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Alternative Synthesis of C_{60}-Diphenylaminofluorene Derivatives for Nonlinear Photonic Applications: Method of Preparation and Characterization

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An alternative synthetic route for the preparation of key intermediate synthons 7-α-bromoacetyl-2-diphenylaminofluorene (α-BrDPAF-H) and 7-α-bromoacetyl-9,9-dialkyl-2-diphenylaminofluorene (α-BrDPAF-C_n) was demonstrated. The latter reactions involved the first step of dialkylation of 2-bromofluorene at C_9 position of the fluorene moiety, the second step of a diphenylamino group attachment at C_2 position of the resulting dialkylfluorene, and the third step of Friedel-Craft acylation of α-bromoacetyl group at C_7 position of dialkylated diphenylaminofluorene. From the intermediates α-BrDPAF-H and α-BrDPAF-C_n, a series of C_{60}-*keto*-DPAF nanostructures, such as the fullerene monoadducts C_{60}(>DPAF-H) and C_{60}(>DPAF-C_n), where n is 2, 4, or 10, were synthesized in a reasonable yield. Molecular mass ions of the dyads C_{60}(>DPAF-H), C_{60}(>DPAF-C_2), C_{60}(>DPAF-C_4), and C_{60}(>DPAF-C_{10}) were clearly detected in positive ion matrix-assisted laser desorption ionization mass spectrum (MALDI–MS) that confirmed the composition mass of each compound synthesized.

Keywords: C_{60} chromophores; diphenylaminofluorene; monodducts; synthetic synthon; nonlinear optical materials.

1 Introduction

Applications of highly fluorescent organic chromophores in conjugation with the C_{60} cage were found to be effective in enhancing the cross-section of simultaneous two-photon absorption of the resulting nanomaterials (1–3). One of the most pronounced chromophores showing an appreciable level of two-photon absorption (2PA) activity is 9,9-dialkyl-2-diphenylaminofluorene (DPAF-C_n). The compound DPAF-C_n consists of an interconnected π-conjugation of double benzene rings with electron-rich characteristics. It serves as the donor component when covalently linked with the strong electron withdrawing C_{60} chromophore. In this arrangement, we applied a weak electron withdrawing functional ketone moiety for the connection of DPAF-C_n and C_{60} cage together by a covalent bond, forming the corresponding C_{60}-*keto*-DPAF-C_n assemblies. The ketone group ensures the electron polarization of the fluorene ring going on the direction from the electron-rich diphenylamino group to the electron-deficient ketone group. That facilitates subsequent photoexcitation events to induce electron transfer from diphenylaminofluorene ring to the C_{60} cage. High molecular polarization is one of several crucial criteria necessary for the enhancement of two-photon absorption cross-sections. Upon laser irradiation, this type of assembly in a form of C_{60}(>DPAF-C_2) dyad was found to exhibit large 2PA cross-sections in both femtosecond and nanosecond regions with significant nonlinear photoresponsive activities (1, 2). Aside from the enhanced 2PA cross-sections, C_{60} cage exhibits a nearly quantitative yield of intersystem crossing process going from the excited singlet state ($^1C_{60}{}^*$) to the triplet state ($^3C_{60}{}^*$) that provides a significant number of excited states in population for appreciable photoinduced reverse saturable absorption (RSA). Combination of large 2PA cross-sections and a high RSA value (4–6) at the ultrafast transient state in femtoseconds to nanoseconds becomes the foundation of nonlinear photonic responses in the molecular C_{60}-*keto*-DPAF-C_n nanostructure system, such as optical power limiting effect (7–10).

Nanostructures of C_{60}-*keto*-DPAF-C_n assemblies also exhibit photoinduced intramolecular electron- or energy-transfer phenomena from DPAF-C_n donor moiety to the C_{60} acceptor cage upon single-photon excitation of either donor or acceptor moieties (10–12). This analogous of photophysics has been extensively reviewed (13–19). The phenomena lead to the formation of corresponding charge-separated $(C_{60}>)^{\bullet -}$–$(DPAF\text{-}C_n)^{\bullet +}$ or triplet C_{60} ($^3C_{60}{}^*>$) excited transient states. Utilization of these transient states to

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enhance their potential applications in the area of molecular electronic devices (20–28), photovoltaic cells (29–37), and photodynamic sensitizing treatments (38–45) was proposed recently.

Success of the design of C_{60}-*keto*-DPAF-C_n nanostructures relies greatly on the development of a synthetic approach leading to efficient preparation of the desirable materials in a high yield. Accordingly, we undertook synthetic evaluation of a possible preparative route for key intermediate precursors aiming to improve the overall efficiency. This resulted in the alternative synthesis of C_{60}(>DPAF-C_n), as shown in Scheme 1.

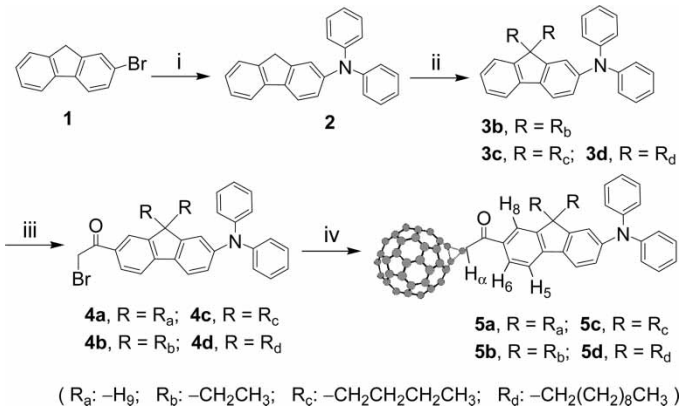
2 Experimental

2.1 Materials

Pure C_{60} (99.5%) was purchased from NeoTech Product Company, Russia and confirmed by thin-layer chromatography (TLC, SiO_2, toluene). Fluorene was purchased from Aldrich Chemicals. Toluene and benzene was dried over sodium or molecular sieves 4.0 Å). The reagents *tris*(dibenzylideneacetone)dipalladium(0), *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), and 2-bromofluorene were purchased from Aldrich Chemicals. All other chemicals were purchased from Acros, Ltd.

