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Synthesis and Characterization of C₆₀ Dyads with Highly Photoactive Dicyanoethylenylated Diphenylaminofluorene Chromophore Antenna

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Synthesis and Characterization of C₆₀ Dyads with Highly Photoactive Dicyanoethylenylated Diphenylaminofluorene Chromophore Antenna

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We designed and synthesized a novel class of highly photoactive C₆₀(>CPAF-C_n) nanostructures for their potential uses as photonic materials, using CPAF-C_n chromophore as the light-harvesting antenna. It is a part of our research effort on developing C₆₀(>DPAF-C_n)-based nonlinear photonic organics. We extended the structural modification by chemical conversion of the keto group in C₆₀(>DPAF-C_n) compound to a 1,1-dicyanoethylenyl moiety with stronger electron-withdrawing ability that resulted in a largely increased electronic polarization of the chromophore conjugate. Structural characterization of several C₆₀(>CPAF-C_n) containing variable alkyl sidechains was made by various spectroscopic methods. Interestingly, the chemical modification leads to a large bathochromic shift of the major absorption band of C₆₀(>CPAF-C_n) in the visible spectrum up to 600 nm and extending the photoresponsive capability of C₆₀-DCE-DPAF nanostructures to longer red wavelengths than the parent C₆₀(>DPAF-C_n) materials.

Keywords: C₆₀ dyads, diphenylaminofluorene, photoactive antenna, photonic fullerene nanomaterials.

1. Introduction

Recent advances in the design of photovoltaic devices based on a mixing heterojunction of C₆₀ derivatives and conjugated polymer thin films promote renewed interest in this alternative energy source (1–8). The main driving force on the utilization of conjugated polymer-based materials relies on their advantages over conventional inorganic crystalline or amorphous silicon-based solar cells including the potential to create lightweight, flexible, and inexpensive modules. In view of these concerns, composites of conjugated polymers and fullerene acceptors become recognizable prime candidates for potential future photovoltaics.

An improved photovoltaic device structure with 6% power conversion efficiency was reported on the tandem cell architecture consisting of a blend composition of poly(3-hexylthiophene), low band-gap polymers, and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) in multilayer junctions (7). Photoconductivity of the pri-

mary photovoltaic device with conjugated polymer-C₆₀-based cells arises from photoinduced electron transfer at the interface from the conjugated polymer donor segments to the fullerene acceptor cages in a heterojunction composite structure. Functionalized fullerene derivatives are electronegative molecules acting as an efficient electron affinitive component when used in conjunction with a variety of donor polymers. Evidently, the parent fullerene cage exhibits a high capacity in accepting multiple electrons consecutively (9). The addition of substituents on fullerenes may progressively reduce the electronegativity of the C₆₀ cage moiety of derivatives. However, limited functionalization of C₆₀ forming donor-fullerene dyads and triads containing carotene-porphyrin (10), porphyrin (11–16), terpyridine or bipyridine ruthenium complex (17,18), ferrocene (19), tetrathiafulvalene (20), and pyrazine (21) were proven to retain its photoinduced charge-transfer or energy-transfer (22,23) efficiency from the chemically attached donor arm to the C₆₀ cage. Alternatively, electrostatic self-assembly approaches using anionic fullerene derivatives (24–26) also provided a useful means for the construction of pre-defined layer structures to facilitate the charge transport. Subsequent efficient separation of the resulting photogenerated hole and

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electron species at the interface contributes to the photo-voltaic characteristics.

Fluorene-derived structures are thermally stable and highly fluorescent. Chemical modification of dialkylfluorenes by the linkage of an electron-rich diphenylamino group effectively converts them into diphenylaminodialkylfluorene (DPAF- C_n) motifs showing electron-donating characteristics. Periconjugative bridging of a C_{60} cage with one or multiple photoresponsive DPAF- C_n antenna forming $C_{60}(>DPAF-C_n)_x$ analogous structures is a logical approach to the design of nanomaterials exhibiting photoinduced ultrafast charge-generation capability (27–32). We have great interest in extending the optical absorption maximum range of DPAF- C_n moieties to longer wavelengths into the red region. Accordingly, we modified the structure of $C_{60}(>DPAF-C_n)$ for light harvesting in a larger range of the visible spectrum by replacing the keto functional group of C_{60} -keto-DPAF assemblies with a highly electron-withdrawing 1,1-dicyanoethylenyl (DCE) bridging group. The chemical modification forms respective C_{60} -DCE-DPAF analogous structures as $C_{60}(>CPAF-C_n)$ derivatives (33). In this report, we describe the preparation method and structural characterization of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-{1,1-dicyanoethylenyl})-9,9-dialkyl-2-diphenylamino-fluorene $C_{60}(>CPAF-C_n)$, where C_n represents either *n*-butyl (C_4), 3,5,5-trimethylhexyl (C_9), or *n*-dodecyl (C_{12}) groups.

2. Experimental

2.1. Materials

Reagents of 2-bromofluorene, *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), tris(dibenzylideneacetone)dipalladium(0), and malononitrile were purchased from Aldrich Chemicals. All other chemicals were purchased from Acros Ltd. Pure C_{60} (99.5%) was purchased from NeoTech Product Company, Russia and used as received.

