X-ray Photoelectron Spectroscopy as a Probe of Intermolecular Interactions in Porphyrin Polymer Thin Films

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High-resolution X-ray photoelectron spectroscopy (XPS) has been applied to a series of free-base and Zn−porphyrin polymers in which the macrocycles are separated by oligo(phenylene vinylene) units (OPV) of different, controllable lengths. Neat films of all the Zn−porphyrin polymers unexpectedly reveal two peaks in the N 1s XPS region (∼400 eV). The peak areas vary with the length of the OPV bridge, suggesting an intermolecular interaction between the porphyrin and linker subunits. A series of XPS analyses were performed to identify the different interactions taking place in these thin films. To inhibit interpolymer interactions, one of the polymers was incorporated into a nonconjugated PMMA matrix, collapsing the N1s spectrum to a single peak at 398.0 eV, relative to the neat film signals at 397.8 and 400.1 eV. In a conjugated matrix of OPV, two peaks remain at 401.7 and 399.5 eV. Extensive vacuum drying of the neat film leads to a single peak at 398.3 eV, suggesting loss of trapped solvent molecules. Ultimately, we attribute the lower energy signal of the neat films to solvent ligation, and the higher energy peak is attributed to interactions between the porphyrins and conjugated bridges on nearby polymer chains. This interpretation is successfully applied to the N 1s XPS data from a previously reported Zn−porphyrin oligomer-based multilayer array.

Introduction

The design and study of supramolecular porphyrin complexes has undergone tremendous growth in recent years. A variety of porphyrin monomers,[1−10] dimers,[11−14] oligomers,[15−18] polymers,[19−23] and nonlinear arrays[24−29] have emerged from new synthetic methods. As the elegance of these systems improves, exceptional control has been gained over their chemical and physical properties. For example, these chromophoric structures are often utilized in the study of energy and electron transfer, particularly as models of light-harvesting, photosynthetic systems.[1,7a,11−16,24,26−30] A continuing challenge in the study of porphyrins and conjugated polymers is the identification of inter- and intramolecular interactions, especially in spin-coated films. It is critical that we advance our understanding of these phenomena if we are to use these materials in applications such as sensors and electrodes,[12,13,21,31−33] optoelectronic devices,[11−16,19,20,29] and catalysts.[2c,3,7a,8a,29] X-ray photoelectron spectroscopy (XPS)

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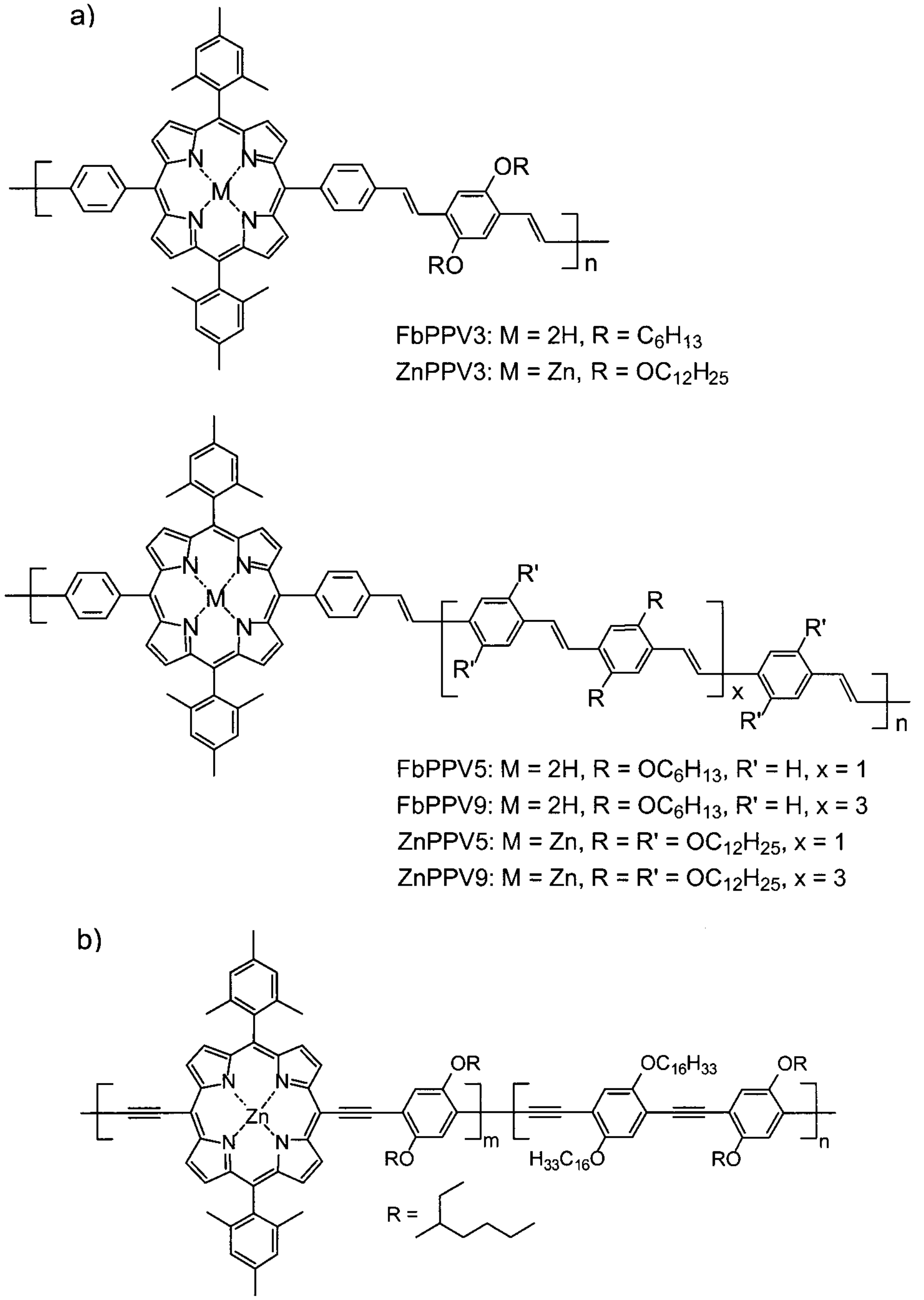