2.2 Spectroscopic Measurements

Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. UV-vis spectra were recorded on a Hitachi U-3410 UV spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker Avance Spectrospin-200 or Bruker AC-300 spectrometer. Mass spectroscopic measurements were measured by using positive ion matrix-assisted laser desorption ionization (MALDI–TOF) technique on a micromass M@LDI-LR mass spectrometer. In a typical measurement, two fractions (100 μl) each from the solution of C_{60}(>DPAF-C_n) (1.0 mg) in chloroform (1.0 ml) and the matrix solution of α-cyano-4-hydroxycinnamic acid (10 mg) in acetone (1.0 ml) were mixed together. From this sample-matrix mixture, a small quantity (2.0 μl) was taken and deposited on the stainless steel sample target plate, dried, and, subsequently, inserted into the ionization source of the instrument. The resulting sample blended or dissolved in the matrix material was irradiated by nitrogen UV laser at 337 nm with 10 Hz pulses under high vacuum. MALDI mass spectra were acquired in reflection mode. Each spectrum was produced by averaging 10 laser shots; at least 25 spectra were acquired from different regions of the sample target. Mass ion peaks were identified for the spectrum using the Mass Lynx v4.0 software.



Sch. 1. *Reagent and reaction condition*: i) diphenylamine, *tris*-(dibenzylidenacetone dipalladium(0) (*cat.*), *rac*-BINAP, *t*-BuONa, toluence, ref;ix; ii) iodoalkane, *t*-BuOK in THF, 0°C-*rt*, 4.0 h; iii) bromoacetyl bromide, $AlCl_3$, THF, reflux; iv) C_{60}, DBU, toluene, *rt*, 4.0 h.

2.3 Synthesis of 2-diphenylaminofluorene 2

The compound 2-bromofluorene **1** (5.0 g, 20.5 mmol), diphenylamine (4.0 g, 23.7 mmol), *tris*-(dibenzylideneacetone)dipalladium(0) (0.045 g, 0.25 mmol), *rac*-BINAP (0.093 g, 0.75 mmol), and sodium *t*-butoxide (3.0 g, 31 mmol) in dry toluene (100 ml) was placed and refluxed for 40 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature, it was diluted with diethyl ether (60 ml) and washed with brine (40 ml) and water (40 ml). The organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified by column chromatography (silica gel) using a mixture of hexane–toluene, 4:1, as the eluent. A chromatographic fraction corresponding to $R_f = 0.4$ on TLC (SiO_2, hexane–toluene, 4:1, as the eluent) was isolated to afford 2-diphenylaminofluorene (5.6 g, 84%); FT-IR (KBr) ν_{max} 3062 (m), 2920 (w), 2850 (w), 1600 (w), 1466 (m), 1447 (s), 1408 (m), 1294 (w), 1175 (w), 1064 (w), 822 (w), 763 (vs), and 728 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 7.67 (t, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 7.0$ Hz, 1H), 7.37–6.96 (m, 14H), and 3.79 (s, 2H).

2.4 Synthesis of 9,9-diethyl-2-diphenylaminofluorene 3b

In a round-bottom flask, a mixture of 2-diphenylaminofluorene **2** (2.5 g, 7.5 mmol), potassium *t*-butoxide (2.0 g, 18 mmol) in dry THF (100 ml) at 0°C was added ethyl iodide (1.3 ml, 16 mmol) over 10 min. The mixture was warmed to ambient temperature under nitrogen atmosphere, and stirred 4.0 more hours. The reaction mixture was washed with brine (40 ml) and water (40 ml). The organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified by column chromatography (silica gel, hexane–EtOAc, 4:1) to give 9,9-diethyl-2-diphenylaminofluorene **3b** (2.6 g, 89%). The product showed as a chromatographic fraction corresponding to $R_f = 0.5$ on TLC (SiO_2, hexane–EtOAc, 4:1, as the eluent); FT-IR (KBr) ν_{max} 3058 (m), 3030 (m), 2956 (s), 2923 (s), 2868

(m), 1584 (vs), 1485 (vs), 1326 (s), 1300 (s), 1268 (s), 751 (s), 733 (s), 698 (s), 694 (s), and 512 (m) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 7.64–7.57 (m, 2H), 7.33–7.23 (m, 7H), 7.15–7.12 (m, 5H), 7.06–6.99 (m, 3H), 1.99–1.87 (m, 4H), and 0.36 (t, $J = 7.3$ Hz, 6H)

2.5 Synthesis of 9,9-di(n-butyl)-2-diphenylaminofluorene 3c

In a round-bottom flask, a mixture of 2-diphenylaminofluorene **2** (0.5 g, 1.5 mmol), potassium *t*-butoxide (0.4 g, 3.36 mmol) in dry THF (40 ml) at 0°C was added *n*-butane iodide (0.36 ml, 3.15 mmol) over 10 min. The mixture was warmed to ambient temperature under nitrogen atmosphere and stirred 4.0 more hours. The reaction mixture was washed with brine (20 ml) and water (20 ml). Organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified by column chromatography (silica gel, hexane–toluene, 4:1) to afford 9,9-di(*n*-butyl)-2-diphenylaminofluorene (0.62 g, 93%). Its chromatographic fraction is corresponding to $R_f = 0.5$ on TLC (SiO_2, hexane–toluene, 4:1, as the eluent); FT-IR (KBr) ν_{max} 3057 (w), 3032 (w), 2960 (w), 2924 (m), 2851 (m), 1718 (s), 1609 (m), 1596 (m), 1483 (s), 1444 (s), 1411 (m), 1186 (m), 1110 (w), 790 (m), and 735 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 7.58–7.54 (m, 2H), 7.30–7.00 (m, 15H), 1.91–1.81 (m, 4H), 1.13–1.01 (m, 4H), and 0.72–0.55 (m, 10H).

