

Synthesis of Oligoquinoline Dendronized Fullerenes for Potential Use in Organic Photovoltaic Devices

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New C60 fullerenes derivatives [G1]-C60 (**1**) and [G2]-C60 (**2**) comprising of phenylenevinylene bridges and phenylquinoline peripheral surface groups were synthesized by 1,3-dipolar cycloaddition reaction of fullerene C60 with azomethine ylide *in situ* generated from [Gx]-CHO dendrons (x = 1 and 2) and sarcosine.

Key Words : C60 fullerenes, Oligoquinoline-functionalized fullerene, Phenylquinoline, Conjugated arylene vinylene dendrons

Introduction

Interest in low cost and efficient conversion of sunlight into electrical energy has led to development of organic materials such as fullerenes and other conjugated polymers. Since discovery of C60 fullerene¹ in 1985, conjugated fullerene C60 derivatives have attracted tremendous attention for uses in the photovoltaic² and a solar energy conversion as well as electron acceptor³ in the light harvesting systems for the fabrication of electronic and optoelectronic devices.⁴ By connecting to electron donor molecular structure as an antenna, fullerene C60 has been demonstrated in multi-component artificial photosynthetic system.⁵

The mechanism of a photovoltaic device involves the illumination of the device to generate electron and holes and collection of current at opposite electrodes due to the electron affinity (EA) and ionization potential (IP) difference.⁶ Fullerene C60 itself is a very strong electron acceptor (*n*-type). Since fullerene C60 is not soluble in common solvents, blend of C60/dendrimers⁷, soluble double cable organic macromolecules such as fullerene functionalized dendrimers⁸ are necessary to investigate for photovoltaic or other electronic applications in thin film devices. We have reported the synthesis of quinoline derived dendrimers and their electronic properties and found that these dendrimers show promising *n*-type semiconducting emissive and electron transport materials in light emitting diodes.⁹ Introduction of *n*-type quinoline dendrons to fullerene C60 is very important due to electron accepting moiety which can be used in photovoltaic device with conjugated polymers such as MEH-PPV. MEH-PPV is usually classified as weak donor material (*p*-type) and easily oxidized. MEH PPV thin films are known as good semiconductor and having excellent thermal stability. In this work, we report the synthesis of two C60-quinoline periphery organic molecules such as [G1]-C60, **1** and [G2]-C60, **2** from aldehyde focused dendrons, **5** and **7** [Gx]-CHO (x = 1 and 2).

Results and Discussion

The structures of [G1]-C60, **1** and [G2]-C60, **2** are shown in Chart 1. The synthesis of [G1]-CHO and [G2]-CHO are depicted in Scheme 1. [G1]-CHO **5** was obtained in two steps from divinyl aldehyde, **3** and bromoquinoline [Go-Br], **4** as previously reported.⁹ To increase the solubility in solvents, the flexible *n*-hexyl chain was introduced in a periphery quinoline moiety. The 1,3-cycloaddition coupling

