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Synthesis and Energy Transfer Properties of Terminally Substituted Oligothiophenes

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Abstract: A series of conjugated anthryl-oligothienyl-porphyrins in which the oligothiophene is terminally linked to the 5-position of a porphyrin and to the 9-position of anthracene has been synthesized, and photoexcited-state properties have been studied by steady-state fluorescence spectra, fluorescence excitation spectra and picosecond time-resolved fluorescence measurements. Due to the spectral position of the anthracene and the porphyrin absorption bands a selective excitation of both end groups is possible, which is demonstrated by the UV−visible absorption spectra. Selective excitation of the anthryl end group leads to a quantitative intramolecular energy transfer to the porphyrin end group in the subpicosecond time scale. The mechanism is discussed in terms of existing theories (Förster/Dexter, superexchange, and intramolecular relaxation).

Introduction

Inspired by the processes of excitation energy transfer and charge separation in biological photosynthetic reaction centers, numerous synthetic model compounds have been studied containing porphyrins either as an acceptor in energy transfer systems[2−8] or as a donor in electron transfer systems.[8−10] Apart from this basic work for the understanding of natural processes such compounds can find application for information transport and storage on the molecular level.[11−13]

In terminally substituted conjugated polyenes with an anthryl group as donor and tetraphenylporphyrin as acceptor we could prove a selective excitation of the anthryl moiety and an intramolecular energy transfer from the excited donor to the emitting acceptor. The mechanism has been identified as an intramolecular relaxation process mediated via the polyene chain.[11,14,15]

With respect to possible applications, polyenes containing more than five double bonds were revealed to have severe disadvantages. They are thermally and photochemically of inadequate stability. Most critical, however, is the competing radiationless deactivation on the polyene subunit resulting in considerable losses of excitation energy. The fluorescence quantum yields decrease from 3.5% in the compounds with three conjugated double bonds to <0.1% in compounds with nine conjugated double bonds.[11a,14b]

To address these problems, especially to improve the fluorescence quantum yields we have synthesized new model compounds which contain oligothiophenes instead of polyenes as conjugated π-systems between the given end groups anthracene and porphyrin. Oligothiophenes are by far more stable than polyenes. They do not isomerize, show high fluorescence quantum yields[16,17] and exhibit a large degree of π-delocalization along the conjugated chain.[18,19]

In this paper we report on the synthesis and the optical properties of anthryl-oligothienyl-porphyrins **1** as new model

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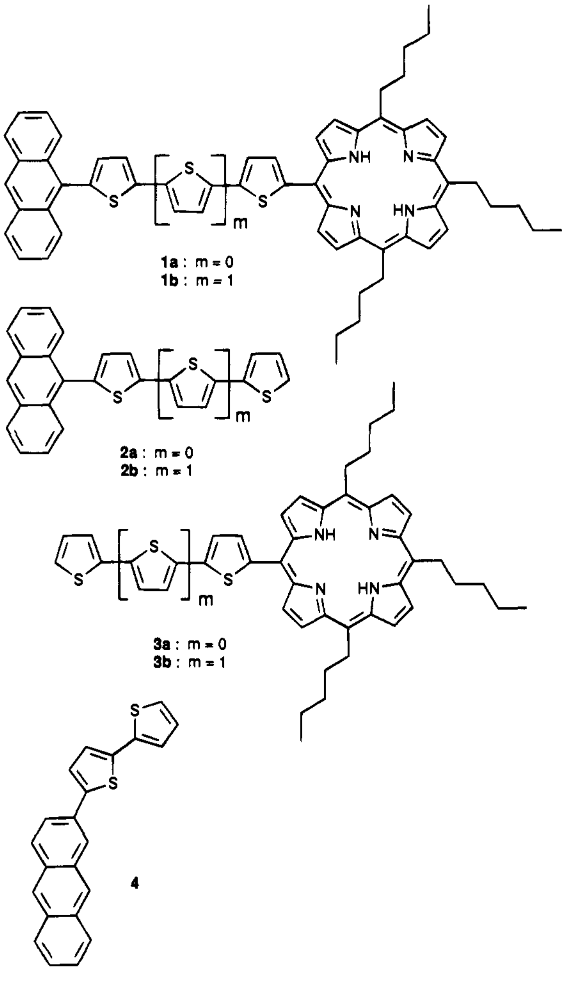
Chart 1



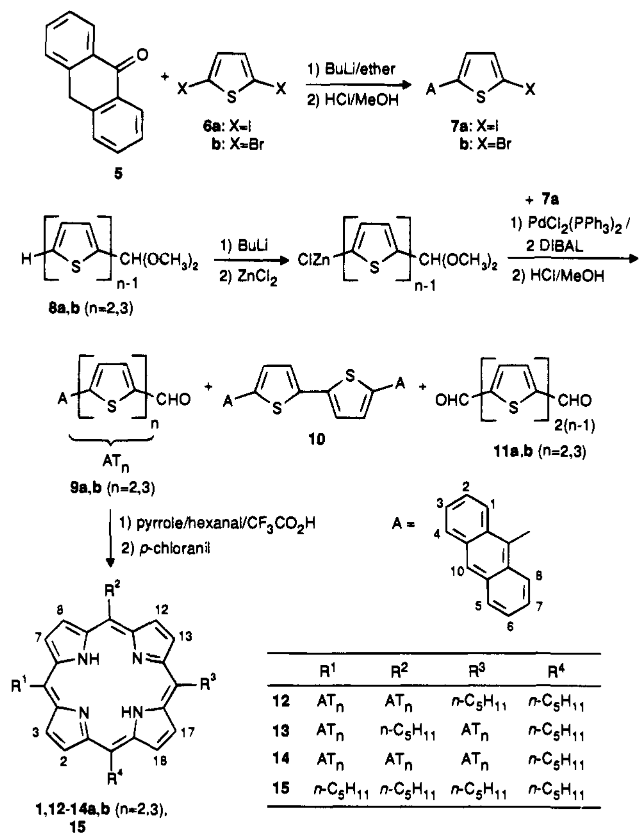
compounds for an intramolecular energy transfer via conjugated bridges. To enhance the solubility of the oligothienyl compounds pentyl side chains had to be incorporated into the meso positions of porphyrin. In addition anthryl-oligothiophenes **2** and **4** as well as oligothienyl-porphyrins **3** representing the donor-chain and the chain-acceptor subunits are included in this work. The physical properties of compounds **2**, published already in a previous paper,[17] are only discussed as far as they are relevant for the understanding of the properties of compounds **1**. In order to demonstrate the high selectivity of anthryl excitation in our energy transfer systems **1**, a comparison of compounds **2a** and **4** with different position of anthracene-bithiophene linkage is of particular interest.

Results

Synthesis. The synthetic sequence leading to compounds **1a,b** is shown in Scheme 1.

2,5-Diiodothiophene **6a** dissolved in diethyl ether was lithiated by *n*-butyllithium in *n*-hexane at −70 °C to 2-lithio-5-iodothiophene which, upon subsequent treatment with anthrone **5** and acidic workup afforded anthrylthienyl iodide **7a** in 77% yield. Analogous, 2-(9-anthryl)-5-bromothiophene (**7b**) was isolated in 66% yield. For elongation of the oligothiophene chain, **7a** was coupled with the protected and zinc-metalated oligothiophene aldehyde **8a,b** in the presence of a catalytic amount of a Pd catalyst[20] generated in situ from $PdCl_2(PPh_3)_2$ and diisobutylaluminium hydride (DIBAL). After treatment with hydrogen chloride in methanol and chromatographic workup the anthryloligothiophene aldehydes **9a,b** were obtained in 42 and 30% yield. As byproducts of the cross-coupling reaction significant amounts of the homodimers **10** and **11a,b** have been isolated.

Scheme 1



	R1	R2	R3	R4
12	AT_n	AT_n	n-C_5H_{11}	n-C_5H_{11}
13	AT_n	n-C_5H_{11}	AT_n	n-C_5H_{11}
14	AT_n	AT_n	AT_n	n-C_5H_{11}
15	n-C_5H_{11}	n-C_5H_{11}	n-C_5H_{11}	n-C_5H_{11}

The porphyrins **1a,b** were prepared by condensation of pyrrole and an appropriate mixture of the aldehydes **9a,b** and 1-hexanal and subsequent oxidation of the porphyrinogen mixture with *p*-chloranil using Lindsey's method.[21] Due to the simultaneous condensation of two aldehydes the formation of the desired porphyrins **1a,b** was accompanied by the formation of tetrapentylporphyrin (**15**) and the other hybrid anthryloligothienyl-pentyl-porphyrins **12**, **13**, and **14**. On the basis of their different aryl contribution MPLC-chromatographic separation on nitrophenyl-modified silica gel was possible giving pure porphyrins **1**, **14**, and **15** and the isomers **12** and **13** (as a mixture) with high HPLC purity (>99%). The yields of the various porphyrins are consistent with a statistical incorporation of the two aldehydes (9−10% **1**, 6−8% **15**, 2% **12/13** (2:1), and 0.4% **14b**).

The synthesis of the oligothienyl-porphyrins **3a,b** was performed analogously from 5-formyl-2,2′-bithiophene (**16a**) and 5-formyl-2,2′:5′,2″-terthiophene (**16b**)[22] (Scheme 2).

After MPLC-purification pure porphyrin fractions of **3**, **15**, **17**, and **18** were obtained.