2.6 Synthesis of 9,9-di(n-decyl)-2-diphenylaminofluorene 3d

In a round-bottom flask, a mixture of 2-diphenylaminofluorene **2** (0.5 g, 1.5 mmol), potassium *t*-butoxide (0.4 g, 3.36 mmol) in dry THF (40 ml) at 0°C was added iodo(*n*-decane) (0.64 ml, 3.00 mmol) over 10 min. The mixture was warmed to ambient temperature under nitrogen atmosphere and stirred 4 more hours. The reaction mixture was washed with brine (20 ml) and water (20 ml). The organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified by column chromatography (silica gel, hexane-toluene, 4:1) to give 9,9-di(*n*-decyl)-2-diphenylaminofluorene **3d** (0.91 g, 99%) showing a chromatographic fraction corresponding to $R_f = 0.6$ on TLC (SiO_2, hexane-toluene, 4:1, as the eluent); FT-IR (KBr) $\bullet_{max}$ 3061 (w), 2920 (m), 2850 (w), 1719 (vs), 1607 (m), 1595 (m), 1443 (m), 1188 (m), 1052 (w), 820 (s), 759 (s), and 735 (s) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 7.62–7.54 (m, 2H), 7.53–6.84 (m, 15H), 1.87–1.81 (m, 4H), 1.20–0.82 (br, 34H), and 0.74–0.55 (br, 4H).

2.7 Synthesis of 7-α-bromoacetyl-2-diphenylaminofluorene 4a

To a suspension of aluminum chloride (0.375 g, 2.80 mmol) in 1,2-dichloroethane (20 ml) at 0°C was added a solution of 2-diphenylaminofluorene **2** (0.43 g, 1.3 mmol) in 1,2 -dichloroethane (10 ml). The mixture was added α-bromoacetyl bromide (0.14 ml, 1.6 mmol) over a period of 10 min. At the end of the addition, the mixture was warmed to ambient temperature and stirred for another 60 h. The solution was diluted by a slow addition of water (50 ml) while maintaining the temperature of reaction mixture below 45°C. Organic layer was washed subsequently with dilute hydrochloric acid (1.0 N, 50 ml), water (2 × 50 ml), dried over magnesium sulfate, and concentrated *in vacuo.* The crude products were purified by column chromatography (silica gel, hexane–EtOAc, 9:1) to afford 7-α-bromoacetyl-2-diphenylaminofluorene **4a** (0.3 g, 51%) with its chromatographic spot corresponding to $R_f = 0.6$ on TLC (SiO_2, hexane–EtOAc, 9:1, as the eluent); FT-IR (KBr) ν_{max} 3017 (w), 2954 (w), 2923 (s), 2850 (m), 1675 (w), 1596 (m), 1491 (m), 1468 (m), 1282 (m), 1215 (s), 1177 (w), 819 (w), 757 (vs), 698 (w), and 668 (m) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.11 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.32–6.74 (m, 12H), and 7.06–7.04 (m, 2H).

2.8 Synthesis of 7-α-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene 4b

To a suspension of aluminum chloride (0.375 g, 2.80 mmol) in 1,2-dichloroethane (20 ml) at 0°C was added a solution of 9,9-diethyl-2-diphenylaminofluorene **3b** (0.5 g, 1.3 mmol) in 1,2-dichloroethane (10 ml). The mixture was added α-bromoacetyl bromide (0.14 ml, 1.6 mmol) over a period of 10 min. At the end of the addition, the mixture was warmed to ambient temperature and stirred for another 10 h. The solution was diluted by a slow addition of water (50 ml) while maintaining the reaction mixture temperature below 45°C. The resulting organic layer was washed subsequently with dilute hydrochloric acid (1.0 N, 50 ml), water (2 × 50 ml), dried over magnesium sulfate, and concentrated *in vacuo.* The crude products were purified by column chromatography (silica gel, hexane–EtOAc, 4:1) to afford 7-α-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **4b** (0.49 g, 74%). Its chromatographic band corresponds to $R_f = 0.6$ on TLC (SiO_2, hexane–EtOAc, 4:1, as the eluent); FT-IR (KBr) ν_{max} 3037 (w), 2966 (s), 2928 (w), 2878 (w), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 7.95 (dd, $J = 8$ Hz, $J = 1.6$ Hz, 2H), 7.92 (d, $J = 1.6$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.28–7.09 (m, 10H), 7.05–7.02 (m, 2H), 4.49 (s, 2H), 2.05–1.84 (m, 4H), and 0.35 (t, $J = 7.3$ Hz, 6H).

