Nonlinear optical studies of fullerene–arylethyne hybrids†

Ryo Hamasaki,[a] Masateru Ito,[a] Mouad Lamrani,[a] Masaya Mitsuishi,[b] Tokuji Miyashita[b] and Yoshinori Yamamoto*[a]

[a]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[b]Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-2-1, Aoba-ku, Sendai 980-8577, Japan

The fullerene–arylethyne hybrids **2** and **3** were synthesized in order to investigate their NLO activities. The β values for **2** and **3** were obtained by hyper Rayleigh scattering measurements. The arylethynyl fullerenes **3a–f** exhibit β values in the range $20-361 \times 10^{-30}$ esu. Interestingly, the β values for **3a,b** are higher than those for **3c–f**; a good correlation was obtained between the Hammett σ_p values of the *para* substituents of **3** and their β values. The ^{1}H-NMR and $E_{1/2}$ data indicate that the fullerene moieties of **3** attract electrons from the arylethynyl groups *in the ground state*. The β values for **2a–c** are higher than those for **3a–f**; the *para*-carborane–fullerene dyad **2c** exhibits an exceptionally high β value (1189×10^{-30} esu). The electronic characteristics of the carbon and boron clusters are discussed.
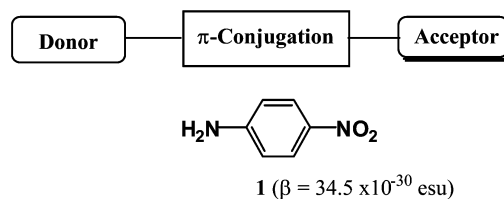
Introduction

Recent years have witnessed a dramatic growth in multidisciplinary research activity involving materials that exhibit quadratic nonlinear optical (NLO) behavior, which have attracted attention owing to their direct application in the development of efficient optical telecommunication networks without electrical-to-optical, and *vice versa*, signal conversion.[1] Such applications require thermally robust materials with highly nonlinear optical responses (first hyperpolarizability, β). The use of organic materials may offer significant advantages over conventional inorganic crystals such as LiNbO$_3$.[2] In the past decade, considerable efforts have been focused on the development of materials with large molecular hyperpolarizabilities. Typical organic NLO compounds include donor (D) and acceptor (A) moieties connected *via* a π-conjugated linker. Until now, most efforts to obtain better hyperpolarizabilities have been directed towards finding both the right combination of D and A and the right length of conjugated bridge between D and A[3] [for example, 4-nitroaniline (**1**); Scheme 1]. On the other hand, we recently reported that combinations of seemingly attractive carboranes and seemingly attractive fullerene linked through an arylethynyl π-system (**2a–c**; Scheme 2) give unexpectedly high β values, with the *para*-carborane derivative **2c** showing the highest β value (1189×10^{-30} esu).[4]

It has been known for many years that *closo*-carboranes are electron-deficient boron clusters with highly polarizable σ-aromatic character[5] and that fullerene is an electron-attracting carbon cluster having highly delocalizable π-electrons.[6] Carboranes (A) containing electron-donor (D) moieties have been synthesized, but their β values were found to be moderate or low.[7] Nevertheless, the fullerene–carborane hybrid dyads **2a–c**, which are seemingly acceptor–acceptor combinations, exhibit unexpectedly high NLO activities; β values of 346, 483, and 1189×10^{-30} esu for **2a–c**, respectively.[4] Accordingly, we decided to investigate systematically whether the fullerene moieties of **2** really act as acceptors in NLO activities, as is believed and often mentioned in the literature.[8,9] We
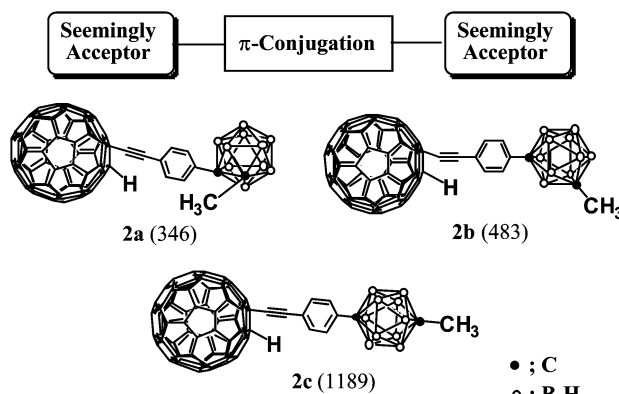
synthesized the arylethynyl fullerenes **3**, in which appropriate electron-donating and electron-withdrawing groups (X) were attached to the *para* position of the phenyl ring (Scheme 3). There was a good correlation between the β values of **3** and the Hammett σ_p values of the X substituents. In this article, we report full details of this interesting result, together with the role of carborane in NLO activities, which explains why compounds **2** exhibit rather high β values.

Experimental

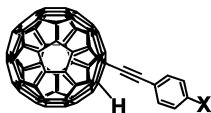NMR, UV-vis, cyclic voltammetry (CV) and hyper Rayleigh scattering (HRS) spectra are provided in the ESI.

