Large concentration-dependent nonlinear optical responses of starburst diphenylaminofluorenocarbonyl methano[60]fullerene pentads[†]

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We demonstrate an approach toward the design of starburst C_{60} -keto-DPAF assembly by applying a starburst macromolecular configuration with C_{60} as the core center, which is encapsulated by multiple bulky groups leading to the increase of intermolecular separation and aggregation barrier. Molecular compositions of the resulting $C_{60}(>DPAF-C_9)_2$ triad and C₆₀(>DPAF-C₉)₄ pentads were clearly confirmed by MALDI-MS (positive ion) detection of protonated molecular mass ions. Both $C_{60}(>DPAF-C_9)_2$ and $C_{60}(>DPAF-C_9)_4$ (structural isomers, **3a** and **3b**) exhibited nonlinear optical transmittance reduction responses in the femtosecond (fs) region with a lower transmittance value for the latter at the high laser power above 80 GW cm⁻². This was attributed to the larger fs 2PA cross-section values of **3a** and **3b** than that of **2** at the same concentration and, apparently, correlated to a higher number of DPAF-C₉ subunits in the structure of 3. As the concentration was decreased to 10^{-4} M, a clear monotonous increase of the σ_2 value change ($\Delta \sigma_2$) from 13.9, 33.2, to 48.1 and $68.2 \times 10^{-48} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ (or 6820 GM for the latter) for the structural variation from the monoadduct 1, bisadduct 2, to tetraadducts 3b and 3a, respectively, was observed. We interpreted the concentration-dependent phenomenon as being due to the high tendency of fullerene-DPAF chromophores to form nanoscale aggregates at concentrations above 10^{-3} M. We also proposed that starburst structures, as exemplified by $C_{60}(>DPAF-C_9)_4$, in a multipolar arrangement resembling encapsulation of C₆₀ by DPAF-C₉ pendants, provide a useful means to increase the degree of molecular dispersion and maintain high nonlinear optical efficiency.

Introduction

Chemical functionalization of C_{60} with organic groups to produce the corresponding monoadducts and bisadducts by converting one or two fullerenyl double bonds into two or four sp³ carbons, respectively, in general does not alter much the overall π -conjugation and photophysical properties of the fullerene cage.^{1–3} In fact, functional modification of C_{60} disrupts symmetry-forbidden transitions of the parent cage and allows more ground state optical absorption of the derivatives in the visible region. Certain structural alterations given the formation of hexaarmed hydrophilic fullerene cages, such as those of hexa(*n*-sulfobutyl)[60]fullerenes (FC₄S) molecules, were proven to allow the occurrence of fullerenyl photoactivation processes in the long wavelength region. Examples of these photoprocesses were demonstrated recently in singlet oxygen generation,⁴ photodynamic therapeutic fibrosarcoma tumor treatment,⁵ and photodynamic antibacterial coatings⁶ with the use of either a red-light laser or a visible light source. During the application, a significant quantity of singlet oxygen produced by FC₄S implied the existence of a photoinduced triplet excited transient state (³C₆₀*) upon irradiation. This observation supports our hypothesis that the attachment of a limited number (≤ 6) of addends onto C₆₀ forming a starburst molecular structure may not adversely affect its ability to form an excited triplet fullerene state, which is considered to be one of the crucial prerequisites for the reverse saturable absorption (RSA) and optical limiting properties of C₆₀-derived materials.⁷⁻⁹ The phenomenon of RSA is related to the wellrecognized fact that excited states of C₆₀ are more polarizable with larger absorption cross-sections than those of the ground states. The near co-existence of fullerenyl singlet and triplet excited states fits well with the required facile generation of populated excited states for obtaining strong nonlinear optical responses¹⁰ and the enhanced excited state absorption.^{7,11} These RSA properties have been applied as the fundamental principle in the development of effective materials for protection from high-intensity laser pulses.¹²⁻²¹

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[†] Electronic supplementary information (ESI) available: MALDI-TOF mass spectrum of C₆₀(>DPAF-C₉) **1**; comparison profiles of MALDI-TOF mass spectra among C₆₀(>DPAF-C₉), C₆₀(>DPAF-C₉)₂, and C₆₀(>DPAF-C₉)₄; MALDI-TOF mass spectrum of C₆₀(>DPAF-C₉)₄ **3b**; comparison of ¹³C NMR spectra of C₆₀(>DPAF-C₉)₄ and C₆₀(>DPAF-C₉)₂; procedure of proton integration ratio measurement and the calculation of proton counts in ¹H NMR spectra of C₆₀(>DPAF-C₉), C₆₀(>DPAF-C₉)₂, and C₆₀(>DPAF-C₉)₄. See DOI: 10.1039/b615697e

Nonlinear absorption behavior of C₆₀ appeared to be dominated by the reverse saturable absorption in the visible region and the two-photon absorption (2PA) process in the NIR-IR region.²²⁻²⁴ Recently, large enhancement of molecular 2PA cross-sections in the NIR region has been achieved by periconjugation of C₆₀ with conjugated chromophores or grafted polymers.^{25–29} One typical example of such conjugated chromophores was given by 9,9-diethyldiphenylaminofluorene (DPAF-C₂) which produces fluorescence emission centered at 498 nm in CHCl₃ upon excitation (\sim 400 nm) near the ground state optical absorption peak maximum.³⁰ The emission is efficiently quenchable by C₆₀ intermolecularly in a solution mixture of methano[60]fullerene and DPAF- C_n or intramolecularly in the case of the conjugated molecule C_{60} (>DPAF-C₂) via energy transfer in nonpolar solvents, such as toluene, benzene, and CS₂. This energy transfer is plausible since the lowest excited singlet energies of $C_{60}(>^1DPAF^*-C_2)$ and ${}^{1}C_{60}^{*}(>DPAF-C_{2})$ were estimated to be 2.74 (452 nm) and 1.74 (714 nm) eV, respectively, in toluene based on steady state fluorescence measurements.³¹ The formation of the fullerene triplet state was evident from the detection of the triplet-triplet absorption band of ³C₆₀*(>DPAF-C₂) at about 730 nm in nanosecond transient absorption measurements after 532 nm pulse laser irradiation, in close resemblance to that of the parent C₆₀ occurring at 750 nm for ³C₆₀* upon similar excitation.³² Therefore, photoexcitation of $C_{60}(>DPAF-C_n)$ by 780 nm irradiation with respect to nearly half of DPAF-C_n's HOMO-LUMO energy gap should facilitate both two-photon absorption of the DPAF- C_n moiety and excited state absorption of the fullerene moiety in a similar wavelength range. Combination of two-photon absorption and ${}^{3}C_{60}*$ absorption in a nearly concurrent event may largely increase the overall nonlinear optical absorption capability of the materials on the ns timescale, in line with the proposed concept of 2PA-RSA combination at the excited states of complex chromophores toward the reduction of optical transmittance at high irradiance.^{33–36} Accordingly, transient absorption data obtained from femtosecond pump-probe experiments at 800 nm on samples of sterically hindered [60]fullerenyl dyad C_{60} (>DPAF-C₉) 1 and triad C_{60} (>DPAF-C₉)₂ 2, where C₉ is 3,5,5-trimethylhexyl, unambiguously verified the occurrence of two-photon excitation processes in air-saturated benzene and subsequent efficient energy transfer from the two-photon pumped DPAF-C₉ moiety to the C₆₀ cage moiety.²⁸ A similar study on $C_{60}(>DPAF-C_9)_2$ in CS_2 (1.0 × 10⁻² M) also indicated good intrinsic fs 2PA cross-sections around $0.824 \times 10^{-48} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ (or 82.4 GM).

Synthetically, C_{60} -DPAF conjugates can be modified to further increase the number of chromophore arms on a single C_{60} cage resulting in a starburst structure for enhancing 2PA cross-sections. In this structural motif, the C_{60} cage serves as a molecular core for attaching multiple 2PA-active chromophore antenna components to harvest light in the visible–NIR wavelength ranges and, subsequently, condense the excited-state energy to the central fullerene core. The approach resembles photoresponsive dendritic chromophore structures synthesized recently that embodied the fluorescence resonance energy transfer (FRET) phenomenon.³⁷ Here, we report the first concentration-dependent 2PA cross-section measurements on starburst hindered diphenylaminofluorenocarbonyl methano-[60]fullerene pentads $C_{60}(>DPAF-C_9)_4$ **3** and the observed significant decrease of relative 2PA cross-section values, especially at high solution concentration (10^{-2} M). In this concentration region, a high tendency for intermolecular clustering and nano-aggregative interactions of this class of materials is believed to exist.

Materials and methods

Reagents and chemicals

Pure C₆₀ (99.5%) was produced from NeoTech Product Company, Russia and confirmed by thin-layer chromatography (TLC, SiO₂, toluene). Reagents of tris(dibenzylideneacetone) dipalladium(0), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 2-bromofluorene, and all other chemicals were purchased from Sigma-Aldrich Chemicals.

