

# Synthesis and characterization of photoresponsive diphenylaminofluorene chromophore adducts of [60]fullerene†

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A class of acceptor–*keto*–donor structures as hindered 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluoreno-methano[60]fullerene  $C_{60}(>>DPAF-C_9)$  and the related bisadducts  $C_{60}(>>DPAF-C_9)_2$  and  $C_{60}(>>DPAF-C_2)_2$  were synthesized. They are derivatives of multiphoton absorptive  $C_{60}(>>DPAF-C_2)$  showing enhanced cross-sections of simultaneous two-photon absorption under laser excitation at 800 nm in nanosecond region. Molecular synthesis of these  $C_{60}$ –DPAF conjugates involved the covalent attachment of a diphenylaminofluorene moiety to methano[60]fullerene *via* a keto linkage for increasing molecular acceptor–donor polarization of the chromophore in conjunction with the fullerene cage. Preparation of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-dialkyl-2-diphenylaminofluorene  $C_{60}(>>DPAF-C_n)$  involved cyclopropanation of  $C_{60}$  with a key synthon 7- $\alpha$ -bromoacetyl-9,9-dialkyl-2-diphenylaminofluorene. Synthesis of this synthon was achieved by a three-steps procedure starting from 2-bromofluorene via dialkylation at  $C_9$  of the fluorene ring, attachment of a diphenylamino group at  $C_2$  of dialkylfluorene, and Friedel–Craft acylation of the  $\alpha$ -bromoacetyl group at  $C_7$  of diphenylaminofluorene. All  $C_{60}$ –DPAF derivatives were fully characterized with the chemical structures confirmed by various spectroscopic analyses and validated by the single-crystal structural analysis data of  $C_{60}(>>DPAF-C_2)$ . Strong solvent-sensitive fluorescence quenching phenomena of  $C_{60}(>>DPAF-C_2)$ ,  $C_{60}(>>DPAF-C_9)$ , and  $C_{60}(>>DPAF-C_9)_2$  were noticed, showing no fluorescence band above 700 nm in more polar solvents, such as DMF, PhCN, and THF, while in less polar solvents (toluene,  $CHCl_3$ , and  $CS_2$ ) a fullerenyl fluorescence band at 700–710 nm was observed. It was attributed to the occurrence of electron transfer *via* the singlet excited state of the fullerene moiety  $^1C_{60}^*(>>DPAF-C_n)$  in the former group of the solvents. On the contrary, energy transfer processes from DPAF- $C_n$  moiety to the fullerene cage are favored in the latter group of the solvents.

## Introduction

Molecular design of photoresponsive chromophores *via* covalent linkage of electron donors onto the  $C_{60}$  acceptor cage stimulates much interest in exploration of photosynthesis mimicking involving sequential intramolecular and intermolecular electron- or energy-transfer events.<sup>1</sup> A large number of the acceptor–donor (A–D) type  $C_{60}$ –D dyads<sup>2,3</sup> have been synthesized using  $C_{60}$  as the acceptor component for this purpose. Many photoinduced transient processes engage mainly one-photon excitation of the  $C_{60}$  cage and donor chromophore moieties followed by either electron- or energy-transfer between these A–D components at the excited state.<sup>1,4</sup> Occurrence of the photoinduced charge generation and

separation phenomena in the composite or nanospheres<sup>5</sup> of  $C_{60}$  dyads and in the ordered structures of bis- and tris-fullerenes,<sup>6</sup> such as elongated wires and entangled spheres, enhances their potential applications in the area of artificial photosynthetic materials,<sup>1</sup> molecular electronic devices,<sup>7</sup> and photovoltaic cells.<sup>8</sup> In the case of the energy-transfer processes taking place from the photoactivated donor moieties to the  $C_{60}$  cage resulting in generation of the triplet  $C_{60}$  excited state ( $^3C_{60}^*$ ) or its derivatives ( $^3C_{60}^*-D$ ), formation of singlet oxygen ( $^1O_2$ ) becomes possible via the triplet energy transfer from the  $^3C_{60}^*$  moiety to molecular oxygen. Examples of efficient singlet oxygen production in biological medium allowed investigation of its cytotoxicity in single-photon excitation based photodynamic therapeutic (PDT) treatment against the tumor and cancer cells *in vitro* and *in vivo* using hydrophilic molecular micelle-like  $C_{60}$  derivatives (FC<sub>4</sub>S) as photosensitizers.<sup>9</sup> High efficiency of singlet oxygen generation of FC<sub>4</sub>S was substantiated in its nanosphere structures.<sup>9c</sup> In several closely related *in vitro* studies, singlet oxygen and oxygenated radicals generated from hydrophilic fullerene derivatives or composites have been implicated in direct or indirect oxidative damage of biomolecules, including selective DNA cleavage,<sup>10</sup> membrane lipid peroxidation,<sup>11</sup> and virus inactivation.<sup>12</sup>

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Simultaneous two-photon absorption (2PA) excitation processes allow the photodynamic applications using a laser light source with the photon energy in the near-infrared range equivalent to nearly a half of HOMO–LUMO energy gap of the photosensitizer. Combination of 2PA and reverse saturable absorption (RSA) at the excited states of complex organic dyes with appreciably large cross-sections was proposed for the potential optical power limiting application of the materials.<sup>13</sup> To achieve multiphoton absorption (MPA)-based applications, enhancement of MPA cross-sections becomes a prerequisite. Observation of simultaneous two-photon excitation of a  $C_{60}$ -*keto*-donor dyad system was reported recently for 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene, denoted  $C_{60}(>>\text{DPAF-C}_2)$  dyad **1a**, synthesized by the attachment of 9,9-diethyl-2-diphenylaminofluorene (DPAF- $C_2$ ) donor subunit at the  $C_7$  carbon position on the  $C_{60}$  cage.<sup>3g</sup> The compound **1a** exhibits large effective molecular two-photon absorption (2PA) cross-sections  $\sigma_2' = 196 \times 10^{-48} \text{ cm}^4 \text{ s}$ . Two-photon excitation has also been demonstrated in the practice of photodynamic therapy-related biomedical investigation with the use of highly penetrating, nondamaging near infrared light in a spectral transparent window of 800–1100 nm in mammalian tissue.<sup>14</sup> The approach has potential to provide a means for improving localization of the PDT-related antibacteria therapy or obtain high-resolution, three-dimensional images of the tissue by depth-resolved contrast using two-photon fluorescence microscopy.<sup>15</sup>

Both  $C_{60}$  acceptor and DPAF donor are involved in simultaneous 2PA excitation processes. We found that an approach using the  $C_{60}$ -*keto*-D assembly structure to a composition of  $C_{60}(>>\text{DPAF-C}_n)$  gave significant improvement of 2PA cross-sections from that of DPAF derivative alone.<sup>3g,3h</sup> In this analog of compounds, the DPAF moiety is linked on methano[60]fullerene by a keto functional group with only one  $\text{sp}^3$  carbon between two conjugative chromophores. DPAF chromophores containing various electron donating and withdrawing substituents exhibit high fluorescent photo-emission quantum yield, two-photon absorptivity, and good resistance to thermal and photooxidative degradation.

Its close linkage to the fullerene cage by a short separation distance of only roughly 2 Å leads to observation of ultrafast photoresponse within 10 ps after a 150 fs laser pulse.<sup>16</sup> Subsequent intramolecular electron-transfer processes of  $C_{60}(>>\text{DPAF-C}_2)$  proceeded with a charge-separation quantum yield of 0.96 in PhCN and a long-lived charge separated states of 150 ns in this donor–acceptor assembly. In non-polar solvent, such as toluene, no charge-transfer states were revealed. Triplet state of the fullerene cage in  $^3C_{60}*(>>\text{DPAF-C}_2)$  was detected, instead, with the lifetime of 33  $\mu\text{s}$ .<sup>16</sup>

Combination of two-photon absorptivity and intramolecular electron- or energy-transfer phenomena of  $C_{60}$ -*keto*-DPAF assemblies may allow us to explore two-photon excitation based photonics. Evidently, the phenomenon of intramolecular two-photon energy transfer from the DPAF moiety to the  $C_{60}$  cage was detected upon the pulsed laser excitation at 800 nm that significantly decreases the DPAF-derived 2PA emission at 450 nm.<sup>3g</sup> Synthetically, the molecule

**1a** can be modified to include multiple two-photon active chromophore arms on a single  $C_{60}$  cage to afford a starburst structure for further enhancing 2PA cross-sections. The concept of multi-dimensional conjugation as an approach to improve cross-sections of 2PA molecules was proposed recently.<sup>17</sup> Our synthesis of monoadducts **1a** and  $C_{60}(>>\text{DPAF-C}_9)$  dyad **1b** was also accompanied with a minor yield of the corresponding bisadducts  $C_{60}(>>\text{DPAF-C}_2)_2$  **2a** and  $C_{60}(>>\text{DPAF-C}_9)_2$  **2b**. That allowed us to investigate this concept by using the  $C_{60}$  cage as a molecular core for attaching multiple chromophore donor moieties, acting as antenna components for light harvesting at visible wavelengths. Accordingly, we report the synthesis and structural characterization of the dyads  $C_{60}(>>\text{DPAF-C}_n)$  with the isolation of the first series of the triads  $C_{60}(>>\text{DPAF-C}_n)_2$ , containing two DPAF arms by the use of hindered alkyl side-chain to increase solubility of chromophore conjugates and minimize the molecular aggregation of DPAF moieties in solution.

## Materials and methods

### General

Pure  $C_{60}$  (99.5%) was purchased from NeoTech Product Company, Russia. Further purification of  $C_{60}$  was made by thin-layer chromatography (TLC,  $\text{SiO}_2$ , toluene). Reagents of 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. Toluene and benzene were dried and distilled over sodium.

### Physical measurements

Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and COSY spectra were recorded on either a Bruker Avance Spectrospin-400 or Bruker AC-300 spectrometer. HMQC spectra were recorded on Bruker-500 SB FT-NMR spectrometer. UV–vis spectra were recorded on a Hitachi U-3410 UV spectrometer. Fluorescence spectra were recorded on a FLUOROLOG (ISA Instruments) spectrofluorometer. Mass spectroscopic studies were performed by the use of either negative ion desorption chemical ionization (DCI<sup>−</sup>) technique with a direct probe on a JEOL JMS-SX 102A mass spectrometer or positive ion fast atom bombardment (FAB<sup>+</sup>) technique with a direct probe on a JEOL SX-102A mass spectrometer. X-Ray single crystal analysis on NONIUS KAPPA CCD diffractometer and elemental analyses of fullerene derivatives were carried out at National Taiwan University, Taiwan.

