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Electron Transport and Ultrafast Spectroscopic Studies of New

Methanofullerenes bearing Heteroatom in exohedral chain

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Abstract

Fullerene derivatives (C60 and C70) have been widely used in excitonic solar cells due to their exceptional electron accepting properties and low reorganization energy. In the recent years, a wide variety of fullerene based n-type materials have been developed showing tremendous potential in the field of organic photovoltaics. However, only a little study has been performed on heteroatom bearing methanofullerenes for opto-electronic properties to be used as n-type organic semiconductor material. In the present study, we report synthesis of two mono substituted methanofullerene derivatives, i.e., C60-Th (Product 1) and C60-TPA (Product 2), having heteroatom (S & N respectively) in exohedral chain attached by ethylene linker on cyclopropane ring and comprehensively studied their photophysical and electrochemical properties. Methanofullerene derivatives have been synthesized using our amine assisted cycloaddition (AACA) reaction method. The structure of synthesized products was established by different spectroscopic techniques. Efficient quenching efficiency was observed in fluorescence emission in mixture with donor polymer P3HT for both the methanofullerenes. Electron transport properties were evaluated by fabricating electron only devices and found 10x and 6x higher than PC61BM for product 1 and 2 respectively. Finally, the charge transfer properties were evaluated in mixture with P3HT by transient absorption spectroscopy to establish ultrafast charge separation and formation of long lived charge separated states. The study suggests both the products show excellent electron transport properties and formation of longer lived charge separated states in mixture with donor polymer to be used as n-type material for organic solar cells.

Key words. Methanofullerene, heteroatom, AACA, transient absorption, spectroscopy, solar cells

2 3 4 5 6 7 8 Bublished 00.05.800 cmber 2019. Downloaded by Neutrighton Trent University on 2/52019 6:57:104 EM 6 2 9 5 4 8 7 1 0 6 8 2 9 5 4 8 7 1 0 6 8 2 9 5 7 0 0 6 8 2 9 5 4 8 7 0 0 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58

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1. Introduction

The development of new organic functional materials is drawing the considerable attention of researchers in the area of organic photovoltaics (OPV) to harvest maximum solar energy and to accomplish the cheaper source of energy demands.¹ Fullerene chemistry has been evolved tremendously since its large scale production reported in 1990² introducing different types of reactions and synthesizing medley of fullerene derivatives with variety of functional groups attached exohedrally.³ Among all the reactions, cycloaddition reactions are the most prevalently used for synthesis of methanofullerene derivatives for different applications including organic solar cells.⁴ The modified fullerenes maintain the anomalous properties of pristine fullerenes like low reorganization energy and high electron affinity.⁵⁻¹¹ For example, attachment of suitable organic moieties over fullerenes results in tuning of energy levels, better molecular interactions as well as their solubility. Introduction of electron donating groups on exohedral addends in methanofullerenes, results in improved solubility as well as increase in open circuit voltage of solar cell devices.¹² These advantages enable modified fullerenes to be used as n-type material in for organic electronics.¹³⁻¹⁵ For the synthesis of methanofullerene derivatives, cyclopropanation by 1,3 dipolar cycloaddition reaction of diazo compounds generated from different precursors, has been exploited extensively. Phenyl[C61]butyric acid methyl ester (PC61BM) and [6,6] Phenyl[C71]butyric acid methyl ester (PC71BM) are the most conventional acceptor materials synthesized by 1,3 dipolar cycloaddition of diazo compound and has been used widely in organic photovoltaics (OPV).¹⁶ We have recently reported the amine assisted cycloaddition (AACA) reaction for the synthesis of [6,6]PC61BM monoadduct and several other methanofullerenes catalyzed by amine under total aerobic conditions for their applications in organic electronics.¹⁷ Although, among myriad of fullerene derivatives several heteroatom bearing fullerene products

are reported (Prato product, fused fullerene etc.) using amines and sulfur derivatives,¹⁸ only a few methanofullerene derivatives are reported with heteroatom in exohedral addend.¹⁹ Recently thiophene containing methanofullerenes were developed and used as electron transport layer in Perovskite solar cells as organic Lewis base to passivate the uncoordinated lead ions.^{20,21} There is still lack of reports on heteroatom containing methanofullerenes with comprehensive study of their opto-electronic and charge transfer properties. More research is required on preparation of methanofullerenes specially using low cost amines and thiophene derivatives for cost effective bulk scale synthesis for large area application.

