Ab initio Density Functional Methods to Probe the Site of Electron Transfer in Fullerene Bearing Dyads and Triads

Melvin E. Zandler, Phillip M. Smith and Francis D'Souza

Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051, USA

Evaluation of the sequence of the site of electron transfer in molecular systems bearing one or more redox active groups, designed for photochemical energy conversion and developing optical devices, is essential information. Knowledge of the redox potential based sequence of electron transfers is an important property needed to arrive at the electron transfer pathways in supramolecular systems. Spectroelectrochemistry is often employed to probe the redox sites. However, difficulties arise when the redox potentials of the different entities are closely located from one another.

In the present study we have explored the utilization of computational methods to predict the sequence of the site of electron transfer in molecular dyads and triads composed of fullerene, ferrocene and nitroaromatic entities (Scheme 1) and the results have been compared to experimental studies. Both semi-empirical (AM1 and PM3) and moderate level *ab initio* (Hartree Fock and Density Functional) methods have been utilized to explore the geometric and electronic properties of these molecular systems. While semi-empirical AM1 and PM3 as well as Hartree Fock *ab initio* methods usually produce a plausible geometry, an incorrect electronic structure, based on the location of the HOMO and LUMO orbitals, is often obtained by these methods. However, as will be demonstrated in the present contribution,[1,2] *ab initio* methods at B3LYP/3-21G(*) level accurately predict both the geometry and the electronic structure in these molecular systems.

Scheme 1
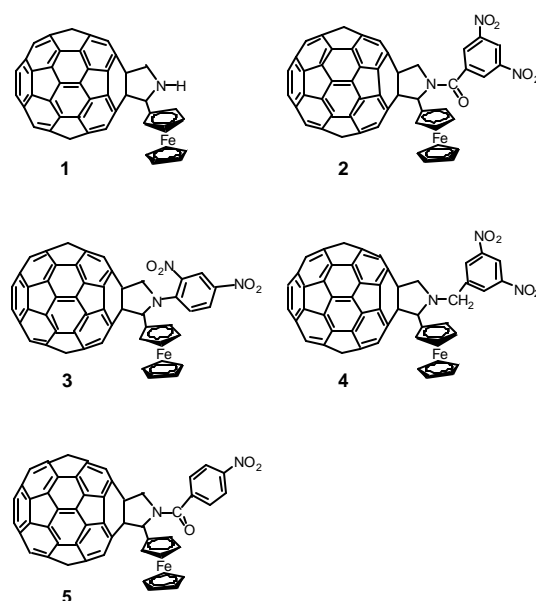
References

1. D'Souza, F.; Zandler, M. E.; Smith, P. M.; Deviprasad, G. R.; Arkady, K.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 649.

2. Zandler, M. E.; Smith, P. M.; Fujitsuka, M.; Ito, O.; D'Souza, F. *J. Org. Chem.* **2002**, *67*, 0000.