2.2. Spectroscopic measurements

Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. 1H NMR and ^{13}C NMR spectra were recorded on either a Bruker Avance Spectrospin-400 or Bruker AC-300 spectrometer. UV-Vis spectra were recorded on a Hitachi U-3410 UV spectrometer. Mass spectroscopic measurements were performed by the use of positive ion matrix-assisted laser desorption ionization (MALDI-TOF) technique on a micromass M@LDI-LR mass spectrometer. The sample blended or dissolved in the matrix material was irradiated by nitrogen UV laser at 337 nm with 10 Hz pulses under high vacuum. Mass ion peaks were identified for the spectrum using the MassLynx v4.0 software.

2.2.1. Synthesis of 7- α -bromoacetyl-9,9-didodecyl-2-diphenylamino-fluorene BrDPAF- C_{12} , 6- C_{12}

To a suspension of aluminum chloride (0.59 g, 4.47 mmol) in 1,2-dichloroethane (30 ml) at 0°C was added a solution of 9,9-didodecyl-2-diphenylamino-fluorene **5** (0.30 g, 1.5 mmol) in 1,2-dichloroethane (30 ml). To it was then added α -bromoacetyl bromide (0.45 g, 1.5 mmol) over 10 min while maintaining the temperature of reaction mixture between 0–10°C. The mixture was warmed to ambient temperature and stirred for an additional 4.0 h. At the end of the reaction, it was quenched by the slow addition of water (100 ml) while maintaining the temperature below 45°C. The organic layer was separated and washed sequentially with dil. HCl (1.0 N, 50 ml) and water (50 ml \times 2). It was dried over sodium sulfate and concentrated *in vacuo* to get the crude product as yellow solids. It was purified by column chromatography (silica gel) using hexane–EtOAc/9:1 as the eluent. A chromatographic fraction corresponding to $R_f = 0.8$ on TLC (SiO₂, hexane–EtOAc/9:1 as the eluent) was isolated to afford 7- α -bromoacetyl-9,9-didodecyl-2-diphenylamino-fluorene BrDPAF- C_{12} , **6- C_{12}** , as a yellow viscous oil in 74% yield (0.87 g). Spectroscopic data of **6- C_{12}** : FT-IR (KBr) ν_{max} 3031 (w), 2953 (m), 2927 (m), 2868 (w), 1675 (s), 1593 (s), 1492 (s), 1465 (m), 1276 (s), 753 (m), and 697 (m) cm^{-1} ; 1H -NMR (500 MHz, CDCl₃, ppm) δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.94 (s, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.63 (dd, $J = 8.8$ Hz, $J = 3.2$ Hz, 1H) 7.30–7.0 (m, 12H), 4.5 (s, 2H), 2.0–1.8 (m, 4H), and 1.4–0.4 (m, 46H).

2.2.2. Synthesis of 7-(1,2-dihydro-1,2-methanofullerene-[60]-61-carbonyl)-9,9-didodecyl-2-diphenylamino-fluorene, $C_{60}(>DPAF-C_{12})$, 1- C_{12}

C_{60} (0.79 g, 1.1 mmol) and 7- α -bromoacetyl-9,9-didodecyl-2-diphenylamino-fluorene **6- C_{12}** (0.87 g, 1.1 mmol) were dissolved in toluene (500 ml) under an atmospheric pressure of nitrogen. To this was added by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.18 ml, 1.2 mmol) and stirred at room temperature for a period of 5.0 h. At the end of stirring, suspending solids of the reaction mixture were filtered off and the filtrate was concentrated to a 10% volume. Methanol (100 ml) was then added to affect precipitation of the crude product, which was isolated by centrifugation. The isolated solid was a mixture of the monoadduct **1- C_{12}** and its bisadduct. Separation of these two products were made by column chromatography (silica gel) using a solvent mixture of hexane–toluene (3:2) as the eluent. The first chromatographic band corresponding to $R_f = 0.7$ on the thin-layer chromatographic plate (TLC, SiO₂, hexane–toluene/3:1) afford 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-didodecyl-2-diphenylamino-fluorene **1- C_{12}** , $C_{60}(>DPAF-C_{12})$, as brown solids (0.62 g, 68% based on recovered C_{60}). Spectroscopic data of **1- C_{12}** : MALDI-MS (TOF) Calcd. for $^{12}C_{111}^{1}H_{67}^{14}N_1^{16}O_1$ m/z 1430; Found, m/z 1430 (M^+); FT-IR (KBr) ν_{max} 2948 (w), 2849 (s), 1680

(s), 1593 (vs), 1498 (s), 1463 (m), 1428 (w), 1274 (s), 752 (s), 696 (s), and 527 (vs) cm⁻¹; ¹H-NMR (200 MHz, CDCl₃, ppm) δ 8.51 (d, *J* = 7.5 Hz, 1H), 8.42 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.39–7.10 (m, 12H), 5.76 (s, 1H), 2.14–1.88 (m, 4H), and 1.50–0.62 (m, 46H).