Physical measurements for material characterization

Infrared spectra were recorded from KBr pellets on a Thermo Nicolet 370 series FT-IR spectrometer. UV-Vis spectra were recorded on a Perkin Elmer Lambda-9 UV/VIS/NIR spectrometer. ¹H NMR and ¹³C NMR spectra in solution were taken on a Bruker Avance Spectrospin-500 spectrometer. Fluorescence spectra were collected on a FLUOROLOG (ISA Instruments) spectrofluorometer. Mass spectroscopic measurements were performed by the use of the positive ion matrixassisted laser desorption ionization (MALDI-TOF) technique on a micromass M@LDI-LR mass spectrometer. In a typical measurement, two fractions (100 µl) each from the solution of $C_{60}(>DPAF-C_9)_x$ (1.0 mg) in chloroform (1.0 ml) and the matrix solution of α -cyano-4-hydroxycinnamic acid (10 mg) in acetone (1.0 ml) were mixed together. From this samplematrix mixture, a small quantity (2.0 µl) was taken and deposited on the stainless steel sample target plate, dried, and subsequently inserted into the ionization source of the instrument. The resulting sample blended or dissolved in the matrix material was irradiated by a nitrogen UV laser at 337 nm with 10 Hz pulses under high vacuum. MALDI mass spectra were acquired in reflection mode. Each spectrum was produced by averaging 10 laser shots; at least 25 spectra were acquired from different regions of the sample target. Mass ion peaks were identified for the spectrum using the MassLynx v4.0 software.

Preparation of $7-\alpha$ -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2diphenylaminofluorene (7)

A modified aluminium chloride quantity compared to the literature procedure was applied.^{30,38} A solution of 9,9di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6** (1.4 g, 2.4 mmol) in 1,2-dichloroethane (30 ml). was added to a suspension of aluminium chloride (1.12 g, 8.4 mmol, 3.5 equiv.) in 1,2-dichloroethane (50 ml) at 0 °C. The mixture was then added to α -bromoacetyl bromide (0.25 ml, 6.5 mmol) dropwise over a period of 5.0 min while maintaining the reaction temperature between 0 and 10 °C. The mixture was slowly warmed to ambient temperature and stirred for an additional 8.0 h. At the end of the reaction, it was quenched by slow addition of ice cold water (100 ml) while maintaining the temperature below 45 °C. The organic layer was separated and washed sequentially with dilute HCl (1.0 N, 50 ml) and water (50 ml, twice). The liquid was dried over magnesium sulfate and concentrated *in vacuo* to obtain the crude product as a crystalline yellow solid. Further purification was carried out by column chromatography (silica gel) using a mixture of hexane–EtOAc (9 : 1) as the eluent. A chromatographic fraction corresponding to $R_{\rm f} = 0.6$ on TLC (SiO₂, hexane–EtOAc 9 : 1 as the eluent) was isolated to afford 7- α -bromoacetyl-9,9-di(3,5,5-trimethyl-hexyl)-2-diphenylaminofluorene 7 as a yellow viscous oil in 68% yield (1.2 g). The spectroscopic characteristics of 7 were identical to the reported data.²⁹

Synthesis of the [60]fullerenyl monoadduct 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene, $C_{60}(>DPAF-C_9)$ 1, and the corresponding bisadduct C_{60} [methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]₂, $C_{60}(>DPAF-C_9)_2$ 2

A modified reagent quantity compared to the literature procedure was applied.³⁰ C₆₀ (700 mg, 0.97 mmol) dissolved in toluene (600 ml) was added to 7-a-bromoacetyl-9,9di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene 7 (686 mg, 0.97 mmol, 1.0 equiv.) under an atmospheric pressure of nitrogen. To this solution was added 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 0.18 ml, 1.16 mmol) and the resulting mixture was stirred at room temperature for a period of 5.0 h. At the end of the stirring period, suspended solids of the reaction mixture were filtered off, washed with toluene, 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. Analytical thin-layer chromatography (TLC, SiO₂) of the solid sample indicated a mixture of several products at different $R_{\rm f}$ values. Only two major narrow bands were isolated by column chromatographic separation on silica gel using a solvent mixture of hexane-toluene (1 :2) as the eluent. The first chromatographic band, corresponding to a spot at $R_{\rm f} = 0.85$ on the analytical TLC plate using a mixture of hexane-toluene (2:3) as the eluent, afforded the monoadduct 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino-fluorene, C₆₀(>DPAF-C₉) 1, as a brown solid (680 mg, 68% based on recovered C₆₀ of 135 mg). Spectroscopic data of 1: MALDI-MS (TOF) calcd for ¹²C₁₀₅¹H₅₅¹⁴N¹⁶O *m*/*z* 1345.4; found, *m*/*z* 1349, 1348, 1347, 1346 (MH⁺), 894, 877, 862, 855, 845, 840, 802, 704, 687, 683, 672, 665, 650, 631, 629, 612, and 585; FT-IR (KBr) v_{max} 3435 (br), 2947 (s), 2922, 2861 (m), 1678, 1593 (vs), 1491 (s), 1464, 1426, 1402, 1347 (w), 1274 (s), 1199 (s), 1185, 1155 (w), 1028 (w), 816 (w), 752 (s), 695 (s), 576, and 526 (vs) cm^{-1} ; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.47 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.26 (m, 6H), 7.13 (m, 4H), 7.05 (m, 2H), 5.67 (t, J =4.0 Hz, 1H), 2.1-1.9 (m, 4H), 1.3-1.1 (m, 4H), and 0.9-0.6 (m, 30H).

The second chromatographic band, corresponding to a spot at $R_{\rm f} = 0.73$ on the analytical TLC plate using a solvent mixture of hexane–toluene (2 : 3) as the eluent, gave the bisadduct C_{60} (methanocarbonyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)₂, C_{60} (>DPAF-C₉)₂ **2**, as a brownish solid in 9% yield (130 mg). Spectroscopic data of **2**: MALDI-MS (TOF) calcd for ${}^{12}C_{150}{}^{1}H_{110}{}^{14}N_{2}{}^{16}O_{2}$ *m/z* 1970.8; found, *m/z* 1974, 1973, 1972, 1971 (M⁺), 1347, 1346, 870, 861, 710, 705, 672, 666, 630, 629, 612, and 583; FT-IR (KBr) ν_{max} 3429 (br), 3163, 2951 (s), 2922, 2863, 1680, 1595 (vs), 1492 (vs), 1465, 1420, 1400, 1316(w), 1277, 1200, 1156 (w), 1093, 1030 (w), 816 (w), 753, 670 (s), and 527 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.5–8.1 (m, 4H), 7.9–7.4 (m, 4H), 7.24 (m, 12H), 7.12 (m, 8H), 7.05 (m, 4H), 5.8–5.3 (m, 2H), 2.1–1.8 (m, 8H), 1.35–1.15 (m, 8H), and 1.1–0.5 (m, 60H).

Synthesis of the [60]fullerenyl tetraadducts C_{60} [methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]₄, C_{60} (>DPAF-C₉)₄ 3a and 3b

Finely divided C₆₀ (550 mg, 0.76 mmol), 7-α-bromoacetyl-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene (3.24 g, 4.6 mmol, 6.0 equiv.), and anhydrous toluene (500 ml) were placed in a reaction flask under nitrogen atmosphere. The mixture was stirred at ambient temperature until a clear solution was obtained. To this solution was added 1,8diazabicyclo[5.4.0]undec-7ene (DBU, 850 mg, 5.5 mmol, 7.2 equiv.). The reaction mixture was stirred at room temperature for a period of 8.0 h to result in a fine-solid suspended solution. Solid particles in the solution were filtered off and washed with toluene. The combined filtrate was concentrated to 50 ml. To this concentrated liquid was added methanol (100 ml) to effect precipitation of the crude products, which were isolated by centrifugation. The crude solids were washed with methanol (3 \times 20 ml) and subsequently purified by column chromatography (silica gel) using a solvent mixture of hexane-toluene (3 : 1) as the eluent. Prior to column chromatography, the crude sample was evaluated on analytical TLC plates to observe at least 4 product spots each in a different relative quantity. However, only two major fractions were collected by column chromatography separation and subsequently repurified separately on preparative TLC plates [SiO₂, 2000 µm layer thickness, using a solvent mixture of hexane-toluene (4:1) for the less polar fraction and hexanetoluene (3:1) for the more polar fraction as the eluent]. During the TLC separation, only a center narrow dense band was isolated to afford the [60]fullerenyl multiadducts. These two product fractions were identified to be the tetraadducts: C₆₀[methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]₄ 3a, corresponding to the chromatographic band at $R_{\rm f} = 0.5$ on the analytical TLC plate using hexane-toluene (2 : 3) as the eluent, as a brownish solid in 18% yield (440 mg); and 3b, corresponding to the chromatographic band at $R_{\rm f} = 0.25$ on the analytical TLC plate, as a brownish solid in 7% yield (170 mg). All other unidentified minor products from column chromatography were accounted for a total 470 mg.

