramolecular energy transfer in **1** is faster than 10 ps. The mechanism of this ultrafast energy transfer can be explained by different theories[5] such as Förster's (through-space), Dexter's/superexchange (through-bond), and intramolecular relaxation. From our experimental results, however, a clear distinction cannot be made so far.[4,6]

In an effort to get deeper insight in the energy transfer, we have studied the role of the mediator unit: By introduction of a rigid, nonconjugated spacer unit the through-bond interactions via the π-system can be suppressed. Consequently, the mediator function of the oligothiophene is switched off. However, it is known from the literature[7] that in the case of nonconjugated spacers of comparable length Dexter energy transfer can occur

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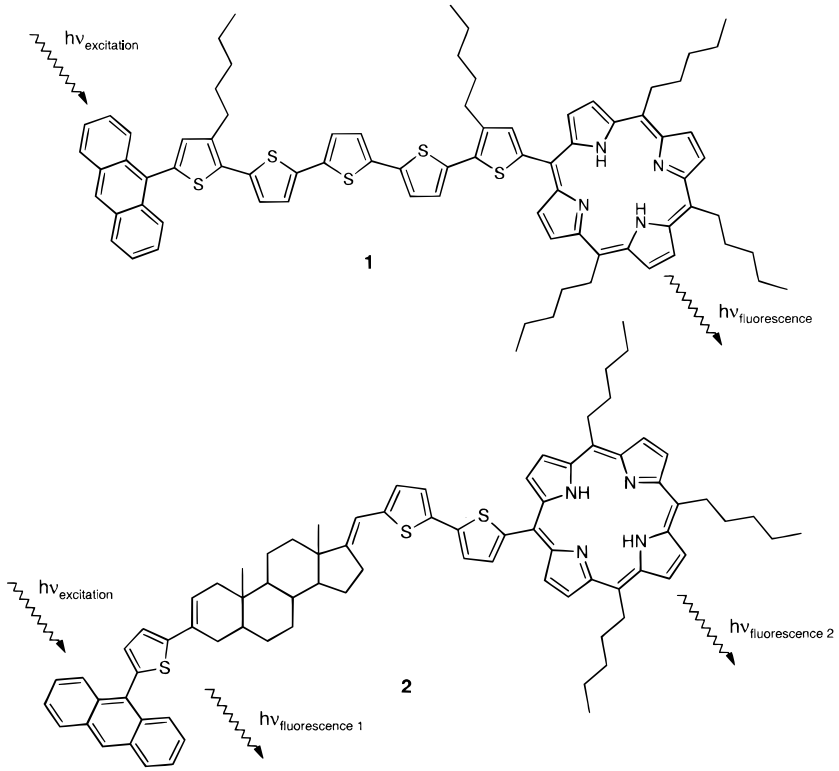
Chart 1



with transfer rates of 10^9 s^{-1}. For our studies, we have synthesized the new model compound **2** with a rigid steroid (androstene) spacer within the oligothiophene chain (Chart 1). The spacer was incorporated in such a manner that we get an anthrylthiophene donor unit and a bithienylporphyrin acceptor unit with elongation of conjugation, respectively (Chart 1). This geometry leads to a difference of length of about 2 Å between the bridging molecules in **1** and **2**.[8] It is of interest to see if the energy transfer properties in **2** will change as against **1**. If in **2** the Dexter mechanism dominates the energy transfer, the transfer rate should be lowered drastically (from $>10^{11}$ s^{-1} to 10^9 s^{-1}) and in addition to the typical porphyrin emission donor emission should occur as illustrated in Figure 1.

In the present paper we report on the synthesis and photophysical properties of the steroid-bridged porphyrin **2**. The optical properties of the anthrylthienylandrostenone unit **6** (Scheme 1) are of particular interest, since it represents the donor part of the supermolecule **2**. The influence of the spacer on the intramolecular energy transfer is discussed by comparison of **2** with the conjugated system **1**.

Results and Discussion

Synthesis. The proposed synthetic route to model compound **2**—linkage of the donor anthracene to the steroid unit followed by extension to the donor-bridge-thienyl compound **8** and introduction of the acceptor porphyrin (Scheme 1)—enables also the access to the molecular subunits required as reference compounds for physical investigations.

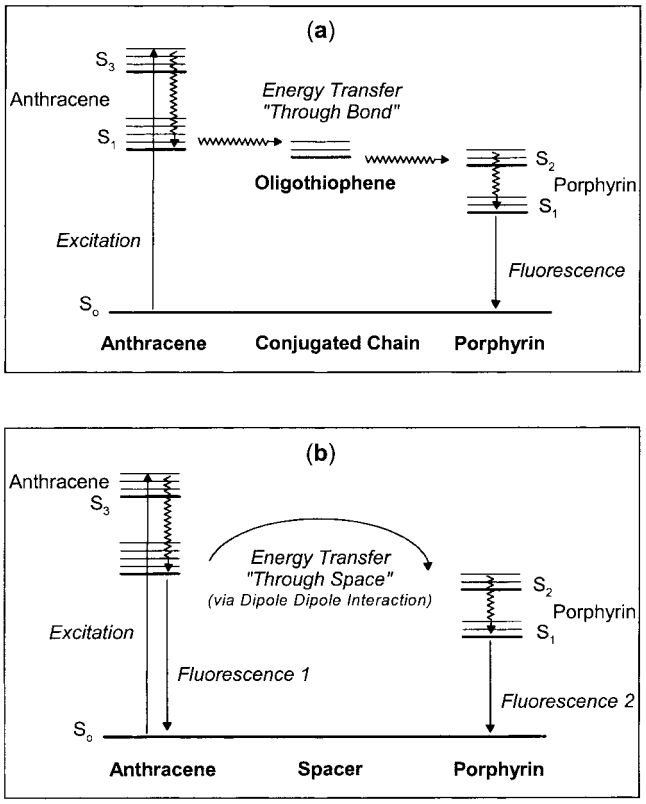


Figure 1. Schematic illustration of the intramolecular energy transfer (a) in the conjugated supermolecule **1**, and (b) in the steroid-bridged supermolecule **2**.

