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

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Abstract - Triazoline fullerenes are strong electron acceptors that could form novel donor-acceptor dyads with metallocenes exhibiting efficient and improved electron transfer dynamics. Reports in literature have cited Fullerene-Ferrocene donor–spacer-acceptor dyads prepared by Diels-Alder cycloaddion[1,3-dipolar] reaction[1]. Fullerotriazolines can form a rare class of fullerene derivatives through the reaction of C_{60} with azides. In comparision to the most studied acceptor NMFP(N-methyl fulleropyrrolidine), the present investigation takes advantage of the electronegative character of the two nitrogen atoms covalently linked to the C_{60} core in the triazidine fullerene. Based on the above, we can calculate the electronic structure of the dyad[2], and investigate the ground state charge transport behavior of the dyad as well as understanding the basic aspects of 'Sprintronics' in creating spin polarized current in the desired donor-acceptor dyads by varying the metallocene type. Keeping these things in mind Ferrocene azide has been synthesized by taking the starting material ferrocene methanol, and has been characterized by different spectroscopic method (IR,NMR)[3]. Donor-Bridge-Accepter(D-B-A) dyadic molecular designs have been discussed with transition metal based donor complexes and triazolinic fullerene C_{60} acceptors.

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[4]. The design of functional dyad covalently linked electron donors and acceptors is a valuable approach towards electron transport. Incorporation 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 and charge recombination processes. Fullerenes, and in particular the readily available C_{60}, possess a wide range of physical and chemical properties that makes them interesting building blocks for supramolecular assemblies and new materials [5]. The remarkable electron acceptor property of ground state C_{60}, 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 temperarure. 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). Ferrocenetosylate-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 ferrocenetosylate (0.676 gm, 0.00182 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.

Ferroceneazide - FT-IR (KBr) in cm-1

815, 848 ,890, 923, 1012, 1036, 1067, 1124, 1106, 1187, 1214, 1569, 2021, 2924 ,2924 cm-1.

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.

FT-IR (KBr) v/cm-1 - 1462, 1425, 580 (C_{60}), 528 (C_{60}).1H NMR (400 MHz, CDCl3) δ 4.39 (s, 5H), 7.2 (d, 4H), 7.9 (s, 2H).
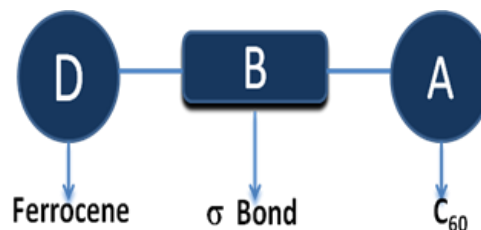
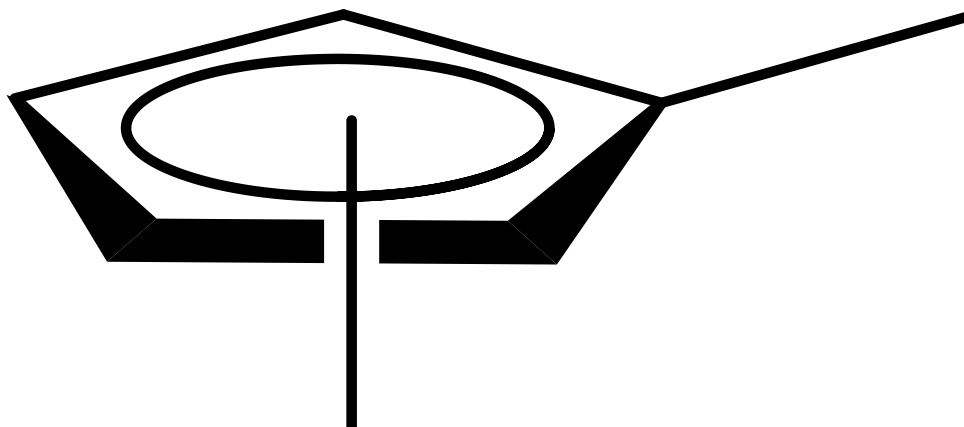**Scheme 1: Schematic diagram for D-B-A**