As outlined in Scheme 3, 9-anthrylbithiophene **2a** has been obtained from **5** and 5-bromo-2,2′-bithiophene (**19**)[23] in a yield of 58%. 9-Anthrylterthiophene **2b** was prepared in 48% yield

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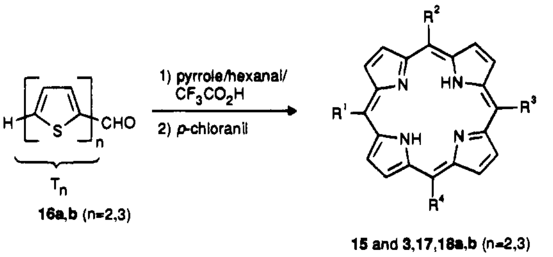
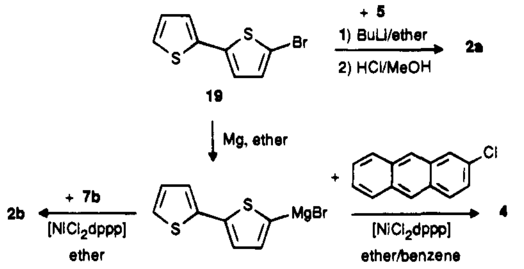
Scheme 2



	R1	R2	R3	R4
17	T_n	T_n	n-C_5H_{11}	n-C_5H_{11}
18	T_n	n-C_5H_{11}	T_n	n-C_5H_{11}

Scheme 3



by the NiCl$_2$dppp-catalyzed cross-coupling reaction of the Grignard reagent from **19** with anthrylthienylbromide **7b**. Also by Kumada coupling reaction of the Grignard reagent from **19** with 2-chloroanthracene in diethyl ether and benzene as cosolvent 5-(2-anthryl)-2,2′-bithiophene (**4**) was synthesized in 63% yield.

Absorption Spectra. Figure 1 shows the UV–visible spectra of anthrylterthienylporphyrin **1b** together with the bichromophoric subsystems **2b** and **3b** and the individual chromophores anthracene, terthiophene, and tetrapentylporphyrin. In spite of the direct attachment of the π-systems anthracene and terthiophene as well as terthiophene and porphyrin, the electronic interactions of these π-systems are only weak, and the individual molecular subunits can be recognized in the spectra of the supermolecules. The most characteristic features are the S_0–S_3 absorption of the anthracene at 258 nm and the Soret band of the porphyrin at 422 nm. The four Q-bands of porphyrin in the spectral region from 500 to 700 nm are clearly evident, too. In the UV absorption range up to 400 nm there are contributions coming from the porphyrin, the anthracene, and the terthiophene chromophore. However, in contrast to the intensive anthracene absorption the contribution of porphyrin and oligothiophene at 258 nm is negligible. The contribution of the anthryl-oligothienyl absorption is clearly demonstrated by the absorption spectra of **1b**, **12b/13b**, and **14b** (Figure 2) showing a linear increase of the extinction in this spectral region with an increasing number of anthrylterthienyl subunits and a well resolved vibronic structure in **14b**, originating from the anthracene S_0-S_1 transition. A linear increase of the extinction coefficient is also given at 258 nm where the anthryl group possesses a strong absorption band.

Although all absorption bands may be ascribed to the individual molecular subunits, electronic interactions between them are not negligible. All peak maxima exhibit slight red shifts and the absorption coefficients at the peak positions are reduced because of a broadening of the bands. Observed red shifts for the Soret band are 4 nm in **1b** and **3b**, 10 nm in **12b/13b** and **17b** (or **18b**), and 18 nm in **14b**. The red shifts of the anthryl S_0–S_3 absorption are 3 nm in **2b** and in **1b** compared to the anthracene absorption.

For the bithienyl bridge in **1a** spectral changes in the absorption of the porphyrin and the anthryl bands are less pronounced, which is demonstrated by the UV–visible data in Table 1. These observations suggest that there is less electronic coupling between the component parts for the bithienyl than for the terthienyl bridge. The bithienyl chromophore itself

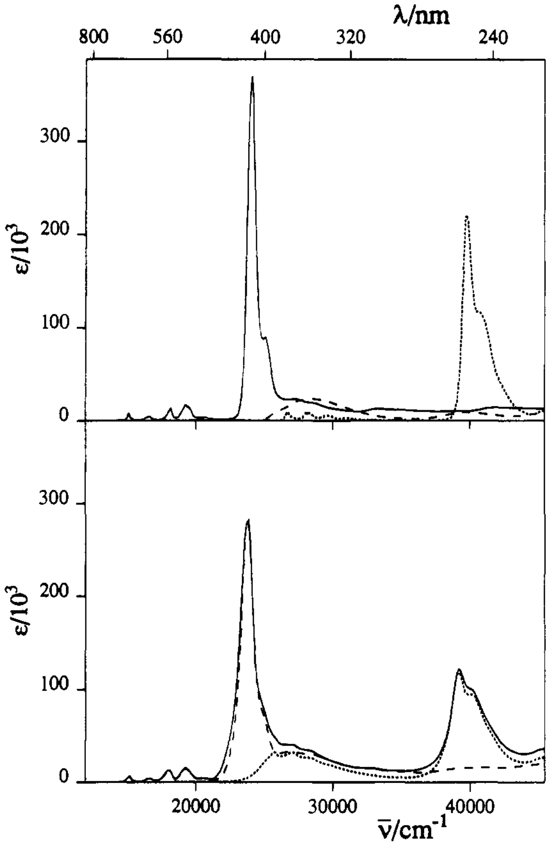


Figure 1. Absorption spectra (n-hexane, T = 295K) of anthrylterthienylporphyrin **1b** and model compounds containing the chromophores anthracene, terthiophene, and porphyrin. Top: **15** (—), 2,2′:5′,2″-terthiophene (— —), anthracene (- -). Bottom: **1b** (—), **2b** (- -), **3b** (— —).

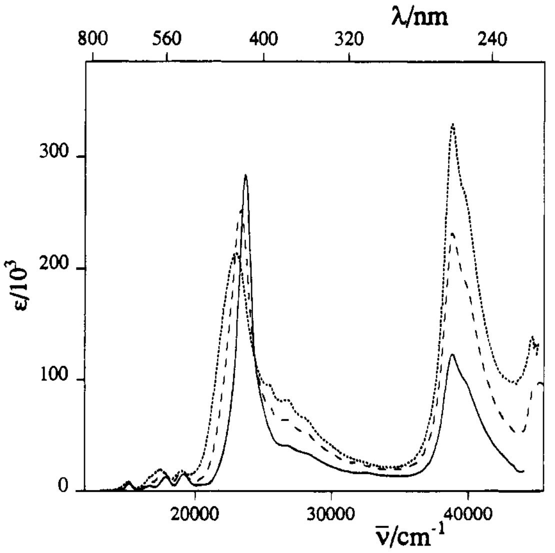


Figure 2. Absorption spectra (dichloromethane, T = 295K) of anthrylterthienylporphyrins **1b** (—), **12b/13b** (— —) and **14b** (- -).

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Table 1. UV/vis Absorption Maxima of Anthryloligothienylporphyrins **1**, **12/13**, and **14**, Oligothienylporphyrins **3**, **17**, and **18** and Anthryloligothiophenes **2** in Comparison with the Model Chromophores Anthracene (**A**), Bithiophene (**T$_2$**), Terthiophene (**T$_3$**), and Porphyrin **15** in Dichloromethane at 20 °C

	λ [nm] (ε [10^3 L·mol^{-1}·cm^{-1}])									
compd	anthracene $S_0 \rightarrow S_3$	bithiophene[a]	anthracene/terthiophene/porphyrin			porphyrin $S_0 \rightarrow S_2$	porphyrin $S_0 \rightarrow S_1$			
A	255(190)		342(5)	359(8)	378(7)					
15		302[a](11)	347[b](15)	365(18)	399(72)	417(410)	519(14)	554(9)	600(4)	658(7)
1a	258(122)	306(20)	351[b](26)	370(31)		421(320)	522(15)	559(12)	600(5)	657(7)
12a/13a[c]	258(220)	308(30)	353(39)	370(45)	390[b](49)	426(255)	524(15)	564(13)	599(6)	657(6)
3a		306(20)	348[b](20)	368(23)		420(330)	521(14)	558(11)	599(5)	656(7)
17a		309(30)	350[b](26)	370[b](28)		426(284)	524(16)	562(12)	597(6)	657(7)
18a		310(28)		367[b](26)		426(260)	522(15)	562(15)	600[b](5)	657(10)
2a	257(130)	317(14)	352(11)	370(13)	390(12)					
T$_2$		302(12)								
1b	258(124)		355[b](34)	374[b](41)		422(284)	522(15)	559(13)	599(5)	657(8)
12b/13b[c]	258(236)		354[b](51)	374(63)	392[b](75)	428(252)	525(17)	565(17)	600[b](8)	659(9)
14b	258(329)		354[b](66)	374(83)	392[b](99)	435(222)	526(17)	573(20)	598[b](12)	663(8)
3b			352[b](30)	374(33)		421(281)	521(14)	558(12)	599(5)	656(7)
17b			352[b](47)	375(51)		427(248)	524(16)	564(14)	600[b](7)	656(7)
18b[d]			353[b]	375		428	522	564	600[b]	659
2b	258(116)		357(26)	373(31)	392(31)					
T$_3$			355(22)							

[a] The bithiophene band is superimposed by absorptions of the porphyrin as can be seen from **15**. [b] Shoulder. [c] The ratio of the isomers **12a/13a** is 94:6, of the isomers **12b/13b** 70:30. [d] Extinction coefficients not determined.