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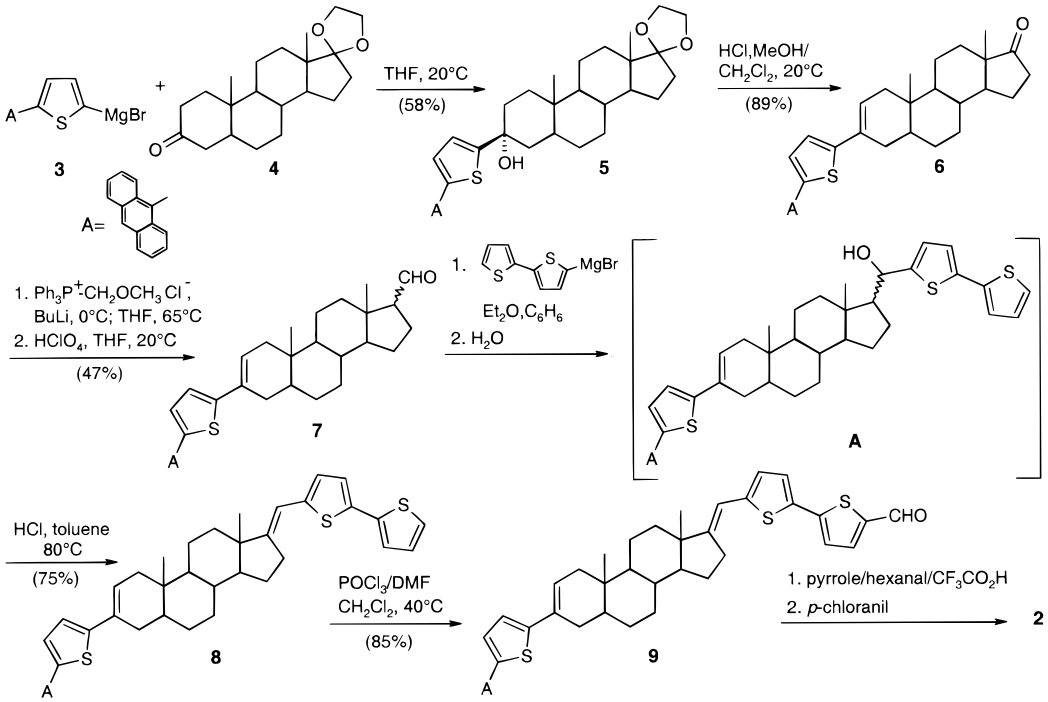
(8) The length of the quinquethiophene bridge in **1** is about 19 Å and the length of the thiophene/androstene/bithiophene bridge in **2** is about 21 Å, determined by molecular modeling studies (BIOSYM, Insight II, Discover 95.0/3.00, CVFF−Forcefield).

Scheme 1



The steroid component **4** was prepared according to literature methodology[9] starting from *epi*-androsterone. Anthrylthienyl bromide,[6,10] isolated in an improved yield of 86%, was converted with a 3-fold excess of magnesium into the Grignard reagent **3** which reacted with **4** to give the anthrylthienyl-substituted steroid derivative **5** in 58% yield. The treatment with concd HCl in methanol/dichloromethane results in regioselective elimination of water with simultaneous removal of the acetal protecting group to give compound **6** in 89% yield. The reaction of **3** with **4** under acidic workup led directly to **6** in 68% total yield.

We were also interested in the anthrylthienyl donor component without the steroid double bond as a reference compound. However, all attempts failed to hydrogenate the double bond in the steroid unit catalytically under mild conditions with Pd/C, H_2 in methanol/toluene.[11] Besides the steroid, the anthryl group was hydrogenated, and educt **6** completely decomposed in the course of hydrogenation.

The keto group in the 17 position of the steroid unit in **6** was successfully transformed to an aldehyde function under extension by one C-atom via Wittig reaction using (methoxymethyl)triphenylphosphonium chloride.[12] The phosphonium salt was deprotonated with *n*-BuLi at 0 °C and then reacted with **6** in boiling THF, since at low temperatures of −40 °C to 0 °C[12] ketone **6** reacted very slowly. A total of 10 equiv of the ylide were added. Triphenylphosphine and unreacted **6** were separated by column chromatography. After acidic hydrolysis with aqueous $HClO_4$ followed by chromatographic purification, aldehyde **7** was isolated in 47% yield.

The bithiophene was linked to the formyl group via Grignard reaction.[13] Starting from 5-bromo-2,2′-bithiophene, the Grignard reagent was prepared[6] and reacted with steroid aldehyde **7** at room temperature in diethyl ether/benzene. The acid-catalyzed water elimination from intermediates **A** in dichloromethane/methanol as solvent gave, besides **8** in 52% yield, the byproducts 3-[5-(9-anthryl)-2-thienyl]-17α- and 17*β*-[(2,2′-bithien-5-yl)-methoxymethyl]-5α-androst-2-enes by S_N1 reaction with methanol. Therefore the solvent mixture was replaced by toluene. In the acidic medium HCl/toluene, water was eliminated at 80 °C, giving derivative **8** in 75% yield. Under these reaction conditions, the S_N1 concurrent reaction could be suppressed. Both byproducts can be converted to **8** by treatment with HCl in toluene at 80 °C. UV−vis absorption spectra confirm the existence of derivative **8** as the trans-isomer. Due to steric reasons, only the trans configuration allows a planar orientation, which leads to a detectable extension of the conjugated bithienyl π-system.