Spectroscopic data of the nonpolar tetraadduct **3a**: MALDI-MS (TOF) calcd for ${}^{12}C_{240}{}^{1}H_{220}{}^{14}N_4{}^{16}O_4$ *m/z* 3221.6; found, *m/z* 3228, 3227, 3226, 3225, 3224, 3223, 3222 (M⁺), 2639, 2619, 2560, 2599, 2597, 2540, 2127, 2104, 2102,

1972, 1563, 1547, 1543, 1479, 1468, 1456, 1347, 878, 870, 857, 827, 629, 612, and 531; FT-IR (KBr) v_{max} 3421 (br), 2952 (vs), 2924 (vs), 2866, 1681, 1595 (vs), 1493 (vs), 1465, 1421, 1377 (w), 1347 (w), 1277, 1200, 1156 (w), 1029, 819, 752, 697 (s), 525, and 475 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.5–8.0 (m, 8H), 7.9–7.5 (m, 8H), 7.24 (m, 20H), 7.1–6.9 (m, 28H), 5.6–5.0 (m, 4H), 2.4–1.7 (m, 16H), 1.4–1.1 (m, 16H), and 1.1–0.5 (m, 120H).

Spectroscopic data of the polar tetraadduct **3b**: MALDI-MS (TOF) calcd for ${}^{12}C_{240}{}^{14}H_{220}{}^{14}N_4{}^{16}O_4$ *m*/*z* 3221.6; found, *m*/*z* 3228, 3227, 3226, 3225, 3224, 3223, 3222 (M⁺), 2785, 2770, 2757, 2755, 2754, 2753, 2731, 2730, 2680, 2658, 2622, 2599, 2145, 2130, 2128, 2106, 2105, 2104, 1974, 1972, 1958, 1067, 1003, 948, 947, 946, 827, 629, 612, and 531; FT-IR (KBr) v_{max} 3434 (br), 2951 (s), 2924 (vs), 2864, 1683, 1594 (vs), 1492 (vs), 1466, 1420 (w), 1363 (w), 1316 (w), 1278, 1211, 1177 (w), 1089, 819, 752, 697 (s), 525, and 474 (br) cm⁻¹; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.6–8.1 (m, 8H), 7.9–7.5 (m, 8H), 7.24 (m, 20H), 7.11(m, 20H), 7.03 (m, 8H), 5.6–4.9 (m, 4H), 2.2–1.8 (m, 16H), 1.4–1.1 (m, 16H), and 1.1–0.4 (m, 120H).

Optical absorption measurements

Optical absorption and transmission spectra, in the range of 180–1200 nm, of $C_{60}(>DPAF-C_9)_x$ (x = 1, 2, or 4) samples dissolved in CS₂ were determined in a 1 mm thick quartz cuvette with a UV-Vis-NIR spectrophotometer (Model UV 3600, Shimadzu, Kyoto, Japan).

Two-photon absorption cross-section (σ_2) and nonlinear optical transmittance measurements

Two-photon absorption cross-section (σ_2) and nonlinear optical transmittance measurements of $C_{60}(>DPAF-C_9)_x$ (where x = 1, 2, or 4) samples in a CS₂ solution were carried out with femtosecond Z-scans and energy-dependent transmission counting at the wavelength of 780 nm. To reduce accumulative thermal effects and to minimize the contribution of triplet-triplet state absorption in $C_{60}(>DPAF-C_9)_x$, we employed 150 fs laser pulses at 1 kHz repetition rate. Laser pulses were generated by a mode-locked Ti : sapphire laser (Quantronix, IMRA), which seeded a Ti : sapphire regenerative amplifier (Quantronix, Titan), and focused onto a 1 mm thick quartz cuvette containing a solution of $C_{60}(>DPAF-C_9)_x$ with a minimum beam waist of ~12 µm. By adding CS₂ to $C_{60}(>DPAF-C_9)_x$, the concentration of the samples was adjusted to either 1.0×10^{-4} , 1.86×10^{-3} , or 1.0×10^{-2} M for the measurement. Incident and transmitted laser powers were monitored as the cuvette was moved (or Z-scanned) along the propagation direction of the laser pulses.

Two-photon absorption is described by the change in the absorption coefficient $\Delta \alpha = \beta I$, where β and I are the 2PA coefficient and the light intensity, respectively. The 2PA coefficient can be extracted from the best fitting between the Z-scan theory³⁹ and the data. The 2PA cross-section value was then calculated from the 2PA coefficient by the formula $\sigma_2 = \beta \hbar \omega / N$, where $\hbar \omega$ is the photon energy and N is the number of molecules.

Results and discussion

The compounds 9,9-dialkyldiphenylaminofluorenes (DPAF- C_n) are electron donors (D) and highly fluorescent materials showing emission at ~ 450 nm upon photoexcitation at <400 nm. Conjugation with the C₆₀ acceptor (A) cage facilitates intramolecular electron- and energy-transfer events from the DPAF moiety to the fullerene moiety in C₆₀-DPAF assemblies at an ultrafast kinetic rate of >10 ps after 150 fs laser irradiation.³¹ In a nonpolar solvent, such as toluene, the triplet state of the fullerene cage in ${}^{3}C_{60}$ *(>DPAF-C₂) has a lifetime of 33 μ s.³¹ As we extended this linear D-A arrangement to include multiple DPAF- C_n attachments on one C_{60} cage, corresponding starburst A-(D)_n or C_{60} -(DPAF- C_n _x structures were formulated. In this structural motif, the C_{60} cage becomes a molecular core and multiple DPAF- C_n subunits are photoactive antenna components to harvest light from the visible (for single photon excitation) to the near infrared (for two-photon excitation) wavelength ranges. Subsequent transfer of the excited-state energy to the central fullerene core may enhance its reverse saturable absorption capability. In a very dilute solution giving a nearly molecularly separated state of each C_{60} -(DPAF- C_n)_x, interference of intermolecular energy transfer and excited state quenching may be minimized. As their concentration increases in the materials application, molecular aggregation and coalescence becomes a common phenomenon that may significantly affect the photoresponsive efficiency of the compound. One approach to extend and maintain the molecular photoefficiency in highly concentrated solution or the solid state is to apply highly bulky groups in the structure as a physical barrier to favor molecular separation. One recent example was given by hindered $C_{60}(>DPAF-C_9)$ and $C_{60}(>DPAF-C_9)_2$, where C₉ is a 3,5,5-trimethylhexyl group, showing enhanced 2PA cross-section values and nonlinear optical responses.²⁸ Reduction to some extent of the molecular aggregation in a dense solution without much decrease of the chromophore density is believed to be responsible for this enhancement.

Cluster formation of fullerenes in solution can be a frequent occurrence during sample preparation owing to a strong tendency for hydrophobic attraction among fullerene cages *via* weak intermolecular van der Waals interactions in nonpolar solvents, such as benzene, toluene, and CS_2 .^{40,41} Evidently, the phenomenon exists even in fairly dilute toluene solution in a concentration of 2×10^{-4} M showing fractal clusters (C_{60})_n ($n \ge 3$) with sizes >1.2 nm as well as single C_{60} molecules.⁴² The quantum efficiency of the triplet population can be considerably depleted in the form of particles and clusters, *via* triplet–triplet annihilation.

In the presence of an extended aromatic DPAF ring in the $C_{60}(>DPAF-C_2)$ structure, strong fullerenyl π -interactions were found to drive the molecular assembly over DPAF-C₂ subunits into a highly ordered array of the fullerene cages in its single crystal structure.³⁰ The structural arrangement also forces planar DPAF-C₂ rings to orient side-by-side with no direct π - π interaction between DPAF moieties, indicating stronger interactions among C₆₀ cages than among DPAFs or between C₆₀ and DPAF. Therefore, it may require at least four DPAF-C_n subunits, such as in C₆₀(>DPAF-C₉)₄, to

encapsulate the C₆₀ cage in addition to the attachment of hindered 3,5,5-trimethylhexyl groups on the C₉ position of the fluorene ring to prevent direct intermolecular stacking contact of both fullerene cages and DPAF-C_n rings. In addition, when C₆₀ cages are wrapped by four hindered dialkylated chromophores, enhanced solubility of the resulting macromolecule should lead to a larger amount of C₆₀ cages being drawn into the solvent for a highly concentrated solution.

