Anthryloligothienylporphyrins: Energy Transfer and Light-Harvesting Systems

Martin S. Vollmer, Frank Würthner, Franz Effenberger,* Peter Emele, Dirk U. Meyer, Thomas Stümpfig, Helmut Port,* and Hans C. Wolf

Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday

Abstract: In this paper we report on the synthesis and photophysical properties of the energy-transfer system **2a**, in which a quinquethiophene bridge is terminally linked to the 5-position of a porphyrin and to the 9-position of an anthracene group. The photoexcited-state properties were studied by steady-state fluorescence and picosecond time-resolved fluorescence measurements as well as fluorescence excitation spectroscopy. The weak electronic interaction of the subunits anthracene, quinquethiophene and porphyrin results in localized excited states, which are seen in UV/Vis absorption spectra. In **2a**, a highly selective excitation of the anthracene donor leads to quantitative intramolecular energy transfer to the emitting porphyrin acceptor via the quinquethiophene bridge. The efficiency of energy transfer and the fluorescence properties are both independent of the length of the oligothiophene chain, as demonstrated by comparison with the model compounds **1**. Various explanations for the mechanism of intramolecular energy transfer are discussed. Introduction of additional anthrylquinquethienyl units into the porphyrin ring results in an increase in the intensity of the characteristic absorption bands and fluorescence nearly proportional to the number of chromophores.

Keywords: chromophores • light-harvesting system • molecular devices • oligothiophenes • porphyrins

Introduction

The transfer of electronic excitation energy within and between molecules plays an important role in organic photochemistry and photophysics.[1,2] In photosynthesis, the initial steps are the collection of light energy and energy transfer to the photosynthetic reaction centre.[3] In the last few years, numerous synthetic model compounds and supramolecular assemblies containing porphyrins as chlorophyll analogues have been studied.[4–6] Such model systems not only contribute to our understanding of photosynthesis, but also provide an entry to molecular electronics and molecular optics,[7–9] which could enable us to realize transport of information on a molecular level by ultrafast energy- and electron-transfer processes.[10]

Synthetic light-harvesting systems are normally designed as mimics of the natural photosynthetic pigments with a wide frequency range.[5c,10d] Model systems with chromophores which select a small frequency range have been synthesized and investigated, especially by Lindsey et al.[10b–e,11] In these systems metalloporphyrin donor chromophores (antennae) are linked to free base emitting porphyrin acceptors via conjugated π systems. In a supermolecule of this type, for example, an intramolecular energy transfer with high efficiency has been detected.[11a] The peripheral metalloporphyrin absorption at 547 nm is 7.4 times that of the central free base porphyrin, proving frequency selection in the visible region.[11] The energy transfer is slowed down by reducing the coplanarity between linker and porphyrin, and is therefore assumed to proceed through bond.[10d]

In a recent publication[12] we described the intramolecular energy-transfer properties of the trichromophoric supermolecules **1a,b** containing the anthracene donor, the porphyrin acceptor and a conjugated oligothiophene bridge. This type of light-conversion molecular device (J.-M. Lehn[8b]) operates in a three-step mode: absorption → energy transfer → emission (Figure 1). The anthracene acts as an antenna and transfers the energy of absorbed light via the oligothiophene π bridge to the porphyrin acceptor.

Although the three conjugated subunits are directly attached, a highly selective excitation of the anthracene at 254 nm (up to 90%) is possible because of the torsion between the planes of the anthracene and the oligothiophene

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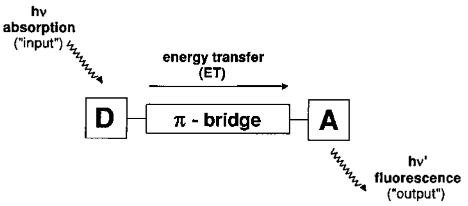
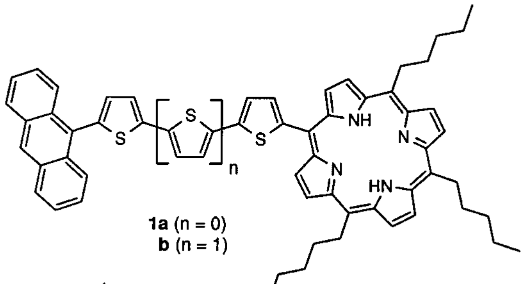


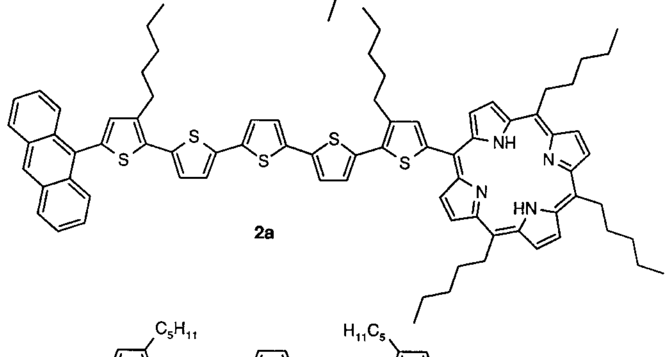
Figure 1. Schematic illustration of the light-conversion molecular device.

unit. We were able to prove quantitative intramolecular energy transfer via the oligothiophene chain to the emitting porphyrin acceptor.[12] Oligothiophenes have become an increasingly important class of molecules in material science. They function not only as structurally defined model compounds for electrically conducting polythiophenes[13,14] but also as stable molecular materials for optical and electronic devices.[15] Recently, photoswitchable molecular wires based on oligothiophenes have been synthesized and studied.[16] Extending our research in the field of oligothiophenes as mediators (molecular photonic wires) between photoactive donor/acceptor end-groups,[12] we wanted to enlarge the donor/acceptor distance by incorporation of longer oligothiophenes and to study their influence on the intramolecular energy transfer.

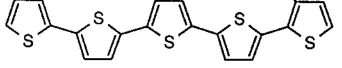
In the present paper we report on the synthesis and the photophysical properties of the new model compound **2a** with a quinquethiophene bridge. To enhance the solubility, pentyl chains had to be incorporated into the oligothiophene and porphyrin subunits. In addition, the optical properties of the π bridge **3** as well as of the bichromophoric units donor/bridge **4a** and bridge/acceptor **5a** are discussed in this paper. The comparison of oligothiophenes with the previously studied polyenes[17] as π bridges in energy-transfer systems with respect to dependence on chain length is of particular interest. Furthermore, we have investigated the introduction of two, three and four anthrylquinquethienyl units into one porphyrin. The anthrylquinquethienylporphyrin **2e**, in which the porphyrin is substituted with the maximum of four anthracene antennae (Scheme 2), should result in a maximum of UV light-harvesting effect.



1a (n = 0)
b (n = 1)



2a



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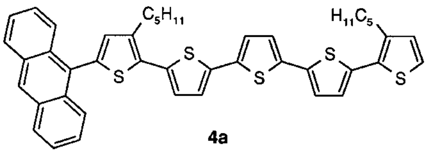
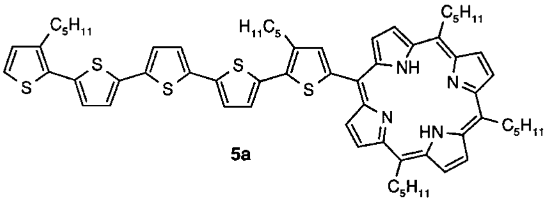