Figure 1. (a) Free-base and zinc porphyrin polymers with oligo(phenylene vinylene) bridges, Fb/ZnPPVn. (b) Zinc porphyrin oligomer with oligo(phenylene ethynylene) bridge, ZnPPEPE3.

can aid in this endeavor by describing the effect of chemical environments on the electron density about specific atoms in the solid state.[4,13]

Modification at the periphery of the porphyrin ring has been well documented to induce intramolecular effects on the overall electronic structure.[2,3,7,8] Intermolecular interactions may also influence the physical and electronic properties in the solid state.[5] The core electron binding energies (BE) of the central nitrogen atoms in a porphyrin are strongly affected by perturbations to the macrocycle, making N 1s XPS a sensitive probe of changes in charge distribution.[4,6a] However, XPS does not typically distinguish between the effects of inter- and intramolecular interactions. Furthermore, although XPS has been widely used to study porphyrin monomers in the solid state,[3−6,9,10] data are available for relatively few multiporphyrin systems.[13,17]

We have previously reported the synthesis and characterization of a series of polymers in which porphyrin units were linked by oligo(phenylene vinylene) bridges of different, controllable lengths (Fb/ZnPPVn), as shown in Figure 1a.[21] We have also synthesized porphyrin oligomers with oligo(phenylene ethynylene) bridges (e.g., ZnPPEPE3, Figure 1b).[17,22] Similar

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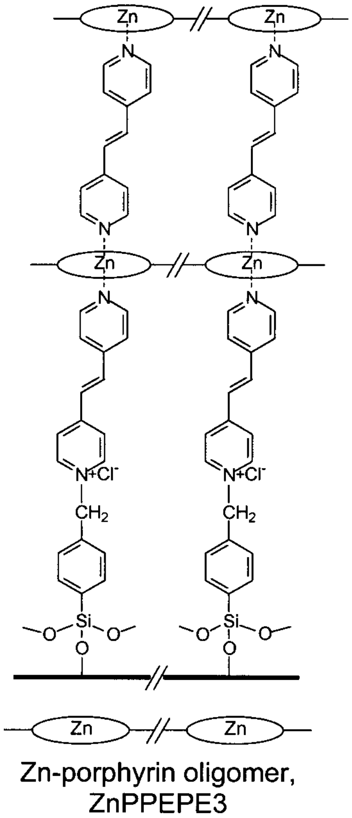

Figure 2. Idealized structure of self-assembled ZnPPEPE3 multilayer array.

polymers utilizing a variety of aryleneethynylene groups between porphyrins have recently been reported by Yamamoto and co-workers.[23] The exceptional structural control exercised in such systems has resulted in materials with tunable photophysical and electronic properties.[21,22]

In an effort to inhibit intermolecular interactions between oligomeric ZnPPEPE3 chains, this fully conjugated material was subsequently incorporated into a multilayer architecture via self-assembling coordination chemistry.[17] In this system, porphyrin units were coordinated to a pyridinium-terminated coupling layer on glass substrates. Additional layers were assembled by axial coordination to dipyridyl spacers (Figure 2).

N 1s XPS was performed on the multilayer system as a means of probing its molecular structure. An amorphous thin film of the Zn−porphyrin oligomer (Figure 1b) was examined as a control sample. The XPS results were unusual in that both the amorphous film and ordered self-assembled array (Figure 2) revealed two N 1s signals.[17] To the best of our knowledge, such an XPS result had not previously been reported.

Typically, free-base porphyrin monomers reveal two peaks, with 1:1 areas. The higher binding energy corresponds to the protonated nitrogen, the lower energy signal to the nonprotonated atom.[2a] In metalloporphyrin monomers, the four identical nitrogen atoms generate a single N 1s XPS signal.[4] XPS on Zn−porphyrin dimers reported by Polzonetti et al also reveals a single N 1s peak.[13] The same would be expected of our larger arrays, unless the nitrogen atoms were experiencing multiple chemical environments. We hypothesized that inadequate coordination between the porphyrinic zinc atoms and the dipyridyl spacers lead to localized intermolecular interactions between oligomer chains in the multilayer assemblies.[17]

To determine the nature of these interactions, we performed an XPS study on a series of structurally related porphyrin polymers (Fb/ZnPPVn, Figure 1a). These materials were prepared as both neat films and spin-coated mixtures in conjugated oligomer and nonconjugated polymer matrixes. Here we report a detailed analysis in which XPS is used as a means of identifying the types of intermolecular interactions that occur in porphyrin copolymer films and assemblies. The goal of this work is to provide a foundation for the characterization of future porphyrin polymers and molecular architectures.