Synthesis and structural characterization of C₆₀-DPAF conjugates

Preparation of the dyad C₆₀(>DPAF-C₉) 1, 7-(1,2-dihydro-1,2methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene, and the triad $C_{60}(>DPAF-C_9)_2$ 2, C₆₀[methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]2, followed a modified synthetic procedure reported recently.30 The modification included the use of a larger quantity of aluminium chloride (3.5 equiv.) in a Friedel-Crafts acylation reaction with α-bromoacetyl bromide than the reported amount to obtain a good product yield of 7-a-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene 7. Isolation and purification of 2 were achieved by the collection of only a narrow, major chromatographic band on preparative TLC plates corresponding to a spot at $R_{\rm f} = 0.73$ on the analytical TLC plate using a solvent mixture of hexane-toluene (2 : 3) as the eluent. Synthesis of starburst C₆₀-DPAF conjugates was carried out by using multiple equivalents of α -bromo-DPAF-C₉ 7 per C₆₀ under similar reaction conditions. However, a greater quantity of 7 than 2.0 equiv. used in the reaction resulted in a distribution of bisadducts, trisadducts, and tetraadducts along with other minor higher multiadducts with little control. Therefore, we applied a maximum quantity of 7 of 6.0 equiv. for this reaction by considering the bulky size of DPAF-C₉ with a sufficient reaction time to complete the highest possible number of chromophore attachments on each C_{60} . The approach minimizes the products containing lower numbers of DPAF-C9 arms and maximizes the product yield of high multiadducts that simplifies the product separation. Evidently, at least 4 chromatographic spots were clearly visible on analytical TLC plates, each in a different relative quantity. Among them, only two major fractions were collected by column chromatographic separation and subsequently repurified individually as a narrow band on preparative TLC plates (SiO₂) to afford the major multiadduct products identified later to be [60]fullerene pentad isomers. No significant quantities of [60]fullerene hexaads or higher adducts were isolable. The first fraction of these two products, corresponding to the chromatographic band at $R_{\rm f} = 0.5$ on the analytical TLC plate using hexane-toluene (2:3) as the eluent, is less polar. It was found to be the tetraadduct C₆₀(>DPAF-C₉)₄, C₆₀[methanocarbonyl-7-(9,9 $di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]_4$ 3a, in the form of a brownish solid in 18% yield. The next major polar fraction, corresponding to the chromatographic band at $R_{\rm f}$ = 0.25 on the analytical TLC plate, was the second tetraadduct 3b isolated as a brownish solid in 7% yield. All other product fractions in a combined quantity accounted for another roughly 20% yield of minor, unidentified tetraads, pentaads, or hexaads.

The chemical structures of 1 and its related monoadduct C_{60} (>DPAF-C₂) were well characterized by spectroscopic methods with the latter also by X-ray single crystal structural analyses.³⁰ Their spectroscopic data greatly aided the structural correlation, characterization, and identification of 2, 3a, and **3b** in this report. Monofunctionalization of C_{60} occurs only on one-half of the sphere leaving the other half-sphere intact. Accordingly, the infrared spectrum of 1 (Fig. 1b) showed two sharp characteristic bands at 576 and 526 cm^{-1} in nearly identical peak positions to those of pristine C_{60} (Fig. 1a) at 575 and 526 cm^{-1} , respectively. Therefore, these two sharp bands are characteristically useful as structural indicators for the bisadducts and tetraadducts if all functional groups are attached on C₆₀ in the same half-sphere. In comparison with the molecular diameter of C₆₀, the size of the 7-keto-9,9di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene (DPAF-C₉, Scheme 1) moiety is relative bulky and can be considered as a hindered arm. It is plausible to assume that the attachment of two DPAF-C9 arms on one C60 should result in regioisomers each with two DPAF-C₉ subunits located at a separation distance sufficient to accommodate the gyration radius of these chromophore arms. A large reduction in intensity of two sharp bands at 576 and 526 cm^{-1} in the infrared spectrum (Fig. 1c) of the triad $C_{60}(>DPAF-C_9)_2$ revealed only a minor quantity of a regioisomer with two DPAF-C₉ subunits located on the same half-sphere in the isolated major chromatographic band. These two sharp bands disappeared fully in the infrared spectra (Fig. 1d and e) of the pentad isomers C_{60} (>DPAF-C₉)₄ 3a and 3b, indicating a distribution of four bulky DPAF-C9 subunits around the full sphere of C_{60} . Undoubtedly, the IR spectra of all C₆₀-DPAF conjugates 1, 2, 3a, and 3b displayed nearly identical profiles of the bands corresponding to the optical absorption of the DPAF-C₉ moiety. It included the characteristic band centered at 1683 cm⁻¹, corresponding to absorption of a keto group bridging a methano[60]fullerene $(C_{60}>)$ cage and a fluorene moiety, shifted by roughly 50 cm⁻¹



Fig. 1 Infrared spectra of (a) pure C_{60} , (b) $C_{60}(>DPAF-C_9)$ **1**, (c) $C_{60}(>DPAF-C_9)_2$ **2**, (d) $C_{60}(>DPAF-C_9)_4$ **3a**, and (e) $C_{60}(>DPAF-C_9)_4$ **3b**, all showing a nearly identical characteristic carbonyl absorption band at 1683 cm⁻¹ largely shifted from 1720 cm⁻¹.



Scheme 1 Reagents and conditions: i. $(CH_3)_3CCH_2CH(CH_3)CH_2-CH_2-OMs$, *t*-BuOK, THF, 10 °C to rt, 15 h; ii. diphenylamine, tris(dibenzylideneacetone)dipalladium(0) (cat.), *rac*-BINAP (cat.), *t*-BuONa, toluene, reflux, 8.0 h; iii. bromoacetyl bromide, AlCl₃, ClCH₂CH₂Cl, 0 °C to rt, 8.0 h; iv. C₆₀, DBU, toluene, rt, 5.0 h.

from the normal carbonyl stretching band at $1720-1750 \text{ cm}^{-1}$ due to the influence of the fluorene ring structure.

The molecular weight of the triad **2** was clearly confirmed by positive ion matrix-assisted laser desorption ionization mass spectrum (MALDI-MS), using α -cyano-4-hydroxycinnamic acid as the matrix, displaying a group of mass peaks with a maximum peak intensity centered at m/z 1972, as shown in Fig. 2. Analysis of this group in Fig. 2b indicated the molecular ion mass (M⁺) of **2** at m/z 1971 with following protonated MH⁺ and isotope peaks at m/z 1972–1974. It was followed by a group of mass peaks centered at m/z 1346 matching well with that of the monoadduct **1** resulting from the loss of exactly one CH₂(DPAF-C₉) (m/z 626) subunit from the molecular mass. In the low mass ion region, several major peaks at m/z 612–629 corresponding to the mass of DPAF-C₉ (m/z 612) and CH(DPAF-C₉) (m/z 625) were also observed revealing facile fragmentation at the bonds immediately next to the C₆₀ and methano[60]fullerene cage. The relatively simple spectrum in the high mass region revealed the good stability of the aromatic *keto*-diphenylaminofluorene moiety under MALDI-MS measurement conditions.

In the MALDI-MS investigation of the tetraadducts 3a and **3b**, a significantly higher laser power than that used in the measurement of 2 was necessary to overcome the low intensity of the mass ion above m/z 3000. However, application of a high laser power created additional mass ion peaks as spectral contaminants with one or two carbon mass units $(m/z \ 15, 24,$ or higher, etc.) higher than the molecular ion or fragmented ion masses. In the high mass region, a group of sharp mass ion peaks corresponding to the molecular mass of C₆₀(>DPAF- C_{9}_{4} 3a at m/z 3222 (M⁺) and its isotope peaks at m/z 3222– 3228 were detected, as shown in Fig. 3. Two additional groups of higher mass ions at m/z 3247 (M + 24)⁺ and 3263 were, presumably, the result of the high laser power conditions. The next major group of mass fragmentation peaks occurring at m/z 2599 (Fig. 3a) matched well with the mass of protonated $C_{60}(>DPAF-C_9)_3$ by the loss of one CH(DPAF-C_9) group (m/z 625) from **3a**. Further fragmentation of the C₆₀(>DPAF- C_{9}_{3} mass peak to give the corresponding $C_{60}(>DPAF-C_{9})_{2}$ and $C_{60}(>DPAF-C_9)$ mass ions at m/z 1972 and 1347, respectively, was also observed at a relatively low intensity. In the low mass ion region, two sharp peaks at m/z 612 and 629 corresponding to the mass of DPAF-C₉ and CH_x(DPAF-C₉), respectively, were detected at a high peak intensity, implying fast loss of two CH(DPAF-C₉) groups after the C₆₀(>DPAF- C_9)₃ fragment. These mass spectral data evidently substantiated the mass composition of **3a** as $C_{60}(>DPAF-C_9)_4$. The mass ion peak at m/z 2104 was the result of decarboxylation fragmentation of a C_{60} (>DPAF-C₉)₂-(α -cyano-4-hydroxycinnamic acid) adduct generated under the high voltage MALDI-MS conditions.