2.2.3. General procedure for the synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-{1,1-dicyanoethylene})-9,9-dialkyl-2-diphenylaminofluorene C₆₀(>CPAF-C_n), 2-C_n

A mixture of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-dialkyl-2-diphenylaminofluorene, C₆₀(>DPAF-C_n) **1-C_n** (0.19–0.24 g, 0.17 mmol) and malononitrile (29 mg, 0.34 mmol) dissolved in dry chloroform (30 ml) was added pyridine (52 mg, 0.68 mmol) with stirring under nitrogen atmospheric pressure. To this solution, titanium tetrachloride (0.20 ml, excess) was added in one portion. After stirring at room temperature for a period of 5.0 min, the reaction mixture was quenched with water (30 ml). The resulting organic layer was washed several times with water (100 ml each), dried over magnesium sulfate, and concentrated *in vacuo* to afford the crude orange red solid product. It was purified by preparative thin-layer chromatography (TLC, silica gel, chloroform). A product fraction collected at *R_f* = 0.3–0.5 (hexane–toluene/3:2) was identified to be 7-(1,2-dihydro-1,2-methanofullerene[60]-61-{1,1-dicyanoethylene})-9,9-dialkyl-2-diphenylaminofluorene **2-C_n**, C₆₀(>CPAF-C_n), as orange-red solids in a yield of (0.2–0.3 g, 49–65%).

Spectroscopic data of C₆₀(>CPAF-H), **2-H**: MALDI–MS (TOF) Calcd. for ¹²C₉₀¹H₁₉¹⁴N₃ *m/z* 1142; found, *m/z* 1142 (M⁺); UV-Vis (toluene, 1.0 × 10⁻⁵ M) λ_{max} (ε) 322 (9.6 × 10⁴) and 482 (3.1 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3059 (w), 3027 (w), 2962 (m), 2925 (m), 2874 (w), 2846 (w), 2216 (m), 1592 (vs), 1488 (s), 1276 (s), 1118 (s), 1072 (s), 817 (m), 747 (m), 697 (s), and 526 (s) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.32 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.30–7.07 (m, 12H), 5.55 (s, 1H), and 3.97 (s, 2H).

Spectroscopic data of C₆₀(>CPAF-C₂) **2-C₂**: MALDI–MS (TOF) Calcd. for ¹²C₉₄¹H₂₇¹⁴N₃ *m/z* 1198; Found, *m/z* 1198 (M⁺); UV-Vis (toluene, 1.0 × 10⁻⁵ M) λ_{max} (ε) 327 (1.9 × 10⁵) and 481 (4.9 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3027 (w), 2954 (m), 2925 (s), 2854 (m), 2224 (m), 1594 (vs), 1491 (m), 1281 (s), 1096 (s), 819 (m), 754 (s), 577 (w), and 527 (m) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.16 (d, *J* = 7.6 Hz, 1H), 8.04 (s, Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.30–7.05 (m, 12H), 5.56 (s, 1H), 2.09–1.92 (m, 4H), and 0.34 (t, *J* = 7.0 Hz, 6H).

Spectroscopic data of C₆₀(>CPAF-C₄) **2-C₄**: MALDI–MS (TOF) Calcd. for ¹²C₉₈¹H₃₅¹⁴N₃ *m/z* 1254; Found, *m/z* 1254 (M⁺) and 1255 (MH⁺); UV-Vis (toluene, 1.0 × 10⁻⁵ M) λ_{max} (ε) 323 (1.5 × 10⁵) and 485 (4.0 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3027 (w), 2954

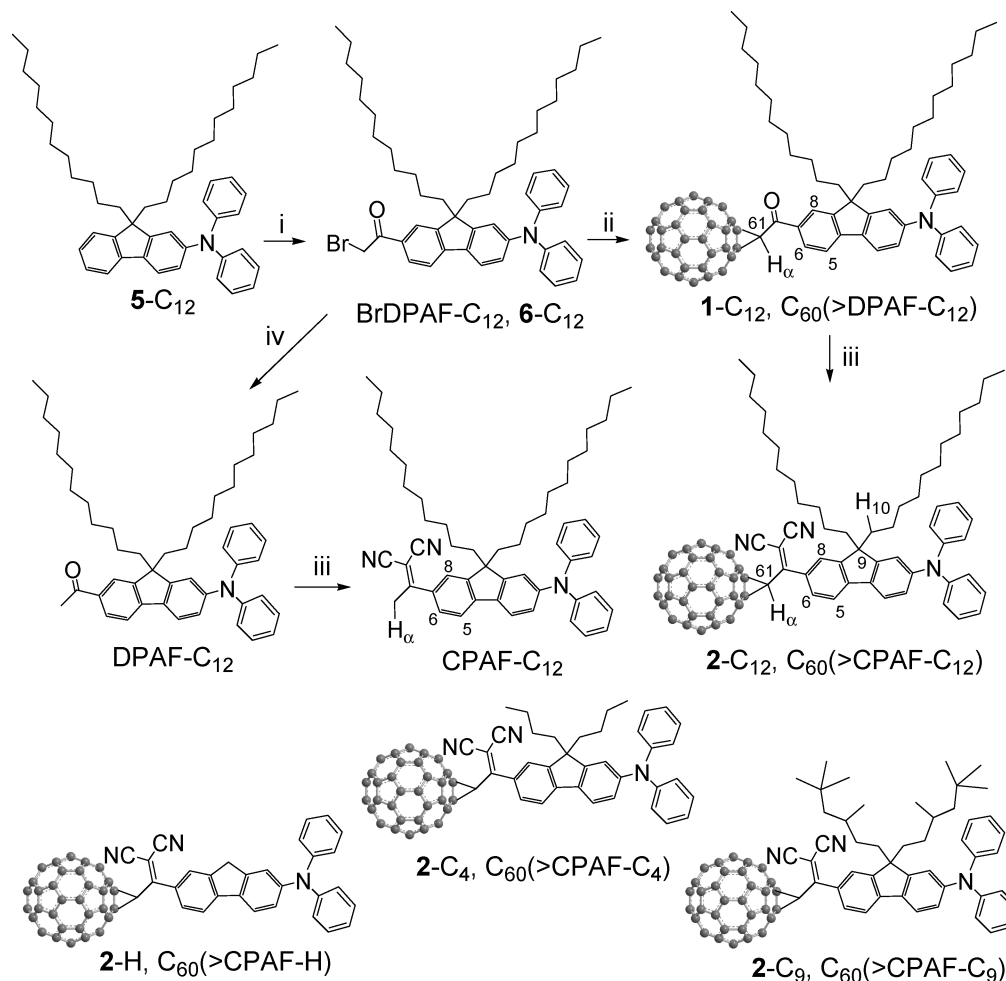
(m), 2925 (s), 2854 (m), 2224 (m), 1594 (vs), 1491 (m), 1281 (s), 1096 (s), 819 (m), 754 (s), 577 (w), and 527 (m) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.15 (d, *J* = 8.2 Hz, 1H), 8.05 (s, Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.34–7.05 (m, 12H), 5.58 (s, 1H), 2.03–1.88 (m, 4H), and 1.08–0.63 (m, 14H).

