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## Introduction

Porphyrins and their tetrapyrrolic relatives are important compounds because of their various roles in biology as light absorbers, redox centers and binding sites for small molecules, and because of their applications (real and potential) in artificial photosynthesis, molecule-based (opto)electronics and data processing, sensing, medical imaging and treatment, and related areas. Many of these applications use both the light-absorbing and redox properties of porphyrins to convert light energy into electrochemical potential. For actual device applications, the incorporation of porphyrins into conducting or semiconducting media is especially convenient because it allows photoinduced charge separation involving a porphyrin followed by charge migration to an electrode and thence into an electronic circuit. However, given the plethora of literature on porphyrin chemistry, relatively few conducting or semiconducting porphyrin polymers in which the porphyrin forms the polymer backbone (rather than a side chain) have been reported. Much of the research on conducting porphyrin polymers has been carried out by electropolymerization of porphyrin monomers to give semiconducting films on electrodes,1-16 although some examples of solution chemical methods for formation of long porphyrin oligomers or polymers have been reported.<sup>17-31</sup> We have reported the electrochemical preparation and properties of polyporphyrins<sup>32,33</sup>

# Synthesis and spectroscopic properties of a soluble semiconducting porphyrin polymer

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A semiconducting porphyrin polymer that is solution processable and soluble in organic solvents has been synthesized, and its spectroscopic and electrochemical properties have been investigated. The polymer consists of diarylporphyrin units that are linked at *meso*-positions by aminophenyl groups, thus making the porphyrin rings an integral part of the polymer backbone. Hexyl chains on two of the aryl groups impart solubility. The porphyrin units interact only weakly in the ground electronic state. Excitation produces a local excited state that rapidly evolves into a state with charge-transfer character (CT) involving the amino nitrogen and the porphyrin macrocycle. Singlet excitation energy is transferred between porphyrin units in the chain with a time constant of *ca.* 210 ps. The final CT state has a lifetime of several nanoseconds, and the first oxidation of the polymer occurs at *ca.* 0.58 V vs. SCE. These properties make the polymer a suitable potential excited state electron donor to a variety of fullerenes or other acceptor species, suggesting that the polymer may find use in organic photovoltaics, sensors, and similar applications.

and polyporphyrin-fullerene dyads<sup>34</sup> based on monomers featuring both a free *meso*-position and a *meso*-aminophenyl group. Electropolymerization generates semiconducting polymers in which porphyrin macrocycles are joined by aminophenyl linkers reminiscent of polyaniline. Although these and other electropolymerized porphyrins are interesting and potentially useful materials, both their study and their applications are limited by the fact that they are bound as thin films to electrodes from which they cannot be removed, and are essentially insoluble in liquids.

We now report the synthesis and spectroscopic properties of a structurally closely related porphyrin polymer which is prepared by chemical reaction in solution; soluble in a variety of organic solvents including tetrahydrofuran, chlorobenzene, anisole, and benzonitrile; and solution processable *via* spin coating, drop casting or other methods. This polymer (**P**-(**PN**)<sub>*n*</sub>, Fig. 1) has the same polymeric backbone as the electropolymers we reported earlier, and features 3,5-dihexyl substituted phenyl groups at two *meso*-positions. These hexyl chains greatly increase the solubility of the polymer relative to the electrochemically produced polymers, which had mesityl groups at these two *meso*-positions.

## **Results and discussion**

#### Synthesis and characterization

Zinc monomer **PBr** was synthesized from readily available precursors by a series of reactions (see Experimental section),



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Fig. 1 Structure and synthesis of porphyrin polymer **P-(PN)**<sub>n</sub>. Synthetic details are given in the text.

and the polymer  $P-(PN)_n$  was prepared by palladium-catalyzed coupling of **PBr** (Fig. 1). The catalyst was prepared *in situ* in tetrahydrofuran by mixing palladium( $\pi$ ) acetate and bis[(2diphenylphosphino)phenyl] ether, and then adding an excess of cesium carbonate. Polymerization ensued, leading to the zinc form of the polymer. Treatment with trifluoroacetic acid in dichloromethane removed the zinc to yield free base **P**-(**PN**)<sub>*n*</sub>. Column chromatography was used to remove impurities and any remaining monomer. Subsequently, chromatography was used to separate the polymer into three fractions, **A**, **B**, and **C**. Details of a typical preparation of the polymer are given in the Experimental section.

Based on the order of elution in column chromatography, fractions A, B, and C were postulated to contain  $P-(PN)_n$  of increasing average molecular weight, respectively. Inductively coupled plasma elemental analysis showed that there was no detectable palladium in any of these fractions. Mass spectrometry was consistent with this assumption. Analysis was performed using MALDI-TOF instrumentation and a diphenylbutadiene matrix. This technique was not quantitative because the higher oligomers did not volatilize readily in the mass spectrometer. Thus, the ratios of peak heights does not correspond to the relative abundances of the various chains, but the technique verified the presence of the expected polymeric material and allowed some conclusions about average chain length to be drawn. All three fractions showed that no monomer was present, and chain lengths up to at least 13 units could be detected unambiguously. Longer chains were present in these samples, but their low volatility coupled with a tendency of the material to associate with itself in the mass spectrometer prevented their quantification. The mass spectrum of fraction A showed large contributions of chains with 2-7 units plus longer chains. Fraction **B** was less easily volatilized in the mass spectrometer than **A**, and showed smaller signals for chains with 2, 3, 4 and 6 porphyrins, but significant peaks for 5-unit and longer chains. Fraction **C** was dominated by high molecular weight polymer that did not volatilize, and the signal to noise obtained was therefore low. Chain lengths up to 13 were observed, but most of the material likely consists of longer chains.

The polymer was also investigated by <sup>1</sup>H-NMR spectroscopy. Solutions of the polymer in deuterated chloroform were studied at 400 MHz. The spectra obtained were characterized by very broad resonances due to the long chain lengths and possible aggregation of the chains. The broadness of the resonances also accentuated resonances from minor impurities with sharp resonances, and this complicated analysis. However, for samples of all three types, resonances expected for the postulated structure were observed, thus confirming the structure. An attempt was made to estimate chain lengths by comparison of the integrals of unique protons at the ends of the polymer chains (i.e. the meso- and beta-protons of the terminal porphyrin which lacks a meso-amino group, and the aryl and amino protons of the terminal porphyrin at the other end of the chain) with those of the aliphatic protons of the hexyl side chains of the internal porphyrins. This method was only approximate, as overlapping resonances and large differences in relaxation times are present, but suggested that fraction A contained significant amounts of chains with an average length of about 6 porphyrin units, whereas fractions B and C had average chain lengths of at least 20 units.

Several model compounds were prepared, including a model<sup>32</sup> **MP** for the porphyrin **P** at the end of the chain, a model **MPN** for the porphyrin at the amino end of the polymer chain, and a dimer **MP-PN** model for a two-porphyrin section of the polymer. These are shown in Fig. 2, and details of their preparation are reported in the Experimental section.