A comparison of the ¹H NMR spectra of 1, 2, 3a, and 3b is shown in Fig. 4, where the chemical shift values of all the protons of $C_{60}(>DPAF-C_9)$ were used as the reference for the proton assignment of the bisadducts and tetraadducts. Interestingly, the α -proton (H $_{\alpha}$, next to the carbonyl group) peak of 1 appeared as a triplet-like signal, perhaps due to longrange ${}^{1}H{}^{-1}H$ coupling, at δ 5.67 (Fig. 4a) with a large downfield shift of 1.15 ppm from that of 7 (δ 4.52, singlet). It was accompanied by three groups of phenyl proton peaks of H₅, H₆, and H₈ of the DPAF moiety showing corresponding chemical shifts at 7.82 (d, J = 8 Hz), 8.46 (d, J = 8 Hz) and 8.33 (s), respectively. Benzyl proton (H₉) peaks at δ 1.9–2.1 are apparently indicative of non-equal H₉s showing two groups of multiplets, instead of one triplet. Peak splitting of benzyl protons is caused by steric hindrance of the adjacent bulky diphenylamino group. In the case of $C_{60}(>DPAF-C_9)_2$, a comparable ¹H NMR spectrum (Fig. 4b) to that of Fig. 4a was obtained. Accordingly, we assigned multiplet peaks at δ 8.1-8.5 (4H), 7.63-7.8 (2H), 5.3-5.8 (2H), and 1.8-2.1 (8H) to the chemical shifts of H₆-H₈/H_{6'}-H_{8'}, H₅/H_{5'}, H_a/H_b, and H₉protons, respectively, of 2. Considering two possible sterically non-equivalent CH(DPAF-C9) subunits and the peak splitting pattern of H_6 , H_5 , H_a , and H_9 as the reference,



Fig. 2 Positive ion MALDI-TOF mass spectra of the bisadduct C_{60} (>DPAF-C₉)₂ 2.



Fig. 3 Positive ion MALDI-TOF mass spectra of the tetraadduct C₆₀(>DPAF-C₉)₄ 3a.

the profile of the α -proton peak in the region of δ 5.3–5.8 was separated into two groups at δ 5.3–5.55 and 5.55–5.8 with a proton integration ratio of roughly 2.5: 1. This revealed the same molecular ratio of two possible regioisomers of C_{60} (>DPAF-C₉)₂ in a similar molecular polarity. By applying the analyses made on its IR spectrum, the minor regioisomer might contain two CH(DPAF-C₉) arms on the same halfsphere, whereas the major regioisomer might contain two CH(DPAF-C₉) arms located on opposite half-spheres. As the spectrum extended to those of C_{60} (>DPAF-C₉)₄ 3a and 3b, as shown in Fig. 4c and d, a slight upfield shift of the α -proton multiplet to δ 4.9–5.6 with increasing complexity was detected. In principle, a large number of four DPAF-C₉ addends per C₆₀ as in 3a and 3b, giving a close resemblance to molecular encapsulation of C₆₀, should increase significantly the spatial crowdedness surrounding the fullerene cage and decrease the degree of freedom for each DPAF-C9 arm to rotate freely around the C_{61} -(C=O) bond. This reduces the peak resolution

of α -protons H_a, H_b, H_c, and H_d of **3** and, thus, further broadens their peak profiles. Therefore, based on the peak profiles of H₆/H₆//H₆"/H₆", H₈/H₈"/H₈", and H₅/H₅'/H₅"/ H₅" of **3a** (Fig. 4c) and **3b** (Fig. 4d) at δ 7.65–8.5, both with reasonably close similarity in peak resolution and shape to those of **2** (Fig. 4b) in the same chemical shift region, we suggest a small possible number of non-isolable regioisomers, such as that of **2**, in the narrow chromatographic fractions of **3a** and **3b**.

Relative integration ratios of aromatic proton peaks at δ 7.0–8.6 in the ¹H NMR spectra of C₆₀(>DPAF-C₉), C₆₀(>DPAF-C₉)₂, and C₆₀(>DPAF-C₉)₄ can be used as the value for quantitative counting of the total aromatic protons that, in turn, correlate directly to the number of DPAF-C₉ units per molecule. The compound 1,4-diazabicyclo[2.2.2]octane (DABCO) is a symmetrical molecule showing only one singlet ¹H peak at δ 2.78 for 12 protons in a chemical shift region containing no aliphatic proton peaks of



Fig. 4 ¹H NMR spectra of (a) $C_{60}(>DPAF-C_9)$ **1**, (b) $C_{60}(>DPAF-C_9)_2$ **2**, (c) $C_{60}(>DPAF-C_9)_4$ **3a**, and (d) $C_{60}(>DPAF-C_9)_4$ **3b** in CDCl₃ with relative integration values, which were calibrated by the use of an internal DABCO standard at the same concentration for (a)–(d), indicated in parentheses.

the DPAF-C₉ moiety. Therefore, this proton peak taken in a known applied concentration can be used as an internal standard for proton counting of the peaks shown in the ¹H NMR spectra of Fig. 4a–d. The procedure of relative integration ratio measurements and the calculation are given as a part of the ESI.[†] Consequently, the results showed total numbers of aromatic protons of **1** (Fig. 4a), **2** (Fig. 4b), and **3** (Fig. 4c and d) in good agreement with the corresponding chemical structures containing one, two, and four DPAF addends, respectively, per C₆₀ cage. The data provided further confirmation of the structural composition of these compounds.

Two-photon absorption cross-section (σ_2) measurements of C₆₀-DPAF conjugates at a high laser power

In the present study, two-photon absorption (2PA) properties of $C_{60}(>DPAF-C_9)_x$ (where x = 1, 2, and 4) dissolved in CS₂ were investigated with femtosecond Z-scans measurements at 780 nm. To correlate the 2PA data with the results of energydependent nonlinear transmission studies, a relatively high energy power source at 163 GW cm^{-2} (or 24.5 mJ cm^{-2}) was applied. This power intensity range also facilitates the signal detection on the same sample at a low solution concentration of 1.0×10^{-4} M. However, high laser-pulse irradiation of fullerene solutions has been reported to cause thermally induced scattering effects.^{11,43} Therefore, recently measured 2PA cross-section values of two C₆₀-DPAF conjugates C₆₀(>DPAF-C₉) and C₆₀(>DPAF-C₉)₂ using a low laser power of 10-30 GW cm⁻² in both femtosecond and nanosecond regions²⁸ were used as the reference. To prevent much deviation of measured 2PA cross-section values from intrinsic two-photon absorptions, effort was taken to reduce accumulative thermal effects to a possibly low level and to minimize the contribution of triplet-triplet state absorption in these

fullerenyl chromophores by employing ultrafast 150 fs laser pulses at 1 kHz repetition rate. Nevertheless, it cannot rule out completely the contribution of thermally induced scattering effects to result in somewhat larger measured 2PA crosssections. By assuming this thermal effect on the scattering is similar for all $C_{60}(>DPAF-C_9)_x$ solutions, the 2PA data should be qualitatively useful for comparison analyses. Prior to 2PA measurements, the concentrations of all $C_{60}(>DPAF-C_9)_x$ solutions in CS₂ was adjusted to 1.86×10^{-3} M which gives a linear (or low-fluence) transmittance (*T*) of 88.6% at a nearly identical intensity for all samples at 780 nm, as shown in Fig. 5. As the concentration was increased to 1.0×10^{-2} M, the solution transmittance of 1, 2, 3a, and 3b decreased to slightly different levels of 77, 82, 80, and 82%,



Fig. 5 UV-Vis-NIR transmission spectra of $C_{60}(>DPAF-C_9)$ **1**, $C_{60}(>DPAF-C_9)_2$ **2**, $C_{60}(>DPAF-C_9)_4$ **3a**, and $C_{60}(>DPAF-C_9)_4$ **3b**, with the latter four compounds dissolved in CS₂ in the concentrations indicated.



Fig. 6 Open-aperture Z-scans of 1 mm thick solutions of (a)/(b) $C_{60}(>DPAF-C_9)_4$, (c) $C_{60}(>DPAF-C_9)_2$, and (d) $C_{60}(>DPAF-C_9)$ in CS_2 in comparison with the sum of the individual model components $[C_{60}$ and $CH_3(DPAF-C_9)]$, performed at the same concentration of 1.0×10^{-4} M and irradiance of 163 GW cm⁻². The data are vertically shifted for clear presentation. Solid lines are the theoretical fit for two-photon absorption.

respectively, at 780 nm. A relatively small deviation of transmittance intensity for the monoadduct $C_{60}(>DPAF-C_9)$ solution might be attributed to its higher tendency to aggregate in at high concentration than the rest of the multiadducts. Molecular aggregation of 1 and 2 was expected to result in broadening and the shift of their optical absorption bands from the maxima at 326 (for the fullerene cage) and 410 (for the DPAF moiety) nm to a slightly longer wavelength along with a shift of the transmission edge from roughly 570 to 680 nm.

