REPORT DOCUMENTATION PAGE

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1. REPORT DATE (DD-MM-YYYY) 31-05-2004
2. REPORT TYPE Final
3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE
Synthesis and Study of fullerene-based Photovoltaic and Two-photon Absorptive Conjugate Materials

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7. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. DISTRIBUTION /AVAILABILITY STATEMENT
Approve for Public Release: Distribution Unlimited.

10. SUPPLEMENTARY NOTES

11. ABSTRACT
We have achieved in the synthesis of several modified fluorened monoadducts of C60 showing high cross-sections of two-photon absorption (TPA). Conclusively, we substantiated our proposal that multi-adduct chromophore structures in close vicinity of the C60 cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced two-photon absorption optical properties. Accordingly for this study, several monoadducts and novel multiadduct analogues of C60-diphenylaminofluorene C60(DPAF)-derivatives were synthesized and characterized by various spectroscopic methods.

In summary, effective molecular TPA cross-sections of one branched alkyl derivative C60(DPAF-C2) in CS2 was found to be 2.51 \times 10^{-48} cm^4-sec/molecule, which is slightly higher than the TPA cross-sections value (196 \times 10^{-48} cm^4-sec/molecule) obtained for our first generation C60(DPAF-C2) monoadduct. It is more than double in the cross-sections of its parent linear DPAF analogue and in a comparable value with that of the current TPA benchmark octupolar analogue AF350 with \sigma_0^* = 278 \times 10^{-48} cm^4-sec/molecule. As the structure of C60-diphenylaminofluorene conjugate is extended from monoadduct to bisadduct analogous, effective molecular TPA cross-sections of C60(DPAF-C2) was found to be 622 \times 10^{-48} cm^4-sec/molecule. This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date.

12. SECURITY CLASSIFICATION OF:

13. LIMITATION OF ABSTRACT

14. NUMBER OF PAGES

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES

19. NAME OF RESPONSIBLE PERSON

19a. CONTRACT NUMBER
F49620-03-1-0334

19b. TELEPHONE NUMBER (Include area code)

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18
Synthesis and Study of fullerene-based Photovoltaic and Two-photon Absorptive Conjugate Materials

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SUMMARY OF REPORT

During the funded research period and extended period to early 2004, we have achieved in the synthesis of several modified fluoreted monoadducts of C₆₀ showing high cross-sections of two-photon absorption (TPA). Consequently, we substantiated our proposal that multi-adduct chromophore structures in close vicinity of the C₆₀ cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced two-photon absorption optical properties. Accordingly for this study, several monoadducts and novel multiadduct analogues of C₆₀-diphenylaminofluorene C₆₀(>DPAF)ₙ derivatives were synthesized and characterized by various spectroscopic methods.

In summary of measured TPA properties of C₆₀-diphenylaminofluorene conjugates, effective molecular TPA cross-sections of one branched alkyl derivative C₆₀(>DPAF-C₉) in CS₂ under a linearly polarized 800 nm pulsed beam was found to be 251 ×10⁻⁴⁸ cm⁴·sec/molecule, which is slightly higher than the TPA cross-sections value (196 ×10⁻⁴⁸ cm⁴·sec/molecule) obtained for our first generation C₆₀(>DPAF-C₂) monoadduct, reported previously. It is more than double in the cross-sections of its parent linear DPAF analogue. It is also in a comparable value with that of the current TPA benchmark for AFX series of chromophore, denoted as octupolar analogue AF350, which showed σ₂' = 278 ×10⁻⁴⁸ cm⁴·sec/molecule at 800 nm pumping in THF. As the structure of C₆₀-diphenylaminofluorene conjugate is extended from monoadduct to bisadduct analogous, effective molecular TPA cross-sections of C₆₀(>DPAF-C₉)₂ in CS₂ under a linearly polarized 800 nm pulsed beam was found to be 622 ×10⁻⁴⁸ cm⁴·sec/molecule. This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date. The effective molecular TPA cross-sections value increases significantly by a factor of nearly 2.5 from that of C₆₀(>DPAF-C₉). We propose hypothetically that a certain degree of hyperconjugation between of the C₆₀ cage and the extended π-orbital of keto-DPAF moieties may make effective large area coverage of TPA cross-sections.

Optical absorption of these samples indicated a systematic increase in relative intensity of the fluorene band centered at 415 nm as the number of DPAF addend increases. Fluorescence of diphenylaminofluorene chromophore in all C₆₀(>DPAF)ₙ derivatives as n = 1, n = 2, n = 3, and n = 4 in o-dichlorobenzene and chloroform was found to be efficiently quenched as the direct covalent bond attachment of diphenylaminofluorene moieties to the fullerene cage facilitates efficient intramolecular electron or energy transfer processes.
In regard to optical limiting measurements of diphenylaminofluorene monoadduct of fullerene C_{60}(>DPAF-C_{18}) using a laser source at 532 nm with a 10 ns pulse, we observed the occurrence clear non-linear optical absorption behavior at the on-set incident laser power intensity of 100 MW/cm^2. The initial transmittance of the solution is roughly 55–60%. As the incident power intensity increases above 100 MW/cm^2, the transmitted power intensity is not linearly proportional to the incident intensity. The deviation progressively lowered the transmittance to 30% at the incident power intensity of 1200 MW/cm^2 that allowed a transmitted power intensity of 400 MW/cm^2.

**STATEMENT OF OBJECTIVES**

This research project focuses mainly on (A) the design and synthesis of fullerene-based two-photon absorptive (TPA) conjugate materials for sensor and personnel protection applications with a minor effort on (B) the design and synthesis of starburst fullerene-linked conjugated oligomer for grafting on the surface of interconnected TiO_2 nanoparticles toward fabrication of photovoltaic cells and modules. In the event of sufficient funding provided, we will increase the research activity of photovoltaic study using C_{60} derivatives as acceptors in conjunction with TiO_2 materials.

