

Directional Synthesis of a Dye-Linked Conducting Homopolymer

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Abstract: We report a new synthesis of a 10,20-diphenyl-5,15-bis(4-cyanophenyl)porphyrin (**1**) and its reduction to give 10,20-diphenyl-5,15-bis(4-formylphenyl)porphyrin (**2**). When the conducting polymer poly(2',5'-dioctyl-4,4''-terphenylenecyanovinylene) was prepared in the presence of **2**, we obtained a three-domain structure, compound **3**, consisting of two homopolymer blocks (J domains) with the porphyrin dye molecule (P domain) in the middle. The JPJ assembly was subjected to photophysical studies where we showed that the J domain could serve as a light-harvesting antenna for the P domain.

Conducting polymers and in particular the application of conducting polymers for diverse functions such as light-emitting diodes,¹ all polymer displays,² all polymer electronic circuits,³ and all polymer solar cells⁴ have received recent attention. With respect to polymer-based solar cells, it is anticipated that the proper synthesis and organization of large multidomain organic molecules could lead to efficient polymer-based solar cells. In particular, an assembly that contains a dye molecule and one or more different conducting polymer domains is of interest. There are, however, many aspects that must be considered for the successful application of such a concept to the synthesis of a large molecule that fulfills these requirements. Most importantly, a conducting polymer synthesis must be available that allows for the integration of a dye molecule into the polymer backbone. The possibility of having porphyrin dyes incorporated into the backbone of a conducting polymer has been explored by Jones et al.,^{5–7} while the synthetic approach did not provide a means of incorporating just one dye molecule. Further multiporphyrin arrays⁸ and their light-harvest-

ing properties have also been examined in great detail by Lindsey et al.^{9–12} with particular emphasis on the influence of the molecular design upon the energy transfer properties. Recently,¹³ the directional synthesis, energy level, and photophysical characterization of the poly-2',5'-dioctyl-4,4''-terphenylenecyanovinylene system (J domain) and similar molecules¹⁴ was reported.

This type of polymerization is particularly suited for the purpose of attaching a polymer string to a molecule containing one or more aldehyde groups.

In this paper, we present the synthesis of a porphyrin-based dye molecule containing two aldehyde functionalities and its incorporation into the polymer backbone of the J domain. The major advantage of the directional synthetic approach, which gives a regioregular polymer, is that only one dye molecule will be sandwiched between any two polymer blocks. While the distribution of molecular weights of the individual J domains is statistical, there will in each polymer molecule be only one incorporated porphyrin dye molecule. The chemical structure obtained is outlined in Chart 1 along with a schematic representation of the assembly. Following on from the synthesis we show how the J domain can be used as a light harvesting antenna for the P domain in accordance with the well-known photophysical properties of porphyrin dyes and assemblies.¹⁵

The studies and reports of porphyrins are vast and these versatile dye molecules have many desirable photophysical properties such as very high extinction coefficients¹⁶ and the possibility of phosphorescence¹⁷ under the right conditions. In terms of synthesis and molecular structure they offer the possibility of having a 90° or 180° substitution pattern with two different substituents, and many reports on the efficient regioselective synthesis of porphyrins with one, two, three, or four different substituents also exist.^{18,19} In our case, we would like the conducting polymer blocks to extend in opposite directions from the dye molecule (180° substitution pattern). For this purpose, we synthesized the porphyrin **2** via the procedure outlined in Scheme 1.

