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

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Figure S1. MALDI–TOF mass spectrum of the monoadduct C$_{60}$(>DPAF-C$_9$) (M$^+$: m/z 1345) 1 in α-cyano-4-hydroxycinnamic acid matrix.
**Figure S2.** Comparison of MALDI–TOF mass spectrum profiles among (a) the monoadduct C$_{60}$(>DPAF-C$_9$) (1, M$^+$, m/z 1345), (b) the bisadduct C$_{60}$(>DPAF-C$_9$)$_2$ (2, M$^+$, m/z 1971), and (c) the tetraadduct C$_{60}$(>DPAF-C$_9$)$_4$ (3a, M$^+$, m/z 3222).
**Figure S3.** MALDI–TOF mass spectrum of the nonpolar tetraadduct \( C_{60}(\text{>DPAF-C}_9)_4 \) (M\(^+\): \( m/z \) 3222) \( 3b \) in \( \alpha \)-cyano-4-hydroxycinnamic acid matrix.

In the high mass region, a group of sharp mass ion peaks corresponding to the molecular mass of \( C_{60}(\text{>DPAF-C}_9)_4 \) \( 3b \) at \( m/z \) 3222 (M\(^+\)) and its isotope peaks at \( m/z \) 3222–3228 were detected, as shown in Fig. S3. Two additional groups of higher mass ions at \( m/z \) 3246 (M+24)\(^+\) and 3263 were, presumably, the result of high laser power conditions. The next major group of mass fragmentation peaks occurring at \( m/z \) 2599 (Fig. 3Sa) matched well with the mass of protonated \( C_{60}(\text{>DPAF-C}_9)_3 \) by the loss of one CH(DPAF-C\(_9\)) group (\( m/z \) 625) from \( 3b \). Further fragmentation of \( C_{60}(\text{>DPAF-C}_9)_3 \) peak to give the corresponding \( C_{60}(\text{>DPAF-C}_9)_2 \) mass ions at \( m/z \) 1972 was also observed in 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-C\(_9\) and CH\(_4\)(DPAF-C\(_9\)), respectively, was detected in a very high peak intensity, implying fast loss of two CH(DPAF-C\(_9\)) groups after the \( C_{60}(\text{>DPAF-C}_9)_3 \) fragment. These mass spectrum data evidently substantiated the mass composition of \( 3b \) as \( C_{60}(\text{>DPAF-C}_9)_4 \). The mass ion peaks at \( m/z \) 2754, 2730, 2127, and 2104 were the result of decarboxylation fragmentation of \( C_{60}(\text{>DPAF-C}_9)_2-(\alpha\text{-cyano-4-hydroxycinnamic acid}) \) and \( C_{60}(\text{>DPAF-C}_9)_2-(\alpha\text{-cyano-4-hydroxycinnamic acid}) \) adducts generated under high voltage MALDI–MS conditions.
Figure S4. Comparison of $^{13}$C NMR spectra of the monoadduct $C_{60}(\geq\text{DPAF-C}_9)$ 1 and the bisadduct $C_{60}(\geq\text{DPAF-C}_9)_2$ 2, showing nearly identical profile of aliphatic carbon peaks with an increase number of fullereryl carbon peaks at $\delta$ 140–148 accounted for proposed two major regioisomers in the isolated narrow TLC fraction.
Analysis of the total aromatic proton counts of (a) the monoadduct $C_{60}(>\text{DPAF-C}_9)$ (1, M.W. 1345), (b) the bisadduct $C_{60}(>\text{DPAF-C}_9)_2$ (2, M.W. 1971), and (c) the tetraadduct $C_{60}(>\text{DPAF-C}_9)_4$ (3a and 3b, M.W. 3222) based on the proton integration calibration using DABCO as an internal standard.

$^1$H NMR spectra of $C_{60}(>\text{DPAF-C}_9)$, $C_{60}(>\text{DPAF-C}_9)_2$, and $C_{60}(>\text{DPAF-C}_9)_4$ showed the total aromatic and aliphatic proton integrations consistent with the corresponding chemical structure containing one, two, and four DPAF addends, respectively, using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the internal reference for counting the proton integration intensity.

The number of protons per molecule was estimated by the total proton integration in the $^1$H NMR spectrum using an internal standard of 1,4-diazabicyclo[2.2.2]octane (DABCO) with a known quantity and a formula as follows.

$$\frac{I_f}{N_{pf}} \frac{M_f}{m_f} = \frac{I_d}{N_{pd}} \frac{M_d}{m_d}$$

where $I_f$ is total proton integration of the compound, $N_{pf}$ is the number of protons of the compound, $M_f$ is the molecular weight of the compound, $m_f$ is the weight of the compound sample used, $I_d$ is total proton integration of DABCO, $N_{pd}$ is the number of protons of DABCO, $M_d$ is the molecular weight of DABCO, and $m_d$ is the weight of DABCO sample used.