In the first subject of objective, we design and synthesize fullerene-based two-photon absorptive conjugated unsymmetrical starburst and dendritic macromolecules aiming to increase the dimensionality of two-photon absorption chromophore moiety. The first phase of the approach involves synthesis of several monoadduct and bisadducts of C_{60}-diphenylaminodiethylfluorene (C_{60}-DPAF) conjugates. In the next phase of the project, we will extend the synthetic work into the preparation of more complex trisadducts and tetrakisadducts of C_{60}-diphenylaminodiethylfluorene conjugates. That makes the C_{60} cage as an effective dimensionality coordinator and linker of highly condensed and packed diphenylaminodiethylfluorene moiety in 3D. The compound consists of direct bonding of multiple TPA absorptive chromophores on a C_{60} cage resulting in a starburst structure. The synthesis requires modified fullerene chemistry to be developed for providing conjugative chemical bonding between fluorene subunits and the fullerene cage. Coupling of fullerene π-orbitals with electron-accepting (A) characteristics, and the π-electron-donating (D) diphenylaminodiethylfluorene moieties produces 3-D (D_1)n-A-(D_2)m macromolecules.

Extension of the C_{60}-DPAF structure from linear to starburst should progressively enhance the solubility of resulting conjugates. If D_1 is well-defined monoadduct (n = 1), the total proton integration of D_2 moieties over the proton integration ratio of the D_1 moiety will allow us to determine the number of n and m in the isolated product of (D_1)n-A-(D_2)m macromolecules, using ^1H NMR spectroscopic method.

Upon modification of D_1 and D_2 DPAF moieties to incorporate long alkyl chains and highly branched alkyl chains, the softening temperature of the resulting (D_1)n-A-(D_2)m...
macromolecules may be lowered into a range of 60–80 °C for easy processing of coating. High enthalpy uptake at the thermal melting transition may be used to enhance the heat dispersion upon sharp heating-up of the film material by an external laser power source.

Utilization of symmetrical octahedral hexamethofullerene as a connecting center allows us to design a single macromolecule of starburst C_{60}(DPAF)_6 or 12. The use of hexanitrofullerene as a precursor core for attaching 6 TPA-active arms should lead to unsymmetrical starburst macromolecules for inhibiting ordered packing of TPA moieties in the solid state. All these C_{60}-DPAF dyes are ideal for systematic study of structure-property relationship, the number density, spatial effect, and synergistic interactions, as cooperative effect, of individual TPA-responsive subunits within the 3-D molecular systems.

Based on our recent study on the photoinduced transient spectroscopy of C_{60}-DPAF monoadduct, solvent-dependent behavior of both intramolecular electron-transfer and energy-transfer from photoexcited DPAF moiety to the C_{60} cage was observed. Application of these phenomena based on (D_1)_(n)-A-(D_2)_(m) macromolecules may include photodynamic therapy, drug delivery, and electrooptical devices.

**RELATED MATERIALS APPLICATIONS**

At least two types of optical physical properties of C_{60}-DPAF, conjugates were studied.

**(A) Two-photon absorption properties** of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-(3,5,5-trimethylhexyl)-2-diphenylaminofluorene monoadduct [C_{60}(>DPAF-C_9)] and bisadduct C_{60}(methanocarboxyl-9,9-(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)₂ [C_{60}(>DPAF-C_9)₂].

As an effort to reduce the melting point of the two-photon absorbing material and minimize the dimerization or aggregation of the fullerene-DPAF conjugates, we modify the structure to used branched 3,5,5-trimethylhexyl groups for increasing the steric hindrance around the planar DPAF moiety.

As shown in the Scheme 1, the synthetic route included preparation of the key intermediate 7-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene 4 from 7-bromo-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene 3. Synthesis of α-bromoacetyl-diphenylaminofluorene 4 was found to be effective using direct Friedel-Crafts acylation of the compound 3 with α-bromoacetyl bromide (1.2 equiv.) in presence of aluminum chloride (1.1 equiv.). This reaction was carried out in 1,2-dichloroethane at 0 °C to ambient temperature for a period of 4.0 h to afford the yellow crystalline product of 4 in a roughly 65% yield. Subsequent Bingel cyclopropanation reaction of α-bromoacetylfluorene derivative 4 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 h led to formation of isomerically pure [6,6] closed fullerene monoadduct 5 of 7-(1,2-dihydro-
Scheme 1. Reagents and synthetic conditions: i, Et–I, NaOH, TBA–Br, toluene, 60 °C, 8 h; ii, diphenylamine, tris(dibenzylideneacetone)dipalladium(0) (cat), rac-BINAP (cat), t-BuONa, toluene, 110 °C, 8 h; iii, bromoacetyl bromide, AlCl₃, ClCH₂CH₂Cl, 0 °C to r.t., 4 h; iv, C₆₀, DBU, toluene, r.t., 5 h.
1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene [C_{60}(>DPAF-C_9)] as greenish brown solids in 70 % yield (based on recovered C_{60}). This reaction also accompanied with the corresponding bisadduct 6 of C_{60}(methanocarbonyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)_2 [C_{60}(>DPAF-C_9)_2] as brownish solids in a minor quantity of roughly 10%. Separation of 5 (R_f = 0.6) and 6 (R_f = 0.3) was carried out via thin-layer chromatography (TLC, SiO_2) using a solvent mixture of hexane:toluene/3:2 as eluent.