4a



5a

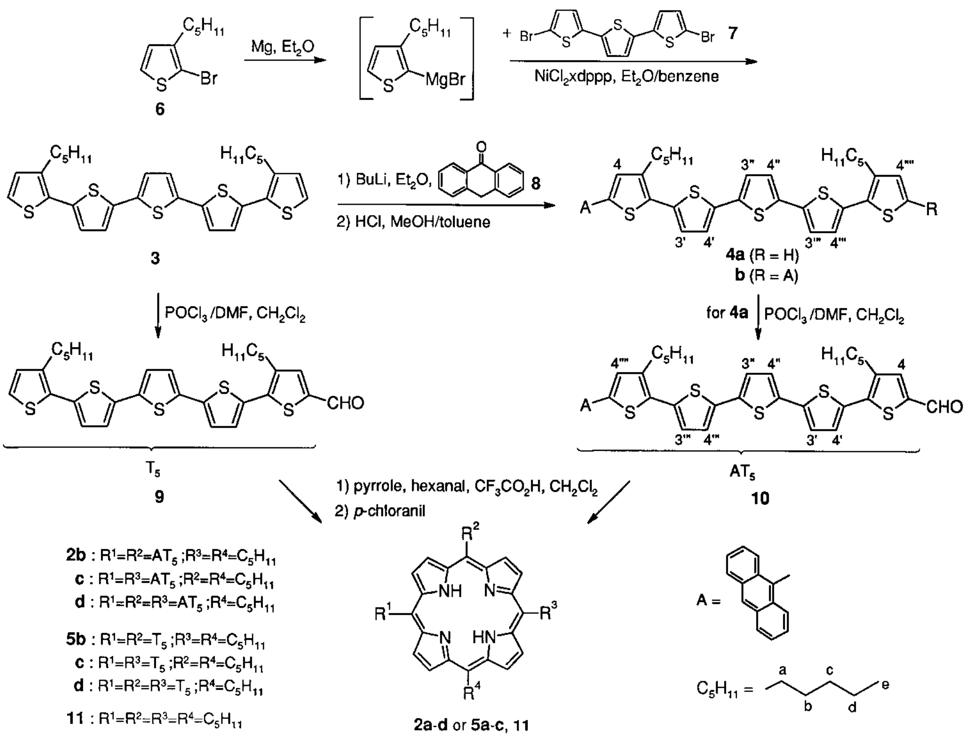
Results and Discussion

Synthesis: The synthetic strategy developed for the preparation of the trichromophoric system anthracene/quinquethiophene/porphyrin **2a** should also serve for the bichromophores anthracene/quinquethiophene **4a** and quinquethiophene/porphyrin **5a**, which are required as reference compounds for the photophysical investigations. Consequently, the quinquethiophene unit should be prepared first and subsequently the respective donor or acceptor component should be linked. Pentyl groups are incorporated into both the porphyrin end-group, as in compounds **1a**,**b**, and the quinquethiophene bridge to provide readily soluble chromophores **5a** and **2a**, respectively. The synthetic approach to the model compounds **2a**, **3**, **4a**, and **5a** from 2-bromo-3-pentylthiophene **6** and 5,5″-dibromoterthiophene **7** is illustrated in Scheme 1.

We have described the synthesis of dipentylquinquethiophene **3** by Kumada cross-coupling reaction in a previous paper.[18] Lithiation of **3** with *n*BuLi in diethyl ether at room temperature and subsequent reaction with anthrone **8** at −78 °C gave the desired 9-anthryl-substituted dipentylquinquethiophene **4a** after acid treatment in 51% yield. The dianthryl compound **4b**, formed as a by-product in 6% yield, could be separated by MPLC on silica gel with *n*-hexane/dichloromethane (15:1) as eluent.

In analogy to the preparation of 5-formyldipentylquinquethiophene **9** by Vilsmeier–Haack formylation (Scheme 1),[18] the corresponding 9-anthryl-substituted aldehyde **10** was synthesized. The formylation agent was generated from DMF and phosphoryl chloride in dichloromethane and added in about 4.5-fold excess at 40 °C to a solution of **4a** in dichloromethane to give compound **10**. After separation of unconverted starting material **4a** by chromatography on silica gel, **10** was isolated in 79% yield. Only traces of the diformylated product, with a second formyl group in the 10 position of anthracene, could be detected by ^{1}H NMR spectroscopy.

As in the synthesis of compounds **1** already published,[12] the porphyrins **2a** and **5a** were prepared by acid-catalyzed condensation of pyrrole and a mixture of aldehyde **9** or **10** and



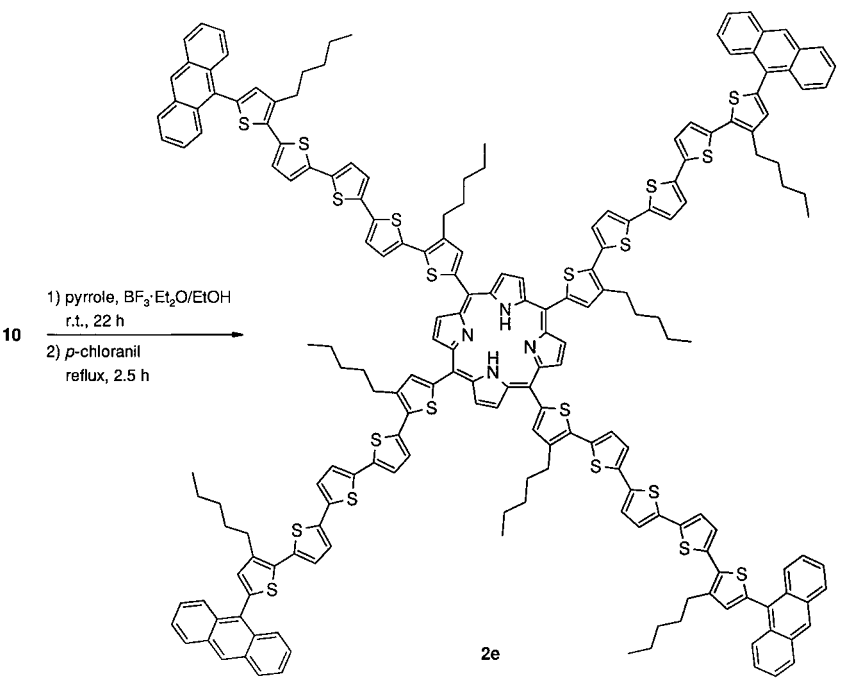
Scheme 1. Synthesis of the model compounds **2**–**5**.

1-hexanal (ratio 1:3) in dichloromethane and subsequent oxidation of the porphyrinogen mixture with *p*-chloranil according to the procedure developed by Lindsey et al.[19] In the case of the condensation reaction of the aromatic aldehyde **9** with hexanal we chose a total concentration of 2.5×10^{-3} mol L^{-1}, which caused a deceleration of the condensation reaction in comparison to literature data.[12,19] An excess of trifluoroacetic acid was necessary. After 28 hours the reaction mixture was oxidized with *p*-chloranil. Despite an aldehyde concentration of 4×10^{-3} mol L^{-1} in the case of compound **10**, the reaction rate is comparable to that with **9**. The oxidation was initiated after 24 hours.

Noncyclized compounds as well as unreacted aldehydes **9** and **10** were separated by chromatography on silica gel. Compound **9** could be reisolated in 23% yield, **10** in 51% yield. The synthesis of the porphyrins **2a** and **5a** was accompanied by the formation of tetrapentylporphyrin (**11**) as well as the other anthrylquinquethienylpentylporphyrins **2b**–**d** and quinquethienylpentylporphyrins **5b**–**d**, respectively. The corresponding fourfold aryl-substituted porphyrins, for example **2e**, could not be detected by HPLC-UV. In both cases the separation of the products was possible by MPLC on nitrophenylpropyl-modified silica gel on the basis of the different aryl contribution. The isomers **5b/c** were isolated as a mixture and, as **5d**, were only analyzed by HPLC-UV detection. The yields of the porphyrins **5a**–**c** are consistent with the expected statistical ratio, whereas the amount of **11** was markedly higher (**5a**: 4%, **5b/c**: 2%, **11**: 6%). The yields of porphyrins **2a**–**d** and **11** (**2a**: 7%, **2b/c**: 3%, **2d**: 0.5%, **11**: 5%) agree with the statistical ratio. The isomers **2b/c** were isolated and characterized as a mixture. The energy-transfer system **2a** and the bichromophoric systems **4a** and **5a** could be obtained in high purity (HPLC > 99%) and were characterized by ^{1}H NMR, elemental analysis, FAB mass spectroscopy and different methods of optical spectroscopy.

