# Modulation of Dark Conductivity over a 1 × $10^{-12}$ to 1 × $10^{-5}$ S/cm Range Through Ancillary Group Modification in Amorphous Solids of Ethyne-Bridged (Porphinato)zinc(II) Oligomers

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Semiconducting organic π-conjugated oligomers and polymers find utility in light-emitting diodes,[1a] photovoltaic cells,[1b] field-effect transistors,[1c] supercapacitors,[1d] and nonlinear optics.[1e] Significant synthetic effort has focused on engineering small band gap oligomers and polymers with appreciable room-temperature dark conductivity (DC).[2] DC measurements of such undoped organic semiconductors are taken typically in the absence of external stimuli (light, heat, dopants, etc). The genesis of charge carriers that gives rise to conduction in these systems stems from either (i) impurities,[15] (ii) shallow traps,[15,17] (iii) intrinsic charges,[2,4,5] (iv) thermal population of the conduction band,[3] or (v) charge injection from metal electrodes.[17] Experiments involving polymeric or oligomeric materials that feature appropriate ionization potentials, no intrinsic charges, no thermally generated carriers, and undetectable impurity levels manifest DCs controlled by charge injection from the electrode materials. In such studies, relative DC values depend upon the nature of intermolecular interactions in the solid, the magnitude of the carrier mobility, and the concentration of injected charge carriers.[15,17]

Common design features of π-conjugated organic materials that feature substantial DC include graphene-like[3] fused aromatic ring systems and alternating donor–acceptor (D–A) repeat units.[4] Alternating D–A motifs have been shown to drive substantial charge-transfer character along the conjugated backbone and DC values as high as 1 × $10^{-3}$ S/cm.[2b] Small molecule charge-transfer salts and charge-neutral radical crystals probed in such experiments display DCs approaching >1 × $10^{-4}$ S/cm.[5] Recent reports have underscored the importance of maximizing π-orbital overlap between oligomeric and polymeric chains in the solid state[6] and inspired efforts to design molecular building blocks with structural features that promote face-to-face stacking of aromatic components in the solid state.[7] From a practical standpoint, one would like to develop oligomers or polymers that not only have large-magnitude electronic coupling along the conjugated backbone but also have sufficient amorphous through-space electronic interactions such that crystallinity is not required for device applications.[8]

The modest one-electron oxidation and reduction potentials of (porphinato)metal compounds make these species promising building blocks for semiconducting organic materials.[9] Along these lines, (porphinato)metal and (phthalocyaninato)metal complexes featuring redox active metal–ligand systems have demostrated DCs as high as 1 × $10^{-2}$ S/cm;[10] discotic liquid crystalline materials derived from these units have been shown to feature enhanced photoconductive and

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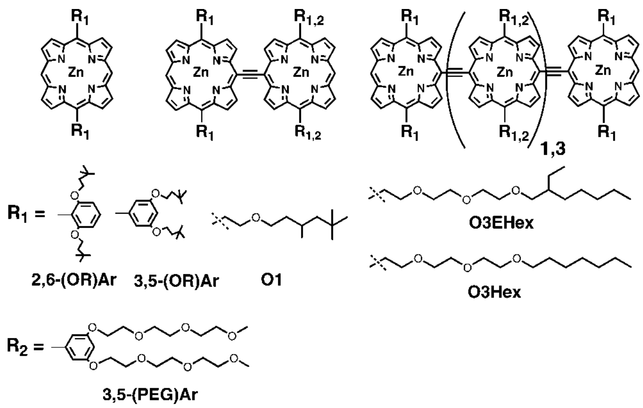
**Chart 1. PZn$_n$ Structures**[a]




[a] Exemplary abbreviation: A **PZn$_3$** oligomer in which all three macrocycles bear O1 substituents is termed **PZn$_3$O1**; see the Supporting Information for details.

photovoltaic properties because of enhanced intermolecular $\pi$-cofacial interations.[11] Alternative strategies have focused on enhancing linear $\pi$-conjugation between (porphinato)metal species to produce rigid-rod oligomers and polymers with diminished potentiometric ($E_p$; $E_{1/2}^{0/+} - E_{1/2}^{-/0}$) and optical ($E_{op}$) band gaps.[12,13]

Previous studies of *meso*-to-*meso* ethyne-bridged (porphinato)zinc(II) oligomers (**PZn$_n$** compounds; Chart 1) demonstrate that modest oligomer lengths give rise to low-energy, high-oscillator-strength $\pi$–$\pi$* absorptions that are polarized exclusively along the long molecular axis.[13] Variable-temperature solution-phase X-band EPR spectroscopic data for the cation radical states of these species show that [**PZn$_n$**]$^+$ structures possess the largest hole polaron delocalization lengths yet measured for a conjugated material (~75 Å), which remain invariant over a 4–298 K temperature domain.[13f] These data suggest that undoped, **PZn$_n$**-derived solid-state materials have the potential to exhibit impressive DC values.

