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Conjugated Porphyrin Polymers: Control of Chromophore Separation by Oligophenylenevinylene Bridges

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Recently a great effort has been devoted to the design and synthesis of large porphyrin arrays including dendrimers,[1] linear oligomers,[2] and polymers.[3,4] These macromolecular, chromophoric structures have a variety of uses in the study of electron and energy transfer and potential application to solar energy conversion,[2] catalysis, nonlinear optics materials,[3a] sensors, and molecular wires.[3c] Though porphyrin macromolecules have found increasing applications in many areas,[1-4] there are few porphyrin polymers in which the chromophoric units are linked within an extended conjugated polymer. More significantly, synthetic strategies that provide for systematic variation of the distance between the chromophoric units within polymeric systems have not been reported. Porphyrin polymers are also typically insoluble in common organic solvents,[3] limiting both characterization and application. Here we report the synthesis, characterization, and preliminary energy-transfer dynamics of a new series of conjugated polymers in which porphyrin units are linked by oligophenylenevinylenes of different, controllable lengths.

The porphyrin polymers described here offer several advantages for photoinduced electron-transport applications: (1) The polymers are highly soluble in common organic solvents and can be processed into optical quality thin films from solution at room temperature. (2) The porphyrin subunits have tunable photophysical and electronic properties. (3) The extended conjugation of the system, when the porphyrin rings are coplanar with the oligophenylenevinylene bridge,[5] provides for potential electrical conductivity in the charged state. (4) The electrochemical properties of the porphyrins can be selected to provide for long-range charge-transport and storage investigations. Given the similarity of poly(phenylenevinylene) (PPV) to the bridges used here, these investigations may provide insight into future development of more traditional LED or conducting materials.[6]

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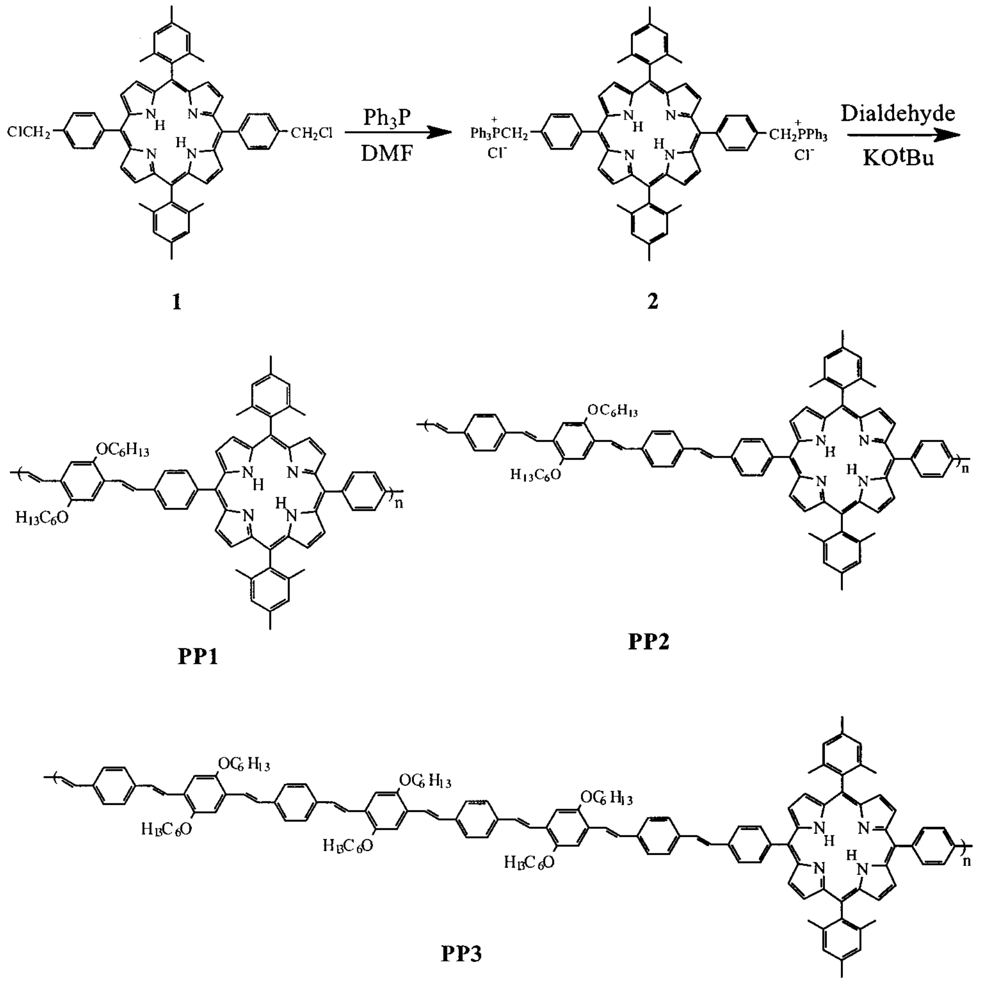
Scheme 1. Synthetic Scheme for Porphyrin Monomer and Polymers.