1 ($\beta = 34.5 \times 10^{-30}$ esu)

Scheme 1

2a (346)   **2b** (483)

2c (1189)

$\bullet$; C
$\circ$; B-H

Scheme 2

3a: X=CF₃, 3b: X=Cl, 3c: X=H,
**3d: X=Me, 3e: X=OMe, 3f: X=NMe₂**

Scheme 3

Instrumentation

Fluorescence and UV-vis absorption spectra were measured with a Hitachi F-4500 spectrofluorophotometer and a Hitachi U-3000 UV-vis spectrometer, respectively. The HRS measurements were carried out by using a q-switched Nd : YAG laser (spectron LS-412; fwhm 6 ns) as an incident light beam. The fundamental light intensity [$\gamma = 1064$ nm, $I(\omega)$] was varied by rotating a half-wave plate positioned between two polarizers. The HRS signal, $I(2\omega)$ was detected by a photomultiplier (Philips model XP 2020Q) as a function of $I(\omega)$. Both incident fundamental light and HRS light signals were fed into two gated integrators (Stanford Research Systems model SR250) and output signals from the gated integrators were A–D converted and analyzed on a personal computer. NMR spectra were recorded at frequencies of 300 MHz for ¹H and 150 MHz for ¹³C, from CDCl₃–CS₂ solutions. FAB mass spectra were obtained using a JEOL JMS-HX110 spectrometer using *m*-nitrobenzyl alcohol matrices.

Materials

C₆₀ (99.5%) was purchased from MER Corp. The phenylacetylene derivatives **4a–f** were prepared according to the published procedure.[10] The fullerene–carborane dyads **2a–c**[4] and phenylethynylfullerene **3c**[11] were synthesized by the reported procedures.

General procedure for the synthesis of 3

Under a scrupulously dry Ar atmosphere, a 1.5 M *n*-hexane solution of *n*-BuLi (0.2 ml, 0.3 mmol) was added to a THF solution (1.5 ml) of the appropriate phenylacetylene derivative **4** (0.3 mmol) at 0 °C. The solution became yellowish orange and was left at room temperature for 15 min. A THF solution (6.0 ml) of C₆₀ (72 mg, 0.1 mmol) was sonicated for 30 min. at 30 °C under a dry Ar atmosphere. The solution of lithiated **4** was added slowly to the C₆₀ solution. The mixture turned dark green and was stirred vigorously for 15 min. After addition of CF₃COOH (2 ml), the solvents were evaporated. Silica gel column chromatography (with *n*-hexane, Et₂O, then CH₂Cl₂ as eluents) of the resulting brown–black crude products gave compounds **3** in the yields indicated in Table 1.
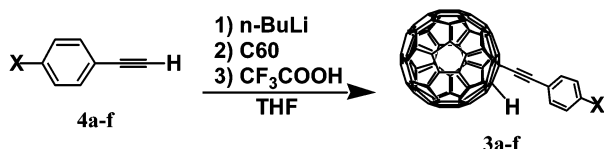
1-{4-(2-Methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)phenyl}-ethynyl-1,2-dihydrofullerene-60 (2a).[4] ¹H-NMR: δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 1H), 1.78 (s, 3H). ¹³C-NMR: δ 151.12, 150.66, 146.52, 146.42, 146.37, 146.22, 145.73, 145.69, 145.48, 145.45, 145.44, 145.34, 144.67, 144.44, 143.21, 142.99, 142.62, 142.58, 142.05, 141.97, 141.75, 141.66, 141.61, 140.39, 140.37, 135.92, 135.21, 132.38, 131.33, 131.21, 130.89, 125.07, 100.39, 95.13, 82.02, 61.63, 55.32, 29.79. MS (FAB⁺) *m/z*: 978 (M⁺); 817.0 [M⁺ − (1-Me-1,2-C₂B₁₀H₁₁)]; 721 (C₆₀H); 720 (C₆₀); 257 (1-CCPh,2-Me-1,2-C₂B₁₀H₁₀); 234 (1-Me,2-Ph,1,2-C₂B₁₀H₁₀); 158 (1-Me,2-C₂B₁₀H₁₀).

Table 1 Yields of **3** from the reaction of fullerene with **4**

Compound	X	Yield (%)
3a	CF₃	20
3b	Cl	6
3c	H	39[a]
3d	Me	40
3e	OMe	44
3f	NMe₂	47

[a]Ref. 11.

1-{4-(7-Methyl-1,7-dicarba-*closo*-dodecaboran-1-yl)phenyl}-ethynyl-1,2-dihydrofullerene-60 (2b).[4] ¹H-NMR: δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 1H), 1.82 (s, 3H). ¹³C-NMR: δ 151.18, 150.84, 147.50, 147.22, 146.49, 146.31, 146.28, 146.13, 146.11, 145.67, 145.45, 145.40, 145.34, 145.25, 144.58, 144.38, 143.12, 142.91, 142.52, 142.49, 141.99, 141.95, 141.90, 141.72, 141.59, 141.53, 140.28, 135.92, 135.74, 135.10, 131.88, 128.00, 122.97, 93.78, 82.59, 61.69, 55.06, 24.56. MS (FAB⁺) *m/z*: 977 (M⁺ − H); 817.0 [M⁺ − (1-Me-1,7-C₂B₁₀H₁₁)]; 744 [M⁺ − (1-Me,7-Ph,1,7-C₂B₁₀H₁₀)]; 721 (C₆₀H); 720 (C₆₀); 258 (1-CCPh,7-Me-1,7-C₂B₁₀H₁₀); 234 (1-Me,7-Ph,1,7-C₂B₁₀H₁₀); 158 (1-Me-1,7-C₂B₁₀H₁₀).