Experimental Section

Materials. All solvents and chemicals were used as received unless otherwise noted. Dichloromethane was purchased from EM Science. Free-base (Fb) and zinc(II) tetraphenyl porphyrin (ZnTPP) was purchased from Midcentury Chemical. Polymethyl methacrylate (PMMA, M_w: 996,000 by GPC) and polystyrene (PS, M_w: 280,000 by GPC) were purchased from Aldrich.

The series of free-base and zinc porphyrin polymers bridged by oligo(phenylene vinylene) linkages (Fb/ZnPPVn, Figure 1a) was synthesized using previously reported methods.[21] The oligo(phenylene vinylene) dialdehyde (OPV) was prepared by slight modification of a method reported by Wang and Wasielewski,[34] employing hexyloxy rather than decyloxy sidechains. The oligo(phenylene ethynylene)-bridged zinc porphyrin oligomer (ZnPPEPE3, Figure 1b) and multilayer architectures (Figure 2) were prepared as described earlier.[17] Neat films of each porphyrin material were prepared for XPS analysis by spreading a very small quantity of the solid powder on indium foil and lightly pressing with a clean spatula.

Preparation of Spin-Coated Thin Films. Solutions prepared for spin-coating consisted of 20 and 50% (w/w) mixtures of ZnPPV5 in PMMA, PS, and OPV, dissolved in 10 mL of dichloromethane. These solutions were concentrated by blowing a stream of nitrogen across the surface until they became slightly viscous.

Standard glass microscope slides (VWR Scientific) were cut into 1.5 × 1.5 cm segments and washed first with copious amounts of acetone then with ultrapure deionized water. Slides were then immersed in "piranha" solution (3:7 (v/v) 30% H_2O_2 and concentrated H_2SO_4; caution, highly corrosive) and heated to $\sim$90 °C in a water bath for 1 h. The slides were again thoroughly washed in ultrapure deionized water, dried under a stream of nitrogen, and then heated in vacuo to $\sim$140 °C for 1 h to remove residual surface water.[35] Upon returning to room temperature, the substrates were spin-coated with the 20 and 50% (w/w) porphyrin-containing solutions using in-house equipment.

Methods. X-ray photoelectron spectroscopy (XPS) was performed using a modified PHI model 5500 multi-probe spectrometer. The instrument contains a hemispherical analyzer that has apertures for spot sizes of 30−800 μM. Monochromatized Al Kα X-ray excitation was produced by a 7 mm Al filament. This filament is capable of decreasing the charge broadening typically associated with monochromatized beams using this geometry for the analysis of insulating samples. In addition, charge compensation was accomplished by means of a neutralizer filament operating under optimum conditions. The X-ray source operated at 14 keV and 350 mA. Irradiation effects were monitored as a function of time in order to determine the sensitivity of

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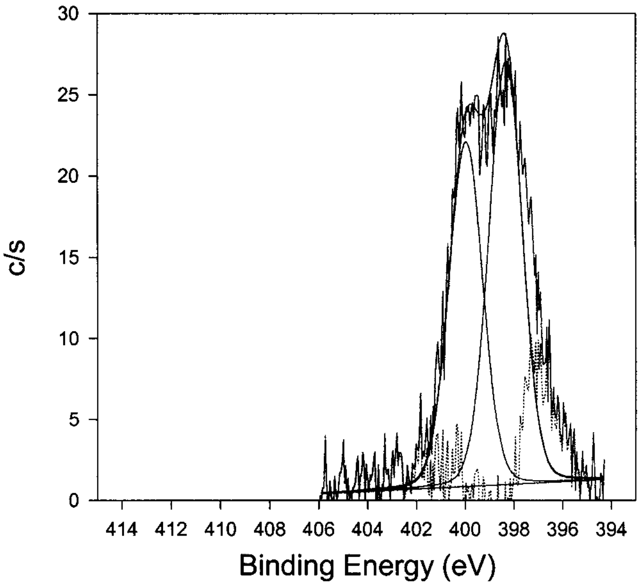

Figure 3. N 1s XPS of FbPPV5 neat film on indium foil. Solid lines indicate original data and fitted curves. Dotted line indicates residuals from fitted curve.

the samples to degradation. Survey and high-resolution spectra were collected at 65° to the detector with pass energy resolutions of 187.5 and 11.75 eV, respectively. The linearity of the binding energy scale was calibrated against the Au $4f_{7/2}$ (84.0 eV) and the Cu $2p_{3/2}$ (932.6 eV) photoemission lines by standard procedures. The measured binding energies were referenced to the C 1s line at 284.8 eV. The high-resolution spectra for the regions of interest were curve fitted using MultiPak 6.0 (Physical Electronics), a version of MatLab. Curve fitting was performed using Gaussian−Lorentzian shapes with a Shirley background. Minimization was performed using standard procedures for curve-fitting routines.