2.9 Synthesis of 7-α-bromoacetyl-9,9-di(n-butyl)-2-diphenylaminofluorene 4c

To a suspension of aluminum chloride (0.375 g, 2.80 mmol) in 1,2-dichloroethane (20 ml) at 0°C was added a solution of 9,9-di(*n*-butyl)-2-diphenylaminofluorene **3c** (0.58 g,

1.3 mmol) in 1,2-dichloroethane (10 ml) with a subsequent addition of α-bromoacetyl bromide (0.14 ml, 1.6 mmol) over a period of 10 min. At the end of the addition, the mixture was warmed to ambient temperature and stirred for another 48 h. The solution was diluted by a slow addition of water (50 ml) while maintaining the reaction mixture temperature below 45°C. The resulting organic layer was washed sequentially with dilute hydrochloric acid (1.0 N, 50 ml), water (2 × 50 ml), dried over magnesium sulfate, and concentrated *in vacuo*. The crude products were purified by column chromatography (silica gel, hexane–EtOAc, 3:2) to afford 7-α-bromoacetyl-9,9-di(*n*-butyl)-2-diphenylaminofluorene **4c** (0.65 g, 88%) with its chromatographic band corresponding to $R_f = 0.8$ on TLC (SiO_2, hexane–EtOAc, 3:2, as the eluent); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.02–7.97 (m, 2H), 6.99 (d, $J = 8.03$ Hz, 1H), 6.48 (d, $J = 8.28$ Hz, 1H), 7.36–7.05 (m, 12H), 4.56 (s, 2H), 1.91–1.60 (m, 4H), 1.13–1.01 (m, 4H), and 0.72–0.55 (m, 10H).

2.10 Synthesis of 7-α-bromoacetyl-9,9-di(n-decyl)-2-diphenylaminofluorene 4d

To a suspension of aluminum chloride (0.375 g, 2.80 mmol) in 1,2-dichloroethane (20 ml) at 0°C was added a solution of 9,9-di(*n*-decyl)-2-diphenylaminofluorene **3d** (0.90 g, 1.47 mmol) in 1,2-dichloroethane (10 ml) with a subsequent addition of α-bromoacetyl bromide (0.14 ml, 1.6 mmol) over a period of 10 min. At the end of the addition, the mixture was warmed to ambient temperature and stirred for another 48 h. The solution was diluted by a slow addition of water (50 ml) while maintaining the reaction mixture temperature below 45°C. The organic layer was washed subsequently with dilute hydrochloric acid (1.0 N, 50 ml), water (2 × 50 ml), dried over magnesium sulfate, and concentrated *in vacuo*. The crude products were purified by column chromatography (silica gel, hexane–toluene, 3:2) to afford 7-α-bromoacetyl-9,9-di(*n*-decyl)-2-diphenylaminofluorene **4d** (1.06 g, 97%) with its chromatographic band corresponding to $R_f = 0.8$ on TLC (SiO_2, hexane–toluene, 4:1 as the eluent); FT-IR (KBr) ν_{max} 3062 (w), 3034 (w), 2953 (w), 2924 (m), 2852 (m), 1675 (w), 1595 (m), 1492 (m), 1466 (w), 1279 (m), 820 (w), 752 (w), and 692 (m) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 7.98–7.92 (m, 2H), 7.65 (d, $J = 8.10$ Hz, 1H), 7.60 (d, $J = 8.28$ Hz, 1H), 7.31–7.00 (m, 12H), 4.51 (s, 2H), 1.98–1.86 (m, 4H), 1.20–1.05 (br, 34H), and 0.89–0.82 (br, 4H).

2.11 Synthesis of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-2-diphenylaminofluorene 5a

To a mixture of C_{60} (0.266 g, 0.37 mmol) and 7-α-bromoacetyl-2-diphenylaminofluorene **4a** (0.15 g, 0.33 mmol) in dry toluene (300 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.05 ml, 0.33 mmol) under nitrogen atmosphere. After stirring at room temperature for a period of 5.0 h under nitrogen, the reaction mixture was concentrated to a volume of approximately 15 ml. Crude products were precipitated by the addition of methanol and isolated by centrifugation. It was further purified by column chromatography (silica gel, hexane–toluene, 3:2) to afford 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-2-diphenylaminofluorene **5a** (0.084 g, 23%) with its chromatographic band corresponding to $R_f = 0.4$ on TLC (SiO_2, hexane–toluene, 3:2); MALDI–MS (TOF) calcd. for $^{12}C_{87}{}^{1}H_{19}{}^{14}N_1{}^{16}O_1$ m/z 1093; found, m/z 1093 (M^+); FT-IR (KBr) ν_{max} 2950 (m), 2920 (s), 2851 (m), 1675 (m), 1593 (s), 1508 (m), 1489 (w), 1458 (s), 1261 (m), 1070 (m), 1027 (m), and 801 (m) cm^{-1}; UV-vis (THF, 2.0×10^{-5} M) λ_{max} (ε) 254 (1.9×10^5), 323 (4.7×10^4), and 391 (3.9×10^4 L/mol-cm) nm; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 8.60–8.55 (m, 2H), 7.95 (d, $J = 8.78$ Hz, 1H), 7.80 (d, $J = 8.28$ Hz, 1H), 7.39–7.09 (m, 12H), 5.76 (s, 1H), and 4.03 (s, 2H).