In this context, in the current work we have synthesized two new methanofullerene derivatives having heteroatom in exohedral addend. In product 1 (C60-Th), thiophene ring end unit is attached on fullerene exohedrally via cyclopropane ring and ethylene linker. The other Product 2,(C60-TPA), contains triphenylamine end group attached to fullerene exohedrally in same manner as Product 1 (figure 1). Thiophene and triphenylamine both are electron rich groups and act as energy absorbing centers.²² Both the molecules have been synthesized by AACA process from their diazo intermediate. The synthesized molecules have been characterized by UV-vis, FTIR, NMR spectroscopy and MALDI-TOF mass spectrometry for the establishment of their structure. HOMO-LUMO energy levels of products have been calculated by cyclic voltammetry. Thermal stability was confirmed by thermal gravimetric analysis (TGA). The electron mobility of the products was also evaluated by making electron only devices. Photoluminescence and time resolved fluorescence study was performed to establish efficient charge transfer interactions between methanofullerene and donor P3HT polymer. Finally to further support the efficient charge transfer and generation of charge separated states, we performed transient absorption

spectroscopy in mixture with P3HT. Both the materials show excellent acceptor properties with ultrafast charge separation.



Figure 1. Chemical structure of Product 1 (C60-Th) and Product 2 (C60-TPA).

2. Experimental Section

2.1. Materials and Characterization

Thiophene-3-Carboxaldehyde, 4-(Diphenylamino) benzaldehyde, p-toluenesulfonyl hydrazide, triethylamine and Poly(3-hexyl)thiophene were purchased from SigmaAldrich and used without further purification. [60]Fullerene was purchased from AlfaAesar. All solvents were used after drying and were purchased from Alfa Aesar. Fourier Transform Infrared spectroscopy (FTIR) was done on Perkin Elmer FTIR Spectrum 2. The sample was ground with anhydrous KBr and pallets were prepared to record the spectrum from 4000 to 500 cm⁻¹. A background in air was done before samples. UV-vis absorption spectroscopy measurement was performed on Shimadzu UV-vis spectrophotometer (UV-1800) for 25 μ M solutions and spin coated films. Products were also characterized for ¹H NMR on Jeol 400 MHz spectrometer in deuterated chloroform (CDCl₃) using tetramethylsilane (TMS) as internal standard. We were not able to record ¹³C NMR due to low concentration of products. MALDI-TOF-TOF mass spectrometry AB SCIEX used to determine the molecular weight of the products using α -cyano 4-hydroxy cinnamic acid matrix. Three electrode standard configuration was used for cyclic voltammetry (CV) measurements

using a platinum wire as counter electrode. Ag wire as reference electrode and Pt-disc as working electrode. 0.1 M TBAPF₆ (tetra-n-butylammonium hexafluorophosphate) was used as supporting electrolyte and 1 mM solution of methanofullerene in o-dichlorobenzene (o-DCB) was used to perform the experiment. Current vs Voltage was measured on an Autolab potentiostate. Fluorescence measurements were performed on Varian (CARY eclipse) Fluorescence Spectrophotometer in 25 µM solution and also in films. A solid sample holder assembly was used to record the fluorescence in films. Horiba Jobin Yvon (Fluorohub) was used to record time resolved fluorescence in 25 µM toluene solution but were not able to measure in films due to instruments limitation. Ultrafast transient absorption spectroscopy was performed using optical pulse from Ti:Sapphire laser amplifier (35 fs, 4 mJ/pulse, 1 KHz, 800 nm). A beam splitter was used to split the pulse into two beams. An optical parametric amplifier (TOPAS, Light Conversion) was employed on the high intensity beam (pump) to vary the wavelength from 190 nm to 2600 nm. The weak intensity beam (probe) was propagated through a CaF_2 crystal to generate white light continuum (WLC). A computer-controlled delay stage was used to optically delay the probe beam with respect to pump beam. In the current study we used 450 nm wavelength as a pump beam at normal incidence and the changes in absorption was detected by using a gated CMOS detector. The time resolved study was performed using HELIOS (Ultrafast systems) spectrometer and life times were estimated by global fitting.