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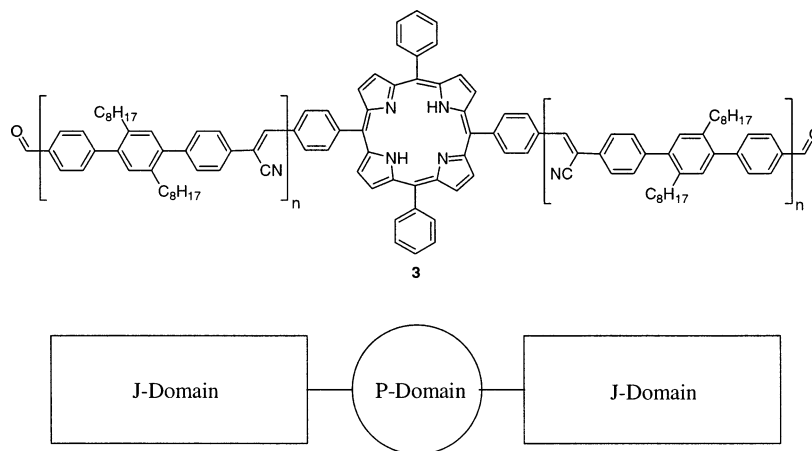
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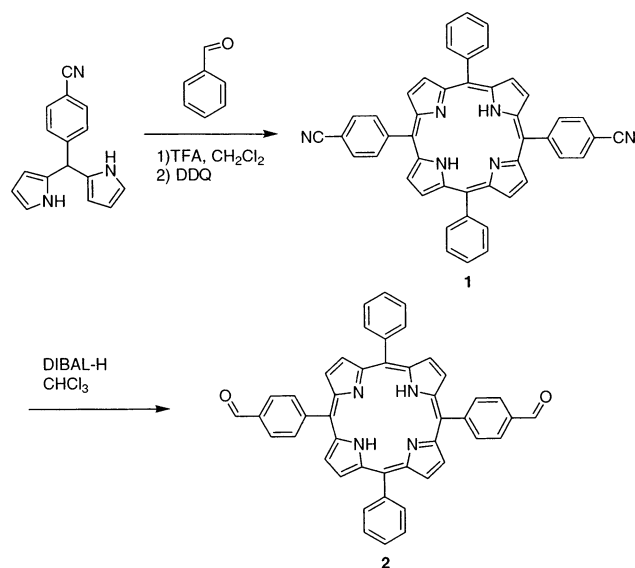
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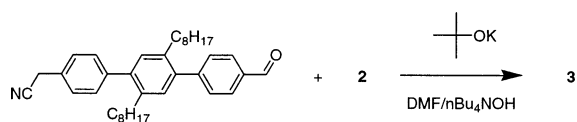
CHART 1



SCHEME 1



SCHEME 2



While compound **2** has been reported,²⁰ it was by a different route that in our hands proved to be unattractive. The polymerization of 4'-cyanomethyl-2',5'-dioctyl-4-formylterphenyl in the presence of **2** proceeded smoothly in DMF by addition of a small amount of *n*-Bu₄NOH (aq) and was complete in a short amount of time. The molar ratio of 4'-cyanomethyl-2',5'-dioctyl-4-formylterphenyl to **2** was kept at 26:1, thus in principle giving an average chain length of thirteen monomer units in each J domain. The procedure is outlined in Scheme 2.

The molecular weights and the distribution of molecular weights was investigated by UV-vis, NMR, and SEC using both refractive index and UV-vis detection. From the UV-vis solution spectra the average ratio of J to P could be obtained on the basis of the extinction

coefficients, and this indicated a J/P ratio of 20:1. ¹H NMR was used to give a J/P ratio based on the ratio of the porphyrin NH-proton signals or end groups signals with the entire aromatic region. The porphyrin NH-protons and the aldehyde protons from the end of the J domains are easily discernible as they are observed at negative ppm values and very high positive ppm values, respectively. This also gave a J/P ratio of 20:1. Finally, SEC was used to give an indication of the molecular weights and more notably the distribution of molecular weights. The JPJ aggregate is assumed to be a rigid rod, and this makes it difficult to obtain an exact molecular weight based on the SEC data which we compare with a polystyrene standard that is assumed to be globular in solution. The combination of the three different techniques that together probe both chemical signatures and hydrodynamic volume does allow us to confirm that the average molecular weight of our product is in the anticipated range. While many attempts were made to obtain mass spectral data using MALDI-TOF it failed in our hands.

The well-known spectral changes of the porphyrin system upon interaction with strong acid^{21,22} were explored in the context of the JPJ aggregate. The UV-vis properties are as expected and shown in Figure 1 where it is observed that the acidification with H₂SO₄ leads to only a slight hyperchromic shift for J domain absorption (at 350 nm). The spectroscopic properties of various acid salts of porphyrin have been reported.^{21,22}

The differences between the UV-vis spectra obtained in solution and in the solid state (spin-coated films) were a slight red-shift in the position of the absorption maxima in the solid films which is consistent with earlier observations on solution versus film UV-vis properties of the pure J domain.¹³

The emission spectra of spin-coated films of JPJ are shown in Figure 2. In both the base and acid form (obtained by adding a small amount of H₂SO₄ to the solution before spincoating), the J-domain emission is a broad featureless peak in the 400–550 nm region (maxima at 430 nm). The corresponding solution spectra are very similar.