### Synthesis of 2-bromo-9,9-diethylfluorene (5a)

To a solution of 2-bromofluorene **4** (2.5 g, 10.2 mmol) in toluene (40 ml) was added tetra-*n*-butylammonium bromide (1.83 g, 5.7 mmol) as a phase transfer agent. A freshly prepared solution of aqueous sodium hydroxide (25 ml, 50% w/w) was added in one portion to the solution. The mixture turned orange and became viscous. To this bilayer solution was added iodoethane (2.4 ml, 30 mmol). The mixture was stirred at 60 °C

for overnight. The reaction mixture was then diluted with ethyl acetate (25 ml) and washed several times with water. The organic layer was dried over magnesium sulfate and the solution concentrated to give the crude product which was purified by column chromatography (silica gel, hexane as eluent). A chromatographic fraction corresponding to  $R_f = 0.8$  on thin-layer chromatography (TLC,  $\text{SiO}_2$ , hexane as eluent) was isolated to afford colorless oil of 2-bromo-9,9-diethylfluorene **5a** (2.5 g) in 81% yield. The compound **5a** gave crystalline white solids after standing. Spectroscopic data of **5a**: FAB<sup>+</sup>-MS calcd for  $^{12}\text{C}_{17}\text{H}_{17}^{79,9}\text{Br}_1$   $m/z$  301; found,  $m/z$  301; FT-IR (KBr)  $\nu_{\text{max}}$  3060 (w), 2964 (vs), 2919 (s), 2876 (s), 2852 (s), 1598 (w), 1570 (w), 1443 (vs), 1404 (s), 1378 (s), 1255 (m), 1132 (m), 1061 (m), 1004 (m), 876 (m), 823 (s), 781 (s), 767 (vs), 733 (vs), 569 (m), and 418 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.61–7.59 (m, 1H), 7.49–7.46 (m, 1H), 7.38–7.36 (m, 2H), 7.25–7.23 (m, 3H), 1.94–1.91 (m, 4H), and 0.24 (t,  $J = 8\text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  152.0, 149.2, 140.3, 140.16, 129.9, 127.3, 126.9, 126.0, 122.7, 120.9, 120.9, 119.6, 56.1, 32.5, and 8.3.

#### Synthesis of 2-bromo-9,9-di(3,5,5-trimethylhexyl)fluorene (**5b**)

To a solution of 2-bromofluorene **4** (4.0 g, 16.3 mmol) in dry tetrahydrofuran (150 ml) was added potassium *t*-butoxide (5.5 g, 49.0 mmol) resulting in orange suspension. The mixture was stirred at room temperature for a period of 20 min. The suspension was cooled below 10 °C and added a tetrahydrofuran solution of 3,5,5-trimethylhexyl mesylate (11.0 g, 49.0 mmol) dropwise over a period of 30 min. Gradual color change of the reaction mixture from deep red to deep purple was observed by stirring overnight. At the end of the reaction, it was quenched by addition of water and extracted with ethyl acetate, dried over sodium sulfate, and concentrated *in vacuo* to give the crude product which was purified by column chromatography (silica gel, hexane as eluent). A chromatographic fraction corresponding to  $R_f = 0.8$  on TLC ( $\text{SiO}_2$ , hexane as eluent) was isolated to afford 2-bromo-9,9-di(3,5,5-trimethylhexyl)fluorene **5b** (7.6 g) as colorless oil in a yield of 94%. Spectroscopic data of **5b**: FAB<sup>+</sup>-MS calcd for  $^{12}\text{C}_{31}\text{H}_{45}^{79,9}\text{Br}_1$   $m/z$  497; found,  $m/z$  496 and 498; FT-IR (KBr) similar to that of **5a**;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.65–7.62 (m, 1H), 7.55–7.51 (m, 1H), 7.46–7.41 (m, 2H), 7.35–7.27 (m, 3H), 2.1–1.8 (m, 4H), and 1.35–0.38 (m, 34H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  152.8, 150.2, 140.2, 140.1, 129.8, 127.5, 126.9, 126.1, 122.8, 121.0, 120.9, 119.7, 55.1, 50.7, 50.7, 37.7, 32.8, 32.7, 30.9, 29.9, 29.5, 29.4, 22.4, and 22.4.

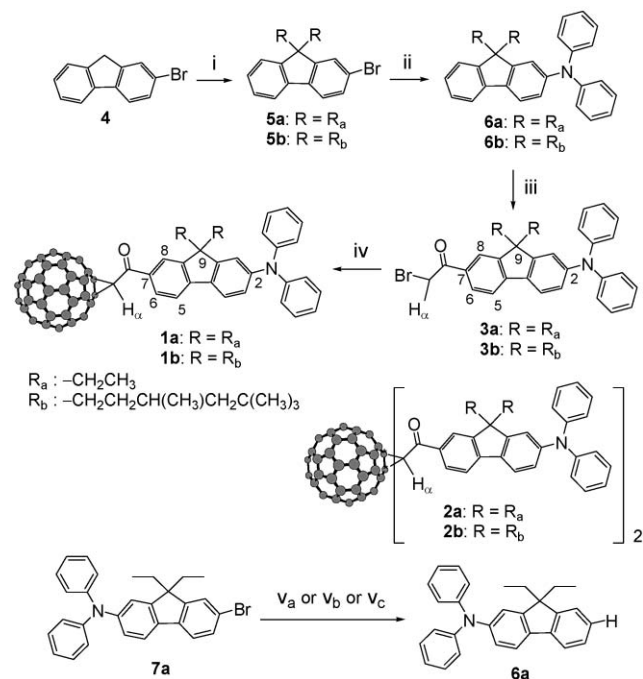
#### Synthesis of 9,9-diethyl-2-diphenylamino fluorene (**6a**)

A mixture of 2-bromo-9,9-diethylfluorene **5a** (2.44 g, 8.1 mmol), diphenylamine (1.43 g, 8.5 mmol), tris(dibenzylideneacetone)dipalladium(0) (18 mg, 0.25 mmol%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 37 mg, 0.75 mmol%), and sodium *t*-butoxide (1.08 g, 11.3 mmol) in dry toluene (100 ml) was heated to refluxing temperatures for a period of 8.0 to 10.0 h under nitrogen atmosphere. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (60 ml), and washed with brine (40 ml) and

water in sequence. The resulting organic layer was dried over sodium sulfate and concentrated *in vacuo* to give the crude product. It was purified by column chromatography (silica gel) using a mixture of hexane–toluene, 9 : 1, as eluent. A chromatographic fraction corresponding to  $R_f = 0.6$  on TLC ( $\text{SiO}_2$ , hexane–toluene, 4 : 1, as eluent) was isolated to afford 9,9-diethyl-2-diphenylamino fluorene **6a** as white amorphous low melting solids in a yield of 98% (3.1 g). Spectroscopic data of **6a**: FAB<sup>+</sup>-MS calcd for  $^{12}\text{C}_{29}\text{H}_{27}^{14}\text{N}_1$   $m/z$  389; found,  $m/z$  389; FT-IR (KBr)  $\nu_{\text{max}}$  3058 (m), 3030 (m), 2956 (s), 2923 (s), 2868 (m), 1584 (vs), 1485 (vs), 1448 (s), 1326 (s), 1300 (s), 1268 (s), 751 (s), 733 (s), 698 (s), 694 (m), and 512 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  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,  $J = 7.3\text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  151.2, 149.8, 148.0, 147.1, 141.2, 136.7, 129.1, 126.8, 126.3, 123.7, 123.7, 122.7, 122.4, 120.3, 119.4, 119.1, 56.0, 32.6, and 8.5.

#### Synthesis of 9,9-diethyl-2-diphenylamino fluorene (**6a**) via the step $v_c$ of Scheme 1

To a cooled solution of 7-bromo-2-diphenylamino-9,9-diethylfluorene **7a** (1.0 g, 2.1 mmol) in dry THF (20 ml) at  $-78\text{ }^\circ\text{C}$  under nitrogen atmospheric pressure was added *n*-BuLi in hexane (0.53 ml, 1.6 M, 8.5 mmol) over a period of 5 min. The reaction mixture was stirred for an additional period of 4.0 h while the bath temperature was raised slowly to  $-20\text{ }^\circ\text{C}$ . It was quenched with saturated ammonium chloride solution



**Scheme 1** Reagents and conditions: i. Et-I, NaOH, TBA-Br, toluene, 60 °C, 8.0 h; ii. diphenylamine, tris(dibenzylideneacetone)dipalladium(0) (cat.), *rac*-BINAP (cat.), *t*-BuONa, toluene, 110 °C, 8.0 h; iii. bromoacetyl bromide,  $\text{AlCl}_3$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , 0 °C to rt, 4.0 h; iv.  $\text{C}_{60}$ , DBU, toluene, rt, 5.0 h; v\_a, Mg,  $\alpha$ -bromoacetyl bromide, THF,  $\Delta$ ; v\_b, *n*-butyllithium,  $\alpha$ -bromoacetyl bromide, THF,  $-78\text{ }^\circ\text{C}$  to  $-30\text{ }^\circ\text{C}$ ; v\_c, *n*-butyllithium, THF,  $-78\text{ }^\circ\text{C}$ ,  $\text{NH}_4\text{Cl}$ .



( $\text{NH}_4^+\text{Cl}^-$ ). The products were extracted by chloroform ( $2 \times 20$  ml) and the combined organic extracts were washed with aqueous saturated ammonium chloride followed by water. The organic layer was dried over anhydrous sodium sulfate, concentrated *in vacuo*, and purified on thin-layer chromatographic plates (TLC,  $R_f = 0.6$  using hexane–toluene, 4 : 1, as eluent) to give 9,9-diethyl-2-diphenylaminofluorene **6a** as viscous colorless oil, which solidified upon standing, in 95% yield (780 mg).

#### Synthesis of 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene (**6b**)

A mixture of 9,9-di(3,5,5-trimethylhexyl)-2-bromofluorene **5b** (5.9 g, 11.9 mmol), diphenylamine (2.4 g, 14.2 mmol) tris(dibenzylideneacetone)dipalladium(0) (27 mg, 0.25 mmol%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 89 mg, 0.75 mmol%) and sodium *t*-butoxide (1.6 g, 16.6 mmol) in dry toluene (150 ml) was heated to refluxing temperatures for a period of 8.0 to 10.0 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature, it was diluted with diethyl ether (60 ml), washed with brine (80 ml), and further washed with water. The diethyl ether layer was dried over sodium sulfate and concentrated *in vacuo* to give the crude product, which was purified by column chromatography (silica gel) using hexane as eluent. A chromatographic fraction corresponding to  $R_f = 0.6$  on TLC ( $\text{SiO}_2$ , hexane as eluent) was isolated to afford 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6b** as colorless oil in 97.5% yield (6.8 g). Spectroscopic data of **6b**:  $\text{FAB}^+$ -MS calcd for  $^{12}\text{C}_{43}^{1}\text{H}_{55}^{14}\text{N}_1$   $m/z$  585; found,  $m/z$  585;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.6–7.52 (m, 2H), 7.3–7.19 (m, 7H), 7.15–7.05 (m, 5H), 7.05–6.94 (m, 3H), 1.99–1.75 (m, 4H), and 1.29–0.38 (m, 34H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  151.9, 150.4, 148.0, 147.0, 140.9, 136.6, 129.2, 129.1, 126.7, 126.3, 124.1, 123.7, 122.6, 122.4, 120.3, 119.4, 119.1, 54.8, 50.9, 37.9, 33.1, 34.0, 30.9, 29.9, 29.4, 22.5, and 22.5.