2.12 Synthesis of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene 5b

To a mixture of C_{60} (0.72 g, 1.0 mmol) and 7-α-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **4b** (0.49 g, 0.96 mmol)) in dry toluene (500 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.13 ml, 0.96 mmol) under an atmospheric pressure of nitrogen. After stirring at room temperature for a period of 5.0 h, the reaction mixture was concentrated to a volume of approximately 20 ml. Crude products were precipitated by the addition of methanol and subsequently isolated by centrifugation. It was further purified by column chromatography (silica gel, hexane–toluene, 3:2) to afford 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene **5b** (0.77 g, 67%) with its chromatographic band corresponding to $R_f = 0.4$ on TLC (SiO_2, hexane–toluene, 3:2, as the eluent); MALDI–MS (TOF) calcd. for $^{12}C_{91}{}^{1}H_{27}{}^{14}N_1{}^{16}O_1$ m/z 1149; found, m/z 1149 (M^+); FT-IR (KBr) ν_{max} 3029 (w), 2963 (s), 2921 (m), 2853 (w), 1677 (s), 1591 (vs), 1492 (s), 1276 (s), 1276 (s), 750 (s), 695 (s), and 524 (m) cm^{-1}; UV-vis (THF, 2.0×10^{-5} M) λ_{max} (ε) 253 (1.3×10^5), 323 (2.3×10^4), and 395 (1.9×10^4 L/mol-cm) nm; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.5 (dd, $J = 7.8$ Hz, $J = 1.25$ Hz, 1H), 8.3 (s, 1H), 7.85 (d, $J = 8$ Hz, 1H), 7.68 (d, $J = 8$ Hz, 1H), 7.34–7.03 (m, 12H), 5.71 (s, 1H), 2.20–1.87 (m, 4H), and 0.42 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 189.6, 153.0, 149.1, 148.2, 147.9, 147.6, 146.9, 145.6, 145.4, 145.3, 145.1, 145.3, 145.1, 145.0, 144.9, 144.6, 144.3, 143.9, 143.7, 143.3, 143.1, 143.0, 142.9, 142.8, 142.5, 142.2, 142.1, 140.9, 139.7, 136.6, 134.2, 133.5, 129.3, 129.0, 124.5, 123.2, 122.8, 121.8, 119.2, 118.1, 72.7, 56.4, 44.4, and 8.7.

2.13 Synthesis of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(n-butyl)-2-diphenylaminofluorene 5c

To a mixture of C_{60} (0.74 g, 1.05 mmol) and 7-α-bromoacetyl-9,9-di(*n*-butyl)-2-diphenylaminofluorene **4c** (0.6 g, 1.05 mmol)) in dry toluene (500 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.15 g, 1.05 mmol) under nitrogen atmosphere. After stirring at room temperature for a period of 5.0 h, the reaction mixture was concentrated to a volume of approximately 20 ml. Crude products were precipitated by the addition of methanol and isolated by centrifugation. It was further purified by column chromatography (silica gel, toluene–EtOAc, 9:1) to afford greenish brown solids of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(*n*-butyl)-2-diphenylaminofluorene **5c** (0.66 g, 52%); MALDI–MS (TOF) calcd for $^{12}C_{95}$ $^{1}H_{35}$ $^{14}N_1$ $^{16}O_1$ m/z 1205; found, m/z 1205 (M^+); FT-IR (KBr) ν_{max} 3059 (w), 3034 (w), 2953 (m), 2922 (vs), 2852 (s), 1724 (m), 1592 (s), 1491 (s), 1489 (w), 1275 (m), 1197 (w), 1104 (w), 1027 (w), 906 (m), 752 (w), 731 (m), and 696 (m) cm^{-1}; UV-vis (THF, 2.0×10^{-5} M) λ_{max} (ε) 254 (1.5×10^5), 323 (3.3×10^4), and 396 (2.7×10^4 L/mol-cm) nm; ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.52 (d, $J = 8.3$ Hz, 1H), 8.41 (s, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8$ Hz, 1H), 7.41–7.11 (m, 12H), 5.77 (s, 1H), 2.11–1.89 (m, 4H), 1.20–1.05 (m, 4H), and 0.79–0.71 (m, 10H); ^{13}C-NMR (500 MHz, $CDCl_3$, ppm) δ 189.0, 154.2, 151.9, 148.6, 148.0, 147.4, 146.0, 145.8, 145.7, 145.6, 145.5, 145.4, 145.1, 145.1, 145.0, 144.7, 144.4, 144.1, 143.7, 143.4, 143.4, 143.2, 142.9, 142.7, 142.6, 142.5, 141.6, 141.4, 140.0, 137.1, 134.3, 129.7, 129.3, 124.9, 123.7, 123.5, 123.2, 122.2, 119.7, 118.5, 77.7, 77.4, 77.3, 77.2, 73.1, 55.7, 45.0, 40.3, 26.5, 23.4, and 14.3.

2.14 Synthesis of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(n-decyl)-2-diphenylaminofluorene 5d

To a mixture of C_{60} (0.6 g, 0.82 mmol) and 7-α-bromoacetyl-9,9-di(*n*-decyl)-2-diphenylaminofluorene **4d** (0.59 g, 0.804 mmol) in dry toluene (500 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.11 ml, 0.80 mmol) under nitrogen atmosphere. After stirring at room temperature for a period of 5.0 h under nitrogen, the reaction mixture was concentrated to a volume of approximately 20 ml. At the end of the reaction, crude products were precipitated by addition of methanol with the solids isolated by centrifugation. It were purified by column chromatography (silica gel, hexane–toluene, 3:2) to afford 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(*n*-decyl)-2-diphenylaminofluorene **5d** (0.64 g, 58%) with its chromatographic band corresponding to $R_f = 0.5$ on TLC (SiO_2, hexane–toluene, 3 : 2, as the eluent); MALDI–MS (TOF) calcd. for $^{12}C_{107}$ $^{1}H_{59}$ $^{14}N_1$ $^{16}O_1$ m/z 1373; found, m/z 1373 (M^+); FT-IR (KBr) ν_{max} 2956 (s), 2922 (s), 2852 (s), 1727 (w), 1676 (w), 1593 (s), 1491 (m), 1463 (s), 1275 (m), 1201 (w), 1186 (w), 1070 (m), 1035 (w), 923 (m), 753 (w), and 696 (m) cm^{-1}; UV-vis (THF, 2.0×10^{-5} M) λ_{max} (ε) 250 (1.0×10^5), 323 (1.2×10^4), and 399 (8.9×10^3 L/mol-cm) nm; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.50 (d, $J = 8.0$ Hz, 1H), 8.42 (s, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.37–7.07 (m, 12H), 5.76 (d, 1H), 2.02–2.90 (m, 4H), 1.35–1.07 (m, 32H), and 0.90–0.71 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 189.8, 164.0, 148.6, 148.0, 147.4, 146.0, 145.8, 145.6, 145.1, 145.1, 145.0, 144.3, 144.3, 143.7, 143.5, 143.4, 143.4, 143.2, 142.9, 142.7, 142.5, 141.7, 141.2, 139.9, 137.1, 136.4, 135.2, 129.7, 126.3, 124.9, 123.6, 122.2, 116.6, 77.9, 77.8, 77.5, 77.4, 77.1, 73.1, 55.8, 45.1, 40.7, 32.3, 30.6, 30.2, 30.1, 29.8, 29.7, 24.6, 23.5, 23.2, and 14.5.