Both C_{60} and diphenylaminofluorene components are photoresponsive chromophores capable of undergoing simultaneous two-photon excitation, making contributions to the two-photon absorption cross-section value. To differentiate the molecular contribution vs. the number-sum component contribution to the measured 2PA cross-section values (σ_2) and to gain an insight of the structure-property relationship leading to the enhancement of σ_2 , we carried out comparative Z-scans (Fig. 6) to include measurements based on the cumulative number-sum of individual C60 and CH3(DPAF- C_9) components in the same composition ratio as their corresponding conjugated compounds $C_{60}(>DPAF-C_9)_x$. For comparison purposes, the Z-scans were performed in CS₂ with a concentration of 1.0 \times 10⁻⁴ M. As a result, a systematic increase of σ_2 from 12.7 $\times 10^{-48}$ cm⁴ s photon⁻¹ molecule⁻¹ (or 1270 GM) for the combination of one C_{60} and one $CH_3(DPAF-C_9)$ model component to 29.6 and 46.4 × 10^{-48} cm⁴ s photon⁻¹ molecule⁻¹ (or 4640 GM for the latter) for the combination of one C60 with two and four CH3(DPAF-C₉) components, respectively, was observed, as shown in Table 1. At a relatively low concentration of 1.0×10^{-4} M, a unimolecular process of either C₆₀ or CH₃(DPAF-C₉) model component in response to laser excitation may be expected. Based on this assumption and the simple cumulative sum of 2PA data measured, the average 2PA contribution of one molecular fraction of CH₃(DPAF-C₉) component to the σ_2 value can be estimated to be roughly $11-12 \times 10^{-48}$ cm⁴ s photon⁻¹ molecule⁻¹. This implied that DPAF-C₉, being the major structural moiety in $C_{60}(>DPAF-C_9)_x$, is responsible for photoexcitation in 2PA processes at 780 nm. The implication is reasonable since we believe the 2PA peak of structurally modified C_{60} to be at wavelengths >950 nm.²⁴

Similar open-aperture Z-scans carried out under an irradiance of 163 GW cm⁻² were taken for **1**, **2**, **3a**, and **3b** in CS₂ in three concentrations from 1.0×10^{-4} to 1.0×10^{-2} M giving the plots shown in Fig. 7. These Z-scans displayed positive signs for absorptive nonlinearities. All calculated values of 2PA coefficient β and cross-sections σ_2 of these chromophores are listed in Table 1, where nonlinear absorption in neat carbon disulfide was also measured and included as the reference which gave the β value of 0.03 cm GW⁻¹ in a similar range as the value (0.05 cm GW⁻¹)

Table 1 Two-photon absorption cross-section values ($\sigma_2 = \beta \hbar \omega / N$) of C₆₀(>DPAF-C₉)_x (x = 1, 2, or 4) and the sum of their individual molecular components, measured at 780 nm with 150 fs laser pulses and I = 163 GW cm⁻²

Chromophore/solvent	[<i>C</i>]/M	β /cm GW ⁻¹	$\sigma_2/10^{-48} \text{ cm}^4 \text{ s}$ photon ⁻¹ molecule ⁻¹	$\sigma_{2,adj}/10^{-48} \text{ cm}^4 \text{ s}$ photon ⁻¹ molecule ⁻¹ a	$\Delta \sigma_{2,adj}/10^{-48} \text{ cm}^4 \text{ s}$ photon ⁻¹ molecule ⁻¹
CS ₂		0.03			
$C_{60} + 1 [CH_3(DPAF-C_9)]$	1.0×10^{-4}	0.033	12.7	9.3	
$C_{60}(>DPAF-C_9) 1/CS_2$	1.0×10^{-4}	0.036	25.3	21.9	13.9
	1.86×10^{-3}	0.080	11.4	8.0	7.7
	1.0×10^{-2}	0.100	2.9	0.3	
$C_{60} + 2 [CH_3(DPAF-C_9)]$	1.0×10^{-4}	0.037	29.6	26.2	
$C_{60}(>DPAF-C_9)_2 2/CS_2$	1.0×10^{-4}	0.041	46.4	43.0	33.2
	1.86×10^{-3}	0.088	13.2	9.8	9.0
	1.0×10^{-2}	0.130	4.2	0.8	
$C_{60} + 4 [CH_3(DPAF-C_9)]$	1.0×10^{-4}	0.041	46.4	43.0	
$C_{60}(>DPAF-C_9)_4$ 3a/ CS_2	1.0×10^{-4}	0.051	88.6	85.2	68.2
	1.86×10^{-3}	0.120	20.4	17.0	9.9
	1.0×10^{-2}	0.280	10.5	7.1	
C ₆₀ (>DPAF-C ₉) ₄ 3b/CS ₂	1.0×10^{-4}	0.045	63.3	59.9	48.1
	1.86×10^{-3}	0.097	15.2	11.8	9.7
	1.0×10^{-2}	0.160	5.5	2.1	
^{<i>a</i>} Calibrated σ_2 values to the	e reported data col	lected at $1.0 \times 10^{\circ}$	0^{-2} M using a lower laser e	energy source of 10-30 GW c	$cm^{-2}.^{28}$



Fig. 7 Open-aperture Z-scans of 1 mm thick solution of $C_{60}(>DPAF-C_9)$, $C_{60}(>DPAF-C_9)_2$, and $C_{60}(>DPAF-C_9)_4$ in CS_2 performed at different concentrations of (a) 1.0×10^{-4} , (b) 1.86×10^{-3} , and (c) 1.0×10^{-2} M with an irradiance of 163 GW cm⁻². Solid lines are the theoretical fit for two-photon absorption.

reported recently.⁴⁴ As thermally induced scattering effects caused by high irradiances may influence the accuracy of overall 2PA cross-sections measured, we undertook the measurement of Z-scans of $C_{60}(>DPAF-C_9)_4$ **3a** in CS₂ (1.86 × 10⁻³ M) at different irradiances, as shown in Fig. 8a, with the resulting 2PA cross-section values plotted as a function of the laser power intensity in Fig. 8b. Interestingly, the σ_2 values apparently remain nearly constant in approximately a straight line across the irradiance range from 40 GW cm⁻² up to 600 GW cm⁻² without an obvious increase, confirming the independence of the σ_2 values from the laser power intensity. This can be interpreted as the thermally induced scattering contribution being either fluctuation



Fig. 8 (a) Open-aperture Z-scans at different excitation irradiances for $C_{60}(>DPAF-C_9)_4$ **3a** with experimental data presented as scatter graphs and fitting curves, calculated by Z-scan theory,³⁸ as solid lines and (b) irradiance independence of the σ_2 profile of **3a** in two concentrations indicated.

insensitive or relatively constant over the irradiance range. Thus, the observed change $(\Delta \sigma_2)$ in the nonlinear absorption could be purely due to the different 2PA processes.

In the comparison of σ_2 values among $C_{60}(>DPAF-C_9)_x$ samples collected at 1.0×10^{-4} M concentration, a consistent reduction of the transmittance in Fig. 7a–d is indicative of a larger 2PA coefficient of each $C_{60}(>DPAF-C_9)_x$ compound than that for the sum of compositional model components. Accordingly, an increase of 2PA cross-sections by 2.0, 1.6, 1.9, and 1.4 times their corresponding model component σ_2 values for 1, 2, 3a, and 3b, respectively, revealed clearly the contribution of extending molecular branching and π -conjugative polarization of donor–acceptor moieties to the 2PA enhancement over the simple cumulative number-sum effect.

Most importantly, we observed a significantly large increase of 2PA cross-sections of all $C_{60}(>DPAF-C_9)_x$ compounds in a consistent trend upon decreasing the solution concentration from 1.0×10^{-2} to 1.0×10^{-4} M in CS₂ (see Fig. 9). Since 2PA cross-sections for 1 and 2 at 2.0 and 1.0×10^{-2} M in CS₂ were reported with values of 0.306 and 0.824 × 10^{-48} cm⁴ s photon⁻¹ molecule⁻¹ (or 30.6 and 82.4 GM), respectively, using a lower laser energy source of 10– 30 GW cm⁻²,²⁸ these two values were used for the calibration by reducing the measured σ_2 value of 2 at 1.0×10^{-2} M to the same amount as the reported one. Correspondingly, all other



Fig. 9 Concentration dependence of 2PA cross-section values σ_2 of C₆₀(>DPAF-C₉), C₆₀(>DPAF-C₉)₂, and C₆₀(>DPAF-C₉)₄ in CS₂.

 σ_2 values measured were then deducted by the same quantity of 3.4×10^{-48} cm⁴ s photon⁻¹ molecule⁻¹, which accounted for the partial factor arising from the thermally induced scattering, ^{11,43} to the new $\sigma_{2,adj}$ values, as shown in Table 1. As an example for 1, the $\sigma_{2,adi}$ values were adjusted to be 8.0 and 21.9×10^{-48} cm⁴ s photon⁻¹ molecule⁻¹ (or 800 and 2190 GM) at concentrations of 1.86 \times 10⁻³ and 1.0 \times 10⁻⁴ M, respectively, showing a clear increase of 2PA crosssections upon decrease of the concentration. The systematic increase of the σ value, $\Delta \sigma_{2,adj}$, at incremental decreases of the concentration was calculated as listed in Table 1. Interestingly, regardless of the multiadduct structure, the $\Delta \sigma_{2,adj}$ values in the high concentration range $(10^{-3}-10^{-2} \text{ M})$ were relatively close to each other in a narrow range of 7.7–9.9 \times 10⁻⁴⁸ cm⁴ s photon⁻¹ molecule⁻¹, revealing domination of the aggregation factor over the difference of the molecular structures. As the degree of molecular separation increases at a low concentration of 10^{-4} M, a clear leap of the $\Delta \sigma_{2,adi}$ values from 13.9, 33.2, to 48.1 and 68.2×10^{-48} cm⁴ s photon⁻¹ molecule⁻¹ for the modification of starburst structures going from the monoadduct 1, bisadducts 2, to tetraadducts 3b and 3a, respectively, was found. This observation implied the significance of branched fullerenyl multiadducts in enhancing the 2PA cross-sections at the laser power range related to the nonlinear power transmission application.