The dramatic change in the UV-vis properties of the P domain upon acidification is reflected in the fluores-

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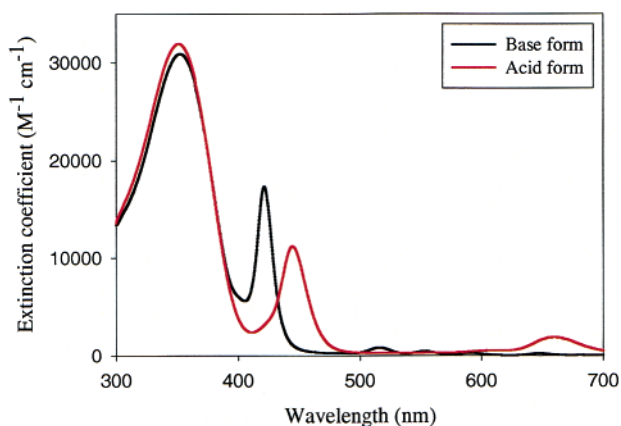


FIGURE 1. UV-vis spectra of the JPJ domain recorded in chloroform solution in the acid form or base form.

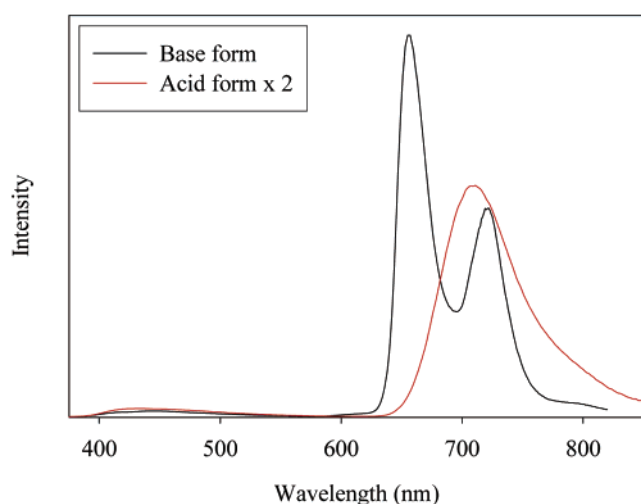


FIGURE 2. Emission spectra of spin-coated JPJ films. The spectra have been scaled to reflect the relative quantum yields of the acid and base form (note that the acid form has been multiplied by 2).

cence emission spectrum in both solution (degassed chloroform) and spincoated film; in the base form the porphyrin gives two peaks at 655 and 721 nm, but in acid form only one broad peak at 709 nm. Further lifetime of the P domain is decreased (see Table 1), and the quantum yield is increased in solution but decreased in the solid phase. The fluorescence from J domain is not affected by acid. Time-resolved emission spectroscopy (TRES) of the base form of JPJ in CHCl_3 shows that emission from the porphyrin is delayed around 1 ns compared to the emission from the J domain. We interpret this as the time it takes for the two domains to change geometry and allow for transfer energy from J to P. We assume that the majority of energy transfer is through-bond²³ and very little is through-space in solution.²⁴ However, when acid is added to the solution TRES shows that energy transfer occurs almost instantaneously (<0.1 ns). This is supported by the well-known structural change of the porphyrin skeleton when adding protons. The geometry

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TABLE 1. Lifetimes, Quantum Yields, and TRES Data for TPP and JPJ under Both Basic and Acidic Conditions^a

	<i>P</i> (ns)	Δt (ns)	quantum yield (%)
J in CHCl_3			0.009
J in film			0.08
TPP ^b (base form) in CHCl_3	14		0.13
TPP (acid form) in CHCl_3	2.9		0.24
JPJ in CHCl_3 (base form)	8.1	1	0.009 (0.45)
JPJ in CHCl_3 (acid form)	1.5	<0.1	0.011 (0.60)
JPJ film (base form)	4.8	<0.1	0.36 (0.97)
JPJ film (acid form)	2.9	<0.1	0.18 (0.91)

^a Δt is the observed delay in emission from the P domain compared the emission from the J domain in the JPJ assembly. Values in parentheses are the relative contribution from the P domain to the total quantum yield. ^b Reference 29.

of the base form is such that the porphyrin system is near-planar with the torsion angle of the substituent phenyl rings at right angles^{25,26} leading to poor overlap with the J domain. Upon protonization, the geometry of the porphyrin becomes nonplanar and the torsion angle between the substituent phenyl rings and the porphyrin system becomes nearly coplanar,^{27,28} allowing for good overlap and fast energy transfer. These structural effects have been shown by crystallization of the acid and base form. The faster energy transfer in the acid form also increases the relative contribution to the overall quantum yield from P as expected. In the spincoated films energy transfer is fast whether acid is added or not, possibly due to through-space energy transfer. The effect of acid leads to a shortening of the lifetime in solution and to both a shortening of the lifetime and a lowering of the quantum yield in the solid. We ascribe this to the interactions with the anion.

