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Synthesis, Light Harvesting, and Energy Transfer Properties of a Zinc Porphyrin Linked Poly(phenyleneethynylene)

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ABSTRACT: The synthesis of a zinc porphyrin linked conjugated homopolymer is presented. The synthetic strategy employed a directional polymerization of 1-iodo-2,5-dioctyl-4′-ethynyltolane in the presence of [10,20-bis(3,5-bis-*tert*-butylphenyl]-5,15-diethynylporphinato]zinc(II) (**12**) or [10,20-bis(3,5-bis-*tert*-butylphenyl]-5,15-dibromoporphinato]zinc(II) (**10**). In the case of **12** the reaction was found to give a polymer product with a constant ratio of zinc porphyrin to incorporated monomer units regardless of the molecular weight. In the case of **10**, however, the ratio of zinc porphyrin to incorporated monomer units decreased with increasing molecular weight of the polymer product. The polymer products were separated into fractions using preparative SEC. Studies of the energy transfer properties from the polymer to the zinc porphyrin revealed that there was little energy transfer in solution but quantitative energy transfer in the solid state. The polymer products proved difficult to handle in terms of device construction where a thin polymer film is sandwiched between two electrodes. We found this to be a consequence of the palladium catalysis employed during the polymerization. We finally discuss the issues concerning the problems with remnants from the Pd catalyst in the polymer samples and their removal.

Introduction

Since the discovery in 1974 of doped polyacetylene showing electrical conductivity,[1] there has been a large interest in conjugated polymers and their application for e.g. light-emitting diodes,[2] polymer electronic circuits,[3] and polymer solar cells.[4]

Recently, the synthesis of a three-domain (JPJ) and a five-domain (PF_4) structure were reported.[5,6] The three-domain structure consisted of two homopolymer blocks (J domains) with a porphyrin dye molecule (P domain) in the middle. In this three-domain structure, the J domains were poly(2′,5′-dioctyl-4,4″-terphenylenecyanovinylene), and the distribution of the individual incorporated monomer units was a broad distribution. The P domain was a 5,10,15,20-tetraphenylporphyrin derivative, and there was only one porphyrin molecule in each JPJ unit. In contrast to JPJ the PF_4 consisted of four oligofluorene (F domains) linked to a porphyrin dye molecule (P domain). A very interesting property observed for these three-domain and five-domain structures was that both the J and the F domain served as a light-harvesting antenna for the P domain. We decided to investigate and evaluate the use of poly(phenyleneethynylene)s as the backbone of the light-harvesting polymer chains for the porphyrin dyes and have two alkyl groups on every second phenyl ring to obtain solubility[7] and reduce the distortion of the backbone.[8]

In this paper we present a synthesis of a conjugated homopolymer of the poly(phenyleneethynylene) type. We discuss two different synthetic strategies toward linking the conjugated homopolymer blocks via a zinc porphyrin to give the three-domain structure NPN, as shown in Figure 1.

We present studies of the optical properties of the compounds with a focus on the band gap, the quantum efficiency of the fluorescence, and the lifetimes. These studies were performed on the homopolymer, poly[(2,5-dioctyltolanyl)ethylene] (N_n), on the NPN structure with a broad distribution and on fractions with a narrow distribution prepared by preparative size exclusion chromatography (SEC). Finally, we discuss the problems concerning the use of Pd as a catalyst for the polymerization due to the catalyst remnants contained in the polymer product and provide a solution to this problem in the context of this work.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a 250 MHz Bruker NMR spectrometer at 300 K unless otherwise stated. All spectra were recorded in $CDCl_3$ with TMS as an internal reference. Compound **5**[9] and 1,4-dioctylbenzene[10] were prepared according to the procedures described in the literature. Compounds **9**−**12** were prepared according to the procedures reported by Plater et al.[11] with the exception that compound **11** was purified by preparative SEC before deprotection of the TMS groups. Detailed descriptions of synthetic procedures and analytical data for compounds **1**, **2**, **3**, **4**, **6**, **7**, and **8** can be found in the Supporting Information. Electroactive device preparation is described in detail in the Supporting Information.

Liquid Chromatography Methods. The apparatus for the SEC consists of a preparative system with a 3 mL injection loop. The detector is a UV−vis diode array with a spectral resolution of 1 nm. A 16-port switch valve allows for separation into fractions. Two different column systems were used. They consisted of DVB linked polystyrene gel columns comprising a guard column and two gel columns. One system had a 100 Å and a 1000 Å column in succession, and the other had a 500 Å and a 10000 Å column in succession. The eluent was chloroform, and the flow rate was 20 mL/min with a pressure of 75 bar. The molecular weight was calculated on the basis of polystyrene standards having molecular weights of 515 000, 127 000, 68 000, 36 300, 19 000, 10 900, 3250, and 1360. In all cases the polydispersity of the standards was smaller than 1.007.

Photophysical Methods. The UV−vis solution spectra were recorded in dry $CHCl_3$ degassed with argon. Emission spectra and lifetimes were recorded in degassed $CHCl_3$. The absorption maximum was kept below 0.07. All emission spectra are corrected. Quantum yields where measured rela-

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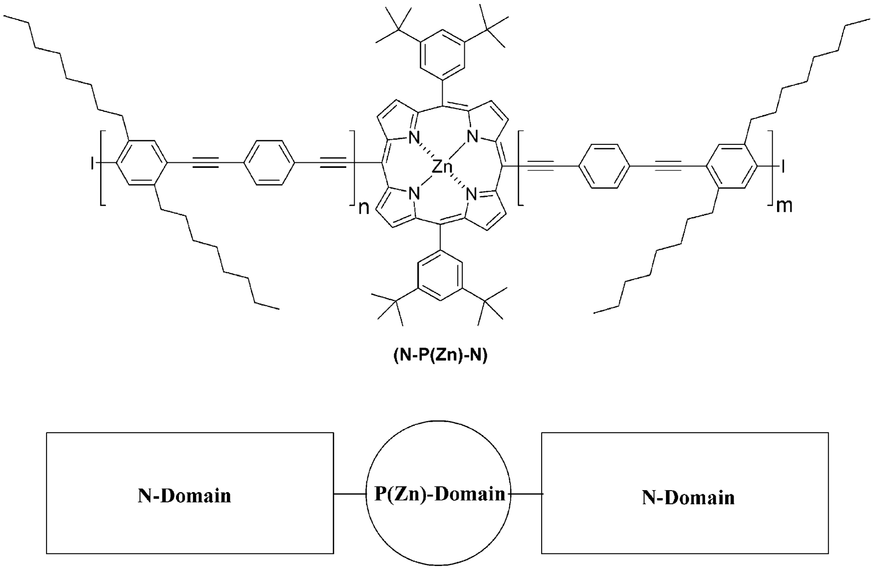


Figure 1. Three-domain structure of the NPN dye linked homopolymer.

tive to DPA.[12] The UV−vis solid-state spectra were recorded on spin-coated films of the polymers.