Table 1. Measured TPA cross-section values by using a pulsed tunable dye laser working at 800 nm and ~8 ns laser pulses.*

<table>
<thead>
<tr>
<th>Chromophore / solvent</th>
<th>(\lambda_{\text{max}}/\text{nm} ) (linear absorption)</th>
<th>(\sigma_2 \times 10^{-20} \text{ cm}^4/\text{GW-molecule} )</th>
<th>(\sigma_2^* \times 10^{-48} \text{ cm}^4/\text{sec-molecule} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF350 / THF</td>
<td>400</td>
<td>112</td>
<td>278</td>
</tr>
<tr>
<td>C_{60}(&gt;DPAF-C_9) / CS_2</td>
<td>410</td>
<td>102</td>
<td>251</td>
</tr>
<tr>
<td>C_{60}(&gt;DPAF-C_9)_2 / CS_2</td>
<td>410</td>
<td>251</td>
<td>622</td>
</tr>
<tr>
<td>C_{60}(&gt;DPAF-C_9) / THF</td>
<td>41.1</td>
<td>102</td>
<td></td>
</tr>
</tbody>
</table>

* Experimental uncertainty ±15%. The measurements were made by Guang S. He, Qingdong Zheng, Changgui Lu, and Paras N. Prasad at Institute for Lasers, Photonics and Biophotonics, SUNY, Buffalo.

Effective TPA cross-section values of 5, 6, and AF-350 in a solution concentration of 0.02 M were obtained by measuring the nonlinear transmissivity of a given sample as a function of the intensity of the input laser beam. The beam was provided by a pulsed tunable dye laser working at ~800 nm wavelength, ~8 ns pulse duration, and 10 Hz repetition rate. An optical path-length of 1.0 cm was applied. As a result, molecular two-photon absorption cross-sections \(\sigma_2\) in an unit of \(\text{cm}^4/\text{GW-molecule}\) were obtained from the nonlinear absorption coefficient \(\beta\) of the sample. As shown in Table 1, an effective molecular TPA cross-sections value of \(102 \times 10^{-48} \text{ cm}^4/\text{sec-molecule}\) for C_{60}(>DPAF-C_9) 5 in THF under a linearly polarized 800 nm pulsed beam was obtained. It correlated to a lower solubility of 5 in THF that gave some scatterings at a high concentration of 0.02 M. Possible aggregation of 5 in THF into nanoparticles can not be ruled out.

Interestingly, effective molecular TPA cross-sections \(\sigma_2^* = h\nu\sigma_2\) of C_{60}(>DPAF-C_9) 5 in CS_2 under a linearly polarized 800 nm pulsed beam was found to be \(251 \times 10^{-48} \text{ cm}^4/\text{sec-molecule}\), which is slightly higher than the TPA cross-sections value \((196 \times 10^{-48} \text{ cm}^4/\text{sec-molecule})\) obtained for our first generation C_{60}(>DPAF-C_2) monoadduct, reported previously. It is more than double in the cross-sections of its parent linear DPAF analogue.
Table 2. Measured TPA cross-section values by using a pulsed tunable dye laser working at 775 nm and ~160 fs laser pulses.

<table>
<thead>
<tr>
<th>Chromophore/solvent</th>
<th>$\lambda_{\text{max}}$/nm (linear absorption)</th>
<th>$\sigma_2$ ($\times 10^{-20}$ cm$^4$/GW-molecule)</th>
<th>$\sigma_2'$ ($\times 10^{-48}$ cm$^4$/sec/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF350 / THF</td>
<td>400</td>
<td>0.600</td>
<td>1.49</td>
</tr>
<tr>
<td>C$_{60}$($&gt;$DPAF-C$_9$) / CS$_2$</td>
<td>410</td>
<td>0.123</td>
<td>0.306</td>
</tr>
<tr>
<td>C$_{60}$($&gt;$DPAF-C$_9$)$_2$ / CS$_2$</td>
<td>410</td>
<td>0.332</td>
<td>0.824</td>
</tr>
</tbody>
</table>

Under similar measurement conditions for the consistency in comparison of materials optical properties, a comparable data of 5 with those of several good TPA chromophores, such as the octupolar analogue AF350 showing $\sigma_2' = 278 \times 10^{-48}$ cm$^4$-sec/molecule at 800 nm pumping in THF, was made. As AF-350 being the current TPA benchmark for AFX series of chromophore, TPA characteristics of the linear A-$sp^3$-D monoadduct of C$_{60}$-DPAF 5 in the nanosecond regime are apparently approaching one of the best candidates for the TPA based technology evaluation. Since the number density is a significant factor in enhancing the TPA cross-sections, the fullerene cage should serve well as a nucleus center of the fluorene dye in increasing the dimensionality. Furthermore, this result also suggests that C$_{60}$ with multiple DPAF branches may lead to similar interactions reported for a three-armed oxadiazole-triarylamine system similar to AF-350.

Accordingly, effective molecular TPA cross-sections of C$_{60}$($>$DPAF-C$_9$)$_2$ 6 in CS$_2$ under a linearly polarized 800 nm pulsed beam was found to be $622 \times 10^{-48}$ cm$^4$-sec/molecule. This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date. Apparently, by extending from the monoadduct analogous of fullerene to its bisadduct analogous, the effective molecular TPA cross-sections value increase significantly by a factor of nearly 2.5. We propose hypothetically that a certain degree of hyperconjugation between of the C$_{60}$ cage and the extended $\pi$-orbital of two keto-DPAF moieties may make effective large area coverage of two-photon absorption cross-sections. The result substantiated our proposal that multi-adduct chromophore structures in close vicinity of the C$_{60}$ cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced TPA optical properties.

**Optical limiting properties** of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-cobynyl)-9,9-diocotadecanyl-2-diphenylaminofluorene monoadduct [C$_{60}$($>$DPAF-C$_{18}$)].

Optical limiting measurements of C$_{60}$-DPAF conjugates were made using a sample of diphenylaminofluorene monoadduct of fullerene C$_{60}$($>$DPAF-C$_{18}$) and a laser source at 532 nm with a 10 ns pulse. The experiments were performed in THF solution at incident laser power
intensity in the range of 0.1 to 1.2 $\times 10^3$ MW/cm$^2$ at U.S. Army Soldier, Biological, Chemical Command, Natick Soldier Center, Massachusetts.