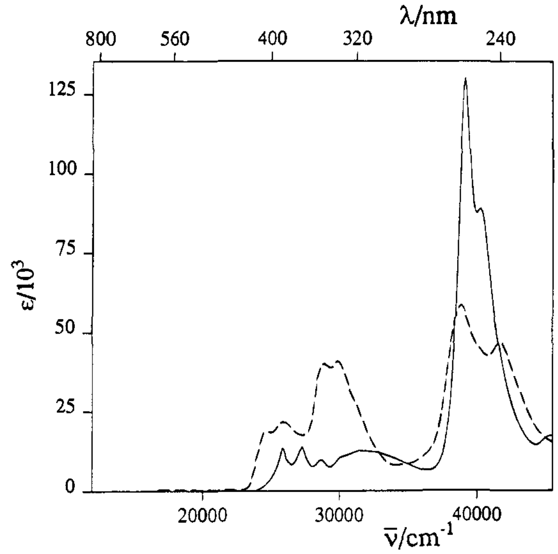

Figure 3. Absorption spectra (*n*-hexane, T = 295K) of anthrylbithiophenes **2a** (—) and **4** (– –).

is absorbing around 300 nm, clearly separated from transitions of the anthryl group (Table 1).

Figure 3 shows the UV–visible spectra of the anthrylbithiophenes **2a** and **4**. Due to the sterically less hindered anthryl linkage in 2-position the extinction of the anthracene S_0–S_3 band in **4** is reduced by more than 50% and additional bands, which result from high electronic coupling between anthracene and bithiophene, appear between 300 and 400 nm. Therefore a selective anthryl excitation can be excluded in **4** in contrast to **2a** with the linkage in 9-position of anthracene.

Most important for our investigations on intramolecular energy transfer processes in conjugated π-systems is the fact that for all anthracene-oligothiophene-porphyrin molecules a predominant, highly selective excitation of the terminal 9-anthryl group at 258 nm is possible.

Fluorescence Spectra. The emission spectra of tetrapentylporphyrin **15**, terthienylporphyrin **3b**, anthrylterthiophene **2b**, and the anthrylterthienylporphyrins **1b** and **14b** are shown in Figure 4. The spectra are normalized to the same maximum intensity. All porphyrin compounds **1**, **3**, **12b/13b**, and **14b** show the Q^*_{x00} and the Q^*_{x01} emission bands which are typical for porphyrins.[24] The emission bands of **1b** are broadened and slightly red-shifted (7 nm) with respect to the emission bands of **15**. For **14b** the Q^*_{x00} and Q^*_{x01} bands are no longer resolved.

The fluorescence spectra are independent of the excitation wavelength. Even excitation in the area of the strong anthracene-like transition at 258 nm does not reveal additional emission bands. Especially there is neither anthracene- nor anthrylterthiophene-type emission of the molecules in the spectral region between 370 and 600 nm.

Also shown in Figure 4 are the fluorescence excitation spectra (detection energy 715 nm) of compounds **1b**, **2b**, **3b**, **14b**, and **15** together with their absorption spectra. The two transitions characteristic for the porphyrin absorption are seen in the fluorescence excitation spectra, the Q-bands in the spectral region between 500 and 660 nm and the most intensive Soret band at 420 nm. At 258 nm in the fluorescence excitation spectra of **1b** and **14b** a band is resolved which can be clearly interpreted as the anthracene S_0–S_3 absorption by comparison with the fluorescence excitation and absorption spectrum of **2b**. For **14b** the intensity of this transition is three times larger corresponding to the three-fold substitution with anthrylterthiophene. Upon excitation at 258 nm for both **1b** and **14b** the typical porphyrin emission is observed indicating the energy transfer from anthracene to the porphyrin chromophore. By comparison of the fluorescence excitation and the absorption spectra the efficiency of the energy transfer can be determined.[2,3,5] For both compounds **1b** and **14b** no remarkable difference is seen in the efficiency of energy transfer from the anthracene to the porphyrin end group; it is estimated to be at least 98%.

The optical behavior of the porphyrin compounds **1a** and **14a** containing the bithiophene bridge is analogous. Also these compounds show an intramolecular energy transfer of at least 98%.

In Table 2 the fluorescence quantum yields in *n*-hexane and dichloromethane solutions are shown.

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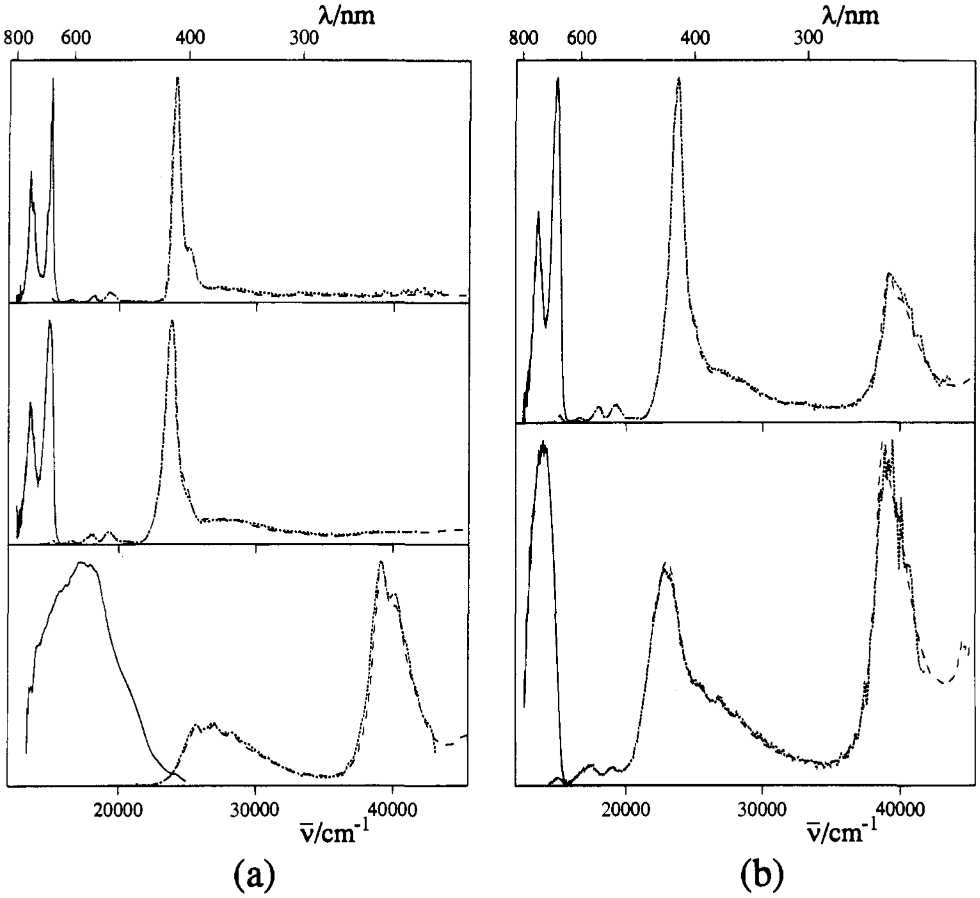

Figure 4. Fluorescence (—), fluorescence excitation (- -) and absorption (— —) spectra (T = 295 K). Fluorescence spectra are independent of excitation wavelength, fluorescence excitation spectra independent of detection wavelength. All spectra are normalized to the same maximum intensity: (a) top, **15**; middle, **3b**; bottom, **2b** (*n*-hexane) and b) top, **1b** (*n*-hexane); bottom, **14b** (dichloromethane).

Table 2. Fluorescence Lifetimes and Fluorescence Quantum Yields of Compounds **1**–**3**, **12b**/**13b**, **14b**, **15** in *n*-Hexane Solution at Temperatures of 295 K and 180 K, Respectively

	τ^{295} [ps]	τ^{180} [ps]	ϕ^{295} [%]^{a}	ϕ^{180} [%]^{a}
15	11200	11600	11	13
3a	4700	5000	9	11
1a	4400	4500	9	12
3b	3800	4000	8	10
1b	3600	3700	9	12
12b/13b^{b}			7^{c}	12^{c}
14b			6^{c}	11^{c}
2a^{d}	<10/900	27/950	0.6/9.4	1/13
2b^{d}	10/650	40/670	0.3/5.2	1/9

[a] Experimental errors ±1–2%. [b] The ratio of the isomers **12b**/**13b** is 70:30. [c] In dichloromethane; for **1b** there is no difference in ϕ for the solvents *n*-hexane and dichloromethane. [d] **2a** and **2b** show dual fluorescence. The first value corresponds to the instantaneously appearing normal emission, the second to the red-shifted emission of the relaxed molecules.

The energy transfer systems **1a,b** show, within the experimental errors, at 295 and 180 K the same fluorescence quantum yield of about 10% as **15**. The increasing number of anthrylterthiophene substituents in compounds **12b**/**13b** and **14b** causes a decrease of the quantum yield at 295 K. At 180 K, however, the quantum yields are not dependent on the number of substituents.

In Figure 5 the time-resolved fluorescence spectra and fluorescence decays of **1b** and **2b** are shown.