Poly[(2,5-dioctyltolanyl)ethynylene] (N_n). A 250 mL round-bottom flask was dried using a heat gun and flushed with argon. Compound **8** (1.36 mmol, 0.750 g) was placed in the flask and dissolved in 40 mL of piperidine. The solution was flushed with argon for 30 min before the catalyst Pd(PPh_3)$_4$ (30 mg, ≈2 mol %) and the cocatalyst CuI (25 mg, ≈10 mol %) were added under an argon atmosphere. After the addition of the catalyst the mixture was stirred under an argon atmosphere overnight at room temperature. A yellow precipitate quickly formed. The following day the reaction mixture had solidified. Dry THF (50 mL) was added, and the solution was heated to reflux temperature. The precipitate dissolved, and the solution was stirred for another 5 h at reflux. The solution was then poured into 300 mL of methanol, and a yellow precipitate formed. Filtration on a glass filter gave a yellow solid that was washed with both cold methanol and cold diethyl ether and dried on the filter. The wet product was kept for further use. Attempts to dry the product in a vacuum oven at RT gave a darkened product that was no longer soluble in common solvents. This behavior has been observed earlier.[15] The total yield based on a completely dried sample was 0.35 g (95%) (the wet product weighed 0.6 g containing 40% w/w solvent and was conveniently stored in this form).^{1}H NMR δ: 0.76−0.95 (m, 6H), 1.13−1.50 (m, 20 H), 1.50−1.83 (m, 4H), 2.70−2.90 (m, 4H), 7.31−7.43 (broad s), 7.43−7.60 (broad s) (7.31−7.60, 6H).

Porphyrin Linked Polymer with a Constant Porphyrin-to-Monomer Ratio (NPN A). A 100 mL round-bottom flask was dried using a heat gun and flushed with argon. Compound **8** (7.24×10^{-4} mol, 0.400 g) and compound **12** (6.26×10^{-5} mol, 0.050 g) were placed in the flask and dissolved in 50/30 mL dry triethylamine/THF. The solution was flushed with argon for 30 min before the catalyst Pd(PPh_3)$_4$ (20 mg, ≈2 mol %) and the cocatalyst CuI (15 mg, ≈10 mol %) were added under an argon atmosphere. After the addition of the catalyst the mixture was refluxed overnight and was next day poured into 300 mL of methanol. The following day a green precipitate formed that was filtered on a glass filter−funnel. The filter cake was washed with both cold methanol and cold diethyl ether and was dried in the air to give 0.271 g of polymer. ^{1}H NMR δ: 0.76−2.18 (m), 2.20 (m) (0.76−2.20, 490 H), 2.81 (broad s, 53 H), 6.80−8.18 (m, 90 H), 8.71−9.06 (m, 4 H), 9.48−9.94 (m, 4 H).

Porphyrin Linked Polymer with One Porphyrin Moiety in Each Polymer Chain (NPN B). A 100 mL round-bottom flask was dried using a heat gun and flushed with argon. Compound **8** (2.19×10^{-3} mol, 1.212 g) and compound **10** (2.12×10^{-4} mol, 0.198 g) were placed in the flask and dissolved in 50/30 mL dry triethylamine/THF. The solution was flushed with argon for 30 min before the catalyst Pd(PPh_3)$_4$ (50 mg, ≈2 mol %) and the cocatalyst CuI (40 mg, ≈10 mol %) were added under an argon atmosphere. After the addition of the catalyst the mixture was refluxed overnight and was poured into 300 mL of methanol. The following day a green precipitate formed that was filtered on a glass filter−funnel. The filter cake was washed with both cold methanol and cold diethyl ether and was dried in the air to give 1.021 g of polymer. ^{1}H NMR δ: 0.73−1.03 (m, 190 H), 1.03−1.91 (m, 740 H), 2.15 (m, 8 H), 2.32 (m, 9 H), 2.56 (m, 13 H), 2.82 (broad s, 76 H), 6.31−6.61 (m, 14 H), 6.79−8.16 (m, 286 H), 9.01 (m, 4 H), 9.79 (m, 4 H).

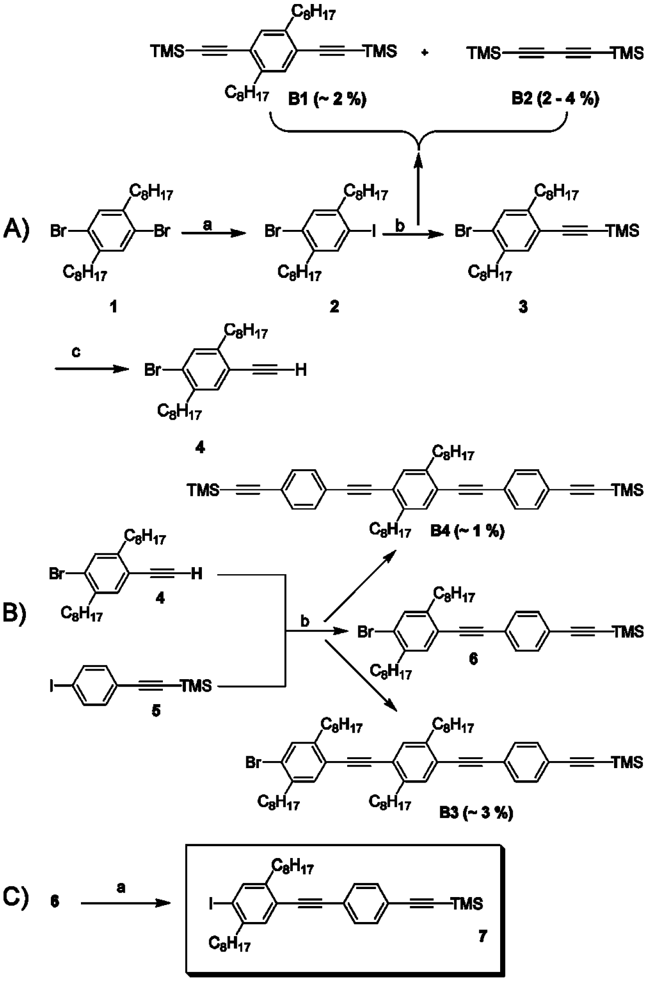
Diethylammonium Diethyldithiocarbamate (DDC). DDC was prepared by the method described in the literature for sodium methyltiocarbamate.[16] Carbon disulfide (0.15 mol, 11.42 g) was added dropwise to a solution of diethylamine (0.4 mol, 29.25 g) in diethyl ether (350 mL), and after a while small colorless crystals were formed. The material was collected on a filter and washed with copious amounts of diethyl ether and dried in a vacuum oven. The yield was 19.29 (58%); mp 81−82 °C. ^{1}H NMR δ: 1.24 (t, 6H, $^3J = 7.3$ Hz), 1.37 (t, 6H, $^3J = 7$ Hz), 3.15 (q, 4H, $^3J = 7.3$ Hz), 4.10 (q, 4H, $^3J = 7$ Hz), 8.27 (broad s, 2H). ^{13}C NMR δ: 12.09, 13.05, 41.70, 48.54. Anal. Calcd for $C_9H_{22}S_2$: C, 48.60; H, 9.97; N, 12.60; S, 28.83. Found: C, 48.73; H, 10.17; N, 12.54; S, 28.37.