Aldehyde **9** was prepared from **8** via Vilsmeier−Haack formylation.[14] After 7 h reaction time and addition of 4 equiv of Vilsmeier reagent, compound **9** was isolated in 85% yield. A byproduct resulting from formylation at the 10 position of the anthracene group was also detected by ^{1}H NMR spectroscopy. Interestingly, the methoxy-substituted byproducts (see above) were converted directly to aldehyde **9** under Vilsmeier−Haack reaction conditions. Presumably the HCl liberated during the formylation step effected E1 elimination of methanol.[11]

The linkage of porphyrin to give model compound **2** was performed according to the methodology developed by Lindsey[15] by acid-catalyzed condensation of pyrrole and a mixture of aldehyde **9** and hexanal (ratio 1:3) and

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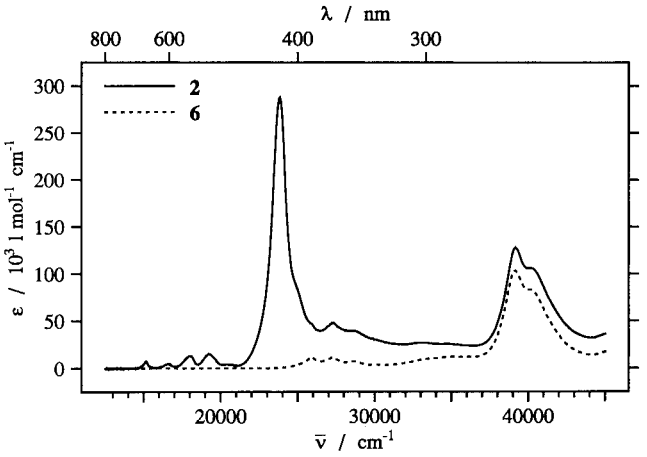

Figure 2. Absorption spectra of **2** and **6** in *n*-hexane at $T = 295$ K.

subsequent oxidation of the porphyrinogen mixture with *p*-chloranil. The concentration of the reaction mixture amounted to 5×10^{-3} mol/L. The oxidation was initiated after 20 h. Besides the desired compound **2**, tetraphenylporphyrin as well as the aromatic polysubstituted porphyrins were detected (HPLC), which could be separated on nitrophenyl-modified silica gel by MPLC. The byproducts were not isolated and characterized. In contrast to formerly described porphyrin syntheses,[4,6] starting aldehyde **9** was completely reacted. However, due to the intensive purification steps, the steroid-bridged porphyrin **2** was isolated only in 2.5% yield with high HPLC purity (>95%). For the photophysical investigations, compound **2** was purified up to >99.8% HPLC purity. Porphyrin **2** was characterized by ^{1}H NMR and UV−vis spectroscopy as well as by FAB mass spectrometry.

Absorption Spectra. The quantitative absorption spectra of **2** and **6** in *n*-hexane at room temperature are shown in Figure 2. The spectrum of the donor subunit **6** exhibits the typical anthracene $S_0 \rightarrow S_1$ absorption above 25000 cm^{-1} and the strong $S_0 \rightarrow S_3/S_0 \rightarrow S_4$ absorption at 37000−43000 cm^{-1}.

The absorption spectrum of **2** corresponds to a superposition of the spectra of the donor **6** and the bithiophene−porphyrin acceptor subunit, which is dominated by the porphyrin Soret band at 24000 cm^{-1} and the Q_x/Q_y bands in the region of 15000−20000 cm^{-1}.

Time-Resolved Fluorescence Spectra of 6. To analyze the photophysical properties of supermolecule **2**, a characterization of the donor subunit **6** is crucial.

Figure 3 (top) shows the fluorescence of **6** in *n*-hexane at $T = 180$ K after excitation at 37594 cm^{-1}. The quasi-cw spectrum [0−8700 ps] exhibits a broad band at 18000 cm^{-1} with a distinct shoulder at 22000 cm^{-1}. In time-resolved fluorescence two spectral contributions are clearly separated: The spectrum in the time interval directly after the ps-pulse excitation [0−75 ps] reveals a broad band at 22000 cm^{-1} whereas the spectrum at later times (3800−8700 ps) is dominated by a second band at 18000 cm^{-1}. These two contributions will be denoted as "blue" and "red" component, respectively.

The analysis of the transients (Figure 3, bottom traces) confirms the distinction of two contributions: The transient at 22000 cm^{-1} shows an instantaneous rise and a decay with $\tau^{blue}_{decay} = 70$ ps, whereas the transient at 16000 cm^{-1} exhibits a rise-time of $\tau^{red}_{rise} = 70$ ps and a decay-time of $\tau^{red}_{decay} = 1700$ ps.

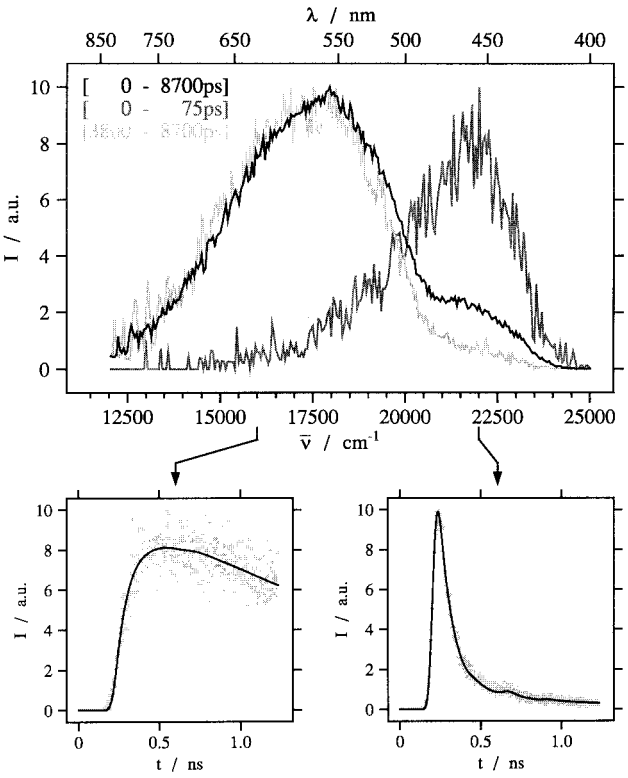

Figure 3. Time-resolved fluorescence spectrum of **6** in *n*-hexane at $T = 180$ K (top). Fluorescence transients at 16000 and 22000 cm^{-1}, respectively; experimental dots with biexponential fits (bottom).

