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Synthesis of C_{60}-diphenylaminofluorene dyads with two-photon absorbing characteristics

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Abstract

Linear A–sp^3–D molecular conjugates as 9,9-dialkyl-2-diphenylaminofluorene (DPAF-C_n)–C_{60} monoadducts were demonstrated using methanoketo unit as a linker to bridge the DPAF donor moiety and the fullerene acceptor chromophore together within a short distance of roughly 2.0 Å. Target products of C_{60}-diphenylaminofluorene dyads C_{60}(>DPAF-C_2) and C_{60}(>DPAF-C_{18}) were synthesized using Bingel cycloproanation reaction from the corresponding 7-α-bromoacetyl-9,9-dialkyl-2-diphenylaminofluorene precursors. Both dyads C_{60}(>DPAF-C_2) and C_{60}(>DPAF-C_{18}) were characterized by spectroscopic methods and simultaneous two-photon excitation measurements, showing large two-photon absorption cross-sections in the nanosecond regime.

Keywords: Fullerene derivative, diphenylaminofluorene, two-photon absorption, donor-acceptor conjugate, photonic organics.

1. Introduction

Molecular excitation by simultaneous two-photon absorption (2PA) leads to nonlinear dependence of the process in creating excited state at a much higher energy level than its ground state band gap energy. Subsequent release of this energy gives the corresponding fluorescence at a shorter optical wavelength than that produced from the one-photon excitation process. To make simultaneous multiple photons pumping process effective for materials application, 2PA-active polyaromatic or extensively conjugated chromophoric molecules exhibiting large photon-absorption cross-sections are desirable. Potential 2PA-based photonic applications using a focused laser beam include 3D optical data storage, 3D microfabrication [1-3], two-photon upconverted lasing [4], optical power limiting [5], two-photon based fluorescence microscopy, and photodynamic therapy [6-10].

Two-photon absorption cross-section value of organic dye molecules was progressively increased via extensive research effort over a number of years. Most of systematic modifications were made by changing the electronic structure to increase molecular polarity and dimensionality [11]. That included several strategies employed to increase the donor strength and conjugation length [12], extension of molecular dimensionality by multibranched derivatives [13], dendrimer [14], and octapolar molecules [15]. Evidence led to the conclusion that 2PA cross-section value increases with the increase in conjugation length and ability to promote charge polarization from the donor moiety to the acceptor moiety via π-electrons. However, little is known on 2PA chromophores consisting of A–sp^3–D motif, particularly, using the C_{60} cage as an electron acceptor (A) and 2-diphenylamino-9,9-dialkylfluorene (DPAF-C_n) as an electron donor (D) segment. This molecular system brings the donor segment into a close surrounding area of the fullerenic π-current without a direct conjugative bond.

In this article, we describe the synthetic procedure for the preparation of C_{60}-diphenylaminofluorene conjugates with different alkyl pendants on C_9 position of DPAF-C_n for the study of their nonlinear photonic characteristics in nanosecond region. We are interested in learning the effectiveness of long alkyl (C_{18}) pendent substitution on DPAF for improving (i) solubility of the resulting C_{60}-DPAF dyad and (ii) effective two-photon absorption cross-section. In addition, C_{60} derivatives exhibit nonlinear optical properties and are 2PA-active molecules. Structural combination of C_{60} with other 2PA chromophore may provide an essential approach for enhancing simultaneous multi-photon excitation activities.

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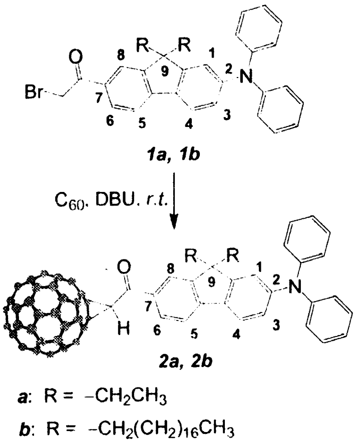
2. Results and Discussion