In the upper part, the fluorescence spectra of **2b** measured in two different time intervals (early: 0–50 ps, late: 300–7000 ps) after ps-laser pulse excitation at 366 nm are plotted. The measurements reveal two differing spectral components. This dual fluorescence after photoexcitation is explained by a conformational change in the excited state.[17] Whereas the ground-state molecules exist in an orthogonal conformation of the two chromophores anthracene and terthiophene, the red-shifted and late emission is attributed to a more planarized conformation of the molecule in the excited state. The dynamic of this dual fluorescence is quantified by evaluating the decay curves of the two spectral components. The relaxed state is populated with the same time constant (rise time 40 ps) as that of the precursor decay (35 ps). Further experimental details on the behavior of anthryloligothiophenes in the excited state are given in the literature.[17]

In the lower part of Figure 5 the time-resolved fluorescence spectrum of **1b**, measured in the time interval 0–5000 ps at 180 K, is shown (excitation 366 nm). This spectrum is independent of the chosen time interval and similar to the stationary spectrum of this compound at 295 K (see Figure 4). At short times the fluorescence transient (see inset of Figure 5) reveals an increase of the fluorescence which is faster than the response time of the apparatus (<10 ps). The decay is monoexponential with a time constant of 3700 ps. In accord with the stationary spectra no emission in the spectral region above 600 nm could be detected which would be typical for anthracene or anthrylterthiophene. An upper limit for the quantum yield of some residual fast emission, not detectable by the very sensitive measurements at short time intervals in the spectral range between 370 and 600 nm, is 10^{-4}%.

Discussion

Localization of Electronic States. The absorption spectra of all compounds investigated in this work reveal that linking

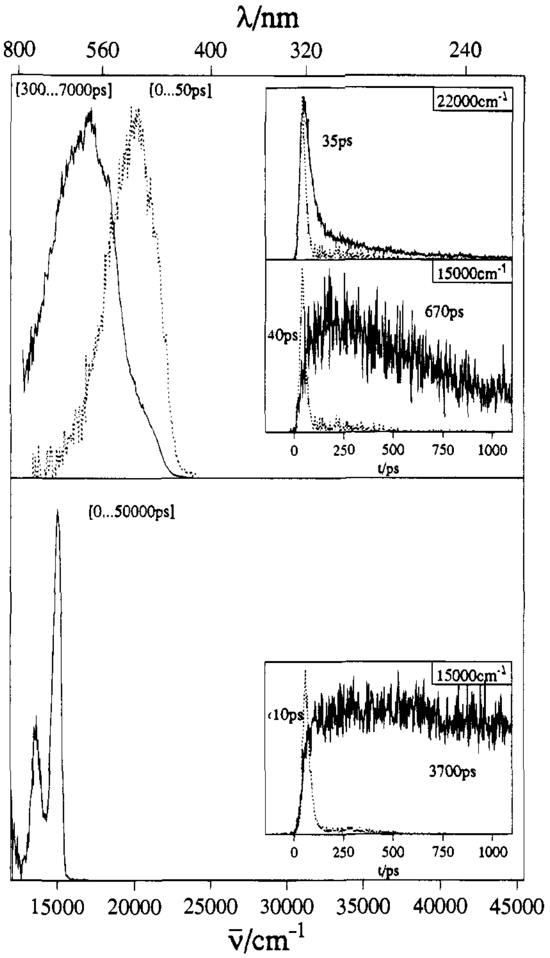

Figure 5. Time resolved fluorescence spectra detected in different time intervals after picosecond pulse excitation and fluorescence transients (insets) of **2b** (top) and **1b** (bottom) in *n*-hexane at $T = 180$ K. Top: time intervals between 0 and 50 ps (- -) and between 300 and 7000 ps (—). Insets: transients detected at 20 000 and 15 000 cm^{-1} and respective time constants. (- -) Pulse response of the apparatus. Bottom: time interval between 0 and 50 000 ps. Inset: detail of transient detected at 15 000 cm^{-1}. Rise time below 10 ps and decay time 3700 ps. (- -) Pulse response of the apparatus.

the molecular components at well-chosen positions does not significantly perturb the ground and the Franck–Condon-excited states of the individual chromophores. For similarly built-up anthryl-polyenyl-porphyrins it has been shown both experimentally[11,14] and theoretically[15] that changes in the electronic levels of the anthryl group are smallest if the conjugated polyene chain is linked to the 9-position of anthracene. This is mainly due to a steric hindrance of the subunits in this position which prevents their coplanar arrangement. The selective excitation of the anthryl donor can be referred to this sterical induced distorsion of the anthryl moiety against the conjugated π-system. The torsion angle for the 9-linkage of the anthryl group with the oligothiophene chain (72°) is larger than in anthrylpolyenes (56°) as has been demonstrated by crystallographic studies and AM1 calculations.[19c] As a result of the more twisted conformation the anthryl absorption bands are sharper and less red-shifted in the oligothiophene model compounds. Furthermore, there are no additional bands originating from electronic transitions between mixed molecular levels of the different partners as has been observed for anthrylpolyenes.[25]

The influence of distorsion is clearly demonstrated by comparison of the anthrylbithiophenes **2a** and **4**. In the sterically stronger hindered **2a** with anthryl linkage in 9-position, electronic coupling between the subunits is markedly weaker than in the far less hindered **4**. Therefore the extinction of the UV absorption band of the anthracene unit in **2a** is twice as high as in **4**.

The observed differences in the porphyrin absorption bands of compounds **1** and **3**, with respect to the porphyrin **15**, are very small concerning both line-broadening and energy shifts. In comparison with polyenyl compounds[11,14] a much better separation of the absorption bands of the conjugated oligothiophene chain and the porphyrin terminal group is achieved, too.

Altogether, the results of the absorption measurements demonstrate that different π-systems may be combined to form a supermolecule in such a way that they retain the identity of their electronic levels to a large extent.

From the extinction coefficients of **1** and **3** at 258 nm the selectivity of anthryl excitation (S_0–S_3) is estimated to be 88% for **1a** and 86% for **1b**. For **12/13** and **14** with two and three anthryloligothienyl subunits the selectivity of anthryl excitation is even higher.

From the emission spectra of **1**, **12/13**, and **14** it clearly follows that the emitting S_1-state is localized on the porphyrin terminal group. The slight red-shift and line-broadening of the porphyrin emission is explained by a reduced symmetry of the porphyrin and a weak coupling with the conjugated chain. Although no emission from the other subcomponents (anthracene and oligothiophene) are observable in these supermolecules, we conclude from this porphyrin emission that the segmental character found for the supermolecules in their ground-state is prevailed in the excited state. This behavior is in contrast to that of the two-component molecules **2** which show complex emission properties. It was found a distinct time-dependent change from an ultrafast "blue" anthracene-like emission to a delayed "red" emission component originating in the molecule as a whole. On the basis of temperature-dependent steady-state and time-resolved fluorescence measurements we assume an enlargement of the π–π interaction of the two molecular subunits anthracene and oligothiophene in the excited state by means of a partial planarization of the two chromophores.[17] It is important to point at the fast decay of the "blue" emission (and the corresponding rise time of the "red" emission) of about 10 ps at room temperature (**2a** and **2b**) and of 27 ps (**2a**) and 40 ps (**2b**) at 180 K, where the solvent exhibits a higher viscosity. At temperatures below 120 K (frozen solution), however, the torsional motion between the molecular subunits is frozen in, and only the "blue" anthracene-like emission is observable. With regard to the instantaneous appearance of the porphyrin emission (< 10 ps) for compounds **1** at temperatures between 4.2 and 295 K and for all excitation wavelengths such conformational changes do not seem to have a bearing on the intramolecular energy transfer from anthracene to porphyrin. Apparently the coupling of the two terminal groups anthracene and porphyrin is strong enough that the energy transfer can take place faster than any conformational changes.

Singlet–Singlet Energy Transfer. The lack of emission from subcomponents other than the porphyrin indicates that the energy transfer within the supermolecule from the anthracene to the porphyrin terminal substituent is very efficient in **1**,**12/13**, and **14**. On the basis of the perfect matching of absorption and excitation spectra we conclude that the energy transfer efficiency Q is at least 98% for all investigated anthryloligothienylporphyrins. Taking that value for Q into account together with the measured lifetime of the blue emission in the reference

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molecules **2a** and **2b** (Table 2) the rates k_{ET} for the intramolecular energy transfer can be calculated according to eq 1

$$k_{ET} = \frac{1}{\tau_1} = \frac{Q}{1-Q} \cdot \frac{1}{\tau_b} \qquad (1)$$

The calculated values for k_{ET} lead to energy transfer times $\tau_{ET} = 1/k_{ET}$ in **1a** and in **1b** of about 100 and 500 fs, respectively, in *n*-hexane at $T = 295$ K (500 fs and 800 fs at $T = 180$ K). These estimated values for the energy transfer time are in accordance with the experimental finding for the rise time of the porphyrin fluorescence to be much faster than 10 ps (the detection limit of the apparatus).

It is also an important feature of these model compounds that the absorption and excitation spectra match perfectly in the whole spectral range between 200 and 800 nm. Therefore singlet–singlet energy transfer is the only important quenching process for excited anthracene and oligothiophene. Other relaxation pathways like rapid internal conversion on the conjugated chain that have been observed in porphyrin-polyene systems after excitation of the polyene moiety[2,5,11,14] have not been found for these oligothiophene compounds.