3 Results and Discussion

In the recent synthesis of C_{60}(>DPAF-C_n) analogous chromophore conjugates, the key intermediate precursor 7-α-bromoacetyl-9,9-dialkyl-2-diphenylaminofluorene **4** was prepared by a three-step reaction involving dialkylation of commercially available 2-bromofluorene **1** at C_9 position of the fluorene ring followed by diphenylamination of the resulting product 2-bromo-9,9-dialkylfluorenes, leading to the precursor compound 9,9-dialkyl-2-diphenylaminofluorene **3**. In this synthetic route, it can be modified by performing the diphenylamination reaction of **1** first followed by the second step of dialkylation reaction on the resulting product 2-diphenylaminofluorene **2**. By the use of the latter procedure, a new unalkylated 7-α-bromoacetyl-2-diphenylaminofluorene intermediate **4a** becomes available for the synthesis of a novel C_{60}-DPAF conjugate as 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-2-diphenylaminofluorene **5a,** having the most least hindrance on the fluorene ring. The compound **5a** may facilitate intermolecular aggregation by π-interactions among planar fluorene moieties. As the intermolecular aggregation of C_{60}-*keto*-DPAF-C_n nanostructures was suggested to present a problematic issue in the effort of multiphoton absorption cross-section enhancement of this type of materials, compound **5a** may serve as reference material for examination of the hypothesis. Accordingly, in the alternative synthesis of the key intermediate **4**, the starting 2-bromofluorene was allowed to react with diphenylamine in the presence of sodium *t*-butoxide, *tris*(dibenzylideneacetone)dipalladium(0) catalyst, and *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand in toluene at refluxing temperatures for a period of 40 h under an atmospheric pressure of nitrogen. The resulting amination product 2-diphenylaminofluorene **2** was isolated as a white amorphous solid in 84% yield after column chromatographic purification.

Dialkylation of **2** was carried out with either ethyl iodide, *n*-butyl iodide, or *n*-decyl iodide in toluene in the presence of potassium *t*-butoxide in dry THF (40 ml) at 0°C to

ambient temperature for a period of 4.0 h. The resulting corresponding products, 9,9-diethyl-2-diphenylaminofluorene **3b**, 9,9-di(*n*-butyl)-2-diphenylaminofluorene **3c**, or 9,9-di(*n*-decyl)-2-diphenylaminofluorene **3d** were obtained in 89%, 93%, or 99%, respectively. Purification of **3b**−**3d** was carried out by column chromatography (silica gel, hexane-toluene, 4:1) with a chromatographic band corresponding to $R_f = 0.5$–0.6 on thin-layer chromatography (TLC, SiO_2, hexane-toluene, 4:1, as the eluent). Subsequent Friedel-Crafts acylation of **2** and **3b**–**3d** at C_7 position of diphenylaminofluorene moiety was achieved with α-bromoacetyl bromide and a suspension of aluminum chloride (1.8–2.0 equiv.) in 1,2-dichloroethane at 0°C to ambient temperature for a period of 60 h to afford the corresponding 7-α-bromoacetyl-2-diphenylaminofluorene **4a**, 7-α-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **4b**, 7-α-bromoacetyl-9,9-di(*n*-butyl)-2-diphenylaminofluorene **4c**, and 7-α-bromoacetyl-9,9-di(*n*-decyl)-2-diphenylaminofluorene **4d** in 51, 74, 88, and 97% yield, respectively, after column chromatography with their chromatographic band corresponding to $R_f = 0.6$ for **4a** (TLC, SiO_2, hexane-EtOAc, 9:1, as the eluent), 0.6 for **4b** (TLC, SiO_2, hexane-EtOAc, 4:1, as the eluent), 0.8 for **4c** (TLC, SiO_2, hexane-EtOAc, 3:2, as the eluent), and 0.8 for **4d** (TLC, SiO_2, hexane-toluene, 4 : 1 as the eluent).

Attachment of a substituted DPAF-H or DPAF-C_n unit to C_{60} leading to the formation of dyads **5a**–**5d** was accomplished by the treatment of α-bromoacetyl fluorene derivatives **4a**–**4d**, respectively, with C_{60} in toluene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv.) at ambient temperature for a period of 5.0 h. Proceedings of this reaction were monitored by TLC technique for the indication of monoaddition vs bisaddition in the reaction mechanism. As a result, formation of fullerenyl bisadducts persists even with only one equivalent of α-bromoacetyl fluorene applied. Therefore, chromatographic separation of [6,6]-cyclopropanyl fullerene bisadducts from the main monoadduct product became necessary. This separation procedure was made by column chromatography (silica gel) using a solvent mixture of hexane–toluene in a ratio of 3:2 as the eluent with the isolation of its chromatographic band corresponding to $R_f = 0.4$ on a TLC plate under the same eluent conditions to afford the monoadduct 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-2-diphenylaminofluorene **5a** as C_{60}(>DPAF-H) in a yield of 23%. A similar sequence of workup procedures were performed for the isolation of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene ($R_f = 0.4$) as C_{60}(>DPAF-C_2) **5b**, 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(*n*-butyl)-2-diphenylaminofluorene as C_{60}(>DPAF-C_4) **5c**, and 7-(1,2-dihydro-1,2-methano[60]-fullerene-61-carbonyl)-9,9-di(*n*-decyl)-2-diphenylaminofluorene ($R_f = 0.5$) as C_{60}(>DPAF-C_{10}) **5d** in a yield of 67, 52, and 58%, respectively.