Chart 1 shows a family of **PZn$_n$** structures that feature a wide range of peripheral ancillary substituents that confer substantial solubility. Note that O1, O3Hex, and O3EHex substituents provide **PZn$_n$** oligomers with solubilities similar to that evinced for the Chart 1 derivatives bearing 2,6- and 3,5-dialkoxyphenyl [2,6-(OR)Ar, 3,5-(OR)Ar, and 3,5-(PEG)Ar] peripheral substituents, but do so without augmenting steric bulk above and below the porphyrin plane. Hence,

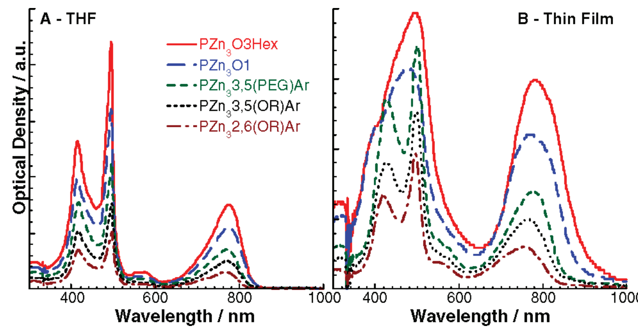



**Figure 1.** Comparative **PZn$_3$** electronic absorption spectra in (A) THF solvent and (B) thin solid films, as a function of the nature of macrocycle peripheral substituents. Note that these **PZn$_3$** oligomers possess virtually identical vis and NIR absorption band extinction coefficients; spectra have been displayed and offset on the optical density ordinate for clarity. Additional solution and thin film spectroscopic data are available in the Supporting Information.

**PZn$_n$O1**, **PZn$_n$O3Hex**, and **PZn$_n$O3EHex** oligomers are anticipated to exhibit larger intermolecular interactions in the solid state relative to previously studied **PZn$_n$** benchmarks featuring 2,6- and 3,5-dialkoxyphenyl ancillary groups.

Insight into the nature of solid-state interchain electronic interactions can be gleaned from electronic absorption spectroscopy. Figure 1 examines the degree to which **PZn$_3$** peripheral substituents influence intermolecular interactions in both solutions and thin films. In dilute (micromolar) THF solution (see Figure 1A and Supporting Information), **PZn$_3$O1**, **PZn$_3$O3Hex**, **PZn$_3$O3EHex**, **PZn$_3$2,6-(OR)Ar**, and **PZn$_3$3,5-(OR)Ar** manifest superimposable electronic absorption spectra, suggesting that these species exhibit little or no aggregation under these conditions. In the solid state, **PZn$_3$2,6-(OR)Ar** and **PZn$_3$3,5-(OR)Ar** display electronic absorption spectra remarkably similar to that evinced in THF solution; in contrast, **PZn$_3$O1**, **PZn$_3$O3Hex**, and **PZn$_3$O3EHex** thin film spectra exhibit broadened absorption manifolds, and a redistribution of B- and Q-state oscillator strength to long wavelengths, consistent with the hypothesis that these species feature enhanced intermolecular porphyrin–porphyrin $\pi$–$\pi$ interactions in the solid state.

XRD (small, intermediate, and wide-angle) and TGA/DTA measurements were performed to interrogate the solid-state morphology and stability of **PZn$_5$O3Hex** powder samples (see the Supporting Information). Small-angle XRD data showed the material to be amorphous with no discernible diffraction peaks, whereas analogous wide-angle data displayed several broad diffraction peaks centered at 26.2, 12.6, 11.0, and 4.3 Å, where the 12.6, 11, and 4.3 Å diffraction intensities were weak relative to that at 26 Å. The 26 Å interlayer spacing is consistent with that observed for other rigid-rod conjugated polymers with similar sidechains, and thus suggests some degree of lamellar structure within theses amorphous samples.[14] Aerobic DTA measurements (Supporting Information) reveal no melting point or phase

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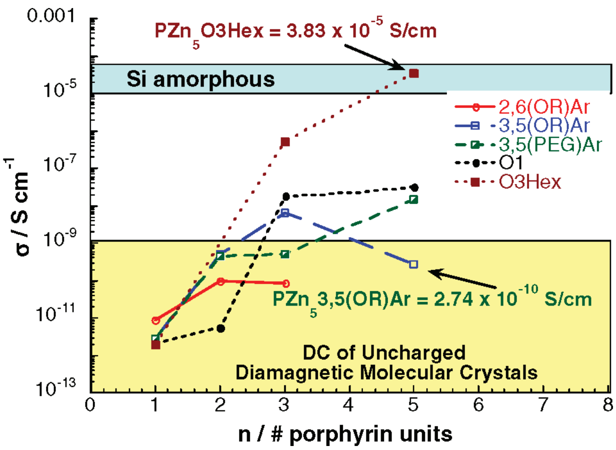