Table 1. Spectral Positions $\tilde{\nu}$ and Lifetimes τ of the Two Components of the Dual Fluorescence of 6 in *n*-Hexane[a]

compd	$\tilde{\nu}^{180K}_{max}$ (cm^{-1})	$\tau^{180\ K}$ (ps)	$\tau^{295\ K}$ (ps)
6	22000, 17500	70 (1700)	10 (1000)
9A-T_1	23000, 19000	50 (290)	<10 (290)
9A-T_2	21500, 17000	27 (950)	<10 (900)
9A-T_3	20000, 17000	40 (670)	10 (650)

[a] The 9-anthryloligothiophenes 9A-T_n ($n = 1-3$) are listed for comparison. The data for 9A-T_n are taken from refs 17a and 18.

The two components are dynamically coupled since τ^{blue}_{decay} and τ^{red}_{rise} are equal. **6** therefore exhibits a dual fluorescence.[16] This is analogous to the behavior of anthryloligothiophenes reported earlier[17] (**6** is closely comparable to anthrylbithiophene, see Table 1). In correspondence to the anthryloligothiophenes, the observed dual fluorescence is ascribed to arise from a conformational relaxation in the excited state. While in the ground state, the anthracene and thiophene moieties are almost perpendicular, and they become more planar in the excited state. This results in a larger π-delocalization and a lowering of the energy of the excited state. In time-resolved measurements therefore a blue anthracene-like fluorescence directly after the pulse-excita-

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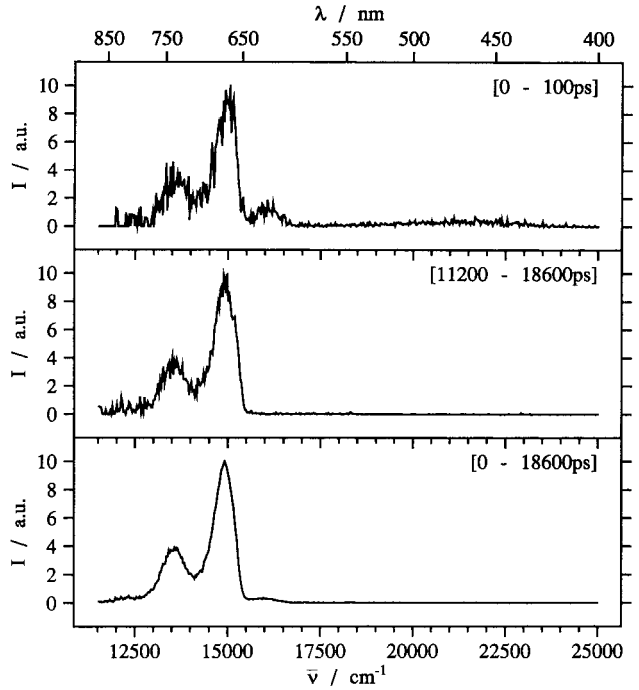

Figure 4. Time-resolved fluorescence spectra of **2** in *n*-hexane at $T = 180$ K. The blue region above 17500 cm^{-1} is shown in detail in Figure 5.

tion and a dynamically coupled delayed red fluorescence from the relaxed excited state can be observed.

It must be emphasized that this dual fluorescence is not a result of energy transfer between the anthracene and the thiophene moieties but rather of a geometry change and energy relaxation within the bichromophoric molecule. A detailed investigation of the dual fluorescence of anthrylthiophenes has previously been reported.[17]

Time-Resolved Fluorescence Spectra of 2. With the knowledge of the photophysical properties of **6** described above, we can now examine the supermolecule **2**. The fluorescence spectrum of **2** after excitation of the anthracene moiety at 37594 cm^{-1} is shown in Figure 4. The quasi-cw spectrum [0−18600 ps] (bottom trace) exhibits a typical porphyrin fluorescence with the overlapping Q_x-bands and Q_y-bands at 13600 cm^{-1}/15000 cm^{-1} and 15000 cm^{-1}/16400 cm^{-1}, respectively. The Q_x- and Q_y-bands result from the NH-tautomerism and are also observed in other porphyrin compounds.[19]

The time-resolved spectra (Figure 4, top) exhibit two additional features: The Q_y-band is pronounced in the early time interval [0−100 ps] because of its faster decay-time compared to Q_x (1400 ps versus 4700 ps). This is a known behavior of porphyrin compounds (e.g. tetraphenylporphyrin[20]). In the time window of the first 100 ps after excitation an additional weak and broad fluorescence between 17500 and 25000 cm^{-1} with a very fast decay-time can be observed. This band is shown in Figure 5 in comparison with the blue component of the donor-part **6**. The two spectra are identical. Hence, **2** exhibits an emission from the locally excited donor-subunit.