2.2. General method of synthesis of Chalcone 1a and Chalcone 2a.^{17a} Acetophenone (2 mM) and Thiophene-3-carboxaldehyde for **1a** (2 mM), or 4-(Diphenyl)amino benzaldehyde for **2a** (2 mM) were dissolved in 20 mL ethanol. After dissolution 40 % NaOH solution (10 mL) was added with continuous stirring at room temperature and the progress of reaction was monitored by TLC. Finally the reaction mixture was precipitated using dilute HCL (20%). Crude product

was filtered and washed many times with water and purified by column chromatography using ethyl acetate: n-hexane (70:30) as eluent.

Yield: ~90 %. **1a**: FTIR (cm⁻¹) 3086, 2927, 1662, 1592, 1443, 1278, 1208, 1011, 919, 718, 623; ¹H NMR (CDCl₃, δ) (ppm) 7.25 (1H), 7.29 (1H), 7.3 (1H), 7.4 (2H), 7.5 (2H), 7.7 (1H), 7.9 (2H). **2a**: FTIR (cm⁻¹) 3054, 1670, 1578, 1503, 1327, 1202, 1010, 753, 704; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 6.9 (2H), 7.1 (8H), 7.4 (7H), 7.7 (2H), 7.9 (2H).

2.3 General method of synthesis of Hydrazone (1b) and Hydrazone (2b) of chalcone (1a & 2a)^{17a}: The tosyl hydrazone was prepared by refluxing a solution of chalcone 1a or chalcone 2a (0.5 mM), p-toluene sulfonyl hydrazide (1.1 equivalent) in methanol (50 mL) with continuous stirring for ~6 hour. Crystals of hydrazone precipitate out of solution on cooling and dried after washing with cold methanol.

Yield: ~75 %. **1b**: FTIR (cm⁻¹,v) 3203, 3021, 1616, 1310, 1194, 1044, 751; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 2.36 (3H), 6.22 (1H), 6.88 (1H), 7.01 (2H), 7.06 (1H), 7.19 (1H), 7.27 (3H), 7.40 (2H), 7.45 (2H), 7.7 (2H). **2b**: FTIR (cm⁻¹,v) 3192, 3059, 2921, 1677, 1585, 1489, 1268, 1150, 1010, 759; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 2.3 (3H), 6.7 (1H), 6.9 (2H), 6.9-7.11 (10H), 7.25-7.30 (9 H), 7.6 (2H), 7.7 (2H).

2.4 General method for synthesis of methanofullerenes, C60-Th (1) & C60-TPA (2)^{17a}: Hydrazone, 1b or 2b (0.25 mM) was dissolved in dichloromethane (10 mL) and cooled down to 0°C. A catalytic amount of triethyl amine (0.9 mL) was added and stirred for three hours at this temperature. A solution of C₆₀ (0.5 equivalent) in o-dichlorobenzene (20 mL) was added and temperature was raised to 85-90 °C. Stirring was continued for 8 hours followed by precipitation with methanol. Precipitate was collected by centrifugation. Crude product was loaded on silica gel column (200 mm x 18 mm) for purification using toluene/hexane (70:30) mixture as eluent.

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Unreacted fullerene was isolated as the first fraction followed by purple colored monoadduct i.e., [5,6] fulleroid. Refluxing [5,6] isomers in o-dichlorobenzene for 5 hours converts totally to wine colored [6,6]methanofullerene by thermal isomerisation.

Product 1: Yield: ~30 %; FTIR (cm⁻¹,v) 2972, 1454, 1314, 1268, 1014, 794; ¹H NMR (CDCl₃, 400 MHz), δ (ppm) 6.75 (1H), 6.86 (1H), 6.96 (1H), 7.12 (2H), 7.3-7.8 (5H); HR-MS (MALDI-TOF): m/z for C73H10S, calculated 918.8312; found 917.8234 (M-1).

