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Conjugated Chromophore Arrays with Unusually Large Hole Polaron Delocalization Lengths

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Extensive experimental data identify the magnitude of the polaron/soliton delocalization length as a primary determinant of the measured value of charge/spin mobility in conjugated electronic materials.[1] The maximal such intrachain delocalization distances observed in processable organic semiconductors range between 20 and 30 Å;[2] interestingly, these effective conjugation length benchmarks established in acetylene-, phenylenevinylene-, and aryleneethynylene-based polymers have evolved little over the past three decades, despite extensive synthetic modifications to these classic conjugated backbones. Fundamental theoretical frameworks developed for charge transfer reactions point to the importance of low inner-sphere reorganization energy (λ_i) to maximize the spatial extent of cation and anion radical wave functions and fix low activation barriers for charge hopping.[3] Here we show that oligomers based on low λ_i (porphinato)zinc(II) (PZn) units[4] delineate conjugated materials having the largest hole polaron delocalization lengths yet measured.

Electron paramagnetic resonance (EPR) spectroscopy can probe charge/spin mobility in conjugated structures;[1] for example, narrowing of the electron spin resonance line width for a conjugated material, relative to that evinced by the localized magnetic moment of the building block monomer, signals the extent of charge/spin delocalization and provides a spectroscopic handle with which to assess the migratory behavior of such species in π-conjugated oligomers. Figure 1 displays such ambient temperature EPR data for the cation radical states of *meso*-to-*meso* ethyne-bridged (porphinato)zinc(II) oligomers (**PZn*n*** species).[5]

EPR spectroscopy shows that the cation radical state of the **PZn$_1$** benchmark possesses a g value of 2.003 ± 0.0005, with an overall envelope line width of 6.0 ± 0.1 G at 298 K (Figure 1, Supporting Information). The line width is governed primarily by the hyperfine interaction $H_{\mathrm{hf}} = \Sigma \vec{S}\cdot A_i \cdot \vec{I}_i$ (where S and I_i refer to the respective electron spin and nuclear spin, and A_i denotes the magnitude of the interaction); in these species, the line width is dominated by ^{14}N and ^{1}H hyperfine couplings. The hyperfine structure characteristic of the **PZn$_1$** cation radical EPR spectrum derives from the fact that it possesses a highest occupied molecular orbital (HOMO) derived from a_{2u} symmetry;[6] due to the substantial N-centered electron density in this orbital, the four equivalent pyrrole nitrogen atoms thus give rise to $2I + 1$ hyperfine lines, with a nitrogen hyperfine coupling of 1.41 ± 0.05 G, a value consistent with that measured previously for related (porphinato)metal cation radical species using this technique.[6a] Note that **PZn$_2$−PZn$_7$** also possess a_{2u}-derived HOMOs;[5e] hence, similar hyperfine coupling interactions contribute to the observed [**PZn$_2$−PZn$_7$**]$^+$[SbCl$_6$]$^-$ spectra (Figure 1). Likewise, consistent with the aromatic nature of these radical systems, [**PZn$_2$−PZn$_7$**]$^+$[SbCl$_6$]$^-$ display measured g values of 2.003 ± 0.0005.

The EPR data obtained for the cation radical states of **PZn$_1$−PZn$_7$** bear a number of noteworthy characteristics. In these experiments, [**PZn*n***]$^+$[SbCl$_6$]$^-$ species were probed under magnetically dilute conditions (~50−100 μM). The absence of any significant intermolecular exchange interaction was verified by the observed Curie−Weiss behavior for these **PZn*n***$^+$ species; Figure 2 highlights the strict paramagnetic behavior of the **PZn$_5$**$^+$ spin system. Note that the Figure 1 EPR spectra for [**PZn$_2$−PZn$_7$**]$^+$[SbCl$_6$]$^-$ show no resolved hyperfine structure; importantly, as the conjuga-