The fourfold anthrylquinquethienyl-substituted porphyrin **2e**, not detected by HPLC-UV when trifluoroacetic acid was used as catalyst, was formed by reaction of aldehyde **10** with pyrrole in a molar ratio 1:1 under BF$_3$/ethanol[20] catalysis (Scheme 2). After repeated purification by MPLC on nitrophenylpropyl-modified silica gel, **2e** was isolated in 3.5% yield with high purity (HPLC >98%). Compound **2e** was characterized by ^{1}H NMR and different methods of optical spectroscopy as well as by matrix-assisted laser desorption/ionisation mass spectrometry (MALDI). Because of the presence of the pentyl groups, **2e** is readily soluble in nonpolar solvents.

Photophysical properties—absorption spectra: In the energy-transfer systems a weak electronic coupling of anthracene,



Scheme 2. Synthesis of the light-harvesting system **2e**.

oligothiophene and porphyrin is required to address selectively both the donor and the acceptor terminal group. Figure 2 shows the absorption spectrum of **2a** compared with the individual subunits anthracene, dipentylquinquethiophene **3** and porphyrin, as well as the spectra of the bichromophoric systems **4a** and **5a**. The trichromophoric system **2a** exhibits the typical anthracene S_3 absorption in the UV region (230–260 nm) where quinquethiophene and the porphyrin group hardly absorb. The contributions of the quinquethiophene absorption and the anthracene S_1 absorption dominate at 300–400 nm. The characteristic features of porphyrin are the intensive Soret band at 419 nm as well as the Q-bands in the absorption range between 450 to 700 nm. The weak electronic interaction between the terminal groups and the oligothiophene bridge caused by steric distorsion is evident in the slight broadening and red shift of the bands with reduced extinction coefficients (Table 1). However, the characteristic absorption bands of the bichromophores **4a** and **5a** and of the trichromophoric system **2a** can be ascribed to the individual molecular subunits. Obviously the supermolecules exhibit localized excited states. Bands which originate from electronic transitions between mixed molecular levels of the subunits are not observed.

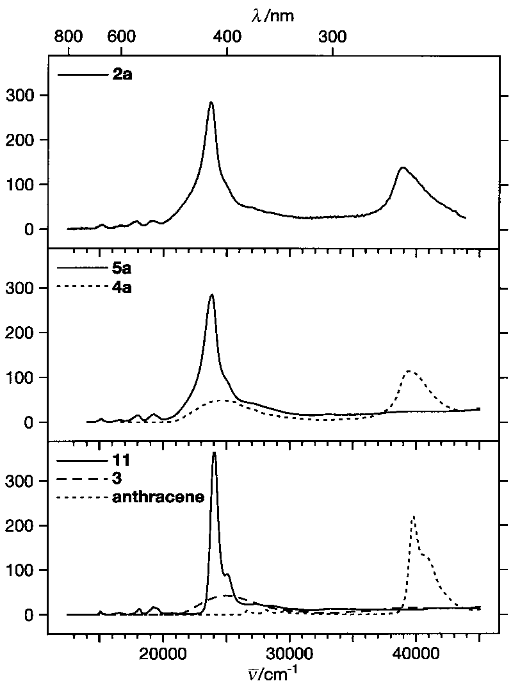


Figure 2. Absorption spectra (*n*-hexane, $T = 295$ K). Top: anthrylquinquethienylporphyrin (**2a**); middle: anthrylquinquethiophene (**4a**) and quinquethienylporphyrin (**5a**); bottom: anthracene, dipentylquinquethiophene (**3**) and tetrapentylporphyrin (**11**).

The localization results from the sterically induced torsion between the anthryl moiety and the oligothiophene bridge of about 90°, confirmed by AM1 calculations,[21] and caused by the linkage of anthracene in the 9 position. Thus, an intensive anthracene-type UV absorption at 254 nm is maintained in the energy-transfer systems. From the extinction coefficients of **2a** and **5a** at 254 nm the selectivity of anthryl excitation is estimated to be 82 %. For compounds **1a** and **1b**, with shorter thiophene chains, selectivities of 88 % (for **1a**) and 86 % (for **1b**) were estimated.[12]

Table 1. UV/Vis absorption maxima of anthrylquinquethienylporphyrin (**2a**), quinquethiophene (**3**), anthrylquinquethiophene (**4a**) and quinquethienylporphyrin (**5a**) in comparison with the model chromophores anthracene and tetrapentylporphyrin (**11**) in *n*-hexane at 20 °C.

	λ_{max}, nm (ε, $\mathrm{M^{-1}cm^{-1}}$)			
	Anthracene (S_0-S_3)	Anthracene (S_0-S_1)/ oligothiophene/ porphyrin	Porphyrin (S_0-S_2)	Porphyrin (S_0-S_1)
anthracene	246 (112000) [a]	323 (2800)		
	252 (220000)	339 (5500)		
		356 (8500)		
		374 (8500)		
3	252 (14500) [b]	401 (41800)		
4a	254 (114000)	406 (48800)		
11	239 (11400) [b]	300 (10800)	416 (370000)	519 (14300)
		398 (73000)		551 (11400)
				602 (4300)
				662 (7100)
5a	254 (24000) [b]	303 (17400)	419 (285200)	519 (17300)
		353 (23800)		555 (15000)
				601 (4700)
				659 (7400)
2a	254 (129600)	301 (18700)	419 (283600)	519 (17700)
		351 (33600)		555 (15300)
		368 (46300)		601 (4600)
				659 (7200)

[a] Shoulder. [b] Absorption in the range of the anthracene S_3 band.

In the electronic ground state communication between the anthracene donor and the porphyrin acceptor moieties becomes obvious from the absorption spectra of **2a** and **5a** (Figure 2). In both systems, intensity and position of the porphyrin absorption bands are identical. However, in the energy-transfer system **2a** the porphyrin Soret band is slightly broadened, indicating the weak electronic influence of the anthracene donor on the porphyrin acceptor.

The comparison of the absorption spectra of quinquethiophene-bridged compound **2a** (10 conjugated double bonds) with the corresponding polyene-bridged compound **12a**[17b] (nine conjugated double bonds) is of particular interest (Figure 3). As can be seen from the figure, the considerable electronic interaction between the chromophores in **12a** results in highly broadened bands with reduced extinction

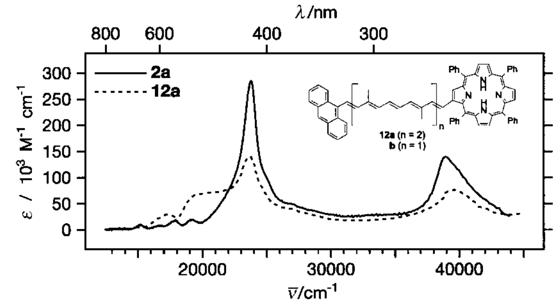


Figure 3. Absorption spectra (*n*-hexane, $T = 295$ K) of anthrylpolyenylporphyrin (**12a**, 9 conjugated double bonds) and anthrylquinquethienylporphyrin (**2a**, 10 conjugated double bonds).

coefficients. Between 400–700 nm additional bands appear, which can be ascribed to mixed electronic states.[17b]

Altogether, the greater torsion between the chromophores in the anthryloligothienylporphyrins as well as the well-chosen linkage of the π systems anthracene, oligothiophene and porphyrin provides a supermolecule with retention of the identity of individual electronic levels and highly selective anthryl excitation.

The similarity of the UV/Vis spectra of the unsubstituted quinquethiophene with those of dipentylquinquethiophene **3** indicates that, as expected, the electronic and steric influence of the pentyl chains is negligible.[22] Consequently, unfavourable effects on the mediator properties of the oligothiophene did not occur.