Spectroscopic data of C₆₀(>CPAF-C₉) **2-C₉**: MALDI–MS (TOF) Calcd. for ¹²C₁₀₈¹H₅₅¹⁴N₃ *m/z* 1394; Found, *m/z* 1394 (M⁺) and 1395 (MH⁺); UV-Vis (toluene, 1.0 × 10⁻⁵ M) λ_{max} (ε) 326 (1.5 × 10⁵) and 482 (4.5 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3027 (w), 2954 (m), 2924 (s), 2854 (w), 2224 (m), 1594 (vs), 1491 (s), 1282 (s), 1096 (vs), 819 (m), 754 (m), 697 (m), and 527 (s) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.12 (d, *J* = 8.2 Hz, 1H), 8.07 (s, Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.26–7.00 (m, 12H), 5.52 (t, *J* = 1.9 Hz 1H), 2.1–2.0 (m, 4H), and 1.86–0.44 (m, 34H).

Spectroscopic data of C₆₀(>CPAF-C₁₂) **2-C₁₂**: MALDI–MS (TOF) Calcd. for ¹²C₁₁₄¹H₆₇¹⁴N₃ *m/z* 1479; Found, *m/z* 1479 (M⁺) and 1480 (MH⁺); UV-Vis (toluene, 1.0 × 10⁻⁵ M) λ_{max} (ε) 326 (1.5 × 10⁵) and 468 (4.2 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3064 (w), 3036 (w), 2954 (m), 2923 (s), 2851 (w), 2224 (m), 1594 (vs), 1538 (w), 1492 (s), 1279 (s), 1186 (m), 1105 (vs), 820 (w), 753 (m), 697 (m), and 527 (s) cm⁻¹; ¹H-NMR (200 MHz, CDCl₃, ppm) δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.06 (s, Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.40–7.06 (m, 12H), 5.59 (s, 1H), 2.4–1.7 (m, 4H), and 1.50–0.71 (m, 46H).

3. Results and discussion

In the chemical conversion of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-didodecyl-2-diphenylaminofluorene, C₆₀(>DPAF-C₁₂), **1-C₁₂**, to 7-(1,2-dihydro-1,2-methanofullerene[60]-61-{1,1-dicyanoethylene})-9,9-didodecanyl-2-diphenylaminofluorene C₆₀(>CPAF-C₁₂), **2-C₁₂**, it involves a structural modification from a keto group of **1-C₁₂** to a 1,1-dicyanoethylenyl (DCE) group. The conversion was made by using malononitrile as a reagent. Prior to this reaction, a recently reported reaction sequence for the preparation of 7-bromoacetyl-9,9-didodecanyl-2-diphenylaminofluorene **6-C₁₂** (BrDPAF-C₁₂) was applied as the key intermediate precursor molecule (30), as shown in Scheme 1. This intermediate was prepared by Friedel-Crafts acylation reaction of 9,9-didodecanyl-2-diphenylaminofluorene **5-C₁₂** at C₇ position of fluorene moiety with α-bromoacetyl bromide and aluminum chloride in 1,2-dichloroethane at 0 °C to ambient temperature for 4.0 h. Synthesis of the compound **5-C₁₂** was made by the amination of 2-bromo-9,9-didodecanylfluorene **4-C₁₂** using diphenylamine as a reagent in the presence of tris(dibenzylideneacetone)dipalladium(0) catalyst, *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) ligand, and sodium *t*-butoxide in toluene at refluxing



Sch. 1. Reagents and conditions: (i) α -bromoacetyl bromide, AlCl₃, ClCH₂CH₂Cl, 0°C to rt, 4.0 h; (ii) C₆₀, DBU, toluene, rt, 5.0 h; (iii) malononitrile, pyridine, TiCl₄, rt, 5.0 min; (iv) (*n*-Bu)₃SnH (4.0 equiv.), toluene, 70°C, 24 h.