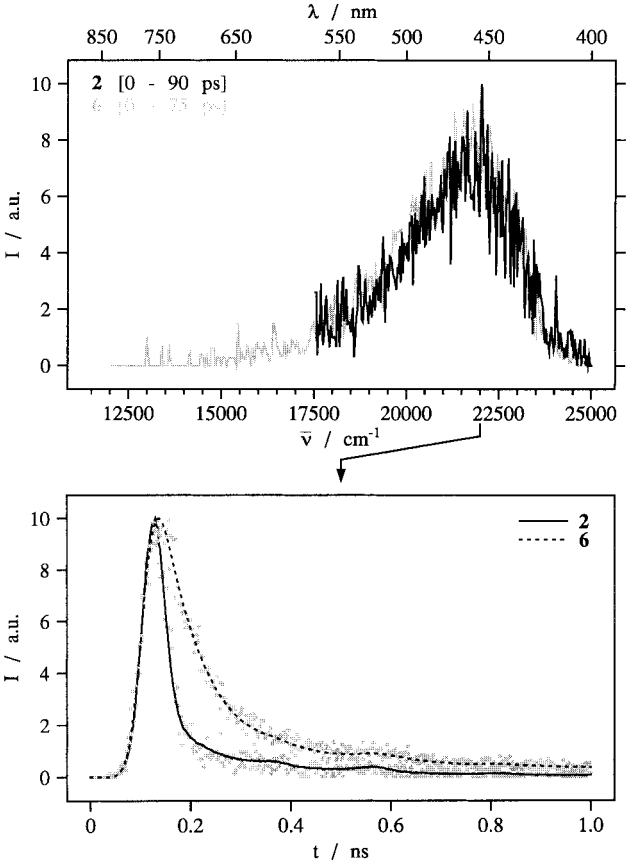

Figure 5. Time-resolved fluorescence spectra (short time interval after excitation) of **2** and **6** in *n*-hexane at $T = 180$ K (top). Comparison of the transients at 22000 cm^{-1} together with exponential fitting curves (bottom). The spectrum of **2** is limited to the region of 17500−25000 cm^{-1} for comparison purposes. For the complete spectrum of **2** dominated by the porphyrin emission, see Figure 4.

The transients at 22000 cm^{-1} are shown in Figure 5 (bottom). The decay-time of this band of **2** cannot be determined exactly, because it is faster than the time resolution of our single photon counting setup. The upper limit is $\tau \leq 10$ ps. Therefore the fluorescence decay of **2** at 22000 cm^{-1} is significantly shorter than the decay of the blue component of **6**.

Due to the shortening of the lifetime, the donor fluorescence is definitely not caused by impurities but results from a competition between energy transfer to the acceptor moiety and radiative deactivation of the donor part. From the shortening of the lifetime, the energy transfer efficiency can be calculated. We assume that the intrinsic decay rate of the donor k_D (for radiative and nonradiative decay in the absence of the acceptor) is not changed by the acceptor. The energy transfer to the acceptor is an additional deactivation pathway for the donor enhancing its decay rate k'_D (eq 1).

$$k'_D = k_D + k_{ET} \stackrel{!}{=} nk_D \qquad (1)$$

The energy transfer efficiency is given as follows in eq 2:

$$\Phi_{ET} = \frac{k_{ET}}{k'_D} = \frac{k_{ET}}{k_D + k_{ET}} = \frac{(n-1)k_D}{nk_D} = \frac{n-1}{n} \qquad (2)$$

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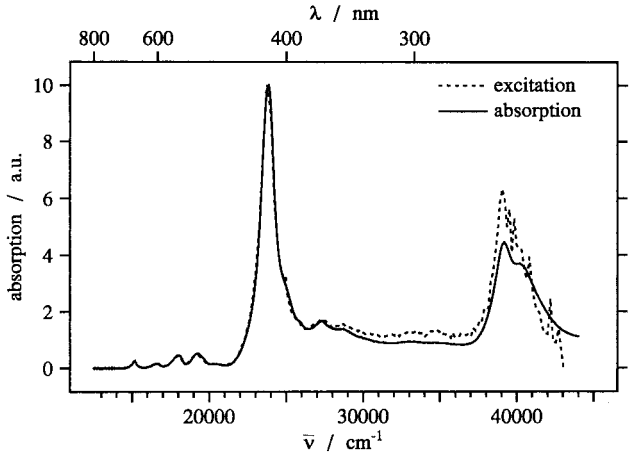

Figure 6. Comparison of the excitation spectrum (detection at 15000 cm^{-1}) of **2** in *n*-hexane at $T = 295$ K with the absorption spectrum.

In our case the shortening of the lifetime of the donor is $n \geq 7$, which results in a transfer efficiency of $\Phi_{ET} \geq 6/7 \approx 86\%$.

By integration of the donor-emission and the acceptor-emission of **2** for the quasi-cw spectrum, the energy transfer can be quantified more precisely. Considering the selectivity of the excitation and the quantum efficiencies of donor and acceptor (approximately 10%), an upper limit of 1% for the donor emission can be given. Thus the efficiency of the energy transfer is at least 99%.

In former studies we have already investigated polyenes with anthracene donor and porphyrin acceptor groups which contain saturated spacer units such as androstane and bicyclooctane, respectively, within the conjugated chain.[21,22] In contrast to the oligothiophene compounds, however, the polyene compounds are thermally and photochemically of inadequate stability which made the optical investigations difficult.[21] In all supermolecules based on polyenes, only the porphyrin emission was detected independent of the position of the spacer. In some cases also donor type emissions were observed; however, it could be proved that they were caused by (photochemically produced) impurities—in contrast to **2** no shortening of the lifetime appeared.[23] Hence **2** is the first system in our series of anthrylporphyrins which exhibits a donor fluorescence although the transfer efficiency is close to 100%.

Excitation Spectra. The energy transfer can also be proved by fluorescence excitation spectroscopy. The excitation spectrum of **2** (detected at 15000 cm^{-1}) is shown in Figure 6 in comparison with the absorption spectrum. From the close similarity of both spectra and especially from the appearance of the anthracene type absorption band in the excitation spectra, an efficient intramolecular singlet−singlet energy transfer from the donor to the acceptor can be concluded. However, an exact quantification is not possible due to limitations of the excitation intensity correction in the UV-region.

