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

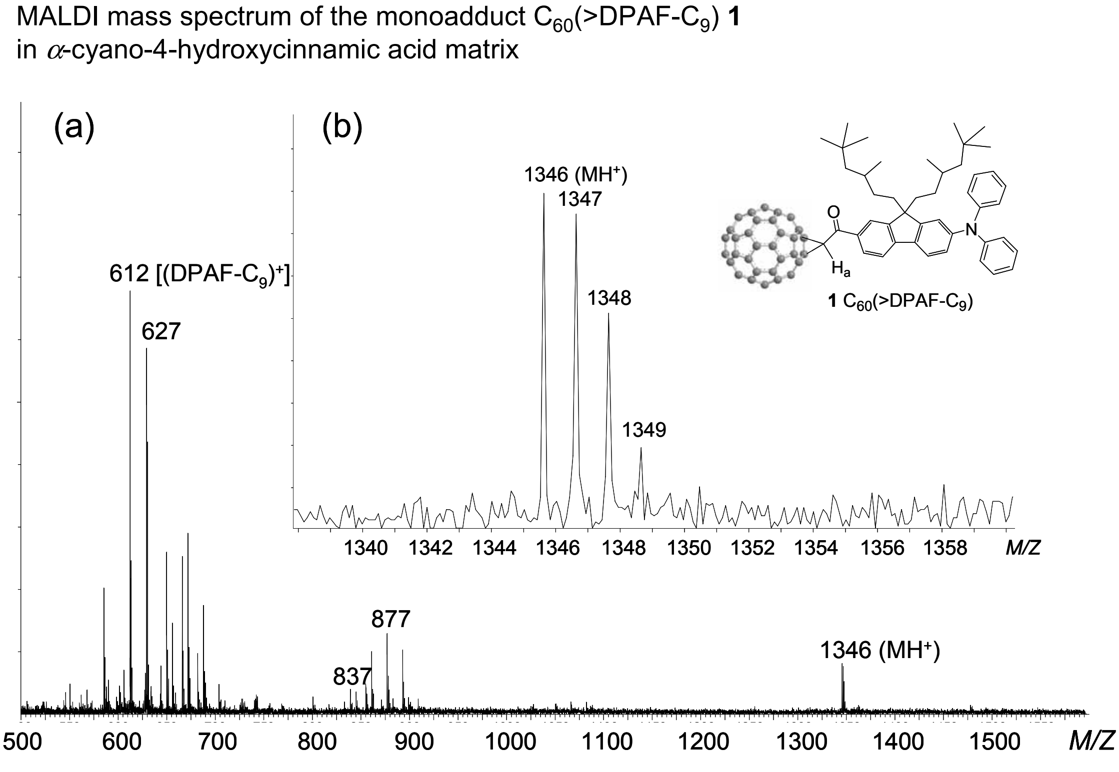
Hendry I. Elim,[a] Robinson Anandakathir,[b] Rachel Jakubiak,[c] Long Y. Chiang,*[b] Wei Ji,*[a] and Loon-Seng Tan*[c]

[a] *Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore, E-mail: phyjiwei@nus.edu.sg; Fax: 65-67776126; Tel: 65-68742664*

[b] *Department of Chemistry, University of Massachusetts Lowell, Lowell, MA 01854, USA. E-mail: Long_Chiang@uml.edu; Fax: (978)-934-3013; Tel: (978)-934-3663*

[c] *Air Force Research Laboratory, AFRL/MLBP, Wright-Patterson Air Force Base, Dayton, OH 45433, USA. E-mail: Loon-Seng.Tan@wpafb.af.mil; Fax: (937)-255 -9157; Tel: (937)-255-9141*

Figure S1. MALDI–TOF mass spectrum of the monoadduct C_{60}(>DPAF-C_9) (M^+: *m/z* 1345) **1** in *a*-cyano-4-hydroxycinnamic acid matrix.



MALDI mass spectrum of the monoadduct C_{60}(>DPAF-C_9) **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).