Fluorescence spectra: The fluorescence spectra of tetrapentylporphyrin **11**, quinquethienylporphyrin **5a** and anthrylquinquethienylporphyrin **2a** are shown in Figure 4. The spectra are normalized to the same maximum intensity. Porphyrin **11** exhibits the two typical porphyrin emission bands ($Q^*_{x,00}$, $Q^*_{x,01}$) in the region between 650 and 800 nm.[12] The emission spectra of **2a** and **5a** are nearly identical and reveal, in comparison with **11**, the characteristic fluorescence of the porphyrin end-group. However, the emission bands of **2a** and **5a** are broadened and slightly red-shifted because of the reduced symmetry of the porphyrin and its weak coupling to the oligothiophene chain. The fluorescence spectra are independent of the excitation wavelength. It is remarkable that in **2a** even excitation of the intensive anthracene transition leads to typical emission of the porphyrin end-group. Neither anthracene-type nor anthrylquinquethienyl-type emission could be detected, although these subunits possess high fluorescence quantum yields.[23] This fluorescence behaviour indicates that all the excitation energy is transferred to the porphyrin end-group.

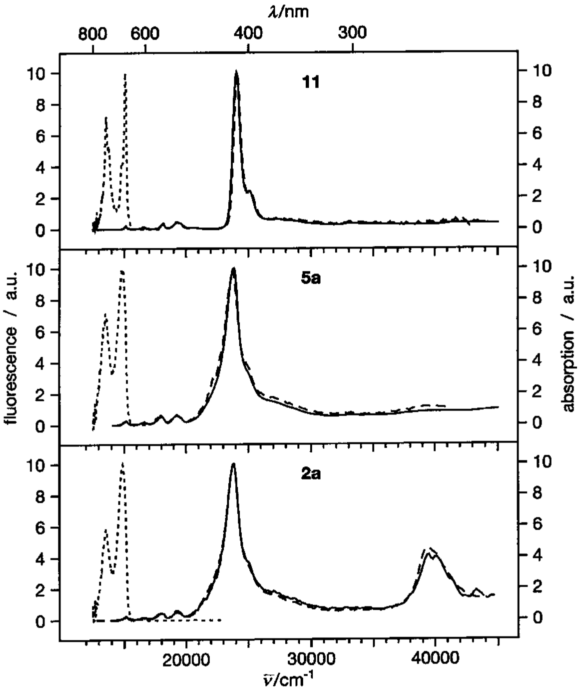


Figure 4. Fluorescence (····), fluorescence excitation (—) and absorption spectra (- - - -) (*n*-hexane, 295 K, arbitrary units [a.u.]). Top: tetrapentylporphyrin (**11**); middle: quinquethienylporphyrin (**5a**); bottom: anthrylquinquethienylporphyrin (**2a**). Fluorescence spectra are independent of the excitation wavelength, fluorescence excitation spectra independent of the detection wavelength. All spectra are normalized to the same maximum intensity.

Excitation spectra: Figure 4 also shows the fluorescence excitation spectra of compounds **11**, **5a**, and **2a**, together with the absorption spectra. By excitation spectroscopy, the dependence of the intensity of the porphyrin emission on the excitation wavelength is detected (detection energy 714 nm). All compounds show very good correspondence of absorption and excitation spectra. Besides the transitions characteristic for the porphyrin group, the excitation spectrum of **2a** shows an intense absorption band in the region between 230–280 nm that clearly corresponds to the anthracene S_0-S_3 absorption. Therefore, excitation of the anthryl group at 254 nm leads to the typical fluorescence of the porphyrin group as a result of intramolecular energy transfer within the supermolecule.

The efficiency of energy transfer can be determined by comparison of excitation and absorption spectra.[12] Absorption and excitation spectra in **2a** are nearly identical. Thus the energy-transfer efficiency from the anthracene to the porphyrin group is estimated to be at least 98%. This is also the case in the energy-transfer systems **1a** and **1b**. Overall, in supermolecules containing a bithiophene, terthiophene or quinquethiophene bridge, the intramolecular energy transfer is independent of the chain length and nearly quantitative in all cases.

In contrast to the oligothiophene compounds, the previously studied energy transfer in the polyene-bridged systems could not be quantified unambiguously. Competing radiationless deactivation processes within the polyene chain are mainly responsible for the low correspondence of absorption and excitation spectra.[17c,24]

Fluorescence quantum yields, fluorescence lifetimes and time-resolved measurements: The fluorescence quantum yields in *n*-hexane solutions are shown in Table 2. Tetrapentylporphyrin **11** possesses a fluorescence quantum yield of about 10%. The energy-transfer system **2a** as well as the shorter systems **1** show, within experimental error, the same fluorescence quantum yield as **11** at 295 and 180 K. We conclude that in the oligothiophene compounds the fluorescence quantum yields are independent of the chain length.

In the anthrylpolyenylporphyrins **12** studied previously, the fluorescence quantum yields decrease rapidly with increasing chain length of the polyene[17c,24] (Table 2). A high radiationless deactivation through the polyene chain leads to deactivation of the entire system. Furthermore, reversible energy transfer between the porphyrin group and the polyene can result in quenching of the porphyrin fluorescence. Similar findings are described by Gust and Moore et al.[25] as well as by Osuka et al.[26] for polyene (carotenoid)–porphyrin dyads. These quenching processes are not observed in the anthryl-

Table 2. Fluorescence quantum yields of tetrapentylporphyrin (**11**), quinquethienylporphyrin (**5a**) and anthryloligothienylporphyrins **1a,b**, **2a** in comparison with tetraphenylporphyrin (TPP), polyenylporphyrin (P_9-TPP) and anthrylpolyenylporphyrins **12** with different polyene chain length in *n*-hexane solution at 295 K.

Oligothiophenes			Polyenes		
	Φ (%) [a]			Φ (%) [a]	
	180 K	295 K		180 K	295 K
11	13	10	TPP	13	10
1a	12	9	**12c** [b]	3.5	–
1b [c]	12	9	**12b**	1.5	–
2a [c]	13	10	**12a**	< 0.1	–
5a	–	10	P_9-TPP [d]	< 0.1	–

[a] Experimental errors ± 20%. [b] 1-(9-Anthryl)-4-methyl-6-(5,10,15,20-tetraphenylporphyrin-2-yl)-hexatriene. [c] In dichloromethane. [d] 3,8,11,16-Tetramethyl-1-(5,10,15,20-tetraphenylporphyrin-2-yl)-1,3,5,7,9,11,13,15,17-nonadecanonaene.

oligothienylporphyrins. They are obvious particularly when comparing supermolecule **2a**, with 10 conjugated double bonds, and the corresponding polyene **12a**, with nine double bonds, which differ dramatically in fluorescence quantum yields (Table 2).

Fluorescence lifetimes were determined from the monoexponential decay at 295 K. The lifetime of tetrapentylporphyrin **11** amounts to 11.2 ns, while the lifetime of the energy-transfer system **2a** decreases to 3.5 ns, compared to 4.4 and 3.6 ns for **1a** and **1b**, respectively. The lifetimes of the porphyrin-type fluorescences are obviously independent of the chain length. Time-resolved fluorescence measurements of **2a** at different time intervals (early: 0–200 ps, late: 200–50000 ps) after ps laser excitation at 366 nm correspond to the stationary spectrum at 295 K (see Figure 4). The rate of energy transfer was also deduced from time-resolved measurements. The fluorescence signal appears instantaneously (< 10 ps) with the pulse response of the apparatus, indicating an ultrafast energy transfer (faster than 10 ps).

Intramolecular energy transfer: The photophysical investigations reveal a nearly quantitative and extremely fast energy transfer in the supermolecules **1a,b**[12] and **2a**. The energy transfer is indubitably due to an intramolecular mechanism. Reabsorption (trivial mechanism) and intermolecular energy-transfer processes can be excluded, since the measured transfer efficiencies are independent of concentration. The perfect correspondence of absorption and excitation spectra in the whole spectral range between 200 and 800 nm indicates that singlet–singlet energy transfer to the porphyrin endgroup is the only important quenching process after excitation, especially after selective excitation of the anthracene donor.