Product 2: Yield: ~32 %; FTIR (cm⁻¹,v) 2916, 1591, 1487, 1257, 1018, 729; ¹H NMR (CDCl₃, 400 MHz), δ (ppm) 6.21 (1H), 6.84 (1H), 6.93-7.16 (6H), 7.26-7.30 (4H), 7.37-7.54 (4H), 7.72-7.94 (5H); HR-MS (MALDI-TOF): m/z for C87H21N, calculated 1080.1014; found 1079.0936 (M-1).

2.5. Fabrication of electron only devices^{17c}

2.5.1. Preparation of zinc oxide precursor solution

The solution of zinc oxide (ZnO) has been prepared by dissolving 1 g (4.5 mM) zinc acetate dihydrate (Zn(CH₃CO₂)₂.2H₂O) in 10 mL methoxyethanol with 0.254 mL monoethanolamine (MEA) as stabilizing agent at room temperature. The mixture solution was then stirred at 60 °C for about 2 hours until a clear and homogenous solution was obtained.

2.5.2. Current–voltage characteristics.

Electron only devices with the ITO/ZnO/Product 1 or 2/Al architecture were fabricated on a cleaned ITO coated glass substrate with sheet resistance of 20 Ohm/sq under ambient conditions. Substrates were ultrasonically cleaned with detergent, distilled water, acetone and isopropyl alcohol and dried in vaccum oven. The ZnO precursor solution was spin coated onto the substrates at 3000 rpm followed by annealing at 250°C for 30 minutes. Methanofullerene solution (20, 30 & 40 mg/mL) in chlorobenzene were prepared and spin coated at 1000 rpm on

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top of the electron transport layer followed by annealing at 120 °C for 15 min. Finally, the cathode material i.e., a 100 nm Al layer was deposited on top of active layer under high vaccum to complete the device structure. Film thickness was measured using calibrated Ellipsometer (J A Woolam, Model: Vase). The J–V characteristics were recorded using a calibrated computer controlled Keithley 236 source meter under dark.

3. Results and Discussion

The most accepted approach for synthesis of methanofullerene is via diazoalkane intermediate from tosyl hydrazone precursor in pyridine in presence of sodium methoxide under inert atmosphere.^{23,24} This process is very hazardous and causes high impact on environment due to disposals during material synthesis. Amine assisted cycloaddition reaction has been found less hazardous and more energy efficient over other methods for methanofullerene synthesis as the reaction is performed under aerobic conditions without using pyridine and sodium methoxide.²⁵ AACA method makes bulk synthesis of methanofullerene feasible at very cheap prices required for commercialization of OPV. In the present work, we have synthesized two different methanofullerene derivatives bearing heteroatoms (Figure 1) by our AACA method.

For the synthesis of methaonofullerene, chalcone was prepared in first step via Claisen-Schmidt condensation of acetophenone with respective ketone (Scheme 1). The reaction of thiophene-3-carboxaldehyde and 4-(Diphenyl)amino benzaldehyde with acetophenone forms enone 1a and 2a respectively where, α , β double bond is present on phenyl ketone. Hydrazones (1b and 2b) were prepared from their respective chalcone in methanol using p-toluenesulfonyl hydrazide. After tosylation, diazo intermediate was generated at 0° C in presence of tertiary amine as catalyst under aerobic conditions. The fullerene (C60) solution in *o*-DCB was added *insitu* and reaction

was carried out for 8 hrs at 90° C as shown in Scheme 1 (A & B) and the progress of reaction was monitored by thin layer chromatography (TLC). The reaction mixture was precipitated using methanol and subjected to column chromatography for purification. Kinetically favorable product, [5,6] open fulleroid is converted into thermodynamically stable [6,6] methanofullerene by refluxing in *o*-DCB for 5 hours.



Scheme 1. Synthesis of (A) Product 1 (C60-Th) and (B) Product 2 (C60-TPA) (i) ethanol, 40% NaOH solution, rt; (ii) p-toluenesulfonyl hydrazide (1.2 eq.), methanol, reflux, 24 hours; (iii) dichloromethane, triethyl amine, 0 °C, 3 hours; (iv) C_{60} in *o*-dichlorobenzene, 90 °C, 8 hours; (v) *o*-DCB, reflux, 5 hours.