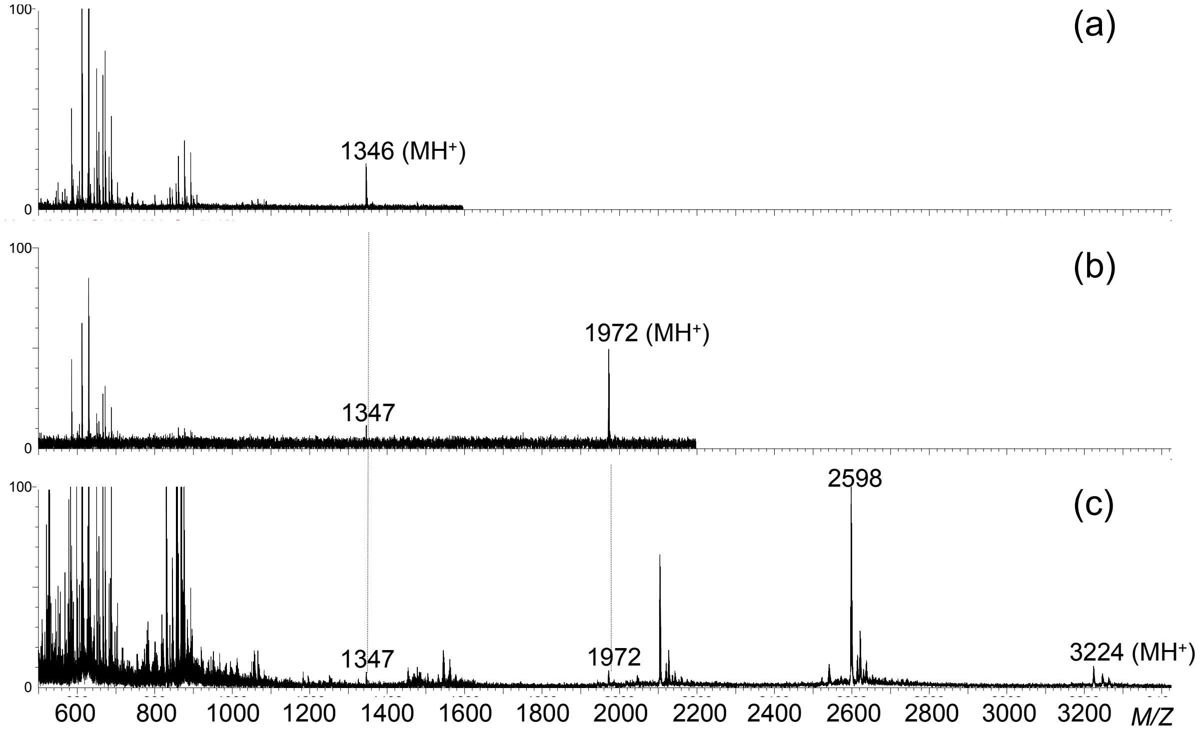
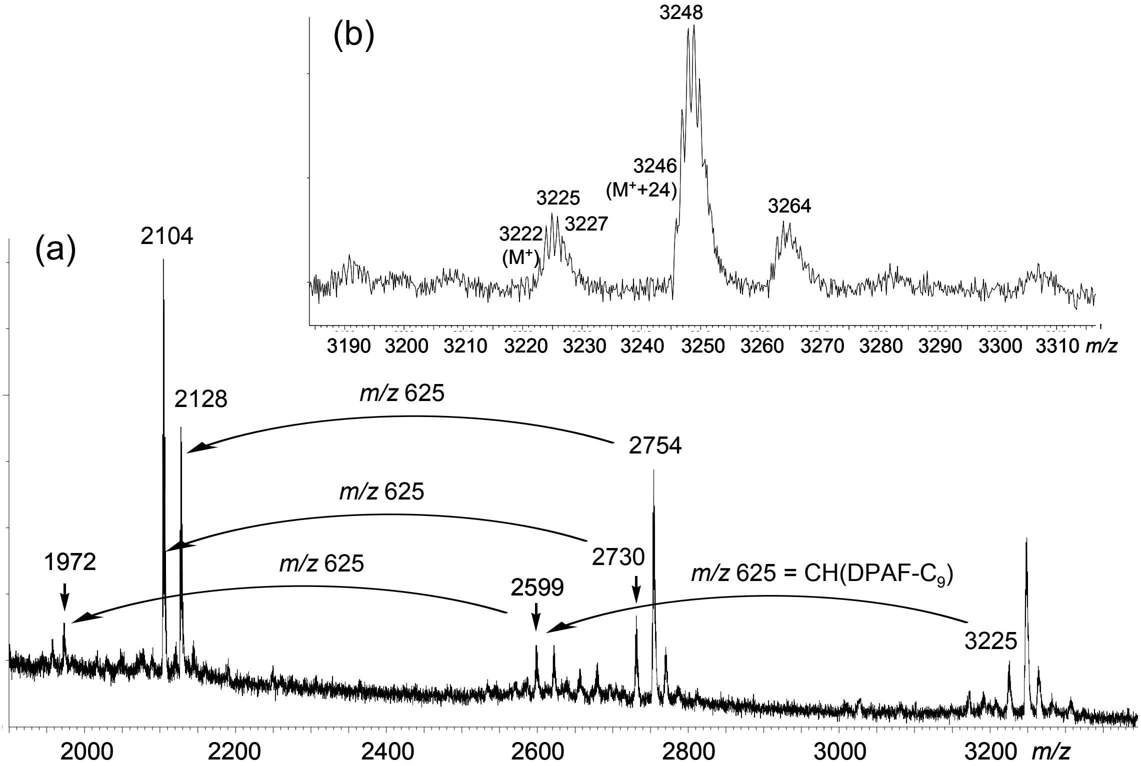