Fullerene molecule is composed of fully conjugated hexagons and pentagons. The carbon-carbon double bond located between two pentagons is the most reactive center to chemical functionalization. Any direct covalent bond linkage on the surface of C_{60} converts one C=C bond into two fullerenic sp^3 carbons. Covalent attachment of a diphenylaminofluorene moiety on C_{60} can be made via either the nucleophilic reaction of diphenylaminofluorenic anion or cyclopropanation reaction to place DPAF in a close neighborhood around the cage. We utilized the latter approach for constructing A–sp^3–D motif. Synthetic procedure of cyclopropanation reaction was reported by Bingel [16]. It involves in situ generation of anionic α-carbon of α-bromomalonate diester to initiate the nucleophilic attack on biscyclopentadienic olefin moiety of C_{60}. Subsequent replacement of the bromine atom of the intermediate species results in the formation of a cyclopropane ring with one extended extra carbon on C_{60}, denoted C_{61}. Accordingly, we prepared recently the first linear monoadduct of C_{60} as 9,9-diethyl-2-diphenylaminofluorenoketomethano[60]fullerene dyad **2a**, C_{60}(>DPAF-C_2). Compound **2a** was found to exhibit solvent-dependent intramolecular electron and energy transfer phenomena [17]. In this molecular system, photoinduced electron transfer from DPAF to the fullerene cage occurs in polar solvent, such as PhCN and DMF, whereas photoinduced energy transfer from excited DPAF to the fullerene cage in ground state dominates in nonpolar solvent, such as $PhCH_3$, using the nanosecond laser excitation at 532 nm where the C_{60} cage exhibits low optical absorption. Effective quenching of DPAF fluorescence in the excitation processes was observed.

Synthesis of C_{60}-DPAF dyads was carried out by functionalizing biscyclopentadienic olefin moiety of C_{60} with 9,9-dialkyl-2-diphenylaminofluorene with the alkyl group being either ethyl or octadecyl group at C_9 position of the diphenylaminofluorene ring. The use of long octadecyl group in replacement of the ethyl group was intended to increase the steric hindrance at DPAF moieties, minimize their aromatic ring-stacking aggregation, and enhance the solubility of resulting C_{60} dyad in the solvent that facilitates 2PA measurements.

A key step of synthetic preparative procedure of C_{60}(>DPAF-C_2) **2a** and 9,9-dioctadecyl-2-diphenylaminofluorenoketo-methano[60]fullerenes **2b**, C_{60}(>DPAF-C_{18}), is shown in Scheme 1. It involved Bingel cyclopropanation reaction [16] using corresponding 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorenes **1a** and 7-bromoacetyl-9,9-dioctadecyl-2-diphenylaminofluorenes **1b** as reaction intermediates. Thus, the treatment of **1a** or **1b** (1.0 equiv.) with C_{60} was performed in toluene using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base at ambient temperatures for a period of 5 h under nitrogen atmosphere. At the end of reaction, the resulting mixture was filtered and the filtrate partially concentrated via solvent removal. Subsequent work-up and application of a chromatographic separation procedure to remove starting materials and the residual byproducts from the crude material afforded the products **2a** (R_f = 0.6, SiO_2, hexane:toluene/3:2) or **2b** (R_f = 0.6, SiO_2, hexane:toluene/ 3:2) respectively, in an isolated yield of approximately 70% (with calibration of recovered C_{60}) after further purification on thin-layer chromatography. Intermediates of α-bromoacetyl-diphenylaminofluorenes **1a** and **1b** were prepared from commercially available 2-bromofluorene via a similar sequence of reactions described previously [18]. The reaction sequence included (a) dialkylation at C_9 of 2-bromofluorene with a mesyl derivative of appropriate alkanol in the presence of potassium *t*-butoxide for generation of the fluorenyl anion, (b) introduction of a diphenylamino group at C_2 of the fluorene ring using Buchwal–Hartwig procedure in the presence of $Pd_2(dba)_3$ catalyst in a catalytic amount and a ligand BINAP [19], and (c) Friedel-Crafts acylation for attaching a bromoacetyl group at C_7 position using anhydrous aluminum chloride as a reagent. An overall yield of the products **1a** or **1b** in nearly 66% was achieved after column chromatography purification.



Scheme 1. Key synthetic step of cyclopropanation reaction for preparation of fullerene dyads C_{60}(>DPAF-C_2) **2a** and C_{60}(>DPAF-C_{18}) **2b**.

During the first step reaction of dialkylation at C_9 of 2-bromofluorene, incomplete reaction occurred often with contamination of mono-alkylated byproduct if alkyl halide was used instead of alkanol mesylate. In case of diphenylamino group attachment on fluorene, a lesser amount of the 2-diphenylaminofluorene product was obtained by using a P(*o*-tolyl)$_3$/Pd catalyst system. Apparently, the combination of $Pd_2(dba)_3$ and BINAP gave a more effective condensation reaction. Effort for attachement of α-bromoacetyl group on the fluorene ring by 7-bromo-9,9-dialkyl-2-diphenylaminofluorene was not successful using either bromide-lithium metathesis with *n*-BuLi or Grignard complex that led to protonated 9,9-dialkyl-2-diphenylaminofluorene instead of **1a** or **1b**.

The structure of all reaction products was characterized by various spectroscopic methods. ^{1}H NMR spectrum of