ES9

Hybrid Redox Polyether-Metalloporphyrin: Synthesis and Application to Chemical Analysis of the Melts

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The preparation and electrochemical characterization are described for a new class of metallo-porphyrins in which four oligomeric ethylene glycol chains are attached to each porphyrin structure. The resulting redox polyether hybrids are viscous liquids at room temperature, highly concentrated in porphyrin site (~ 0.4 M), and dissolve large quantities of lithium salts. Microelectrode voltammetry and chronoamperometry have been used to assess the charge transport rates for various reactions in the undiluted melt state of the polyether-porphyrin. The apparent diffusion coefficients, DAPP, vary over a wide range depending on the specific redox reaction and on the amount of added lithium electrolyte. The largest DAPP values are found for redox reactions centered on the porphyrin ring, while the smallest values are seen for the Fe III/II reaction. This difference is ascribed to enhanced charge transport by an electron hopping mechanism in the former cases. The temperature- dependence for DAPP was used to examine activation parameters. The interaction of polyether-porphyrin melts with the axial ligand, (CO, pyridines, NO) and electroatalytic effect for oxygen reduction were were also examined by voltammetry.