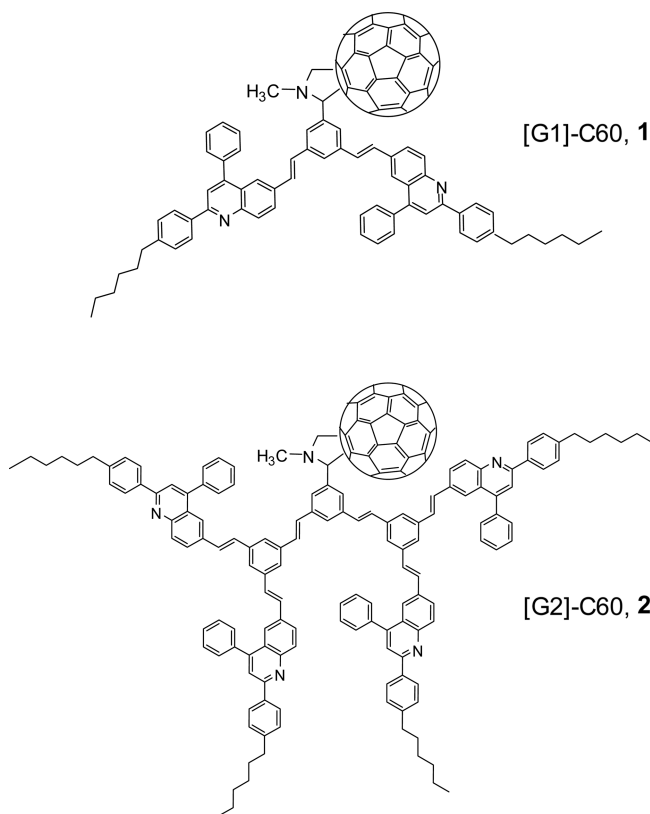
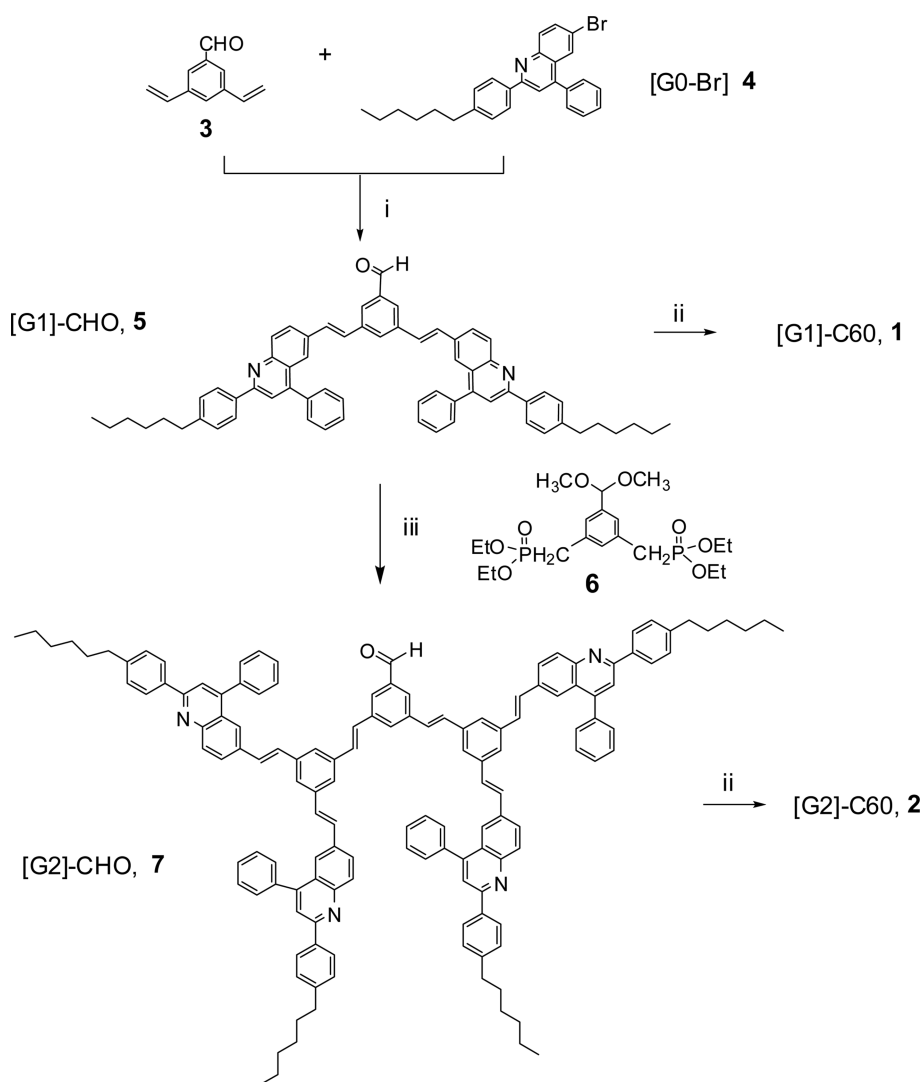


Chart 1. Chemical structures of quinoline based fullerenes: [G1]-C60 (**1**) and [G2]-C60 (**2**).



Scheme 1. Reagents and conditions: (i) TBAB, K_2CO_3 , $Pd(OAc)_2$, DMF (ii) Fullerene C60, *N*-methylglycine, toluene, reflux (iii) **6**, 2.2 equiv. $KOC(CH_3)_3$, THF/aq. HCl.

reaction between [G1]-CHO derived *in situ* azomethine ylide¹⁰ and fullerene C60 was successfully accomplished to lead to [G1]-C60 (**1**) dendron with 37% yield. Generation of azomethine ylide was carried out using commercially available sarcosine in toluene.