In Table 1, lifetimes, quantum yields, and TRES data are shown. In all cases, the lifetime of the J domain was lower than 1 ns and is omitted. Tetraphenylporphyrine (TPP) is used as a model compound for the P domain and is shown for comparison.

The major difference between the solution and solid-phase spectra is that the overall quantum yield of JPJ is much larger in solid phase (around 30-fold) than in solution. This is expected because there are less degrees of conformational freedom and therefore fewer pathways leading to nonradiative processes. This effect is clearly seen for pure J where the quantum yield increases 9-fold.

The energy balance can be summarized as absorption, emission, transfer, and nonradiative processes as shown in Figure 3. From this it is clear that the J domain acts as a very efficient antenna for light harvesting for the P domain, especially in the solid phase.

Recent developments have incorporated a perylene-based dye into a conducting polymer by hydrogen bonding³⁰ and covalent bonding.³¹ Neither of the reported systems, however, provide full conjugation between the

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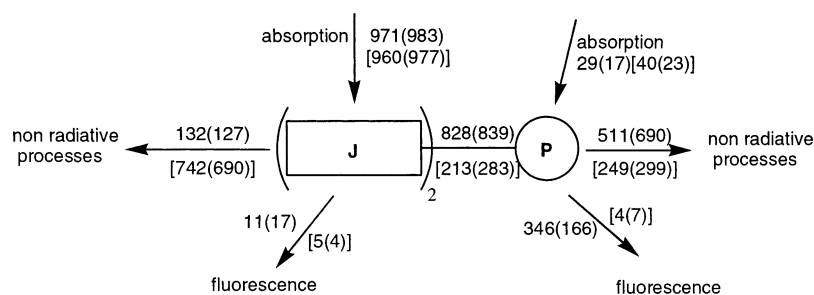


FIGURE 3. Photon balance for JPJ in spincoated film for every 1000 adsorbed photons (acid added) and [CHCl₃ solution (acid added)]. The values indicate the number of photons. The excitation wavelength is set at maximum absorption of the J domain 350 nm.

conducting polymer backbone and the dye molecule as we present in this paper. We believe that this is the explanation for the remarkable increase in the energy transfer from polymer to the dye molecule that we observe. Upon protonization, the systems become more coplanar, and we believe that this is the reason for the shortening of the energy transfer time.

We have presented the synthesis of a new dye linked conducting homopolymer along with the light harvesting properties of the three-domain structure as established using fluorescence spectroscopy.

Experimental Section

All reagents were commercially available. 4''-Cyanomethyl-2',5'-dioctyl-4-formylterphenyl was prepared as described in the literature.¹³

10,20-Diphenyl-5,15-bis(4-cyanophenyl)porphyrin (1). A solution of (4-cyanophenyl)dipyrromethane¹⁸ (2.47 g, 10.0 mmol) and benzaldehyde (1.06 g, 10.0 mmol) was prepared in CH₂Cl₂ (1 L) in a 2-L round-bottomed flask and degassed with argon. TFA (2.00 mL, 26 mmol) was added dropwise over a period of 1 min. The mixture was stirred at room temperature for 30 min, diclorodicyanobenzoquinone (2.27 g, 10.0 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through alumina (4 × 8 cm) and eluted with CH₂Cl₂ until the eluents were light brown (ca. 2 L). The solvent was evaporated to give a black solid that was dissolved in toluene (500 mL) in a 1-L round-bottomed flask. A further portion of diclorodicyanobenzoquinone (2.27 g, 10.0 mmol) was added, and the mixture was refluxed for 1 h. After being cooled to ambient temperature, the mixture was filtered through alumina (4 × 8 cm) and eluted with CH₂Cl₂ until the eluents were colorless (volume 1000 mL). The solvent was evaporated to give purple solid/crystals (1.32 g, 20%): mp > 300 °C; ¹H NMR (250 MHz, CDCl₃, 300 K, TMS) δ -2.8 (s, 2H), 7.8 (d, *J* = 6.3 Hz, 6H), 8.1 (d, *J* = 7.9 Hz, 4H), 8.2 (d, *J* = 7.3 Hz, 4H), 8.3 (d, *J* = 7.9 Hz, 4H), 8.7 (d, *J* = 4.7 Hz, 4H), 8.9 (d, *J* = 4.7 Hz, 4H); ¹³C NMR (63 MHz, CDCl₃, 300 K, TMS) δ 112.8, 118.6, 119.6, 127.5, 128.7, 131.2, 135.2, 135.7, 142.4, 147.7. Anal. Calcd for C₄₆H₂₈N₆: C, 83.11; H, 4.25; N, 12.64. Found: C, 82.81; H, 4.01; N, 12.37.

