Abstract: Open-shell molecules possess unpaired electron density (radical character), which makes them intriguing candidate materials for many optoelectronic applications. Air-stable structures have been reported, but most require lengthy synthetic sequences with limited generality. Our lab has developed a concise strategy for rapidly accessing a variety of bisphenalenyls from commercial starting materials. We used this method to synthesize a neutral biradicaloid, Ph2-s-IDPL, and several novel heteroatom-substituted, π-radical cations. One such molecule is O-substituted (Ph2-PCPL)(OTf), which displays electrostatically-enhanced, intermolecular covalent-bonding interactions that impart remarkable charge transport properties. Specifically, we have discovered that mixing soluble PCPL derivatives with polystyrenesulfonate (PSS) enables the formation of water-processable, n-type conductive organic films that demonstrate high optical transparency (>94% transmission), electrical conductivity (σrt < 117 S/cm), and electron mobility (μe < 27 cm2 V-1 s-1). In these composites, PSS not only serves as a counterion, but also promotes n-doping and solution-phase aggregation, which leads to molecular ordering in the solid-state. We have also discovered a N-substituted, red emissive, π-radical cation [(Ph2-PQPL)(OTf)] that is structurally distinct from all other luminescent radicals, and achieves rare antiambipolar charge transport in field-effect transistors. N-substituted bisphenalenyls also display self-sensitized and reversible reactivity with dioxygen that shows potential for use in colorimetric oxygen sensors and for acid-triggered singlet oxygen release.