#### Spectroscopic properties

Monomers. The spectroscopic properties of model compounds were investigated in order to aid in the elucidation of the



Fig. 2 Structures of model monomeric and dimeric porphyrins.



Fig. 3 Spectra of model compounds in 2-methyltetrahydrofuran. Absorption spectra of MP (red), MPN (black), and MP-PN (blue) and corrected emission spectra of MP (red dash), MPN (black dash) and MP-PN (blue dash). All spectra have been normalized for ease in comparison.

spectroscopic properties of the polymer. The absorption spectra in 2-methyltetrahydrofuran solution of model porphyrin MP, which has only hydrogen at meso-position 15, and model MPN, which has an aminotolyl group at the corresponding position, are shown in Fig. 3. The spectrum of MP is typical of free base porphyrins with a sharp Soret band at 413 nm and four Q-band maxima at 509, 544, 588 and 642 nm. The spectrum of MPN, on the other hand, has a broad Soret band at 428 nm and broad Q-band absorption, with maxima at 521, ca. 570, ca. 590, and 675 nm. Thus, the presence of the meso-amino group in MPN leads to significant distortion of the spectrum, relative to those of other free base tri- or tetraarylporphyrins. Differences are also seen in the fluorescence emission spectra (Fig. 3). The spectrum of MP is similar to that of other triarylporphyrins, with maxima at 649 and 713 nm. Molecule MPN, on other hand, shows an emission peak at 714 nm, with a shoulder at ca. 775 nm.

These results suggest that the excited state of **MPN** is significantly perturbed from that of other porphyrins due to the presence of the *meso*-amino group. We investigated the solvent dependence of the spectra in order to get more information about this perturbation. Five solvents were investigated: acetonitrile ( $\varepsilon = 37.5$ ), 1-decanol ( $\varepsilon = 8.1$ ), 2-methyltetrahydrofuran ( $\varepsilon = 7.0$ ), toluene ( $\varepsilon = 2.4$ ) and cyclohexane ( $\varepsilon = 2.0$ ). The absorption spectra of **MP** and **MPN** showed relatively small solvent effects over this range of solvents. Porphyrin **MP** also showed only small shifts in emission. The shortest-wavelength emission band of **MP** is found at 647 nm in both cyclohexane and acetonitrile. On the other hand, larger solvent effects were observed for **MPN** in emission (Fig. 4). The main emission band appears at 696 nm in cyclohexane and 720 nm in acetonitrile.

It is clear from these studies that the energy of the relaxed first excited singlet state of **MPN** has a significant dependence on solvent polarity, as illustrated by the emission results, whereas that of **MP** shows only small effects. Upon increasing the dielectric constant of the solvent from 2.0 to 37.5, the shortest wavelength emission band of **MPN** shifts by 24 nm to longer wavelengths, whereas there is no observed shift in the corresponding emission of **MP**. The Stokes shift for **MPN** in 2-methytetrahydrofuran is 38 nm, whereas that for **MP** is



**Fig. 4** Fluorescence emission from a solution of **MPN** with excitation at 420 nm. The spectra are normalized at the emission maximum. Solvents were cyclohexane (solid), toluene (dashed), 2-methyltetrahydrofuran (dash-dot), 1-decanol (dash-dot-dot), and acetonitrile (dot).

only 7 nm. Clearly, more polar solvents stabilize the excited state of **MPN** relative to the ground state. These data suggest that the excited state of **MPN** has significant charge-transfer (CT) character, and the more polar solvents stabilize the charge-transfer state. Presumably this state arises from increased electron donation from the amino group to the porphyrin macrocycle in the excited state, giving the amino group more positive character.

Because the excited state behavior observed in **MP** and **MPN** is also expected to play a role in the photochemistry of the polymer, we investigated the emission of the model compounds as a function of time after excitation. Fluorescence decays were measured using the single photon timing technique. The emission spectrum of **MP** in 2-methyltetrahydrofuran was measured at 8 wavelengths in the 620–760 nm region, and the spectra were fitted globally to derive decay-associated spectra (DAS). The data were fitted well as a single exponential decay ( $\chi^2 = 1.06$ ) with a time constant of 9.53 ns. Such an excited state lifetime is typical for porphyrins of this general type.

The decay-associated spectra from time-resolved fluorescence experiments on **MPN** are shown in Fig. 5. The decays were multiexponential in all of the solvents investigated. Two components were observed in cyclohexane, 2-methyltetrahydrofuran and acetonitrile, and four components were seen in 1-decanol. In all solvents, a relatively long-lived component was observed. The shape of this component is similar to that of the emission spectra shown in Fig. 4: this is expected, as this component is mainly responsible for the steady-state emission spectrum. The lifetime ranges from 7.2 ns in cyclohexane, the least polar solvent, to 4.9 ns in acetonitrile, the most polar solvent. We ascribe this emission to the charge-transfer excited state discussed above.

The shorter-lived components are assigned to local excited (LE) states of **MPN** that evolve into the final charge-transfer state with the indicated time constants. Consistent with this assignment is the fact that the emission maxima of these states are all found at slightly shorter wavelengths than those of the CT states, indicating that these LE states are of higher energy than the CT state. The results in decanol most clearly show that the decays of the emissions of these shorter-lived states



**Fig. 5** Decay-associated emission spectra in various solvents of **MPN** with excitation at 520 nm. (a) Cyclohexane: 7.2 ns (circles), 190 ps (squares); (b) 2-methyltetrahydrofuran: 5.7 ns (circles), 100 ps (squares); (c) acetonitrile: 4.9 ns (circles), 120 ps (squares); (d) 1-decanol: 5.4 ns (circles), 1.96 ns (squares), 380 ps (diamonds), 63 ps (triangles).

(positive amplitudes in Fig. 5d) have the same time constants as a rise of emission amplitude in the region of CT emission (negative amplitudes in Fig. 5d). This indicates that the LE states decay to give the CT state. Decanol is a viscous solvent that may retard intramolecular motions that accompany relaxation of the LE states to the CT state, and permit observation of relaxations that are too fast to measure in the other solvents. It is also possible that different hydrogen bonding interactions between decanol and the *meso*-amino group of **MPN** play a role.

**Dimer.** We now turn to dimer **MP-PN**, which features a porphyrin bearing a *meso*-amino group linked *via* this moiety to a porphyrin with only a hydrogen atom at one *meso* position.