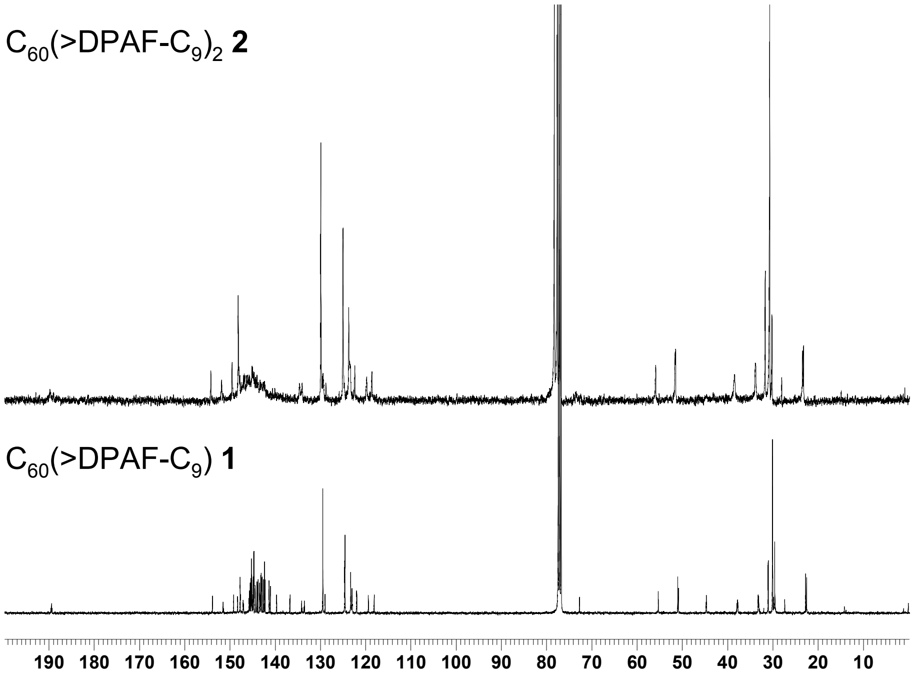