Results

High-resolution XPS was performed on each of the porphyrin materials prepared as neat films on indium foil and 20 and 50% (w/w) mixtures of ZnPPV5 in polymer and oligomer matrixes spin-coated on glass. As a control, spin-coated ZnTPP at 20% (w/w) in polymer and oligomer matrixes was also examined. All samples exhibited a strong peak in the C 1s region, which was set to 284.8 eV in order to maintain consistency throughout this study. Survey spectra revealed a N 1s signature after acquisitions as short as 6.5 min. Data indicative of two N 1s peaks appeared in the high-resolution spectra after as little as 70 min. The N 1s region of the mixtures was scanned for at least 470 min in order to obtain sufficient signal-to-noise ratios for well-resolved analyses. No significant sample degradation was evident, even during the course of the 820 min of irradiation required for acquisition of the weakest signals.

Neat Porphyrin Films. XPS of a neat film of the FbTPP monomer yielded two sharp, well-resolved peaks in the N 1s region. They were of roughly equivalent areas, with binding energies (BE) of 400.2 and 398.0 eV, corresponding to the protonated and nonprotonated nitrogen atoms, respectively. A neat film of the ZnTPP monomer, which has four equivalent nitrogen atoms, exhibited a single N 1s peak at 398.9 eV. Taking into account any differences in the relative C 1s energies, these results agree very well with previous literature reports.[3a,4a,6a,10]

Neat films of free-base porphyrin polymers FbPPV3, FbPPV5 (Figure 3), and FbPPV9 all show two N 1s signals. The energies of each peak vary only slightly throughout the series. The peak areas for the three- and five-unit bridged polymers are identical; the lower energy peaks (at 398.2 and 398.4 eV, respectively) account for 55.2% of the total N 1s signal. The relative peak areas are reversed for FbPPPV9, with 57.6% of the area in the higher energy signal at 400.0 eV. The XPS data from the free-base systems are summarized in Table 1.

Table 1. N 1s XPS Results for Neat Films of Free-Base Porphyrin Monomer and Polymers[a]

Porphyrin	N1 1s (eV)	N2 1s (eV)	ΔN (eV)
FbTPP	400.2 (49.4)	398.0 (50.6)	2.0
FbPPV3	400.1 (44.8)	398.2 (55.2)	1.9
FbPPV5	400.0 (44.8)	398.4 (55.2)	1.6
FbPPV9	400.0 (57.6)	398.2 (42.4)	1.8

[a] Numbers in parentheses indicate the relative peak areas for each component.

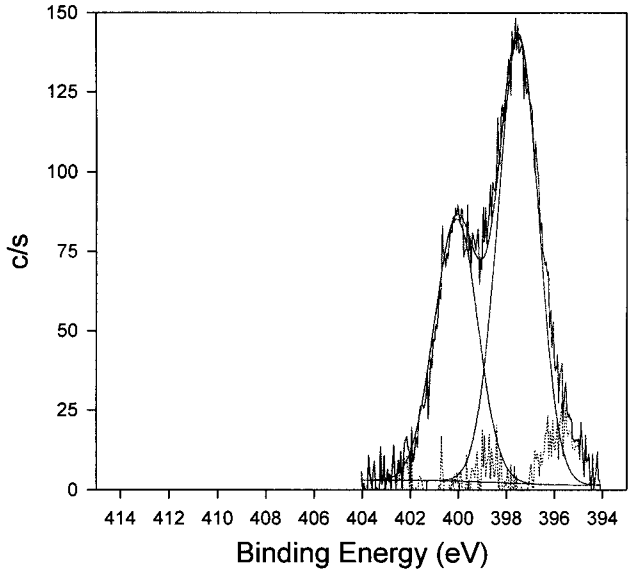

Figure 4. N 1s XPS of ZnPPV5 neat film on indium foil. Solid lines indicate original data and fitted curves. Dotted line indicates residuals from fitted curve.

Table 2. N 1s XPS Results for Neat Films of Zinc Porphyrin Monomer and Polymers[a]

Zn−Porphyrin	N1 1s (eV)	N2 1s (eV)	ΔN (eV)
ZnTPP		398.9	
ZnPPV3	400.8 (9.1)	398.5 (90.9)	2.3
ZnPPV5	400.1 (47.4)	397.8 (52.6)	2.1
ZnPPV9	399.9 (35.5)	398.6 (64.5)	1.3

[a] Numbers in parentheses indicate the relative peak areas for each component.

XPS of zinc porphyrin polymers ZnPPV3, ZnPPV5 (Figure 4), and ZnPPV9 also surprisingly reveals two N 1s signals. This result contrasts sharply with the single peak typically observed for metalated porphyrin monomers. The peak energies and relative areas for the neat films are listed in Table 2. The 400.8 eV peak of ZnPPV3 accounts for only 9.1% of the N1s signal. Analysis of ZnPPV5 and ZnPPV9 reveals an increase in the area of the higher energy peaks (400.1 and 399.9 eV, respectively) by at least a factor of approximately four. After vacuum drying ZnPPV5 for 5 days at room temperature, XPS revealed only a single N 1s peak at 398.3 eV. The nature of these observations will be explored in detail below.