Thus, it is a model for P-(PN)<sub>1</sub>. The absorption spectrum of MP-PN (Fig. 3) features a Soret maximum at 410 nm with a strong shoulder at ca. 425 nm. The Q-band region is broad, with absorption maxima discernable at 512, ca. 550, 587, and ca. 670 nm. The spectrum is essentially a linear combination of the spectra of MP and MPN, with very minimal changes due to interactions between the chromophores. The fluorescence emission spectrum of MP-PN with excitation at 520 nm is very similar to that of MPN (Fig. 3). There is only minimal emission around 650 nm, where MP emits. Both porphyrins have some absorbance at 520 nm, yet emission from PN dominates the spectrum. This indicates that singlet excitation energy is rapidly transferred from the excited singlet state of MP to PN. This is expected because the linkage between the two chromophores is short, and the emission of MP overlaps well with the absorption of the longest-wavelength Q-band of PN. These conditions favor rapid singlet-singlet energy transfer by the Förster-type (dipole-dipole) mechanism.<sup>35,36</sup> Thus, in dimer MP-PN, the two chromophores appear to not interact strongly in the ground state, and to exhibit efficient energy transfer in the excited state.

Additional information concerning **MP-PN** comes from timeresolved fluorescence studies. Fig. 6a shows the DAS for **MP-PN** in 2-methyltetrahydrofuran with excitation at 520 nm. The DAS features a long-lived component (6.0 ns) with a shape similar to that of the CT emission from **MPN** which is assigned to decay of the **MP-<sup>1</sup>PN** charge-transfer state. Additional decay components of 540 ps and 36 ps have maxima at slightly shorter wavelengths than does the CT state, and the shapes of the DAS prove that these shorter components decay to form the final CT state.



Fig. 6 Decay-associated emission spectra with excitation at 520 nm in 2-methyltetrahydrofuran solution. (a) **MP-PN**, 6.0 ns (circles), 540 ps (squares), 36 ps (triangles); (b) **P-(PN)**<sub>n</sub>, 5.4 ns (circles), 1.1 ns (triangles), 200 ps (squares).



Fig. 7 Absorption spectra of **MP-PN** (solid) and **P-(PN)**<sub>n</sub> (dash) in 2-methyltetrahydrofuran, absorption spectrum of **P-(PN)**<sub>n</sub> as a film on glass (dash-dot-dot), and emission with excitation at 520 nm of **MP-PN** (dash-dot) and **P-(PN)**<sub>n</sub> (dot). The absorption spectra have been normalized at the Soret maximum. The emission spectra show emission intensity ratios with excitation of solutions of equal absorbance at 520 nm.

We ascribe these components to LE states similar to those noted above for MPN alone. It is tempting to ascribe one of these components instead to energy transfer from <sup>1</sup>MP-PN. However, this could not be verified unambiguously. As mentioned earlier, MPN alone shows similar short components, especially in 1-decanol. In addition, a cyclic pentamer, PN5, has been prepared (to be described elsewhere), and its DAS in various solvents show similar components. Energy transfer from a porphyrin having only a hydrogen atom on a *meso*-position is impossible in this pentamer due to the absence of such a porphyrin. Thus, energy transfer from <sup>1</sup>MP-PN to yield MP-<sup>1</sup>PN definitely occurs in MP-PN, but its time scale cannot be unambiguously deduced from our measurements. Ideally, excitation of MP only with observation of emission from <sup>1</sup>PN could allow determination of such transfer, but as seen in Fig. 3, there is no suitable wavelength for such an experiment.

**Polymer.** With the results for model compounds in hand, we now examine the spectroscopic properties of the polymer  $P-(PN)_n$ . Experiments were performed on fraction **B** from the synthesis discussed above. The absorption spectrum in 2-methyltetrahydrofuran of the polymer, which consists of a range of chain lengths, is shown in Fig. 7, along with that of dimer **MP-PN** for comparison. The Soret band appears at 415 nm in the polymer (*vs.* 410 for **MP-PN**), and is very broad, with no sharp peak in the region where **MP** absorbs. This is due to the higher ratio of **PN** to **P** in the oligomeric material. Absorption in the Q-band region is broad, with maxima at 520, 575, and 664. In fact, the Q-band region appears very similar to the corresponding region for **MPN** (Fig. 3). Thus, the spectrum indicates limited ground-state interaction between the porphyrin units.

The absorption spectrum of  $\mathbf{P}$ -( $\mathbf{PN}$ )<sub>*n*</sub> when cast as a film on a glass slide is also shown in Fig. 7. The spectrum has similar features to those of the solution spectrum, but the peaks are broader and shifted to longer wavelengths.

Excitation of a solution of  $P(PN)_n$  in 2-methyltetrahydrofuran at 520 nm yielded the emission spectrum shown in Fig. 7.

The shape of the emission is similar to that of the emission of **MP-PN** as well as that of **MPN** (Fig. 3), indicating that emission arises entirely from the **PN** subunits. With identical absorbance at the excitation wavelength, the emission of  $P-(PN)_n$  is about 10 times weaker than that from **MP-PN**.

A time-resolved study of the emission of P-(PN), was performed in 2-methyltetrahydrofuran, with excitation at 520 nm. As shown in Fig. 6b, the main emission component has a decay time constant of 5.4 ns, which is only slightly shorter than that for MP-PN. Additional decay components were observed, as was the case with the dimer and MPN monomer. These had values of 200 ps and 1.1 ns. We assign these short components to LE states that decay to give the longer-lived CT state, as occurs in the monomer and dimer. We assume that the shorter-lived transient states in P-(PN), and MP-PN decay into the longest-lived emitting states, as was seen in MP-PN. Without knowing the yields of the conversion of the LE states into the CT state for each molecule, we cannot determine whether a portion of the 10-fold quenching in emission intensity in the polymer relative to MP-PN may be due to differences in the rates of processes that occur in both compounds, or to processes not present in the model dimer.

**Fluorescence anisotropy and energy transfer.** In principle, singlet–singlet energy transfer between porphyrin units in the polymer is possible. We isolated, by careful and repeated chromatography, a fraction of polymer containing essentially pure **P-(PN)**<sub>3</sub> in order to investigate this phenomenon. Fluorescence anisotropy decay measurements were carried out on **MP-PN** and **P-(PN)**<sub>3</sub> in 2-methyltetrahydrofuran solution at ambient temperatures (Fig. 8). The molecules were excited at 680 nm where the porphyrins bearing *meso*-amino substituents absorb and the fluorescence anisotropy was measured at 780 nm, where



Fig. 8 Fluorescence anisotropy decays with excitation at 680 nm and detection at 780 nm. (a) Dimer **MP-PN**. The white line is a best exponential fit to the data with a time constant of 635 ps. (b) Tetramer **P-(PN)**<sub>3</sub>. The white line is a best exponential fit to the data with a time constants of 105 ps and 1.49 ns.