temperatures for 8.0 to 10 h under nitrogen atmosphere. Whereas, the compound 4-C₁₂ was prepared by the didodecanylation of commercially available 2-bromofluorene 3. Addition of a DPAF-C₁₂ subunit to C₆₀ leading to the formation of dyads 1-C₁₂ and 1-C₄ was accomplished by the treatment of α -bromoacetylfluorene derivative 6-C₁₂ and 6-C₄, respectively, with C₆₀ in toluene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv.) at ambient temperature for 5.0 h. Conversion of the keto group of 1-C₁₂ or 1-C₄ to the corresponding 1,1-dicyanoethylenyl group was carried out by the reaction using malononitrile as a reagent, pyridine as a base, and titanium tetrachloride as a deoxygenation agent in dry toluene at ambient temperature for a short period of 5.0 min to afford 7-(1,2-dihydro-1,2-methanofullerene[60]-61{1,1-dicyanoethylene})-9,9-didodecyl-2-diphenylaminofluorene 2-C₁₂, C₆₀(>CPAF-C₁₂), or 7-(1,2-dihydro-1,2-methanofullerene[60]-61{1,1-dicyanoethylene})-9,9-dibutyl-2-diphenylaminofluorene 2-C₄, C₆₀(>CPAF-C₄), respectively, as orange red solids in 67% yield (based on recovered C₆₀) after purification.

Structural characterization of C₆₀(>CPAF-C₁₂) and C₆₀(>CPAF-C₄) was performed using various spectroscopic techniques. Evidence of the CPAF moiety bridging on the methano[60]fullerene cage by a 1,1-dicyanoethylenyl group can be seen clearly in the infrared spectra of 2-C₁₂ and 2-C₄ as both showing a strong optical absorption band of cyano (–C≡N) stretching vibration centered at 2224 cm⁻¹ with the complete disappearance of carbonyl stretching vibration at 1680 cm⁻¹ for 1-C₁₂ (Figure 1(c)) and three typical fullerene derivative signals at 753, 697, and 527 cm⁻¹ for the unfunctionalized half-cage sphere, as shown in Figure 1(e). This cyano absorption band also matches well with that of the model compound CPAF-C₁₂ (Figure 1(d)) at the same wavenumber.

In the UV-Vis spectra of 2-C₁₂ in toluene, the chemical modification also leads to a large bathochromic shift of nearly 70–86 nm in the long wavelength absorption band from that of C₆₀(>DPAF-C₁₂) (1-C₁₂) centered at 399 nm (λ_{max}). For example, optical absorption of C₆₀(>CPAF-C₁₂) (Figure 2Ac) gave two major bands

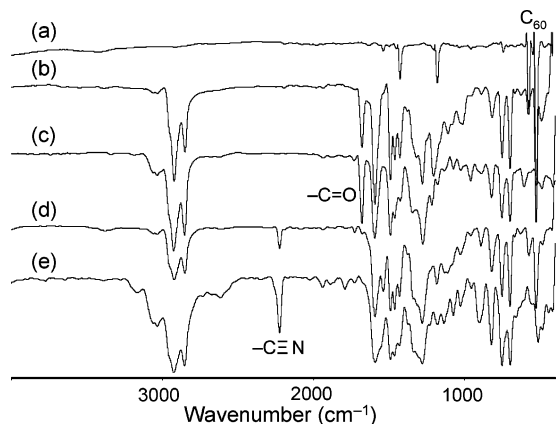


Fig. 1. Infrared spectra of (a) pristine C₆₀, (b) DPAF-C₁₂, (c) C₆₀(>DPAF-C₁₂), (d) CPAF-C₁₂, (e) C₆₀(>CPAF-C₁₂), showing the cyano absorption band centered at 2224 cm⁻¹.

(λ_{\max}) at 326 (1.5×10^5) and 468 (4.2×10^4 L/mol-cm) in toluene (1.0×10^{-5} M), whereas C₆₀(>CPAF-C₄) displayed similar two absorption bands at 323 (1.5×10^5) and 485 (4.0×10^4 L/mol-cm), as shown in Figure 2Ab. The former band matches approximately with that of the fullerene moiety and is, thus, assigned to the absorption of C₆₀ cage. The latter band fits well with a slightly longer wavelength than the main optical absorption of CPAF-C₁₂ (Scheme 1). A slight variation of the absorption intensity observed among the main absorption bands of C₆₀(>CPAF-C₂), C₆₀(>CPAF-C₄), C₆₀(>CPAF-C₉), and C₆₀(>CPAF-C₁₂) may be indicative of a variable degree of intermolecular association in toluene. Accordingly, we conducted the

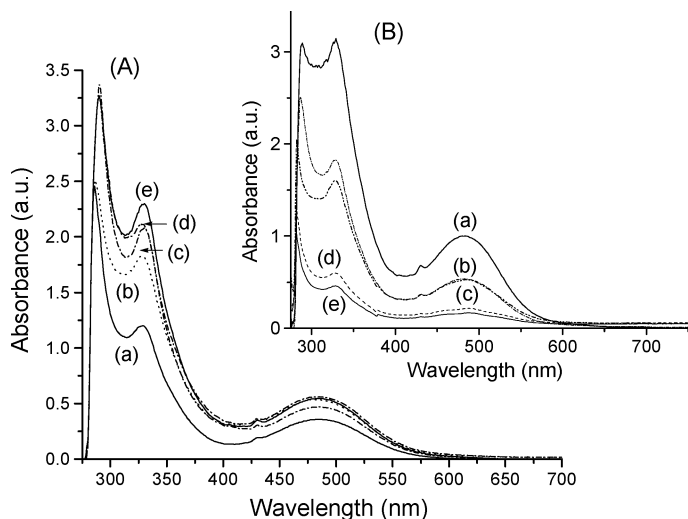


Fig. 2. UV-Vis spectra of (A) (a) C₆₀(>CPAF-H) 2-H, (b) C₆₀(>CPAF-C₄) 2-C₄, (c) C₆₀(>CPAF-C₁₂) 2-C₁₂, (d) C₆₀(>CPAF-C₉) 2-C₉, (e) C₆₀(>CPAF-C₂) 2-C₂, in toluene at a concentration of 1.0×10^{-5} M. (B) UV-Vis spectra of C₆₀(>CPAF-C₁₂) at a concentration of (a) 4.0×10^{-5} , (b) 2.0×10^{-5} , (c) 1.0×10^{-5} , (d) 0.5×10^{-5} , and (e) 0.25×10^{-5} M in toluene.