The Wittig reaction has been widely used to synthesize conjugated, conducting polymers.[6a−e] Recently, the Wittig reaction has also been used in constructing porphyrin dimers, trimers, and a starlike pentamer.[1] By further exploration of this methodology, we have synthesized linear, conjugated porphyrin polymers as shown in Scheme 1. The key to the preparation of these polymers is the synthesis of the appropriately functionalized porphyrin phosphonium salts **2**. We first synthesized 5,15,-bis(chloromethylphenyl)-10,20-bis(mesityl)-porphyrin (**1**).[8] The porphyrin phosphonium salts were then prepared by reaction of this porphyrin with triphenyl phosphine. The reaction of porphyrin phosphonium salt and various oligophenylenevinylene dialdehydes[8] led to porphyrin polymers with different linkage lengths.

The porphyrin polymers were prepared through the Wittig reaction of the porphyrin bisphosphonium salt and related dialdehyde in a mixture of absolute ethanol and anhydrous methylene chloride catalyzed by potassium *tert*-butoxide under N_2.[8] The reaction is facile even under room-temperature conditions. To increase the solubility of porphyrin polymers, long alkoxyl substituents were attached to the oligophenylenevinylene, a common strategy in soluble polymer preparation.[6] The mesityl substituents on the porphyrin ring also contribute to the solubility.[2a−d] All the porphyrin polymers were easily characterized by NMR, UV−vis, gel permeation chromatography (GPC), and fluorescence due to their solubility in common organic solvents such as tetrahydrofuran, chloroform, and toluene.

The final molecular weight of the polymers depends on the temperature and the ratio of ethanol and methylene chloride. The molecular weight of the polymers determined by GPC increased with decreasing bridge length; M_n = 6692 for PP3, M_n = 7517 for PP2, M_n =12 230 for PP1. The polydispersity of these systems varied from 1.4 to 2. Although the molecular weights of PP3 and PP2 are relatively low, they can be cast to form durable, optical-quality films. The structure of the polymers was clearly confirmed by ^{1}H NMR. In the case of PP1, no or very weak reasonance peaks at about 10.04 ppm (CHO) and 5.0 ppm ($CH_2^+PPh_3Cl^-$) indicated the relatively low density of end groups, consistent with GPC results. For PP2 and PP3, integration of the aldehyde peaks suggested a relatively large percentage of end groups consistent with the lower molecular weight of the polymers. Two broad peaks at 6.8−6.9 ppm were assigned to the *cis*-vinylene protons. These peaks disappeared, and the two peaks at 7.3−7.5 ppm

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(8) See Supporting Information.

(9) Cis−trans polymer mixtures can be converted to the all-trans polymer by heating a chloroform solution of the polymer in the presence of a catalytic amount of iodine.