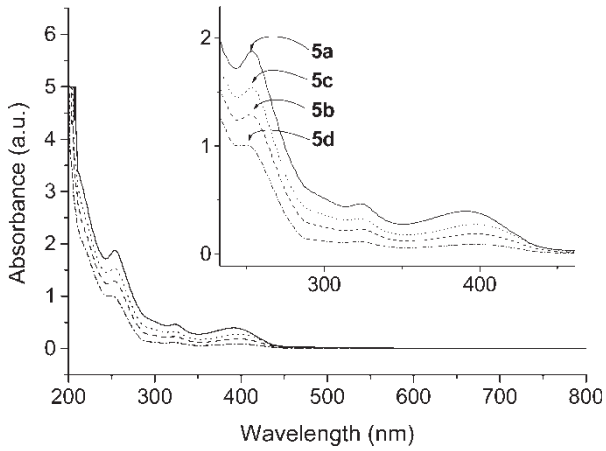


Fig. 1. UV-Vis spectra C_{60}(>DPAF-H) 5a, C_{60}(>DPAF-C_2) 5b, C_{60}(>DPAF-C_4) 5c and C_{60}(>DPAF-C_{10}) 5d in THF at a concentration of 2.0×10^{-5} μ.

Structural characterization of the dyads C_{60}(>DPAF-H), C_{60}(>DPAF-C_2), C_{60}(>DPAF-C_4), and C_{60}(>DPAF-C_{10}) was made via various spectroscopic methods. Evidence of the attachment of a DPAF-C_n moiety on the methano[60]fullerene cage by a ketone bridging group was observed in the infrared spectra of **5a**–**5d** as all of them showing a strong optical absorption band of carbonyl stretching centered at 1675–1680 cm^{-1}. This absorption band in a roughly 50 cm^{-1} shift from the normal carbonyl stretching band at 1720–1750 cm^{-1} was reasoned by the influence of fluorene ring structure. Optical absorption of C_{60}(>DPAF-H) **5a** in THF gave three major bands at 254 ($\varepsilon = 1.9 \times 10^5$), 323 ($\varepsilon = 4.7 \times 10^4$), and 391 nm ($\varepsilon = 3.9 \times 10^4$ L/mol-cm), whereas C_{60}(>DPAF-C_2), C_{60}(>DPAF-C_4), and C_{60}(>DPAF-C_{10}) displayed similar three absorption bands at 253 (1.3×10^5), 323 (2.3×10^4), and 395 (1.9×10^4 L/mol-cm) nm for **5b**, at 254 ($\varepsilon = 1.5 \times 10^5$), 323 ($\varepsilon = 3.3 \times 10^4$), and 396 ($\varepsilon = 2.7 \times 10^4$ L/mol-cm) nm for **5c**, and at 250 ($\varepsilon = 1.0 \times 10^5$), 323 ($\varepsilon = 1.2 \times 10^4$), and 399 ($\varepsilon = 8.9 \times 10^3$ L/mol-cm) nm for **5d**, respectively, in their UV-vis spectra, as shown in Figure 1. The former two bands match approximately with those of the parent fullerene moiety (C_{60}>). The latter band fits well with the previously reported main optical absorption of 7-α-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (α-BrDPAF-C_2) centered at 299 ($\varepsilon = 2.4 \times 10^4$) and 406 ($\varepsilon = 2.7 \times 10^4$ L/mol-cm) nm, attributed to diphenylaminofluorene moiety (8). Nearly absorptive superimposition of the combined spectra of two independent chromophores containing either the fullerene cage or diphenylaminofluorene revealed no ground-state interaction between these two moieties present in the molecule of **5a**–**5d**.

Assignment of all proton peaks in ^{1}H-NMR spectra of the dyads C_{60}(>DPAF-H), C_{60}(>DPAF-C_4), and C_{60}(>DPAF-C_{10}) was made by using the previously reported chemical shifts for the protons of C_{60}(>DPAF-C_2) as the reference (8). Accordingly, the α-proton (H_α next to the carbonyl group) peaks of **5a** (Figure 2a), **5c** (Figure 2c), and **5d** (Figure 2d) appeared as a singlet at δ 5.76, a triplet at δ

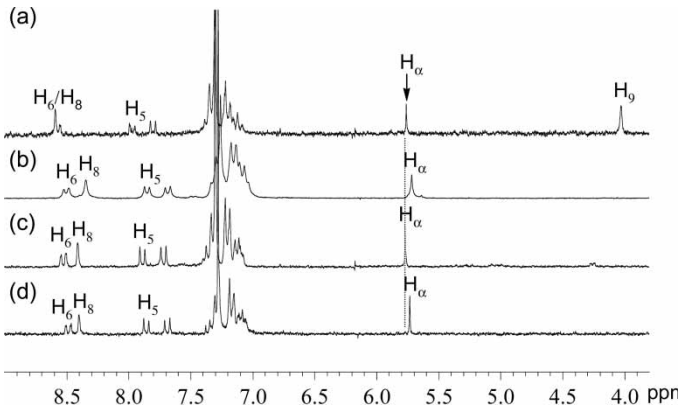


Fig. 2. ^{1}H-NMR spectra of (a) C_{60}(>DPAF-H) **5a**, (b) C_{60}(>DPAF-C_2) **5b**, (c) C_{60}(>DPAF-C_4) **5c**, (d) C_{60}(>DPAF-C_{10}) **5d**.