Further on an important difference between oligothiophenes and polyenes attached to porphyrins is found for the quenching of the porphyrin emission by the conjugated chain molecule. While polyenes cause significant quenching of the porphyrin emission, the fluorescence quantum yields of both oligothienylporphyrins and anthryloligothienylporphyrins are the same at 295 and 180 K (and equal to the porphyrin **15** itself). For anthrylpolyenylporphyrins we have previously reported a substantial decrease in porphyrin fluorescence quantum yields when an anthrylpolyenyl group was attached.[11,14] This decrease is depending on the chain length of the polyene. The fluorescence quantum yields vary from 3.5% for a polyene bridge with three double bonds to 1.5% for one with five double bonds and about 0.1% for one with nine double bonds.[11a,14b,26] Similar results by Gust and Moore on polyene-porphyrin dyads[2] reflect the existence of additional quenching pathways by the polyene which obviously are absent in oligothiophenes. For carotenoid-porphyrin dyads Osuka and co-workers have shown that a reversible energy transfer may occur between porphyrin and carotenoid polyenes which, in combination with a very rapid internal conversion of excitation energy on the carotenoid part, is responsible for the quenching of the porphyrin emission.[5] It seems probable that this rapid internal conversion on polyenes also accounts for the reduced energy transfer efficiency from excited (carotenoid) polyenes to porphyrins. This view is confirmed by a comparison of the lifetimes (at 295 K) of excited bithiophene (100 ps),[17] terthiophene (150 ps),[17] and carotenoid polyenes (ca. 10 ps).[5b] Accordingly the fluorescence quantum yields of oligothiophenes are high, e.g., 1.0% for bithiophene and 5.6% for terthiophene,[17] whereas fluorescence quantum yields of polyenes containing more than five double bonds are unmeasurable low ($<10^{-4}$%).[5,25,26]

The results presented here show clearly that oligothiophenes are by far better suited conjugated chain molecules with regard to an energy transfer without loss of excitation energy as is desirable for an application in molecular electronics.

The fluorescence quantum yields and the high transfer efficiencies of anthryloligothienylporphyrins also suggest that oligothiophene-based molecules substituted with appropriate chromophores may be useful as energy collectors in synthetic (solar) energy conversion schemes.[2] Actually it is observed that the anthryloligothiophene moiety functions as an efficient light-collecting antenna system, which substantially increases the absorption cross section in the UV-range of molecules like **14b** with respect to the unsubstituted porphyrin.

Mechanism of Energy Transfer. From the spectroscopic findings in emission and photoexcitation it is clear that the energy transfer from anthracene to porphyrin must be due to an intramolecular mechanism. Reabsorption or intermolecular transfer can be ruled out since the measured transfer efficiencies are independent on concentration. With regard to the perfect matching of the absorption and the excitation spectra also in the region of the anthryl S_1-absorption it is reasonable to assume that this state is involved in all energy transfer processes reported in this work.

The mechanism of intramolecular energy transfer is discussed in terms of Coulombic interactions (Förster), of exchange interactions (Dexter)[27] and intramolecular relaxation.

(a) Coulombic interactions operate via the electromagnetic field and therefore require no direct contact between the energy donor and the acceptor molecules. According to Förster's theory[28] an energy transfer via Coulombic interaction depends on the spectral overlap between the emission band of the donor and the absorption band of the acceptor and on the fluorescence quantum yield of the donor as well as on the distance and relative orientation between the donor and the acceptor dipoles. If the coupling between the subunits anthracene, oligothiophene and porphyrin is small enough, Förster's (weak coupling) theory should be valid and the Förster radii can be evaluated. The anthryl end group as the emitting donor leads to Förster radii of 50–70 Å. If the anthryl-oligothiophene subunit is considered as the emitting group, the Förster radii are 20–30 Å. The distances between the emitting donor and absorbing acceptor in compounds **1** are between 10 and 15 Å. Therefore the efficiency of a possible Förster energy transfer could approach 100%.

(b) The Dexter-mechanism[29] also might be considered to explain the energy transfer. Exchange interactions occur via special overlap of electronic orbitals and require direct contact between the interacting partners. Because of the small overlap of the wave functions, due to the large distance between donor and acceptor, a direct Dexter-transfer is less probable. However, a Dexter-transfer mediated by the oligothiophene excited states (via superexchange or through-bond interaction) could be possible.[30,31]

(c) The energy transfer could also occur via unidirectional intramolecular energy relaxation.[15,32] The red shift in the absorption spectra indicates a certain coupling between anthracene and oligothiophene and between oligothiophene and porphyrin. Thus, due to electronic-vibronic coupling, energy can be transferred from the anthracene end group to the porphyrin end group.

Each of the mechanisms discussed is sufficient to explain the intramolecular energy transfer in compounds **1**. From the experimental results a clear distinction cannot be made.

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Conclusion

The present studies have proved an efficient energy transfer close to 100% in a given direction from an excited anthracene donor to an emitting porphyrin acceptor via the conjugated oligothiophene chain. In contrast to previously studied polyene chains, oligothiophenes combine the properties of interest for an application in photonic systems: high transfer efficiencies without radiationless deactivation of the excitation energy by the conjugated chain, no quenching of the acceptor emission, and a high thermal and photochemical stability.

As an important outcome of these investigations, the individual molecular subunits—although directly attached to each other—maintain their spectroscopic identity in the given architecture. The 9-anthryl donor may be addressed with high selectivity and therefore represents an excellent UV-"antenna" in conjugated energy transfer systems.

The singlet–singlet energy transfer is discussed in terms of several possible mechanisms (Förster/Dexter, superexchange, and intramolecular relaxation) which cannot be differentiated experimentally. Current investigations are focussed on the incorporation of other molecular species into the oligothiophene chain which are suited to interrupt and to switch the energy transfer between the terminal chromophores.

Experimental Section

General Methods. Melting points were determined on a Büchi SMP-20 apparatus with a silicon bath and are uncorrected. The melting behavior of the porphyrins is characterized by softening beginning ca. 10–40 °C below the given melting points. ^{1}H NMR spectra were recorded on a Bruker ACF 250 MHz spectrometer in $CDCl_3$ as solvent and are reported in ppm downfield from TMS. High resolution mass spectra were obtained with a Varian MAT 711 electron impact spectrometer at 70 eV by using the peak-matching method. Mass spectral analyses of high molecular weight compounds (> 1000 mass units) were performed in the fast-atom bombardment (FAB) mode on a Finnigan MAT 95 spectrometer (20 kV caesium, NBA matrix). The porphyrin parent molecular ion ($[M + H]^+$ or $M^{\bullet +}$) invariably formed the most intense peak. High performance liquid chromatography (HPLC) was performed on a Waters 600 E System employing a Waters 991 Photodiode Array Detector. A Macherey and Nagel Nucleosil 5-NO_2, 200/8/4 mm analytical column was used with *n*-hexane/dichloromethane mixtures as eluent. Medium pressure liquid chromatography (MPLC) was performed at 6–20 bar pressure using glass columns of different size, packed with Nucleosil 1525-NO_2, grain size 0.015–0.025 mm (Macherey and Nagel).

Optical Measurements. Optical spectra were measured in the indicated solvents at concentrations of 10^{-5} to 10^{-6} mol/L 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 avoid oxygen. The cw-fluorescence and fluorescence excitation spectra were performed using standard techniques: 450 W Xenon lamp and two 0.25 monochromators as excitation source (bandwidth 2 nm FWHM), 1 m double monochromator (bandwidth 1 nm FWHM), and cooled photomultiplier with photon counting as detection set-up.

The time-resolved emission spectra were recorded using time correlated single photon counting after ps laser excitation at 27 300 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 set-ups. Fluorescence quantum yields were measured relative to anthracene in *n*-hexane ($\Phi_f = 0.30$ at 295 K[34]).

Syntheses. 2-(9-Anthryl)-5-iodothiophene (7a). At −70 °C under argon *n*-BuLi in *n*-hexane (1.6 N, 31 mL, 50 mmol) was added to a stirred solution of **6a** (16.9 g, 50 mmol) in diethyl ether (120 mL). After stirring for 30 min anthrone (**5**) (7.84 g, 40 mmol) was added portionwise. The mixture was stirred for 3 h at −70 °C, then allowed to warm up to room temperature (16 h), poured into ice-cold 0.5 N HCl, and extracted with diethyl ether. The combined extracts were neutralized with aqueous sodium bicarbonate and dried (Na_2SO_4). The solvent was evaporated, and the solid residue was dissolved in hot methanol. With vigorous stirring 5 N HCl (5–10 mL) was added dropwise until elimination was complete (DC control). On cooling to 0 °C the product precipitated and was chromatographed on silica gel with *n*-hexane/toluene and recrystallized from *n*-hexane/toluene (9:1) to give 11.9 g (77%) **7a** as a yellow solid: mp 161–162 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ(thiophene) 6.89 (1 H, d, $^3J_{3,4} = 3.6$ Hz, H3), 7.46 (1 H, d, $^3J_{4,3} = 3.7$ Hz, H4), δ(anthracene) 7.47 (4 H, m, H2,3,6,7), 7.91 (2 H, m, H1,8), 8.04 (2 H, m, H4,5), 8.55 (1 H, bs, H10). Anal. Calcd for $C_{18}H_{11}IS$: C, 55.97; H, 2.87; I, 32.86; S, 8.30. Found: C, 56.16; H, 2.93; I, 32.73; S, 8.11.