![1H NMR spectra of C60(>DPAF-C9), C60(>DPAF-C9)2, and C60(>DPAF-C9)4 showing the total aromatic and aliphatic proton integrations consistent with the corresponding chemical structure containing one, two, and four DPAF addends, respectively, using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the internal reference for counting the proton integration intensity. The number of protons per molecule was estimated by the total proton integration in the 1H NMR spectrum using an internal standard of 1,4-diazabicyclo[2.2.2]octane (DABCO) with a known quantity and a formula as follows.

$$\frac{I_f}{N_{pf}} \frac{M_f}{m_f} = \frac{I_d}{N_{pd}} \frac{M_d}{m_d}$$

where $I_f$ is total proton integration of the compound, $N_{pf}$ is the number of protons of the compound, $M_f$ is the molecular weight of the compound, $m_f$ is the weight of the compound sample used, $I_d$ is total proton integration of DABCO, $N_{pd}$ is the number of protons of DABCO, $M_d$ is the molecular weight of DABCO, and $m_d$ is the weight of DABCO sample used.
For the sample 1 solution containing monoadduct C$_{60}$(>DPAF-C$_9$)$_1$ (7.6 mg, 11 mM) and DABCO (0.48 mg, 8.6 mM) in CDCl$_3$ (0.5 ml), the aromatic protons at $\delta$ 7.0–8.6 gave a total integration account of 21.4 in $^1$H NMR spectrum (a) that leads to the following results.

\[
\frac{I_f \cdot M_f}{N_{pf} \cdot m_f} = \frac{I_d \cdot M_d}{N_{pd} \cdot m_d} \rightarrow \frac{21.4}{7.6 \text{ mg}} = \frac{1345}{12 \text{ mg}} = 12.0 \quad 112
\]

Thus, $N_{pf} = 16.2$ aromatic protons for C$_{60}$(>DPAF-C$_9$)$_1$ (theoretical value is 16).

For the sample 2 solution containing bisadduct C$_{60}$(>DPAF-C$_9$)$_2$ (10.1 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in CDCl$_3$ (0.5 ml), the aromatic protons at $\delta$ 7.0–8.6 gave a total integration account of 39.1 in $^1$H NMR spectrum (b) that leads to the following results.

\[
\frac{I_f \cdot M_f}{N_{pf} \cdot m_f} = \frac{I_d \cdot M_d}{N_{pd} \cdot m_d} \rightarrow \frac{39.1}{10.1 \text{ mg}} = \frac{1970}{12 \text{ mg}} = 12.0 \quad 112
\]

Thus, $N_{pf} = 32.6$ aromatic protons for C$_{60}$(>DPAF-C$_9$)$_2$ (theoretical value is 32).

For the sample 3 solution containing tetraadduct C$_{60}$(>DPAF-C$_9$)$_4$$_3$ (16.5 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in CDCl$_3$ (0.5 ml), the aromatic protons at $\delta$ 7.0–8.6 gave a total integration account of 78.1 in $^1$H NMR spectrum (c) that leads to the following results.

\[
\frac{I_f \cdot M_f}{N_{pf} \cdot m_f} = \frac{I_d \cdot M_d}{N_{pd} \cdot m_d} \rightarrow \frac{78.1}{16.5 \text{ mg}} = \frac{3220}{12 \text{ mg}} = 12.0 \quad 112
\]

Thus, $N_{pf} = 65.3$ aromatic protons for C$_{60}$(>DPAF-C$_9$)$_4$$_3$ (theoretical value is 64).

For the sample 4 solution containing tetraadduct C$_{60}$(>DPAF-C$_9$)$_4$$_3$ (16.5 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in CDCl$_3$ (0.5 ml), the aromatic protons at $\delta$ 7.0–8.6 gave a total integration account of 77.1 in $^1$H NMR spectrum (d) that leads to the following results.

\[
\frac{I_f \cdot M_f}{N_{pf} \cdot m_f} = \frac{I_d \cdot M_d}{N_{pd} \cdot m_d} \rightarrow \frac{77.1}{16.5 \text{ mg}} = \frac{3220}{12 \text{ mg}} = 12.0 \quad 112
\]

Thus, $N_{pf} = 64.5$ aromatic protons for C$_{60}$(>DPAF-C$_9$)$_4$$_3$ (theoretical value is 64).

The number of aromatic protons per molecule estimated from the spectra (a), (b), (c), and (d) agrees well with the monoadduct, bisadduct, and tetraadduct structures of 1, 2, and 3a and 3b, respectively.