

Available online at www.sciencedirect.com



Chemical Physics Letters 414 (2005) 198-203



www.elsevier.com/locate/cplett

A new fullerene C_{60} -didodecyloxy benzene dyad: An evidence for ground state electron transfer

S. Shankara Gayathri¹, Archita Patnaik *

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Received 5 July 2005; in final form 28 July 2005 Available online 16 September 2005

Abstract

Synthesis, complete spectroscopic characterization and cyclic voltammetric measurements of a new didodecyloxybenzene– C_{60} dyad is described. The dyad showed distinct ground state intramolecular charge transfer as predicted from molecular orbital calculations and complimented by absorption and fluorescence spectroscopic behavior along with cyclic voltammetric studies, in solvents of varying polarity. The ab initio B3LYP/3-21G(d) electronic structure calculations are indicative of a non-planar ground state structure, 8 kJ/mol lower in energy than the planar structure. A ~13° dihedral angle between the benzene ring and the oxygen of the alkoxybenzene moieties of the dyad is attributed to the antibonding interactions associated with the HOMO components. © 2005 Elsevier B.V. All rights reserved.

1. Introduction

The possibility of replacing silicon with new organic semiconductors in photovoltaic devices is a promising task for large area applications. Thus, a variety of dyads are synthesized with covalently linked electron donor and acceptor fragments capable of undergoing light induced electron transfer [1–4]. Molecular bridges are built into these dyads in order to induce a long lived charge-separated (CS) state for potential use in subsequent charge stabilization processes [5]. As electron acceptors, quinones [6,7], radialenes [8] and fullerene[60] [9] have been used, among which C_{60} is widely used; as in such systems, C_{60} retains its redox properties as well as photophysical properties. The low reorganization energy of C_{60} [10] affords various unique photoinduced phenomena, such as, fast charge separation, charge recombination (CR) in C₆₀-based systems. C₆₀ derivatives fabricated as electrodes display photovoltaic properties and some are employed in self-assembled monolayers and Langmuir-Blodgett films to realize high solar energy conversion efficiency [11,12]. The donor molecules employed to the C60-dyad component are aromatic amino compounds [13,14], tetrathiafulvalenes (TTF) [6,15,16], ferrocene [17,18], porphyrins [19,20], oligothiophenes [21], etc. Oxygen containing donors like alkoxybenzenes [22,23], furans [24], pyrans [16] have also been used to form charge transfer (CT) complexes with C_{60} . Alkoxy groups in benzene rings give rise to low oxidation potentials due to their strong π -resonance electron donating ability [22]. Functionalization of C_{60} as pyrazoline [23] and oxazole [24] derivatives or with donors like TTF [15] gave rise to intramolecular ground state CT complexes with a CT band at around 470 nm shifting towards longer wavelengths upon increasing the polarizability of the solvent. Further, C₆₀ derivatized as [6,6]-phenyl-C₆₁-butyric acid-methyl ester (PCBM) has been studied extensively as electron-acceptor fragments in the bulk heterojunction photovoltaic cells [25,26].

^{*} Corresponding author. Fax: +9144 2257 4202.

E-mail addresses: gaya3shank@yahoo.com (S.S. Gayathri), archita59@yahoo.com (A. Patnaik).

¹ Present address: Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

^{0009-2614/\$ -} see front matter @ 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2005.08.043

The above literature reports prompted us to synthesize a dyad with PCBM and didodecyloxy benzene as acceptor and donor compounds. At the design stage a hydrophobic–hydrophilic–hydrophobic network was aimed to study its molecular self-organization. Herein, we report the synthesis, electronic structure and the ground state electronic properties of C_{60} -didodecyloxy benzene dyad.