With a known fluorescence lifetime τ_D of the separated donor molecule and measured transfer efficiency Q, the rate k_{ET} of the intramolecular energy transfer and thus the energy-transfer time τ can be calculated according to Equation (1).

$$k_{ET} = (1/\tau) = Q/[\tau_D\,(1 - Q)] \qquad (1)$$

Transfer efficiencies > 98% ($Q > 0.98$) result in transfer times $\tau < 8$ ps in model compound **2a** with anthrylquinquethiophene as donor unit ($\tau_D = 370$ ps). With a transfer efficiency of 99.9%, for example, a transfer time of 0.5 ps is evaluated. These estimated values of energy-transfer times agree with the experimental finding for a rise time of the fluorescence signal < 10 ps (the detection limit of the apparatus, see above).

In the following, the mechanism of intramolecular energy transfer[1a] is discussed in terms of a) the Förster mechanism (dipole–dipole interaction),[27] b) the Dexter mechanism,[27c,d,28] and c) intramolecular relaxation.[1a,29]

The Förster mechanism describes the energy transfer between donor and acceptor substituents through space via Coulombic interaction, and therefore direct contact between both substituents is not required. Förster's theory is applicable to supermolecules such as **2a**, considering that donor and acceptor group retain their spectroscopic identity owing to a weak electronic coupling between the molecular subunits. For the calculation of Förster radii, the spectral overlap of donor emission and acceptor absorption bands and the fluorescence quantum yield of the corresponding donor must be considered. Furthermore, the distance between donor and acceptor group as well as the orientation of the chromophores, that is, the orientation of transition dipole moments, are critical parameters. For the anthracene/porphyrin pair in **2a**, a Förster radius R_0 of about 50 Å was calculated with the assumption of a mean orientation of the chromophore dipoles. A parallel orientation of the dipoles leads to a Förster radius of about 70 Å. If the bichromophoric anthrylquinquethiophene unit in **2a** is considered as donor, the Förster radii for the anthrylquinquethiophene/porphyrin pair are 24–29 Å.

The distance between anthracene and porphyrin in **2a** was estimated by molecular modelling[30] to be 26 Å in the energetically optimized conformation (Figure 5), while a maximum bend of the oligothiophene chain leads to a distance of 15 Å. Consideration of the anthrylquinquethiophene unit as donor gave distances of 7–12 Å. Despite variable distances and independent of whether the donor is considered to be anthracene or anthrylquinquethiophene, Förster transfer efficiencies Q_F of 99% are calculated from

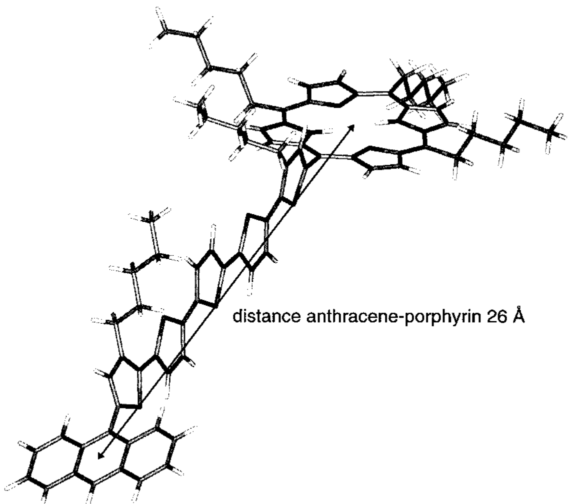


Figure 5. Structure of compound **2a** obtained by molecular modelling.

Equation (2). These results, as well as literature data,[12] demonstrate that the small electronic interaction between anthracene, oligothiophene and porphyrin in supermolecules **1** and **2a** allows an energy transfer of Förster type.

$$Q_F = \frac{1}{1 + (R/R_0)^6} \qquad (2)$$

The Dexter mechanism describes energy transfer by exchange interactions, that is, the excited electron, localized on the donor group, is exchanged with an electron of the acceptor group. Therefore, the Dexter transfer requires direct contact between donor and acceptor electronic orbitals. In the supermolecules **1** and **2a** a Dexter transfer mediated by the oligothiophene orbitals might be possible either by superexchange or by through-bond interaction (Dexter cascade).[31]

Intramolecular relaxation: If the electronic interaction between the subunits in the energy-transfer systems is high enough, the energy could also be transferred by electronic vibronic coupling. This energy transfer by unidirectional intramolecular relaxation is illustrated schematically in Figure 6. After selective excitation of the anthracene donor, intramolecular relaxation takes place via excited states of the oligothiophene to the lowest excited state of the molecule that is localized on the porphyrin end-group. Intramolecular relaxation was also considered for the mechanism of the energy transfer in anthrylpolyenylporphyrins.[17,29a] The estimated energy transfer of these systems in the femtosecond (fs) range corresponds well with the temporal appearance of the porphyrin emission in anthryloligothienylporphyrins.

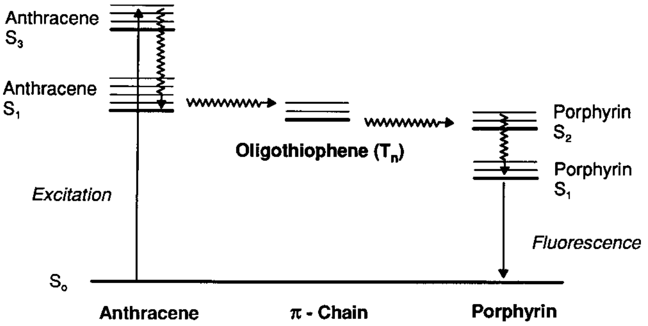


Figure 6. Schematic illustration of the unidirectional intramolecular energy transfer by intramolecular relaxation (the relative energetic position of T_n actually depends on the chain length *n*).

Thus, each of the mechanisms discussed is sufficient to explain the intramolecular energy transfer. From the optical investigations of anthryloligothienylporphyrins no unequivocal statement about the actual most effective mechanism can be made.

Light-harvesting systems: The porphyrins **2** are also of particular interest as synthetic organic light-harvesting systems. The absorption spectra of compounds **2a**–**e** with increasing numbers of anthrylquinquethienyl substituents are summarized in Figure 7. As can be seen from the figure, the intensity of the characteristic absorption bands changes nearly in proportion to the chromophoric ratio. This quantitative relationship is expressed very clearly through the dependence of the intensity of the anthracene S_3 absorption (230–280 nm) on the number of anthryl groups. At 257 nm the extinction coefficients increase continuously from 140000 $\mathrm{L\,mol^{-1}\,cm^{-1}}$ in **2a** to 466000 $\mathrm{L\,mol^{-1}\,cm^{-1}}$ in **2e**. The selectivity of anthryl excitation in **2e** amounts to about 90% compared with 82% in **2a**. The porphyrin bands (Soret band 400–500 nm, Q-bands >500 nm), however, show increasing red shift and broadening from **2a** to **2e**. This effect can be ascribed not only to overlapping oligothiophene absorption but also to an enhanced electronic coupling of porphyrin. The Q-bands between 550 and 650 nm in **2e** appear broad and structureless.

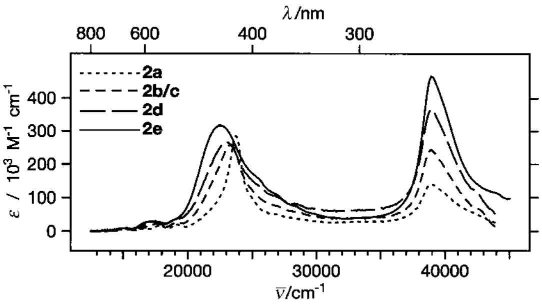


Figure 7. Absorption spectra (CH_2Cl_2, $T = 295$ K) of anthrylquinquethienylporphyrins **2a**–**e**. At $\lambda = 257$ nm the extinction coefficients ε ($\mathrm{L\,mol^{-1}\,cm^{-1}}$) are 140000 for **2a**, 244000 for **2b/c**, 367000 for **2d** and 466000 for **2e**.