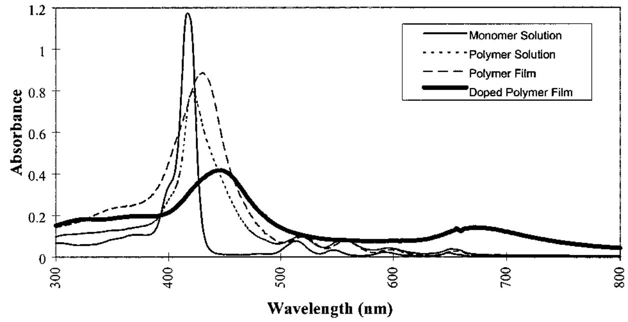

Figure 1. UV−vis absorption spectra of the representative polymer (PP3) and the porphyrin monomer (1) in tetrahydrofuran (THF) solution and the same polymer as a doped and undoped thin film.

increased after thermal isomerization, confirming formation of the trans structure.[9]

The thermal properties of the polymers were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). There were no phase transitions observed between 0 and 250 °C by DSC. The decomposition temperature is about 390 °C for the polymers. Incorporation of the porphyrin into what is effectively a polyphenylenevinylene chain greatly enhanced the thermal stability relative to PPV.

The optical characterization of these new materials provides some insight into their electronic structure. Shown in Figure 1 are the UV−vis spectra for a representative polymer and porphyrin monomer in THF solution. The absorption maxima of the porphyrin Soret bands (422 nm) were all slightly red shifted and broader than that of the corresponding porphyrin monomer (418 nm) due to π-conjugation effects.[5a] There was no significant difference in the UV−vis spectra as a function of the length of the bridge. No splitting of the Soret bands was observed, suggesting that there may be limited electronic interaction in the ground state between the porphyrin units in solution,[1a,b] though a lack of splitting does not preclude electronic communication.[2a−f]

Also shown in Figure 1 are the UV−vis absorption spectra of a representative doped and undoped polymer films (PP3). High-quality thin films could be obtained by casting toluene solutions of the polymers onto glass slides. The maximum absorption at 430 nm of the undoped film was significantly red shifted compared to the spectra in THF solution. This may be due to $\pi-\pi$ stacking effects in the solid state as observed previously for derivatized porphyrins.[11,12] After chemical doping with nitromethane solutions of anhydrous $FeCl_3$, a new broad-band absorption feature appears at low energy, consistent with formation of a bandgap in the conducting form of the polymer. Preliminary results have shown that the undoped films are completely insulating with conductivities less than 10^{-12} S/cm. After doping, the conductivity of the film increased to $\sim 10^{-6}$ S/cm.

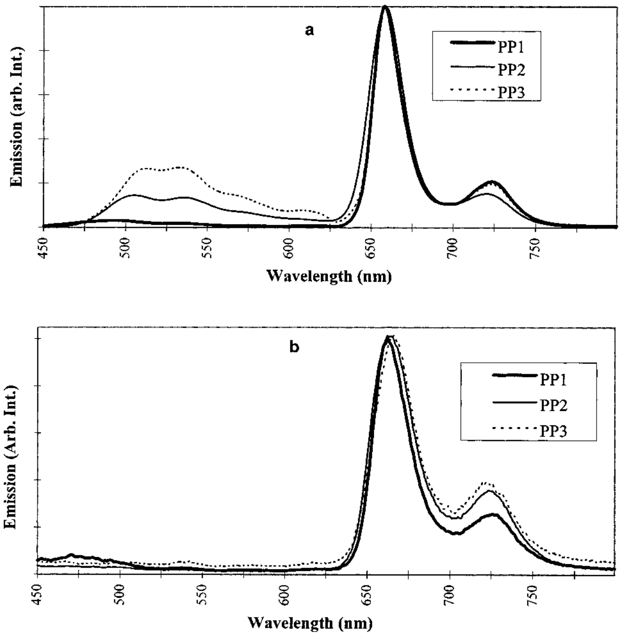

Figure 2. Normalized emission spectra recorded on (a) THF solutions of the three porphyrin polymers recorded at 4 nm slits with 422 nm excitation and (b) thin films of the porphyrin polymers excited at 422 nm and recorded at the front surface of the film.