2. Experimental section

2.1. General and materials

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AdvanceTM 400 MHz Fourier transform NMR spectrometer. The IR spectra were recorded on JASCO FTIR 410 spectrometer. MALDITOF-MS spectra were acquired on Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) with 2,5-dihydroxybenzoic acid as matrix. Elemental analyses were performed on a Perkin–Elmer 2400 series CHNS/O Analyser. Melting points were measured with a Cintex melting point apparatus and uncorrected. Cyclic voltammetric measurements were carried out on an CHI 608B Electrochemical workstation (CH Instruments, USA) with Glassy Carbon working and Platinum counter electrodes, and Silver wire as the pseudoreference electrode, n-Bu₄NPF₆ as the supporting electrolyte with internally added ferrocene in acetonitrile:toluene (1:4 v/v) and CH_2Cl_2 solvent under argon atmosphere. The solvents used for cyclic voltammetry were purchased from Merck Limited and were further purified according to standard procedures [27]. The measurements were done at argon atmosphere. Absorption measurements were done on Varian Cary 5E UV–vis spectrophotometer. The solvents used were of UV grade and the donors aniline and pyridine were purified prior to use. Ferrocene and TTF were purchased from Aldrich Chemicals, USA and were used without further purification. Steady-state fluorescence spectra were measured on Jobin Yvon fluorolog-3-11 spectrofluorimeter with a resolution of 0.2 nm.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the dyad 5 is shown in Scheme 1 and the complete procedure is given in supporting information. Compound 6 was prepared as previously reported [28]. The alkylation of the 3,4-dihydroxy benzoate followed by deprotection of the ethyl ester gave the corresponding acid that served as the donor addend for the subsequent tether-functionalisation with the PCBM. Further the presence of this donor in the dyad made it well soluble in most of the common organic solvents



Scheme 1. (a) $C_{12}H_{25}Br$, K_2CO_3 , 18-crown-6, butanone, 24 h, reflux; (b) NaOH, $H_2O:C_2H_5OH$ (1:4), 8 h, reflux; (c) SOCl₂, 3 h, reflux; hydroquinone, CH₂Cl₂, pyridine, 6 h, reflux; (d) DCC, *o*-DCB, 6, 12 h, 0–25 °C.

such as CH₂Cl₂, CHCl₃, tetrahydrofuran, toluene, *o*dichlorobenzene, benzonitrile, dioxan, etc. The dyad was fully characterized by ¹H and ¹³C NMR, FTIR, MALDI-MS, and UV–vis spectroscopy.

3.2. Molecular orbital calculations

Density functional theory (DFT) calculations at a moderate level with B3LYP/3-21G(d) basis set often yielded correct geometry and electronic structures, agreeing with experimental results [18,20]. In the present investigation, structure optimization was done using GAUSSIAN 03 suite of programs [29], in order to probe the equilibrium geometry and the electronic structure of the dyad. Fig. 1a shows the geometry optimized structure on Born–Oppenheimer potential energy surface leading to a dyad length of 34.56 Å, a bridge length of 11.22 Å and a total dipole moment of of 8.9 D.

The molecular orbital energy levels of the individual donor and acceptor molecules as compared to those of the dyad in Fig. 1d shows the lowest occupied molecular orbital (LUMO) energy levels of the acceptor compare well with LUMO of the dyad and the highest occupied molecular orbital (HOMO) energy levels of the donor are closer in energy with the HOMO energy level of the dyad implying the localization of the HOMO and LUMO energy levels on the donor and acceptor parts of the dyad.

The molecular orbital isosurfaces in Fig. 1 shows the majority of the electron distribution of the LUMO to be located on the C_{60} spheroid and of the HOMO is located on the alkoxybenzene donor with a small orbital coefficient spread on to the bridge, suggesting a

weak charge transfer interaction between the donor and the C_{60} moiety in the ground state. The alkoxy groups of the donor have significant amplitude in the HOMO, contributed by the 2p orbitals on the oxygen atoms of didodecyloxy groups situated perpendicular to the plane of benzene ring. These oxygen 2p orbitals appear with phases opposite to the adjacent orbitals on the benzene ring resulting in antibonding interactions that destabilize the HOMO and produce radical ion pair in the dyad. Further, a deviation from planarity, i.e., a dihedral angle of $\sim 13^{\circ}$ was noted between the benzene and the oxygen of the alkoxybenzene moiety leading to a distorted configuration. To understand this, a single point energy calculation was performed with the dihedral angle set to zero, thus enforcing a rigid rotation on the molecule to adopt a planar configuration. The energy of this planar structure lies only 8 kJ/mol higher in energy than the optimized structure and is viewed as the energy barrier for the molecule to attain planarity.