#### 7- $\alpha$ -Bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (**3a**)

To a suspension of aluminium chloride (375 mg, 2.8 mmol) in 1,2-dichloroethane (15 ml) at 0 °C was added a solution of 2-diphenylamino-9,9-diethylfluorene **6a** (1.0 g, 2.6 mmol) in 1,2-dichloroethane (15 ml). It was added by  $\alpha$ -bromoacetyl bromide (0.27 ml, 3.1 mmol) over 10 min while maintaining the temperature of reaction mixture between 0–10 °C. The mixture was warmed to ambient temperature, stirred for an additional 4.0 h, and then quenched by slow addition of water (50 ml) while maintaining the temperature below 45 °C. The organic layer was isolated and washed sequentially with dil. HCl (1.0 N, 50 ml) and water (50 ml, 2  $\times$ ). It was dried over sodium sulfate and concentrated *in vacuo* to give a crystalline yellow solid. The crude solid product was purified by column chromatography (silica gel) using hexane–toluene, 3 : 2, as eluent. A chromatographic fraction corresponding to  $R_f = 0.3$  on TLC ( $\text{SiO}_2$ , hexane–toluene, 3 : 2, as eluent) was isolated to afford 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3a** as yellow crystalline solids in 66% yield (865 mg). Spectroscopic data of **3a**:  $\text{FAB}^+$ -MS calcd for  $^{12}\text{C}_{31}^{1}\text{H}_{28}^{79.9}\text{Br}_1^{14}\text{N}_1^{16}\text{O}_1$   $m/z$  510; found,  $m/z$  509 and 511; Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{BrNO}$ : C, 72.94; H, 5.49; N, 2.74; found: C, 73.22; H, 5.62; N, 2.54; UV–vis ( $\text{CHCl}_3$ ,  $2.0 \times 10^{-5}$  M)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 299 ( $2.4 \times 10^4$ ) and 406 nm ( $2.7 \times 10^4$  L mol $^{-1}$  cm $^{-1}$ ); FT-IR (KBr)  $\nu_{\text{max}}$  3037 (w), 2966 (s), 2928 (m), 2878 (w), 1674 (s), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm $^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.95 (dd,  $J = 8$  Hz,  $J = 1.6$  Hz 1H), 7.92 (d,  $J = 1.4$  Hz, 1H), 7.65 (d,  $J = 8$  Hz, 1H), 7.60 (d,  $J = 8$  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);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  191.0, 152.8, 150.3, 148.9, 147.3, 134.3, 131.6, 129.3, 129.2, 128.9, 124.4, 123.1, 122.8, 121.6, 118.8, 118.1, 56.2, 32.4, 31.2, and 8.47.

72.94; H, 5.49; N, 2.74; found: C, 73.22; H, 5.62; N, 2.54; UV–vis ( $\text{CHCl}_3$ ,  $2.0 \times 10^{-5}$  M)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 299 ( $2.4 \times 10^4$ ) and 406 nm ( $2.7 \times 10^4$  L mol $^{-1}$  cm $^{-1}$ ); FT-IR (KBr)  $\nu_{\text{max}}$  3037 (w), 2966 (s), 2928 (m), 2878 (w), 1674 (s), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm $^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.95 (dd,  $J = 8$  Hz,  $J = 1.6$  Hz 1H), 7.92 (d,  $J = 1.4$  Hz, 1H), 7.65 (d,  $J = 8$  Hz, 1H), 7.60 (d,  $J = 8$  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);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  191.0, 152.8, 150.3, 148.9, 147.3, 134.3, 131.6, 129.3, 129.2, 128.9, 124.4, 123.1, 122.8, 121.6, 118.8, 118.1, 56.2, 32.4, 31.2, and 8.47.

#### 7- $\alpha$ -Bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene (**3b**)

To a suspension of aluminium chloride (792 mg, 6.0 mmol) in 1,2-dichloroethane (30 ml) at 0 °C was added a solution of 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6b** (3.17 g, 5.4 mmol) in 1,2-dichloroethane (30 ml). It was then added by  $\alpha$ -bromoacetyl bromide (0.57 ml, 6.5 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 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 crystalline yellow solids. It was purified by column chromatography (silica gel) using hexane–EtOAc, 9 : 1, as eluent. A chromatographic fraction corresponding to  $R_f = 0.7$  on TLC ( $\text{SiO}_2$ , hexane–EtOAc, 9 : 1, as eluent) was isolated to afford 7- $\alpha$ -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **3b** as yellow viscous oil in 67% yield (2.6 g). Spectroscopic data of **3b**:  $\text{FAB}^+$ -MS calcd for  $^{12}\text{C}_{45}^{1}\text{H}_{56}^{79.9}\text{Br}_1^{14}\text{N}_1^{16}\text{O}_1$   $m/z$  706; found,  $m/z$  705 and 707; UV–vis ( $\text{CHCl}_3$ ,  $2.0 \times 10^{-5}$  M)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 407 nm ( $3.8 \times 10^4$  L mol $^{-1}$  cm $^{-1}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.94 (m, 2H), 7.63 (d,  $J = 8$  Hz, 1H), 7.58 (d,  $J = 8$  Hz, 1H), 7.27–6.97 (m, 12H), 4.46 (t,  $J = 4$  Hz, 2H), 2.08–1.79 (m, 4H), and 1.31–0.39 (m, 34H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  190.9, 153.4, 150.8, 148.8, 147.6, 146.9, 134.1, 131.5, 129.2, 128.7, 124.3, 124.3, 123.0, 123.0, 122.9, 121.6, 118.8, 118.0, 55.0, 50.8, 50.7, 37.6, 33.0, 32.9, 31.5, 30.9, 29.8, 29.3, 29.3, 22.4, and 22.4.

#### Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene, the monoadduct $\text{C}_{60}(>\text{DPAF-C}_2)$ **1a**, and the bisadduct, $\text{C}_{60}[\text{methanocarbonyl-7-(9,9-diethyl-2-diphenylaminofluorene)}]_2$ , $\text{C}_{60}(>\text{DPAF-C}_2)_2$ **2a**

$\text{C}_{60}$  (1.0 g, 1.4 mmol) and 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3a** (0.7 g, 1.4 mmol) were dissolved in toluene (700 ml) under an atmospheric pressure of nitrogen. To this was added by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.2 ml, 1.4 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 effect precipitation of the crude product, which was isolated by centrifugation. The isolated solid was a mixture of the monoadduct **1a** and bisadduct **2a**. Separation of **1a** and **2a** were made by column chromatography (silica gel) using a solvent mixture of hexane–toluene (3 : 2) as eluent. The first chromatographic band corresponding to  $R_f = 0.6$  on the thin-layer chromatographic plate (TLC, SiO<sub>2</sub>, hexane–toluene, 3 : 2) afford 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene **1a**, the monoadduct C<sub>60</sub>(>DPAF-C<sub>2</sub>), as greenish brown solid (780 mg, 71% based on recovered C<sub>60</sub>). Spectroscopic data of **1a**: FAB<sup>+</sup>-MS calcd for <sup>12</sup>C<sub>91</sub><sup>1</sup>H<sub>27</sub><sup>14</sup>N<sub>1</sub><sup>16</sup>O<sub>1</sub>  $m/z$  1149; found,  $m/z$  1150; DCI<sup>+</sup>-MS calcd for <sup>12</sup>C<sub>91</sub><sup>1</sup>H<sub>27</sub><sup>14</sup>N<sub>1</sub><sup>16</sup>O<sub>1</sub>  $m/z$  1149; found,  $m/z$  1149; Anal. Calcd for C<sub>91</sub>H<sub>27</sub>NO: C, 95.03; H, 2.34; N, 1.2; found: C, 94.58; H, 2.63; N, 1.00; UV-vis (CHCl<sub>3</sub>, 2.0 × 10<sup>−5</sup> M)  $\lambda_{\max}$  (ε) 260 (1.5 × 10<sup>5</sup>), 328 (6.4 × 10<sup>4</sup>), and 410 nm (4.7 × 10<sup>4</sup> L mol<sup>−1</sup> cm<sup>−1</sup>); FT-IR (KBr)  $\nu_{\max}$  3029 (w), 2963 (s), 2921 (m), 2875 (w), 2853 (w), 1677 (s), 1591 (vs), 1492 (s), 1276 (s), 750 (s), 695 (s), and 524 (s) cm<sup>−1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.48 (dd,  $J = 8$  Hz,  $J = 1.6$  Hz, 1H), 8.32 (d,  $J = 1.6$  Hz, 1H), 7.83 (d,  $J = 8$  Hz, 1H), 7.66 (d,  $J = 8$  Hz, 1H), 7.29–7.11 (m, 10H), 7.07–7.03 (m, 2H), 5.69 (s, 1H), 2.13–1.89 (m, 4H), and 0.40 (t,  $J = 8$  Hz, 6H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 189.6, 153.0, 150.8, 149.1, 148.2, 147.9, 147.6, 146.9, 145.6, 145.4, 145.3, 145.1, 145.0, 144.9, 144.7, 144.6, 144.6, 144.3, 143.9, 143.7, 143.3, 143.1, 143.0, 143.0, 142.9, 142.8, 142.5, 142.2, 142.2, 142.1, 141.2, 140.9, 139.7, 136.6, 134.2, 133.5, 129.3, 129.0, 124.5, 123.2, 123.1, 122.8, 121.8, 119.2, 118.1, 72.7, 56.4, 44.4, 32.5, and 8.7.

The second chromatographic band corresponding to  $R_f = 0.3$  on the thin-layer chromatographic plate (TLC, SiO<sub>2</sub>, hexane–toluene, 3 : 2) gave the bisadduct C<sub>60</sub>[methanocarbonyl-7-(9,9-diethyl-2-diphenylaminofluorene)]<sub>2</sub>, C<sub>60</sub>(>DPAF-C<sub>2</sub>)<sub>2</sub> **2a**, as brownish solids in a minor quantity of roughly 11% yield (170 mg). Spectroscopic data of **2a**: FAB<sup>+</sup>-MS calcd for <sup>12</sup>C<sub>122</sub><sup>1</sup>H<sub>54</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>2</sub>  $m/z$  1578; found,  $m/z$  1579; Anal. Calcd for C<sub>122</sub>H<sub>54</sub>N<sub>2</sub>O<sub>2</sub>: C, 92.77; H, 3.42; N, 1.77; found: C, 92.60; H, 3.05; N, 1.94; UV-vis (CHCl<sub>3</sub>, 2.0 × 10<sup>−5</sup> M)  $\lambda_{\max}$  (ε) 254 (1.2 × 10<sup>5</sup>), 308 (8.4 × 10<sup>4</sup>), and 406 (7.8 × 10<sup>4</sup> L mol<sup>−1</sup> cm<sup>−1</sup>); FT-IR (KBr)  $\nu_{\max}$  3029 (w), 2959 (s), 2920 (m), 2850 (w), 1677 (s), 1592 (vs), 1490 (s), 1277 (s), 752 (s), 696 (s), and 525 (s) cm<sup>−1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.7–8.2 (m, 4H), 7.9–7.7 (m, 2H), 7.7–7.5 (m, 2H), 7.4–7.2 (m, 20H), 7.2–7.0 (m, 4H), 5.6–5.3 (m, 2H), 2.1–1.9 (m, 8H), and 0.40 (m, broad, 12H).

**Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene, the monoadduct C<sub>60</sub>(>DPAF-C<sub>9</sub>) **1b**, and the bisadduct, C<sub>60</sub>[methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]<sub>2</sub>, C<sub>60</sub>(>DPAF-C<sub>9</sub>)<sub>2</sub> **2b****

C<sub>60</sub> (1.0 g, 1.38 mmol) and 7-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **3b** (970 mg, 1.38 mmol) were dissolved in toluene (700 ml) under an atmospheric pressure of nitrogen. To this was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.2 ml, 1.38 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 cause precipitation of the crude product, which was isolated by centrifugation. The isolated solid was a mixture of the monoadduct **1b** and bisadduct **2b**. Separation of **1b** and **2b** were made by column chromatography on silica gel using a solvent mixture of hexane–toluene, 3 : 2, as eluent. The first chromatographic band at  $R_f = 0.45$  on the thin-layer chromatographic (TLC, SiO<sub>2</sub>) plate using hexane–toluene, 3 : 2, as eluent afford C<sub>60</sub>(>DPAF-C<sub>9</sub>) monoadduct 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **1b**, as greenish brown solids (960 mg, 70% based on recovered C<sub>60</sub>). Spectroscopic data of **1b**: FAB<sup>+</sup>-MS calcd for <sup>12</sup>C<sub>105</sub><sup>1</sup>H<sub>55</sub><sup>14</sup>N<sup>16</sup>O  $m/z$  1345; found,  $m/z$  1345 and 1346; Anal. Calcd for C<sub>105</sub>H<sub>55</sub>NO: C, 93.68; H, 4.08; N, 1.04; found: C, 93.52; H, 3.88; N, 0.95; UV-vis (CHCl<sub>3</sub>, 2.0 × 10<sup>−5</sup> M)  $\lambda_{\max}$  (ε) 263 (1.7 × 10<sup>5</sup>), 326 (5.7 × 10<sup>4</sup>), and 410 nm (4.4 × 10<sup>4</sup> L mol<sup>−1</sup> cm<sup>−1</sup>); FT-IR (KBr)  $\nu_{\max}$  3029 (w), 2946 (s), 2860 (m), 1677 (s), 1591 (vs), 1490 (s), 1463 (s), 1423 (s), 1273 (s), 1198 (s), 750 (s), 695 (s), and 525 (s) cm<sup>−1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.48 (d,  $J = 8$  Hz, 1H), 8.34 (s, 1H), 7.83 (d,  $J = 8$  Hz, 1H), 7.67 (d,  $J = 8$  Hz, 1H), 7.35–7.02 (m, 12H), 5.69 (t,  $J = 4$  Hz, 1H), 2.2–1.8 (m, 4H), and 1.28–0.48 (m, 34H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 189.3, 153.7, 151.4, 149.1, 148.2, 148.20, 147.6, 147.6, 146.9, 145.6, 145.4, 145.3, 145.1, 145.0, 144.9, 144.7, 144.6, 144.6, 144.5, 143.9, 143.7, 143.3, 143.1, 143.1, 143.0, 142.9, 142.9, 142.8, 142.5, 142.2, 142.1, 141.2, 140.9, 139.6, 136.6, 134.0, 133.5, 129.4, 128.9, 124.5, 123.2, 122.8, 121.8, 119.3, 118.0, 72.6, 55.2, 50.9, 44.6, 38.2, 33.2, 30.9, 30.0, 29.5, and 22.6.

The second chromatographic band corresponding to  $R_f = 0.25$  on TLC gave the bisadduct C<sub>60</sub>(methanocarbonyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)<sub>2</sub>, C<sub>60</sub>(>DPAF)<sub>2</sub> **2b**, as brownish solids in 14% yield (190 mg). Spectroscopic data of **2b**: FAB<sup>+</sup>-MS calcd for <sup>12</sup>C<sub>150</sub><sup>1</sup>H<sub>110</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>2</sub>  $m/z$  1971; found,  $m/z$  1971; UV-vis (CHCl<sub>3</sub>, 2.0 × 10<sup>−5</sup> M)  $\lambda_{\max}$  (ε) 255 (1.9 × 10<sup>5</sup>), 310 (1.1 × 10<sup>5</sup>), and 406 nm (8.5 × 10<sup>4</sup> L mol<sup>−1</sup> cm<sup>−1</sup>); FT-IR (KBr)  $\nu_{\max}$  3029 (w), 2946 (s), 2860 (m), 1677 (s), 1591 (vs), 1490 (s), 1463 (s), 1423 (s), 1273 (s), 1198 (s), 750 (s), 695 (s), and 525 (s) cm<sup>−1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.6–8.4 (m, 4H), 7.9–7.4 (m, 4H), 7.32–7.04 (m, 24H), 5.7–5.4 (m, 2H), 2.2–1.6 (m, 8H), and 1.3–0.2 (m, 68H). <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>, ppm) δ 189.8, 154.1, 151.8, 151.7, 149.4, 148.1, 148.0, 147.7, 147.5, 146.9, 146.8, 146.6, 146.2, 146.0, 145.9, 145.7, 145.5, 145.0, 145.0, 144.9, 144.8, 144.7, 144.5, 144.3, 144.0, 143.9, 143.7, 143.6, 143.3, 143.3, 143.1, 143.0, 143.0, 142.9, 142.6, 142.5, 142.3, 142.3, 142.2, 142.1, 140.9, 140.5, 140.0, 139.8, 139.7, 139.5, 134.5, 134.0, 129.8, 129.5, 129.3, 128.65, 124.9, 123.6, 122.3, 119.6, 118.5, 73.4, 73.2, 55.6, 51.3, 51.2, 44.4, 44.4, 42.9, 38.2, 38.2, 38.1, 33.6, 33.5, 33.5, 31.4, 30.4, 29.9, 27.7, 23.1, and 22.9.

## Results and discussion

Molecular conjugation of C<sub>60</sub>, which exhibits the reverse-saturable absorption capability, and the diphenylaminodi-alkylfluorene (DPAF-C<sub>*n*</sub>) component with relatively broad

optical absorption in the visible wavelength region is considered in our design of new photonic materials. The conjugation may lead possibly to, for example, the light-harvesting efficiency enhancement of fullerene-chromophore derivatives in the visible region. Accordingly, covalent coupling of fullerene  $\pi$ -orbitals with electron-accepting (A) characteristics and  $\pi$ -electron-donating DPAF- $C_n$  (D) moieties produces a three-dimensional  $C_{60}$ -(D) $_n$  molecular system. Aside from its strongly electron-deficient properties with the capability of accepting multiple electrons,  $C_{60}$  is attractive owing to its multiple reactive sites available for attaching up to six or more photoactive arms. We propose a direct chemical bonding of multiple DPAF derivatives on a  $C_{60}$  cage in close vicinity, forming a spherical star-like structure, for enhancing the overall cross-section of two-photon absorption and reducing the ability of 2PA chromophores to aggregate and order.

In our approach using  $C_{60}$ -*keto*-donor assembly structure for the construction of photoresponsive  $C_{60}$ -dyads, a fluorene moiety was chosen because of its inherent thermal and photochemical stability. Aromatic  $C_2$  and  $C_7$  positions of the fluorene ring can be modified with either electron-rich or electron-withdrawing substituents for the alteration of its electronic properties. Simultaneous attachment of alkyl groups at  $C_9$  position should increase the solubility of the resulting  $C_{60}$ -fluorene dyad. The first diphenylaminofluoreno-methano[60]fullerene dyad  $C_{60}$ (>DPAF- $C_2$ ) **1a** was prepared by a synthetic procedure depicted in Scheme 1. It involved synthesis of the key intermediate 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3a**, starting from commercially available 2-bromofluorene **4**, prior to attachment of the fluorene moiety to the  $C_{60}$  cage by a keto linker. The linkage places the diphenylaminofluorene moiety in a close neighborhood of the  $C_{60}$  cage.

Diethylation of **4** was carried out with ethyl iodide in toluene in the presence of aqueous sodium hydroxide and a phase transfer agent, tetra-*n*-butylammonium bromide, at 60 °C for a period of 8.0 h. The resulting product 2-bromo-9,9-diethylfluorene **5a** was obtained as colorless semisolid in 81% yield after thin-layer chromatographic (TLC) purification ( $SiO_2$ ,  $R_f$  = 0.8, hexane) or column chromatography. Its structure was confirmed by detection of the molecular ion mass at  $m/z$  301 in positive ion fast atom bombardment mass spectrum (FAB<sup>+</sup>-MS) and <sup>1</sup>H NMR spectrum. The latter displayed the characteristic resonance of ethyl groups with six terminal methyl protons appearing as a triplet at  $\delta$  0.24 and a broad multiplet between  $\delta$  1.94–1.91 corresponding to four methylene protons at  $\alpha$  position to fluorenyl benzylic carbon. Amination of **5a** was performed by Buchwald's procedure<sup>18</sup> 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 temperatures for 8.0 to 10 h under nitrogen atmosphere. The product 9,9-diethyl-2-diphenylaminofluorene **6a** was isolated as a white amorphous solid in 98% yield after column chromatographic purification (silica gel, hexane–toluene, 9 : 1,  $R_f$  = 0.6 on TLC using hexane–toluene, 4 : 1, as eluent). Complete disappearance of C–Br stretching vibration was revealed in the infrared spectrum of **6a**. Positive ion FAB mass

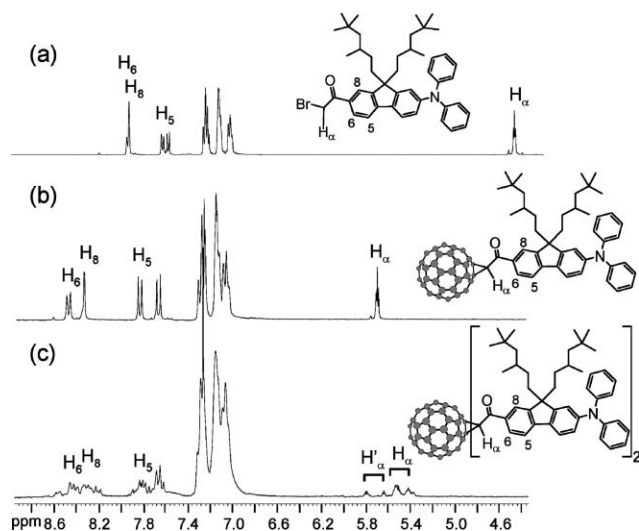
spectrum of **6a** showed a main peak at  $m/z$  389 consisting of its molecular ion mass. Additional structural confirmation was made by <sup>1</sup>H NMR spectroscopic analysis with new resonance observed for the aromatic protons of diphenylamino moiety at  $\delta$  6.99 to 7.64 along with the proton signals of two ethyl groups at  $\delta$  0.36 (t, terminal methyl, 6H) and two groups of multiplet centered at  $\delta$  1.90 and 2.01 for four methylene protons at  $C_9$  position.

