

Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Vast Hole- and Electron-Polaron Spatial Extent in Oligomeric π -Conjugated Porphyrin Arrays PAUL ANGIOLILLO, Saint Joseph's University, JEFF RAWSON, MICHAEL THERIEN, Duke University — *meso*-Ethyne bridged π -conjugated zinc porphyrin oligomers (PZn_n compounds) have been demonstrated to evince lowest excited singlet states that are globally delocalized. It has also previously been shown that hole-polaron states of these oligomers exhibit delocalization lengths that mirror the molecular spatial dimension, 7.5 nm in the case of the heptamer. Here we demonstrate that the electron-polaron states in PZn_n compounds also feature vast areal delocalization. This finding is evidenced by concurrent optical and electron spin resonance measurements, coupled with electronic structure calculations that suggest atypically small reorganization energies for one-electron reduction of these materials. These results are buttressed by electron spin relaxation measurements of PZn_n electron polarons that show that both T₁ and T₂ relaxation times are unusually large, on the order of 10³ ns and 10² ns, respectively. Since rapid charge delocalization defines an important mechanism that mitigates Coulombic stabilization of photogenerated electron-hole pairs to create separated free charge carriers, and spin polarization lifetimes feature prominently in spin currents, these findings identify conjugated materials with exceptional optical, electronic, and spintronic properties.

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Date submitted: 05 Nov 2015

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