Conclusion

We have synthesized and characterized a novel energy transfer system **2** bearing an anthrylthiophene group as donor and a bithienylporphyrin group as acceptor linked together via a rigid androstene bridge. The intramolecular energy transfer has been studied using time-resolved fluorescence as well as fluorescence excitation spectroscopy. After laser excitation of the donor at 266 nm, we could prove an efficient energy transfer to the porphyrin acceptor. Besides the porphyrin fluorescence, a high energetic fluorescence was observed, which originates, as confirmed by full correspondence with the fluorescence spectra of the reference donor molecule **6**, from the donor part of supermolecule **2**. As a consequence of the intramolecular energy transfer, the fluorescence lifetime of the blue emission of supermolecule **2** is shortened compared with the blue emission of **6** by at least a factor 7, and hence the red fluorescence of **6**, which results from consecutive torsional relaxation, is not observed in **2**. In contrast to the conjugated supermolecule **1**, where only porphyrin fluorescence could be observed as a result of a quantitative energy transfer via the oligothiophene chain, in **2** the androstane spacer leads to a partial interruption of energy transfer resulting in evident donor fluorescence. Although the energy transfer efficiency is definitely lowered in **2** as against **1**, it is still in the range of 99%. Therefore we conclude that in **2**, with interrupted π-conjugation, Förster through-space interaction is responsible for the energy transfer across the spacer. In correspondence, also in **1** Förster transfer is assumed to be the most relevant mechanism; however, minor contribution of π through-bond interactions cannot be ruled out.

It must be considered, that the spacer incorporation in **2** does not only interrupt the π-conjugation, it may also influence the parameters which govern the efficiency of Förster-type energy transfer (e.g. the orientation of the chromophores). The small difference of the transfer efficiencies in **1** and **2** is not necessarily caused by the interruption of π through-bond interactions in **2**.

These investigations have shown that in our series of anthryloligothienylporphyrins Förster-type energy transfer plays a predominant role.

Experimental Section

General Procedures. All melting points are uncorrected. ^{1}H NMR spectra were recorded with TMS as the internal standard at 250 MHz. Preparative column chromatography was carried out on silica gel S (Riedel-de Haen, size: 0.032−0.063 mm) or Florisil (Fluka). Preparative medium-pressure liquid chromatography (MPLC) was performed at 5−10 bar on Nucleosil 1525 NO_2 (Macherey Nagel, size: 10 ± 5 μm, $N = 4090$, $S = 3.7$) columns (35×3 cm). HPLC was performed on a Nucleosil 5-NO_2, 200/8/4 analytical column (Macherey Nagel) and *n*-hexane/dichloromethane as eluent at a flow rate of 1 mL/min. GC for reaction control was carried out on a capillary column (20 m) with SDPE 08. Fast-atom bombardment (FAB) mass spectra were obtained using a NBA matrix. All solvents were dried and distilled. The reactions were carried out in dried glassware under argon atmosphere.

(Methoxymethyl)triphenylphosphonium chloride was purchased from Fluka, and pyrrole, hexanal, and *n*-hexane (Uvasol) from Merck. 5-(9-Anthryl)-2-bromothiophene and 5-bromo-2,2′-bithiophene were prepared according to refs 6 and 10, 17-(ethylenedioxy)-5α-androstan-3-one (**4**) according to ref 9.

3β-[5-(9-Anthryl)-2-thienyl]-17-(ethylenedioxy)-3α-hydroxy-5α-androstane (5). Grignard reagent **3** was prepared from Mg (0.215 g, 8.85 mmol) in 5 mL of diethyl ether with 1,2-dibromoethane as entrainer and dropwise addition of a solution of 5-(9-anthryl)-2-bromothiophene[6] (1.0 g, 2.95 mmol) in 25 mL of diethyl ether/benzene (3:2) within 45 min. After

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heating to reflux for 3 h (GC control), the reaction mixture was allowed to cool to room temperature, a solution of **4** (0.88 g, 2.65 mmol) in 20 mL of THF was added dropwise, and the reaction mixture was stirred for further 4 h. After hydrolysis with ice−water, the organic phase was separated and concentrated. The aqueous phase was extracted with dichloromethane. The organic phases were combined, washed with water, dried ($MgSO_4$), and concentrated. Chromatography on silica gel with dichloromethane and recrystallization from toluene/*n*-hexane gave 0.92 g (58%) of **5** as light yellow needles: mp 186−187 °C; ^{1}H NMR ($CDCl_3$) δ 0.75−2.37 (m, 22 H), 0.86 (s, 3H), 0.95 (s, 3 H), 3.82−3.95 (m, 4 H), 7.05 (d, J = 3.6 Hz, 1 H), 7.24 (d, J = 3.6 Hz, 1 H), 7.42−7.52 (m, 4 H), 7.88−7.92 (m, 2 H), 8.02−8.06 (m, 2 H), 8.52 (s, 1 H). Anal. Calcd for $C_{39}H_{44}O_3S$: C, 79.01; H, 7.48; S, 5.41. Found: C, 79.05; H, 7.58; S, 5.21.

3-[5-(9-Anthryl)-2-thienyl]-5α-androst-2-en-17-one (6). Concd HCl (1 mL) was added to a solution of **5** (0.597 g, 1.09 mmol) in methanol (125 mL) at room temperature, and the reaction mixture was stirred for 18 h. After hydrolysis with ice−water, the reaction mixture was extracted with dichloromethane. The extracts were combined, washed with a solution of $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Chromatography on silica gel with dichloromethane and recrystallization from *n*-hexane/ethyl acetate (2:1) afforded 0.51 g (89%) of **6** as yellow crystals: mp 241−242 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.84−2.53 (m, 18 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 2.42−2.53 (m, 2 H), 6.15−6.17 (m, 1 H), 7.02 (d, J = 3.6 Hz, 1 H), 7.12 (d, J = 3.6 Hz, 1 H), 7.38−7.50 (m, 4 H), 7.94−8.04 (m, 4 H), 8.51 (s, 1 H); UV (*n*-hexane) λ_{max} 386.0 nm (ϵ 11200), 366.0 (11100), 348.0 (6800), 333.0 (3300), 280.0 (11400), 256.0 (109300). Anal. Calcd for $C_{37}H_{38}OS$: C, 83.73; H, 7.22; S, 6.04. Found: C, 83.63; H, 7.26; S, 5.76.