Friedel–Crafts acylation<sup>19</sup> of **6a** at  $C_7$  position of diphenylaminofluorene moiety was achieved with  $\alpha$ -bromoacetyl bromide and aluminium chloride in 1,2-dichloroethane at 0 °C to ambient temperature for 4.0 h to afford 7- $\alpha$ -bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3a** as yellow semi-crystalline solids in 66% yield after column chromatography (silica gel, hexane–toluene, 3 : 2,  $R_f$  = 0.3 on TLC). As anticipated, positive ion FAB mass spectrum of **3a** showed a main peak at  $m/z$  510 consisting with its molecular ion mass. Infrared spectrum of **3a** displayed a strong carbonyl stretching absorption band centered at 1674 cm<sup>−1</sup> indicating the presence of  $\alpha$ -bromoacetyl group. Characteristic signal of two methylene protons ( $H_\alpha$ ) of  $\alpha$ -bromoacetyl group appeared as a singlet at  $\delta$  4.50 in <sup>1</sup>H NMR spectrum of **3a**. Attachment assignment of the  $\alpha$ -bromoacetyl group at  $C_7$  position of the fluorene moiety was made by a new carbonyl carbon peak at  $\delta$  191.0 of <sup>13</sup>C NMR spectrum and clear downfield shift of phenyl protons at  $C_5$ ,  $C_6$ , and  $C_8$  of fluorene unit to  $\delta$  7.65 (d,  $J$  = 8 Hz), 7.95 (dd,  $J$  = 8 Hz,  $J$  = 1.6 Hz) and 7.92 (d,  $J$  = 1.4 Hz), respectively, from those of **6a** in <sup>1</sup>H NMR spectrum. In addition, elemental analyses of C, H, and N atoms were found to agree well with theoretically calculated weight percentage values.

Similar reaction conditions were used for the synthesis of the key intermediate 7- $\alpha$ -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **3b** from 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6b** with  $\alpha$ -bromoacetyl bromide (1.2 equiv.) in the presence of aluminium chloride (1.1 equiv.) at 0 °C to ambient temperature for 4.0 h. The product was obtained in roughly 67% yield. Positive ion FAB mass (FAB<sup>+</sup>-MS) spectrum of **3b** showed a main peak at  $m/z$  705 and 707 consisting with its molecular ion mass. The chemical shift of two  $H_\alpha$  protons of **3b** appeared as a triplet at  $\delta$  4.46 in <sup>1</sup>H NMR spectrum (Fig. 1a). The doublet peak at  $\delta$  7.63 was assigned to the chemical shift of phenyl proton ( $H_5$ ) at  $C_5$ . The most downfield-shifted multiplet peak at  $\delta$  7.94 with an integration intensity corresponding to two protons ( $H_6$  and  $H_8$ ) is the chemical shift of phenyl protons at  $C_6$  and  $C_8$  of the fluorene unit.

Addition of a substituted DPAF unit to  $C_{60}$  leading to the formation of dyads **1a** and **1b** was accomplished by the treatment of  $\alpha$ -bromoacetylfluorene derivative **3a** and **3b**, 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 5.0 h.<sup>20</sup> Systematic evaluation of the reaction mixture by TLC technique revealed the need of excess **3a** and **3b** for full utilization of  $C_{60}$  in the cyclopropanation reaction. However, a higher quantity of  $\alpha$ -bromoacetyl fluorine than 1.0 equiv. used in the reaction resulted in an increased yield of bisaddition and trisaddition products of  $C_{60}$  detectable by a lower  $R_f$  value on an analytical TLC plate. Formation of





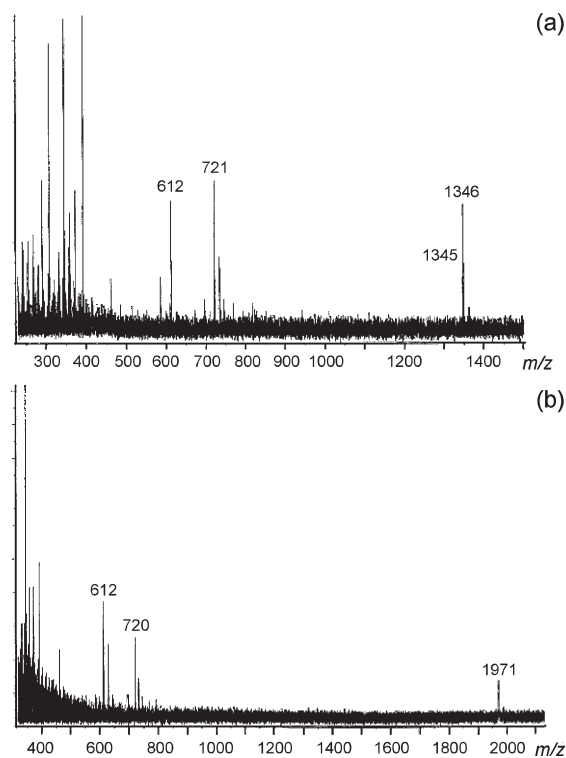
**Fig. 1**  $^1\text{H}$  NMR spectra of (a) the parent 7- $\alpha$ -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene **3b**, (b) the monoadduct  $\text{C}_{60}(>\text{DPAF-C}_9)$  **1b**, and (c) the bisadduct  $\text{C}_{60}(>\text{DPAF-C}_9)_2$  **2b** in  $\text{CDCl}_3$ .

fullerenyl bisadduct persists even with only one equivalent of  $\alpha$ -bromoacetylfluorene 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, 3 : 2, as eluent. The first chromatographic band corresponding to  $R_f = 0.6$  on a TLC ( $\text{SiO}_2$ ) plate afforded the monoadduct **1a**, 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylamino fluorene [ $\text{C}_{60}(>\text{DPAF-C}_2)$ ], or **1b** ( $R_f = 0.45$ , TLC,  $\text{SiO}_2$ ), 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene [ $\text{C}_{60}(>\text{DPAF-C}_9)$ ], both as greenish brown solids in a similar yield of more than 50% (or 71% based on recovered  $\text{C}_{60}$ ). The second chromatographic band corresponding to  $R_f = 0.3$  on TLC gave the corresponding bisadduct **2a**,  $\text{C}_{60}[\text{methanocarbonyl-7-(9,9-diethyl-2-diphenylamino fluorene)}]_2$  [ $\text{C}_{60}(>\text{DPAF-C}_2)_2$ ], as brownish solids in a minor yield of roughly 11%. Similarly, the bisadduct **2b** ( $R_f = 0.25$ , TLC,  $\text{SiO}_2$ ),  $\text{C}_{60}[\text{methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene)}]_2$  [ $\text{C}_{60}(>\text{DPAF-C}_9)_2$ ], was isolated in a yield of 14%.

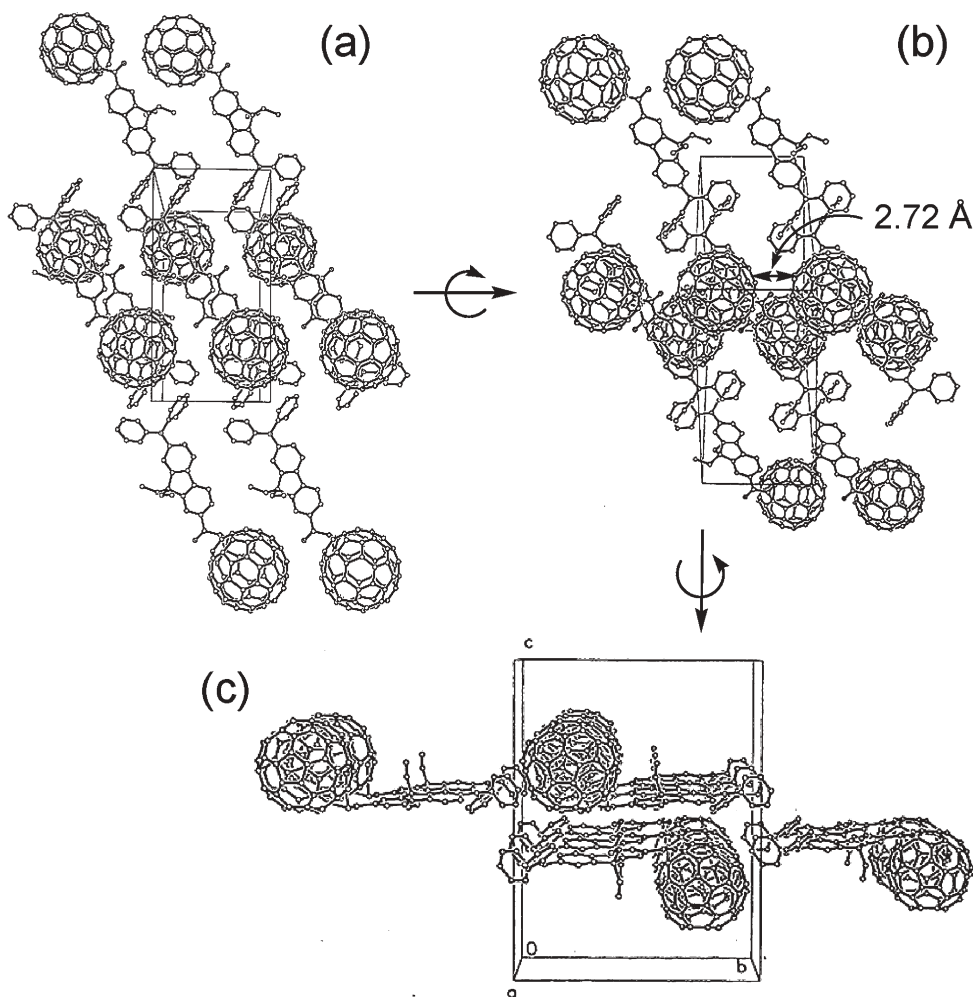
Evidence of the DPAF moiety bridging on the methano[60]-fullerene cage by a keto group can be seen in the infrared spectra of **1a** and **1b** as both showing a strong optical absorption band of carbonyl stretching centered at  $1677\text{ cm}^{-1}$  with three typical fullerene derivative signals at 750, 695 and  $524\text{ cm}^{-1}$ . The former absorption band matches well with that of **3a** and **3b**, however, in a roughly  $50\text{ cm}^{-1}$  shift from the normal carbonyl stretching band at  $1720\text{--}1750\text{ cm}^{-1}$  due to influence of the fluorine ring structure. The molecular ion mass of **1a** was clearly detected in both negative ion desorption chemical ionization mass spectrum (DCI $^-$ -MS), by a group of mass peaks with a maximum peak intensity centered at  $m/z$  1149 ( $\text{M}^+$ ), and positive ion fast atom bombardment mass spectrum (FAB $^+$ -MS) at  $m/z$  1150 ( $\text{M}^+$ ). That clearly provides

evidence of the composition mass of fullerene–fluorene dyad **1a**. In a separate measurement, the molecular ion mass of bisadduct  $\text{C}_{60}(>\text{DPAF-C}_2)_2$  **2a** was detected in FAB $^+$ -MS at  $m/z$  1578 and 1579 ( $\text{M}^+$ ). It was followed by a group of mass peaks centered at  $m/z$  1149 matching well with that of the monoadduct **1a** with the loss of one 7-aceto-9,9-diethyl-2-diphenylamino fluorene subunit from the molecular mass. In the case of **1b** and **2b**, positive ion FAB mass spectrum displayed a group of sharp mass peaks at  $m/z$  1345 and 1346, corresponding to the molecular ion mass of  $\text{C}_{60}(>\text{DPAF-C}_9)$  **1b**, with no mass fragmentation peaks in the range of  $m/z$  800–1330 following the molecular ion peak, as shown in Fig. 2a. The next major group of mass fragmentation peaks occurred at  $m/z$  721 corresponding to the ion mass of the  $\text{C}_{60}$  cage. The relatively simple spectrum in the higher mass region revealed high stability of aromatic diphenylamino fluorene moiety under FAB $^+$ -MS measurement conditions. That led to the bond cleavage occurring only at the cyclopropanyl carbon conjunction bonds bridging fullerene and DPAF moieties. Similar FAB $^+$ -MS spectrum profile (Fig. 2b) was observed for the bisadduct  $\text{C}_{60}(>\text{DPAF-C}_9)_2$  **2b** showing the corresponding molecular ion mass at  $m/z$  1971, followed by no mass fragmentation peaks until  $m/z$  720 corresponding to the ion mass of  $\text{C}_{60}$ .