The compound of $C_{60}(>\text{DPAF-C}_{18})$ was synthesized using a similar reaction sequence scheme shown in Scheme 1 involving Friedel-Crafts acylation of 7-bromo-9,9-dioctadecanyl-2-diphenylaminofluorene with $\alpha$-bromoacetyl bromide in presence of aluminum chloride and Bingel cyclopropanation reaction of the resulting $\alpha$-bromoacetylfluorene derivative with $C_{60}$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Purification of $C_{60}(>\text{DPAF-C}_{18})$ was made by the chromatographic method (SiO$_2$, toluene-THF).

As a result, we observed the occurrence clear non-linear optical absorption behavior at the on-set incident laser power intensity of 100 MW/cm$^2$. The initial transmittance of the solution is roughly 55–60%. As the incident power intensity increases above 100 MW/cm$^2$, the transmitted power intensity is not linearly proportional to the incident intensity. The deviation progressively lowered the transmittance to 30% at the incident power intensity of 1200 MW/cm$^2$ that allowed a transmitted power intensity of 400 MW/cm$^2$. Reproducible optical limiting behavior of at least two other samples of $C_{60}$-diphenylamino-dialkylfluorene ($C_{60}$-DPAF) conjugates was obtained very recently. These preliminary results indicated the possibility of formulating processible optical limiting polymer composites containing dispersion of $C_{60}$-DPAF conjugates. The use of double long octadecanyl side chains on the diphenylaminofluorene moiety decreases significantly solid characteristics of the material. Accordingly, semi-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1a.png}
\caption{Optical limiting characteristics of $C_{60}(>\text{DPAF-C}_{18})$ at the maximum incident laser power intensity of $1.0 \times 10^3$ MW/cm$^2$. Measurements were carried out by Dr. Brian Kimball, U.S. Army Soldier, Biological, Chemical Command, Natick Soldier Center, Massachusetts.}
\end{figure}
solid paste of C₆₀(>DPAC-C₁₈) in the presence of a small portion of octadecane can be made at ambient temperature. Further study on the formulation of C₆₀(>DPAC-C₁₈) for producing the corresponding optical limiting liquid will be pursued.

![Graph showing transmitted intensity vs. incident intensity.](image)

**Figure 1b.** Optical limiting characteristics of C₆₀(>DPAC-C₁₈) at the maximum incident laser power intensity of 1.2 x 10³ MW/cm².

INTRODUCTION OF SYNTHETIC DESIGN

Intermolecular and intramolecular electron transfer processes in functionalized fullerenes¹⁻⁶ were widely studied with the C₆₀ cage as a potent electron acceptor in donor-acceptor assemblies, by taking advantage of its unique spherical shape for 3D attachments, electron delocalization capability, high chemical reactivity for functionalization, and rich electrochemical redox properties⁷⁻¹³. A variety of phorphyrin analogue donor moieties in conjugation with C₆₀ ⁴⁻¹⁸ forming the corresponding dyads were synthesized and widely explored for the study of photoinduced electron or energy transfer phenomena between donor and acceptor components, whereas the use of highly fluorescent diphenylnaphthofluorene (DPAC) in conjugation with C₆₀ for the similar investigation was only recently reported ¹⁹, ²⁰ by us. In addition, diphenylnaphthofluorene chromophore with large two-photon cross-sections can be utilized in photonic applications. High photostability of the fullerene cage may be advantageous in the photonic applications where a high intensity light source is used. Challenges are to increase the molecular two-photon cross-sections, without shifting the two-photon absorption peak away much from 800 nm, and the effective high TPA concentration in medium or density in solid state without inducing strong π-π interaction stacking of chromophores.

Our study addresses the utilization of DPAC as a donor moiety acting as an antenna component for efficient light harvesting at visible wavelengths. That leads to the synthetic study
for preparation of several C₆₀-derived two-photon absorbing dendritic and starburst macromolecules to cooperatively enhancing the cross-sections value. Structure of these fullerene derivatives incorporates modified analogous of diphenylaminodiethylfluorene-based moieties. Combination of the C₆₀ capability to exhibit reverse-saturable absorption in the visible region and the optical absorption of DPAF materials in the near-IR region may provide fundamental insights on the design of new and robust, broadband nanophotonic materials. Direct chemical bonding of multiple DPAF derivatives on a C₆₀ cage forming a spherical star-like structure may enhance the overall cross-section of two-photon absorption and reduce the ability of TPA chromophores to aggregate orderly. The coupling of fullerenic π-orbitals with electron-accepting (A) characteristics and the π-electron-donating (D) diphenylaminodiethylfluorene moieties produces a 3-D system of (D)ₙ-A-(D)ₙ.

Accordingly, we observed the first two-photon absorbing characteristics [19] of a C₆₀-DPAF conjugate linked by a keto functional group, in close resemblance to those reported for DPAF fluorophore-based 2D and 3D structures.[21-24] In addition, triarylamine derivatives usually bear a role of hole-transport mechanism in organic electroluminescent display devices.[25, 26] It is thus of our great interest to examine C₆₀-DPAF dyads in a donor-acceptor assembly using DPAF as a polarizable π-electron donor with inherent thermal and photochemical stability. This type of molecular assemblies may lead to potential applications in two-photon absorption based optoelectronics, organic light emitting diodes,[27] field-induced effect transistors,[28] and photovoltaic devices.[29, 30]

The first linear dyad, 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene as C₆₀(>DPAF), was found to be a highly two-photon absorbing chromophore with large cross-sections.[19] According to the hypothesis made in recent reports [22] on several DPAF related derivatives, enhancement of two-photon absorption cross-sections can be realized as their dimensionality is progressively increased. We investigate this analogy by the synthesis of several C₆₀(>DPAF)ₙ conjugates with a systematic increase of the number of DPAF addends per C₆₀ cage to postulate a simulation of the corresponding dimensional increase with the multiaddend attachment, followed by the measurement of their two-photon absorption cross-sections. Multidimensional C₆₀(>DPAF)ₙ derivatives with enhanced two-photon absorption cross-sections may encompass important biological significance and lead to the development of technology related to photodynamic therapy, fluorescence bio-imaging, 3D optical data storage, and optical power limiting. In this article, we report the synthesis, material characterization, optical absorption, and fluorescence measurements of a linear C₆₀-DPAF dyad 4 and several fullerene derivatives 5, 6 and 7 with multiple DPAF addends, showing effective quenching of the most of DPAF fluorescence.
RESULTS AND DISCUSSION ON SYNTHETIC MATERIAL PREPARATION