#### Paper

emission is also from the PN components. Fluorescence anisotropy will decay with time constants related to overall tumbling of the molecule in solution and also energy transfer between porphyrins, which results, in effect, in reorientation of the transition dipole. The anisotropy decay for dimer MP-PN was well fitted by a single exponential time constant of 635 ps. This is ascribed to rotational tumbling of the molecule in solution. The decay for tetramer P-(PN)<sub>2</sub> required two exponential components with time constants of 105 ps (49% of the decay) and 1.49 ns (51% of the decay). The 1.49 ns component is due to overall tumbling of the molecule, and is longer than the corresponding component in MP-PN because of the larger size of the molecule. The 105 ps component is assigned to energy transfer between adjacent mesoaminoporphyrins, and corresponds to an approximate time constant for singlet-singlet energy transfer of 210 ps. Although two adjacent porphyrin moieties are relatively close together spatially their excited states are isoenergetic, which results in a relatively small spectral overlap integral in the Förster equation<sup>36</sup> for singletsinglet energy transfer and relatively slow energy transfer compared to systems in which the spectral overlap integral is large (e.g., energy transfer from zinc porphyrins to free base porphyrins).

#### **Electrochemical properties**

The cyclic voltammograms of the polymer and model compounds were obtained in benzonitrile solution with tetra-nbutylammonium hexafluorophosphate as supporting electrolyte. As reported previously,<sup>32</sup> monomer MP shows two irreversible overlapping oxidation peaks in the region 0.9-1.1 V vs. SCE and a third irreversible peak around 1.3 V. These potentials are similar to the first and second oxidation potentials of 5,10,15,20tetraphenylporphyrin in benzonitrile (1.08 and 1.25 V)37 and the redox potential of aniline in acetonitrile (0.90 V).<sup>38</sup> The lack of reversibility is consistent with formation of an electropolymerized film on the platinum electrode. Fig. 9a shows cyclic voltammograms for dimer MP-PN in benzonitrile. The solubility of the dimer and the polymer were low in this solvent, which resulted in a large capacitive current contribution to the voltammogram. The first potential sweep shows oxidations at 0.58 V and 1.04 V that are essentially irreversible. The peak at 1.04 V is assigned to the first oxidation of the porphyrin with the free meso-position by analogy to monomer MP and the second oxidation of PN. The peak at 0.58 V is assigned to the first oxidation of porphyrin PN, which bears both a meso-amino functionality and an aniline ring. This value is consistent with redox potentials for other porphyrins with meso-amino substituents.<sup>39</sup> As can be seen in Fig. 9a, the second and subsequent voltage scans of MP-PN show irreversible behavior under these conditions, and each sweep results in less current than the previous scan. This is consistent with formation of a film of some sort on the electrode, although MP-PN cannot form polymer chains, as does MP.

Turning now to polymer  $P(PN)_n$ , the voltammograms in Fig. 9b, it is clear that the behavior is generally similar to that observed for the dimer **MP-PN**, although the peaks are not well resolved due to lack of solubility, the irreversible behavior and deposition of a film on the electrode. Oxidation waves at *ca.* 0.6



Fig. 9 Cyclic voltammograms for (a) dimer **MP-PN** and (b) polymer **P-(PN)**<sub>n</sub> in deaerated benzonitrile containing tetra-*n*-butylammonium hexafluoro-phosphate. Voltage was swept at 100 mV s<sup>-1</sup>.

and 1.0 V vs. SCE are observed. The 0.6 V wave is ascribed to oxidation of porphyrin molecules within the polymer chain, and the 1.0 V wave is due to the second oxidation of these porphyrins and any contributions from the terminal porphyrins.

## **Experimental section**

#### Synthesis

The preparation of **MP** was reported previously.<sup>32</sup> The <sup>1</sup>H NMR spectra were recorded on a Varian Inova 400 or a Varian Inova 500 spectrometer. Mass spectra were obtained on a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). Ultraviolet-visible ground state absorption spectra were measured on a Shimadzu UV2100U spectrometer.

**3,5-Dihexylbenzaldehyde (1).** To a flask containing 4.0 g (13 mmol) of methyl-3,5-dihexylbenzoate<sup>40</sup> and 80 mL of

tetrahydrofuran (THF) was added 0.50 g (13 mmol) of lithium aluminum hydride (LAH) in small quantities until the ester had been reduced to the corresponding alcohol. The progress of the reaction was followed by thin layer chromatography (THC) (hexanes/10% ethyl acetate). The reaction mixture was cooled in ice water and small lumps of ice were added to the reaction flask to quench excess LAH. The resulting suspension was filtered through celite and the residue was washed with dichloromethane/10% methanol. The filtrate was evaporated to dryness, and the residue was redissolved in dichloromethane (100 mL) and then washed with aqueous citric acid followed by aqueous sodium bicarbonate. The organic layer was dried over anhydrous sodium sulfate and concentrated to a viscous oil by evaporation of the solvent at reduced pressure. This material was dissolved in dichloromethane (100 mL) and to the stirred solution was added portions of activated manganese dioxide such that the alcohol was converted to the corresponding aldehyde. The progress of the reaction was followed by TLC (hexanes/10% ethyl acetate). Once the reaction was complete, the suspension was filtered through Celite and the residue was washed with dichloromethane/20% methanol solution (100 mL). The filtrate was evaporated to dryness and the residue was chromatographed on silica gel (hexanes/5% ethyl acetate) to give 1 as a viscous oil (2.92 g, 81% yield).<sup>1</sup>H NMR (400 MHz)  $\delta$  0.88 (6H, t, J = 6 Hz, -CH<sub>3</sub>), 1.31-1.38 (12H, m, -CH<sub>2</sub>-), 1.59-1.67 (4H, m, -CH<sub>2</sub>-), 2.65  $(4H, t, J = 8 Hz, -CH_2)$ , 7.26 (1H, s, Ar-H partially obscured by CDCl<sub>3</sub>), 7.51 (2H, s, Ar-H), 9.97 (1H, s, -CHO); MALDI-TOF-MS m/z calcd for C<sub>19</sub>H<sub>30</sub>O<sub>1</sub> 274.2, obsd 273.8.

5,15-Bis-(3,5-dihexylphenyl)porphyrin (2). To a flask containing 3.30 g (22.6 mmol) of 2,2'-dipyrromethane, 6.20 g (22.7 mmol) of 3,5-dihexylbenzaldehyde (1) and 2.3 L of chloroform was added 1.72 mL of boron trifluoride diethyl etherate. Stirring under an argon atmosphere was carried out in the dark for 30 min. A 5.14 g portion of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was added to the reaction mixture and stirring was continued for 1 h. The dark solution was reduced in volume to approximately 1 L by distillation of the solvent at reduced pressure and then gently shaken with aqueous sodium bicarbonate (1 L). Once the two layers had separated the organic phase was washed a further three times with fresh bicarbonate solution. The organic layer was then concentrated to a viscous oil by distillation of the solvent at reduced pressure and this oil was chromatographed on silica gel (hexanes/dichloromethane, 5:1 to 3:1). The appropriate fractions were combined, the solvent was evaporated and the residue was recrystallized from dichloromethane/methanol to give 3.56 g of 2 (40% yield). <sup>1</sup>H NMR  $(400 \text{ MHz}) \delta - 3.08 (2\text{H, s}, -\text{NH}), 0.92-0.95 (12\text{H, t}, J = 7 \text{ Hz}, -\text{CH}_3),$ 1.37-1.45 (16H, m, -CH2-), 1.50-1.58 (8H, m, -CH2-), 1.92-1.85 (8H, m, -CH<sub>2</sub>-), 2.92 (8H, t, J = 8 Hz, -CH<sub>2</sub>-), 7.43 (2H, s, Ar-H), 7.91 (4H, s, Ar-H), 9.12 (4H, d, J = 5 Hz, β-H), 9.38 (4H, d, J = 5 Hz, β-H), 10.30 (2H, s, meso-H); MALDI-TOF-MS m/z calcd for C<sub>56</sub>H<sub>70</sub>N<sub>4</sub> 798.6, obsd 798.5; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 408, 503, 537, 576, 631 (nm).