General Procedure for the Removal of Pd from Polymer Samples Using DDC. The polymer was dissolved in the minimum amount of chloroform. DDC (5 equiv relative to the Pd employed in the catalyst) was added, and the solution was stirred for 5 min. The solution was poured into methanol (10 time the volume of chloroform) and the polymer precipitated. The precipitate was filtered and washed with methanol and diethyl ether.

Results and Discussion

Monomer Synthesis. The synthesis of the monomer unit is shown in Scheme 1. The synthesis involves the readily available compounds 1,4-dibromo-2,5-dioctylbenzene (**1**) and 1-(4-iodophenyl)-2-trimethylsilylacetylene (TMSA). The first step (Scheme 1A) is a bromine−iodine exchange of compound **1** using *n*-BuLi in THF at −78 °C. The bromoiodo compound (**2**) was cross-coupled with TMSA by Pd/Cu catalysis in the following step to form the 1-(4-bromo-2,5-dioctylphenyl)-2-trimethylsilylacetylene (**3**). In this step it was found important that the coupling reaction took place at low temperature to increase the selectivity between iodo vs bromo substitution. Even at 273 K we obtained ~2% of

Scheme 1. Synthetic Procedure Leading to the Monomer Unit 1-Iodo-2,5-dioctyl-4′-trimethylsilylethynyltolane (7)[a]



[a] (a) (1) n-BuLi, THF, (2) I_2; (b) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (c) K_2CO_3, MeOH, CH_2Cl_2. Compounds B1−B4 were side products isolated from the reaction mixtures in step b.

1,4-di(trimethylsilylethynyl)-2,5-dioctylbenzene (**B1**) and 2−4% of 1,4-ditrimethylsilylbutadiyne (**B2**) as byproducts which were detected by ^1H and ^{13}C NMR, GC-MS, and MALDI TOF. The TMS group was removed by K_2CO_3, and the 4-bromo-2,5-dioctylphenylethynylene (**4**) was obtained.[17] The monomer unit 1-iodo-2,5-dioctyl-4′-trimethylsilylethynyltolane (**7**) was then obtained by an additional two-step reaction. The first step being a Sonogashira cross-coupling reaction between compound **4** and 1-(4-iodophenyl)-2-trimethylsilylacetylene (**5**) (Scheme 1B) to obtain 1-bromo-2,5-dioctyl-4′-trimethylsilylethynyltolane (**6**). The final step was a standard bromine−iodine exchange.

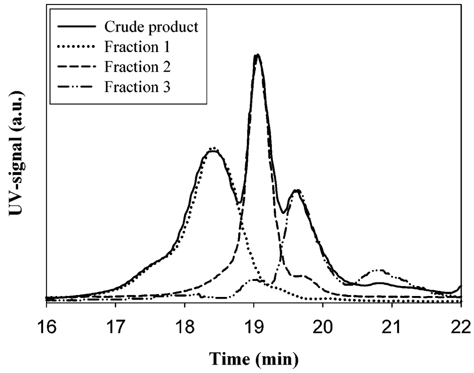


Figure 2. SEC traces of the crude product when synthesizing **11** using the Sonogashira reaction. The crude product was separated into fractions using preparative SEC, which gave a reasonably pure fraction of the desired product (fraction 2).

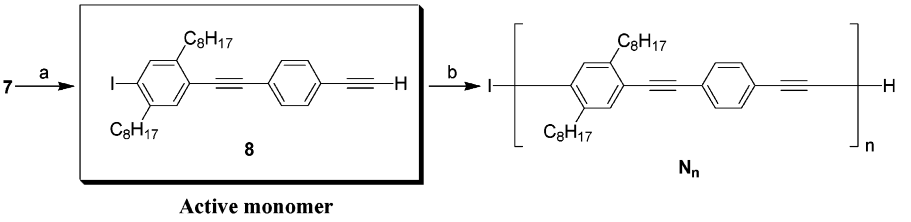
The Sonogashira reaction for this type of molecules has been described by others[13] and generally works quite well. Most authors, however, never comment on the fact that the Sonogashira alkynyl−aryl cross-coupling cannot be performed without significant side reactions. Known byproducts are 1,4-diarylbutadiynes, 1,4-diarylbuta-2-en-1-ynes, and the trimerization product 1,3,5-triarylbenzene.[18−20] Of those byproducts we have only detected butadiynes, and this was in connection with the synthesis of compound **3**. With ^1H and ^{13}C NMR and MALDI TOF we instead detected ~3% 1-bromo-2,5-dioctyl-4′-(4′′-trimethylsilylethynylphenyl)ethynyltolane (**B3**) as a byproduct during the synthesis of compound **6**. Furthermore, we found ~1% of compound **4**. We believe this to be a result of incomplete reaction. We also detected ~1% of 1,4-dioctyl-2,5-bis((4′-trimethylsilylethynylphenyl)ethynyl)benzene (**B4**). The presence of **B4** is a result of the difficulty in separating **B1** from compound **3**. The R_F values in n-heptane of compounds **4**, **6**, **B3**, and **B4** are 0.58, 0.38, 0.25, and 0.08, so it was possible by flash chromatography to separate **6** from the byproducts. The removal of byproducts in this step was found to be essential in order to control the later polymerization process. As a consequence, compound **6** was obtained in low yield. It should be noted that, besides the above-mentioned byproducts, we have detected some minor byproducts, but the amount of these was so small that we could not determine the structures.

Porphyrin Synthesis. The porphyrin subunit should have a structure that allowed for attachment of the polymer blocks in the 5,15-positions. We chose the synthetic scheme presented by Plater et al.[11] due to the possibility of large scale synthesis. The reported procedure allowed for the synthesis of the porphyrin (**9**) (see Scheme 4) on a 100 g scale of sufficient purity for the synthesis of the zinc dibromoporphyrin (**10**).

It was possible to obtain **10** in high purity, which we ascribe to the fortuitous low solubility of **10** making the alleviation of byproducts relatively easy. Plater et al. also reported the synthesis of bisethynylporphyrin (**12**) through Sonogashira coupling of TMSA onto **10** followed by removal of the TMS groups. The synthesis of **12,** however, proved very difficult in our hands, and while a product was obtained the analytical data showed that it consisted of oligomers and other impurities. SEC revealed many different components as shown in Figure 2. We decided to purify the crude product by preparative SEC and isolated the purified fraction of **11**. The similarity between the ^1H NMR spectra for the crude fraction and the purified product was striking, and it was virtually impossible to establish the extent of impurities from the ^1H NMR spectra alone, so a technique like SEC is absolutely needed.

We propose that the large molecular weight impurities are oligomers of **12** to account for the similarities in the ^1H NMR spectra and for the fact that the UV spectra of the fractions were very similar and contained the signatures of a zinc porphyrin. The purified fraction containing mainly **11** could be deprotected followed by recrystallization from chloroform, and the product was filtered using a 0.45 μm filter to give pure **12**. Similar

Scheme 2. Synthetic Procedure Leading to the Homopolymer Poly[(2,5-dioctyltolanyl)Ethynylene] (N_n)[a]



[a] (a) K_2CO_3, MeOH, CH_2Cl_2; (b) $Pd(PPh_3)_4$, CuI, piperidine.

