Unraveling to the Ground State Electronic Structure of a Synthesized Fullerene–Metalloocene Functional Dyad

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INTRODUCTION

The ability of electron or charge transport over long distances is essential to the development of solar energy conversion systems and molecule-based electronics. The design of functional dyad covalently linked electron donors and acceptors is a valuable approach towards electron transport. Incorpotation of a spacing unit into donor-bridge-acceptor molecular assemblies allows control of the distance and angles between the donor-acceptor sites that subsequently governs the rate and charge recombination processes. Fullerenes, and in particular the readily available C₆₀, possess a wide range of physical and chemical properties that makes them interesting building blocks for supramolecular assemblies and new materials. The remarkable electron acceptor property of ground state C₆₀ is capable of accommodating as many as six electrons in solution. It displays a reduction potential of (-0.44V) vs standard calomel electrode (SCE) in presence of DCM (Dichloromethane) [6]. Efficiency of long distance electron transfer

EXPERIMENTAL SECTION

Synthesis of ferrocene-triazole-ferrocene

Synthesis of ferrocenetosylate;

To a solution of 0.5 gm (0.00231 mol, 1 equiv) of ferrocene methanol, 10 mL of triethyl amine was added and refluxed for 10 min. This mixture was then cooled (00C) and 0.659 gm (0.0034 mol, 1.5 equiv) of p-toluene sulfonyl chloride (PTSL) were added under nitrogen atmosphere in presence of catalytic amount(50 mg) of DMAP (dimethylaminopyridine). The mixture was then stirred for 24 h at room temperature. The crude material so formed, was purified by column chromatography (silica gel) using dichloromethane as eluent and was characterized by FTIR.

Ferrocenemethanol-FT-IR(KBr), in cm⁻¹ 815, 848, 890, 923, 1012, 1042, 1106, 1189, 1235, 1350, 1383, 2353, 2830, 2924, 3235, 3437 (OHstr). Ferrocenotosylate-FT-IR(KBr) in cm⁻¹ 815, 848, 890, 923, 1012, 1036, 1067, 1124, 1106, 1187, 1214, 1569, 1647, 2490, 2529, 2924.

Synthesis of ferroceneazide

To a solution of ferrocenotosylate (0.676 gm, 0.0018 mol), sodium azide 0.6 gm (0.00915 mol, 5 equiv) in 20 mL of dry acetonitrile was added in room temperature. The reaction mixture was refluxed (at 800C) with stirring under nitrogen atmosphere for 24 h. After then mixture was cooled at room temperature, water (100 mL) was added, and the mixture was extracted with CH₂Cl₂. The organic phase was dried over anhydrous magnesiumsulfate, and then the solvent was evaporated. Further purification was accomplished by column chromatography (silicagel) using CH₂Cl₂ as the eluent.
Synthesis of ferrocene-triazole-fullerene

To a hot solution (60°C) of [60]fullerene (72 mg, 0.1 mmol) in 6 mL of dry toluene under nitrogen atmosphere, ferroceneazide (24.1 mg, 0.1 mmol) in dry toluene (1 mL) was added dropwise. The resulting solution was stirred at 60°C overnight. Further purification was accomplished by column chromatography (silica gel) using cyclohexane/toluene (1:1) as the eluent.

RESULT AND DISCUSSION

In order to design D - B – A systems with predictable electron transfer properties, it is essential to understand how the electronic structure and composition of the bridge plays a role in governing the rates of electron transfer [7]. Electron transfer in D - B - A systems occurs most often by a superexchange mechanism involving virtual bridge states [8]. Qualitatively, the superexchange mechanism results in three observed trends in electron transfer rates:(a) increasing bridge length decreases the rate; (b) charge transport through a fully conjugated bridge is faster than through a saturated bridge; (c) a larger energy gap between the starting state of the charge transfer process and the relevant virtual bridge states leads to decreased electron transfer rates [9].

The important components of a dyad are the donor and the acceptor molecules whose properties govern the charge separation in the dyad. Since the donor can act as an acceptor for an even stronger donor, these two terms cannot be strictly used separately. There are certain functionalities that are likely to make a material an electron acceptor with respect to most other materials. The important requisite for a good donor is that it should have low ionisation potential and of that of an acceptor is to have a good electron affinity. The bridge not only provides a molecular skeleton to which the chromophores are added-on at well defined separations and orientations, but also provides a medium that modulates the intramolecular electron transfer dynamics by superexchange/tunneling mechanisms. Thus, the bridge plays an important role in determining the electron transport rates in a dyad molecule. Depending upon the nature of the bridge, the charge separation and recombination is controlled.

The molecular orbital energy levels of the individual donor and the acceptor molecules as compared to those of the dyad in fig-3, calculated by using Gauss
03(DFT,B3LYP,6-31G) show a fair comparison between the energy of the lowest unoccupied molecular orbital (LUMO) of the acceptor, LUMO of the dyad. Similarly, the energy of the highest occupied molecular orbital (HOMO) of the donor is closer to the HOMO energy level of the dyad. This observation implies the localization of the HOMO and the LUMO of the individual donor and acceptor moieties respectively on the donor and the acceptor dyad.

**CONCLUSIONS**

The dyad’s HOMO lying on the donor with partial extension onto the bridge and the LUMO on the acceptor side indicated a good electronic communication between the donor and the acceptor moieties of the dyad. An improved electronic band gap (0.073 eV) implied the donor-bridge-acceptor network to be transport active.

**ACKNOWLEDGEMENT**

The authors thank IIT, Madras for providing lab facilities to PH and JJ Gandy fellowship to BN. Support of the UGC (DRS) and the FIST (DST) to the department is also highly acknowledged.

**REFERENCES**