3.3. Solution phase redox behavior and intramolecular electron transfer

Determination of redox potentials in the formed molecular donor-acceptor type systems is important to probe the existence of charge transfer (CT) interactions between the donor and the acceptor in the ground state and also to evaluate its energetics. The electrochemical behaviour of the compounds 4, 5 and C₆₀ were studied using cyclic voltammetry (CV) at room temperature on glassy carbon working electrode in toluene/acetonitrile (TL/ACN, 4:1 v/v) solvent mixture with tetrabutyl



Fig. 1. Ab initio B3LYP/3-21G(d) calculated (a) geometry optimized structure, (b) frontier HOMO and (c) frontier LUMO of the didodecyloxy benzene–fullerene C_{60} dyad. (d) Comparison of the HOMO and LUMO energy levels for the donor, the dyad and the acceptor.

Table 1 Half wave potentials $[E_{1/2} = (E_{pa} + E_{pc})/2]$ of the dyad 5^{a} in volts measured vs. the potential for the redox couple of internally added Fc/Fc⁺

Compound	E_1^{ox}	$E_2^{\rm red}$	$E_3^{\rm red}$	$E_4^{\rm red}$	$E_5^{\rm red}$
C ₆₀		-0.94	-1.39	-2.14	
5	$+0.80^{b}$	-1.06	-1.50	-2.08	-2.61
5 in CH ₂ Cl ₂	+0.50b	-1.35	-1.76	-2.28	
2	+0.60b				

^a Working electrode: glassy carbon; counter electrode: platinum; reference: $Ag|Ag^+$ as pseudo reference electrode; supporting electrolyte: 0.1 M TBAPF₆; solvent: toluene/acetonitrile (4:1 v/v) unless specified.

^b Irreversible according to CV.

ammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The CVs were acquired under argon atmosphere and are summarized in Table 1 (see Fig. 2).

The dyad exhibited three pairs of reversible $(E_2^{\text{red}}, E_3^{\text{red}}, E_4^{\text{red}})$ and one pair of quasi reversible (E_5^{red}) redox waves corresponding to the fullerene core (Fig. 2). In general, these reduction potential values are shifted to more negative values in respect to C_{60} . This shift stems from the saturation of a double bond in the C_{60} core that raises the LUMO energy of the resulting organo-fullerene moiety. Further, these shifts of the order of ~100 mV suggest a partial ground state CT from the donor to the C_{60} moiety.

On the anodic side, the dialkoxybenzene moiety presents good donor strength with one one-electron irreversible wave (E_1^{ox}) at around +0.80. These values are anodically shifted as compared with that of **2** by ~200 mV, indicating the existence of an appreciable degree of ground state intramolecular CT supported by the molecular orbital calculations. Further, the presence of the ester groups in the dyad's bridge helps in facilitating



Fig. 2. Cyclic voltammograms of the dyad 5, 1mM toluene:acetonitrile (4:1 v/v); and in CH₂Cl₂; supporting electrolyte: 0.1 M TBAPF₆; scan rate: 500 mV/s; working electrode: glassy carbon.



Fig. 3. Absorption spectra of the dyad **5** in solvents of varying polarity. Inset: expanded view of the 431 nm peak showing the red shifts with increasing solvent polarity.

the electron transport. The influence of ester group on the electronic properties of dyads has been widely discussed by Prato et al. [30,17].

Further to prove this CT behavior, CV experiments were performed in a more polar solvent CH_2Cl_2 under similar conditions and the results are shown in Table 1. The ground state CT behavior becomes more evident from the larger shifts of order of 300 and 200 mV in comparison with that of C_{60} and the dyad, respectively, in TL/ACN solvent (Fig. 2).

3.4. Solvatochromism in solvents of varying dielectric constants

Absorption spectrum of the dyad showed a characteristic feature at 431 nm, characteristic of [6,6]-bridged monoadducts. Further, a weak absorption at 697 nm is assigned to 0-0 transition is also observed [23,24]. The HOMO-LUMO gap estimated as 1.7 eV compares reasonably with the overestimated calculated value of 2.3 eV from DFT B3LYP/3-21G(d). Another broad feature in 450–650 nm region in Fig. 3 represents the visible transitions in the dyad which is indicative of the strong electron donating capability of the present donor. This band is weaker or almost absent in the case of other dyads with weak electron-donating groups [23]. Similar broad bands have been attributed to weak electronic interactions between donor and acceptor moieties and have been reported for intramolecular CT in other C₆₀-based dyads [15,17], or intermolecular CT transitions with added donors [31]. With changing solvents polarizability [32], the above absorption bands shifted appreciably attributing to the formation of intramolecular ground state charge transfer complex.