Figure 8 shows fluorescence and excitation spectra of the light-harvesting systems **2a**–**e**. All compounds **2** exhibit the typical porphyrin emission band (600–800 nm) which appears as a structured band in the case of **2a** only (Figure 8). In the range of the intense anthracene S_3 absorption, the excitation and absorption spectra of **2a**–**e** correspond very well, indicating a nearly quantitative energy transfer in these compounds from the anthracene antennae to the porphyrin acceptor. The intensity of porphyrin fluorescence increases in proportion to the number of absorbing anthracene antennae.

Conclusions

Terminally donor/acceptor-substituted oligothiophenes represent excellent candidates for molecular photonic wires designed to transfer excitation energy in a given direction. The individual molecular subunits anthracene, oligothiophene and porphyrin, although attached in conjugation, essentially maintain their spectroscopic identity in the supermolecules. The anthracene donor represents a UV antenna and can be excited with high selectivity (up to 90%). After excitation we could prove a quantitative intramolecular energy transfer (>98%) from the anthracene donor to the emitting porphyrin acceptor through the oligothiophene bridge. In contrast to previously studied polyenes, in the oligothiophenes neither radiationless deactivation of the excitation energy through the conjugated chain nor quenching of the acceptor emission

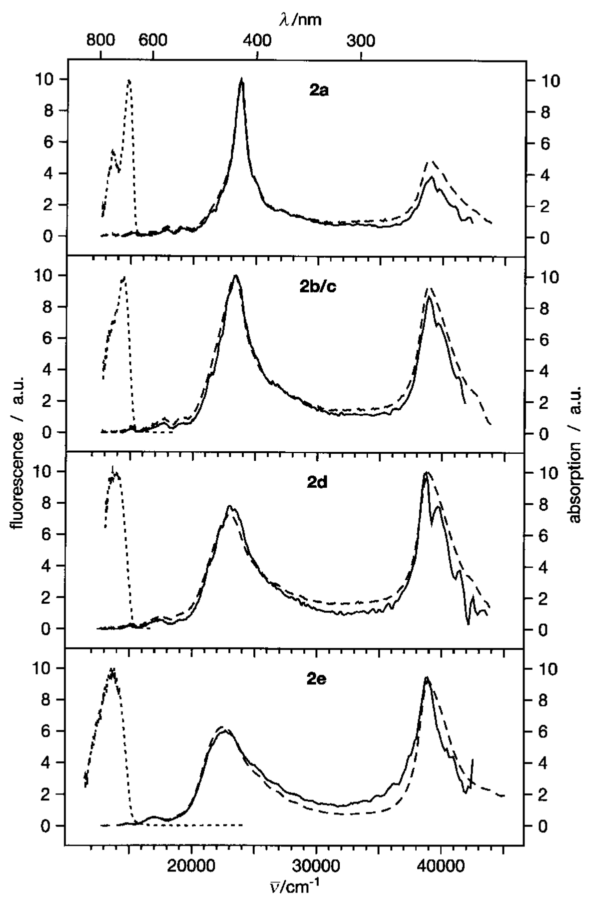


Figure 8. Absorption (- - - -), excitation (—) (detected at the maximum of the fluorescence band) and fluorescence spectra (····) (CH_2Cl_2, $T = 295$ K, arbitrary units [a.u.]) of porphyrins **2a–e**.

could be observed. As a result, the fluorescence quantum yields of the porphyrin emission are high and independent of the oligothiophene chain length.

The mechanism of the ultrafast (< 10 ps) intramolecular singlet–singlet energy transfer can be explained with different theories like Förster's, Dexter's, superexchange or intramolecular relaxation. However, from our experimental results no clear distinction can be made. In continuing this research we shall focus our investigations on the interruption of the π conjugation in oligothiophenes by incorporating saturated spacer molecules in order to control the mechanism of energy transfer.

Experimental Section

General methods: Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC250F (250 MHz) with TMS as internal standard; signals with an asterisk cannot be assigned unambiguously. Preparative column chromatography was carried out on glass columns of different size packed with silica gel S (Riedel–de Haen, grain size 0.032–0.063 mm). Medium-pressure liquid chromatography (MPLC) was performed at 5–10 bar on glass columns (50 cm × 4 cm) packed with Nucleosil 1525 NO_2 (Macherey Nagel, grain size 10 ± 15 μm; N = 1895, S = 3.2) and a Pharmacia LKB 2141 Variable Wavelength Monitor. HPLC was performed on a Waters 600E System with a Waters 991 Array Detector using a Nucleosil 5-NO_2, 200/8/4 analytical column (Macherey Nagel) and *n*-hexane/dichloromethane mixtures as eluent. Mass spectral analyses were performed in the fast-atom bombardment (FAB) mode on a Finnigan MAT 95 spectrometer (20 kV caesium, NBA matrix). All solvents were dried and distilled. The reactions were carried out under argon atmosphere in dried glassware. The following compounds were prepared according to known procedures: 2-bromo-3-pentylthiophene (**6**) and 5,5″-dibromo-2,2′:5′,2″-terthiophene (**7**),[18,32] 3,3′′′′-dipentyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene (**3**) and 5-formyl-3,3′′′′-dipentyl-2,2′:5′,2″: 5″,2‴:5‴,2′′′′-quinquethiophene (**9**).[18]

Optical measurements: Optical spectra were measured in the indicated solvents at concentrations of 10^{-5} to 10^{-6} mol L^{-1} in order to maintain low optical densities and to exclude intermolecular interactions. The solvents (Merck Uvasol) were used as purchased. Absorption spectra were recorded on a Perkin–Elmer Lambda 7 spectrophotometer at 293 K. For fluorescence, fluorescence excitation, and time-resolved fluorescence measurements the solutions were degassed by repeated freeze–pump–thaw cycles to remove oxygen. The cw-fluorescence and fluorescence excitation spectra were performed by standard techniques: 450 W Xenon lamp and 0.25 m double monochromator as excitation source (bandwidth 2 nm FWHM), 1 m double monochromator (bandwidth 1 nm FWHM), and cooled photomultiplier with photon counting as detection setup.

The time-resolved emission spectra were recorded with time-correlated single photon counting after ps laser excitation at 25000, 27300 and 37594 cm^{-1}. By means of fitting the transients deconvoluted with the response of the detection system the time-resolution is about 10 ps. A detailed description is given in the literature.[33] All spectra were corrected for the spectral responses of the experimental setups. Fluorescence quantum yields were measured relative to anthracene in *n*-hexane ($\Phi_f = 0.30$ at 295 K[34]).

5-(9-Anthryl)-3,3′′′′-dipentyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene (4a): A 1.6 M solution of *n*BuLi in *n*-hexane (0.41 mL, 0.65 mmol) was added dropwise to a solution of **3** (300 mg, 0.54 mmol) in dry diethyl ether (10 mL) through a syringe over 10 min under Ar atmosphere. After stirring at room temperature for 1 h, the suspension was cooled to −78 °C. A cold (−78 °C) solution of **8** (84.84 mg, 0.44 mmol) in dry diethyl ether (20 mL) was added dropwise through a syringe to the suspension over 20 min, followed by dry diethyl ether (10 mL). The reaction mixture was stirred at −78 °C for 2.5 h, and then allowed to warm to room temperature (16 h). The mixture was poured into ice-cold water/HCl (5:1, 50 mL) and stirred for 1 h. The organic phase was separated and the aqueous phase extracted three times with CH_2Cl_2 (50 mL each). The combined extracts were concentrated in vacuo and taken up in MeOH/toluene (1:1, 40 mL). Conc. HCl (5 mL) was added and the reaction mixture was heated to 85 °C for 30 min. After addition of CH_2Cl_2 (150 mL), the mixture was hydrolyzed with ice (150 g). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (50 mL). The combined extracts were washed with a solution of sodium hydrogencarbonate and water, dried (Na_2SO_4) and concentrated. To remove unreacted **8** the residue was chromatographed on silica gel with CH_2Cl_2 as eluent followed by *n*-hexane/CH_2Cl_2 (5:1). Compounds **3**, **4a** and **4b** were separated by MPLC on silica gel with *n*-hexane/CH_2Cl_2 (15:1) (flow 30 mL min^{-1}, detection wavelength 260 and 430 nm) to give 95 mg (24 %) **4a** as an orange solid and 14.3 mg (3 %) **4b** as a red solid.