Table 1. Data from the SEC and UV−Vis Analysis for All Three Polymers[a]

compound	M_w [g/mol]	PDI	absorbance ratio	N/P ratio	cross-linkage (UV−vis M_w)[b]
N_n	92 300	2.90			
NPN A crude	19 299	2.12	2.5	8.5	
fraction 1	66 020	1.18	2.5	8.5	
fraction 2	41 255	1.16	3	10.0	
fraction 3	22 175	1.15	2.5	8.5	
fraction 4	13 058	1.18	2.5	8.5	
fraction 5	8 373	1.11	2.5	8.5	
fraction 6	4 727	1.09	2.5	8.5	
fraction 7	2 839	1.03	2	6.9	
NPN B crude	36 949	4.09	3	10.0	3.2[c] (n.a.)
fraction 1	92 275	1.07	6.5	22.2	9.1 (10200)
fraction 2	60 246	1.21	5	17.1	7.5 (8000)
fraction 3	31 612	1.28	4.5	15.4	4.3 (7300)
fraction 4	14 225	1.19	3.5	12.0	2.4 (5850)
fraction 5	9 239	1.24	2.5	8.5	2.1 (4350)
fraction 6	4 074	1.39	2	6.9	1.1 (3700)
fraction 7	1 534	1.17	1.5	5.1	−[d] (2900)

[a] The absorbance ratio is the ratio of the absorbance from the N_n polymer (at 381 nm) and the porphyrin (at 451 nm). The N/P ratio listed in this table is the ratio between the N and P units based on their individual extinction coefficients. (see the section Method B: Polymerization in the Presence of Dibromoporhyrin for the results). [b] Molecular weights of 425 and 750 g mol^{-1} were used respectively for the monomer and the porphyrin constituents in the polymer. [c] Estimated from the increase in molecular weight from 11 546 to 36 949 g mol^{-1} on standing. [d] A value for cross-linking of 0.5 is obtained since the extinction coefficient for N is overestimated at low molecular weights. A value <1 has no physical meaning in terms of cross-linkage; it has therefore not been shown.

problems have been described earlier by Tomizaki et al.,[21] where a seemingly pure product in terms of porphyrin content (NMR and UV−vis data) turned out to be a mixture of molecules with different size (i.e., different molecular weights) when SEC was used. This could be oligomers or higher porphyrin components (geländer molecules).

Homopolymer Synthesis. Scheme 2 shows the synthetic procedure of the conjugated homopolymer. Employing Sonogashira cross-coupling conditions following standard methods, the iodine-terminated homopolymer poly[(2,5-dioctyltolanyl)ethynylene] (N_n) was obtained. We have used $Pd(PPh_3)_4$ as catalyst instead of $Pd(PPh_3)_2Cl_2$ to minimize the formation of the butadiyne byproducts, where two terminal acetylenes are coupled when reducing Pd(II) to Pd(0). Pd(0) is most probably the active species in the catalytic cycle for the Sonogashira cross-coupling reaction.[22] The molecular weight (M_w) of the polymer N_n was determined using SEC, and the results are listed in Table 1. Measurements on electroative devices prepared using N_n showed that it contained residual palladium, which were confirmed by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) measurements. The content of Pd in the N_n polymer was determined to 49.3 mg/kg. The Pd was removed by using DDC (see the section Problems with Pd).

Porphyrin Linked Homopolymer Synthesis. We attempted two different strategies to synthesize a molecule with the general structure NPN, as shown in the lower part of Figure 1. While the two different procedures shown in Scheme 4 both accord with the general structure depicted above, they differ in the way the polymer segments are coupled to the porphyrin nucleus. The only difference is the distance from the porphyrin to the first phenyl ring bearing octyl substituents. The proximity of the octyl substituents in the case of NPN A reduces the degree of conjugation between the polymer segment and the porphyrin system due to steric effects.

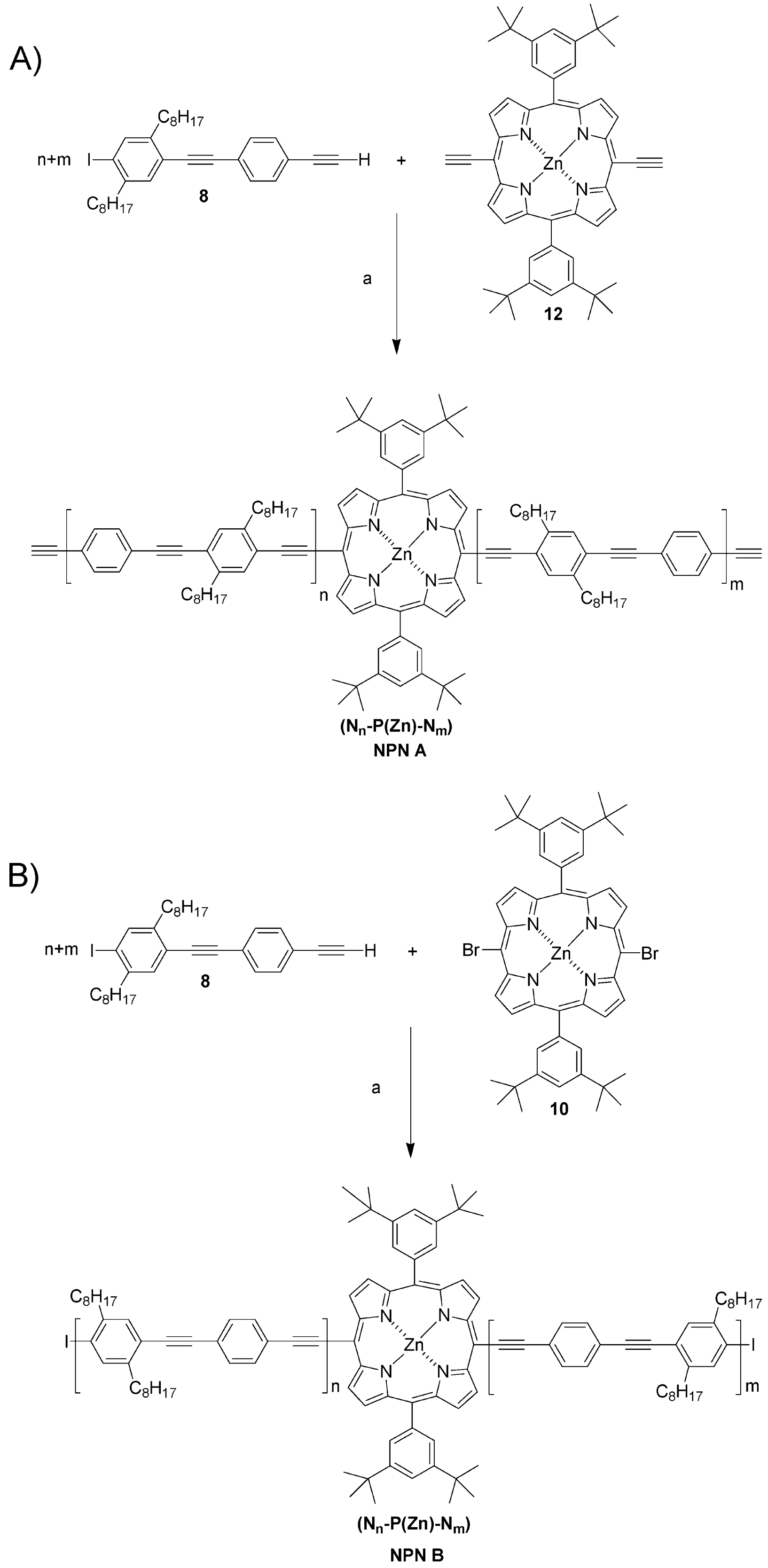
Therefore, there would be a difference between the electronic properties of the NPN A polymer and the NPN B polymer. (This was confirmed by the differences in the UV−vis spectra for the two products.)