Figure S3. MALDI–TOF mass spectrum of the nonpolar tetraadduct $C_{60}(>DPAF\text{-}C_9)_4$ (M^+: *m/z* 3222) **3b** in *a*-cyano-4-hydroxycinnamic acid matrix.



In the high mass region, a group of sharp mass ion peaks corresponding to the molecular mass of $C_{60}(>DPAF\text{-}C_9)_4$ **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 $C_{60}(>DPAF\text{-}C_9)_3$ by the loss of one CH(DPAF-C_9) group (*m/z* 625) from **3b**. Further fragmentation of $C_{60}(>DPAF\text{-}C_9)_3$ peak to give the corresponding $C_{60}(>DPAF\text{-}C_9)_2$ 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_x(DPAF-C_9), respectively, was detected in a very high peak intensity, implying fast loss of two CH(DPAF-C_9) groups after the $C_{60}(>DPAF\text{-}C_9)_3$ fragment. These mass spectrum data evidently substantiated the mass composition of **3b** as $C_{60}(>DPAF\text{-}C_9)_4$. The mass ion peaks at *m/z* 2754, 2730, 2127, and 2104 were the result of decarboxylation fragmentation of $C_{60}(>DPAF\text{-}C_9)_3$-($\alpha$-cyano-4-hydroxycinnamic acid) and $C_{60}(>DPAF\text{-}C_9)_2$-($\alpha$-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}(>DPAF-C_9) **1** and the bisadduct C_{60}(>DPAF-C_9)$_2$ **2**, showing nearly identical profile of aliphatic carbon peaks with an increase number of fullerenyl carbon peaks at δ 140–148 accounted for proposed two major regioisomers in the isolated narrow TLC fraction.



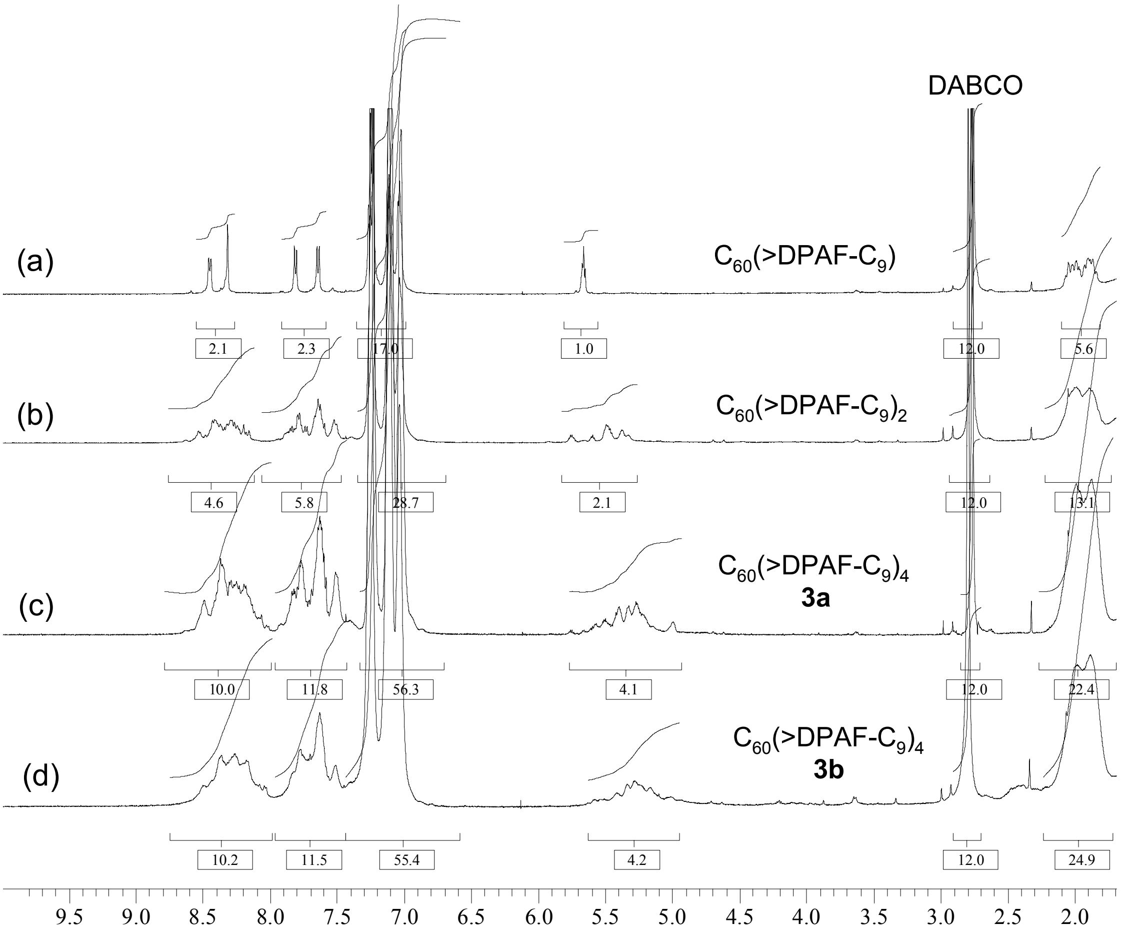
Analysis of the total aromatic proton counts of (a) the monoadduct C_{60}(>DPAF-C_9) (1, M.W. 1345), (b) the bisadduct C_{60}(>DPAF-C_9)$_2$ (2, M.W. 1971), and (c) the tetraadduct C_{60}(>DPAF-C_9)$_4$ (3a and 3b, M.W. 3222) based on the proton integration calibration using DABCO as an internal standard

