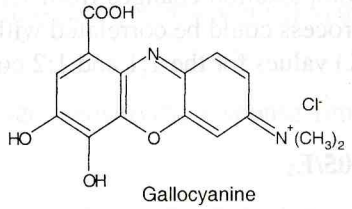
Coulombic interaction of anionic bromopyrogallol Red (BPR) with cationic Fe(II) complexes of gallocyanine and their electrochemical studies

W K Chandima and P M Jayaweera*
Department of Chemistry, University of Sri Jayewadenepurapura, Nugegoda

Transition metal centers coordinated to catecholate type ligands have attracted the attention of many scientists due to their ability to increase the efficiency of nonporous dye sensitized photoelectrochemical cells. The nature of the lowest electronic transition state and redox properties of these complexes provide valuable information when designing such systems. The two complexes Fe(II)(C_2O_4)$_2$gallocyanine and Fe(II)(gallocyanine)$_3$ where, gallocyanine is 7-dimethylamino-4-hydroxy-3-oxo-phenoxazine-1-carboxylic acid were synthesized and characterized by spectroscopic and electrochemical techniques. The chatecholate part of the ligand shows o-quinone/o-semiquinone and o-semiquinone/o-catecholate (i.e.o-Sq/o-Cat) redox couples.



Gallocyanine

Absorption spectrum recorded in DMSO solution shows a band at 599 nm for the uncoordinated gallocyanine ligand. This peak appearing for the uncoordinated ligand arises due to a $\pi \rightarrow \pi^*$ transition. Absorption data suggest that the lowest electron transition has a Metal-to-Ligand Charge Transfer (MLCT) character for the two metal complexes (λ~800 nm). The Cyclic (CV) and Square Wave Voltammetric (SWV) data in DMSO indicate (e.g. *inserted* Fig. I), that the redox values of gallocyanine are reduced by the addition of anionic BPR. The same behavior was observed for the Fe(II)gallocyanine complexes. The drop of oxidation potentials may well be due to the strong coulombic interactions that take place between anionic BPR and cationic gallocyanine ligand. The MLCT character and the strong interaction of anionic BPR would provide better mix-dye systems in photovoltaic devices.

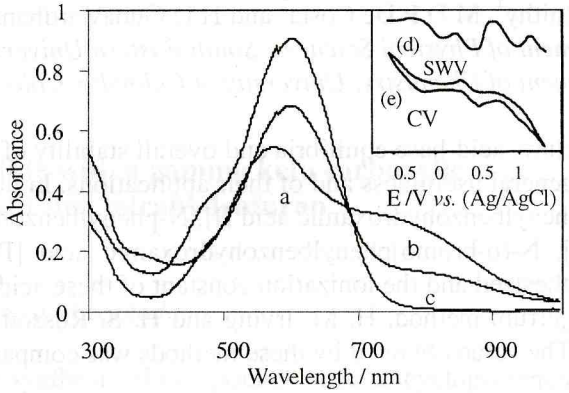


Fig. 1 Absorption spectra of (a) Fe(II)(C_2O_4)$_2$gallocyanine complex. (b) Fe(II)(gallocyanine)$_3$ complex , (c) gallocyanine free ligand. Inserted: SWV and CV of Gallocyanine in the presence of BPR. Solvent DMSO.