The structure of product 1 & 2 has been analyzed by different spectroscopic techniques. The FTIR spectra of fullerene product 1 clearly shows aromatic C-H stretching at 3096 cm⁻¹ and C=C bond stretching at 1621 cm⁻¹. While the FTIR spectra of product 2 shows aromatic C-H stretchings at 3057, 3024 cm⁻¹ and C=C bond stretching at 1627 cm⁻¹. ¹H NMR spectroscopy further confirm the purity and formation of [6,6] methanofullerenes. The ¹H NMR spectrum of product 1 shows the appearance of ethylene protons at 6.75 and 6.86 ppm and other aromatic

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protons appear between 6.96-7.8 ppm. Product 2 shows the chemical shift at 6.2 and 6.8 ppm for ethylene protons with other aromatic protons between 7.0-7.7 ppm (19H) being indicative for the formation of product.²⁶ Mass analysis further confirmed the formation of monoadduct for both the products (See SI).

3.1. Steady State Absorption Spectroscopy

Absorption spectroscopy is a widely used technique to confirm the conversion of [5,6] fulleroid into [6,6] methanofullerene. The peak at ~ 697 nm confirms the formation of [6,6] adduct which is not present in [5,6] adduct.²³ Figure 2A and S15 show the comparative absorption spectra of product 1 & 2 in chloroform solution (25 μ M) in visible range. Both the products show similar absorption to PC61BM, the widely used acceptor material in organic solar cells. Absorption spectra shows clear appearance of peaks at 430 and 697 nm for product 1 and at 433 and 702 nm for fullerene adduct 2 confirming the [6,6] addition on fullerene core and formation of methanofullerene. The optical band gap has been calculated from absorption spectra were also recorded in thin films (spin coated 25 μ M chloroform solution at 1000 rpm) which show broad absorption in the whole visible region and extended absorption up to 800 nm due to aggregate formation in solid state. Both the products show higher absorption than reference PC61BM in films.



Figure 2. Comparative UV-visible absorption spectra of Product 1 (C60-Th) and Product 2 (C60-TPA) and PC61BM in (A) chloroform solution and (B) Spin coated films.

3.2. Thermal properties

The thermogravimetric analysis was performed to study the thermal stability of materials for optimization of annealing temperature of films during device fabrication. The TGA thermograms are shown in Figure 3. Both the methanofullerene derivatives show no weight loss up to 150 °C and only 10% weight loss up to 200 °C as observed in earlier cases.^{17a} Both the materials show \sim 50% weight loss up to 900 °C. For optimization of annealing temperature of films, the thermal stability information is prerequisite and here we find that the films of both the products can be annealed at 120 °C.



Figure 3. TGA of Product 1 (C60-Th) and Product 2 (C60-TPA) under N_2 flow of 20 mL min⁻¹ at 10 °C min⁻¹ temperature ramping.

3.3. Electrochemical Analysis

Electrochemical studies of products were evaluated by cyclic voltammetry (CV) to determine the redox potentials and HOMO-LUMO levels of the synthesized methanofullerene derivatives. Figure 4 shows the cyclic voltammogram of methanofullerene derivatives and data are summarized in Table 1. Both the products show well defined quasi-reversible reduction potentials indicating their n-type semiconductor nature.¹⁷ Product 1 showed three clear reduction peaks at -1.29, -1.66 and -2.10 V whereas in product 2, two reversible reductions at -1.31 and - 1.68 V were observed (Figure 4 A & B) for fullerene reduction. Product 2 also showed one electron oxidation of triphenylamino group at ~0.46 V. HOMO-LUMO energy levels were calculated using the empirical formula $E_{HOMO/LUMO=}$ -($E_{onset(red/ox)}$ +4.8 eV). LUMO energy levels were estimated to be -3.7 and -3.68 eV respectively for product 1 & 2 using the onset reduction potential which is lower than PC61BM.²⁷ From oxidation onset, HOMO energy level was calculated to be 5.59 eV and 5.13 eV for product 1 and product 2 respectively. Using HOMO-LUMO energy levels, the electrochemical band gap was calculated to be 1.89 eV and 1.45 eV for

product 1 & 2 respectively. These values are within the error range compared to optical band gap mentioned earlier.²⁸ Although LUMO energy levels are same for both the products, HOMO has uplifted in product 2 due to presence of electron rich triphenylamine group causing a low oxidation potential, therefore, and thus lowering the band gap of product 2.