The molecular structure of  $\text{C}_{60}(>\text{DPAF-C}_2)$  was confirmed by the X-ray crystallographic analysis of a single crystal grown in  $\text{ClCH}_2\text{CH}_2\text{Cl}$ . Perspective 3-D ORTEP view of molecular unit cell packing is displayed in Fig. 3. A highly ordered array of the fullerene cages along the  $a$ -axis of the unit cell was observed with the planar diphenylamino fluorene (DPAF)



**Fig. 2** Positive ion FAB mass spectrum (direct probe) of (a)  $\text{C}_{60}(>\text{DPAF-C}_9)$  **1b** and (b)  $\text{C}_{60}(>\text{DPAF-C}_9)_2$  **2b**, showing the corresponding molecular ion mass at  $m/z$  1345 and 1971, respectively.



**Fig. 3** Molecular packing of  $C_{60}( > \text{DPAF-C}_2 )$  **1a** in a single crystal unit cell showing a highly ordered array of the fullerene cages along the  $a$ -axis. Interchange among different views of (a), (b), and (c) can be made by rotation along the axis indicated.

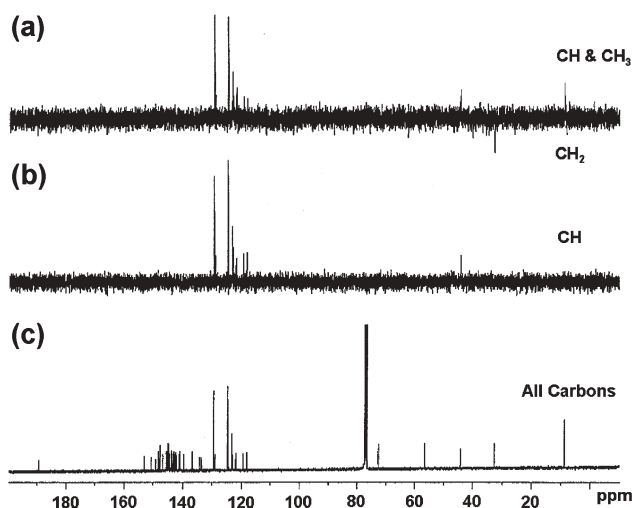
rings located next to each other in the  $a$ - $b$  plane of the unit cell, showing no direct  $\pi$ - $\pi$  interaction between DPAF rings (Fig. 3c). That revealed the intermolecular forces involved in the molecular assembly of  $C_{60}( > \text{DPAF-C}_2 )$  being dominated by the strong fullereryl  $\pi$ -interactions. The closest distance between two neighboring  $C_{60}$  cages was found to be 2.72 Å along the  $a$ -axis (Fig. 3b). Two single-bond lengths connecting the methanocarbon and two fullereryl carbons in the cyclopropanyl ring were found to be 1.498 Å and 1.487 Å. The distance between two fullereryl carbons in the cyclopropanyl ring of **1a** is 1.628 Å, longer than the normal single C-C bond length, that leads to three angles of cyclopropanyl ring as 66.13°, 56.61°, and 57.26° with the former largest angle located at the methanocarbon. The crystallographic data collection and structural refinement information are as follows: empirical formula,  $C_{91}H_{27}NO$ ; formula weight, 1150.14; crystal system, monoclinic; space group,  $P2_1/n$ ;  $T = 295(2)$  K; unit cell dimensions  $a = 10.00100(10)$  Å,  $b = 19.5790(2)$  Å,  $c = 25.7150(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 93.0510(10)^\circ$ ,  $\gamma = 90^\circ$ ; volume  $V = 5028.11(9)$  Å<sup>3</sup>

† CCDC reference numbers 183726. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515055h

with  $Z = 4$ ;  $R_{\text{int}} = 0.0396$ ; abs. coefficient  $0.089 \text{ mm}^{-1}$ ;  $R_1 = 0.0524$  and  $wR_2 = 0.1279$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.0786$  and  $wR_2 = 0.1510$  for all data.†

With the molecular structure of **1a** resolved, we are able to assign all proton peaks in its  $^1\text{H}$  NMR spectrum. The  $\alpha$ -proton ( $H_\alpha$ , next to the carbonyl group) peak of **1a** and **1b** appeared as a singlet and triplet, respectively, at  $\delta$  5.69 (Fig. 1b) with a large downfield shift of roughly 1.2 ppm from that of **3a** and **3b**. It was also accompanied with downfield shift of all phenyl proton at  $C_5$ ,  $C_6$ , and  $C_8$  of the fluorene moiety to 7.83 (d,  $J = 8$  Hz), 8.48 (dd,  $J = 8$  Hz,  $J = 1.6$  Hz) and 8.32 (d,  $J = 1.6$  Hz) for **1a** and to 7.83 (d,  $J = 8$  Hz), 8.48 (d,  $J = 8$  Hz), and 8.34 (s) for **1b**, as shown in Fig. 1b. In the case of the bisadducts  $C_{60}( > \text{DPAF-C}_2 )_2$  **2a** and  $C_{60}( > \text{DPAF-C}_9 )_2$  **2b**, comparable  $^1\text{H}$  NMR spectra were obtained. For example, using the spectrum of **1b** as the reference, we assigned the multiplet peaks at  $\delta$  7.7–7.9 (2H), 8.2–8.35 (2H), and 8.35–8.6 (2H) in Fig. 1c for the chemical shift of  $H_5$ ,  $H_8$ , and  $H_6$  protons of **2b**, respectively. There are two groups of proton peaks at  $\delta$  5.35–5.6 and 5.6–5.85 in a different integration intensity accounted for a total of two  $H_\alpha$  protons. That revealed two possible regioisomers of the bisadduct in a molecular ratio of roughly 1 : 2.8 in the

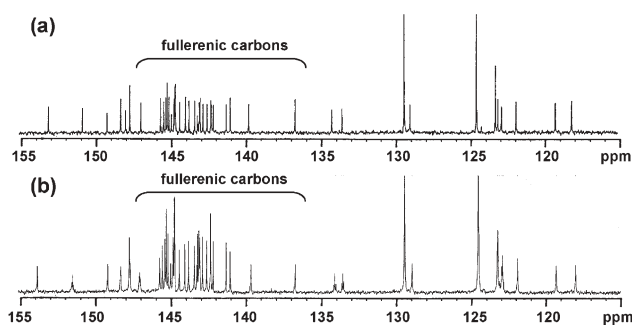




**Fig. 4**  $^{13}\text{C}$ -DEPT NMR spectrum of the dyad  $\text{C}_{60}(>\text{DPAF-C}_2)$  **1a** in  $\text{CDCl}_3$  showing (a) upward signals for CH and  $\text{CH}_3$  carbons and downward signals for  $\text{CH}_2$  carbons, (b) the upward CH carbon signal, and (c) the rest of non-protonated fullerene carbon signals.

isolated, chromatographically non-separable fraction, as a result of the large DPAF moiety size and a close similarity of the molecular polarity between regioisomers.

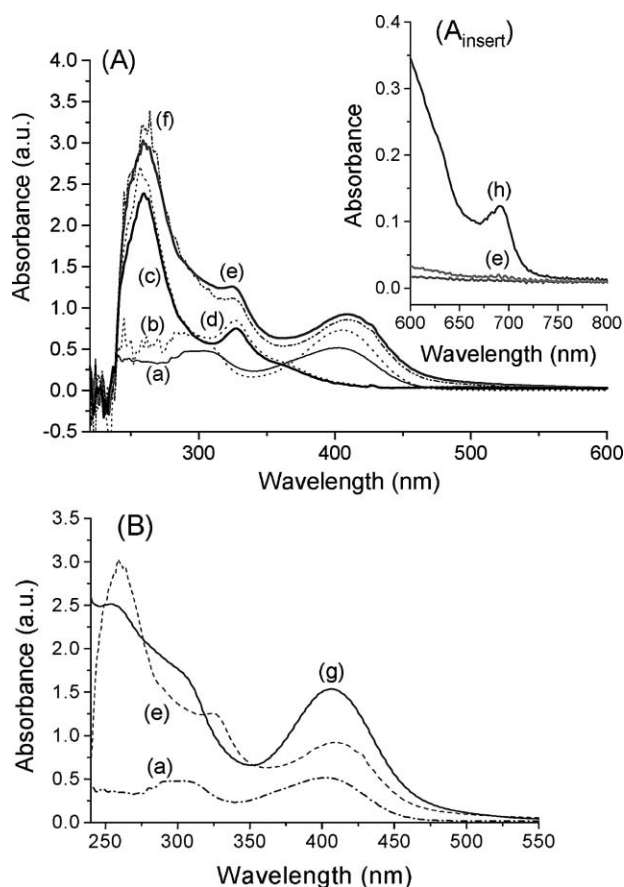
DEPT (distortionless enhancement by polarization transfer) measurement of  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{60}(>\text{DPAF-C}_2)$  (Fig. 4) provides a good method for identification of carbon groups in the structures of **1a** and **1b**. Accordingly,  $^1\text{H}$ -decoupled  $^{13}\text{C}$  signals appear upward for the carbon atoms directly bonded with one or three  $^1\text{H}$  nuclei or downward for the carbon atoms directly bonded with two  $^1\text{H}$  nuclei. Combination of Fig. 4a and 4b allowed differentiation of terminal methyl and methylene carbon peaks at  $\delta$  8.7 and 32.5, respectively, corresponding to ethyl groups attached at  $\text{C}_9$  of **1a**. Most importantly, the chemical shift of cyclopropanyl carbon next to the keto group was found to be  $\delta$  44.4 showing an upward carbon peak in Fig. 4b due to bonding with one  $\text{H}_\alpha$  atom. The remaining two fullerene  $\text{sp}^3$  carbon and  $\text{C}_9$  peaks appeared at  $\delta$  72.7 and 56.4, respectively. The most downfield peak at  $\delta$  189.6 was assigned to the bridging carbonyl carbon (Fig. 4c). All other fullerene carbons appeared as a total of 29 peaks in the region of  $\delta$  136 to 147 accounted for 58  $\text{sp}^2$  carbons of the fullerene cage, indicating clearly a  $\text{C}_2$  symmetry