Addition of trifluoroacetic acid (TFA) to the dyad in various solvents did not show any observable change in the absorption intensity, peak position and shape indicating absence of any proton acceptance by the dyad from TFA in these solvents.

3.5. Emission behavior of the dyad from steady-state fluorescence spectra

The fluorescence spectra of the dyad were acquired at room temperature in solvents of varying polarity upon excitation at 431 nm and are shown in Fig. 4. Each spectrum with a peak maximum at \sim 706 nm and a shoulder above 760 nm are typical of monoadduct derivatives of C₆₀. Hence, emission from the singlet excited state of C₆₀ is thus inferred. Further, the dyad shows solvatochromic red shifts from 766 nm in CCl₄ ($\varepsilon = 2.24$) to 789, 785 and 792 nm in polar CH₂Cl₂ ($\varepsilon = 8.93$), benzonitrile ($\varepsilon = 26$) and CS_2 ($\varepsilon = 2.24$, highly polarizable), respectively. A similar CT character has been assigned in isoxazolofullerene-donor (donor = dimethylaniline, ferrocene, furan) dyads to CT character [24,33]. It is also noted that the fluorescence quenching is more marked on moving from a non-polar solvent to the more polar benzonitrile. Thus, the intramolecular CT interaction of the dyad in the ground state leads to quenching of fluorescence in the excited state, probably because of the high degree of CT in excited state in more polar solvents. Further, an attempt made to correlate the stokes shifts with the orientational polarizability as given by Lippert-Mataga equation did not yield linear variation. This may be due to the fact that the equation fails for elongated molecules like the present dyad where ellipsoid form will be more appropriate [34].



Fig. 4. Fluorescence spectra (normalized at 650 nm) of the dyad 5 in solvents of varying polarity.

4. Conclusion

The present investigation has successfully dealt with a molecular design, synthesis and structure characterization of a new PCBM acceptor-based dyad, the didodecyloxy benzene– C_{60} with alkoxy substituents in the benzene ring, contributing a stronger electron donating capability to the donor. Sufficient antibonding interactions between the alkoxy group and the benzene ring revealed the destabilization of the HOMO which results in the formation of radical ion pair. Pronounced intramolecular charge transfer as revealed by absorption and electrochemical investigations justify the dyad to be depicted as C_{60}^{δ} –donor^{δ +} in the ground state.

Acknowledgement

This work is supported by Department of Science and Technology (DST), Government of India under Grant No. SP/SI/H-37/2001.

Appendix A. Supplementary data

The synthetic procedure for the dyad **5** preparation is available at www.sciencedirect.com. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.cplett.2005.08.043.

References

- F. Fungo, L. Otero, C.D. Borsarelli, E.N. Durantini, J.J. Silber, L. Sereno, J. Phys. Chem. B 106 (2002) 4070.
- [2] M.A. Loi, P. Denk, H. Hoppe, H. Neugebauer, C. Winder, D. Meissner, C. Brabec, N.S. Sariciftci, A. Gouloumis, P. Vazquez, T. Torres, J. Mater. Chem. 13 (2003) 700.
- [3] A.S. Lukas, P.J. Bushard, M.R. Wasilewski, J. Phys. Chem. A 106 (2002) 2074.
- [4] M.R. Wasilewski, Chem. Rev. 92 (1992) 435.
- [5] J.G. Vos, R.J. Forster, T.E. Keyes, in: Interfacial Supramolecular Assemblies, Wiley, West Sussex, England, 2003.
- [6] Y. Yamashita, M. Tomura, J. Mater. Chem. 8 (1998) 1933.
- [7] T.W. Kim, H. Lee, D. Byun, D. Kang, Thin Solid Films 331 (1998) 8.
- [8] K. Takahashi, Y. Tarutani, Chem. Commun. (1994) 519.
- [9] N. Martin, L. Sanchez, B. Illescas, I. Perez, Chem. Rev. 98 (1998) 2527.
- [10] H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, Chem. Phys. Lett. 263 (1996) 545.
- [11] M. Maggini, G. Possamai, E. Menna, G. Soccrano, N. Camioni, G. Ridolfi, G. Casalbore-Miceli, L. Franco, M. Ruzzi, C. Corvaja, Chem. Commun. (2002) 2028.
- [12] H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 123 (2001) 100.
- [13] S. Komamine, M. Fujitsuka, O. Ito, K. Morikawi, T. Miyata, T. Ohno, J. Phys. Chem. 104 (2004) 11497.
- [14] K.G. Thomas, V. Biju, D.M. Guldi, P.V. Kamat, M.V. George, J. Phys. Chem. 103 (1999) 8864.