**5-Bromo-10,20-bis-(3,5-dihexylphenyl)porphyrin (3).** To a flask containing 1.00 g (1.25 mmol) of 2 and 200 mL of chloroform was added 223 mg (1.25 mmol) of *N*-bromosuccinimide. After stirring the reaction mixture for 15 min, TLC (hexanes/ dichloromethane, 2:1) indicated that the product was present together with lesser amounts of the starting material and the dibrominated porphyrin. The reaction mixture was concentrated to a viscous oil by evaporation of the solvent at reduced pressure and this oil was chromatographed on silica gel (hexanes/dichloromethane, 4:1 to 3:1) to give 1.17 g of 3 (68% yield). <sup>1</sup>H NMR (400 MHz)  $\delta$  –2.97 (2H, s, –NH), 0.93 (12H, t, *J* = 7 Hz, –CH<sub>3</sub>), 1.36–1.44 (16H, m, –CH<sub>2</sub>–), 1.48–1.56 (8H, m, –CH<sub>2</sub>–), 1.83–1.91 (8H, m, –CH<sub>2</sub>–), 2.89 (8H, t, *J* = 8 Hz, –CH<sub>2</sub>–), 7.43 (2H, s, Ar–H), 7.85 (4H, s, Ar–H), 8.99 (2H, d, *J* = 4 Hz, β-H), 9.00 (2H, d, *J* = 4 Hz, β-H), 9.28 (2H, d, *J* = 4 Hz, β-H), 9.73 (2H, d, *J* = 5 Hz, β-H), 10.16 (1H, s, *meso*-H); MALDI-TOF-MS *m*/*z* calcd for C<sub>56</sub>H<sub>69</sub>N<sub>4</sub>Br 876.5, obsd 876.4; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 416, 512, 547, 588, 645 (nm).

5-(4-t-Butylphenylcarbamate)-10,20-bis-(3,5-dihexylphenyl)porphyrin (4). To a heavy walled glass tube was added 1.00 g (1.14 mmol) of 3, 3.64 g (11.4 mmol) of 4-(boc-amino)benzeneboronic acid pinacol, 4.83 g (22.8 mmol) of tribasic potassium phosphate and 20 mL of THF. The suspension was flushed with a stream of argon gas for 10 min, 132 mg (0.11 mmol) of tetrakis-(triphenylphosphine)palladium(0) was added and the argon flushing procedure was continued for an additional 10 min. The tube was sealed with a Teflon<sup>™</sup> screw plug and warmed to 67 °C. After 17 h, the tube was cooled and TLC (hexanes/dichloromethane, 1:1) of the contents indicated that all the starting material had been consumed. The reaction mixture was filtered through Celite and the filtrate was concentrated to dryness by evaporation of the solvent. The residue was chromatographed on silica gel (hexanes/dichloromethane, 2:1 to 1:1) to give 985 mg (87% yield) of 4. <sup>1</sup>H NMR (400 MHz)  $\delta$ -2.98 (2H, s, -NH), 0.92 (12H, t, J = 7 Hz, -CH<sub>3</sub>), 1.32-1.42 (16H, m, -CH2-), 1.46-1.56 (8H, m, -CH2-), 1.64 (9H, s, -CH3), 1.82-1.88 (8H, m,  $-CH_2$ -), 2.88 (8H, t, J = 8 Hz,  $-CH_2$ -), 6.83 (1H, s, -NH), 7.41 (2H, s, Ar-H), 7.75 (2H, d, J = 8 Hz, Ar-H), 7.82 (4H, s, Ar-H), 8.13 (2H, d, J = 8 Hz, Ar-H), 8.89 (2H, d, J = 4 Hz, β-H), 8.93  $(2H, d, J = 4 Hz, \beta-H), 9.04 (2H, d, J = 4 Hz, \beta-H), 9.32 (2H, d, J)$ J = 4 Hz,  $\beta$ -H), 10.19 (1H, s, meso-H); MALDI-TOF-MS m/z calcd for C<sub>67</sub>H<sub>83</sub>N<sub>5</sub>O<sub>2</sub> 989.6, obsd 989.6; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 414, 510, 545, 584, 639 (nm).

5-Bromo-15-(4-tert-butylphenylcarbamate)-10,20-bis-(3,5dihexylphenyl)porphyrin (5). To a 1 L flask containing 2.90 g (2.93 mmol) of 4 and 400 mL of chloroform was added 547 mg (3.07 mmol) of N-bromosuccinimide. The solution was stirred for 20 min, after which time TLC (hexanes/dichloromethane, 1:1) indicated that the reaction was complete. The reaction mixture was washed with aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated to dryness by distillation of the solvent under reduced pressure. The resulting material was chromatographed on silica gel (hexanes/dichloromethane, 5:2 to 3:2) to give 2.81 g (90% yield) of 5. <sup>1</sup>H NMR (400 MHz)  $\delta$  -2.74 (2H, s, -NH), 0.91 (12H, t, J = 7 Hz, -CH<sub>3</sub>), 1.34-1.41 (16H, m, -CH2-), 1.46-1.52 (8H, m, -CH2-), 1.64 (9H, s, -CH<sub>3</sub>), 1.81-1.88 (8H, m, -CH<sub>2</sub>-), 2.87 (8H, t, J = 8 Hz, -CH<sub>2</sub>-), 6.82 (1H, s, -NH), 7.41 (2H, s, Ar-H), 7.75 (2H, d, J = 8 Hz, Ar-H), 7.82 (4H, s, Ar-H), 8.10 (2H, d, J = 8 Hz, Ar-H), 8.82 (4H, s,  $\beta$ -H), 8.92 (2H, d, J = 4 Hz,  $\beta$ -H), 9.65 (2H, d, J = 5 Hz,  $\beta$ -H); MALDI-TOF-MS m/z calcd for C<sub>67</sub>H<sub>82</sub>N<sub>5</sub>O<sub>2</sub>Br 1067.6, obsd 1067.5; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 422, 520, 556, 597, 654 (nm).