Synthetic procedure of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene monoadduct [4, C₆₀(DPAF)] is outlined in Scheme 2. Starting synthon 1 was conveniently synthesized by a reported procedure [21] starting from fluorene. It involved diethylolation of fluorene at the C₉ carbon position using ethylbromide as a reagent to give 9,9-diethylfluorene. Subsequent monobromination of 9,9-diethylfluorene with N-bromosuccinimide afforded 2-bromo-9,9-diethylfluorene. Iodination of 2-bromo-9,9-diethylfluorene with iodic acid to 2-bromo-7-ido-9,9-diethylfluorene was further converted to 7-bromo-9,9-diethyl-2-diphenylaminofluorene 1 via copper catalyzed amination reaction with diphenylamine.

\[ \text{Scheme 2. Reagents and the reaction condition, ia, Mg, } \alpha\text{-bromoacetyl bromide, THF; ib, } n\text{-butyllithium, } \alpha\text{-bromoacetyl bromide, THF; ic, } n\text{-butyllithium, THF, NH₄Cl; ii, AlCl₃, } \alpha\text{-bromoacetyl bromide, 1,2-dichloroethane; iii, C₆₀, DBU, toluene.} \]

The basis of the synthetic scheme to the product 4 relies on preparation of the key intermediate 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene 3 from 7-bromo-9,9-diethyl-2-diphenylaminofluorene 1. Effort to convert the compound 1 to 3 was made using bromide-
lithium metathesis with n-ButLi as a reagent at -78 °C followed by treatment of the resulting 7-lithium-2-diphenylamino-9,9-diethylfluorene with α-bromoacetyl bromide at low temperatures to replace the more reactive bromide atom. Alternatively, a Grignard complex was used instead of the lithium reagent. It was prepared from 1 with magnesium and subsequent treatment of the resulting Grignard intermediate with bromoacetyl bromide. In both cases, the reaction failed to give the expected product 3, protonated 9,9-diethyl-2-diphenylaminofluorene 2 was formed instead. Apparently, the α-proton of α-bromoacetyl bromide is readily removed by either lithium or Grignard reagent. Structure of the product 2 was confirmed by its FAB mass spectrum showing the molecular ion at m/z 389 and the corresponding fragmentation pattern. This spectrum is identical to that of 2 obtained by the quenching reaction of 7-lithium-2-diphenylamino-9,9-diethylfluorene intermediate with ammonium chloride. Synthesis of α-bromoacetyl diphenylaminofluorene 3 was found to be effective using direct Friedel-Crafts acylation of the compound 2 with α-bromoacetyl bromide (1.2 equiv.) in presence of aluminum chloride (1.1 equiv.). This reaction was carried out in 1,2-dichloroethane at 0 °C to a ambient temperature for a period of 4.0 h to afford the yellow crystalline product of 7-bromoacetyl-9,9-

Figure 2. 1H NMR spectra of the starting α-bromoacetyl diphenylaminofluorene derivative 3 and C₆₀(>DPAF) monoadduct 4 in CDCl₃.

diethyl-2-diphenylaminofluorene 3 in a roughly 66% yield.

Compound 3 showed a characteristic infrared band centered at 1674 cm⁻¹ in the FT-IR spectrum corresponding to the optical absorption of carbonyl stretching in 3 indicating attachment of α-bromoacetyl group on the fluorine moiety. The molecular mass of 3 was confirmed by its positive ion mass spectrum (FAB⁺-MS) showing a group of molecular ion peaks with a maximum peak intensity at m/z 509 and 511. Subsequent Bingel cyclopropanation [31] reaction of α-bromoacetylfluorene derivative 3 with C₆₀ in toluene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv.) at ambient temperature for 5 h led to
formation of isomerically pure [6,6] closed fullerene monoadduct 4 of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene \([C_{60}(\text{DPAF})]\) as greenish brown solids in 71 % yield (based on recovered \(C_{60}\)). This reaction also accompanied with the corresponding bisadduct 5 of \(C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_2 \ [C_{60}(\text{DPAF})_2]\) as brownish solids in a minor quantity of roughly 11%. Separation of 4 \((R_f = 0.6)\) and 5 \((R_f = 0.3)\) was carried out via thin-layer chromatography (TLC, SiO\(_2\)) using a solvent mixture of hexane:toluene/3:2 as eluent.

The compound \(C_{60}(\text{DPAF})\) showed a strong absorption band of carbonyl stretching centered at 1677 cm\(^{-1}\) with typical fullerene derivative signals at 750, 695 and 534 cm\(^{-1}\) in FT-IR spectrum, consistent with the ketone formation that bridges fluorene and fullerene moieties. Observation of a group of mass peaks with a maximum peak intensity centered at \(m/z\) 1149 in negative ion desorption chemical ionization mass spectrum (DCl–MS) of 4 clearly provides evidence of the molecular ion and composition of fullerene-fluorene dyad 4.

![CH & CH\(_2\)
CH\(_2\)
CH
All Carbons](image)

**Figure 3.** \(^{13}\)C–DEPT NMR spectrum of methanofullerene-diphenylaminofluorene dyad \(C_{60}(\text{DPAF})\) 4 in CDCl\(_3\).

