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Probing Polaron Dynamics and Transport in Multiporphyrin Conjugated Arrays by EPR and Optical Spectroscopy PAUL ANGIOLILLO, Saint Joseph's University, JEFF RAWSON, MICHAEL THERIEN, Duke University — The nature of mobile charge carriers and their transport in organic conducting and semiconducting materials is still an area requiring deeper understanding. Unlike in classical metals, charge carriers are not represented well by bare charges but rather as polarons. Hole and electron polarons were chemically generated in a systematic series of meso-to-meso ethyne-bridged (porphinato)zinc arrays (PZn_n), spanning a linear dimension of 1.4 nm to 7.5 nm. Determination of the spin distribution through the nuclear hyperfine interaction suggest that both hole and electron polarons are extensively delocalized over the extent of the molecule at 298 K. Low temperature studies at 77 K further reveal that the polaronic states maintain their ability to explore the extent of the molecule. Concomitant optical absorption spectroscopy of the hole polaronic states in these oligomers further supports the delocalized nature of the excitation. Electron spin relaxation in organic materials devoid of heavy atoms is dominated by the nuclear hyperfine interaction. This decreased interaction manifest itself in a simultaneous decrease in the spin lattice relaxation rate (increase in spin lattice relaxation time T_1) with oligomer size as determined through progressive microwave saturation with relaxation times on the order of 1μs at 298 K. These data demonstrate exceptional and unprecedented charge dynamics and polaron delocalization lengths.

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