Monoanthryl unit 4a: M.p. 110–112 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.91$, 0.93 (each t, $J = 7.0$ Hz, 6H, H-e), 1.34–1.50 (m, 8H, H-c,d), 1.67, 1.79 (each tt, $J = 7.7$ Hz, 4H, H-b), 2.78, 2.94 (each t, $J = 7.8$ Hz, 4H, H-a), 6.94 (d, $J = 5.2$ Hz, 1H, H4′′′′), 7.02 (s, 1H, H4), 7.03* (d, $J = 3.7$ Hz, 1H), 7.10–7.14* (m, 4H), 7.17* (d, $J = 3.5$ Hz, 1H), 7.18 (d, $J = 5.0$ Hz, 1H, H5′′′′), 7.42–7.52 (m, 4H, anthracene H2,3,6,7), 8.02–8.05 (m, 4H, anthracene H1,4,5,8), 8.53 (s, 1H, anthracene H10); $C_{44}H_{40}S_5$ (729.1): calcd C 72.48, H 5.53, S 21.99; found C 72.67, H 5.71, S 21.55.

Dianthryl unit 4b: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.94$ (t, $J = 7.2$ Hz, 6H, H-e), 1.33–1.50 (m, 8H, H-c,d), 1.80 (tt, $J = 7.5$ Hz, 4H, H-b), 2.94 (t, $J = 7.7$ Hz, 4H, H-a), 7.03 (s, 2H, H4,4′′′′), 7.14 (d, $J = 4.1$ Hz, 2H, H3′,4‴), 7.15 (s, 2H, H3″,4″), 7.18 (d, $J = 3.8$ Hz, 2H, H4′,3‴), 7.43–7.53 (m, 8H, anthracene H2,3,6,7), 8.02–8.06 (m, 8H, anthracene H1,4,5,8), 8.53 (s, 2H, anthracene H10); MS(FAB): *m*/*z* 904.1 [$M^{\cdot+}$].

5′′′′-(9-Anthryl)-5-formyl-3,3′′′′-dipentyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene (10): A solution of **4a** (0.55 g, 0.76 mmol) in CH_2Cl_2 (6 mL) was heated to reflux and a solution of the Vilsmeier reagent (2.5 mL, 1 mL ≈

0.8 mmol) [prepared by addition of phosphoryl chloride (3.29 g, 21.46 mmol) to DMF (1.7 g, 23.26 mmol) in dry CH_2Cl_2 (25 mL) at room temperature and stirring for 2 h[18]] was added, followed by another 1.5 mL after 3 h. After stirring for a further 3.5 h, a solution of sodium hydrogencarbonate (1M) was added, and the reaction mixture stirred for 2 h. After dilution with water, the organic phase was separated and the aqueous phase extracted several times with CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4) and concentrated. The residue was chromatographed twice on silica gel with CH_2Cl_2 to give **10** as effervescent oil that was powdered and dried under high vacuum over paraffin: yield 0.45 g (79 %); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.93$ (d, $J = 6.9$ Hz, 6 H, H-e), 1.37 – 1.45 (m, 8 H, H-c,d), 1.65 – 1.83 (m, 4 H, H-b), 2.83, 2.94 (each t, $J = 7.8$ Hz, 4 H, H-a), 7.03 (s, 1 H, H4′′′′), 7.14* (2d, $J = 3.9$ Hz, 2 H), 7.16* (d, $J = 3.9$ Hz, 1 H), 7.17 (d, $J = 3.8$ Hz, 1 H, H4′), 7.19* (d, $J = 3.9$ Hz, 1 H), 7.22 (d, $J = 3.8$ Hz, 1 H, H3′), 7.42 – 7.52 (m, 4 H, anthracene H2,3,6,7), 7.60 (s, 1 H, H4), 8.01 – 8.06 (m, 4 H, anthracene H1,4,5,8), 8.53 (s, 1 H, anthracene H10), 9.83 (s, 1 H, CHO); $C_{45}H_{40}OS_5$ (757.1): calcd C 71.39, H 5.32, S 21.18; found C 71.34, H 5.33, S 20.23; MS(FAB): *m*/*z* 757.5 [*M* + H].

General procedure for the synthesis of porphyrins 2 and 5 following ref. [12]: A solution of pyrrole, 1-hexanal and aldehyde **9** or **10** in dry CH_2Cl_2 was stirred for 15 – 30 min under an Ar atmosphere in the absence of light. Trifluoroacetic acid was added through a syringe, and the reaction mixture stirred for 24.5 h (**2a**) or 26 h (**5a**) (monitored by observation of the porphyrin band by UV/Vis). The oxidation was initiated by addition of *p*-chloranil, and the reaction mixture refluxed for 2 h. After cooling to room temperature, the reaction mixture was neutralized with sodium carbonate and Florisil® (Fluka) and stirred for 14 h (**2a**) or 1 h (**5a**). The solution was filtered, concentrated and worked up as described.

5-[5′′′′-(9-Anthryl)-3,3′′′′-dipentyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethienyl-5-yl]-10,15,20-tripentylporphyrin (2a): Prepared as described from **10** (0.56 g, 0.74 mmol), 1-hexanal (0.22 g, 2.21 mmol), pyrrole (0.20 g, 2.98 mmol), trifluoroacetic acid (0.84 g, 7.37 mmol), *p*-chloranil (0.54 g, 2.21 mmol) and CH_2Cl_2 (750 mL); initiation of condensation by addition of 1 equiv trifluoroacetic acid followed by 0.5 equiv each after 2.5, 7 and 20.5 h; neutralization and filtration through a Florisil column (8 × 10 cm), which was subsequently treated several times with CH_2Cl_2 and CH_2Cl_2/MeOH (1:1), concentration of the combined filtrates and chromatography on silica gel with CH_2Cl_2 to separate unreacted **10** (yield 287 mg, 51 %); separation of the porphyrin mixture by MPLC (Nucleosil 1525 NO_2, flow 30 mL min^{-1}, *n*-hexane/CH_2Cl_2 (gradient from 80:20 to 75:25 for separation of **11**, 67:33 to 50:50 for separation of **2a**)), repurification of the porphyrin fractions by chromatography on silica gel with CH_2Cl_2, subsequent MPLC and recrystallization from acetone/MeOH to give 68 mg (7.3 %) **2a** as a bright blue-violet solid; m.p. 115 °C (sintering > 84 °C); HPLC purity 99.8 %; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.58$ (br s, 2 H, NH), 0.92 – 1.04 (m, 15 H, H-e), 1.37 – 1.65 (m, 14 H, H-c,d), 1.72 – 1.84 (m, 8 H, H-b,c), 1.93 – 2.02 (tt, $J = 7.3$ Hz, 2 H, H-b), 2.46 – 2.58 (m, 6 H, H-b), 2.96, 3.15 (each t, $J = 7.7$ Hz, 4 H, H-a), 4.90 – 5.00 (m, 6 H, H-a), 7.04 (s, 1 H, H4′′′′), 7.15* (d, $J = 3.8$ Hz, 1 H, H4′′′), 7.17* (d, $J = 3.8$ Hz, 1 H, H4′′), 7.19* (m, $J = 3.7$ Hz, 2 H, H3′′,3′′′), 7.25* (d, $J = 3.6$ Hz, 1 H, H4′), 7.31 (d, $J = 3.9$ Hz, 1 H, H3′), 7.43 – 7.52 (m, 4 H, anthracene H2,3,6,7), 7.71 (s, 1 H, H4), 8.02 – 8.06 (m, 4 H, anthracene H1,4,5,8), 8.53 (s, 1 H, anthracene H10), 9.19 (d, $J = 4.9$ Hz, 2 H, porphyrin H3,7), 9.41 (d, $J = 4.9$ Hz, 2 H, porphyrin H2,8), 9.48 (AB system, m, $J = 4.9$ Hz, 2 H, porphyrin H12,18), 9.52 (AB system, m, $J = 4.9$ Hz, 2 H, porphyrin H13,17); $C_{79}H_{82}N_4S_5$ (1247.9): calcd C 76.04, H 6.62, N 4.49, S 12.85; found C 76.03, H 6.75, N 4.51, S 12.69.