\(^1\)H NMR spectra of 3 and 4 in CDCl\(_3\) exhibits the expected features with correct integration ratios as shown in Fig. 2. The corresponding spectrum of compound 3 shows one singlet proton peak at \(\delta 4.49\), corresponding to two methylene protons of \(\alpha\)-bromoacetyl group, and several
groups of aromatic proton peaks at δ 7.65 (d, J = 8 Hz), 7.95 (dd, J = 8 Hz, J = 1.6 Hz) and 7.92 (d, J = 1.4 Hz) corresponding to the chemical shift of the protons located at C_5, C_6, and C_8 atoms, respectively, of the fluorene moiety. Further reaction of 3 with C_{60} to 4 caused a clear large downfield chemical shift of the α-proton adjacent to the carbonyl group to δ 5.69, appearing as a singlet peak. It also accompanied with downfield chemical shifts of most of other fluorene protons at C_5, C_6, and C_8 to δ 7.83 (d, J = 8 Hz), 8.48 (dd, J = 8 Hz, J = 1.6 Hz), and 8.32 (d, J = 1.6 Hz), respectively, due to influence of the π-electronic structure of the fullerene cage. 13C-DEPT NMR spectrum of 4 (Fig. 3) showed a characteristic carbonyl carbon peak appearing at δ 189.5 and terminal methyl and methylene carbon peaks at δ 8.6 and 32.5, respectively, corresponding to ethyl groups attached at C_9 consistent with the structure of 4. All sp^2 fullerene carbons appear as a total of 28 peaks in the region of δ 136 to δ 147 with two sp^3 fullerene carbon peaks appearing at δ 72.6, indicating clearly a C_2 symmetry axis along the plane of two sp^3 fullerene carbons. Those are 13C NMR characteristics of typical methano[60]fullerene monoadducts confirming the overall structure of dyad 4.

![Graph](image)

**Figure 4.** UV-Vis absorption spectra of the parent diphenylaminofluorene derivative 3, C_{60}(>DPAF) monoadduct 4, and the fullerene core as C_{60}(>COOEt)_2] in chloroform at a concentration of 2.0 x 10^{-5} M.

UV-Vis absorption spectrum (Fig. 4) of C_{60}(>DPAF) dyad 4 showed three strong absorption bands centered at 259, 327 and 410 nm. Two of these bands centered at 259 and 327 nm are assigned to the optical absorption of the fullerene cage based on the comparison with that of methano[60]fullerene monomalonate diethylester C_{60}(>COOEt)_2] while the third band centered at 410 nm is attributed to the DPAF moiety. The assignment reveals domination of the
optical absorption of the fullerene cage in the UV region whereas the optical absorption of DPAF covers the visible region. Therefore, optical spectrum of the dyad 4 is a virtual superimposition of absorptions independently contributed from two chromophore moieties present in the molecule, indicating no appreciable ground state electronic interaction between two $\pi$-conjugated systems separated by a $sp^3$ carbon.

In a solution of o-dichlorobenzene, DPAF 3 dye displays a strong fluorescence maximum centered at 497 nm (Fig. 5) upon photoexcitation at 385 nm. Under the same photoexcitation conditions and solution concentration, the emission spectrum of C$_{60}$ and dyad 4 shows no and only an insignificant residual fluorescence, respectively, covering from 420 to 550 nm, as shown in the inset of Fig. 5. The observation indicated a nearly quantitative quenching of the DPAF fluorescence by the fullerene cage due to possible intramolecular electron or energy transfer processes. Efficiency of these processes decreases in the mixture of compound 3 and C$_{60}$ in an equal molar quantity, as shown by the reduction in intensity of fluorescence maximum at 497 nm to 50% of the parent value without C$_{60}$. Intermolecular electron or energy transfer processes involve a biomolecular collision and are concentration dependent. Direct attachment of DPAF moieties onto one C$_{60}$ cage increases the efficiency and kinetic rate of these transient processes. Interestingly, a weak fluorescence band of dyad 4 centered around 714 nm (inset of Fig. 5), which is the emission characteristic of methano[60]fullerene derivatives, was detected that may reveal the existence of neutral (uncharged) ground state of the fullerenic moiety.

![Fluorescence emission profile of diphenylaminofluorene derivative 3, C$_{60}$(>DPAF) monoadduct 4, C$_{60}$, and (C$_{60} + 3$) upon photoexcitation at 385 nm in o-dichlorobenzene at a concentration of 2.0 x 10$^{-5}$ M.](image)

**Figure 5.** Fluorescence emission profile of diphenylaminofluorene derivative 3, C$_{60}$(>DPAF) monoadduct 4, C$_{60}$, and (C$_{60} + 3$) upon photoexcitation at 385 nm in o-dichlorobenzene at a concentration of 2.0 x 10$^{-5}$ M.
Characterization of the $C_{60}$(>DPAF)$_2$ bisadduct 5 was performed using the negative ion desorption chemical ionization mass spectroscopic study. The DCl–MS spectrum showed a group of mass peaks with a peak maximum at $m/z$ 1579 corresponding to the molecular ion mass of 5 consisting of two DPAF addends per $C_{60}$ cage. Synthesis of $C_{60}$-DPAF conjugates containing a higher number of DPAF addends than 2 was performed by the treatment of $C_{60}$ molecules with 8 equivalents of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene 3 in presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. Reaction progress was constantly monitored by taking samples for the TLC examination on sequential change of fullerene derivatives. Evidently, disappearance of $C_{60}$ in the solution mixture was detected after 10 min of the reaction with systematic increase in intensity of two TLC spots corresponding to the monoadduct of $C_{60}$(>DPAF) and the bisadduct of $C_{60}$(>DPAF)$_2$ derivatives with lower chromatographic polarity for the former. Intensity of these spots gradually decreased to an insignificant value after 6 h of the reaction. It accompanied with a number of new TLC spots in higher chromatographic polarity. The latter chromatographic profile remained almost constant even up to 36 h of the reaction. After a standard workup procedure, the crude products comprising of a mixture of $C_{60}$-DPAF conjugated derivatives were subjected to purification by repetitive preparative thin layer chromatographic (PTLC) separations until a narrow chromatographic band being isolated.