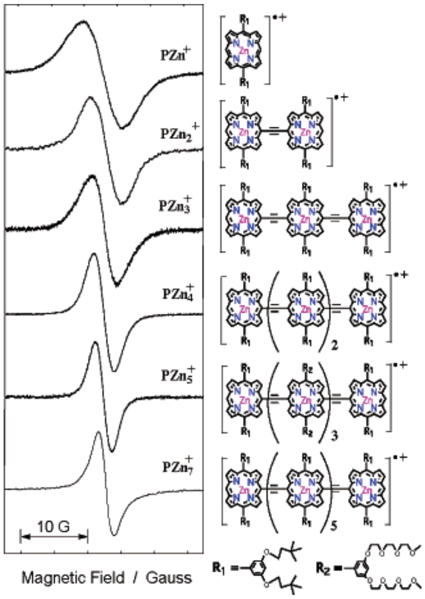

Figure 1. X-band EPR spectra of the cation radical (hole polaron) states of **PZn$_1$−PZn$_7$**. Experimental conditions: [**PZn*n***$^+$] = 50−100 μM, solvent = CH$_2$Cl$_2$, modulation amplitude = 1.0 G at 100 kHz, T = 298 K.

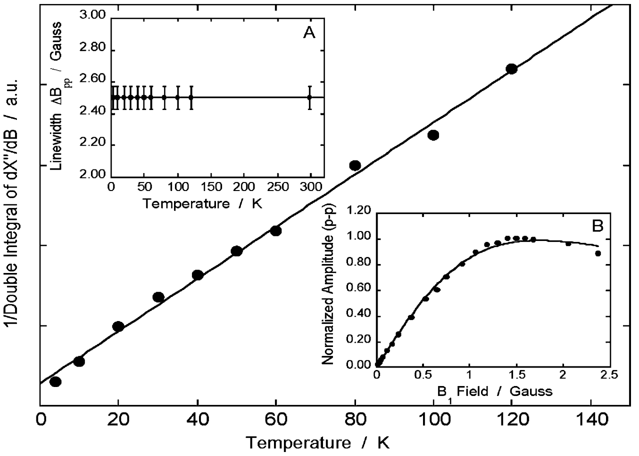

Figure 2. Curie−Weiss plot for [**PZn$_5$**]$^+$[SbCl$_6$]$^-$; the solid line is a fit to the Curie−Weiss law $\chi = C/(T - \theta)$ with $\theta \sim -8$ K ([**PZn$_5$**$^+$] = 100 μM, solvent = CH$_2$Cl$_2$). Inset A: EPR line width of [**PZn$_5$**]$^+$[SbCl$_6$]$^-$ as a function of absolute temperature. Inset B: Progressive microwave power saturation of [**PZn$_5$**]$^+$[SbCl$_6$]$^-$ at 298 K; the solid line represents a theoretical fit of the data.[8]

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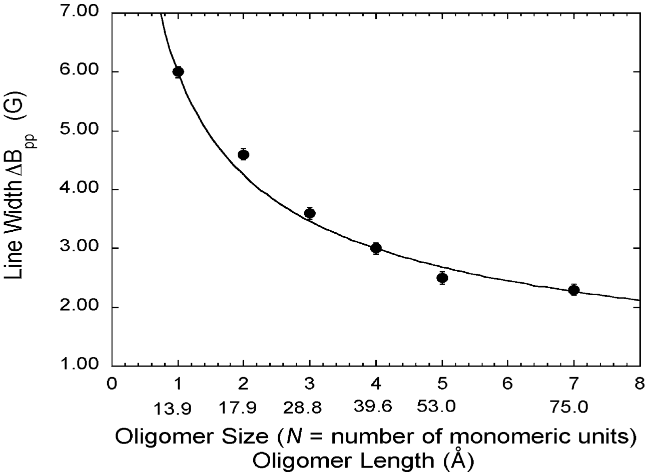

Figure 3. Plot of EPR peak-to-peak line width of the radical cation (hole polaron) states of $\mathbf{PZn_1}$−$\mathbf{PZn_7}$ at 298 K. The abscissa gives oligomer size represented by number of monomeric **PZn** units *N* and oligomer length in Å. The solid line is a fit to $6.0/N^{1/2}$ G.

tion length increases, the peak-to-peak line width ($\Delta B_{\mathrm{p-p}}$) concomitantly decreases, spanning 6.0 ($\mathbf{PZn_1}^+$) to 2.3 G ($\mathbf{PZn_7}^+$) at 298 K. Further, the EPR spectra acquired for the radical cation states of $\mathbf{PZn_2}$−$\mathbf{PZn_5}$ exhibit strict Gaussian line shapes, congruent with noninteracting spin systems with no significant exchange interaction.

