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Charge and Spin Delocalization in Novel Porphyrin Oligomers P.

FRAIL, K. SUSUMU, M.J. THERIEN, Dept. of Chemistry, Univ. of Pennsylvania, Philadelphia, PA 19104, P.J. ANGIOLILLO, Dept. of Physics, St. Joseph's University, Philadelphia, PA 19131, J.M. KIKKAWA, Dept. of Physics & Astronomy, Univ. of Pennsylvania, Philadelphia, PA 19104 — We discuss a new class of meso-to-meso ethyne-bridged (porphinato)zinc(II) oligomers with potential for TFT, FET, photovoltaic, magnetic, and spintronic applications on both a single molecule and bulk level. As the series progresses from dimer through heptamer, intramolecular electronic delocalization results in red-shifted optical transitions (2.0 eV-1.4 eV) and motional narrowing of the EPR signal. The former is consistent with potentiometrically determined HOMO-LUMO gaps, while the latter indicates spin delocalization lengths that span the molecular length scales of these structures (20 -75 Angstroms). Generally, solubilizing appendages impose steric restrictions which can largely prevent such properties from transferring to the bulk phase. Through systematic modification of these appendages, the intermolecular resistance can be lowered dramatically. Resistivities measured for undoped oligomers can vary over 2-5 orders of magnitude for a given conjugation length. These large changes in resistivity correlate with the nature of the $\pi - \pi$ interactions made possible in the bulk phase. The doped species of these systems will also be discussed along with photoconductive properties. This work partially supported by DARPA/ONR N00015-01-0831.

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