Fluorescence spectra (422 nm excitation) of the polymers in dilute THF solution (1×10^{-6} M) are shown in Figure 2a. Two emission manifolds are observed. The low-energy bands (640−750 nm) are independent of the length of oligophenylenevinylene bridges and have an emission lifetime of 9.8 ± 1 ns in each case. The low-energy features can be attributed to the porphyrin subunits within the polymer chain. The higher energy emission bands at 450−600 nm increase in intensity and red shift with increasing bridge length. These features could be assigned to the oligophenylenevinylene bridge based on model studies of the bridge prior to polymerization. The emission lifetime of this higher energy state, monitoring at 560 nm, was 500 ps for the PP3 system. The quantum yield of the emission was also enhanced as the bridge length increased; $\Phi_{em} = 0.10$, 0.13, and 0.23 for PP1, PP2, and PP3.[12] The increase in the emission quantum yield was dominated by the observed emission from the bridge, though there was a slight increase in emission quantum yield from just the porphyrin band relative to the monomer ($\Phi_{em,porph} =$ 0.10, 0.11, 0.15, and 0.02 for PP1, PP2, PP3, and monomer, respectively).[13]

There was a significant shift in the emission intensities of the polymers when cast as thin films (Figure 2b). The thin-film fluorescence spectra are dominated by the porphyrin bands at low energy with only a slight red shift compared to solution (Figure 2a). Emission lifetime measurements were substantially increased but could not be determined with local instrumentation. Noticeably absent in the thin-film spectra are the emission bands at higher energy assigned to the oligophenylenevinylene bridge.

One conclusion that could be drawn from the absorption and emission data is that in the solid-state energy

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(12) Emission measurements and lifetimes were determined on an SLM 48000S emission lifetime fluorimeter. All solutions were bubble deoxygenated with N_2 prior to running. Quantum yields were determined by relative actinometry using either tetraphenylporphyrin or zinc tetraphenylporphyrin as the standard.

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transfer from the higher energy bridge state to the lower energy porphyrin units was taking place. Further support for this conclusion is found by comparing the absorption spectra to the excitation spectra in the solution and solid state. The results of fluorescence excitation experiments monitoring the emission either at 550 or 724 nm in solution show that the absorptions that lead to the two emissions are consistent with the bridge and monomer absorption spectra, respectively, prior to polymerization. In the solid state, the fluorescence excitation spectrum of the low-energy band (724 nm) overlaps completely with the UV−vis spectrum of the polymer. The excitation spectra results are more consistent with an energy transfer quenching mechanism than electron transfer.

On the basis of these results, we conclude that energy transfer between the bridge and porphyrin subunits is inefficient in solution. It is likely that steric hindrance forces the porphyrin rings out of the plane of conjugation in solution as observed previously for phenyl-substituted porphyrin dimers and oligomers.[2a−f] This would decrease the conjugation through the extended system and result in the dual excited-state emission observed.

In the solid state there is enhanced electronic communication, perhaps leading to energy transfer from the higher energy bridge to the porphyrins. A possible explanation of this observation is that in the solid state the porphyrin subunits are preferentially stacking.[13] This would force the porphyrin rings to be within the same plane as the conjugated bridge in the solid state. While it could be argued that this type of interaction would lead to self-quenching of the porphyrin emission, it has previously been shown that solid state π- stacking of porphyrins can result in enhancement of the emission quantum yield compared to solution.[12] Preliminary X-ray diffraction results from thin polymer films show that they exhibit only short-range order. An alternative hypothesis would be that in the solid state intermolecular $\pi-\pi$ interactions lead to the observed decrease in emission intensity from the bridge-based state. This would mean that the intramolecular energy-transfer rate remains low, as observed in solution. Further investigation into the energy-transfer mechanism is currently underway.

In conclusion, we have developed a new strategy for the preparation of a series of conjugated copolymers in which porphyrin units are linked with oligophenylenevinylene bridges. These new polymers are soluble in common organic solvents, making them processable and easy to characterize both in solution and as spin-coated thin films. Given these enhancements and the increased thermal stability observed, these polymers provide a unique opportunity to explore electronic processes within conducting polymer systems.

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Supporting Information Available: Experimental details (5 pages). Ordering information is given on any current masthead page.

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