Method A: Polymerization in the Presence of Diethynylporphyrin. Our first choice of porphyrin derivative was the diethynylporphyrin **12** since we desired a reactivity of the porphyrin derivative that was comparable or larger than the individual monomers to ensure attachment of the porphyrin molecules to the growing polymer chains during the polymerization reaction.

The polymerization reaction of the monomer **8** in the presence of the deprotected diethynylporphyrin **12** proceeded smoothly, giving a polymer product. The evidence for zinc porphyrin content in the polymer was found by the UV−vis spectrum of the product during SEC analysis. We employed fractionation of the crude polymer product using preparative SEC and obtained seven fractions. The UV−vis spectra of the fractions are shown in Figure 3, and while they show a gradual red shift of the absorption maximum for the polymer component with increasing molecular weight (as expected) the porphyrin content was roughly constant. The ratio of the N and P absorption and the molecular weight (M_w) determined by SEC in the seven fractions are listed in Table 1. The ratio between the porphyrin and polymer showed little variation and did not depend on the molecular weight as expected, if only one porphyrin molecule had been incorporated into each NPN molecule. These results could indicate that not only the NPN A polymer was produced but also a large amount of the buta-1,3-diyn-1,4-diyl byproduct derived from oxidative dimerization (see Scheme 5).

To account for this finding, we assume that a side reaction involving the ethynyl groups of either the growing polymer chain or the porphyrin takes place. In the case of the polymerization starting from the diethynylporphyrin the growing polymer chain will always expose an ethynyl group and thus be susceptible to oxidative coupling of the ethynyl group to give a butadiyne, which in principle gives a homopolymer

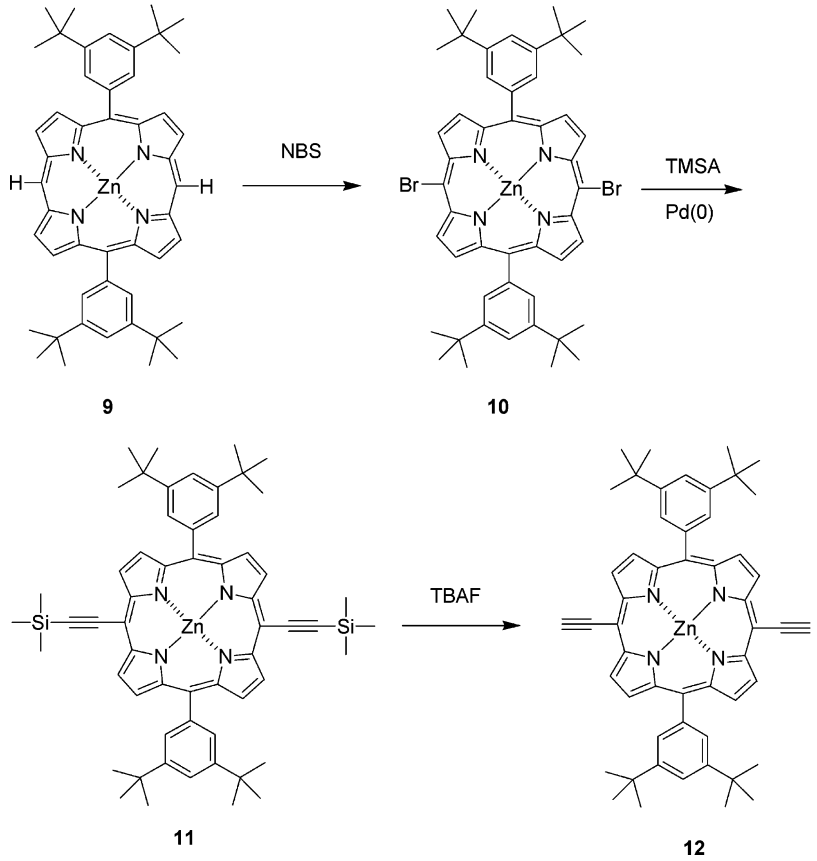
Scheme 3. Two Different Synthetic Producers Leading to the Three-Domain Structure NPN[a]



[a] (a) $Pd(PPh_3)_4$, CuI, Et_3N, THF.

segment with a defect in the growth direction such that both polymer termini present iodine atoms. Such an event, however, does not represent a termination of chain elongation as a monomer or another diethynylporphyrin can react at the iodinated chain end hence continue chain growth. The result is a polymer product with an even distribution of porphyrin molecules with the amount of porphyrin determined largely by the ratio of polymer to monomer in the initial reaction mixture. In conclusion, the synthetic scheme

Scheme 4. Synthetic Procedure of Compounds 9−12



for the incorporation of a single porphyrin molecule between two polymer blocks based on a diethynylporphyrin does not work because of the dimerization side reaction that always takes place during the Sonogashira reaction.

From a synthetic point of view, a small molecule product is generally not affected by a small amount of dimerization (of the order of 1−10%) as means of purification are available (i.e., distillation, crystallization). When employing the Sonogashira reaction for polymerization, however, the defects introduced by the side reaction are accumulated in the polymer product and make the applicability of the Sonogashira reaction for polymerization questionable, if a product with a high degree of regioregularity or directionality is required.

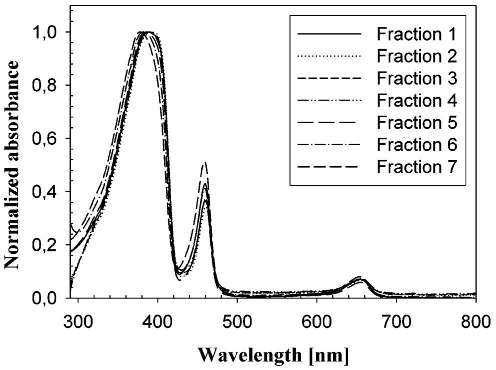
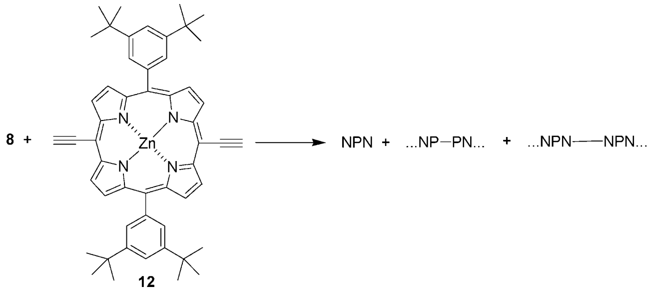


Figure 3. UV−vis spectra of the seven fractions of the NPN A polymer formed during the polymerization of the monomer **8** in the presence of the diethynyl porphyrin **12**. The spectra are normalized according to $\lambda_{\max}$ of the polymer. It can be seen how the absorption of the porphyrin ($\lambda = 451$ nm) does not vary significantly in intensity as a function of the length of the N_n polymers.