1-{4-(12-Methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl}-ethynyl-1,2-dihydrofullerene-60 (2c).[4] ¹H-NMR: δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.05 (s, 1H), 1.23 (s, 3H). ¹³C-NMR: δ 151.28, 150.97, 147.53, 147.25, 146.53, 146.34, 146.31, 146.15, 145.71, 145.61, 145.51, 145.41, 145.36, 145.27, 144.61, 144.42, 143.14, 142.95, 142.54, 142.50, 142.01, 141.93, 141.76, 141.61, 141.55, 140.30, 140.28, 136.74, 135.96, 135.12, 131.66, 127.43, 122.55, 93.47, 82.72, 61.72, 55.01, 25.57. MS (FAB⁺) *m/z*: 977 (M⁺ − H); 817.0 [M⁺ − (1-Me-1,12-C₂B₁₀- H₁₁)]; 744 [M⁺ − (1-Me,12-Ph-1,12-C₂B₁₀H₁₀)]; 721 (C₆₀H); 720 (C₆₀); 258 (1-CCPh,12-Me-1,12-C₂B₁₀H₁₀); 234 (1-Me,12-Ph-1,12-C₂B₁₀H₁₀); 158 (1-Me-1,12-C₂B₁₀H₁₀).

1-(4-Trifluoromethylphenyl)ethynyl-1,2-dihydrofullerene-60 (3a). ¹H-NMR: δ 7.92 (d, *J* = 9 Hz, 2H), 7.74 (d, *J* = 9 Hz, 2H), 7.13 (s, 1H). ¹³C-NMR: δ 151.16, 150.70, 147.59, 147.31, 146.54, 146.41, 146.36, 146.21, 145.74, 145.70, 145.50, 145.48, 145.43, 145.33, 144.66, 144.44, 143.20, 142.98, 142.61, 142.57, 142.05, 141.97, 141.76, 141.66, 141.61, 140.38, 135.94, 135.24, 132.39, 130.67 (q, *J*₍C–F₎ = 33 Hz), 126.25, 125.43 (m), 123.67 (q, *J*₍C–F₎ = 271 Hz), 94.61, 82.17, 61.64, 54.99. MS (FAB⁺) *m/z*: 891 (M⁺ + H), 745 (M⁺ − CF₃C₆H₄), 720 (C₆₀).

1-(4-Chlorophenyl)ethynyl-1,2-dihydrofullerene-60 (3b). ¹H-NMR: δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 1H). ¹³C-NMR: δ 151.41, 151.12, 147.66, 147.38, 146.64, 146.45, 146.42, 146.26, 145.83, 145.71, 145.63, 145.51, 145.48, 145.39, 144.72, 144.52, 143.24, 142.65, 142.61, 142.13, 142.08, 142.02, 141.86, 141.72, 141.65, 140.41, 140.39, 136.05, 135.23, 135.20, 133.37, 128.93, 120.93, 93.22, 82.50, 61.76. MS (FAB⁺) *m/z*: 859 (M⁺ + H), 745 (M⁺ − ClC₆H₄), 720 (C₆₀).

1-Phenylethynyl-1,2-dihydrofullerene-60 (3c).[12] ¹H-NMR: δ 7.77 (m, 2H), 7.45 (m, 3H), 7.13 (s, 1H). ¹³C-NMR: δ 151.51, 151.22, 147.49, 147.21, 146.63, 146.30, 146.27, 146.12, 145.70, 145.60, 145.55, 145.41, 145.33, 145.25, 144.61, 144.42, 143.13, 142.52, 142.49, 142.06, 141.97, 141.93, 141.81, 141.62, 141.54, 140.30, 140.27, 135.99, 135.08, 132.06, 128.91, 128.55, 122.47, 92.24, 84.05, 61.87, 55.03. MS (FAB⁺) *m/z*: 822 (M⁺), 720 (C₆₀)

1-(4-Methylphenyl)ethynyl-1,2-dihydrofullerene-60 (3d). ¹H-NMR: δ 7.69 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.12 (s, 1H), 2.45 (s, 3H). ¹³C-NMR: δ 151.47, 151.38, 147.50, 147.23, 146.57, 146.29, 146.12, 146.11, 145.72, 145.60, 145.56, 145.39, 145.33, 145.25, 144.60, 144.43, 143.11, 142.92, 142.50, 142.47,

141.95, 141.92, 141.81, 141.61, 141.52, 140.29, 140.23, 138.94, 136.04, 135.05, 132.03, 129.23, 119.38, 91.62, 83.90, 61.88, 55.09, 21.62. MS (FAB$^+$) m/z: 837 (M$^+$ + H), 744 (M$^+$ − MeC$_6$H$_4$ − H), 720 (C$_{60}$).

