

E2-36 Molecular mechanics and semi-empirical molecular orbital calculations of pelargonidin, cyanidin, delphinidin and their Ti(IV) complexes

A R Kumarasinghe, Pradeep M Jayaweera

(Dept of Chemistry, University of Sri Jayewardenepura, Nugegoda)

The field computational calculations, particularly in the area of molecular modelling is now widely used to characterize, predict the structures and to understand the stability of chemical systems. Three naturally occurring flower pigments, pelargonidin, cyanidin, delphinidin and their metal complexes (fig. 1) were examined using computational calculation methods as these dye materials have shown remarkable ability to act as potential sensitizers in nanoporous photovoltaic cells.

Computational investigation was performed using HyperChem molecular modelling and quantum mechanics program. Geometry of all the 5 molecules were first optimized using the molecular mechanics geometry optimization method MM+. Subsequently a semi-empirical quantum mechanical calculation, either AM1^[3] or PM3^[4] was used to obtain the final geometry. These fully geometry optimized molecules were used to carry out single point calculations to understand the electronic properties.

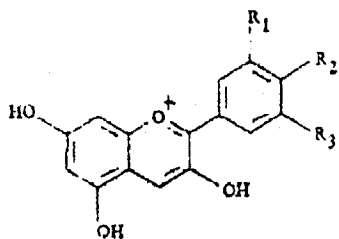


Fig. 1a

Pelagonidine $R_1 = H, R_2 = OH, R_3 = H$

Cyanidine $R_1 = H, R_2 = OH, R_3 = OH$

Delphinidine $R_1 = OH, R_2 = OH, R_3 = OH$

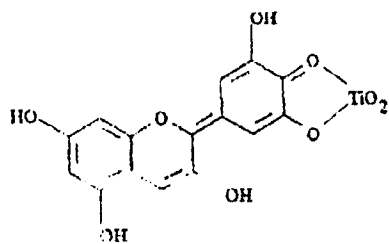


Fig. 1b

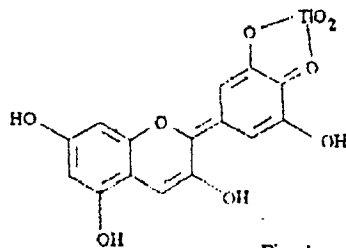


Fig. 1c

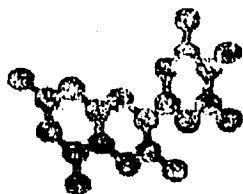


Fig. 1d

Fully optimized geometries of above pigments all show a torsion angle of ca. 17°. This can be easily attributed to the strong repulsion forces operating between positively charged oxygen atom and 6'-H of the phenyl ring. Addition of -OH groups to the phenyl ring reduce energies of both HOMO and LUMO levels by ca. 605 cm⁻¹ wave numbers.

Metal coordinated systems having quinonoid geometry show planarity due to increase in bonding character of the inter-ring C-C bond. Calculated bond lengths are 1.437 Å and 1.357 Å for the free ligand and metal complexed molecule respectively. Hence, substantial overlap of molecular orbitals between the ligand and metal centre makes photo-excited electron ejection from LUMO level of the ligand to the conduction band (CB) of Ti(IV) ion an efficient process. Comparing the coordinated cyanidin and delphinidin systems, energy of the LUMO in delphinidin is 590 cm⁻¹ below cyanidin. Therefore, theoretically we can predict that the photocurrent conversion efficiency of delphinidin should be higher than that of cyanidin coated photocells due to reduction of charge recombination.

Financial assistance by University of Sri Jayewardenepura and NARESA (RG/98/c/05) for the studentship to ARK is acknowledged.