2-(9-Anthryl)-5-bromothiophene (**7b**) was prepared as described for **7a** from 2,5-dibromothiophene (**6b**) (1.21 g, 5 mmol) and **5** (0.70 g, 3.5 mmol): yield 0.78 g (66%); mp 128 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ(thiophene) 6.94 (1 H, d, $^3J_{3,4} = 3.7$ Hz, H3), 7.25 (1 H, d, $^3J_{4,3} = 3.7$ Hz, H4), δ(anthracene) 7.46 (4 H, m, H2,3,6,7), 7.90 (2 H, m, H1,8), 8.03 (2 H, m, H4,5), 8.53 (1 H, bs, H10). Anal. Calcd for $C_{18}H_{11}BrS$: C, 63.73; H, 3.27; Br, 23.55; S, 9.45. Found: C, 63.98; H, 3.32; Br, 23.34; S, 9.19.

5-(9-Anthryl)-2,2′-bithiophene (**2a**) was prepared as described above for **7a** from **19** (1.23 g, 5 mmol) and **5** (0.78 g, 4 mmol) to give 0.80 g (58%) **2a** as a bright yellow solid: mp 162–163 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ(bithiophene) 7.05 (1 H, dd, $^3J_{4',3'} = 3.8$ Hz, $^3J_{4',5'} = 5.0$ Hz, H4′), 7.08 (1 H, d, $^3J_{4,3} = 3.6$ Hz, H4), 7.25 (2 H, m, H3′,5′), 7.37 (1 H, d, $^3J_{3,4} = 3.6$ Hz, H3), δ(anthracene) 7.46 (4 H, m, H2,3,6,7), 7.99 (2 H, m, H1,8), 8.02 (2 H, m, H4,5), 8.53 (1 H, bs, H10). Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.16; H, 4.12; S, 18.72. Found: C, 76.84; H, 4.11; S, 18.63.

5-(9-Anthryl)-2,2′:5′,2″-terthiophene (**2b**). To **19** (0.5 g, 2 mmol) and Mg (0.08 g, 3.2 mmol) in diethyl ether/tetrahydrofuran (1:1, 20 mL) in a 50-mL flame-dried apparatus under argon 1,2-dibromoethane (0.19 g, 1 mmol) was slowly added to entrain the Grignard reaction, and the reaction mixture was heated to reflux for 30 min. The Grignard solution was transferred to the dropping funnel of a second apparatus and was dropped to a solution of **7b** (0.51 g, 1.5 mmol) and $NiCl_2$-dppp[35] (8 mg, 0.015 mmol) in diethyl ether (10 mL). The mixture was stirred at reflux for 15 h, hydrolyzed with cold 0.5 N HCl, and extracted several times with diethyl ether. The combined extracts were washed with 1 N sodium bicarbonate and water, dried (Na_2SO_4), and concentrated. Chromatography on silica gel afforded a mixture of **2b** and 2,2′:5′,2″:5″,2‴-quaterthiophene, which were separated by MPLC (Nucleosil 1525-NO_2, 90:10 *n*-hexane/dichloromethane). After recrystallization from *n*-hexane pure **2b** was obtained as a yellow solid: yield 0.31 g (48%); mp 199–200 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ(terthiophene) 7.05 (1 H, dd, $^3J_{4'',3''} = 3.7$, $^3J_{4'',5''} = 5.1$ Hz, H4″), 7.09 (1 H, d, $^3J_{4,3} = 3.6$ Hz, H4), 7.14 (2 H, AB, $^3J_{3',4'} = 3.8$ Hz, H3′,4′), 7.22 (1 H, dd, $^3J_{3'',4''} = 3.7$, $^4J_{3'',5''} = 1.2$ Hz, H3″), 7.24 (1 H, dd, $^3J_{5'',4''} = 5.2$, $^4J_{5'',3''} = 1.2$ Hz, H5″), 7.37 (1 H, d, $^3J_{3,4} = 3.6$ Hz, H3), δ(anthracene) 7.47 (4 H, m, H2,3,6,7), 7.99 (2 H, m, H1,8), 8.05 (2 H, m, H4,5), 8.54 (1 H, bs, H10). Anal. Calcd for $C_{26}H_{16}S_3$: C, 73.55; H, 3.80; S, 22.65. Found: C, 73.65; H, 3.75; S, 22.86.

5-(2-Anthryl)-2,2′-bithiophene (**4**) was prepared as described for **2b** from **19** (1.44 g, 5.87 mmol), Mg (0.18 g, 7.4 mmol) in diethyl ether (30 mL), 1,2-dibromoethane (0.1 g, 0.53 mmol) at reflux for 3 h.

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The Grignard solution was diluted with diethyl ether/benzene (1:1, 40 mL), transferred to the dropping funnel of a second apparatus, and dropped to a suspension of 2-chloroanthracene (1.0 g, 4.7 mmol) and NiCl$_2$dppp (25.5 mg, 0.047 mmol) in diethyl ether/benzene (2.5:4, 65 mL). The mixture was stirred at reflux for 45 h, hydrolyzed with ice-cold 0.5 N HCl (200 mL) and extracted several times with diethyl ether. The combined extracts were concentrated and resolved in dichloromethane (250 mL). The suspension was washed with 1 N sodium bicarbonate and water and concentrated to 25 mL. The resulting green solid was filtered off, dried over P$_2$O$_5$ and recrystallized twice from toluene to give 1.01 g (63%) **4** as yellow green crystals: mp 259−260 °C; UV (*n*-hexane) λ_{max} 240(ϵ 46), 257(56), 335(39), 347(38), 386(20), 405(18); ^{1}H NMR (250 MHz, CDCl$_3$) δ(bithiophene) 7.06 (1 H, dd, $^3J_{4',5'}$ = 4.9, $^3J_{4',3'}$ = 3.7 Hz, H4′), 7.22 (1 H, d, $^3J_{4,3}$ = 3.8 Hz, H4), 7.24−7.26 (2 H, m, H3′,5′), 7.41 (1 H, d, H3), δ(anthracene) 7.45−7.49 (2 H, m, H6,7), 7.74 (1 H, dd, J = 1.8, J = 8.9 Hz, H3), 7.98−8.04 (3 H, m, H4,5,8), 8.19 (1 H, s, H1), 8.39 and 8.43 (2 H, s, H9,10). Anal. Calcd for C$_{22}$H$_{14}$S$_2$: C, 77.15; H, 4.12; S, 18.73. Found: C, 76.79; H, 4.02; S, 18.56.

5-(9-Anthryl)-5′-formyl-2,2′-bithiophene (9a). Under argon *n*-BuLi in *n*-hexane (1.6 N, 9.4 mL, 15 mmol) was added to a solution of 2-dimethoxymethylthiophene (**8a**)[36] (2.37 g, 15 mmol) in THF (30 mL). After stirring for 20 min at room temperature, the mixture was cooled to 0 °C, and ZnCl$_2$ (2.04 g, 15 mmol) in THF (30 mL) was slowly added. In a second flask equipped with dropping funnel and argon inlet the Pd catalyst was prepared from PdCl$_2$(PPh$_3$)$_2$[37] (180 mg, 0.25 mmol) in THF (20 mL) and diisobutylaluminium hydride (DIBAL) in *n*-hexane (1.0 N, 0.5 mL, 0.5 mmol), and **7a** in THF was added. The zinc-metalated **8a** was transferred to the dropping funnel *via* cannula and dropped to the reaction mixture. After stirring for 4 h at room temperature the solution was poured into 3 N HCl (50 mL). This mixture was stirred for 1 h and then extracted several times with diethyl ether. The extract was washed with water and aqueous sodium bicarbonate and dried (Na$_2$SO$_4$). The solvent was evaporated, and the remaining residue was chromatographed on silica gel with dichloromethane to give after recrystallization from *n*-hexane/toluene 0.74 g (24%) **10**, 1.87 g (42%) **9a**, and 0.32 g (19%) **11a**.

9a: mp 207−208 °C; ^{1}H NMR (250 MHz, CDCl$_3$) δ(bithiophene) 7.13 (1 H, d, $^3J_{4,3}$ = 3.7 Hz, H4), 7.28 (1 H, d, $^3J_{3',4'}$ = 3.9 Hz, H3′), 7.54 Hz (1 H, d, $^3J_{3,4}$ = 3.7 Hz, H3), 7.67 (1 H, d, $^3J_{4',3'}$ = 3.9 Hz, H4′), δ(anthracene) 7.46 (4 H, m, H2,3,6,7), 7.92 (2 H, m, H1,8), 8.03 (2 H, m, H4,5), 8.54 (1 H, bs, H10), 9.87 (1 H, s, CHO). Anal. Calcd for C$_{23}$H$_{14}$OS$_2$: C, 74.57; H, 3.81; S, 17.31. Found: C, 74.81; H, 3.91; S, 17.46;

5,5′-Di-(9-anthryl)-2,2′-bithiophene (10): mp > 300 °C; ^{1}H NMR (250 MHz, CDCl$_3$) δ(bithiophene) 7.14 (2 H, d, $^3J_{4,3}$ = 3.6 Hz, H4,4′), 7.46 (2 H, d, $^3J_{3,4}$ = 3.6 Hz, H3,3′), δ(anthracene) 7,49 (8 H, m, H2,3,6,7), 8.05 (8 H, m, H1,4,5,8), 8.56 (2 H, bs, H10). Anal. Calcd for C$_{36}$H$_{22}$S$_2$: C, 83.36; H, 4.27; S, 12.36. Found: C, 83.23; H, 4.40; S, 12.16;

5,5′-Diformyl-2,2′-bithiophene (11a): mp 216 °C [lit.[38] mp 215−218 °C].