^{1}H NMR spectra of C_{60}(>DPAF-C_9), C_{60}(>DPAF-C_9)$_2$, and C_{60}(>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.



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 δ 7.0–8.6 gave a total integration account of 21.4 in ^{1}H NMR spectrum (a) that leads to the following results.

$$\frac{I_f}{N_{pf}}\frac{M_f}{m_f} = \frac{I_d}{N_{pd}}\frac{M_d}{m_d} \rightarrow \frac{21.4}{N_{pf}}\frac{1345}{7.6\ \text{mg}} = \frac{12.0}{12}\frac{112}{0.48\ \text{mg}}$$

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)$_2$ **2** (10.1 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in $CDCl_3$ (0.5 ml), the aromatic protons at δ 7.0–8.6 gave a total integration account of 39.1 in ^{1}H NMR spectrum (b) that leads to the following results.

$$\frac{I_f}{N_{pf}}\frac{M_f}{m_f} = \frac{I_d}{N_{pd}}\frac{M_d}{m_d} \rightarrow \frac{39.1}{N_{pf}}\frac{1970}{10.1\ \text{mg}} = \frac{12.0}{12}\frac{112}{0.48\ \text{mg}}$$

Thus, N_{pf} = 32.6 aromatic protons for C_{60}(>DPAF-C_9)$_2$ **2** (theoretical value is 32).

For the sample 3 solution containing tetraadduct C_{60}(>DPAF-C_9)$_4$ **3a** (16.5 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in $CDCl_3$ (0.5 ml), the aromatic protons at δ 7.0–8.6 gave a total integration account of 78.1 in ^{1}H NMR spectrum (c) that leads to the following results.

$$\frac{I_f}{N_{pf}}\frac{M_f}{m_f} = \frac{I_d}{N_{pd}}\frac{M_d}{m_d} \rightarrow \frac{78.1}{N_{pf}}\frac{3220}{16.5\ \text{mg}} = \frac{12.0}{12}\frac{112}{0.48\ \text{mg}}$$

Thus, N_{pf} = 65.3 aromatic protons for C_{60}(>DPAF-C_9)$_4$ **3a** (theoretical value is 64).

For the sample 4 solution containing tetraadduct C_{60}(>DPAF-C_9)$_4$ **3b** (16.5 mg, 10 mM) and DABCO (0.48 mg, 8.6 mM) in $CDCl_3$ (0.5 ml), the aromatic protons at δ 7.0–8.6 gave a total integration account of 77.1 in ^{1}H NMR spectrum (d) that leads to the following results.

$$\frac{I_f}{N_{pf}}\frac{M_f}{m_f} = \frac{I_d}{N_{pd}}\frac{M_d}{m_d} \rightarrow \frac{77.1}{N_{pf}}\frac{3220}{16.5\ \text{mg}} = \frac{12.0}{12}\frac{112}{0.48\ \text{mg}}$$

Thus, N_{pf} = 64.5 aromatic protons for C_{60}(>DPAF-C_9)$_4$ **3b** (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.