**Figure 2.** 2-Probe DC data for $\mathbf{PZn}_n$ thin films as a function of the nature of macrocycle ancillary substituents and oligomer length. The established DC ranges for uncharged diamagnetic crystals and amorphous Si are highlighted.[15] Benchmark DC values for representative undoped semiconducting polymers (not shown in figure) include polyacetylene (DC $\sim 1 \times 10^{-5}$ S/cm),[16ab] polythiophene (DC $> 1 \times 10^{-5}$ S/cm),[16c] and polyaniline (DC $\sim 1 \times 10^{-10}$ S/cm).[16b] $\mathbf{PZn}_n$ DC values and standard deviations (see the Supporting Information) were determined from a minimum of 3 independent measurements. $\mathbf{PZn}_n$**O3EHex** data are omitted for clarity. The Supporting Information compiles all 2- and 4-probe DC data.

transition, whereas TGA results show that the onset of decomposition for $\mathbf{PZn}_{3,5}$**O3Hex** is ~220 °C.

DC measurements of both thin film (Figure 2) and pressed pellet samples of $\mathbf{PZn}_n$ oligomers gave consistent results (Supporting Information). Note that measured DCs for these low-molecular-weight oligomers span an impressively wide range ($2 \times 10^{-12}$ to $4 \times 10^{-5}$ S/cm). These data (see Figure 2 and Supporting Information) show that $\mathbf{PZn}_n$ species bearing 2,6-(OR)Ar, 3,5-(OR)Ar, and 3,5-(PEG)Ar solubilizing groups behave as insulators over the $\mathbf{PZn}_1$–$\mathbf{PZn}_5$ length scale. In contrast, $\mathbf{PZn}_n$ species that feature **O1**, **O3Hex**, and **O3EHex** substituents show dramatic augmentation of DC with increasing oligomer length. For example, $\mathbf{PZn}_5$**O3Hex** is $>1 \times 10^4$ times more conductive than $\mathbf{PZn}_5$**3,5-(OR)Ar** in the solid state. Moreover, these $\mathbf{PZn}_n$**O3Hex** derivatives feature a $>1 \times 10^6$-fold increase in measured DC from monomer to pentamer. Congruent with the Figure 1 data, these DC results are consistent with the view that **O1**-, **O3Hex**-, and **O3EHex**-based substituents substantially enhance $\mathbf{PZn}_n$–$\mathbf{PZn}_n$ interchain electronic coupling in the solid state. Because both absorption band broadening and oscillator strength redistribution to longer wavelengths increase in concert with conjugation length in thin film samples of $\mathbf{PZn}_n$**O3Hex** and $\mathbf{PZn}_n$**O1** species (Supporting Information), further improvements in solid-state DC may be realized in samples prepared from larger-molecular-weight $\mathbf{PZn}_n$ oligomers.

We note that $\mathbf{PZn}_n$ samples interrogated in this study were extensively chromatographically purified prior to spin casting and pellet formation (Supporting Information). Solution ESR studies of these pressed pellet and thin film samples demonsrate no detectable spins at millimolar oligomer concentration at maximum gain (see the Supporting Information); these experiments thus place a lower limit on charge-carrier impurites in these $\mathbf{PZn}_n$ oligomers of 1 part in $1 \times 10^{12}$. In this regard, it is notable that thin films of $\mathbf{PZn}_{3,5}$**O3Hex** exposed to air in ambient light for a week exhibited DCs $1 \times 10^2$ to $1 \times 10^3$ times higher than the samples chronicled in the Figure 2 data, which were stored under a vacuum and measured under an inert atmosphere. Cyclic voltammetric studies of $\mathbf{PZn}_{3,5}$ demonstrate appropriate ionization potentials (4.9 and 4.6 eV, respectively) for charge injection from gold electrodes ($\theta_w$ = 5.2 eV) (Supporting Information).[17] These data, coupled with the EPR spectroscopic results and the facts that DC increases with increasing molecular length (diminished $E_p$ and $E_{op}$) and enhanced intermolcular interactions, are all consistent with charge injection from Au electrodes as being the dominant source of charge carriers in these DC measurements.

In summary, these studies (i) show that the dark conductivity of undoped, low-molecular-weight $\mathbf{PZn}_n$ oligomers can rival that of amorphous Si, (ii) demonstrate that sterically unencumbered $\mathbf{PZn}_n$ oligomers give rise to augmented interchain electronic coupling in the solid state and provide electronically functional thin films via direct spin-casting, and (iii) highlight an example where ancillary group modification in a conjugated organic oligomer modulates the measured DC by more than 4 orders of magnitude. Furthermore, the fact that solid-state samples of undoped $\mathbf{PZn}_5$**O3Hex** possess the largest DC yet measured for an amorphous, electronically homogeneous charge-neutral organic material suggests exceptional utility for $\mathbf{PZn}_n$-based oligomers and polymers in organic electronic devices.

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**Supporting Information Available:** Reaction schemes, synthetic procedures, characterization data, details regarding electrical measurements, XRD, TGA/DTA, GPC, potentiometric, and conductivity data (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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