While [G1]-CHO (**5**) showed strong fluorescence in the solution under UV light and was highly soluble in many common organic solvents such as ethyl acetate, $CHCl_3$, CH_2Cl_2 , THF, and toluene, [G1]-C60, **1** did not give any fluorescence under UV light. The next generation of [G2]-CHO dendron, **7** was prepared by Horner-Wadsworth-Emmons coupling reaction between masked diphosphate core reagent, tetraethyl 5-methoxymethyl-1,3-phenylenebis(methylenephosphonate)¹¹ (**6**) and [G1]-CHO (**5**). Subsequently, [G2]-CHO (**7**) was coupled with 1.6 equivalent of C60 *via* 1,3-dipolar cycloaddition to afford the [G2]-C60 dendron **2** as shown in Scheme 1. In contrast to C60, [G2]-C60 dendron is also very soluble in several organic solvents such as $CHCl_3$, CH_2Cl_2 , THF or ethyl acetate presumably because of the hydrophobic hexyl chains attached to

periphery quinoline moieties. All C60-[G1 and G2] products were fully characterized by 1H and ^{13}C NMR spectroscopy. Firm evidence of the correct molecular ion peaks for the structures were obtained from MALDI-TOF (matrix assisted laser desorption-time of flight) mass spectra.

The MALDI-TOF spectrum of [G1]- and [G2]-C60 dendrons (**1** and **2**) is provided in the Supporting Information (Figures 1 and 2). The molecular formula of [G1]-C60 is $C_{127}H_{66}N_3$. The calculated $[M^+]$ and observed average molecular ion peak $[M+H]$ of [G1]-C60 was found to be 1631.5 and 1630.5, respectively. Similarly, the [G2]-C60 dendron shows the average molecular ion peak at 2614.05. Distinct strong peaks (913.9 and 1897.3) were observed in both cases due to the loss of fullerene fragmentation (-720). The supporting information (Figure 3(a) and 3(b)) showed 1H NMR spectra of [G1] and [G2]-C60 dendrons (**1** and **2**). In both case, aromatic and vinyl hydrogens appeared near 8.2–6.8 ppm and periphery hexyl peaks (He-h) were found at 2.71, 1.68, 1.35 and 0.92 ppm. Two doublet set at 4.96/4.23 ppm and one singlet at 4.92 ppm (Hc) clearly demonstrated

the presence of the bridged carbon atoms of the pyrrolidine ring moiety having two diastereomeric hydrogens. In Figure 2(a), one singlet of N-CH₃ was showed at 2.82 ppm and overlapped with CH₂ chains near 2.81 ppm in the case of Figure 1(b). In the case of [G2]-C60 (Figure 3(b)), same chemical shifts were also recorded and showed broader peak pattern compare to [G1]-C60 (Figure 3(a)). The presence of C60 unit was additionally confirmed by ¹³C NMR spectra. C60-G1 dendron and C60-G2 dendron **1**, and **2** showed complicated peaks in the range of 115-160 ppm due to the presence of crowded asymmetric carbons in fullerene C60 and the aromatic rings with clear six aliphatic hexyl carbon peaks.

In conclusion, we have synthesized and presented characterization based on ¹H, ¹³CNMR, and MALDI-TOF MS data for new double *n*-type cable molecules of G_x-C60 (*x* = 1 and 2), **1** and **2**. The structure consist of a electron transport *n*-type conjugated quinoline dendrons with covalently pendant fullerene C60 moieties.

Experimental Section

Potassium carbonate was dried and stored in an oven at 130 °C. Tetrahydrofuran (THF; 99.9%) and chloroform were either used as supplied or purified by standard techniques. All reactions requiring anhydrous conditions were performed in oven-dried glassware under argon or N₂ atmosphere. TLC was performed on precoated glass plate-silica gel 250-um (Baker Si250F; hard surfaced analytical later with 254 nm fluorescent indicator) with detection by UV light. Flash column chromatography was performed on silica gel (230-400 mesh). The ¹H NMR spectra were recorded on a DRX499 (500 MHz) or JEOL (400 MHz). ¹³C NMR spectra were recorded on a WM-500 (125 MHz) spectrometer. The spectra were recorded in CDCl₃ at room temperature. The solvent signals were used as internal standards for both ¹H NMR and ¹³C NMR recordings. Chemical shifts are given in ppm and referenced to internal TMS (tetramethylsilane, δ = 0 ppm). Matrix Assisted Laser Desorption-Time-of-Flight mass spectra (MALDI-TOF MS) were recorded on a Biflex III instrument (Bruker Daltonics, Billerica, MA) equipped with a nitrogen laser (337 nm). Compounds to be analyzed were dissolved in dichloromethane (Sigma, St. Louis, MO) and the MALDI probe was spotted with 1 mL of a 1:1 (v:v) mixture of sample and a saturated solution of *o*-cyano-4-hydroxycinnamic acid (HCCA) (Sigma, St. Louis, MO) in acetonitrile (Sigma). The instrument was operated in the positive ion mode with an accelerating potential of 20 kV and an extraction delay of 500 ns. A spectrum was produced by collecting and averaging data generated from 50 laser pulses.

