

New insights into the electrochemistry of quinoxalinoporphyryns

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New insights are provided into the electrochemistry of quinoxalinoporphyryns which were investigated in several nonaqueous solvents containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The investigated compounds are represented as $(PQ_n)M$ where P is the dianion of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin, Q is a quinoxaline group, $n = 1-4$ and $M = Zn^{II}, Pd^{II}, Cu^{II}, Ni^{II}$ and $Au^{III}(PF_6)$ (see Chart 1). Two oxidations and up to five reductions can be observed for each compound depending on the solvent, central metal ion and number of fused quinoxaline groups. The results from thin-layer UV-visible spectroelectrochemistry in conjunction with the measured half-wave potential of each redox reaction were used to assign the site of electron transfer and characterize the oxidation and reduction products. Several nitro-substituted quinoxalinoporphyryns were also investigated and the redox potentials analyzed by linear free energy relationships. An increase in the number of fused quinoxaline groups on the porphyrin macrocycle generally results in easier reductions and easier oxidations, leading to smaller HOMO-LUMO gaps as compared with the same porphyrins not containing a fused quinoxaline group. However, this was not always the case as discussed in the current paper.

Chart 1 Structures of investigated metalloporphyrins with 1-4 fused quinoxaline groups