10,20-Diphenyl-5,15-bis(4-formylphenyl)porphyrin (2). Compound **1** (500 mg, 0.75 mmol) was dissolved in CHCl₃ (300

mL) and degassed with argon, and DIBAL-H (3 mL, 1 M in toluene) was added dropwise through septa. The reaction mixture was refluxed, monitored by MALDI-TOF, cooled to room temperature, and quenched with saturated NH₄Cl after ca. 1.5 h. The mixture was washed with water (500 mL), and the organic phase was isolated, dried (MgSO₄), and evaporated to give a purple solid. The solid was purified by flash column chromatography (silica, CHCl₃/ethyl acetate (50:1), *R_f* = 0.6, CH₂-Cl₂/ethyl acetate (20:1)). The fractions containing the desired porphyrin were collected, evaporated, and recrystallized from Et₂O/CHCl₃ (4:1) to give a purple solid (84 mg, 17%): mp > 300 °C; ¹H NMR (250 MHz, CDCl₃, 300 K, TMS) δ -2.8 (s, 2H), 7.8 (d, *J* = 6.0 Hz, 6H), 8.2 (d, *J* = 7.4 Hz, 4H), 8.3 (d, *J* = 8.2 Hz, 4H), 8.4 (d, *J* = 8.2 Hz, 4H), 8.8 (d, *J* = 4.7 Hz, 4H), 8.9 (d, *J* = 4.7 Hz, 4H), 10.4 (s, 2H); ¹³C NMR (63 MHz, CDCl₃, 300 K, TMS) δ 119.3, 121.5, 127.5, 128.7, 135.2, 135.9, 136.5, 142.5, 149.2, 192.9. Anal. Calcd for C₄₆H₃₀N₄O₂: C, 82.37; H, 4.51; N, 8.35. Found: C, 82.21; H, 4.19; N, 8.51.

10,20-Diphenyl-5,15-bis(4-(poly-2',5'-dioctyl-4,4''-terphenylene-1-cyanovinylene-2-yl)phenyl)porphyrin (3). Compound **2** (24 mg, 0.036 mmol) was mixed with 4''-cyanomethyl-2',5'-dioctyl-4-formylterphenyl (0.5 g, 0.96 mmol) in DMF (20 mL). The mixture was heated to 60 °C, *t*-BuOK (50 mg, catalyst) dissolved in DMF (1 mL) was added, and the mixture was stirred for 3 min whereupon it became first green and then dark brown/red and a precipitate started to form. *n*-Bu₄NOH (aq) (40%, 0.25 mL) was added, and the mixture was stirred for 10 min at rt. Water (150 mL) was added followed by HCl (aq) (37%) until it was strong green. The mixture was stirred for 5 min. Filtering and drying gave the crude green product as the hydrochloride (0.45 g after drying). The crude product was shaken in chloroform (100 mL) containing Et₃N (1 mL) over the weekend and then filtered to remove a small amount insoluble material. This solution (5 mL) was then used directly for preparative GPC, and the remaining solution was concentrated to a volume of 25 mL that was poured into methanol (400 mL) and evaporated to a volume of 50 mL where the material suddenly precipitated as a light brown material that was filtered and dried to give a dark brown solid in 85% yield (0.42 g): ¹H NMR (250 MHz, CDCl₃, 300 K, TMS) δ -2.78 (broad s, 2H), 0.81 (broad s, 130H), 1.2 (broad s, 450H), 1.5 (broad s, 90H), 2.5 (broad s, 90H), 7.1–8.0 (m, 230H) 10.1 (s, 2H); *M_p* = 7780; *M_n* = 4560; *M_w*/*M_n* = 2.741.

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Supporting Information Available: Photophysical methods, absorption spectra, lifetime decays, and emission spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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