5.77, and a doublet at δ 5.76, respectively, with a large downfield shift of roughly 1.25 ppm from that of **4a**–**4d** (δ 4.49–4.56). It was also accompanied with a downfield shift of the chemical shift of all phenyl protons at C_5, C_6, and C_8 of the fluorene moiety to δ 7.95 (H_5, d, $J = 8.78$ Hz, 1H) and δ 8.60–8.55 (H_6/H_8, m, 2H) for **5a**, to δ 7.88 (H_5, d, $J = 8.0$ Hz, 1H), 8.52 (H_6, d, $J = 8.3$ Hz, 1H), and 8.41 (H_8, s, 1H) for **5c**, and to δ 7.88 (H_5, d, $J = 8.0$ Hz, 1H), 8.50 (H_6, d, $J = 8.0$ Hz, 1H), and 8.42 (H_8, s, 1H) for **5d**, as shown in Figures 2a–2d.

Molecular ion mass of the dyad C_{60}(>DPAF-H) **5a** was clearly detected in positive ion matrix-assisted laser desorption ionization mass spectrum (MALDI−MS), using α-cyano-4-hydroxycinnamic acid as the matrix, displaying a

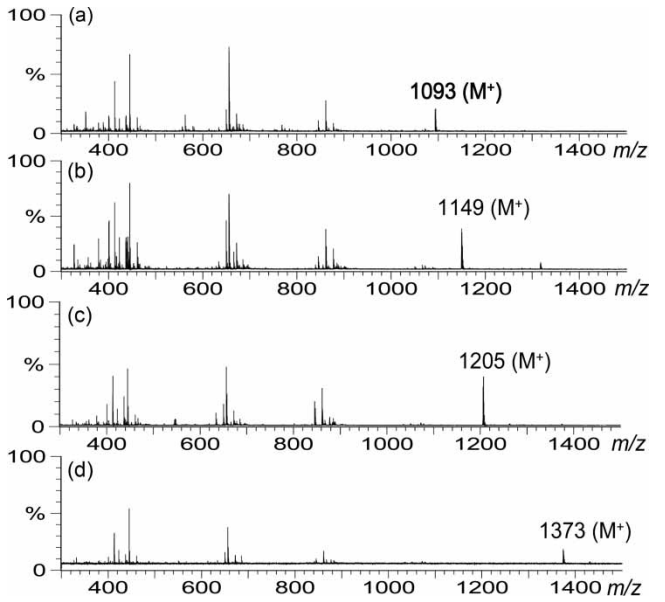


Fig. 3. MALDI–TOF mass spectrum of (a) C_{60}(>DPAF-H) **5a**, (b) C_{60}(>DPAF-C_2) **5b**, (c) C_{60}(>DPAF-C_4) **5c**, and (d) C_{60}(>DPAF-C_{10}) **5d**, showing the corresponding molecular ion mass at m/z 1093, 1149, 1205, and 1373, respectively.

group of sharp mass peaks with maximum peak intensity centered at m/z 1093, as shown in Figure 3a. It was followed by several groups of mass ion peaks with a maximum peak intensity centered at m/z 842, 860, and 656. The former two mass ions were suggested to be related to fragmentation of the fluorene moiety at the central pentagon with the mass corresponded to the loss of one diphenyl-dialkylbenzene subunit from the molecular mass of **5a**–**5d**. In the low mass ion region, several mass ion peaks centered at m/z 350–356 corresponding to the mass of protonated CH_3-DPAF-H (m/z 347) and C_2-DPAF-H (m/z 356) fragments were observed revealing facile fragmentation at the bonds immediately next to the C_{60} cage for **5a**. In the case of C_{60}(>DPAF-C_4) and C_{60}(>DPAF-C_{10}), the spectra displayed a similar fragmentation pattern showing several groups of fragmented mass ion peaks with a maximum peak intensity centered at m/z 842, 860, 658, 444, and 412. The latter two groups of peaks were related to the mass of partial dealkylated diphenylfluorene moieties. The relatively simple spectrum in the high mass region revealed good stability of aromatic *keto*-diphenylaminofluorene moiety under MALDI–MS measurement conditions. In summary, detected molecular ion mass peaks provided clear evidence of the composition mass of fullerene-DPAF-H dyad **5a** and fullerene-DPAF-C_n dyad **5b**−**5d**.

4 Conclusions

An alternative synthetic route for the preparation of key intermediate synthons 7-α-bromoacetyl-2-diphenylaminofluorene (α-BrDPAF-H) and 7-α-bromoacetyl-9,9-dialkyl-2-diphenylaminofluorene (α-BrDPAF-C_n) was demonstrated. The latter reactions involved the first step of dialkylation of 2-bromofluorene at C_9 position of the fluorene moiety, the second step of a diphenylamino group attachment at C_2 position of the resulting dialkylfluorene, and the third step of the Friedel-Craft acylation of α-bromoacetyl group at C_7 position of dialkylated diphenylaminofluorene. From the intermediates α-BrDPAF-H and α-BrDPAF-C_n, a series of C_{60}-*keto*-DPAF nanostructures, such as the fullerene monoadducts C_{60}(>DPAF-H) and C_{60}(>DPAF-C_n), where n is 2, 4, or 10, were synthesized in a reasonable yield. Molecular mass ions of the dyads C_{60}(>DPAF-H), C_{60}(>DPAF-C_2), C_{60}(>DPAF-C_4), and C_{60}(>DPAF-C_{10}) were clearly detected in positive ion matrix-assisted laser desorption ionization mass spectrum (MALDI–MS) that confirmed the composition mass of each compound synthesized. These derivatives are potential simultaneous two-photon absorptive chromophores for nonlinear photonic applications, including optical limiting effect and 2PA-based photodynamic cytotoxicity effect.

5 Acknowledgements

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