concentration-dependent measurements on the sample of C₆₀(>CPAF-C₁₂) from 0.25×10^{-5} M to 4.0×10^{-5} M. A nonlinear relationship of λ_{\max} intensity of the 485 nm band was detected, as shown in Figure 2Ba–2Be, confirming the hypothesis.

The molecular ion mass of C₆₀(>CPAF-C₄) 2-C₄ and C₆₀(>CPAF-C₁₂) 2-C₁₂ was detected in matrix-assisted laser desorption ionization (MALDI) mass spectra (MS), showing a group of mass peaks with a maximum peak intensity at m/z 1254 (M⁺) and 1255 (MH⁺) for 2-C₄ and m/z 1479 (M⁺) and 1480 (MH⁺) for 2-C₁₂. In the case of C₆₀(>CPAF-C₉) 2-C₉, positive ion MALDI mass spectrum (Figure 3b) displayed a group of mass ion peaks at m/z 1394 (M⁺) and 1395 (MH⁺). It was followed by a group of mass peaks centered at m/z 1155, 1141, 1128, and 720 (weak, C₆₀), matching well with the mass of fragmented ion having the loss of two 3,5,5-trimethylhexyl (C₉) subunit and CPAF-C₉ moiety from 2-C₉. The spectrum also showed a major fragmentation peak at m/z 675 that is identical to the molecular mass ion of CPAF-C₉ model compound at m/z 677 (MH⁺), as shown in Figure 3a, giving the clear confirmation of the chemical composition of these analogous of novel nanomaterials 2-C_n.

No other mass fragmentation peaks were found in the range of m/z 750–1100 giving a relatively simple spectrum in the higher mass region of Figure 3b revealed high stability of aromatic diphenylaminofluorene moiety under mass spectroscopic measurement conditions. That led to the bond cleavage occurring mostly at the cyclopropanyl carbon conjunction bonds bridging fullerene and CPAF-C_n moieties.

¹H NMR spectra data of the precursor molecule BrDPAF-C₉, 6-C₉, and the model compound DPAF-C₉ were used as the reference for comparison with those of C₆₀(>CPAF-C_n) synthesized. In the case of 6-C₉, the chemical shift of H _{α} (next to carbonyl group) was detected at δ 4.45 (Figure 4a) while the H _{α} chemical shift of the model DPAF-C₉ was found to be δ 2.65 (Figure 4b) owing to the absence of an electron-withdrawing bromo group. The aromatic carbon peak pattern of ¹³C NMR spectrum (Figure 4c) of DPAF-C₉ was applied for the differentiation of fulleranyl carbon peaks in the spectra of C₆₀(>DPAF-C₉) and C₆₀(>CPAF-C₉). Chemical conversion of keto group of 1-C_n to the corresponding 1,1-dicyanoethylene group of C₆₀(>DPAF-H), C₆₀(>DPAF-C₄), C₆₀(>DPAF-C₉), and C₆₀(>DPAF-C₁₂) was also confirmed by the disappearance of key carbonyl carbon peak at δ 190 in ¹³C NMR spectrum of C₆₀(>DPAF-C_n) and clear upfield shift of α -proton (H _{α} next to 1,1-dicyanoethylene group) chemical shift to δ 5.59 of 2-C₁₂, appearing as a singlet peak. The shift is 0.17 ppm from δ 5.76 for H _{α} (next to carbonyl group) of C₆₀(>DPAF-C₁₂) 1-C₁₂. It was also characterized by large downfield shift of nearly 1.0 ppm from δ 4.6 for the chemical shift of H _{α} peak as a singlet in the spectrum of CPAF-C₁₂. Detailed information of all aromatic protons of C₆₀(>CPAF-C₁₂) and the peak assignments were

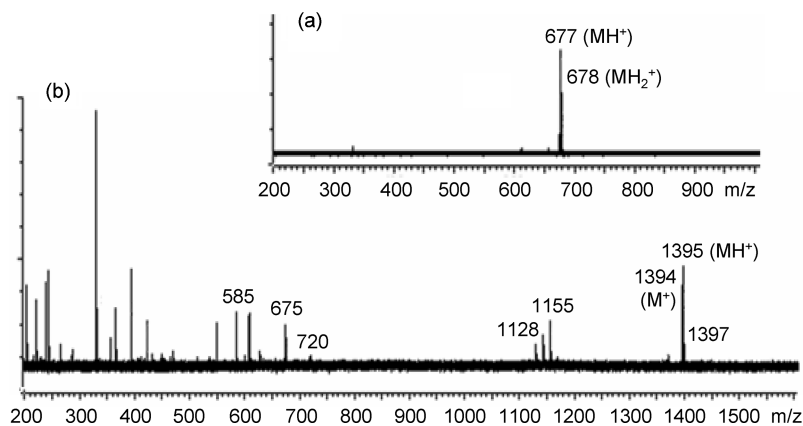


Fig. 3. MALDI-TOF mass spectrum of (a) CPAF-C₉ and (b) C₆₀(>CPAF-C₉) 2-C₉, showing the corresponding molecular ion mass at m/z 677 (MH⁺) and 1394 (M⁺), respectively.