We interpret the concentration-dependent phenomena by the high tendency of fullerene-DPAF chromophores to form nano-aggregates, instead of a molecular dispersion, at concentrations above 10^{-3} M. Nano-aggregation might play a role in reducing 2PA quantum efficiency leading to the decrease of the σ_2 value. The starburst structures of $C_{60}(>DPAF-C_9)_4$ pentad regioisomers **3a** and **3b** gave the largest σ_2 enhancement over the $C_{60}(>DPAF-C_9)$ dyad and the $C_{60}(>DPAF-C_9)_2$ triad when molecular dispersion became possible in dilute solution.

Nonlinear optical transmittance measurements of C₆₀-DPAF conjugates

Nonlinear optical transmittance properties of C_{60} -DPAF conjugates C_{60} (>DPAF- C_9)_x in CS₂ were investigated by



Fig. 10 (a) Nonlinear transmission of $C_{60}(>DPAF-C_9)$, $C_{60}(>DPAF-C_9)_2$, and $C_{60}(>DPAF-C_9)_4$ in CS₂ and (b) the measurement of transient transmission change $(-\Delta T/T)$ in solutions of $C_{60}(>DPAF-C_9)$ and **3a**. All the measurements were conducted with 150 fs laser pulses at $\lambda = 780$ nm. All four samples showed nearly identical linear transmission T = 88.6% for an optical path of 1 mm.

energy-dependent transmission measurements at the wavelength of 780 nm using the same setup as that in 2PA measurements conducted by 150 fs laser pulses, except that the sample was fixed at the focus area when the incident pulse power was varied. Technical details of the measurements were described elsewhere.45,46 Nonlinear transmittance results for 1 mm thick solutions of 1, 2, 3a, and 3b in CS_2 at a medium concentration of 1.86×10^{-3} M are shown in Fig. 10a. All the samples showed a linear transmission (T = 88.6%) with an input intensity of up to 36 GW $\rm cm^{-2}$, or a fluence of 5.4 mJ cm^{-2} . When the incident intensity was increased above 36 GW cm^{-2} , the transmittance began to deviate from the linear transmission line and decrease indicating the initiation of nonlinearity and the limiting effect. The transmitted fluence further departed from linearity upon increasing the incident fluence. A systematic trend showing higher efficiency in reducing optical transmittance with the increase of irradiance level up to <1000 GW cm⁻² was observed for the starburst tetraadducts C₆₀(>DPAF-C₉)₄ than for the bisadduct $C_{60}(>DPAF-C_9)_2$ and the monoadduct $C_{60}(>DPAF-C_9)$. This improvement in lowering the transmittance can be correlated to a higher number of DPAF-C₉ subunits in the structure of 3 than in 1 and 2, consistent with the positive contribution of a starburst structure such as 3 to a larger

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two-photon absorption, concluded by Z-scans in Fig. 7. This correlation was made on the assumption of a similar degree of nonlinear scattering among the solutions.

In the molecular system of $C_{60}(>DPAF-C_n)_x$, simultaneous absorption of two photons energy at 780 nm leads to fast release of the fluorescence emission of DPAF- C_n at roughly 450 nm, which can be utilized for subsequent photoexcitation of the C_{60} cage *via* intramolecular energy transfer. The kinetic rate of following intersystem crossing going from the excited singlet state of the fullerene cage moiety $({}^{1}C_{60}^{*}>)$ to the corresponding triplet state (${}^{3}C_{60}*>$) took place within a 1.4 ns time scale.²⁸ Therefore, triplet-triplet state related absorption processes in the ${}^{3}C_{60}$ *> cage moiety can be neglected in this study since the current measurements were performed by using 150 fs laser pulses. The observed transmittance reduction behavior may be attributed predominantly to the high absorption cross-section of 2PA processes, mainly on DPAF- C_9 moieties, and the excited state absorption of the lowest excited singlet state ${}^{1}C_{60}$ *>. Population of the latter ${}^{1}C_{60}$ *> state can be highly enhanced by ultrafast intramolecular energy transfer from the two-photon pumped excited singlet state of the DPAF-C₉ moiety in $C_{60}(>^1 DPAF^*-C_9)$ to form ${}^{1}C_{60}$ *(>DPAF-C₉), which occurs at rate as fast as 130 fs²⁸ to 15 ps.³¹

Under the conditions of Z-scan experiments, C₆₀(>DPAF- C_{9}_{4} showed surprisingly good photostability, which was evaluated by comparing the absorption spectra before and after laser irradiation. The results showed no difference in the spectral profiles for all the samples used. Even though the laser power applied was relatively high, and possibly had reached above the decomposition threshold of the C₆₀-DPAF molecule, the application of ultrafast irradiation on a femtosecond time scale did not seem to have accumulated sufficient energy to impact the chromophore sample with noticeable damage. To evaluate the recovery time of observed nonlinearities and to reveal the underlying mechanism, we conducted a degenerate pump-probe experiment with 150 fs, 780 nm laser pulses close to the 2PA peak position of C₆₀(>DPAF-C₉) and $C_{60}(>DPAF-C_9)_4$ 3a in CS_2 solution. As shown in Fig. 10b, the maximum transmittance change $(-\Delta T/T)$ in **3a** solution was found to be greater than that in the solution of 1, indicating larger 2PA coefficients and σ_2 values of **3a** than those of 1. Furthermore, the response time of 3a was evaluated to be ~ 15 ps in a time scale necessary for intramolecular energy transfer from the DPAF-C₉ moiety to the methano-[60]fullerene (C_{60} >) moiety. It should be pointed out that an oscillation in the relaxation time was present. The origin of this oscillation is unclear. It may be attributed to the interplay between the 2PA and energy transfer processes.

Conclusions

We demonstrated an approach toward the design of starburst C_{60} -*keto*-DPAF assemblies to extend and maintain the molecular photoefficiency in highly concentrated solution by applying a combination of a starburst macromolecular configuration with C_{60} as an encapsulated core and multiple bulky groups. The structure was made for the progressive increase of the aggregation barrier and the unimolecular

character. The molecular compositions of the resulting $C_{60}(>DPAF-C_9)_2$ triad and $C_{60}(>DPAF-C_9)_4$ pentads were confirmed by the analyses of various spectroscopic data. Both $C_{60}(>DPAF-C_9)_2$ **2** and $C_{60}(>DPAF-C_9)_4$ (**3a** and **3b**) exhibited nonlinear optical transmittance reduction responses in the femtosecond region with a lower transmittance value for the latter in the high laser power region above 80 GW cm⁻². This was attributed to the larger fs 2PA cross-section value of $C_{60}(>DPAF-C_9)_4$ than for **2** at the same concentration and correlated to a higher number of DPAF-C₉ subunits in the structure of **3**.

The observed high 2PA cross-section values were explained by an increasing degree of intramolecular interaction and polarization. As the concentration of the solution was varied systematically to induce molecular separation, a consistently large increase of 2PA cross-sections of all $C_{60}(>DPAF-C_9)_x$ (x = 1, 2, or 4) chromophores in the fs region was observed upon concentration dilution from 1.0×10^{-2} to 1.0×10^{-4} M. The difference of the 2PA cross-section value change ($\Delta \sigma_2$) among all samples in response to variation of the concentration was not sensitive to the compound structure in the high concentration range. However, at a low concentration of 10^{-4} M, $\Delta \sigma_2$ values were evaluated to increase clearly for the structural modification from the monoadduct 1, bisadducts 2, to tetraadducts **3b** and **3a**. This large $\Delta \sigma_2$ value enhancement for 3b and 3a was correlated to the hindered starburst structures which may give a higher degree of molecular separation than 1 and 2. Therefore, we interpreted the concentration-dependent phenomenon by the high tendency of fullerene-DPAF chromophores to form nano-aggregates at concentrations above 10^{-3} M. In fact, nano-aggregation might play a role in reducing the 2PA quantum efficiency leading to the decrease of the σ_2 value. The starburst structure of $C_{60}(>DPAF-C_9)_4$ in a multipolar arrangement resembling encapsulation of C_{60} by multiple DPAF-C₉ chromophores is likely to increase the degree of molecular dispersion at high solution concentration and hamper the aggregation tendency, thus maintaining high nonlinear optical efficiency. These results provided an insight into structural control toward managing molecular and nanoscale aggregation phenomena of C₆₀-based starburst and dendritic suprastructures in the materials design of 2PA-based photonic devices and photodynamic therapeutics.