5-Bromo-15-(4-aminophenyl)-10,20-bis-(3,5-dihexyl-phenyl)porphyrin (6). To a flask containing a solution of 1.5 g (1.40 mmol) of 5 dissolved in 40 mL of dichloromethane was added 60 mL of trifluoroacetic acid. The green solution was stirred under an argon atmosphere for 20 min, whereupon TLC (hexanes/dichloromethane, 1:1) indicated that the reaction was complete. The reaction mixture was diluted with 200 mL of dichloromethane and washed with water (200 mL) several times. The organic layer was then washed with aqueous sodium bicarbonate, dried over anhydrous sodium sulfate and then concentrated to dryness by evaporation of the solvent. The residue was chromatographed on silica gel (dichloromethane/hexanes, 3:4 to 1:1) to give 1.24 g (91% yield) of 6. <sup>1</sup>H NMR (400 MHz)  $\delta$  -2.71 (2H, s, -NH), 0.91 (12H, t, J = 7 Hz, -CH<sub>3</sub>), 1.34-1.42 (16H, m, -CH<sub>2</sub>-), 1.46-1.52 (8H, m, -CH<sub>2</sub>-), 1.81-1.88 (8H, m, -CH<sub>2</sub>-), 2.86 (8H, t, J = 8 Hz, -CH<sub>2</sub>-), 3.98 (2H, s, -NH), 7.02 (2H, d, J = 8 Hz, Ar-H), 7.40 (2H, s, Ar-H), 7.82 (4H, s, Ar-H), 7.94 (2H, d, J = 8 Hz, Ar-H), 8.84 (2H,  $d, J = 5 Hz, \beta - H), 8.87 (2H, d, J = 5 Hz, \beta - H), 8.92 (2H, d, J = 5 Hz, \beta - H), 8.92 (2H, d, J = 5 Hz, \beta - H), 8.87 (2H$  $\beta$ -H), 9.64 (2H, d, J = 5 Hz,  $\beta$ -H); MALDI-TOF-MS m/z calcd for C<sub>62</sub>H<sub>74</sub>N<sub>5</sub>Br 967.5, obsd 967.5; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 423, 521, 559, 598, 656 (nm).

[5-Bromo-15-(4-aminophenyl)-10,20-bis-(3,5-dihexylphenyl)porphyrino zinc(II) (PBr). To a flask containing 1.20 g (1.24 mmol) of 6 and 200 mL of dichloromethane was added 50 mL of a saturated solution of zinc acetate dihydrate in methanol. After stirring for 1 h, TLC (hexanes/methylene chloride, 1:1) indicated that all the starting material had been consumed and a single product had formed. The pink reaction mixture was washed with water (200 mL) several times and then with aqueous sodium bicarbonate; it was then dried over anhydrous sodium sulfate. The solvent was evaporated at reduced pressure and the remaining solid was dried under high vacuum to give 1.21 g (95% yield) of PBr. <sup>1</sup>H NMR (400 MHz)  $\delta$  0.91 (12H, t, J = 7 Hz, -CH<sub>3</sub>), 1.32–1.41 (16H, m, -CH<sub>2</sub>-), 1.45– 1.51 (8H, m, -CH<sub>2</sub>-), 1.80-1.88 (8H, m, -CH<sub>2</sub>-), 2.86 (8H, t, *J* = 7 Hz, -CH<sub>2</sub>-), 3.82 (2H, s, -NH), 6.93 (2H, d, *J* = 8 Hz, Ar-H), 7.38 (2H, s, Ar-H), 7.82 (4H, s, Ar-H), 7.92 (2H, d, J = 8 Hz, Ar-H), 8.86 (2H, d, *J* = 4 Hz, β-H), 8.90 (2H, d, *J* = 4 Hz, β-H), 8.96 (2H, d, J = 5 Hz,  $\beta$ -H), 9.70 (2H, d, J = 5 Hz,  $\beta$ -H); MALDI-TOF-MS m/zcalcd for C<sub>62</sub>H<sub>72</sub>N<sub>5</sub>BrZn 1029.4, obsd 1029.4; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 424, 517(sh), 553, 595 (nm).

**Polymer P-(PN)**<sub>*n*</sub>. To a 250 mL heavy walled glass flask was added 1.00 g (0.97 mmol) of **PBr**, 78 mg (0.15 mmol) of bis[(2-diphenylphosphino)phenyl] ether, 442 mg (1.36 mmol) of cesium carbonate and 200 mL of THF. The suspension was flushed with a stream of argon for 15 min, 21 mg (0.01 mmol) of palladium(II) acetate was added and the argon flushing process was continued for a further 10 min. The flask was sealed with a Teflon<sup>™</sup> screw plug and the reaction mixture was stirred at 67 °C for 42 h. A TLC on silica gel (dichloromethane/hexanes, 1:1) of the reaction mixture indicated that most if not all of the starting material had been consumed and that many other compounds (polymers of different chain lengths) had formed. The reaction mixture was filtered through Celite and the residual material was thoroughly washed with THF. The combined filtrate

was concentrated by distillation of the solvent at reduced pressure and dried under high vacuum. The residue was dissolved in a mixture of dichloromethane (200 mL) and trifluoroacetic acid (200 mL) and stirred under an argon atmosphere for 1 h. The reaction mixture was then diluted with dichloromethane (200 mL) and washed with water followed by aqueous sodium bicarbonate. The solvent was then evaporated and the residue was chromatographed on silica gel (dichloromethane/2% THF, dichloromethane/20% THF and finally dichloromethane/20% THF/10% methanol) to give three fractions **A**, **B** and **C** the weight of each being, 0.43 g, 0.33 g, and 0.21 g. Characterization was performed as discussed in the Results and discussion section.

5-Bromo-15-(4-*tert*-butylphenylcarbamate)-10,20-bis(2,4,6trimethylphenyl)porphyrin (7). To a flask containing a solution of 159 mg (0.203 mmol) of 10-(4-*tert*-butylphenylcarbamate)-5,15bis(2,4,6-trimethylphenyl)porphyrin (8)<sup>32</sup> and 50 mL of chloroform was added 38 mg (0.21 mmol) of *N*-bromosuccinimide. The reaction mixture was stirred for 30 min, at which time the solvent was evaporated at reduced pressure and the residue was chromatographed on silica gel (dichloromethane/hexanes, 1:1) to give 153 mg (92% yield) of 7. <sup>1</sup>H NMR (300 MHz)  $\delta$  –2.59 (2H, s, N–H), 1.63 (9H, s, –CH<sub>3</sub>), 1.83 (12H, s, Ar–CH<sub>3</sub>), 2.63 (6H, s, Ar–CH<sub>3</sub>), 6.82 (1H, s, N–H), 7.28 (4H, s, Ar–H), 7.74 (2H, d, *J* = 8 Hz, Ar–H), 8.10 (2H, d, *J* = 8 Hz, Ar–H), 8.64 (2H, d, *J* = 5 Hz, β-H), 8.73 (2H, d, *J* = 5 Hz, β-H), 8.78 (2H, d, *J* = 4 Hz, β-H), 9.59 (2H, d, *J* = 5 Hz, β-H); MALDI-TOF-MS *m*/*z* calcd for C<sub>49</sub>H<sub>46</sub>N<sub>5</sub>O<sub>2</sub>Br 815.28, obsd 815.29; Uv/vis (CH<sub>2</sub>Cl<sub>2</sub>) 421, 520, 553, 596, 653 (nm).