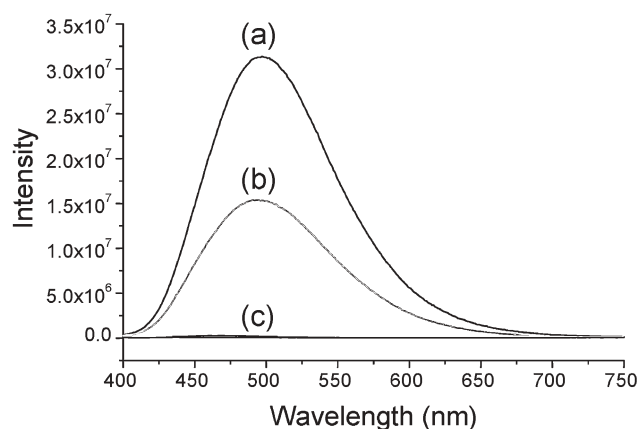
**Fig. 5**  $^{13}\text{C}$  NMR spectra of (a)  $\text{C}_{60}(>\text{DPAF-C}_2)$  **1a** and (b)  $\text{C}_{60}(>\text{DPAF-C}_9)$  **1b** showing close resemblance of a fullerene carbon peak pattern consisting of 29 carbon signals.

axis along the plane of two  $\text{sp}^3$  fullerene carbons, as shown in Fig. 5a. These characteristic carbon signals confirmed the overall chemical structure of dyad  $\text{C}_{60}(>\text{DPAF-C}_2)$ . In  $^{13}\text{C}$  NMR spectrum of the dyad  $\text{C}_{60}(>\text{DPAF-C}_9)$ , the corresponding key signals of  $\text{C}_9$ , carbonyl carbon,  $\alpha$ -carbon, and fullerene  $\text{sp}^3$  carbons were recorded at  $\delta$  55.2, 189.3, 44.6, and 72.6, respectively. Confirmation of a  $\text{C}_2$  molecular symmetry for dyad **1b** as a DPAF monoadduct of  $\text{C}_{60}$  was made by the close resemblance of its fullerene  $\text{sp}^2$  carbon peak pattern to that of **1a**, showing a total of identical 29 peaks (Fig. 5b).

Optical absorption of **1a** gave three major bands at 260 ( $\epsilon = 1.5 \times 10^5$ ), 328 ( $\epsilon = 6.4 \times 10^4$ ), and 410 nm ( $\epsilon = 4.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), whereas **1b** displayed similar three absorption bands at 263 ( $\epsilon = 1.7 \times 10^5$ ), 326 ( $\epsilon = 5.7 \times 10^4$ ), and 410 nm ( $\epsilon = 4.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in their UV-vis spectra (Fig. 6). The former two bands match approximately with those of the model compounds  $\text{C}_{60}(>\text{COPh})$  (Fig. 6Ac) and  $\text{C}_{60}[(\text{CO}_2\text{Et})_2]$  (Fig. 6Ad) containing mainly an optical active fullerene moiety that confirms these absorption bands being attributed to the  $\text{C}_{60}$  cage. The latter band fits well with the main optical absorption of 7-bromoacetyl-9,9-diethyl-2-diphenylamino fluorene (DPAF- $\text{C}_2$ , **3a**, Fig. 6Aa) centered at



**Fig. 6** UV-vis spectra of (A) and (B) as (a) DPAF- $\text{C}_2$  **3a**, (b) DPAF- $\text{C}_9$  **3b**, (c)  $\text{C}_{60}(>\text{COPh})$ , (d)  $\text{C}_{60}[(\text{CO}_2\text{Et})_2]$ , (e)  $\text{C}_{60}(>\text{DPAF-C}_2)$  **1a**, (f)  $\text{C}_{60}(>\text{DPAF-C}_9)$  **1b**, and (g)  $\text{C}_{60}(>\text{DPAF-C}_2)_2$  **2a** in chloroform ( $2.0 \times 10^{-5} \text{ M}$ ). Very weak characteristic steady state absorption band of the methano[60]fullerene moiety of  $\text{C}_{60}(>\text{DPAF-C}_2)$  became visible at roughly 690 nm at a higher concentration of  $4.4 \times 10^{-4} \text{ M}$ , as shown in the insert of (A).



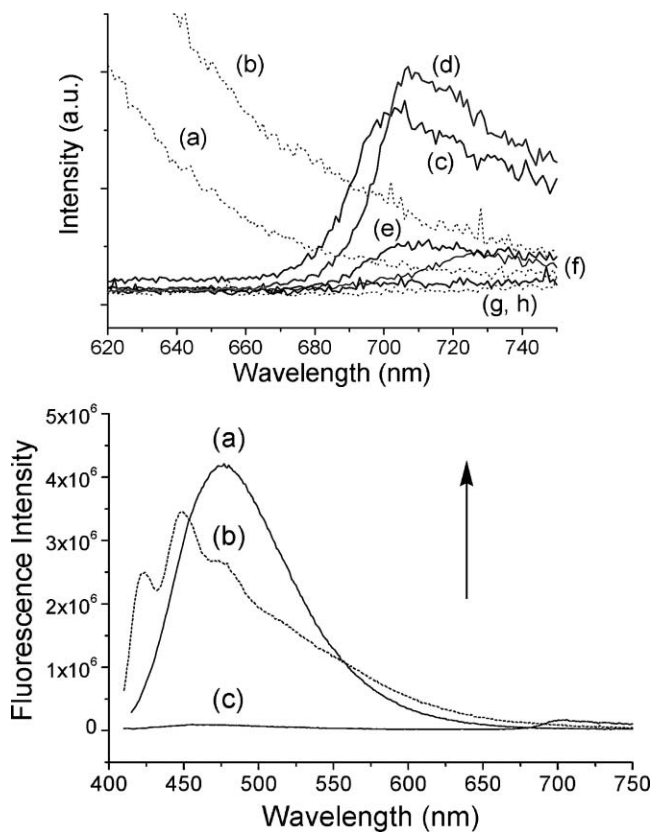
**Fig. 7** Comparison of intermolecular and intramolecular fluorescence quenching efficiency of the system (a) DPAF-C<sub>2</sub> control, (b) an equimolar mixture of C<sub>60</sub> and DPAF-C<sub>2</sub>, and (c) C<sub>60</sub>(>DPAF-C<sub>2</sub>) under 400 nm excitation in CHCl<sub>3</sub> ( $2.0 \times 10^{-5}$  M).

299 ( $\epsilon = 2.4 \times 10^4$ ) and 406 nm ( $\epsilon = 2.7 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) and DPAF-C<sub>9</sub> (**3b**, Fig. 6Ab) at 407 nm ( $3.8 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) that is attributed to the corresponding diphenylaminofluorene moiety. Nearly absorptive superimposition of Figs. 6Ae and 6Af with 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 **1a** and **1b** in chloroform ( $2.0 \times 10^{-5}$  M). In addition, a very weak characteristic steady state absorption band of the methano[60]fullerene moiety of C<sub>60</sub>(>DPAF-C<sub>2</sub>) became visible only at a higher concentration than  $4.4 \times 10^{-4}$  M with the peak maximum appearing at roughly 690 nm, as shown in Fig. 6A(insert). As the number of DPAF addends increases to two in the structure of C<sub>60</sub>(>DPAF-C<sub>2</sub>)<sub>2</sub> **2a**, the absorption intensity of the DPAF components becomes significant and dominates the spectrum with two DPAF bands centered at 308 ( $8.4 \times 10^4$ ) and 406 nm ( $7.8 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) clearly shown in Fig. 6Bg. Intensity of the latter band is almost 1.8-fold higher than that of the monoadduct **1a** (Fig. 6Be), consistent with the composition of the bisadduct **2a**.

Most of C<sub>60</sub>-DPAF conjugates exhibit either intramolecular electron- or energy-transfer phenomena at its photoexcited nanosecond transient states from the DPAF donor moiety to the fullerene acceptor moiety. Diphenylaminofluorene subunits DPAF-C<sub>2</sub> and DPAF-C<sub>9</sub> are highly fluorescent upon photoexcitation at 400 nm showing fluorescence emission with the peak maximum centered at 500 nm. In CHCl<sub>3</sub>, a good solvent for DPAF-C<sub>2</sub> and C<sub>60</sub>(>DPAF-C<sub>2</sub>), intermolecular partial quenching of DPAF-C<sub>2</sub> fluorescence (Fig. 7b) by C<sub>60</sub> was detected at a concentration of  $2.0 \times 10^{-5}$  M that reduced its intensity to less than a half of the control value (Fig. 7a). Covalent attachment of the fullerene cage to diphenylaminofluorene moiety in close vicinity forming the dyad structure of **1a** quenched the fluorescence emission of DPAF-C<sub>2</sub> moiety in a near quantitative yield (Fig. 7c), indicating that the intramolecular energy transfer process from the DPAF-C<sub>2</sub> moiety to the fullerene cage is much more efficient than the

corresponding intermolecular process. In the case of DMF, the reduction of fluorescence at 475 nm to a band intensity of less than 30% was measured upon the same photoexcitation at 400 nm, as shown in steady-state fluorescence spectrum of C<sub>60</sub>(>DPAF-C<sub>2</sub>) (Fig. 8a). This 475 nm fluorescence indicates that the lowest excited singlet energy of C<sub>60</sub>[<sup>1</sup>(DPAF-C<sub>2</sub>)\*] is 2.61 eV in DMF. Strong solvent-sensitive fluorescence emission was observed in these C<sub>60</sub>-DPAF conjugates. For example, multiple fluorescence emission bands of the DPAF-C<sub>2</sub> moiety with the peak maxima appearing at 425, 450, and 475 nm were detected in benzonitrile, as shown in Fig. 8b. We propose that both the heterogeneous molecular aggregation of C<sub>60</sub>(>DPAF-C<sub>2</sub>) and aggregate-solvent interactions contribute to the variation in the shape and intensity of the fluorescence band in polar solvents.

Interestingly, this one-photon excited emission of **1a** was highly suppressed in less polar and non-polar solvents, including CHCl<sub>3</sub>, CS<sub>2</sub>, THF, *o*-dichlorobenzene (*o*-DCB), nitrobenzene and ethyl acetate, showing only a very weak broad band centered at 475 nm. Instead, a low intensity of the fluorescence band with the peak at 700–710 nm was recorded in chloroform, CS<sub>2</sub>, *o*-dichlorobenzene and THF, as shown in the insert of Fig. 8, with appreciable emission intensity in the first two solvents (Figs. 8c and 8d). No fluorescence band of **1a** at either 475 or 700 nm was detectable in nitrobenzene and ethyl acetate. Disappearance of all fluorescence emission may



**Fig. 8** Fluorescence spectra of C<sub>60</sub>(>DPAF-C<sub>2</sub>) **1a** upon 400 nm excitation in the solvents of (a) DMF, (b) PhCN, (c) CHCl<sub>3</sub>, (d) CS<sub>2</sub>, (e) *o*-dichlorobenzene, (f) THF, (g) EtOAc, and (h) nitrobenzene in the presence of air at a concentration of  $2.0 \times 10^{-5}$  M.