It should be noted that N 1s energies of ~400 eV are higher than those typically found in the literature.[2a,3−6,9,10,13] Although there is no significant evidence of X-ray induced sample degradation, the minor contribution of a protonated species is a possibility. It is also likely that differences in N 1s energies

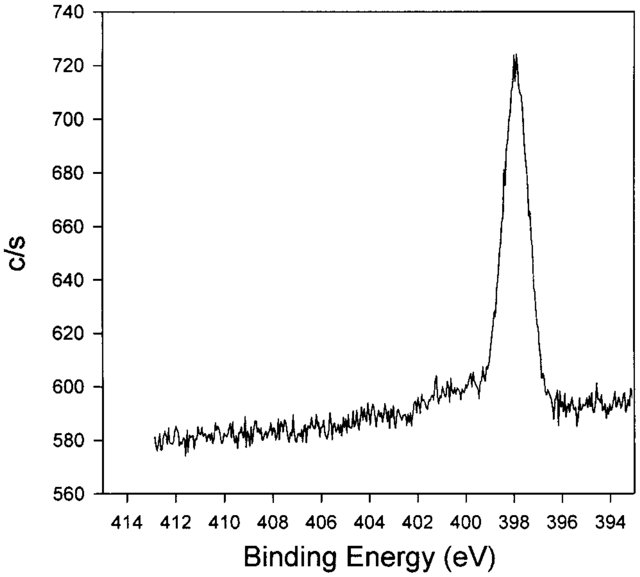

Figure 5. N 1s XPS of 20% (w/w) film of ZnPPV5 in PMMA spin coated onto glass.

relative to other reports correspond directly to the energies used to calibrate the linearity of the binding energy scale (Au $4f_{7/2}$ at 84.0 eV and Cu $2p_{3/2}$ at 932.6 eV) and the C 1s reference signal (284.8 eV).

The difference between the binding energies of the two nitrogen signals (ΔN) is also of significance in the porphyrin polymer series. Typically, in a free-base porphyrin $\Delta N = 2.1 \pm 0.1$ eV, largely independent of any peripheral substituents.[3a] For example, we observe a difference of 2.0 eV for the FbTPP monomer. The porphyrin polymers reveal markedly different results. Table 1 indicates a difference of 1.9 for FbPPV3, 1.6 for FbPPV5, and 1.8 eV for FbPPV9. From the data in Table 2, the difference is 2.3 for ZnPPV3, 2.1 for ZnPPV5, and 1.3 eV for ZnPPV9.

Spin-Coated Films: 20 and 50% (w/w) Porphyrin in Polymer Matrixes. To determine if the occurrence of a second N 1s signal was the result of intermolecular interactions, films were prepared with reduced porphyrin concentrations. This study was carried out on ZnPPV5 as the representative polymer. ZnPPV5 was incorporated into matrixes of polymethyl methacrylate (PMMA), polystyrene (PS), and oligo(phenylene vinylene) (OPV), and then spin coated onto clean glass slides for XPS analysis. In the nonconjugated PMMA matrix, the zinc porphyrin polymer exhibited a single N 1s peak at 398.0 and 398.2 eV for the 20 (Figure 5) and 50% (w/w) samples, respectively. Additionally, one peak was found at 398.5 eV for the 20% sample in PS. In the conjugated OPV matrix at 20% porphyrin, two N 1s signals were observed at 401.7 (29.7% peak area) and 399.5 eV (Figure 6). At 50%, the peaks appeared at 400.1 (48.1% peak area) and 398.2 eV. As described above, N 1s energies of ~400 eV and greater likely result from the choice of reference and calibration signals, as well as possible degradation impurities. Finally, as a control, ZnTPP was also incorporated at 20% (w/w) into PMMA and OPV, revealing a single N 1s peak at 398.2 eV in each matrix.

Self-Assembled Multilayer Architectures. XPS of the porphyrin oligomer ZnPPEPE3 as a neat thin film on indium foil yielded N 1s peaks at 400.1 (56.6% peak area) and 398.4 eV. This material was incorporated into multilayer architectures built upon a self-assembled pyridinium coupling layer on glass, as described previously (Figure 2).[17] XPS of a multilayer sample resulted in a broad N 1s peak due to energetically similar nitrogen species that could not be adequately resolved. Based on data obtained from the amorphous thin film, mathematical deconvolution of this signal revealed two porphyrinic nitrogen species at 400.5 and 399.0 eV, in addition to a peak for the pyridinium coupling layer. There was some evidence of X-ray induced decomposition during extensive irradiation, which could be attributed to pyridinium loss.

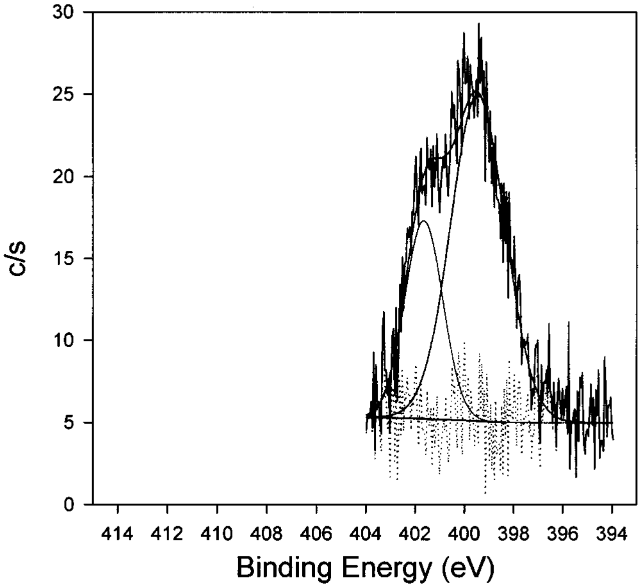

Figure 6. N 1s XPS of 20% (w/w) film of ZnPPV5 in OPV spin coated onto glass. Solid lines indicate original data and fitted curves. Dotted line indicates residuals from fitted curve.