Scheme 5. Illustration of Some of the Possible Byproducts from Cross-Coupling of the Monomer Unit 8 with the Diethynylporphyrin 12



Method B: Polymerization in the Presence of Dibromoporphyrin. In this method we used dibromoporphyrin, **10**, as the source of porphyrin during the polymerization reaction. Seen in light of the finding above, we would expect only one porphyrin molecule to be incorporated in each polymer chain assuming that **10** does not lead to homocoupled byproducts. We would also expect a considerable amount of homopolymer since any dimerization of a pair of ethynyl groups will lead to homopolymers with halogen termini in both ends of the molecule that does not allow for the incorporation of the dibromoporphyrin. From the SEC trace of the crude product it was clear that the synthetic scheme worked in terms of a decreasing porphyrin content with increasing molecular weight. The SEC trace also confirmed the presence of porphyrin in molecules of high molecular weight but revealed nothing about the homopolymer content.

The crude polymer product had a molecular weight (M_w) of 11 546 g/mol and a polydispersity of 3.456. Fractionation of the crude product into seven fractions

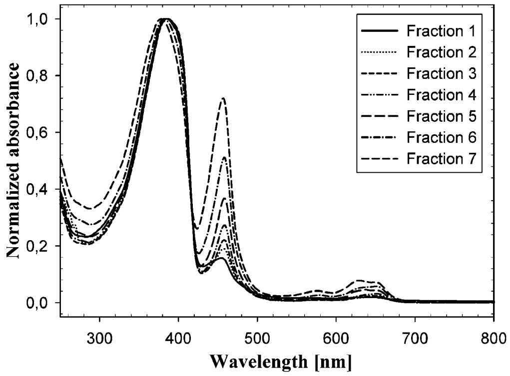


Figure 4. UV−vis spectra of the seven fractions of the NPN B polymer. The spectra are normalized according to $\lambda_{\max}$ for the polymer. It can be seen how the absorption for the porphyrin ($\lambda = 451$ nm and 520−700 nm) varies in intensity as a function of the length of the N_n polymers.

using preparative SEC as above revealed as expected a variation of the porphyrin content in the individual fractions. When SEC analysis was performed on the individual fractions the following day, it was surprising that the molecular weight of the fraction had increased, as if cross-linking of the products took place. The fractions were then left to stand and evaporate in the hood in air for 3 days to allow for completion of the cross-linking process. The resulting solids were boiled in chloroform that dissolved only a part of the polymer product. This finding is consistent with earlier reports on the insolubility of poly(phenyleneethynylene)s once having been subjected to complete drying.[15,18a] The soluble fraction was then refractionated using preparative SEC, and this gave stable molecular weight fractions. It should be noted that the molecular weight of the crude polymer was increased to 36 949 g/mol with a polydispersity of 4.09 during the 3 days. The fractions show the desired variation of the porphyrin content between the individual fractions (see Figure 4). The repurified fractions were used for the emission spectroscopy studies. The UV−vis solution spectra of the seven fractions were recorded, and from these spectra it can be seen that the absorption maximum, $\lambda_{\max}$, as a function of the polymer chain length was red-shifted 9 nm from fraction 7 through fraction 1. From Figure 4 it is observed that the red shift of $\lambda_{\max}$ already stops at fraction 5, which corresponds to approximately a decamer of the N_n in NPN B. These results are in agreement with the results of Jones et al.,[23] who reported studies on oligomers at a precise length of 1,4-phenylene ethynylenes. Brédas et al.[24] have shown that the band gap as a function of n^{-1} (for large $n > 5$) has a linear relationship. The average ratio of N and P in the NPN polymer is obtained on the basis of the measured $\lambda_{\max}$ at 390 nm (absorption mainly from N_n) and 451 nm (absorption mainly from P). The ratio for the N_n and P absorption in the fraction are listed in Table 1 together with the molecular weight (M_w) determined by SEC. From the extinction coefficient for N_n and P (we used the ϵ_{431} in **12** for the absorption at 455 nm) an estimate for the ratio between N and P can be obtained. The two extinction coefficients were determined to be $\epsilon_{390} = 70\,000$ M^{-1} cm^{-1} and $\epsilon_{431} = 240\,000$ M^{-1} cm^{-1}. This indicates a N/P ratio of 22.2:1; 17.1:1; 15.4:1; 12:1; 8.5:1; 6.9:1, and 5:1 for fractions 1 to 7, respectively (see Figure 4).

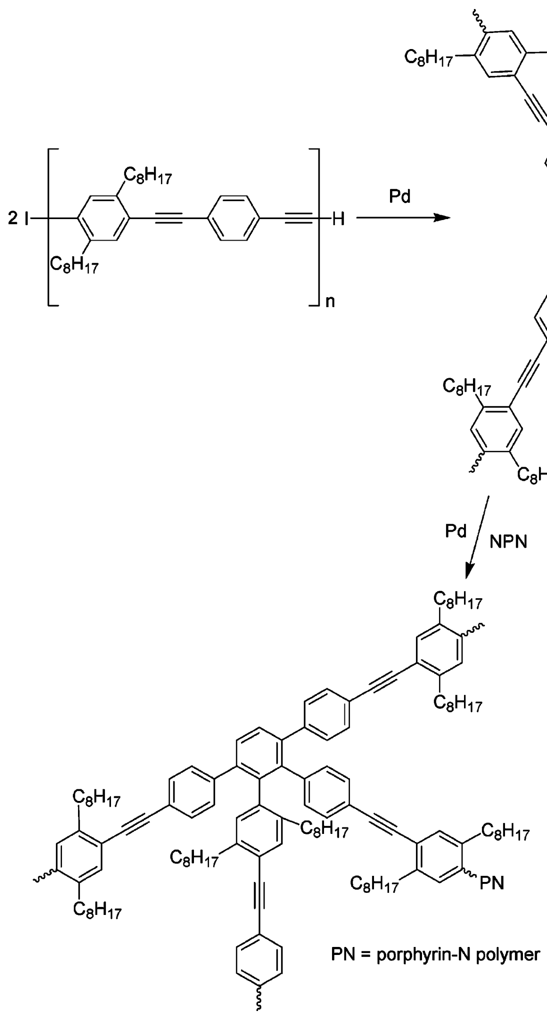
A comparison of the molecular size obtained by UV−vis with the results from the SEC analysis shows a mismatch in both high and low molecular weights. In the low molecular weight range the mismatch is a result of the estimate that the extinction coefficient of both N_n and P is the same in the polymer and for the isolated molecules. In the high molecular weight range the mismatch is due to cross-linking since more than one porphyrin molecule would be present in the cross-linked supermolecules. This means that the molecular weight (M_w) determined by SEC should be given by $M_w = x((N/P)M_{\text{monomer}} + M_{\text{porphyrin}})$, which is in good accordance with our observations (see Table 1). In the equation x is the number of cross-link, N/P is the ratio between the N_n monomer and the porphyrin obtained by the UV−vis measurements, and M_{monomer} and $M_{\text{porphyrin}}$ are the molecular weights monomer and porphyrin, respectively. Further, SEC has a tendency to overestimate the molecular weight of linear rigid molecules when using polystyrene standards. SEC probes the hydrodynamic volume of the polymer, and since polystyrene can be assumed globular in chloroform solution and the polymer systems studied remain linear, this will contribute to the overestimation as the molecular weight increases. This effect has not been taken into account in Table 1. The average of the cross-linking, x, in Table 1 has a value of 3.8 for the seven fractions, which is in good accordance with the value of 3.2 obtained for the molecular weight increase of the homopolymer on standing (not corrected for the weight of the individual fractions).