given as follows. Assignment of H₆ proton peak was made by its most downfielded chemical shift at δ 8.17 (d, $J = 8.0$ Hz, 1H) from that of CPAF-C₁₂ due to through space close contact with the fullerene cage. Its proton coupling with the adjacent H₅ at δ 7.83 (d, $J = 8.0$ Hz, 1H) was revealed by the same coupling constant. The nearly singlet peak at δ 8.06 (s, Hz, 1H) with a small long-range proton coupling was assigned for the proton H₈. Chemical shifts of these phenyl protons at C₆, C₈, and C₅ of fluorene ring

represented downfield shift from δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.94 (s, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), respectively, in the spectrum of 6-C₁₂ (BrDPAF-C₁₂) due to the influence of fulleranyl cage current. That suggested the successful cyclopropanation reaction of CPAF-C₁₂ with C₆₀. The degree of downfielded chemical shift is apparently less than those of the corresponding fluorenyl protons of C₆₀(>DPAF-C₁₂), 1-C₁₂, at δ 8.51 (d, $J = 7.5$ Hz, 1H), 8.42 (s, 1H), 7.88 (d, $J = 7.5$ Hz, 1H), respectively.

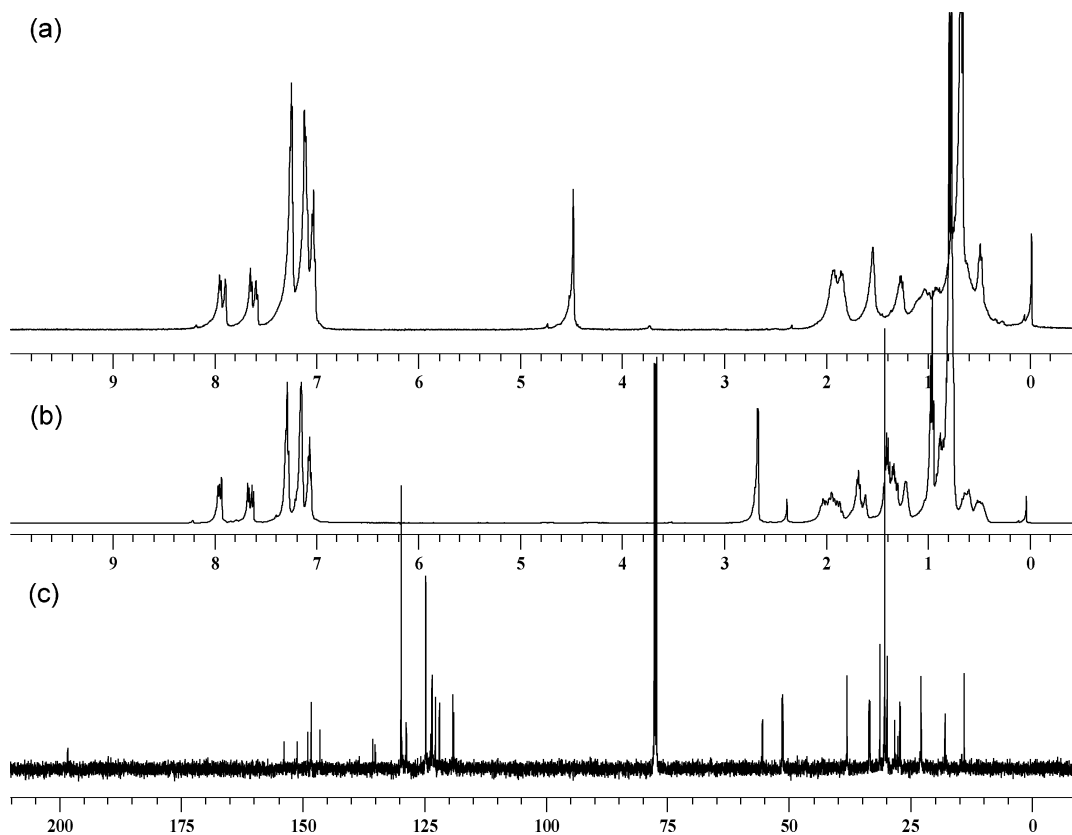


Fig. 4. ¹H NMR spectra of (a) BrDPAF-C₉ 6-C₉ and (b) DPAF-C₉ and (c) ¹³C NMR spectrum of DPAF-C₉.