Preparation of 6 Starting from Compounds 3 and 4. To a solution of **3** [prepared as described above from Mg (1.60 g, 66.0 mmol) in 10 mL of diethyl ether and 5-(9-anthryl)-2-bromothiophene (7.47 g, 22.0 mmol) in 75 mL of diethyl ether/benzene (3:2)] a solution of **4** (6.58 g, 19.8 mmol) in 70 mL of THF was added dropwise. The reaction mixture was stirred for 20 h and then poured onto HCl acidic ice−water. After extraction with dichloromethane, the extracts were combined, concentrated, and taken up in 300 mL dichloromethane/methanol (1:1). As described above, concd HCl was added, and the reaction mixture stirred at room temperature for ca. 5 h. Workup and purification (see above) gave 7.9 g (68%) **6** as yellow solid.

3-[5-(9-Anthryl)-2-thienyl]-17ξ-formyl-5α-androst-2-ene (7). To a vigorously stirred suspension of (methoxymethyl)triphenylphosphonium chloride (55.74 g, 0.163 mol) in 170 mL of THF was added dropwise a 1.6 M solution of *n*-BuLi in *n*-hexane (100.6 mL, 0.161 mol) at 0 °C within 1 h. Five equivalents of this solution (referred to **6**) were added dropwise within 1 h to a solution of **6** (8.63 g, 16.26 mmol) in THF (110 mL) at 65 °C followed by further five equivalents after 4 h. After heating to 65 °C for further 16 h, the reaction mixture was poured onto ice−water, neutralized with diluted HCl, and extracted with dichloromethane. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. By chromatography on silica gel with dichloromethane, 11% of educt **6** was reisolated. The crude product was dissolved in THF (350 mL), a solution of $HClO_4$ (30%, 75 mL) was added, and the reaction mixture was stirred at room temperature for 6.5 h (TLC control). After hydrolysis with ice−water, the reaction mixture was extracted with dichloromethane. The combined extracts were washed with a solution of $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Repeated chromatography on silica gel with dichloromethane and recrystallization from *n*-hexane/ethyl acetate (1:1) gave 4.19 g (47%) **7** as yellow crystals: mp 219−222 °C (partly dec); ^{1}H NMR ($CDCl_3$) δ 0.78−2.58 (m, 21 H), 0.78 (s, 3 H), 0.87 (s, 3 H), 6.16−6.17 (m, 1 H), 7.02 (d, J = 3.5 Hz, 1 H), 7.12 (d, J = 3.5 Hz, 1 H), 7.37−7.50 (m, 4 H), 7.94−8.04 (m, 4 H), 8.51 (s, 1 H), 9.76−9.79 (m, 1 H, isomeric mixture). Anal. Calcd for $C_{38}H_{40}OS$: C, 83.78; H, 7.40; S, 5.88. Found: C, 83.55; H, 7.45; S, 5.67.

3-[5-(9-Anthryl)-2-thienyl]-17-[(2,2′-bithienyl-5-yl)methylidene]-5α-androst-2-ene (8). A solution of (2,2′-bithienyl-5-yl)magnesium bromide [prepared as described above from Mg (0.296 g, 12.19 mmol) in 5 mL of diethyl ether and a solution of 5-bromo-2,2′-bithiophene (1.87 g, 7.62 mmol) in 40 mL of diethyl ether/benzene (5:3)] was added dropwise at room temperature within 30 min to a solution of **7** (4.15 g, 7.62 mmol) in 300 mL of diethyl ether/benzene (1:1). The reaction mixture was stirred for 2 h (TLC control), hydrolyzed with ice−water, and extracted with dichloromethane. Then the aqueous phase was acidified and extracted for the last time with dichloromethane. The combined extracts were washed with water to neutral, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel with dichloromethane.

(a) Intermediate 3-[5-(9-anthryl)-2-thienyl]-17α- and -17β-[(2,2′-bithienyl-5-yl)-hydroxymethyl]-5α-androst-2-enes were dissolved in 340 mL of dichloromethane/160 mL of methanol. Concd HCl (4 mL) was added, and the reaction mixture stirred at room temperature for 4 h followed by workup as described above. Chromatography on silica gel with *n*-hexane/dichloromethane (2:1) and recrystallization from ethyl acetate gave 2.75 g (52%) of **8** as fine yellow crystals: mp > 206 °C (sintering), 224 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.80−2.64 (m, 20 H), 0.88 (s, 3 H), 0.90 (s, 3 H), 6.17−6.18 (m, 1 H), 6.27 (m, 1 H), 6.81 (d, J = 3.7 Hz, 1 H), 7.00 (dd, J = 5.1, 3.7 Hz, 1 H), 7.02 (d, J = 3.5 Hz, 1 H), 7.08 (d, J = 3.7 Hz, 1 H), 7.12 (d, J = 3.5 Hz, 1 H), 7.15 (dd, J = 3.7, 1.1 Hz, 1 H), 7.18 (dd, J = 5.1, 1.1 Hz, 1 H), 7.38−7.50 (m, 4 H), 7.95−8.04 (m, 4 H), 8.51 (s, 1 H); UV (*n*-hexane) λ_{max} 385.0 nm (ϵ 12000), 365.0 (25900), 348.0 (30900), 336.0 (27100), 255.0 (114400), 249.0 (94600). Anal. Calcd for $C_{46}H_{44}S_3$: C, 79.72; H, 6.40; S, 13.88. Found: C, 79.47; H, 6.55; S, 13.74.

(b) Alternative treatment of the intermediate alcohols in toluene with concd HCl at 80 °C for 1 h, chromatography on silica gel with dichloromethane, and drying in high vacuum over paraffin afforded 75% of **8**.