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References

- 1 D. M. Guldi and M. Prato, Acc. Chem. Res., 2000, 33, 69-73.
- 2 D. M. Guldi and P. V. Kamat, *Fullerenes, Chemistry, Physics and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley-Interscience, New York, 2000, pp. 225–281.
- 3 M. Maggini and D. M. Guldi, *Molecular and Supramolecular Photochemistry*, ed. V. Ramamurthy and K. S. Schanze, Marcel Dekker, New York, 2000, vol. 4, pp. 149–196.
- 4 C. Yu, T. Canteenwala, M. E. El-Khouly, Y. Araki, L. Y. Chiang, B. C. Wilson, O. Ito and K. Pritzker, *J. Mater. Chem.*, 2005, 15, 1857–1864.

- 5 C. Yu, T. Canteenwala, H. H. C. Chen, B. J. Chen, M. Canteenwala and L. Y. Chiang, *Proc. Electrochem. Soc.*, 1999, **12**, 234–249.
- 6 C. Yu, T. Canteenwala, L. Y. Chiang, B. Wilson and K. Pritzker, *Synth. Met.*, 2005, **153**, 37–40.
- 7 L. W. Tutt and A. Kost, Nature, 1992, 356, 225-226.
- 8 D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz and T. Pottenger, *Opt. Lett.*, 1993, **18**, 858–860.
- 9 T. H. Wei, T. H. Huang, T. T. Wu, P. C. Tsai and M. S. Lin, *Chem. Phys. Lett.*, 2000, **318**, 53–57.
- 10 Q. L. Zhou, J. R. Heflin, K. Y. Zamani-Khamiri and A. Garito, *Phys. Rev. A*, 1991, **43**, 1673.
- 11 A. Kost, L. W. Tutt, M. B. Klein, T. K. Dougherty and W. E. Elias, *Opt. Lett.*, 1993, **18**, 334–336.
- 12 F. Z. Henari, K. H. Cazzini, D. N. Weldon and W. J. Blau, Appl. Phys. Lett., 1996, 68, 619.
- 13 Y.-P. Sun and J. E. Riggs, Int. Rev. Phys. Chem., 1999, 18, 43.
- 14 J. E. Riggs and Y.-P. Sun, J. Phys. Chem. A, 1999, 103, 485-495.
- 15 Y. L. Song, G. Y. Fang, Y. X. Wang, S. T. Liu, C. F. Li, L. C. Song, Y. H. Zhu and Q. M. Hu, *Appl. Phys. Lett.*, 1999, 74, 332–334.
- 16 M. Maggini, C. D. Faveri, G. Scorrano, M. Prato, G. Brusatin, M. Guglielmi, M. Meneghetti, R. Signorini and R. Bozio, *Chem.-Eur. J.*, 1999, 5, 2501–2510.
- 17 K. Dou and E. T. Knobbe, J. Nonlinear Opt. Phys. Mater., 2000, 9, 269–287.
- 18 Z. B. Liu, J. G. Tian, W. P. Zang, W. Y. Zhou, C. P. Zhang, J. Y. Zheng, Y. C. Zhou and H. Xu, *Appl. Opt.*, 2003, 42, 7072–7076.
- 19 E. Koudoumas, M. Konstantaki, A. Mavromanolakis, S. Couris, M. Fanti, F. Zerbetto, K. Kordatos and M. Prato, *Chem.-Eur. J.*, 2003, 9, 1529–1534.
- 20 G. Kopitkovas, A. Chugreev, J. F. Nierengarten, Y. Rio, J. L. Rehspringer and B. Honerlage, *Opt. Mater.*, 2004, 27, 285–291.
- 21 H. I. Elim, J. Quyang, S. H. Goh and W. Ji, *Thin Solid Films*, 2005, 477, 63–72.
- 22 K. A. Drenser, R. J. Larsen, F. P. Strohkendl and L. R. Dalton, J. Phys. Chem. A, 1999, 103, 2290–2301.
- 23 S. V. Rao, D. N. Rao, J. A. Akkara, B. S. DeCristofano and D. V. G. L. N. Rao, *Chem. Phys. Lett.*, 1998, **297**, 491–498.
- 24 G. Banfi, D. Fortusini, M. Bellini and P. Milani, *Phys. Rev. B:* Condens. Matter, 1997, 56, R10075–R10078.
- 25 L. Y. Chiang, P. A. Padmawar, T. Canteenwala, L.-S. Tan, G. S. He, R. Kannan, R. Vaia, T.-C. Lin, Q. Zheng and P. N. Prasad, *Chem. Commun.*, 2002, 1854–1855.
- 26 P. A. Padmawar, T. Canteenwala, S. Verma, L.-S. Tan, G. S. He, P. N. Prasad and L. Y. Chiang, *Synth. Met.*, 2005, **154**, 185–188.

- 27 Y. Zhao, Y. Shirai, A. D. Slepkov, L. Cheng, L. B. Alemany, T. Sasaki, F. A. Hegmann and J. M. Tour, *Chem.–Eur. J.*, 2005, 11, 3643–3658.
- 28 P. A. Padmawar, J. O. Rogers, G. S. He, L. Y. Chiang, T. Canteenwala, L.-S. Tan, Q. Zheng, C. Lu, J. E. Slagle, E. Danilov, D. G. McLean, P. A. Fleitz and P. N. Prasad, *Chem. Mater.*, 2006, **18**, 4065–4074.
- 29 B. Z. Tang, H. Xu, J. W. Y. Lam, P. P. S. Lee, K. Xu, Q. Sun and K. K. L. Cheuk, *Chem. Mater.*, 2000, **12**, 1446–1455.
- 30 P. A. Padmawar, T. Canteenwala, L.-S. Tan and L. Y. Chiang, J. Mater. Chem., 2006, 16, 1366–1378.
- 31 H. Luo, M. Fujitsuka, Y. Araki, O. Ito, P. Padmawar and L. Y. Chiang, J. Phys. Chem. B, 2003, 107, 9312–9318.
- 32 T. W. Ebbesen, K. Tanigaki and S. Kuroshima, *Chem. Phys. Lett.*, 1991, **181**, 501–504.
- 33 For a review of 2PA-active materials: T. C. Lin, S. J. Chung, K. S. Kim, X. Wang, G. S. He, J. Swiatkiewicz, H. E. Pudavan and P. N. Prasad, *Adv. Polym. Sci.*, 2003, 161, 157–193.
 34 G. S. He, J. D. Bhawalkar, C. F. Zhao and P. N. Prasad, *Appl.*
- 34 G. S. He, J. D. Bhawalkar, C. F. Zhao and P. N. Prasad, *Appl. Phys. Lett.*, 1995, 67, 2433–2435.
- 35 J. E. Ehrlich, X. L. Wu, L.-Y. Lee, Z.-Y. Hu, H. Roeckel, S. R. Marder and J. W. Perry, *Opt. Lett.*, 1997, 22, 1843–1845.
- 36 M. G. Silly, L. Porres, O. Mongin, P.-A. Chollet and M. Blanchard-Desce, Chem. Phys. Lett., 2003, 379, 74–80.
- 37 W. R. Dichtel, J. M. Serin, C. Edder, J. M. J. Frechet, M. Matuszewski, L. S. Tan, T. Y. Ohulchanskyy and P. N. Prasad, J. Am. Chem. Soc., 2004, 126, 5380–5381.
- 38 P. A. Padmawar, T. Canteenwala, S. Verma, L.-S. Tan and L. Y. Chiang, J. Macromol. Sci., Pure Appl. Chem., 2004, 41, 1387–1400.
- 39 M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, 26, 760.
- 40 Q. Ying, J. Marecek and B. Chu, Chem. Phys. Lett., 1994, 219, 214.
- 41 R. V. Hongchuck, T. W. Cruger and J. Milliken, J. Am. Chem. Soc., 1993, 115, 3034.
- 42 L. A. Bulavin, I. I. Adamenko, V. M. Yashchuk, T. Yu. Ogul'chansky, Y. I. Prylutskyy, S. S. Durov and P. Scharff, J. Mol. Liq., 2001, 93, 187–191.
- 43 L. B. Justus, Z. H. Kafafi and A. L. Huston, *Opt. Lett.*, 1993, 18, 1603.
- 44 R. A. Ganeev, A. I. Ryasnyansky, N. Ishizawa, M. Baba, M. Suzuki, M. Turu, S. Sakakibara and H. Kuroda, *Opt. Commun.*, 2004, 231, 431–436.
- 45 H. I. Elim, J. Y. Ouyang, J. He, S. H. Goh, S. H. Tang and W. Ji, *Chem. Phys. Lett.*, 2003, 369, 281.
- 46 H. I. Elim, W. Ji, G. C. Meng, J. Y. Ouyang and S. H. Goh, J. Nonlinear Opt. Phys., 2003, 12, 175.