Discussion

Neat Polymer Films. Free-base porphyrins, since they possess protonated and nonprotonated nitrogen atoms, are known to exhibit two XPS signals of roughly equivalent area in the N 1s region, at approximately 400 eV. These peaks are typically separated by 2.1 ± 0.1 eV in porphyrin monomers.[3a] It is expected that the three free-base porphyrin polymers (FbPPV3, 5, 9) should also present two N 1s peaks, as is shown in Figure 3 and Table 1. The peak areas and ΔN for the polymers deviate noticeably from prior monomer studies and vary with the OPV bridge length, suggesting that the conjugated linker has an effect on the charge distribution at the nitrogen atoms. No systematic trend is observed as a function of increasing OPV length. The binding energy (BE) of the protonated nitrogen atom (N1) is lower relative to FbTPP, whereas the BE of the nonprotonated nitrogen atom (N2) is slightly higher (see Table 1), which is consistent with weak electron-withdrawing and donating effects.

The N 1s XPS of metalloporphyrin monomers reveal a single peak because the four nitrogen atoms are structurally and electronically equivalent. The Zn−porphyrin dimers studied by Polzonetti et al also reveal a single N 1s peak, despite the loss of four-fold symmetry brought about by the meso substituted conjugated linker.[13] The appearance of two N 1s peaks for the three zinc porphyrin polymers (ZnPPV3, 5, 9) is, therefore, unprecedented (see Figure 4). Peak separation clearly decreases with increasing bridge length (see Table 2). Although further study is necessary, variations in ΔN are likely related to changes in the conjugation length of the bridge units. Relative peak areas deviate strongly from typical free-base monomer values and, as described above, are significantly influenced by the length of the OPV unit. Differences in peak areas of up to 10% have been observed from one sample to the next, which could be due to variations in the physical structure of neat films. The N 1s binding energy of 398.9 eV for ZnTPP is between the values of N1 and N2 for the three Zn−porphyrin polymers. The higher energy peak is consistent with electron-withdrawing effects, and the lower energy peak is consistent with electron-donating effects in films of these materials.

The appearance of a second peak could be taken as evidence of demetalation during polymerization or extended X-ray irradiation. However, prior characterization of the porphyrin polymer by UV−vis absorbance and emission measurements on spin-coated neat films and mixtures in other polymer matrixes (i.e., polystyrene) indicates only the presence of the metalloporphyrin, with no detectable free-base impurities.[21] The absorbance and emission maxima of the films are slightly broadened and red-shifted, relative to solutions in THF. Additionally, in the solid state, emission from the OPV bridge units is quenched by intermolecular energy transfer.[21] ^{1}H NMR on the Zn−porphyrin polymers in $CDCl_3$ also demonstrates the absence of free-base species.[21] Furthermore, the N 1s binding energy separation of the Zn−porphyrins deviates strongly enough from that of the typical free-base systems to preclude a return to this configuration. Sample degradation effects, such as protonation, could result in high N 1s energies of ~400 eV. However, no significant changes in the N 1s peak areas or ΔN are observed for the spin-coated films, even after 820 min of X-ray exposure.

Although substitution at the meso positions can affect the binding energies of porphyrin monomers and dimers,[2a,3a] this type of intramolecular interaction does not result in two peaks in the N 1s XPS region.[2a,3−6,9,10,13] Given the observations from our free-base and metalated polymer systems, we are led to hypothesize the occurrence of intermolecular interactions between the porphyrin units and conjugated bridges of nearby polymer chains.

These phenomena are difficult to study on free-base systems because two N 1s peaks will appear regardless of any intermolecular interactions. Hence, we have chosen to focus the remainder of our investigation on the zinc−porphyrin polymers, specifically ZnPPV5, because only one N 1s peak is typically expected for the metalloporphyrins.

Many porphyrin systems experience $\pi-\pi$ interactions in which the macrocycles are held parallel and offset from one another.[36−38] Metalation enhances the magnitude of this interaction by placing a large positive charge in the porphyrin cavity, which interacts with the π electrons of the porphyrins above and below the macrocycle plane.[36−38] For our systems, however, this type of intermolecular interaction is highly unlikely. First, X-ray diffraction experiments on polymer films show no evidence of any order, as has been observed for π-stacking liquid crystalline systems.[39] Furthermore, the strength of $\pi-\pi$ interactions is reduced by coordination of the metal by a ligand,[36−38] a factor whose importance will be explained below. Thus, the unusual XPS results cannot be attributed to porphyrin−porphyrin interactions.

