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An Epr Study of Alkali-Metal-Doped Poly(P-Phenylene) and P-Phenylene Oligomers

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AN EPR STUDY OF ALKALI-METAL-DOPED POLY(p-PHENYLENE) AND p-PHENYLENE OLIGOMERS

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Abstract. Poly(p-phenylene), PPP, and fully-deuterated poly(p-phenylene), DPPP, were heavily doped with lithium, sodium, potassium, rubidium, cesium, and successively with potassium then lithium. Inert atmosphere conditions using alkali naphthalides in THF were used. The spin susceptibility of each of these samples was not Curie-Weiss over the entire temperature range 7 to 300 K. The EPR linewidths at 300 K of donor-doped PPP were dependent on spin-orbit coupling with the alkali metal, varying from a peak-to-peak width at 300 K of 0.5 G for the lithium-doped sample to 5.5 G for the cesium-doped sample. A small decrease in linewidths was noted upon doping of DPPP, these same linewidths equaling 0.35 and 4.5 G. In contrast, the linewidths of Li, K. and Rb graphite complexes are much larger. The linewidth for potassium-doped PPP decreased from 1.9 G at 300 K to 0.45 G at 7 K while the linewidth for potassium-doped p-terphenyl, p-quaterphenyl, and p-sexiphenyl increased. The concentration of unpaired spins at 300 K was approximately 10% of the potassium concentration. These observations suggest that the equilibrium between the radical anion and the dianion (paramagnetic ⟶ diamagnetic) may be important and that alkali metal orbitals and hydrogens do interact with the unpaired electrons on the polymer chain.