	red _{onset} (V)	red ⁻¹ (V)	red ⁻² (V)	red ⁻³ (V)	Ox _{onset} (V)	ox ⁻¹ (V)	LUMO (eV)	HOMO (eV)	Electrochem band Gap (eV)
C60-Th (1)	-1.10	-1.29	-1.66	-2.10	0.79	-	-3.7	-5.59	1.89
C60-TPA (2)	-1.12	-1.31	-1.68	-	0.33	0.46	-3.68	-5.13	1.45

Table 1. Electrochemical data of Product 1 (C60-Th) and Product 2 (C60-TPA).



Figure 4. Cyclic voltammetry curve of (a) C60-Th and (b) C60-TPA (in o-dichlorobenzene (v/s Fc/Fc⁺) with 0.1 M n-Bu₄NPF₆ as a supporting electrolyte at a scan rate of 50 mV s⁻¹.

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3.4. Electron Transport Studies

To ascertain the potential of new methanofullerenes for their applications in organic solar cells, we have fabricated electron only devices at variable thickness to investigate the charge carrier mobility. The solution of methanofullerene products (1 & 2) was prepared in chlorobenzene with varying concentration from 20-40 mg/mL followed by spin coating on top of the ZnO coated ITO substrates under inert conditions. The schematic of device and energy level diagrams are shown in Figure 5.



Figure 5. Schematic of fabricated electron only device with energy level diagram of corresponding layers.

Electron mobility of materials was estimated by the space charge limited current (SCLC) model. At applied voltage above 0.1 V, the curves demonstrate power law dependence i.e. J α V^m where m takes different values over different voltage regimes.²⁹ After the ohmic region, the second region i.e., trap-controlled space charge limited conduction (SCLC) has been observed at the gradient value of 2 at a single energy level inside the band gap; this mechanism can be represented by the following Mott-Gurney equation 1:³⁰

$$J_{SCLC} = \frac{9}{8}\mu_0\varepsilon_0\varepsilon_r \frac{(V-V_{Bi})^2}{L^3}$$
.....Eq. 1

where, J_{SCLC} stands for space charge limited current density, μ_0 is the mobility of organic semiconductor, ε_0 is the vacuum permittivity and ε_r permittivity of medium, L is thickness of organic semiconductor layer and V is applied potential and V_{Bi} is the built-in-potential. Generally charge carrier mobility in organic materials is low due to structural disorder in the films. I-V data was recorded under dark condition. Current density-voltage curves for different concentrations are shown in Figure S16 and S17. At low applied voltage the dependence of J over V is linear and behavior is ohmic (Slope 1). On increasing the voltage the charge carriers are injected and current becomes space charge limited with value of m=2 (Slope 2). Electron mobility values have been calculated by fitting the experimental J-V in the given equation 1. The electron mobility for new methanofullerenes with variable thickness has been summarized in Table 2. The film thickness is an important parameter for the determination of charge carrier mobility. The decreased layer thickness limits the injection of charge carriers into the bulk of material that leads to the reduced charge carrier collection rate resulting in decreased charge carrier mobility. The highest mobility for synthesized acceptors was achieved with 200 nm thickness and the values are 1.02 x 10⁻³ cm²/V.s and 0.6 x 10⁻³ cm²/V.s for product 1 and 2 respectively which is 10x and 6x higher than PC61BM (0.1 x 10⁻³ cm²/V.s).^{17c}

Thickness, nm (uncertainty in	Mobility (cm²/V.s)					
nm)	C60-Th	C60-TPA				
100 (±10)	0.93 x 10 ⁻⁴	0.77 x 10 ⁻⁵				
150 (±26)	7.1 x 10 ⁻⁴	1.12 x 10 ⁻⁴				
200 (±33)	1.02 x 10 ⁻³	0.6 x 10 ⁻³				