Carbamate-protected form of MP-PN (9). To a glass tube was added 86 mg (0.14 mmol) of 10-(4-aminophenyl)-5,15-bis(2,4,6trimethylphenyl)porphyrin,<sup>32</sup> 100 mg (0.122 mmol) of 7, 56 mg (0.17 mmol) of cesium carbonate, 10 mg (0.018 mmol) of bis[(2diphenylphosphino)phenyl] ether and 20 mL of THF. The suspension was flushed with argon for 10 min, 3 mg (0.012 mmol) of palladium acetate was added and the flushing procedure was continued for an additional 5 min. The tube was sealed with a Teflon<sup>®</sup> screw plug and the reaction mixture was warmed to 67 °C for 18 h. Once cool, the solvent was evaporated by distillation at reduced pressure and the residue was chromatographed on silica gel (hexanes/15% ethyl acetate) to give 163 mg of **9** (97% yield). <sup>1</sup>H NMR (300 MHz)  $\delta$  -2.88 (2H, s, N-H), -2.26 (2H, s, N-H), 1.63 (9H, s, -CH<sub>3</sub>), 1.82 (12H, s, Ar-CH<sub>3</sub>), 1.89 (12H, s, Ar-CH<sub>3</sub>), 2.65 (12H, s, Ar-CH<sub>3</sub>), 6.82 (1H, s, N-H), 7.29 (4H, s, Ar-H), 7.30 (4H, s, Ar-H), 7.3 (2H, m, Ar-H partially obscured), 7.73 (2H, d, J = 8 Hz, Ar–H), 8.02 (2H, d, J = 8 Hz, Ar–H), 8.05 (1H, s, N–H), 8.11 (2H, d, J = 8 Hz, Ar–H), 8.65 (2H, d, J = 5 Hz,  $\beta$ -H), 8.73–8.81 (8H, m,  $\beta$ -H), 9.03 (2H, d, J = 5 Hz,  $\beta$ -H), 9.23 (2H, d, J = 5 Hz,  $\beta$ -H), 9.60 (2H, d, J = 5 Hz,  $\beta$ -H), 10.06 (1H, s, meso-H); MALDI-TOF-MS *m/z* calcd for C<sub>93</sub>H<sub>84</sub>N<sub>10</sub>O<sub>2</sub> 1372.68, obsd 1372.68; Uv/vis (CH<sub>2</sub>Cl<sub>2</sub>) 413, 426 (sh), 514, 551, 587, 647, 668 (nm).

**Dyad MP-PN.** Compound 9 (150 mg, 0.109 mmol) was added to a flask along with 30 mL of trifluoroacetic acid. The green solution was stirred under a nitrogen atmosphere for 20 min and then diluted with dichloromethane (150 mL). After washing with water and aqueous sodium bicarbonate, the solution was dried over sodium sulfate and then concentrated by distillation of the solvent at reduced pressure. The residue was chromatographed on silica gel (dichloromethane/20–5% hexanes) to give 125 mg of **MP-PN** (90% yield). <sup>1</sup>H NMR (300 MHz)  $\delta$  –2.88 (2H, s, N–H), –2.25 (2H, s, N–H), 1.82 (12H, s, Ar–CH<sub>3</sub>), 1.89 (12H, s, Ar–CH<sub>3</sub>), 2.64 (12H, s, Ar–CH<sub>3</sub>), 3.98 (2H, s, N–H), 7.03 (2H, d, J = 8 Hz, Ar–H), 7.29 (4H, s, Ar–H), 7.30 (4H, s, Ar–H), 7.03 (2H, d, Ar–H partially obscured), 7.96 (2H, d, J = 8 Hz, Ar–H), 8.02 (2H, d, J = 8 Hz, Ar–H), 8.02 (1H, s, N–H), 8.65 (2H, d, J = 4 Hz,  $\beta$ -H), 8.73– 8.84 (8H, m,  $\beta$ -H), 9.03 (2H, d, J = 5 Hz,  $\beta$ -H), 9.22 (2H, d, J = 4 Hz,  $\beta$ -H), 9.59 (2H, d, J = 5 Hz,  $\beta$ -H), 10.06 (1H, s, *meso*-H); MALDI-TOF-MS *m*/*z* calcd for C<sub>88</sub>H<sub>76</sub>N<sub>10</sub> 1272.63, obsd 1272.62; Uv/vis (CH<sub>2</sub>Cl<sub>2</sub>) 412, 426 (sh), 514, 554, 587, 649, 662 (nm).

Carbamate protected form of MPN (10). To a heavy walled glass tube was added 190 mg (0.23 mmol) of 7, 75 mg (0.70 mmol) of p-toluidine, 106 mg (0.33 mmol) of cesium carbonate, 19 mg (0.04 mmol) of bis[(2-diphenylphosphino)phenyl] ether and 60 mL of THF. The mixture was flushed with argon gas for 15 min, 5.2 mg (0.02 mmol) of palladium acetate was added and the argon gas flushing process was continued for an additional 10 min. The tube was sealed with a Teflon<sup>™</sup> screw plug and the reaction mixture was warmed to 67 °C. After 17 h the reaction mixture was cooled and TLC (hexanes/20% ethyl acetate) indicated that all the starting porphyrin had been consumed. The reaction mixture was filtered through Celite and the residue was washed thoroughly with THF (100 mL). The filtrate was concentrated to dryness by removal of the solvent at reduced pressure and the residue was chromatographed on silica gel (hexanes/5-7.5% ethyl acetate) to give 163 mg of 10 (83% yield). <sup>1</sup>H NMR (400 MHz)  $\delta$  –2.31 (2H, s, N-H), 1.63 (9H, s, -CH<sub>3</sub>), 1.84 (12H, s, Ar-CH<sub>3</sub>), 2.26 (3H, s, Ar-CH3), 2.62 (6H, s, Ar-CH3), 6.81 (1H, s, N-H), 6.87 (2H, d, J = 8 Hz, Ar-H), 6.99 (2H, d, J = 8 Hz, Ar-H), 7.26 (4H, s, Ar-H partially obscured), 7.63 (1H, s, N-H), 7.73 (2H, d, J = 8 Hz, Ar-H), 8.09 (2H, d, J = 8 Hz, Ar–H), 8.59 (2H, d, J = 5 Hz,  $\beta$ -H), 8.60 (2H, d, J = 5 Hz, β-H), 8.74 (2H, d, J = 5 Hz, β-H), 9.27 (2H, d, J = 4 Hz,  $\beta$ -H); MALDI-TOF-MS m/z calcd for C<sub>56</sub>H<sub>54</sub>N<sub>6</sub>O<sub>2</sub> 842.4, obsd 842.4; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 423, 520, 572, 590, 663 (nm).