1-(4-Methoxyphenyl)ethynyl-1,2-dihydrofullerene-60 (3e). ^{1}H-NMR: δ 7.73 (d, J = 9 Hz, 2H), 7.12 (s, 1H), 6.98 (d, J = 9 Hz, 2H), 3.89 (s, 3H). ^{13}C-NMR: δ 151.59, 151.58, 147.57, 147.30, 146.63, 146.35, 146.18, 146.16, 145.78, 145.67, 145.60, 145.43, 145.38, 145.31, 144.65, 144.49, 143.16, 142.98, 142.55, 142.52, 142.09, 141.97, 141.88, 141.66, 141.57, 140.34, 140.27, 136.10, 135.06, 133.56, 114.46, 114.12, 91.00, 83.74, 61.94, 55.17, 55.12. MS (FAB$^+$) m/z: 853 (M$^+$ + H), 744 (M$^+$ − MeOC$_6$H$_4$ − H), 720 (C$_{60}$).

1-(4-N,N-Dimethylaminophenyl)ethynyl-1,2-dihydrofullerene-60 (3f). ^{1}H-NMR: δ 7.66 (d, J = 9 Hz, 2H), 7.12 (s, 1H), 6.75 (d, J = 9 Hz, 2H), 3.06 (s, 6H). ^{13}C-NMR: δ 152.14, 151.95, 150.47, 147.65, 147.38, 146.76, 146.41, 146.25, 146.23, 145.91, 145.89, 145.62, 145.48, 145.45, 145.38, 144.74, 144.61, 143.22, 142.60, 142.58, 142.19, 142.08, 142.04, 141.74, 141.63, 140.41, 140.28, 136.28, 135.09, 133.28, 111.87, 108.99, 90.28, 84.86, 62.13, 55.46, 40.17. MS (FAB$^+$) m/z: 866 (M$^+$ + H), 744 (M$^+$ − MeOC$_6$H$_4$ − H), 720 (C$_{60}$).

Results and discussion

Syntheses of the arylethynyl fullerenes 3

The arylethynyl fullerenes **3** were prepared in one step from the corresponding aryl acetylenes **4**, which were synthesized by the Sonogashira coupling protocol; aryl iodides or bromides were treated with trimethylsilylacetylene under Pd(PPh$_3$)$_4$–CuI-catalyzed conditions.[10] Treatment of **4a–f** with n-BuLi, followed by addition of C$_{60}$ and subsequent treatment with CF$_3$COOH, gave **3a–f** in moderate to low yields[11] (Table 1). The synthesis of compounds **2** was carried out in a similar manner to that described previously;[4] the carborane-substituted phenylacetylenes were synthesized and the coupling reaction between them and fullerene gave the corresponding carborane–fullerene dyads **2**. The arylethynyl fullerenes **3c–f**, having electron-donating groups at the *para* position of the phenyl ring, were obtained in higher yields than **3a,b**, which have electron-withdrawing *para* groups. The lithiated arylethynes of **4a,b** underwent facile polymerization, in comparison with those of **4c–f**, leading to low yields of **3a,b**. The structural

Table 2 UV-vis and ^{1}H-NMR data for **3** and **4**

Compound	X	λ_{max}/nm (log ε)	^{1}H-NMR C$_{60}$H^a	C$_6$H$_4{}^b$
3a	CF$_3$	258 (5.29), 328 (4.76), 431 (3.70)	7.29, 7.74	7.13
4a	—		7.57	—
3b	Cl	258 (5.23), 328 (4.67), 432 (3.52)	7.74, 7.45	7.11
4b	—		7.39, 7.25	—
3c	H	258 (5.09), 328 (4.53), 432 (3.41)^c	7.77, 7.45	7.13
4c	—		7.45, 7.28	—
3d	Me	258 (5.40), 328 (4.87), 433 (3.62)	7.69, 7.27	7.12
4d	—		7.37, 7.11	—
3e	OMe	258 (5.12), 328 (4.56), 430 (3.52)	7.73, 6.98	7.12
4e	—		7.41, 6.82	—
3f	NMe$_2$	258 (5.07), 295 (4.88), 430 (3.75)	7.66, 6.75	7.12
4f	—		7.36, 6.61	—

^{a}Protons on benzene ring. ^{b}Proton on fullerene cage. ^{c}Ref. 12

assignments of **3a–f** were carried out by analytical and spectroscopic techniques (*i.e.* ^{1}H-NMR, ^{13}C-NMR, UV-vis and FAB MS) and full details are given in the ESI. Representative data from the UV-vis and ^{1}H-NMR spectra of **3** and **4** are summarized in Table 2. The ^{1}H-NMR spectra of **3** show a proton on the fullerene skeleton around δ 7.1, which is in good agreement with the chemical shifts reported for protons of related fullerene derivatives.[11] Additionally, the protons on the benzene rings of **3** appear at slightly lower magnetic fields, compared to those of the corresponding compounds **4**, indicating that in the ground state, the fullerene moieties of **3** attract electrons from the benzene ring.