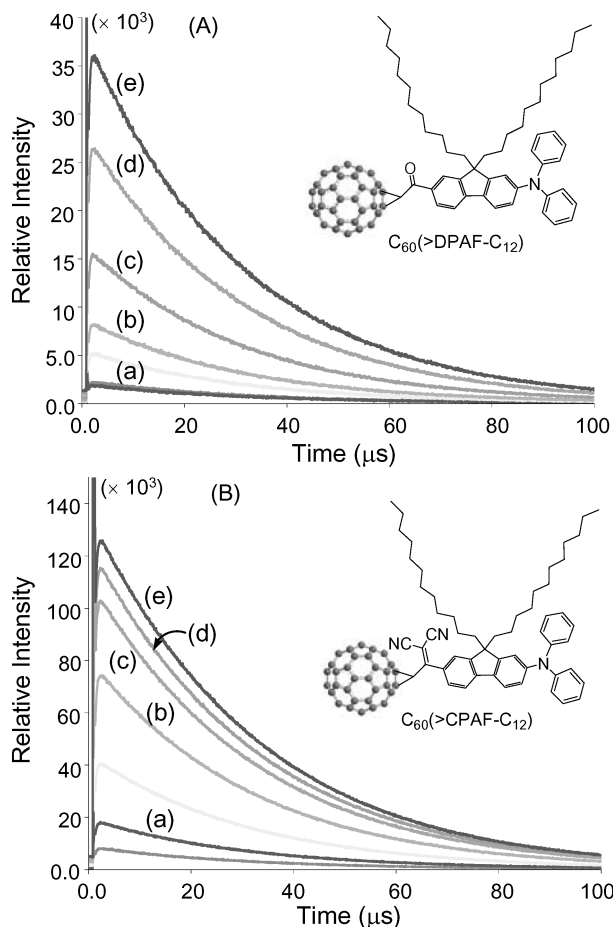


Fig. 5. Time-resolved luminescence of singlet oxygen ($^1\text{O}_2$) derived from (A) $C_{60}(>DPAF-C_{12})$ 1- C_{12} and (B) $C_{60}(>CPAF-C_{12})$ 2- C_{12} at 1270 nm in toluene at a concentration of (a) 2.0, (b) 10, (c) 20, (d) 30, (e) 50 μM upon photoexcitation at 532 nm.

To study and compare the efficiency of intermolecular energy-transfer processes from photoexcited $C_{60}(>^1DPAF^*-C_{12})$ and $C_{60}(>^1CPAF^*-C_{12})$ transient state to the corresponding C_{60} cage, we carried out time-resolved singlet oxygen measurements by direct detection of oxygen's near-IR luminescence emission ($^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition) at 1270 nm corresponding to a singlet-triplet transition state. The fullerene derivatives $C_{60}(>DPAF-C_{12})$ and $C_{60}(>CPAF-C_{12})$ were excited by a frequency-doubled Nd:YLF laser at 523 nm (λ_{max}). The pulse duration was 10 ns and the pulse repetition rate was approximately 3 kHz. The singlet oxygen luminescence was detected by a PMT detector with high sensitivity in the near-IR region. Five bandpass filters (1210 nm, 1240 nm, 1270 nm, 1300 nm, 1330 nm) were placed sequentially in front of the photodetector to sample the spectrum of the luminescence. All measurements were performed using 10 μM or 50 μM concentrations of the fullerene derivatives in toluene.

Formation of $^1\text{O}_2$ becomes possible via the intermolecular triplet energy transfer from $^3C_{60}^*(>CPAF-C_n)$ to O_2 . As a result, we recorded the emission intensity of $^1\text{O}_2$ fluorescence arising from $C_{60}(>DPAF-C_{12})$ 1- C_{12} (Figure 5A) and $C_{60}(>CPAF-C_{12})$ 2- C_{12} (Figure 5B) to be 3.6×10^4 and $1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, in a concentration of $5.0 \times 10^{-5} \text{ M}$ in toluene. The intensity varied as a function of the concentration, the number of laser pulses, and the laser power intensity. The $^1\text{O}_2$ production yield of $C_{60}(>CPAF-C_{12})$ was found in a more than 3.5-folds in intensity higher than its keto analogous 1- C_{12} , indicating large light-harvesting enhancement of CPAF- C_{12} moiety and subsequent efficient triplet state generation of the $C_{60} >$ cage moiety. The lifetimes of singlet oxygen generated from $C_{60}(>CPAF-C_{12})$ and $C_{60}(>DPAF-C_{12})$ in toluene were estimated to be 32 and 31 μs , respectively. The observation revealed the population mechanism of the $^1C_{60}^*(>CPAF-C_{12})$ state arising from the energy-transfer process since the direct photoexcitation of the $C_{60} >$ moiety to $^1(C_{60} >)^*$ is unlikely to occur with the 523 nm light source.

4. Conclusions

We have designed and synthesized a new class of photoresponsive C_{60} -DCE-diphenylaminofluorene (DPAF) nanostructures, where DCE represents the 1,1-dicyanoethylenyl group, for their potential uses as photonic materials, using CPAF- C_n chromophore as the light-harvesting antenna. Photophysical properties of these nanomaterials manifested in the generic structure of $C_{60}(>CPAF-C_n)$ are expected to enhance linear and nonlinear photonic characteristics from those of recently, intensively studied C_{60} -keto-DPAF assemblies as nanophotonic $C_{60}(>DPAF-C_n)_x$ compounds.

We extended the structural modification by chemical conversion of the keto group in $C_{60}(>DPAF-C_n)$ dyad to a 1,1-dicyanoethylenyl moiety with stronger electron-withdrawing ability that resulted in a largely increased electronic polarization of the chromophore conjugate. Structural characterization of several $C_{60}(>CPAF-C_n)$ containing variable alkyl sidechains was made by various spectroscopic methods. Interestingly, the chemical modification leads to a large bathochromic shift of the major absorption band of $C_{60}(>CPAF-C_n)$ in the visible spectrum up to 600 nm and extending the photoresponsive capability of C_{60} -DCE-DPAF nanostructures to longer red wavelengths than the parent $C_{60}(>DPAF-C_n)$ materials.

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