MPN. To a flask containing 150 mg (0.18 mmol) of 10 and 20 mL of dichloromethane was added 20 mL of trifluoroacetic acid. The green solution was stirred at room temperature under an argon atmosphere for 30 min. A TLC (hexanes/20% ethyl acetate) indicated that the reaction was complete. The reaction mixture was diluted with dichloromethane (100 mL) and washed with water  $(2 \times 100 \text{ mL})$  and then with aqueous sodium bicarbonate (100 mL). The solution was dried over anhydrous sodium sulfate and filtered, and the filtrate was concentrated to a purple solid. This material was chromatographed on silica gel (hexanes/25% ethyl acetate) to give 120 mg of MPN (91% yield). <sup>1</sup>H NMR (400 MHz)  $\delta$  -2.31 (2H, s, N-H), 1.84 (12H, s, Ar-CH<sub>3</sub>), 2.26 (3H, s, Ar-CH<sub>3</sub>), 2.62 (6H, s, Ar-CH<sub>3</sub>), 4.01 (2H, s, N-H), 6.86 (2H, d, J = 8 Hz, Ar-H), 6.99 (2H, d, J = 8 Hz, Ar-H), 7.04 (2H, d, J = 8 Hz, Ar-H), 7.24 (4H, s, Ar-H partially obscured), 7.61 (1H, s, N-H), 7.95 (2H, d, J = 8 Hz, Ar-H), 8.59 (2H, d, J = 5 Hz, β-H), 8.61  $(2H, d, J = 5 Hz, \beta-H)$ , 8.80  $(2H, d, J = 5 Hz, \beta-H)$ , 9.27 (2H, d, J)J = 5 Hz,  $\beta$ -H); MALDI-TOF-MS m/z calcd for C<sub>51</sub>H<sub>46</sub>N<sub>6</sub> 742.4, obsd 742.6; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 427, 521, 570, 590, 665 (nm).

Electrochemical measurements. The voltammetric characterization of the redox processes for the molecules was performed with a CHI 620 potentiostat (CH Instruments) using a Pt disk working electrode, a Pt wire mesh counter electrode, and a silver wire quasireference electrode in a conventional three-electrode cell. Electrochemical studies were carried out in anhydrous benzonitrile containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. The working electrode was cleaned between experiments by polishing with diamond paste slurry, followed by solvent rinses. After each voltammetric experiment, ferrocene was added to the solution, and the potential axis was calibrated against the formal potential of the ferrocenium/ferrocene redox couple (taken as 0.45 V *vs.* SCE in dichloromethane).

**Steady-state spectroscopy.** Absorption spectra were measured on a Shimadzu UV-3101PC UV-vis-NIR spectrometer. Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrometer and corrected for detection system response. Excitation was provided by a 75 W xenon-arc lamp and single grating monochromator. Fluorescence was detected 90° to the excitation beam *via* a single grating monochromator and an R928 photomultiplier tube having S-20 spectral response and operating in the single photon counting mode.

Time-resolved fluorescence. Fluorescence decay kinetics were measured using the time-correlated single-photon counting technique. The excitation source was a fiber supercontinuum laser based on a passive modelocked fiber laser and a highnonlinearity photonic crystal fiber supercontinuum generator (Fianium SC450). The laser provides 6 ps pulses at a repetition rate variable between 0.1-40 MHz. The laser output was sent through an Acousto-Optical Tunable Filter (Fianium AOTF) to obtain excitation pulses at the desired wavelength. Fluorescence emission was collected at 90° and detected using a doublegrating monochromator (Jobin-Yvon, Gemini-180) and a microchannel plate photomultiplier tube (Hamamatsu R3809U-50). The polarization of the emission was 54.7° relative to that of the excitation. Data acquisition was done using a single photon counting card (Becker-Hickl, SPC-830). The instrument response function had a FWHM of 50 ps, as measured from the scattering of the sample at the excitation wavelength. The data were fitted with a sum of exponentials decay model at a single wavelength.

### Conclusions

The palladium catalyzed coupling method described here for preparation of  $\mathbf{P}$ -( $\mathbf{PN}$ )<sub>*n*</sub> yields a semiconducting polymer with the porphyrin moieties as part of the polymer backbone that is similar to the polymers previously prepared by electropolymerization.<sup>32,34</sup> Replacement of the mesityl groups used in the electropolymers with 3,5-dihexylphenyl groups yields a soluble polymer that can be studied easily in solution. It is amenable to spin-coating or other film-forming procedures and should be useful for making polymer phases intimately mixed with fullerene phases for construction of bulk heterojunction organic photoelectrochemical cells. Comparison of the spectroscopic properties of the polymer rings *via meso*-aminophenyl groups allows the porphyrin moieties to retain many of the absorption and redox properties of the monomer, rather than

generating a highly delocalized chromophoric system. At the same time, the close similarity in structure between  $P(PN)_n$  and the electropolymers studied previously<sup>32,34</sup> suggest that the polymer chains form a semiconducting material through which positive charge is expected to flow readily. The relatively long excited singlet state lifetime observed for the polymer shows that this state is kinetically competent to inject charge into a suitably located electron acceptor. This in turn suggests that polymers of this type could be useful in organic photovoltaics or light emitting diodes, sensors, or other optoelectronic applications.

The spectroscopic studies of the polymer and model compounds suggest that the presence of an amino group at the *meso*position of a porphyrin leads to formation of initial local excited states that quickly evolve into excited states with charge-transfer character. Presumably, the lone pair electrons of the amino group are somewhat delocalized into the porphyrin macrocycle, leaving a partial positive charge on the amino substituent and a partial negative charge on the macrocycle. The formation of charge transfer states of this general type in molecules with an amino group attached to an aromatic residue with some electron accepting character is widely observed and has been extensively studied, although the exact nature of the CT state has been greatly debated and is still not completely understood.<sup>41</sup>

Energy transfer between porphyrin units along the polymer chain is moderately rapid. The singlet state lifetimes suggest that in a film structure, energy transfer could also occur between adjacent polymer chains. The electrochemical experiments show that the polymer chain is readily oxidized at *ca.* +0.6 V *vs.* SCE, indicating that the excited states of the porphyrin moieties are thermodynamically competent to inject charge into a wide variety of electron acceptors, including typical fullerenes. Thus, porphyrins of this general type have properties that could prove useful in a variety of optoelectronic, sensing and solar energy conversion applications.

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