![Figure 6](image)

**Figure 6.** UV-Vis spectrum of 3, $C_{60}$(>DPAF) 4, $C_{60}$(>DPAF)$_2$ 5, $C_{60}$(>DPAF)$_3$ 6, and $C_{60}$(>DPAF)$_4$ 7 in a concentration of 2 x 10^{-5} M in chloroform.

By using this separation technique, at least two major product bands were isolated for further characterization using negative ion desorption chemical ionization mass spectroscopic measurements. As a result, the DCl–MS spectrum of the product isolated from a narrow upper
band showed a group of mass peaks with a peak maximum at \( m/z \) 2009 corresponding to the molecular ion mass of \( \text{C}_{60}(\text{methanocarboxyl-9,9-diethyl-2-diphenylaminofluorene})_3 \) 6 as \( \text{C}_{60}(\text{DPAF})_3 \), consisting of three DPAF addends per \( \text{C}_{60} \) cage. The second narrow band led to a product showing a group of mass peaks with a peak maximum at \( m/z \) 2437 corresponding to the molecular ion mass of \( \text{C}_{60}(\text{methanocarboxyl-9,9-diethyl-2-diphenylaminofluorene})_4 \) 7 as \( \text{C}_{60}(\text{DPAF})_4 \), consisting of four DPAF addends per \( \text{C}_{60} \) cage. Several additional PTLC bands with higher chromatographic polarity were also isolated each in a small quantity. However, no conclusive DCM–MS data was obtained.

![Graph](image)

Figure 7. Fluorescence spectra of 3, \( \text{C}_{60}(\text{DPAF})_3 \) 4, \( \text{C}_{60}(\text{DPAF})_2 \) 5, \( \text{C}_{60}(\text{DPAF})_3 \) 6, and \( \text{C}_{60}(\text{DPAF})_4 \) 7 in chloroform upon photoexcitation at 385 nm under a concentration of 2 x 10^{-5} M.

\(^1\text{H} \text{NMR spectra of both trisadduct } \text{C}_{60}(\text{DPAF})_3 \text{ and tetraakisadduct } \text{C}_{60}(\text{DPAF})_4 \text{ showed broadening of all proton peaks with an increase in number of aliphatic and aromatic proton peaks. Especially, multiple peak characteristics of } \alpha \text{-proton adjacent to the carbonyl group of 6 and 7 may reveal a mixture of regioisomers in these products. Attempts are underway to separate a single regioisomer from 6 and 7 for the structural identification. } \text{UV-Vis spectra of bisadduct } \text{C}_{60}(\text{DPAF})_2, \text{ trisadduct } \text{C}_{60}(\text{DPAF})_3, \text{ and tetraakisadduct } \text{C}_{60}(\text{DPAF})_4 \text{ are shown in Fig. 6, giving a similar optical absorption wavelength of DPAF moieties to that of monoadduct 4 centered at 410 nm. Evidently, as the number of DPAF addends per } \text{C}_{60} \text{ cage increases in the corresponding derivatives going from monoadduct } \text{C}_{60}(\text{DPAF}) \text{ to tetraakisadduct } \text{C}_{60}(\text{DPAF})_4, \)
extinction coefficients of the visible absorption band at 410 nm increases systematically to a higher value while the sum of overall extinction coefficients of the UV bands corresponding to the optical absorption of fullerene moiety remaining relatively constant among 4, 5, 6, and 7. As the extinction coefficient of UV-Vis absorption bands is proportional to the concentration of absorbent moiety in the solution, a proportional increase in absorption intensity of the DPAF band may allow us to correlate the number of DPAF addends per C_{60} cage among derivatives of 4, 5, 6, and 7 and substantiate their composition. As shown in Fig. 7, fluorescence emission spectra of 3, C_{60}(>DPAF) 4, C_{60}(>DPAF)_{2} 5, C_{60}(>DPAF)_{3} 6, and C_{60}(>DPAF)_{4} 7 all showed efficient fluorescence quenching of diphenylaminofluorene chromophore centered at 497 nm in chloroform upon photoexcitation at 385 nm.

EXPERIMENTAL AND SYNTHETIC PROCEDURE

Fluorene was purchased from Aldrich Chemicals. All other chemicals were purchased from Acros Ltd. A C_{60} sample in a purity of 99.5% was used. Further purification of C_{60} was made by thin-layer chromatography (TLC, SiO_{2}, toluene). Toluene and benzene were dried and distilled over sodium. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker Spectrospin-400 or Bruker AC-300 spectrometer. Mass spectroscopic studies were performed either by use of the positive ion fast atom bombardment (FAB^+) technique with a direct probe on a JEOL SX-102A mass spectrometer or the negative ion desorption chemical ionization (DCI^-) technique with a direct probe on a JEOL JMS-SX 102A mass spectrometer. 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. Fluorescence spectra were recorded on a FLUOROLLOG (ISA Instruments) spectrofluorometer.

Synthesis of 9,9-diethyl-2-diphenylaminofluorene (2)

To a cooled solution (~78 °C) of 7-bromo-2-diphenylamino-9,9-diethylfluorene (1.0 g, 2.1 mmol) in dry THF (20 ml) 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 a period of 4 h while the bath temperature was raised slowly to ~20 °C. It was quenched with saturated ammonium chloride solution (NH_{4} Cl^-). The products were extracted by chloroform (2 x 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, SiO_{2}, R_{f} = 0.9 using hexane:EtOAc in a ratio of 4:1 as eluent) to give 9,9-diethyl-2-diphenylaminofluorene 2 as viscous colorless oil in a yield of 95% (0.78 g). Spectroscopic data of 2: FAB^+–MS m/z 389 (M^+); FT-IR (KBr) \nu_{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) cm\(^{-1}\); ^{1}H NMR
(400 MHz, CDCl₃, 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).