5-(9-Anthryl)-5″-formyl-2,2′:5′,2″-terthiophene (9b) was prepared as described above for **9a** from **8b**[36](1.20 g, 5 mmol) and **7a** (1.55 g, 4 mmol) to give 0.55 g (30%) **9b**: mp 228 °C; ^{1}H NMR (250 MHz, CDCl$_3$) δ(terthiophene) 7.12 (1 H, d, $^3J_{4,3}$ = 3.6 Hz, H4), 7.21 (1 H, d, $^3J_{3',4'}$ = 3.9 Hz, H3′), 7.28 (1 H, d, $^3J_{3'',4''}$ = 4.0 Hz, H3″), 7.33 (1 H, d, $^3J_{4',3'}$ = 3.9 Hz, H4′), 7.43 (1 H, d, $^3J_{3,4}$ = 3.6 Hz, H3), 7.70 (1 H, d, $^3J_{4'',3''}$ = 4.0 Hz, H4″), δ(anthracene) 7.48 (4 H, m, H2,3,6,7), 7.97 (2 H, m, H1,8), 8.06 (2 H, m, H4,5), 8.56 (1 H, bs, H10), 9.88 (1 H, s, CHO). Anal. Calcd for C$_{27}$H$_{16}$OS$_3$: C, 71.65; H, 3.56; S, 21.25. Found: C, 71.60; H, 3.65; S, 21.35.

Anthryl-Bithienyl-Porphyrins 1a, 12a, and 13a. Nitrogen was bubbled for 15 min through a solution of distilled pyrrole (0.40 g, 6 mmol), 1-hexanal (0.45 g, 4.5 mmol) and anthrylbithienylaldehyde **9a** (0.56 g, 1.5 mmol) in CH$_2$Cl$_2$ (650 mL) in a 1 L three-necked round-bottomed flask with reflux condenser and nitrogen inlet, which was shielded from ambient lighting, and then trifluoroacetic acid (0.7 g, 6 mmol) was added *via* syringe. After stirring at room temperature for 2 h the oxidation was initiated by the addition of *p*-chloranil (1.11 g, 4.5 mmol), and the solution was refluxed for 1 h. After cooling to room temperature anhydrous K$_2$CO$_3$ (20 g) was added, and the mixture was stirred for 2 h. The solution was filtered and concentrated to about 50 mL. Silica gel was added, the remaining solvent was removed in vacuo, and the resulting powder was added on a silica gel column poured with CH$_2$Cl$_2$. Elution with CH$_2$Cl$_2$ and combination of all high R_f material afforded 0.25 g of the porphyrins **1a**, **15**, **12a**, **13a**, and **14a**, which were separated by MPLC on Nucleosil 1525 NO$_2$ with *n*-hexane/CH$_2$Cl$_2$ (gradient from 85:15 to 80:20) to give 75 mg (8.3%) of pure **15**, 120 mg (9.3%) of pure **1a**, and 25 mg (1.5%) of a mixture of the isomers **12a/13a**. Each product fraction was crystallized from acetone/methanol.

5-[5′-(9-Anthryl)-2,2′-bithienyl-5-yl]-10,15,20-tripentylporphyrin (1a): violet solid, mp 229−230 °C; MS(FAB) *m/z* 861.4 [M + 1]$^+$. Anal. Calcd for C$_{57}$H$_{56}$N$_4$S$_2$: C, 79.49; H, 6.55; N, 6.51; S, 7.45. Found: C, 79.14; H, 6.63; N, 6.33; S, 7.36.

5,10,15,20-Tetrapentylporphyrin (15):[21] violet solid (HPLC purity 99.9%), mp 128 °C; HRMS(EI) *m/z* calcd for C$_{40}$H$_{54}$N$_4$ 590.4348, found 590.4346.

5,10-Bis-[5′-(9-anthryl)-2,2′-bithienyl-5-yl]-15,20-dipentylporphyrin (12a) and 5,15-bis-[5′-(9-anthryl)-2,2′-bithienyl-5-yl]-10,20-dipentylporphyrin (13a): **12a/13a** (94:6); black solid, MS(FAB) *m/z* 1131.3 [M + 1]$^+$.

UV/vis absorption and ^{1}H NMR data of porphyrins **1a**,**15** and **12a/13a** are listed in Tables 1 and 4.

Anthrylterthienyl-pentyl-porphyrins 1b, 12b, 13b, and 14b were prepared as described above from pyrrole (0.27 g, 4 mmol), 1-hexanal (0.30 g, 3 mmol), anthrylterthienylaldehyde **9b** (0.45 g, 1 mmol), trifluoroacetic acid (0.45 g, 4 mmol), and *p*-chloranil (0.74 g, 3 mmol) in CH$_2$Cl$_2$ (500 mL). The porphyrin mixture (0.40 g) was purified by MPLC on Nucleosil 1525 NO$_2$ with *n*-hexane/CH$_2$Cl$_2$ (gradient from 82:18 to 70:30) to yield 38 mg (6.4%) of pure **15**, 93 mg (9.9%) of pure **1b**, and 32 mg (2.5%) of the isomers **12b/13b** as well as 7 mg (0.4%) of pure **14b**. **1b** was crystallized from acetone/methanol; **12b/13b** and **14b** were crystallized from acetone.

5-[5″-(9-Anthryl)-2,2′:5′,2″-terthienyl-5-yl]-10,15,20-tripentylporphyrin (1b): red solid (HPLC purity >99%), mp 196−198 °C; HRMS(EI) *m/z* calcd for C$_{61}$H$_{58}$N$_4$S$_3$ 942.3824, found 942.3835.

5,10-Bis-[5″-(9-anthryl)-2,2′:5′,2″-terthienyl-5-yl]-15,20-dipentylporphyrin (12b) and 5,15-bis-[5″-(9-anthryl)-2,2′:5′,2″-terthienyl-5-yl]-10,20-dipentylporphyrin (13b): **12b/13b** (70:30), MS(FAB) *m/z* 1295.3 [M + 1]$^+$.

5,10,15-Tris-[5″-(9-anthryl)-2,2′:5′,2″-terthienyl-5-yl]-20-pentylporphyrin (14b): MS(FAB) *m/z* 1647.3 [M + 1]$^+$.

UV/vis absorption and ^{1}H NMR data of porphyrins **1b**, **12b**, **13b**, and **14b** are listed in Tables 1 and 4.

Bithienyl-pentyl-porphyrins 3a, 17a, and 18a were prepared as described above from pyrrole (1.01 g, 15 mmol), 1-hexanal (1.13 g, 11.25 mmol), formylbithiophene **16a** (0.73 g, 3.75 mmol), trifluoroacetic acid (1.7 g, 15 mmol), and *p*-chloranil (2.78 g, 11.25 mmol) in CH$_2$Cl$_2$ (1.5 L). The porphyrin mixture was purified by MPLC on Nucleosil 1525 NO$_2$ with *n*-hexane/CH$_2$Cl$_2$ (88:12) as eluent to give 100 mg (4.5%) of pure **15**, 130 mg (5.1%) of pure **3a**, and 65 mg (2.2%) of the isomers **17a/18a**, which could partly be separated in pure **17a** and pure **18a**. Crystallization of each fraction was performed from acetone/methanol.

5-(2,2′-Bithienyl-5-yl)-10,15,20-tripentylporphyrin (3a): violet solid, mp 84−85 °C. Anal. Calcd for C$_{43}$H$_{48}$N$_4$S$_2$: C, 75.40; H, 7.06; N, 8.18; S, 9.36. Found: C, 75.32; H, 7.06; N, 8.04; S, 9.40.

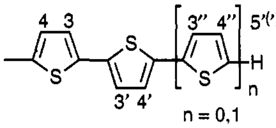
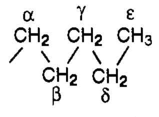
5,10-Di-(2,2′-bithienyl-5-yl)-15,20-dipentylporphyrin (17a): violet solid (HPLC purity 95%), mp 110−115 °C; HRMS(EI) *m/z* calcd for C$_{46}$H$_{42}$N$_4$S$_4$ 778.2292, found 778.2287.

5,15-Di-(2,2′-bithienyl-5-yl)-10,20-dipentylporphyrin (18a): violet solid (HPLC purity >99%), mp 219−221 °C; HRMS(EI) *m/z* calcd for C$_{46}$H$_{42}$N$_4$S$_4$ 778.2292, found 778.2296.

UV/vis absorption and ^{1}H NMR data of porphyrins **3a**,**17a**, and **18a** are listed in Tables 1 and 3.