SHG activities of 3 and correlation between their β values and the Hammett σ_p values of the X substituents

In order to measure hyperpolarizability values with hyper Rayleigh scattering, it is essential that there are no absorptions or emissions around 532 nm, since the resonance and fluorescence around 532 nm enhance the hyperpolarizabilities of **3**, which makes it difficult to obtain accurate β values. The UV-vis absorption spectra of **3a–e** in CHCl$_3$ show two large absorption bands at 258 and 328 nm, which arise from fullerene moieties (Table 2).[11] In the case of **3f**, a strong band appears at 295 nm instead of 328 nm. The NMe$_2$ group is well known as an auxochrome and, in general, the absorption of phenyl rings with NMe$_2$ substituents appears around 300 nm. In this case, the absorption of the phenylacetylene moiety of **3f** appears at 295 nm and an enhanced auxochrome effect due to the NMe$_2$ group is observed. The UV-vis spectrum of **3f** is different from the spectra of **3b–e** because the strong absorption of the (dimethylaminophenyl)acetylene moiety obscures the absorption of the fullerene moiety at 328 nm. The spectrum of **3a** shows a weak absorption at 310 nm. This could be due to the phenylacetylene moiety. In the case of **3b–e**, however, similar absorptions around 300 nm are not observed, perhaps because the strong absorptions of fullerene at 258 and 328 nm obscure any peaks around 300 nm. Furthermore, very weak absorption bands are observed around 430–433 nm (log ε 3.41–3.75), which are presumably due to a forbidden transition; absorption bands around 430 nm are typical of 1,2-dihydrofullerenes.[12] No absorptions are observed at wavelengths greater than 450 nm for CHCl$_3$ solutions of **3a–f**, although C$_{60}$ itself and **3c** in cyclohexane exhibit very weak absorption bands between 470–700 nm with log ε 2.3–3.2. Excitation at 258 and 328 nm produced fluorescence spectra, which show broad band emissions in the range 350–390 nm. The emission spectra are attributed to Raman scattering by CHCl$_3$. Fullerene fluorescence is usually observed around 700 nm and is, in general, measured in cyclohexane.[13] However, in the present case using CHCl$_3$ as solvent, fluorescence spectra around 700 nm were not observed. We attempted to dissolve **3a,b** and **3d–f** in cyclohexane, THF and CH$_3$CN, but were unsuccessful. In conclusion, CHCl$_3$ solutions of **3** (10$^{−4}$ M) did not show significant spectroscopic absorption and emission around the double frequency value 532 nm, allowing us to carry out the measurements necessary to deduce the β coefficients.

HRS measurements were performed to determine the molecular nonlinear optical properties of the dyads. All the measurements were performed at a fundamental wavelength of 1064 nm (see Experimental). The β values for **3a–f** are summarized in Table 3. It should be noted that **3a,b**, which are fullerene–acceptor systems, exhibit much higher β values than **3c–f**, fullerene–donor systems. As expected, the β value for fullerene itself was zero under the same experimental conditions, due to its centrosymmetric structure. Fig. 1 shows a correlation between the β values for **3** and the Hammett σ_p values of the X substituents.

A good correlation between the β values for **3** and the Hammett σ_p values of the X substituents is observed; higher σ_p
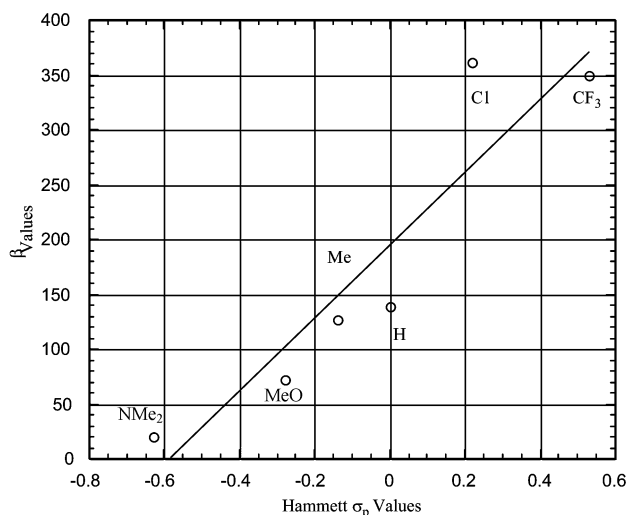
Table 3 Hammett σ_p and β values for **3**

Compound (X)	σ_p	$\beta/10^{-30}$ esu	$\beta_0/10^{-30}$ esu
3a (CF$_3$)	0.53	350	196
3b (Cl)	0.22	361	*ca.* 220
3c (H)	0	139	*ca.* 83
3d (Me)	−0.14	127	*ca.* 76
3e (OMe)	−0.28	72	*ca.* 43
3f (NMe$_2$)	−0.63	20	15

Fig. 1 Plot of Hammett σ_p *versus* β for **3**.

values lead to higher β values, indicating that fullerene acts as an electron-donating group in the excited state. As mentioned above, fullerene acts as an electron-withdrawing group in the ground state, and this is an accepted fact in fullerene chemistry.[6,12] As discussed below, the NLO activities depend on the electronic characteristics of the excited process.