An important mechanism resulting in line width narrowing stems from the averaging of the hyperfine field experienced by the spin system; this averaging originates from either coherent delocalization of the excitation or incoherent hopping on a time scale more rapid than that associated with the hyperfine interaction ($> \sim$1 MHz). Norris has predicted that in the limit of stochastic, near barrierless, one-dimensional charge hopping between *N* equivalent sites the theoretical line width is given by $\Delta B_{\mathrm{p-p}}(N\text{-mer}) = (1/N^{1/2})\Delta B_{\mathrm{p-p}}(\text{monomer})$.[7] This analysis yields a theoretical value of 2.27 G for the heptamer, given that $\Delta B_{\mathrm{p-p}}$ for benchmark monomeric cation radical complexes is 6.0 G at 298 K. Microwave power saturation measurements (Figure 2, inset B) suggest a spin lattice relaxation time of ~1 μs, while variable temperature (VT) experiments over the 4−298 K temperature domain reveal that the EPR line width for $\mathbf{PZn_5}^+$ remains constant, indicating unequivocally that the polaron delocalization length spans 53 Å, even at cryogenic temperatures (Figure 2, inset A; Figure 3). These data demonstrate for the first time fast one-dimensional stochastic hopping at 4 K over spatial domains larger than that spanned by dimeric chromophores and stand in sharp contrast to related phenylene-linked **PZn** oligomers, which show a line width transition to monomer-like peak-to-peak line width values upon freezing of the solvent, indicating abrupt hole localization.[9] Furthermore, these data are remarkable given that (i) polaronic delocalization in conventional conducting polymers attenuates dramatically upon freezing of solvent,[1b,c] and (ii) the largest spatial delocalization of a polaronic state measured previously in a hole-doped conjugated material is significantly smaller (~25 Å).[2,10] While a diverse range of conjugated structures has been described as “molecular wires”,[11] it is important to underscore that none of these compositions possess charge delocalization lengths that rival those manifest by these $\mathbf{PZn}_{\boldsymbol{n}}$ radical cations.

VT $\mathbf{PZn_5}^+$ line shape analyses (Supporting Information) demonstrate that hole migration kinetics are sufficient to maintain a $1/N^{1/2}$ scaling of the $\Delta B_{\mathrm{p-p}}$ line width (Figure 3). The EPR spectral data obtained for the $\mathbf{PZn_7}$ hole polaron state show a line width of approximately 2.3 G; it is noteworthy that the line shape of this species exhibits substantial Lorentzian character (Figure 1). EPR spectroscopic studies of samples of $\mathbf{PZn_7}^+$ at concentrations <100 μM reveal no change in the Lorentzian line shape and thus eliminate the possibility of exchange narrowing as a mechanism for the evolution of a Lorentzian line. While this result requires further investigation, it suggests that the stochastic hopping rate may be slower than that seen in $\mathbf{PZn_2}^+$−$\mathbf{PZn_5}^+$ (fast hopping regime)[7b] or may signal the transition from a global delocalization mechanism for narrowing to that of dynamic line narrowing.[7c]

In summary, given the time scale of the EPR measurement, these data show that either (i) Franck−Condon effects are incapable of driving charge localization in $[\mathbf{PZn_2}$−$\mathbf{PZn_7}]^+$, resulting in cation radical wave functions which are globally delocalized over a spatial domain that is large with respect to established benchmarks for hole-doped conjugated materials, or (ii) polaron hopping rates in these oligomers exceed $10^7\ \mathrm{s}^{-1}$, even at 4 K. Further, these EPR results verify for the first time a Norris-type hole delocalization mechanism[7] over a substantial distance (~75 Å) along a single conjugated backbone and demonstrate that polymeric building blocks having low λ_i values enable the development of conjugated materials having long polaron delocalization lengths. Finally, because charge delocalization length and charge mobility are closely correlated, these data underscore the enormous potential of hole-doped $\mathbf{PZn}_{\boldsymbol{n}}$ structures as an important new class of semiconductor materials.

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Supporting Information Available: Materials, experimental details, EPR spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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