- [15] H. Nishikawa, S. Kojima, T. Kodama, I. Ikemoto, S. Suzuki, K. Kikuchi, M. Fujitsuka, H. Luo, Y. Araki, O. Ito, J. Phys. Chem. A 108 (2004) 1881.
- [16] D.V. Konarev, R.N. Lyubovskaya, N.V. Drichko, E.I. Yudanova, Y.M. Shulga, A.L. Litvinov, V.N. Semkin, B.P. Tarasov, J. Mater. Chem. 10 (2000) 803.
- [17] D.M. Guldi, M. Maggini, G. Soccrano, M. Prato, J. Am. Chem. Soc. 119 (1997) 974.
- [18] F. D'Souza, M.E. Zandler, P.M. Smith, G.R. Deviprasad, K. Arkady, M. Fujitsuka, O. Ito, J. Phys. Chem. A 106 (2002) 649.
- [19] P.A. Liddel, D. Kuciauka, J.P. Sumida, B. Nash, D. Nguyen, A.L. Moore, T.A. Moore, D. Gust, J. Am. Chem. Soc. 119 (1997) 1400.
- [20] F. D'Souza, G.R. Deviprasad, M.E. Zandler, V.T. Hoang, A. Klykov, M. VanStipdonk, A. Perera, M.E. El-Khouly, M. Fujitsuka, O. Ito, J. Phys. Chem. A 106 (2002) 3243.
- [21] N. Armaroli, G. Accorsi, J. Gisselbrechdt, M. Gross, V. Krasnikov, D. Tsamouras, G. Hadziioannou, M.J. Gomez-Escalonilla, F. Langa, J. Eckert, J. Nirengarten, J. Mater. Chem. 12 (2002) 2077.
- [22] T. Khan, J.J.W. McDouall, E.J.L. McInnes, P.J. Skabara, P. Frere, S.J. Coles, M.B. Hursthouse, J. Mater. Chem. 13 (2003) 2490.
- [23] F. Langa, P. de la Cruz, E. Espildora, A. De la Hoz, J.L. Bourdelande, L. Sanchez, N. Martin, J. Org. Chem. 66 (2001) 5033.

- [24] F. Langa, P. de la Cruz, E. Espildora, A. Gonza'lez-Corte's, A. de la Hoz, V. Lopez-Arza, J. Org. Chem. 65 (2000) 8675.
- [25] A. Dhanabalan, J.K.J. van Duren, P.A. van Hal, L.J. van Dongen, R.A. Jannsen, J. Adv. Funct. Mater. 11 (2001) 255.
- [26] L. Chen, D. Godovsky, O. Inganas, J.C. Hummelen, R.A. Jannsen, M. Svensson, M.R. Adersson, Adv. Mater. 12 (2000) 1367.
- [27] W.L.F. Armarego, D.D. Perrin, fourth edn., Purification of Laboratory Chemicals, Butterworth–Heinemann, Elsevier Science, Woburn, MA, 1996, p. 67.
- [28] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, J. Org. Chem. 60 (1995) 532.
- [29] M.J. Frisch et al., GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- [30] M. Prato, M. Maggini, C. Giacometti, G. Soccrano, G. Sandona, G. Farnia, Tetrahedron 52 (1996) 5221.
- [31] M.C. Rath, H. Pal, T. Mukherjee, J. Phys. Chem. A 103 (1999) 4993.
- [32] C. Reichardt, second edn., Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.
- [33] K.B. Simonsen, V.V. Konovalova, T. Kawai, M.P. Cava, L.D. Kispert, R.M. Metzger, J. Becher, Perkin Trans. 2 (1999) 657.
- [34] B. Valeur, in: Molecular Fluorescence, Principles and Applications, Wiley-VCH, Weinheim, 2002.