The dependence on OPV length suggests that the bridge unit specifically interacts with the porphyrin. Similar $\pi-\pi$ interactions have been observed between porphyrins and other aromatic systems.[2d,36,40−43] For example, the presence of a noncoordinated benzene molecule has been reported to perturb the stereochemistry of a Mn−porphyrin through a weak π interaction.[43] A similar effect could result in charge redistribution at the porphyrin nitrogen atoms, generating an additional chemical environment and, thus, a second N 1s peak. However, porphyrin−arene π interactions are unlikely because they are inhibited in the same ways as porphyrin−porphyrin interactions (e.g., ligand coordination).[36−38]

Solvent Ligation and Macrocycle Distortion. In addition to the interpolymer interaction referred to above, ligand coordination could also significantly alter the porphyrin N 1s binding energy. The solvent coordinating properties of metalloporphyrins are well documented.[44] For example, ruthenium^{II} tetraphenylporphyrin can axially coordinate two ligand molecules, such as carbonyl, pyridine, or THF.[45] Zinc^{II} tetraphenylporphyrin typically coordinates one ligand, such as THF,[46] pyridine,[47] or water.[48] Six-coordinate bis(THF)−ZnTPP has been reported in the solid state. However, after exposure to the atmosphere, the crystals readily lost one THF molecule.[49]

XPS was run under ultrahigh vacuum (UHV) conditions. As such, it was expected that any residual solvent in the solid would have been removed. However, after vacuum drying a neat sample of ZnPPV5 for 5 days at room temperature, the photoelectron spectrum was reduced to a single N 1s peak at 398.3 eV. The disappearance of one of the N 1s signals suggested the loss of trapped, coordinated solvent molecules, most likely THF from the synthetic procedures.[21] Thus, the signal at 398.3 eV corresponds to the N 1s binding energy of a four-coordinate Zn−porphyrin polymer species. An intermolecular ligand interaction must represent at least part of the initially observed multi-peak XPS data.

The nondried ZnPPV5 sample exhibits two N 1s peaks at 397.8 and 400.1 eV (Figure 4). The signal at lower BE can now be attributed to solvent ligation, as the four-coordinate porphyrin becomes five-coordinate (see Scheme 1a). Upon coordination, charge flows from the ligand, through the metal atom, to the porphyrin ring.[8b] Based upon Gouterman's four-orbital model,[50] the HOMO a_{2u} level, which has electron density at the porphyrin nitrogen atoms, is destabilized by the added charge from ligand coordination. (The a_{1u} molecular orbital has nodes at these atoms and is much less perturbed.) This correlates well with solution studies on metalloporphyrins by Nappa and

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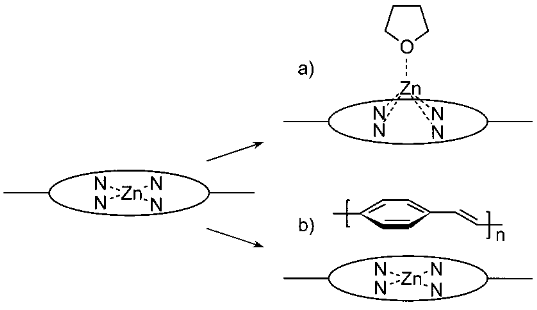
Scheme 1. Representation of the Two Types of Intermolecular Interactions Identified by XPS for Porphyrin Polymers ZnPPVn. (a) Porphyrin and Coordinated Solvent (b) Porphyrin and OPV Bridge on nearby Polymer Chain



Valentine, in which axial ligation results in red-shifted absorbance spectra.[46] The destabilized a_{2u} level is clearly reflected by the decrease in N 1s binding energy from 398.3 to 397.8 eV. The higher energy peak at 400.1 eV does not correlate with Zn−porphyrin monomer XPS energies. This signal must then be the consequence of another type of intermolecular interaction.

Highly substituted and distorted porphyrin monomers also exhibit significant red shifts in absorbance due to destabilized HOMO levels.[7b,10] As such, the lower energy N 1s XPS peak might be partially attributed to a deviation from planarity. This seems unlikely, as four-coordinate ZnTPP is a virtually planar molecule,[42a,47b] and X-ray structures indicate that although ligation pulls the zinc atom out of the porphyrin plane,[42a,46,47a,b,48] this does not significantly distort the entire macrocycle.[42a,48] Furthermore, our porphyrins are not highly substituted, avoiding steric strain that can induce nonplanarity.[7] However, as reported by Williamson and Hill, the presence of nearby arenes (e.g., the OPV bridge of ZnPPV5) could have a steric effect on the porphyrin ring.[43] The possible contribution of macrocycle distortion to the XPS results on neat films, although small, should not be excluded.

Inhibition of Intermolecular Interactions. The XPS results appear to depend on the length of the OPV unit (Tables 1 and 2), suggesting a possible interaction between porphyrin and bridge segments on nearby chains. As described above, solid state mixtures of the porphyrin polymer in conjugated and nonconjugated polymer matrixes were prepared as thin films for XPS analysis. To avoid intermolecular solvent interactions, dichloromethane, a noncoordinating solvent, was used to prepare solutions for this study and should thus exert no influence on the XPS data.

At 20 and 50% (w/w) ZnPPV5 in polymethyl methacrylate, the N 1s spectra collapse to a single peak (Figure 5). The same is true of a 20% mixture in polystyrene. This solid state dilution prevents interaction between porphyrin polymer chains. Therefore, it can be inferred that an interpolymer interaction in neat films of ZnPPV5 is partially responsible for the unusual XPS data. Previously published fluorescence data, in which emission from the OPV bridge units is quenched in neat polymer films, similarly demonstrates an intermolecular interaction among polymer chains. Dilution in a nonconjugated polymer matrix results in a return of the thin film emission by inhibiting such interactions.[21]

To further establish that the conjugated OPV linker plays a role in interpolymer interactions, ZnPPV5 was incorporated into a matrix of three-unit OPV at 20 and 50% (w/w). This not only inhibited interpolymer interactions, but also forced the polymer chains to interact with the conjugated units believed to be responsible for the results in the neat films. At both concentrations, two peaks remained in the N 1s XPS region (e.g., 20% mixture shown in Figure 6). This result is specific to the Zn−porphyrin polymers only, as ZnTPP in PMMA and OPV matrixes reveals a single peak at 398.2 eV.

