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研究论文

羟基卟啉化合物的电化学、顺磁共振及时间分辨光电压性质

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摘要 通过循环伏安法、电子顺磁共振谱和时间分辨电压光谱研究了羟基取代基数目和位置的不同对羟基苯基卟啉化合物的电化学、电子顺磁共振和时间分辨光电压性质的影响. 研究结果表明, 所有氧化还原反应都是在卟啉环上进行的. 卟啉周边取代基数目的增加使得卟啉共轭体系平均电子云密度增大, 导致体系易氧化而难以还原. 对称性增强可能使卟啉化合物的半波电位值向正方向移动, 羟基取代基的给电子效应对于卟啉化合物电化学性质的影响起主导作用. 常态下卟啉分子没有EPR信号, 在光的激发下, 卟啉分子由原来的逆磁性分子变成顺磁性的激发三重态分子, 这种激发三重态分子在分子轨道上具有两个未成对电子, 这两个电子相距很近, 彼此之间发生很强的相互作用而产生电子, 它的*g*值随卟啉共轭体系平均电子云密度增大而变大. 时间分辨光电压是由分子中的自由光声载流子的存在而产生的, 光电压的衰减与分子结构密切相关, 它们的电荷分离速度基本上随卟啉周边羟基取代基数目的增加而减慢.

关键词 羟基苯基卟啉 电化学性质 电子顺磁共振性质 时间分辨光电压性质

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Properties of Electrochemistry, EPR and Time-resolution Photovoltage of a Series of Hydroxyphenyl Porphyrins Compounds

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Abstract The effects of the number and the location of hydroxyl substituents on electrochemistry, EPR and transient photovoltage properties of a series of hydroxyphenyl porphyrins were studied for the first time. The study results indicate that all oxidation-reduction reactions occur on the macroring of porphyrin. With the increase of the number of the periphery substituents of porphyrin, the conjugate system is getting to be easy for oxidation, difficult for reduction. An increase in structure symmetry would cause positive shift of half-wave potential values. The reinto the electron-donation effect of the porphyrin compounds on their electrochemistry property played a main role. At the normal state, porphyrin molecules do not have EPR signal. However, light excitation may cause a transition of porphyrin molecules from singlet to triplet. At the same time, the change from diamagnetism to paramagnetism occurred to porphyrin molecules. In this case, the two un-paired electrons are nearby each other and cause a strong interaction, giving EPR signal with sharp peak at $g=2.000$. The g value increased with an increase in electron cloud density. Time-resolution photovoltage is generated from the free photoacoustic carrier. The decay of photovoltage is closely related to the molecular structure and the separation velocity of their charge, which decreased on the whole with an increase in the number of periphery hydroxyl substituents.

Key words Hydroxyphenyl porphyrin Electrochemistry property EPR property Time resolution Photovoltage property

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