Mixture of 2b/c: Yield 43 mg (3.0 %) as a blue-violet solid; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.60, -2.54$ (2 s, 2 H, NH), 0.87 – 1.05 (m, 18 H, H-e), 1.25 – 1.84 (m, 28 H, H-b,c,d), 1.96 – 2.02 (m, 4 H, H-b), 2.53 – 2.59 (m, 4 H, H-b), 2.96, 3.14 (each t, $J = 7.7$ Hz, 8 H, H-a), 4.94 – 5.00 (m, 4 H, H-a), 7.03, 7.04 (2 s, 2 H, H4′′′′), 7.14 – 7.33 (m, $J = 3.5 – 3.8$ Hz, 12 H, H3′,4′,3′′,4′′,3′′′,4′′′), 7.44 – 7.51 (m, 8 H, anthracene H2,3,6,7), 7.73 (s, 2 H, H4), 8.02 – 8.06 (m, 8 H, anthracene H1,4,5,8), 8.53 (s, 2 H, anthracene H10), 9.19* (s, 1 H, porphyrin H), 9.22 – 9.26* (m, $J = 4.9$ Hz, 3 H, porphyrin H), 9.43 – 9.47* (m, $J = 5.4$ Hz, 3 H, porphyrin H), 9.52* (s, 1 H, porphyrin H); MS(FAB): *m*/*z* 1903.2 [*M* − H].

Porphyrin 2d: Yield 9 mg (0.5 %) as a blue-violet solid.

5-(3,3′′′′-Dipentyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethienyl-5-yl)-10,15,20-tripentylporphyrin (5a): Prepared as described from **9** (0.27 g, 0.47 mmol), 1-hexanal (0.14 g, 1.40 mmol), pyrrole (0.13 g, 1.94 mmol), trifluoroacetic acid (0.53 g, 4.68 mmol), *p*-chloranil (0.34 g, 1.40 mmol) and CH_2Cl_2 (750 mL); initiation of condensation by addition of 1 equiv trifluoroacetic acid followed by F. Effenberger, 0.5 equiv each after 3.5, 7.5 and 23.5 h; neutralization and concentration of the filtrate followed by uptake in CH_2Cl_2, treatment with Florisil for 15 min, filtration and concentration; after chromatography on silica gel with CH_2Cl_2 to separate unreacted **9** (yield 63 mg, 23 %) separation of the porphyrins by MPLC (Nucleosil 1525 NO_2, flow 30 mL min^{-1}, *n*-hexane/CH_2Cl_2 (gradient from 80:20 to 75:25)), repurification of the porphyrin fractions as described above for **2a** to give 19 mg (3.8 %) **5a** as a bright blue-violet solid. M.p. 123 – 124 °C (sintering > 115 °C); HPLC purity > 99.3 %; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.58$ (br s, 2 H, NH), 0.92 – 1.04 (m, 15 H, H-e), 1.25 – 1.85 (m, 22 H, H-b,c,d), 1.93 – 2.02 (tt, $J = 7.6$ Hz, 2 H, H-b), 2.46 – 2.59 (m, 6 H, H-b), 2.80, 3.14 (each t, $J = 7.8$ Hz, 4 H, H-a), 4.89 – 5.00 (m, 6 H, H-a), 6.95 (d, $J = 5.2$ Hz, 1 H, H4′′′′), 7.04* (d, $J = 3.7$ Hz, 1 H, H4′′′), 7.14* (d, $J = 3.9$ Hz, 1 H, H4′′), 7.16* (d, $J = 3.9$ Hz, 1 H, H3′′′), 7.18* (d, $J = 3.8$ Hz, 1 H, H3′′), 7.19 (d, $J = 5.2$ Hz, 1 H, H5′′′′), 7.24* (d, $J = 3.8$ Hz, 1 H, H4′), 7.30 (d, $J = 3.9$ Hz, 1 H, H3′), 7.70 (s, 1 H, H4), 9.19 (d, $J = 4.9$ Hz, 2 H, porphyrin H3,7), 9.41 (d, $J = 4.9$ Hz, 2 H, porphyrin H2,8), 9.47 (AB system, m, $J = 4.9$ Hz, 2 H, porphyrin H12,18), 9.51 (AB system, m, $J = 4.9$ Hz, 2 H, porphyrin H13,17); $C_{65}H_{74}N_4S_5$ (1071.6): calcd C 72.85, H 6.96, N 5.23, S 14.96; found C 72.93, H 6.98, N 5.18, S 14.72.

5,10,15,20-Tetrakis[5′′′′-(9-anthryl)-3,3′′′′-dipentyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethienyl-5-yl]porphyrin (2e): A solution of **10** (205 mg, 0.27 mmol) in dry CH_2Cl_2 (70 mL), pyrrole (18 mg, 0.27 mmol) and ethanol (0.5 mL) was stirred at room temperature for 30 min under Ar atmosphere in the absence of light. The condensation was initiated by addition of $BF_3 \cdot Et_2O$ in CH_2Cl_2 (0.25M, 0.37 mL) followed by addition of further $BF_3 \cdot Et_2O$ (0.3 mL) and CH_2Cl_2 (200 mL) after 8 h. After total of 22 h, *p*-chloranil (49 mg, 0.2 mmol) was added, and the reaction mixture heated under reflux for 2.5 h. After addition of triethylamine (18 mg, 0.18 mmol), the reaction mixture was stirred for 45 min, concentrated and chromatographed on silica gel with CH_2Cl_2. The porphyrin fraction was purified by MPLC (Nucleosil 1525 NO_2, flow 30 mL min^{-1}) with *n*-hexane/CH_2Cl_2 (66:34). Crystallization of **2e** was induced by addition of acetone to a satd solution of **2e** in CH_2Cl_2 to give 7.6 mg (3.5 %) as blue-violet solid. M.p. sintering > 89 °C; HPLC purity > 98 %; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.24 – 9.26$* (m, 6 H, porphyrin), 9.08* (d, $J = 5.2$ Hz, 2 H, porphyrin), 8.52 (s, 4 H, anthracene H10), 8.02 – 8.06 (m, 16 H, anthracene H1,4,5,8), 7.79 (m, 4 H, H4), 7.43 – 7.52 (m, 16 H, anthracene H2,3,6,7), 7.14 – 7.21 (m, $J = 3.8$ Hz, H4′,3′′,4′′, 3′′′,4′′′), 7.04 (s, 4 H, H4′′′′), 3.16, 2.95 (each t, $J = 7.5$ Hz, 16 H, H-a), 1.37 – 2.03 (m, 48 H, H-b,c,d), 0.92 – 1.03 (m, $J = 7.1$ Hz, 24 H, H-e), −2.51 (s, 2 H, NH); MALDI-MS (matrix: sinapic acid): calcd for $C_{196}H_{167}N_4S_{20}$ [M+H$^+$] 3215.8; found 3215.9.

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