Problems with Pd. The problems concerning the removal of Pd catalyst from samples is a large forgotten area in the literature, which only very few authors[25−27] have reported. Earlier work[25] with palladium-catalyzed polymerization using the Heck reaction for the polymerization have unfortunately shown that the removal of palladium catalyst remnants can be problematic. It is probably difficult to envisage complete removal of catalyst remnants in the case of polymeric products. With this paper and two recent ones[25] we hope to start a discussion on this topic. It is very important to be able to remove all of the Pd catalyst, when e.g. a photovoltaic or a light-emitting device of conjugated polymers is produced, because remnants from the Pd catalyst in the form of nanoparticles can lead to a short circuit of the device.

From our experience with the palladium-catalyzed Heck reaction, we would expect some remnants of palladium in both the N_n and the NPN (both A and B) polymer. The remnants of Pd in the N_n were confirmed by ICP-SFMS and determined to be 49.3 mg/kg. We had hoped that the remnants of palladium did not influence the electrical and optical properties of the polymers too much. Unfortunately, when we made a standard electroactive device of the polymers produced by sandwiching the polymer between two electrodes (see Supporting Information) the resistance was as low as 30 Ω.

In connection to removing Pd from our polymers, we have attempted to use diethylammonium diethyldithiocarbamate (DDC) with some success as reported by Jones et al.[26] for solid-state synthesis. The reason for choosing DDC is that it coordinates very strongly to Pd ($\log K\,(\text{Pd[DDC]}_2) = 64.9$)[28] and more strongly than the alkyne groups in the polymers. Furthermore, Briscoe and Humphries[28] have showed that the coordination of DDC to Pd is very fast and that the coordination process is complete after 5 min at room temperature. There were several indications that DDC coordinated to Pd as

Scheme 6. Illustration of a Probable Trimerization Cross-Linkage Process between Two N_n Polymers and a NPN B Polymer[a]



[a] The trimerization process is observed under normal Sonogashira cross-coupling conditions.

expected and thereby removed Pd from the polymers. The indications were that the solution shifted color from yellow to dark brown very quickly (in a few seconds) upon addition of DDC. Furthermore, the precipitated polymer product after the treatment with DDC had a lighter yellow color than the crude polymer product; the resistance through a standard electroactive device geometry (produced by sandwiching the polymer between two electrodes) increased from 30−50 Ω to 0.3−2 MΩ after the treatment with DDC. Our results indicate that DDC very effectively removed or passivated Pd from polymer samples. Unfortunately, there were also some indications that DDC reacted with the polymers. We observed that treatment with DDC, for periods of time longer than 5 min (we attempted 2 and 24 h), led to a dramatic change in some of the properties of the polymers. The polymer became difficult to precipitate from in methanol, and no electroluminescence could be observed when a potential was applied. On the other hand, we had success in removing Pd from the polymer samples without the above-mentioned changes in properties for the polymers, when we used approximately 5 times excess of DDC, compared to the amount of Pd used in the catalyst, and a reaction time between 3 and 5 min. From the UV−vis spectra of the N_n in the solid state (see Supporting Information) it can be seen that

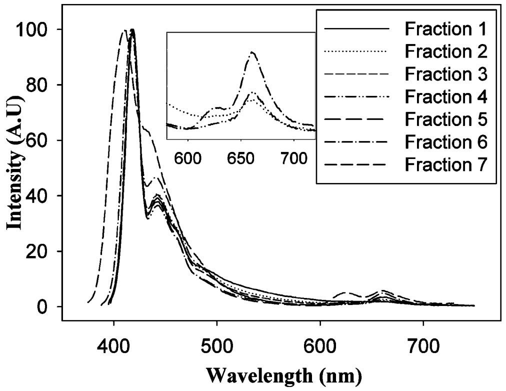


Figure 5. Emission spectra of fractions 1−7 of NPN B in degassed chloroform. The excitation wavelength was set to the maximum absorption of the polymer (around 388 nm). Peak absorption was below 0.07 (concentrations below 10^{-5} M). The inset shows the porphyrin emission of fractions 2, 4, and 6 for comparison.

the optical properties have changed dramatically, when the polymer was treated with DDC for more than 5 min. It should be emphasized that there is little change in the UV−vis spectrum of the polymer, which have been treated with DDC for 5 min compared with the crude polymer. It was not possible to observe the dithiocarbamoyl groups in the ^{1}H NMR spectra recorded on the DDC treated N_n polymer product. By comparing the fluorescence spectra of the N_n polymer in solid state before and after a long DDC treatment time, it can be seen that there were significant changes (see Supporting Information). The changes cannot however explain why the electroactive devices after long DDC treatment time did not show electroluminescence. The quantum yield of fluorescence is approximately constant; there is however a small blue shift of the emission maximum upon DDC treatment and a shoulder at 415 nm that becomes suppressed.

An elementary analysis of the N_n polymer after a 2 h DDC treatment time shows that the polymer contains C, 84.8%; H, 9.1%; N, 0.5%; and S, <0.1% compared with C, 88.4%; H, 9.5%; N, <0.3%; and S, <0.1% for the untreated N_n polymer. The elementary analysis indicates that it is not the DDC group itself that is added to the polymer, since no S could be detected in the polymer. However, we detected a little increase in the contents of N corresponding to one N atom for every six incorporated monomer units. From the elementary analysis we got an indication that it is an N-containing compound that is attached to the polymer by treatment with DDC. While we cannot provide a solid explanation for the reaction between DDC and the polymer, our photophysical and electroactive device measurements show that DDC treatment changes the properties of the polymer. The NPN B polymer has also been treated with DDC with success; electroluminescent devices of the N_n itself and of NPN B polymer were prepared, and the nature of the electroluminescence has been characterized.[29] To decide whether the apparent cross-linkage of the NPN B polymer products could be a result of the content of Pd in the polymers, we performed a search in the literature for a useful model study and found that it has been known for more that 50 years that transition metals catalyze the trimerization of alkynes.[30] In 1997 and 2001, it was further shown by Gevorgyan et al.[31,32] that substituted benzenes can be constructed from enynes and activated alkynes in a [4 + 2] and from