Table 2. Electron mobility values for Product 1 (C60-Th) and Product 2 (C60-TPA)

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3.5 Fluorescence Spectroscopy Study

The fluorescence spectra of mixture of product 1 or 2 with polymer (P3HT) (1:1 weight ratio) have been measured to analyze the quenching efficiency using equation 2,

$$\phi_q = (I_o - I)/I_o \qquad \dots Eq. 2$$

where, I_o is the PL intensity of pure P3HT with same concentration and I is the PL intensity of P3HT:product mixture. P3HT shows strong fluorescence at ~580 nm on excitation with 450 nm wavelength (Figure 6A). In mixture of P3HT:product 1 the fluorescence peak of P3HT is quenched by 60% while in P3HT:product 2 90% quenching was observed (Figure 6A). The decrease in the intensity of emission bands in P3HT: Product (1&2) mixture as compared to neat P3HT shows efficient intermolecular charge transfer and dissociation of photogenerated excitons in P3HT on excitation (Figure 3). We also recorded the fluorescence spectra of neat P3HT and P3HT: Product (1&2) blend films (1:1 weight ratio) using 450 nm excitation wavelength (Figure 6B). The films showed red shifted emission between 600-850 nm for the corresponding red shifted absorption in films. We observed quenching efficiency of ~50-65 % for product 1 & 2, however, 50 weight% PC61BM/P3HT blend films have shown fluorescence quenching efficiency above 95% following charge transfer process.³¹ Further work in underway to optimize the P3HT/Product 1 or 2 weight ratio and annealing temperature to obtain maximum quenching efficiency.

Time correlated single photon counting (TCSPC) was performed to estimate the lifetime of singlet excited state of P3HT and in mixture with product 1 & 2 (1:1 weight ratio) (Figure S18). As reported earlier by us, the study was performed in solution to avoid improper estimation of life time of excited states due to traps in film.^{17a} The singlet excited state relaxation of P3HT at 584 nm showed lifetime of ~0.85 ns.^{17a} The mixture with product 1 and product 2 showed further

reduced decay time to be 0.78 ns and 0.72 ns due to non radiative charge transfer relaxation of excited P3HT molecules. The observed decay time is slightly higher than what we have observed with other methanofullerenes having electron withdrawing groups on exohedral addends.^{17a}



Figure 6. Fluorescence emission spectra of P3HT and mixture with Product 1 (C60-Th) and Product 2 (C60-TPA) (1:1 weight ratio) in (A) chloroform solution and (B) in films using 450 nm excitation wavelength.

We further calculated the electron transfer rate constant for charge separation (k_{ET(CS)}) using the

lifetime estimated by TCSPC using the equation 3.

$$k_{ET(CS)} = \frac{1}{\tau(mixture)} - \frac{1}{\tau(P3HT)}....Eq. 3$$

Product 1 and 2 showed $k_{ET(CS)}$ 1x10⁸ and 2.1x10⁸ s⁻¹ respectively in mixture with P3HT which is

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in the same order of P3HT:PCBM mixture in *o*-DCB (~4.6x10⁸ s⁻¹).³² At this point we need deeper study to understand the lower quenching efficiency and lower rate of electron transfer in these heteroatom bearing methanofullerene compared to our previously reported methanofullerenes in 1:1 weight ration mixture with donor polymer.^{17c} Therefore, we performed transient absorption spectroscopy for neat and mixture with P3HT for both the products to study the excited state dynamics.