Terthienyl-pentyl-porphyrins 3b, 17b, and 18b were prepared as described above from pyrrole (0.402 g, 6 mmol), 1-hexanal (0.450 g, 4.5 mmol), formylterthiophene **16b** (0.414 g, 1.5 mmol), trifluoroacetic acid (0.7 g, 6 mmol), and *p*-chloranil (1.11 g, 4.5 mmol) in CH$_2$Cl$_2$

Table 3. ^{1}H NMR Data of Oligothienylporphyrins **3**, **17**, and **18** and Compound **15** in $CDCl_3$ at 250 MHz[a]

						
compd	porphyrin[b]	H4[c] H3	H3′[c] H4′	H3″[c] H4″	H5′(′)[c]	Hα,β,γ,δ,ε[d]
15	9.46 (8 H), −2.65 (2 H, NH)					4.92 (8 H), 2.52 (8 H), 1.79 (8 H), 1.54 (8 H), 0.98 (12 H)
3a	9.47[e] (4 H, H12,13,17,18), 9.39 (2 H, H2,8), 9.13 (2 H, H3,7), −2.61 (2 H, NH)	7.74 (1 H) 7.56 (1 H)	7.41 (1 H) 7.14 (1 H)		7.34 (1 H)	4.92 (6 H), 2.50 (6 H), 1.77 (6 H), 1.55 (6 H), 0.97 (9 H)
17a	9.44 (2 H, H17,18), 9.40 (2 H, H2,13), 9.15 (2 H, H3,12), 9.08 (2 H, H7,8), −2.61 (2 H, NH)	7.74 (2 H) 7.55 (2 H)	7.40 (2 H) 7.12 (2 H)		7.33 (2 H)	4.88 (4 H), 2.50 (4 H), 1.77 (4 H), 1.55 (4 H), 0.98 (6 H)
18a	9.38 (4 H, H2,8,12,18), 9.18 (4 H, H3,7,13,17), −2.64 (2 H, NH)	7.77 (2 H) 7.57 (2 H)	7.41 (2 H) 7.13 (2 H)		7.34 (2 H)	4.86 (4 H), 2.48 (4 H), 1.73 (4 H), 1.49 (4 H), 0.95 (6 H)
3b[f]	9.45[e] (4 H, H12,13,17,18), 9.36 (2 H, H2,8), 9.07 (2 H, H3,7), −2.77 (2 H, NH)	7.70 (1 H) 7.52 (1 H)	7.26 (1 H) 7.14 (1 H)	7.22 (1 H) 7.01 (1 H)	7.22 (1 H)	4.86 (6 H), 2.44 (6 H), 1.74 (6 H), 1.49 (6 H), 0.91 (9 H)
17b	9.51 (2 H, H17,18), 9.45 (2 H, H2,13), 9.17 (2 H, H3,12), 9.09 (2 H, H7,8), −2.55 (2 H, NH)	7.76 (2 H) 7.56 (2 H)	7.31 (2 H) 7.19 (2 H)	7.27 (2 H) 7.07 (2 H)	7.27 (2 H)	4.95 (4 H), 2.54 (4 H), 1.80 (4 H), 1.57 (4 H), 0.99 (6 H)
18b	9.44 (4 H, H2,8,12,18), 9.21 (4 H, H3,7,13,17), −2.60 (2 H, NH)	7.80 (2 H) 7.59 (2 H)	7.34 (2 H) 7.22 (2 H)	7.28 (2 H) 7.09 (2 H)	7.28 (2 H)	4.95 (4 H), 2.52 (4 H), 1.77 (4 H), 1.55 (4 H), 0.96 (6 H)

[a] Chemical shift values (δ) observed in ppm relative to TMS as internal standard. [b] Coupling constants between pyrrole β-H: $^3J = 4.9$ Hz. [c] Coupling constants $^3J_{3,4} = {}^3J_{3',4'} = {}^3J_{3'',4''} = 3.5-3.8$ Hz, $^3J_{4''('),5''(')} = 4.9-5.2$ Hz, $^3J_{3''('),5''(')} = 0.9-1.1$ Hz. [d] Coupling constants: $^3J = 7.2-8.0$ Hz. [e] AB system. [f] CD_2Cl_2, solvent.

Table 4. ^{1}H NMR Data of Anthryloligothienylporphyrins **1** and **12−14** in $CDCl_3$ at 250 MHz[a]

		oligothiophene[c]			anthracene		
compd	porphyrin[b]	H4 H3	H3′ H4′	H3″ H4″	H1,4,5,8 H2,3,6,7	H10	pentyl[d] Hα,β,γ,δ,ε
1a	9.47[e] (4 H, H12,13,17,18), 9.41 (2 H, H2,8), 9.17 (2 H, H3,7), −2.57 (2 H, NH)	7.78 (1 H) 7.63 (1 H)	7.60 (1 H) 7.20 (1 H)		8.10 (4 H) 7.52 (4 H)	8.56 (1 H)	4.93 (6 H), 2.53 (6 H), 1.78 (6 H), 1.54 (6 H), 0.99 (9 H)
12a	9.47 (2 H, H17,18), 9.44 (2 H, H2,13), 9.21 (2 H, H3,12), 9.15 (2 H, H7,8), −2.54 (2 H, NH)	7.79 (2 H) 7.63 (2 H)	7.60 (2 H) 7.20 (2 H)		8.09 (8 H) 7.51 (8 H)	8.55 (2 H)	4.91 (4 H), 2.52 (4 H), 1.79 (4 H), 1.56 (4 H), 0.99 (6 H)
13a	9.43 (4 H, H2,8,12,18), 9.21 (4 H, H3,7,13,17), −2.61 (2 H, NH)	7.81 (2 H) 7.63 (2 H)	7.59 (2 H) 7.18 (2 H)		8.09 (8 H) 7.51 (8 H)	8.56 (2 H)	4.91 (4 H), 2.52 (4 H), 1.79 (4 H), 1.56 (4 H), 0.99 (6 H)
1b	9.50[e] (4 H, H12,13,17,18), 9.41 (2 H, H2,8), 9.16 (2 H, H3,7), −2.57 (2 H, NH)	7.78 (1 H) 7.60 (1 H)	7.35 (1 H) 7.27 (1 H)	7.47 (1 H) 7.15 (1 H)	8.05 (4 H) 7.49 (4 H)	8.56 (1 H)	4.95 (6 H), 2.53 (6 H), 1.80 (6 H), 1.56 (6 H), 0.99 (9 H)
12b	9.45 (2 H, H17,18), 9.41 (2 H, H2,13), 9.20 (2 H, H3,12), 9.15 (2 H, H7,8), −2.53 (2 H, NH)	7.77 (2 H) 7.58 (2 H)	7.30 (2 H) 7.22 (2 H)	7.47 (2 H) 7.16 (2 H)	8.07 (8 H) 7.49 (8 H)	8.55 (2 H)	4.87 (4 H), 2.50 (4 H), 1.78 (4 H), 1.55 (4 H), 1.00 (6 H)
13b	9.39 (4 H, H2,8,12,18), 9.22 (4 H, H3,7,13,17), −2.59 (2 H, NH)	7.80 (2 H) 7.60 (2 H)	7.32 (2 H) 7.24 (2 H)	7.47 (2 H) 7.17 (2 H)	8.07 (8 H) 7.49 (8 H)	8.55 (2 H)	4.87 (4 H), 2.50 (4 H), 1.78 (4 H), 1.55 (4 H), 1.00 (6 H)
14b	9.51 (2 H, H2,18), 9.28 (2 H, H3,17), 9.20 (4 H, H7,8,12,13), −2.51 (2 H, NH)	7.84[f] (3 H) 7.64[f] (3 H)	7.38[f] (3 H) 7.29 (3 H)	7.47 (3 H) 7.16 (3 H)	8.05 (12 H) 7.49 (12 H)	8.57 (3 H)	5.00 (2 H), 2.56 (2 H), 1.82 (2 H), 1.50 (2 H), 1.00 (3 H)

[a] Chemical shift values (δ) observed in ppm relative to TMS as internal standard. [b] Coupling constants between pyrrole β-H: $^3J = 4.9-5.0$ Hz. [c] Coupling constants $^3J_{3,4} = {}^3J_{3',4'} = {}^3J_{3'',4''} = 3.6-3.8$ Hz. [d] Coupling constants $^3J = 7.2-8.0$ Hz. [e] AB system. [f] Position of the center of two distinguishable doublets of doublets with an intensity relationship of 2:1.

(600 mL). After MPLC-chromatography on Nucleosil 1525 NO_2 with *n*-hexane/CH_2Cl_2 (gradient from 85:15 to 80:20) as eluent 18 mg (2.0%) of pure **15**, 40 mg (3.5%) of pure **3b**, and 32 mg (2.3%) of the isomers **17b** and **18b** (15 mg of pure **17b** and 8 mg of pure **18b**) were obtained. Crystallizations were performed from acetone/methanol.

5-(2,2′:5′,2″-Terthienyl-5-yl)-10,15,20-tripentylporphyrin (3b): red solid (HPLC purity >99.9%), mp 144−154 °C; HRMS(EI) *m/z* calcd for $C_{47}H_{50}N_4S_3$ 766.3198, found 766.3199.

5,10-Di-(2,2′:5′,2″-terthienyl-5-yl)-15,20-dipentylporphyrin (17b): red solid (HPLC purity >96%), mp 196−202 °C; HRMS(EI) *m/z* calcd for $C_{54}H_{46}N_4S_6$ 942.2047, found 942.2039.

5,15-Di-(2,2′:5′,2″-terthienyl-5-yl)-10,20-dipentylporphyrin (18b): red solid (HPLC purity >97%), HRMS(EI) *m/z* calcd for $C_{54}H_{46}N_4S_6$ 942.2047, found 942.2020.

UV/vis absorption and ^{1}H NMR data of porphyrins **3b**, **17b**, and **18b** are listed in Tables 1 and 3.

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