**Synthesis of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (3)**

A sample of 2-diphenylamino-9,9-diethylfluorene (1.0 g, 2.6 mmol) in 1,2-dichloroethane (15 ml) was added to the suspension of aluminum chloride (0.38 g, 2.8 mmol) in 1,2-dichloroethane (15 ml) at 0 °C. Bromoacetyl bromide (0.27 ml, 3.1 mmol) was added over a period of 10 min while maintaining the reaction temperature at 0–10 °C. The reaction mixture was allowed to reach ambient temperature gradually with stirring for 4 h. It was quenched by slow addition of water (50 ml). Organic layer was sequentially washed with dil. HCl (1N, 50 ml) and water (50 ml x 2). The solution was concentrated in vacuo, followed by purification via column chromatography (silica gel) using a solvent mixture of hexane:toluene/3:2 as eluent. After evaporation of the eluent solvent, a crude product of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene 3 as yellow crystalline solids was obtained in a yield of 66% (0.87 g). Further purification was made on thin-layer chromatographic plates (TLC, SiO₂, Rf = 0.3, using hexane:toluene/3:2 as eluent). Spectroscopic data of 3: FAB⁺–MS m/z 509, 511 (M⁺); UV-Vis (CHCl₃, 2.0 x 10⁻⁵ M) λ max (ε) 251 (1.6 x 10⁴), 290 (2.3 x 10⁴), and 408 (2.7 x 10⁴) nm; FT-IR (KBr) ν max 3037 (w), 2966 (s), 2928 (m), 2878 (w), 1674 (s), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.95 (dd, J = 8 Hz, J = 1.6 Hz 1H), 7.92 (d, 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).

**Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]–61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene monoadduct [4, C₆₀(>DPAF)] and bisadduct C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₂ [5, C₆₀(>DPAF)₂]**

C₆₀ (1.0 g, 1.4 mmol) and 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (0.7 g, 1.4 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, 1.4 mmol) and stirred at room temperature for a period of 5 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 monoadduct 4 and bisadduct 5. Separation of 4 and 5 were made by column chromatography (silica gel) using a solvent mixture of hexane:toluene/3:2 as eluent. The first chromatographic band corresponding to Rf = 0.6 on the thin-layer chromatographic plate (TLC, SiO₂, hexane:toluene/3:2) afforded 7-(1,2-dihydro-1,2-methanofullerene[60]–61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene 4 as greenish brown solid of C₆₀(>DPAF) monoadduct in 71% yield (0.82 g, based on recovered C₆₀). The second chromatographic band corresponding to Rf = 0.3 on the thin-layer chromatographic plate (TLC, SiO₂,
hexane:toluene/3:2) gave the bisadduct 5 C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₂ [C₆₀(>DPAF)₂] as brownish solids in a minor quantity of roughly 11% (0.17 g).

Spectroscopic data of 4: negative ion desorption chemical ionization mass spectrum (DCI–MS) m/z 1149 (M⁻); UV-Vis (CHCl₃, 2.0 x 10⁻⁵ M) λₘₐₓ (ε) 256 (1.1 x 10⁵), 327 (4.8 x 10⁴), and 408 (3.5 x 10⁴) nm; FT-IR (KBr) νₘₐₓ 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⁻¹; ¹H NMR (400 MHz, CDCl₃, 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).

Spectroscopic data of 5: FAB⁺–MS m/z 1579 (M⁺); ¹H NMR (400 MHz, CDCl₃, 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 trisadduct C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₃ [6, C₆₀(>DPAF)₃] and tetrakisadduct C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₄ [7, C₆₀(>DPAF)₄]**

A solution of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (0.14 g, 0.28 mmol, excess) in toluene was added to C₆₀ (25 mg, 0.035 mmol) dissolved in dry toluene (25 ml) with stirring under nitrogen. To this solution was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 42 mg, 0.44 ml, 0.28 mmol) with continuous stirring. Reaction progress was monitored by taking samples on the TLC plate for following disappearance of the starting fluorene derivative and C₆₀. After a reaction period of 10 min, the absence of C₆₀ on TLC was noticed. The reaction was allowed to continue with stirring for an additional 36 h with periodical TLC monitoring. At the end of reaction, the mixture was filtered, concentrated in vacuo to give a crude product mixture of 6, 7 and possibly higher adducts. They were separated by different bands on preparative TLC plates (SiO₂) using a mixture of chloroform and hexane as eluent. Further re-purification and separation of each band by additional preparative TLC plates using a solvent mixture with decreasing polarity as eluent allowed a distinguishable narrow brown-yellow band of each sample to be isolated. Subsequent identification of these samples isolated from each purified band by their negative ion desorption chemical ionization mass spectrum (DCI–MS) clarified the molecular mass of a sample from one band corresponding to a regioisomeric mixture of C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₃ [6, a trisadduct C₆₀(>DPAF)₃] in a yield of roughly 28 mg and the other molecular mass of a sample corresponding to a regioisomeric mixture of C₆₀(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)₄ [7, a tetrakisadduct C₆₀(>DPAF)₄] in a yield of roughly 20 mg. The rest of minor bands on TLC plates were also isolated in an insignificant quantity of possibly higher fullerene–DPAF adducts.
Spectroscopic data of 6: DCT–MS m/z 2009 (M⁺); ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.6–8.0 (m, broad, 6H), 7.9–7.7 (m, broad, 3H), 7.7–7.4 (m, broad, 3H), 7.4–7.2 (m, broad, 30H), 7.2–6.9 (m, broad, 6H), 5.2–5.0 (m, 3H), 2.1–1.87 (m, broad, 12H), and 0.34 (t, broad, 18H).
Spectroscopic data of 7: DCT–MS m/z 2437 (M⁺); ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.6–8.0 (m, broad, 8H), 7.9–7.7 (m, broad, 4H), 7.7–7.5 (m, broad, 4H), 7.3–7.2 (m, broad, 40H), 7.2–6.9 (m, broad, 8H), 5.2–5.0 (m, 4H), 2.1–1.8 (m, broad, 16H), and 0.34 (t, broad, 24H).

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