The calculation of β_0 values is essential for determining the energy levels of empty orbitals, which exert the strongest influence on the single harmonic generation (SHG) activity. Considering the correlation between the Hammett σ_p values and the β values for **3**, it is reasonable to conclude that the orbitals of the phenylacetylene moieties around 300 nm exert the strongest influence on the SHG activities. The β_0 values for **3a** and **3f**, which were calculated according to the two-level model, are shown in Table 3. The exact β_0 values for **3b–e** could not be determined because the absorptions of phenylacetylene moieties were not observed, as mentioned above. Accordingly, the β_0 values for **3b–e** were calculated based upon the assumption that the UV absorptions would appear at 300 nm, similarly to those of **3a** and **3f**.

Electrochemical studies of 2 and 3c,d

In order to clarify the role of the fullerene moieties of **3** in the NLO activities and the role of the carboranes of **2** in the high hyperpolarizabilities, the electrochemical behavior of **2a–c** and **3c,d**, which are essentially reflections of the LUMO levels of the fullerene moieties, were studied by cyclic voltammetry in *o*-dichlorobenzene at room temperature. The redox properties of **3a,b** were also examined, but we could not obtain satisfactory data, perhaps because the carbon–halogen bonds of **3a,b** are cleaved under the electrochemical conditions employed. The cyclic voltammograms of **2a** and C$_{60}$ are shown in Fig. 2.[11a] Compounds **2a–c** and **3c,d** show similar CV curves, and reversible reduction waves corresponding to the reduction of fullerene moieties were observed. The redox potentials of **2a–c**, **3c,d** and C$_{60}$ are summarized in Table 4, in which the first reductive potential (E_1^{red}), the first oxidative
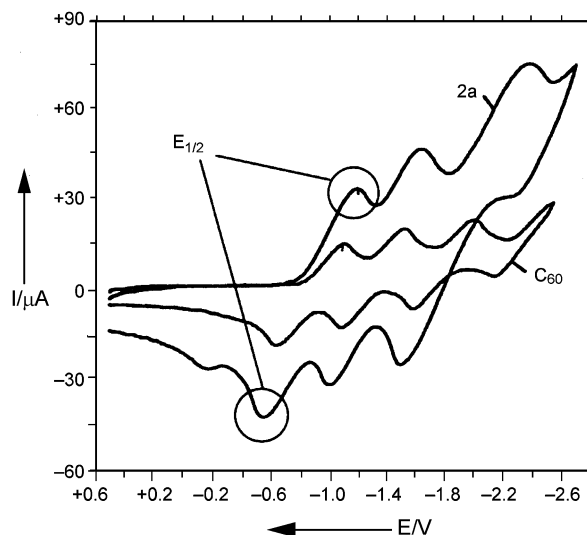
Fig. 2 Cyclic voltammogram of **2a** (5×10^{-3} M) and C$_{60}$ (2.5×10^{-3} M) in *o*-dichlorobenzene {supporting electrolyte 0.1 M *n*-Bu$_4$NClO$_4$; working electrode glassy carbon; counter electrode Pt wire; reference electrode Ag/0.01 N AgNO$_3$ in acetonitrile with 0.1 M *n*-Bu$_4$NClO$_4$ [$E_{1/2}$(ferrocene/ferrocenium) = 180 mV]; scan rate 100 mV s^{-1}}.

Table 4 Redox potentials[a] of C$_{60}$, **2** and **3c,d**

Compound	X	E_1^{red}	E_1^{ox}	$E_{1/2}$[b]
C$_{60}$	—	−1103	−631	−867
2a	*o*-Carborane	−1242	−552	−897
2b	*m*-Carborane	−1210	−581	−896
2c	*p*-Carborane	−1193	−615	−904
3c	H	−1086	−752	−919
3d	Me	−1108	−766	−937

[a]Potentials in mV *vs.* ferrocene/ferrocenium measured in *o*-dichlorobenzene. [b]Of the three quasi-reversible redox peaks, only the $E_{1/2}$ [1/2($E_1^{red} + E_1^{ox}$)] values for the first peaks are listed, the other peaks are shown in the ESI.