The contribution of the conjugated OPV bridge is clear. However, OPV does not participate in a $\pi-\pi$ interaction with the porphyrin. Interacting π systems do not typically distort each other's molecular orbitals,[36] whereas the appearance of two N 1s signals from nondried neat ZnPPV5 (Figure 4) clearly results from such a perturbation, relative to the dried four-coordinate porphyrin. The presence of a metal atom typically encourages $\pi-\pi$ interactions, but they are also inhibited by ligand coordination.[36−38] Although the data indicates a coordination effect, it is not expected to occur at every metal site in ZnPPV5. OPV units could thus interact with ligand-free Zn−porphyrins on nearby polymer chains. As described above, the binding energy of 397.8 eV indicates a gain of electron density due to solvent ligation. The N 1s signal at 400.1 eV indicates a simultaneous loss of electron density from the porphyrin nitrogen atoms in the nondried film.

Unexpectedly, the N 1s peak that remains following extensive drying of the neat film shifts to a lower energy rather than staying at 400.1 eV. In the solid-state, numerous conformations are available to the polymer which could result in multiple intermolecular interactions. Although further investigation is required, a range of N 1s binding energies is possible, all of which may not be apparent from the relatively broad XPS signals (see Figures 4 and 5). In this case, the most prevalent conformation after thorough drying corresponds to the observed binding energy of 398.3 eV.

In the absence of $\pi-\pi$ interactions, another type of interpolymer interaction must be invoked to explain the increase in N 1s binding energy in ZnPPV5. The aromatic system of the phenylene vinylene bridge is likely oriented parallel to the porphyrin ring, based on previous studies.[36] Hence, the proper geometry exists for overlap of the metal d orbitals in the macrocycle plane with both the porphyrin a_{2u} molecular orbital and the OPV π^* orbitals. This interaction would allow the transfer of electron density from the nitrogen atoms, through the metal center, to the unoccupied π^* orbitals of the OPV system. The N 1s binding energy would ultimately increase, resulting in the appearance of the 400.1 eV peak seen in Figure 4. This interaction would similarly apply to neat films of all the Zn−porphyrin polymers (see Table 2). Scheme 1b depicts the intermolecular interaction between the porphyrin and conjugated bridge unit, as identified by this XPS study.

Free-base porphyrin polymers cannot take part in this type of $d-\pi^*$ interaction. However, some favorable orbital overlap of porphyrin and OPV π systems may be possible, because those factors which prevent $\pi-\pi$ interactions are not present (i.e., metal−solvent coordination). Emission spectroscopy on free-base porphyrin polymers also indicates interpolymeric interactions in neat films.[21] Though further study is necessary, it is conceivable that $\pi-\pi$ interactions could be partly responsible for the minor deviations in N 1s peak positions and separation, relative to free-base monomers, as presented in Table 1.

Self-Assembled Multilayer Architectures. In a previous study, we reported the self-assembly of porphyrin oligomer multilayers, which were well ordered in two dimensions.[17] Our initial XPS data exhibited a broad N 1s XPS signal. This was deconvoluted into several peaks, with two of them attributed to the porphyrin nitrogen atoms. The study herein supports our initial hypothesis, which stated that the two N 1s peaks resulted from multiple chemical environments caused by intermolecular interactions between porphyrins and conjugated bridges of nearby oligomer chains. In addition, we can now identify the contribution of coordinated solvent molecules as a further cause of structural defects. Referring to our proposed structure (Figure 2), these defects could have been minimized if there was a means of controlling the oligomer orientation within each layer and if each porphyrin coordinated two bipyridyl ligands. However, zinc−porphyrins typically coordinate a single ligand.[46−48] New systems will, therefore, concentrate on metalloporphyrins capable of six-coordinate complexation and polymers that can better organize in the third dimension.

Conclusion

Data from the N 1s XPS region are useful and sensitive probes of the inter- and intramolecular interactions in porphyrin polymers. Metalloporphyrin monomers and dimers typically show a single N 1s peak.[2a,3−6,9,10,13] The Zn−porphyrin polymers studied in this report are unprecedented in that they display two N 1s peaks. This result suggests the presence of multiple chemical environments at the porphyrin nitrogen atoms. We conclude that they arise from two types of intermolecular interactions. Trapped coordinated solvent molecules increase the electron density at the nitrogen atoms. The N 1s binding energy is lowered, relative to the extensively dried four-coordinate ZnPPV5. The N 1s binding energy is increased by interpolymer interactions between Zn−porphyrins and conjugated OPV segments on nearby chains. Charge is drawn from the nitrogen atoms, through the metal d orbitals, into the unoccupied OPV π^* orbitals. The combination of these interactions is ultimately responsible for the unusual XPS results observed. Similar porphyrin polymers and multilayer arrays are susceptible to the same kinds of interactions and defects. Therefore, XPS is extremely useful in the characterization of these types of solid-state materials.

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