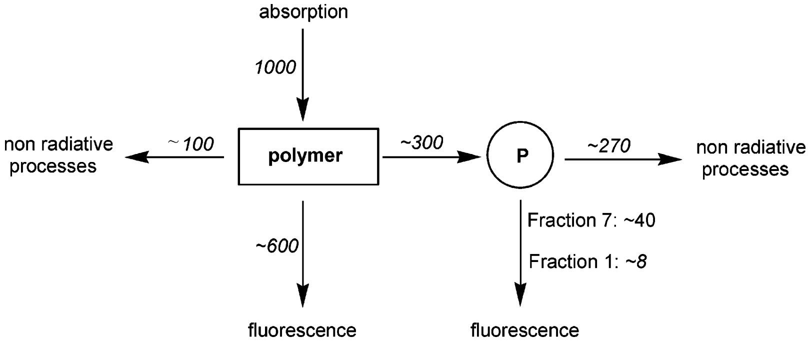


Figure 6. Typical photon balance of the NPN B assembly in dilute degassed chloroform solution. The absorption is arbitrarily set to 1000 photons, and the fluorescence emission was measured. Energy transfer as well as nonradiative decay is calculated from the fluorescence quantum yields of the pure N and P domains. The relative porphyrin emission increases as the N chain length decreases.

terminal alkynes in a [2 + 2 + 2] fashion in the presence of a Pd(0) catalyst. Both reactions proceed under normal Sonogashira conditions without an inert atmosphere. By comparing these model studies of the trimerization of alkynes with the known byproducts[18−20] from a Sonogashira cross-coupling reaction, it is most likely that the apparent cross-linkage of our polymer products are formed by a trimerization process. A probable trimerization process could be that two homopolymers N_n with terminal alkynes (that are not coupled to the porphyrins) are forming an enyne in the presence of the Pd(0) catalysts. This enyne can then react with one of the triple bonds in both N_n and NPN B molecules to form the trimerization cross-linkage (see Scheme 6). This can be used to explain how the molecular weight of a polymer fraction can increase when standing and ultimately form an insoluble product with a high degree of cross-linking. To avoid this trimerization cross-linkage of the polymer, it is very important to remove all the catalyst during precipitation of the polymers.

Fluorescence Measurements. We have performed fluorescence measurements on the N_n and the NPN B polymers. In Figure 5 normalized fluorescence spectra of the seven fractions of NPN B are shown. In all cases the excitation wavelength was set to the maximum absorption of the polymer (around 388 nm). The emission below 600 nm is from the N domain, whereas the porphyrin unit emits around 660 nm. The polymer emission from the seven fractions shows little variation. However, fractions 6 and 7, with the shortest N domains, differ somewhat from the remaining fractions: both spectra are more intense at 440 nm. In addition, the spectrum of fraction 7 is blue-shifted 8 nm compared to the remaining spectra, probably due to the relatively short chain segments (oligomers). Another notable feature is that the polymer emission extends more toward long wavelengths as the N domains gets larger as expected. The most interesting difference is that the porphyrin emission seems to gradually increase as the N domain gets shorter (see inset in Figure 5). We interpret this as a consequence of the fact that the whole polymer chain is probably not perfectly conjugated. Hence, the chain will consist of a number of segments. Thus, with increasing polymer length the more likely it becomes that an exciton gets trapped on a segment that is not in the porphyrin vicinity, and the energy transfer efficiency decreases. Since the N domain fluoresces in the spectral area where the P domain absorbs, a Förster type of energy transfer may be involved. Using the same methodology as described earlier, photon balances could be derived for the individual fractions.[5,33] The fluorescence quantum yields for the pure N domain and pure P domain were determined to be 87% and 10.5%, respectively, using DPA as reference.

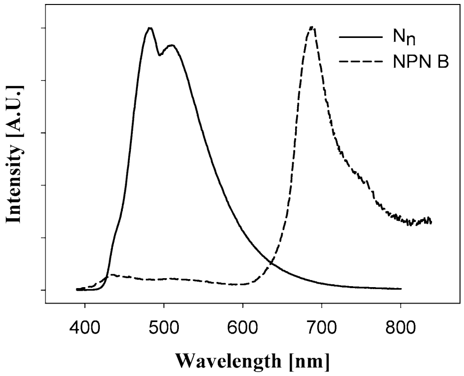


Figure 7. Normalized fluorescence emission from spin-coated films of the N_n polymer (M_w = 92.300 g mol^{-1}) and the NPN B assembly. The polymer emission is almost completely quenched by the porphyrin.

Assuming that the ratio between the fluorescence rate and the nonradiative decay rates are similar in the NPN B assembly as in the model compounds, a photon balance can be calculated from the measured fluorescence emission. This is shown in Figure 6. The overall quantum yield for the NPN B assembly was in general around 60%, which mainly was caused by the N domain emission. The fluorescence from the P domain was limited compared with the N domain. The relative emission of the P domain was found to increase 5-fold going from fraction 1 to 7. This means that in solution (or in a diluted matrix) the polymer length may be crucial in multidomain light-harvesting systems.

Solid-state studies of NPN B shows that whereas energy transfer is limited in solution, it becomes the main deactivation route of the N domain in the solid phase (see Figure 7); thus, N emission is nearly completely quenched by the porphyrin that emit strongly. Thus, in the solid state the chain length is much less important than in solution with regards to efficient energy transfer. The more efficient energy transfer in the solid state seems to be a general rule for this kind of polymer−dye systems.[5,33] The N and P emission are red-shifted by approximately 65 nm compared to the solution spectra. Also, the relative intensity of the N domain and P domain peaks are changed.

The lifetime decay of the pure P domain could be fitted with a single-exponential function, with a decay of 2.4 ns in degassed chloroform. The lifetime decay of the N domain needed a linear combination of two exponential functions to obtain a reasonable fit in degassed chloroform: 259 ps (86%) and 1.6 ps (14%). In the spin-coated film the measured lifetime of the N domain is significantly larger: 1.4 ns (53%) and 2.7 ns (47%). This could be caused by the hampering of some of the deactivation routes that are effective in solution. A side effect is that the exciton has more time to be transferred to a porphyrin unit, and this could be one of the reasons why more efficient energy transfer is observed. Interestingly, the fluorescence lifetime of the porphyrin unit was significantly shorter in the solid state than in solution. The lifetime decay was complex, and a good fit could not be obtained. This is not unexpected since a number of interactions and different local environments are present in the solid NPN B matrix. The average lifetime was approximately 300 ps.

Conclusions

We have presented the synthesis of a new zinc porphyrin linked conjugated polymer. We experienced problems in controlling the nature of polymer product and found that it was a result of many factors: oxidative dimerization and cross-linking of the ethynylene groups and palladium remnants from the catalyst. We thoroughly studied products and the reaction by two different synthetic approaches and demonstrated that a polymer product with one porphyrin molecule inserted in each polymer chain could be obtained by choosing the right synthetic approach. We separated the polymer material into fractions using preparative SEC and studied both the cross-linking of the individual fractions and purified them further to finally perform thorough photophysical studies. We showed the light-harvesting properties of the three-domain structure as a function of the chain length of the N_n polymer. This new zinc porphyrin linked homopolymer shows a very effective energy transfer from the polymer to the porphyrin in solid state. Finally, we have identified some problems concerning remnants of Pd from the catalyst in the polymer product, and devise a procedure for the removal of the Pd remnants such that standard electroactive devices could be constructed.

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Supporting Information Available: General analytical techniques, synthetic procedures, characterization, UV−vis, and fluorescence spectra of the polymer and the DDC-treated polymer, and electroactive device preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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