3-[5-(9-Anthryl)-2-thienyl]-17-[(5′-formyl-2,2′-bithienyl-5-yl)methylidene]-5α-androst-2-ene (9). To a boiling solution of **8** (1.93 g, 2.79 mmol) in 20 mL of dichloromethane was added a solution of the Vilsmeier reagent[14] (2.2 mL, 1 mL ≈ 2.15 mmol of reagent). After 3 h, further 2.2 mL of Vilsmeier reagent was added followed by 1.1 mL after 5 h. After further 2 h, a 1 M $NaHCO_3$ solution was added, and the reaction mixture was stirred for 2 h. Then it was diluted with water and extracted with dichloromethane. The combined extracts were washed with water to neutral, dried (Na_2SO_4), and concentrated. Chromatography on silica gel with dichloromethane and recrystallization from ethyl acetate with addition of some dichloromethane afforded 1.705 g (85%) **9** as orange felted needles: mp 168 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.82−2.72 (m, 20 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 6.17 (br s, 1 H), 6.29 (m, 1 H), 6.87 (d, J = 3.9 Hz, 1 H), 7.02 (d, J = 3.5 Hz, 1 H), 7.12 (d, J = 3.5 Hz, 1 H), 7.21 (d, J = 4.0 Hz, 1 H), 7.28 (d, J = 3.9 Hz, 1 H), 7.37−7.49 (m, 4 H), 7.65 (d, J = 4.0 Hz, 1 H), 7.95−8.04 (m, 4 H), 8.51 (s, 1 H), 9.84 (s, 1 H). Anal. Calcd for $C_{47}H_{44}OS_3$: C, 78.29; H, 6.15; S, 13.34. Found: C, 78.08; H, 6.30; S, 13.31.

3-[5-(9-Anthryl)-2-thienyl]-17-[(5′-(10,15,20-tripentylporphyrin-5-yl)-2,2′-bithienyl-5-yl)methylidene]-5α-androst-2-ene (2). Under Ar atmosphere in the absence of light was stirred a solution of **9** (1.13 g, 1.57 mmol), hexanal (0.47 g, 4.7 mmol), and pyrrole (0.42 g, 6.27 mmol) in dry dichloromethane (1250 mL) for 15−30 min. The condensation was initiated by addition of trifluoroacetic acid (0.715 g, 1 equiv) followed by further 0.358 g after 5 h. After total 20 h, *p*-chloranil (1.16 g, 4.7 mmol) was added, and the reaction mixture was heated to reflux for 2 h. After addition of triethylamine, the reaction mixture was stirred for further 1.5 h, concentrated, and filtered through a silica gel column. To separate porphyrin-containing byproducts, the filtrate was chromatographed on nitrophenyl-modified silica gel by MPLC (*n*-hexane:dichloromethane = 75:25, flow 30 mL/min, detection at 258/420 nm). The product-containing fraction was chromatographed on silica gel with dichloromethane and purified by repeated MPLC to give 0.047

g (2.5%) of **2** as a bright blue-violet solid (HPLC purity >95%). Purification by MPLC and recrystallization from acetone gave **2** with 99.8% HPLC purity: mp > 75 °C (sintering); ^{1}H NMR ($CDCl_3$) δ −2.57 (br s, 2 H), 0.73−2.82 (m, 53 H), 4.90−5.01 (m, 6 H), 6.16−6.18 (m, 1 H), 6.37 (s, 1 H), 6.95 (d, J = 3.8 Hz, 1 H), 7.03 (d, J = 3.5 Hz, 1 H), 7.13 (d, J = 3.5 Hz, 1 H), 7.33 (d, J = 3.8 Hz, 1 H), 7.37−7.51 (m, 4 H), 7.55 (d, J = 3.5 Hz, 1 H), 7.74 (d, J = 3.5 Hz, 1 H), 7.97−8.05 (m, 4 H), 8.42 (s, 1 H), 9.16 (d, J = 4.9 Hz, 2 H), 9.41 (d, J = 4.9 Hz, 2 H), 9.48 (m, 2 H), 9.53 (m, 2 H); UV (*n*-hexane) λ_{max} 659.0 nm (ϵ 8000), 601.0 (4800), 555.0 (13500), 519.0 (16000), 419.0 (259500), 366.0 (48700), 349.0 (40600), 302.0 (28500), 288.0 (27600), 255.0 (127800), 249.0 (107100); FAB-MS Calcd for $C_{81}H_{86}N_4S_3$: 1210.6015 (exact), 1211.6093 (M + H exact). Found: 1211.6080 (M + H).

Photophysical Experiments. All measurements were performed in *n*-hexane (Uvasol) at concentrations $<10^{-4}$ M. The solvent was used without further purification. For fluorescence and excitation spectroscopy, the sample solutions were degassed by repeated freeze−pump−thaw cycles. Absorption spectra were recorded on a Lambda 16 UV/VIS (Perkin-Elmer) spectrophotometer. The fluorescence spectra and transients were measured by using the time-correlated single photon counting technique. A mode-locked Nd:YAG-laser (Quantronix 416) with an external two stage fourth harmonic generation (37594 cm^{-1} ≙ 266 nm) was used as excitation source. The repetition rate was reduced by a pulse picker to 3.8 MHz. The fluorescence was analyzed with a 0.5 m double monochromator with subtractive dispersion (Dilor) and detected with a cooled fast microchannel plate photomultiplier (Hamamatsu 3809U-01). The pulse response of the overall apparatus is about 50 ps (fwhm). By convolution of the model function with the pulse response, the time resolution can be extended to 10 ps.[24] Fluorescence excitation spectra were recorded using a 450 W xenon lamp as a light source. The excitation energy was selected with a 0.25 m double monochromator (2 nm fwhm). The fluorescence was detected with an 1 m double-monochromator and a cooled photomultiplier in photon counting mode. Time-resolved fluorescence spectra were measured by scanning the wavelength of the monochromator and accumulating the emission photons simultaneously in appropriately selected time windows after pulse excitation.

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