potential (E_1^{ox}) and $E_{1/2}$ [1/2($E_1^{red} + E_1^{ox}$)] are shown for simplicity, although three quasi-reversible reduction–oxidation peaks were observed, as shown in Fig. 2 for **2a**. The one-electron reduction of uncharged molecules of **2** and **3c,d** (E_1^{red}), and the one-electron oxidation of **2** and **3c,d** (E_1^{ox}) are more important than further reductions and the oxidations of the charged molecules in the discussion of the electrochemical properties of **2** and **3c,d**. The E_1^{red} values for **2a–c** and **3d** are more negative than that for fullerene itself, and the E_1^{ox} values for **2a–c** and **3c,d** are between −770 and −550 mV. In terms of the electronic properties of **2** and **3c,d**, both the E_1^{red} and E_1^{ox} values are important because they give the information about the electron-transfer ability of the substrates. Accordingly, the $E_{1/2}$ values, which are the average of E_1^{red} and E_1^{ox}, are used for the discussion of the electrochemical properties of the substrates. The $E_{1/2}$ values for **2a–c** and **3c,d** are cathodically shifted compared to that of fullerene, indicating that the electron densities of the fullerene moieties of **2** and **3c,d** are higher than that of C$_{60}$ itself. The increased electron densities are the result of saturation of a carbon–carbon double bond of the fullerenes *via* the attachment of the arylethynyl groups.[11a,14,15] Thus, it is clear that the fullerene moieties of **2** and **3c,d** are much more electron-rich than C$_{60}$ itself in the ground state. The fullerene moieties of **2** attract electrons from the arylethynyl groups, even though electron-withdrawing carboranes are attached to the *para* position of the phenyl groups, and this experimental result is in good agreement with the fact that fullerene is an electron-attracting carbon cluster. It is interesting to consider the order of redox potentials of
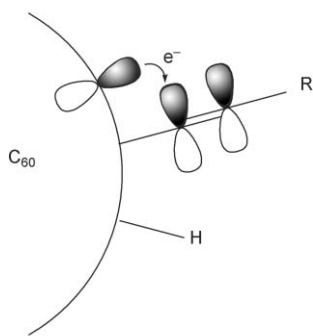
Fig. 3 Interaction between the fullerene π-system and the arylethyne moiety through the sp^3 carbon in **2** and **3**.

the fullerene moieties of **2a–c** and **3c,d** (Table 4). The order of the cathodic shift of the $E_{1/2}$ values is as follows: X = *ortho*-carborane ⩾ *meta*-carborane > *para*-carborane > H > Me. This order indicates that the fullerene moieties of **3c,d** (X = H and Me) are more difficult to reduce, *i.e.* more electron-rich, than those of the carborane derivatives **2**, since Me is an electron-donating group and carboranes are electron-withdrawing groups. As mentioned above, the electron densities of the fullerene moieties of **2** and **3c,d** are higher than that of C$_{60}$ itself, but among them, the $E_{1/2}$ values of **2a–c** exhibit lower cathodic shifts in comparison with those of **3c,d**, as a result of the electron-withdrawing character of the carboranes.

Role of the fullerene moiety in SHG activity

SHG activities are generally influenced by the dipole moments in the ground and excited states. The dipole moments are affected by intramolecular charge transfer. In general, it is expected that charge transfers make β values large. A good correlation between Hammett σ_p values and β values likely indicates that, in the excited state, the fullerene moieties of **2** and **3c,d** act as donors, although they exhibit electron-accepting properties in the ground state, as often mentioned in the literature. Therefore, **2a,c** and **3a,b** exhibit higher SHG activities than **3c,f**. There has been no previous report that fullerene acts as an electron-donating group, to the best of our knowledge.
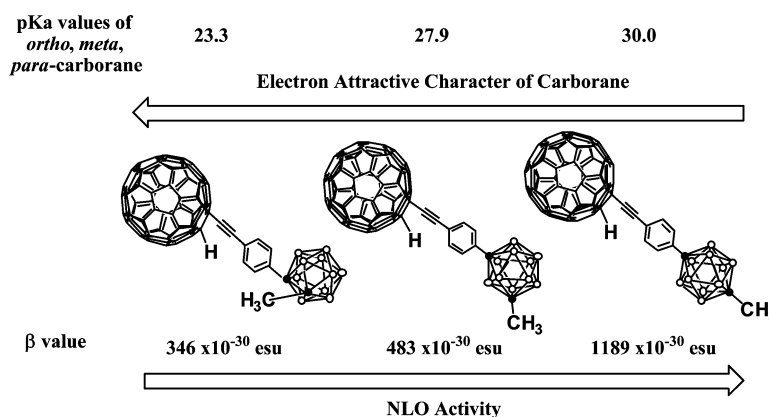
There is a sp^3-carbon between the substituted phenylacetylene moieties and fullerene π-systems in **2** and **3**. Usually there are no strong interactions between the two substituents *via* the sp^3-carbon. As mentioned above, since a clear substituent effect was observed for **2a–c** and **3c,d**, there must be an interaction between the π-spacer and the fullerene cages through the sp^3-carbon atom. Wudl and co-workers have already observed

such a phenomenon, known as periconjugation, wherein their is an expansion of π-conjugation between π-systems on fullerenes and another π-systems.[16,17] Periconjugation is presumably operative in the present system, as shown in Fig. 3. Additionally, longer conjugation systems usually give higher β values. In the case of **2** and **3**, expansion of the π-conjugation systems can account for both the $E_{1/2}$ and β values. To the best of our knowledge, **2** and **3** are the first examples, in which enhancement of the NLO activity was observed through an interaction between C$_{60}$ and a π-spacer.