Fig-2 Synthesis procedure of ferrocene-triazole-fullerene

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 unoccupaid molecular orbital(LUMO) of the acceptor, LUMO of the dyad. Similarly, the energy of the highest occupaid 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.
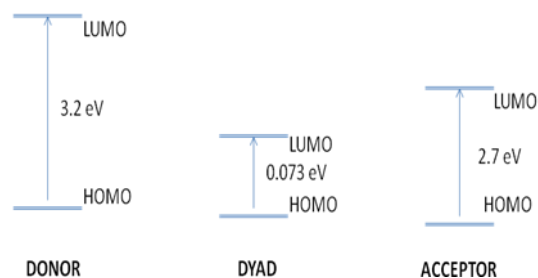

Fig-3 Comparision of HOMO and LUMO energy levels of the individual donor and the acceptor moieties with those of the dyad molecule.

The HOMO and LUMO enrgy ot the dyad depicted in Fig. 4. It can be seen that the LUMO is localized on the C60 moiety whereas the main contribution to the HOMO is from ferrocene d orbitals.
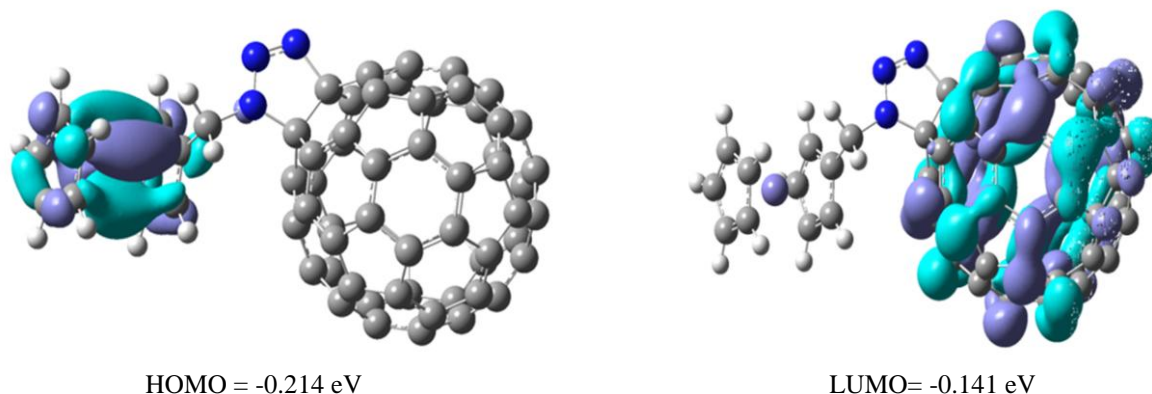

HOMO = -0.214 eV   LUMO= -0.141 eV

Fig -4 Orbital spatial orientation of HOMO, LUMO of the dyad molecule with associated orbital enegies by DFT (B3LYP), 6-31G basis set.

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(0.073eV) implied the donor-bridge-acceptor network to be transport active.

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REFERENCES

[1] D. M. Guldi, S. Gonzalez, N. Martin,A. Anton,J. Garin, J. Orduna J.Org.Chem. 2000, 65,1978.

[2] K.S. Kumar, A. Patnaik Chem phys chem. 2010, 11(17), 3645.

[3] J. Llacay, J. Veciana, J. Vidal-Gancedo, J.L. Bourdelande, R. Gonzalez-Moreno, C. Rovira, J. Org. Chem. 1998, 63, 5201.

[4] J. Jortner, M. A. Ratner, Molecular Electronics;Blackwell:London, 1997.

[5] 6. C. A. Mirkin, W. B. Caldwell Tetrahedron 1996, 52, 5113.

[6] Q. Xie, E. Perez-Cordero, L. J. Echegoyen Am. Chem. Soc. 1992,114, 3978.

[7] A. B. Ricks, G. C. Solomon, M. T. Colvin, A.M. Scott,K. Chen, M. A. Ratner, M. R. Wasielewski J. Am. Chem. Soc. 2010, 132, 15427.

[8] B. Albinsson, M. P. Eng, K. Pettersson, M. U. Winters, Phys. Chem.Chem. Phys. 2007, 9, 5847.

[9] G. C.Solomon, D. Q. Andrews, R. P. Van Duyne, M.A.Ratner, J. Am. Chem. Soc. 2008, 130, 7788.

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