

Electrochemistry of Quinoxalino- and Bis-Quinoxalino-Porphyrins Containing Metal(II) Ions

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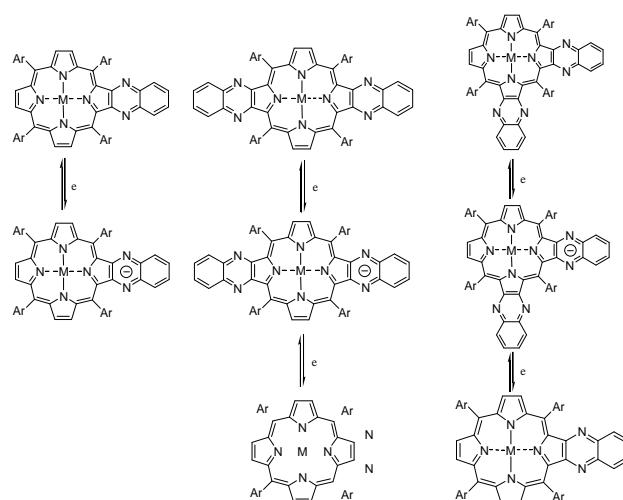
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The electrochemistry of *t*-butyl-tetraphenylporphyrin and *t*-butyl-tetraphenyl-quinoxalinoporphyrin, represented as (P)M and (PQ)M (see Figure 1) were investigated in the different nonaqueous solvents. Electrochemical data showed that the fusion of an electroactive quinoxaline group to an electroactive porphyrin (P \Rightarrow PQ) results in easier reductions of the porphyrin part of the molecule while the quinoxaline-centered redox processes shifts to more negative potentials. The investigated (P)M complexes undergo one or two ring-centered reductions and one or two ring-centered oxidations while additional reductions are seen in the case of (PQ)M. The average HOMO-LUMO gaps for the (P)M and (PQ)M derivatives are 2.26 ± 0.09 V and 2.14 ± 0.08 V, respectively. Both values are smaller than the average separation of 2.33 ± 0.13 V for the corresponding derivatives of (TPP)M.

The fusion of two quinoxaline groups either on the opposite side of porphyrin (P \Rightarrow QPQ) or on the corner side of the porphyrin (P \Rightarrow PQ₂) both result in even easier reductions with the shift in $E_{1/2}$ amount to 20 to 200 mV. (QPQ)M is the most reducible among these four kinds of complexes. The average HOMO-LUMO gaps for the (PQ₂)M and (QPQ)M derivatives is 2.03 ± 0.02 V and 1.93 ± 0.03 V, respectively. Both the values are smaller than the average separation of (P)M and (PQ)M.

UV-visible spectroelectrochemical data indicate that electron density shifts from the porphyrin ring to the quinoxaline group during both the first and second reductions to give π -anion and π -dianion radicals. This agrees with the results from the studies on (PQ)M (see Scheme 1).

Detailed redox properties on these complexes will be reported on the mechanism and electron transfer will be elucidated.



Scheme 1. Mechanism of electron transfer.

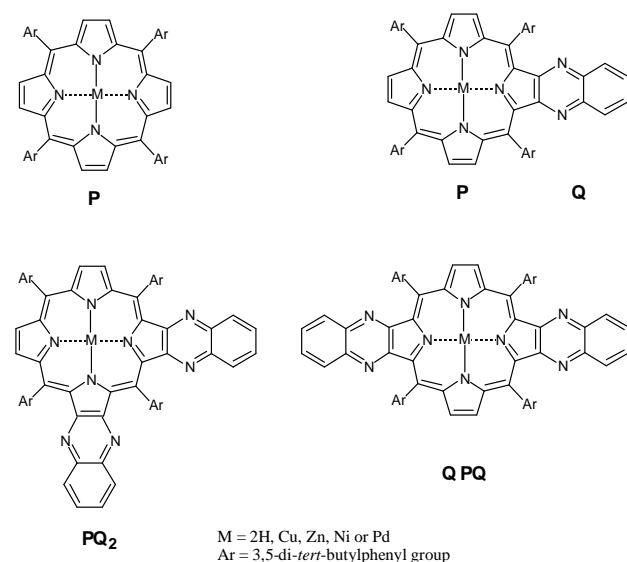


Figure 1. Structures of investigated complexes.