3.6 Transient Absorption Spectroscopy (TAS) Study

Transient absorption spectroscopy was performed for neat P3HT, product 1 & 2 and also in mixture of product 1 or 2 with P3HT in chloroform (1:1 weight ratio). Transient absorption spectra give direct information about the generation of excited states and it also specifies the spectral regions for further electron transport process. The TAS spectra were recorded both in visible and NIR region on excitation (pump) with 480 nm wavelength. For neat P3HT, ground state absorption (GSA) bleaching was observed between ~520-620 nm and stimulated emission appeared at >620 nm after ~ 500 fs (Figure S19). After 1 ps delay, along with GSA, transient absorption appeared at ~740 nm for absorption by photogenerated charges in P3HT. Neat product 1 showed transient absorption at \sim 714, 741 and 767 nm appearing after 5 ps delay time in visible region (Figure S20) while transient absorption at ~ 885 nm and 1030 nm appeared at 2 and 5 ps delay time respectively in NIR region (Figure S21). The transient absorption bands in visible region are due to singlet-singlet transitions and absorption at 885 nm is due to excited singlet states absorption of product 1. Absorption for photogenerated charges appear at ~ 1030 nm.³³ Neat product 2 shows two transient absorption bands at \sim 712 nm and \sim 756 nm for singletsinglet transitions after 5 ps delay time (Figure S22). Similar to product 1, product 2 also shows transient absorption at 885 and 1030 nm for excited singlet state and photogenerated charge

absorption respectively (Figure S23). An interesting observation in TAS spectra of product 1 is the appearance of an extra transient absorption at 767 nm compared to product 2. This transient absorption is similar to what we observed in polymer P3HT for photogenerated charges on thiophene ring. Intramolecular charge transfer interactions between thiophene ring and fullerene facilitated by ethylene linker causes the formation of charged species within the molecule showing transient absorption at ~767 nm. This also causes lower quenching efficiency of P3HT emission in P3HT:Product1 mixture. In TAS of P3HT: Product 1 mixture strong stimulated emission appears at 600 nm, as seen in fluorescence emission spectra, with a lifetime of 249 ps (Figure 7). After 1 ps delay time, the strong transient absorption appears between 700-770 nm with maxima at 766 nm for P3HT cation radical (P3HT⁺) with a lifetime of 1.6 ns (Figure 7A).³⁴ Simultaneously, within 1 ps a transient absorption appears at ~1037 nm for fullerene anion radical (C60⁻) formation (Figure 7B) with a lifetime of 1.5 ns.³³



Figure 7. Transient absorption spectra of Product 1 mixture with P3HT in (A) UV-visible region and (B) NIR region on excitation with 480 nm wavelength. The inset shows the kinetics at 766 and 1037 nm for P3HT⁺ and C60^{-,} charge transfer species respectively.



Figure 8. Transient absorption spectra of product 2 mixture with P3HT in (A) UV-visible region and (B) NIR region. The inset shows the kinetics at 767 and 1037 nm for P3HT^{+.} and C60^{-.} charge transfer species respectively.

On the other hand P3HT:Product 2 mixture shows strong photo bleaching at 530 nm for ground state absorption and ~580 nm for stimulated emission. The absorption for P3HT^{+.} cation radical was observed at 767 nm with lifetime of 1.2 ns as shown in Figure 8A and C60^{-.} anion radical appeared at 1037 nm with lifetime of 1.5 ns (Figure 8B). In both the cases the generation of charge separated states i.e. P3HT^{+.} and C60^{-.} were observed within short delay time of ~ 2 ps. Although the quenching efficiency was \leq 90% in these fullerene derivatives on mixing with

P3HT, ultra fast charge transfer with formation of long lived charge separated states has been observed as required for application in OPV devices.

4. Conclusions

In conclusion, we have synthesized two different methanofullerene derivatives having heteroatoms in exohedral chain via our cost effective AACA process, establishing the versatile application of this process for generation of diazoalkane intermediates bearing different types of groups. The products have been synthesized in good yield and high purity. Electrochemical data shows tuning of LUMO as well as HOMO levels and therefore band gap due to presence of electron donating groups. Both the products show electron transfer rate constant in the same order to P3HT:PC61BM mixtures and generation of charge separated states with nanosecond lifetimes, thus confirming the efficient charge separation on mixing with P3HT. Both the products show higher electron mobility than PC61BM, making them potential candidate to be used as n-type material in organic electronic devices. Also this work shows the tuning of HOMO levels in methanofullerenes by easy substitution with electron donating groups in exohedral chain. Uplifted HOMO levels in acceptor will make them suitable to be used with low band gap polymer with lower HOMO energy levels.

Compliance with Ethical Standards:

The authors declare that they have no conflict of interest.

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Heteroatom bearing methanofullerenes with exciting photophysical and electron transport properties fill in the gap of variety of fullerene derivatives to be used as n-type materials in organic electronics.