Synthesis of [G1]-C60, 1. Round bottomed flask (1 L) and reflux condenser was oven dried and cooled under argon atmosphere. Fullerene (845 mg, 1.17 mmole, 1.2 equiv.) was dissolved in 750 mL of degassed toluene under argon atmosphere at room temperature. [G1]-CHO (864 mg, 0.98 mmol, 1.0 equiv.)¹⁰ and *N*-methylglycine (435 mg, 4.89 mmole, 5.0

equiv.) were added in the presence of argon atmosphere. The purple reaction mixture was refluxed for 22 hr and then cooled down to room temperature. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (100% toluene; *R_f* = 0.20) to give **1** (588 mg, 0.36 mmole, 36.7%). mp 325-328 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.21-7.21 (m., 33H, Ar-H), 4.96 (d, *J* = 9 Hz, 1H), 4.92 (s, 1H, N-C-H), 4.23 (d, *J* = 9 Hz, 1H), 2.82 (s, 3H, N-CH₃), 2.71 (m, 4H, Ar-CH₂), 1.68 (m, 4H, Ar-CH₂-CH₂), 1.35 (m, CH₃-(CH₂)₃-, 12H), 0.92 (m, CH₃-(CH₂)₄-, 6H). ¹³C NMR (CDCl₃) δ 156.02, 153.93, 147.3, 146.22, 145.94, 145.43, 145.31, 144.69, 142.70, 142.24, 129.59, 128.75, 127.42, 126.65, 125.93, 124.93, 124.73, 119.71 (aromatic and vinyl carbons), 83.58 (N-C-H), 77.00 (solvent peak CDCl₃), 70.13, 69.09, 40.25 (N-CH₃), 35.80 (C-Ar), 31.74, 31.34, 28.94, 22.63, 14.10 (CH₃-CH₂) ppm. MALDI-TOF-MS *m/z* calcd for C₁₂₇H₆₅N₃ [M]⁺ = 1631.52, found 1630.5. Base peak *m/e* = 910.7 (M-C60).

Synthesis of [G2]-C60, 2. The synthesis of **7** were performed according to a procedure described in the literature.¹⁰ Round bottomed flask (500 mL) and reflux condenser was oven dried and cooled under argon atmosphere. Fullerene (487 mg, 0.68 mmole, 1.6 equiv.) was dissolved in 360 mL of degassed toluene under argon atmosphere at rt. [G2]-CHO, **7** (784 mg, 0.42 mmol, 1.0 equiv.) and *N*-methylglycine (245 mg, 2.75 mmole, 6.5 equiv.) were added in the presence of argon atmosphere. The purple reaction mixture was refluxed for 24 hr and then cooled down to room temperature. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (100% toluene; *R_f* = 0.18) to give **2** (366 mg, 0.14 mmole, 33.3%). mp 335-339 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.21-7.07 (m., 73H, Ar-H), 4.99 (d, *J* = 9 Hz, 1H), 4.962 (s, 1H, N-C-H), 4.25 (d, *J* = 9 Hz, 1H), 2.81 (s, 3H, N-CH₃), 2.59 (m, 8H, Ar-CH₂), 1.67 (m, 8H, Ar-CH₂-CH₂), 1.35 (m, CH₃-(CH₂)₃-, 24H), 0.99 (m, CH₃-(CH₂)₄-, 12H). ¹³C NMR (CDCl₃) δ 157.03, 149.32, 149.10, 145.06, 139.17, 138.36, 137.40, 130.72, 130.69, 119.93 (aromatic and vinyl carbons), 83.40 (N-C-H), 77.00 (solvent peak CDCl₃), 70.18, 69.19, 41.25 (N-CH₃), 35.79 (C-Ar), 31.80, 31.29, 29.04, 22.68, 14.43 (CH₃-CH₂) ppm. MALDI-TOF-MS *m/z* calcd for C₂₀₁H₁₃₂N₅ [M]⁺ = 2614.05, found 2617.3. Base Peak *m/e* = 1896.3 (M-C60).

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