Higher β values due to carborane moieties

The final question is why **2**, containing carborane, exhibit higher β values in comparison with **3a,b**, bearing electron-withdrawing groups, and why the *para*-carborane derivative **2c** exhibits the highest β value among the carborane-appended molecules. It is well known that *closo*-carboranes are electron-deficient boron clusters with highly polarizable σ-aromatic character, which means delocalization of electrons in the cages. Accordingly, not only in NLO materials,[7] but also in ordinary organic reactions,[18,19] *closo*-carboranes are often used as electron acceptors. For example, the pK_a values of C–H bonds in simple *closo*-carboranes are shown in Scheme 4. The order of C–H acidity in simple *closo*-carboranes is *ortho* > *meta* ≫ *para*,[20] *i.e.* the *ortho*-carborane has the most acidic proton, or, in other words, the greatest electron-attracting ability among these isomers. However, the order of β values is *ortho* < *meta* ≪ *para*-substituted derivative, the *para*-carborane derivative exhibiting the highest β value among **2a–c** (Scheme 4).

We think that the σ-aromaticity of the carborane structural framework is key to understanding the phenomena mentioned above. The σ-aromaticity makes carboranes very stable by delocalizing electrons on the cage, even though they are electron deficient. This character also allows the two carbons in carborane cage to interact with each other very easily and occurs even in the case of *para*-carborane, in spite of the distance between the carbon atoms.[21,22] In the case of **2**, such an interaction affects the β values because one of the two carbons combines with the phenylacetylene–fullerene moiety. We assume that, during the excitation process, the electron density at the carbon on carborane cage which is linked to fullerene through the π-spacer increases due to the electron-donating ability of C$_{60}$, leading to significant differences in electron density between the carbon near the donor and the other carbon. The electronegativities of carbon (2.5) and boron (2.0) indicate that the electron-attracting ability of carbon in carborane is higher than that of boron. Consequently, charge transfer occurs from the electron-rich carbon to the other carbon in the exited state. Such an interaction between two carbons by σ-aromaticity produces a new conjugation system

| pKa values of *ortho, meta, para*-carborane | 23.3 | 27.9 | 30.0 |

Electron Attractive Character of Carborane

| β value | 346 x10^{-30} esu | 483 x10^{-30} esu | 1189 x10^{-30} esu |

NLO Activity

Scheme 4

in carborane in addition to the phenylacetylene–C_{60} π-conjugation system. Thus, compounds **2** possess not only a π-conjugation system due to phenylacetylene and C_{60}, but also a σ-conjugation system due to the carboranes. It has been shown that there are interactions between the carbon in carborane and aromatic substituents on it.[21] Taking these results together, it is now clear that the conjugation system of **2** is longer than that of **3**. It is widely accepted that longer π-conjugation systems make β values higher. Consequently, the difference between the carboranes in **2** and the more common acceptors in **3** is the presence of σ-aromaticity; compounds **2**, having longer π- and σ-conjugations, exhibit higher SHG activities than compounds **3**.

Finally, it should be mentioned that the NLO activity of the *para*-carborane derivative **2c** is higher than those of **2a,b**. The two carbons in *ortho*-carborane are adjacent, whereas the two carbons of *para*-carborane occupy the 1- and 12-positions in the icosahedral cage. The difference between the three carborane isomers is the distance between the two carbons in their cages. As mentioned above, these carbons interact with each other through σ-aromaticity and a more extended conjugation system leads to higher NLO activity. Among compounds **2**, the *para*-carborane derivative has the longest distance between these two carbons. The longer the distance between carbons, the longer the σ-conjugation system and, hence, the higher the β value. This is why the order of the β values for compounds **2** is *para* ≫ *meta* > *ortho*-carborane derivatives. It is now clear that carboranes are special acceptors which not only have electron-attracting ability, but also act as prolonged conjugation systems.

Conclusion

The fullerene–acceptor systems **3a,b** give higher β values (SHG activities 350 and 361 × 10^{-30} esu, respectively) than the fullerene–donor systems **3c–f** (137, 127, 72 and 20 × 10^{-30} esu, respectively). Furthermore, **2a–c**, having carboranes at the *para* position of the phenyl ring of the fullerene–arylethyne hybrids exhibit significantly higher β values (346, 483 and 1189 × 10^{-30} esu, respectively) than those for **3a–f**. Among the *ortho-*, *meta-* and *para*-carborane derivatives **2a–c**, the *para* derivative **2c** shows an exceptionally high β value of 1189 × 10^{-30} esu. A good correlation was obtained between the β values of compounds **3** and the Hammett $σ_p$ values of their *para* substituents, X, indicating that the fullerene moieties of **3** act as electron-donating groups *in the excited state*. The redox properties of **2** and **3c,d** indicate that the fullerene moiety acts as an acceptor *in the ground state*, which is in good agreement with the accepted view that fullerene is an electron-attracting carbon cluster. The high SHG activities of the carborane–fullerene dyads **2** are most probably due to the electron-donating character of fullerene in the excited process, together with the electron-withdrawing nature of the carborane clusters. The exceptionally high β value for the *para*-carborane derivative **2c** is due to the synergistic effect of the prolonged conjugation and electron-withdrawing effect of *para*-carborane.

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