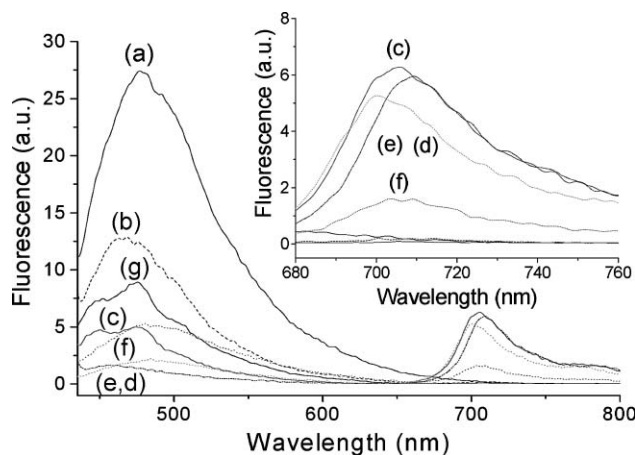
be the result of severe molecular aggregation and the related quenching effect, due to low solubility of **1a** in these solvents. The observed fluorescence band at  $>700$  nm was compared to that of methanofullerene  $C_{60}(>>CH_2)$  at 717 nm in toluene,<sup>16</sup> revealing its source arising from the fullerene cage moiety. Therefore, this fluorescence band can also be correlated to the lowest excited singlet energy of  $^1C_{60}^*(>>DPAF-C_2)$  and estimated to be 1.74–1.75 eV in  $CHCl_3$ . The fullereryl fluorescence intensity of **1a** was fully quenched in polar solvents including DMF and benzonitrile shown as the profiles (a) and (b) in the insert of Fig. 8. Large decrease in fluorescence of the fullerene moiety may indicate the occurrence of charge-separation due to electron transfer from DPAF- $C_2$  moiety to the fullerene cage via the singlet excited state  $^1C_{60}^*(>>DPAF-C_2)$  in polar solvents as determined by the transient spectroscopic measurements in nanosecond region.<sup>16</sup> Contrary phenomena were detected in non-polar solvent, such as toluene, using the same measurement demonstrating favorable energy transfer processes occurring from photo-excited DPAF- $C_2$  moiety to  $C_{60}$ . Accordingly, we assume similar energy transfer processes occurring during photo-excitation of **1a** in  $CHCl_3$  and  $CS_2$  for the detection of extended fluorescence emission above 720 nm corresponding to the energy of excited fullerene state. Comparable solvent-dependent fluorescence emission was recorded in fluorescence spectra of  $C_{60}(>>DPAF-C_9)$  **1b** upon 420 nm excitation in various solvents of  $CHCl_3$ ,  $CS_2$ , toluene, DMF, *o*-DCB, THF, and PhCN at a concentration of  $2.0 \times 10^{-5}$  M, as shown in Fig. 9. No fluorescence band above 700 nm was observed in DMF, PhCN, and THF indicating that these three solvents as a group exhibit similar fluorescence behavior of **1b** while toluene,  $CHCl_3$ , and  $CS_2$  representing the other group of the less polar solvents showing a fluorescence band centered at 704, 701, and 709 nm (the insert of Figs. 9c, 9d, and 9e), respectively, in an intensity relatively higher than those in Fig. 8 for **1a**. One explanation is made by the sufficient steric hindrance induced by two 3,5,5-trimethylhexyl groups attached at  $C_9$  carbon of the fluorene unit in the structure of **1b** resulting in aggregation inhibition and molecular stacking

difficulty of both fullerene cage and fluorene ring. This decreases the aggregation-induced fluorescence quenching effect making the band comparatively visible.

In the case of the bisadduct  $C_{60}(>>DPAF-C_9)_2$  **2b** containing one more DPAF- $C_9$  subunit than **1b**, its fluorescence spectra in all solvents, except  $CS_2$ , exhibited the DPAF- $C_9$  fluorescence band in intensity stronger than those of **1b**, as shown in Fig. 10. Specifically, a visible increase of peak intensity profile in  $CHCl_3$  (Fig. 10d) and *o*-dichlorobenzene (Fig. 10f) revealed incomplete fluorescence quenching of the DPAF- $C_9$  moieties by the fullerene cage, *via* energy transfer, in these solvents. We assume the cause of full fullereryl fluorescence suppression of **2b** in DMF, PhCN, and THF, similar to **1a**, arising from the formation of charge-separated states  $C_{60}^{\bullet-}$  and  $(>>DPAF-C_9)^{\bullet+}$ . A noticeable red shift of the peak maximum to 500–560 nm in all solvents, except toluene, was detected. That can be correlated to the decreased lowest excited singlet energy of  $C_{60}[>^1(DPAF-C_2)^*]_2$  at 2.48–2.21 eV, slightly lower than that of **1b**. Attachment of multiple hindered 3,5,5-trimethylhexyl groups in the structure of **2b** making direct intermolecular stacking contact of fullerene cages and diphenylaminofluorene rings more difficult. That may give better presentation of solvent-dependent molecular fluorescence characteristics. These results provide a better understanding on the use of highly fluorescent DPAF- $C_9$  addends as the antenna components for the construction of  $C_{60}(>>DPAF-C_9)_x$  starburst fullerene multiads to harvest light energy. As the photoinduced electron- and energy-transfer processes become crucial to the therapeutic method for photodynamic treatments, further investigation of these intramolecular phenomena in the molecular system of  $C_{60}(>>DPAF-C_n)_x$  facilitates their uses as one-photon or two-photon absorption-based photosensitizers.

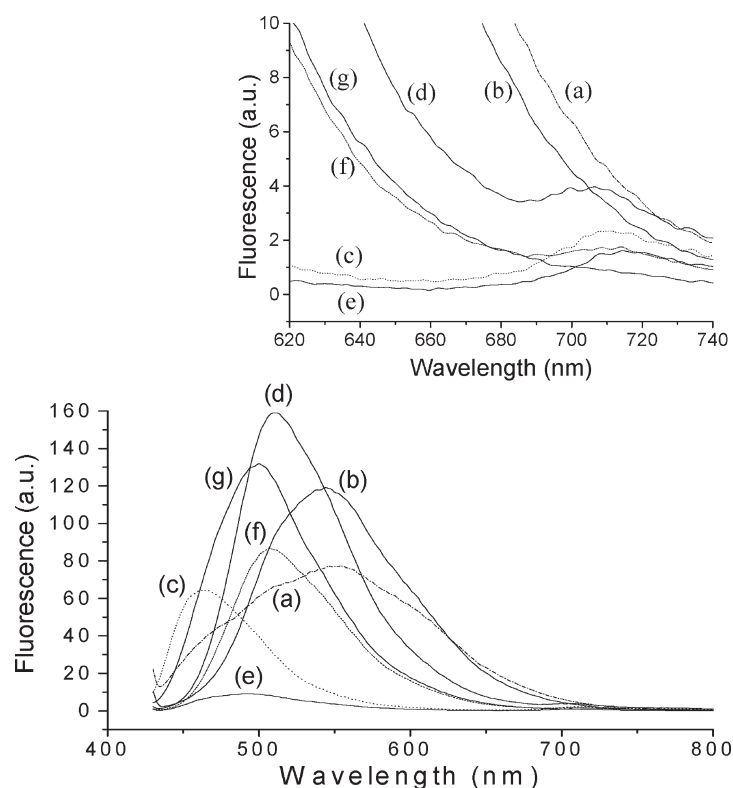
## Conclusion

Novel  $C_{60}$ -*keto*-acceptor structures as hindered 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene monoadduct of methano[60]fullerene  $C_{60}(>>DPAF-C_9)$  and the related bis-adducts  $C_{60}(>>DPAF-C_9)_2$  and  $C_{60}(>>DPAF-C_2)_2$  were synthesized. All  $C_{60}$ -DPAF derivatives were fully characterized with their chemical structure confirmed by various spectroscopic analyses. X-Ray structural analysis on a single crystal of  $C_{60}(>>DPAF-C_2)$  validated its structural composition and the basic molecular structure of similar dyads. Strong solvent-sensitive fluorescence quenching phenomena of  $C_{60}(>>DPAF-C_2)$ ,  $C_{60}(>>DPAF-C_9)$ , and  $C_{60}(>>DPAF-C_9)_2$  were observed, showing no  $C_{60}$ -based fluorescence band above 700 nm in DMF, PhCN, and THF as a group of the solvents exhibiting similar fluorescence behavior while toluene,  $CHCl_3$ , and  $CS_2$  representing the other group of the less polar solvents showing a fullereryl fluorescence band at 700–710 nm. It was attributable to the occurrence of electron transfer via the singlet excited state of the fullerene moiety as  $^1C_{60}^*(>>DPAF-C_n)$  in the former group of the solvents. Contrarily, energy transfer processes from DPAF- $C_n$  moiety to the fullerene cage are favored in the latter group of the solvents. These results appear to support our design rationale for these  $C_{60}$ -DPAF conjugates with the covalent attachment of diphenylaminofluorene



**Fig. 9** Fluorescence spectra of  $C_{60}(>>DPAF-C_9)$  **1b** upon 420 nm excitation in  $N_2$ -saturated solutions of (a) DMF, (b) PhCN, (c) toluene, (d)  $CHCl_3$ , (e)  $CS_2$ , (f) *o*-dichlorobenzene, and (g) THF in a concentration of  $2.0 \times 10^{-5}$  M.





**Fig. 10** Fluorescence spectra of  $C_{60}(>>DPAF-C_9)_2$  **2b** upon 420 nm excitation in  $N_2$ -saturated solutions of (a) DMF, (b) PhCN, (c) toluene, (d)  $CHCl_3$ , (e)  $CS_2$ , (f) *o*-dichlorobenzene, and (g) THF in a concentration of  $2.0 \times 10^{-5}$  M.

moiety to methano[60]fullerene *via* a keto linkage in terms of increased molecular polarization. The approach has recently resulted in an enhanced two-photon response of the corresponding compound  $C_{60}(>>DPAF-C_2)$  upon laser excitation at 800 nm in nanosecond region.<sup>3g</sup> Furthermore, high electron affinity of the fullerene moiety of  $C_{60}(>>DPAF-C_2)$  was also substantiated by its cyclic voltammograms displaying a reversible pattern of redox waves with the first, second, and third half-wave reduction potential  $E_1^{red}$ ,  $E_2^{red}$ , and  $E_3^{red}$  values recorded at  $-1.00$ ,  $-1.39$ , and  $-1.88$  V, respectively, vs  $Fc/Fc^+$ ,<sup>16</sup> in a close agreement to those of the parent  $C_{60}$  in  $CH_3CN$ -toluene ( $E_1^{red} = -0.98$ ,  $E_2^{red} = -1.37$ , and  $E_3^{red} = -1.87$  vs  $Fc/Fc^+$ ).<sup>21</sup> With highly fluorescent DPAF moiety functioning as the light harvesting unit and the  $C_{60}$  cage working as the electron accepting and transport unit, these new  $C_{60}(>>DPAF-C_n)_x$  materials may exhibit potential in photovoltaic and photodynamic treatment applications.

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