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Carborane–fullerene hybrids as a seemingly attractive–attractive dyad with high hyperpolarizability†

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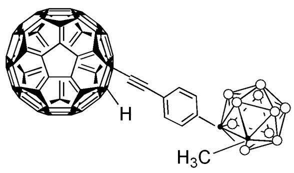
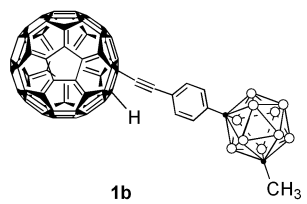
A combination between seemingly attractive carboranes and fullerene through an ethynyl π-system (compounds 1a–c) gives unexpectedly high β-values, thereby providing a guideline that in certain cases a seemingly A–A system becomes a promising complementary combination for obtaining high hyperpolarizability; the β values of 1a, 1b and 1c were 346, 483, and 1189 × 10^{-30} esu, respectively.

Quadratic nonlinear optical (NLO) materials have increasingly attracted attention owing to their direct application in the development of efficient optical telecommunication networks lacking electrical-to-optical, and *vice versa*, signal conversion.[1] Such application requires thermally robust materials with highly nonlinear optical (NLO) response (first hyperpolarizability β). The use of organic materials may offer significant advantages over conventional inorganic crystals. Typical organic NLO compounds include Donor (D) and Acceptor (A) moieties bridged by a π-conjugated linker. Until now, most efforts to obtain better hyperpolarizability (β) have been directed to finding both the right combination of D and A species and the right length of the conjugated bridge between D and A.[2] It has been known for many years that *closo*-carboranes are *electron deficient boron clusters* having highly polarizable σ-aromatic character.[3] Previously carboranes (A) containing certain donor (D) groups were synthesized, but their hyperpolarizable properties were not satisfactory.[4] More recently it has been recognized that fullerenes are *electron attracting carbon clusters* having highly delocalizable π-electrons.[5] Actually, fullerenes (A) containing electron donor (D) moieties have been reported,[6] but there are no NLO studies on those compounds at all, to the best of our knowledge. It occurred to us that carborane–fullerene dyads bridged by an appropriate linker might exhibit an interesting NLO response, in spite of the fact that both groups are electron attracting clusters, since both clusters have highly polarizable electrons. We wish to report that a combination between seemingly attractive carboranes and fullerene through an ethynyl π-system (compounds **1a**–**c**) gives unexpectedly high β-values, thereby providing a guideline that in certain cases a seemingly A–A system becomes a promising complementary combination for obtaining high hyperpolarizability.

The synthetic procedure for **1a** is shown in Scheme 1 (see ESI.†) The *meta*- and *para*-carborane analogues, **1b** and **1c**, were prepared in a similar manner.[7]

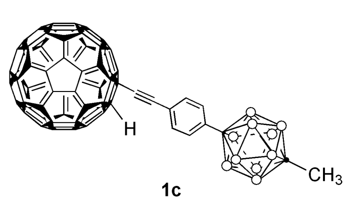


1a



1b

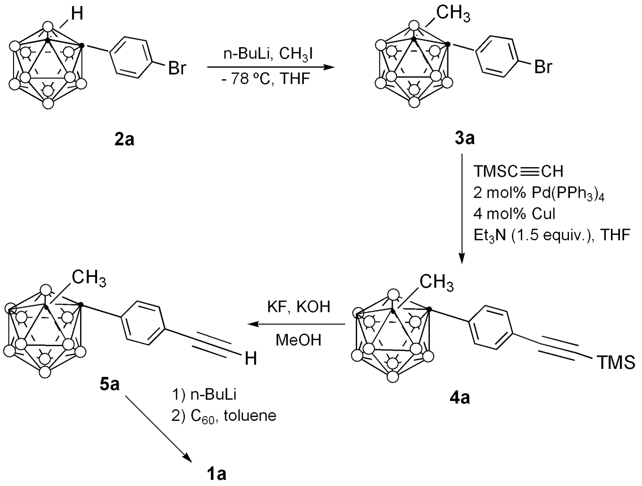
· ; C
○ ; B–H



1c

For clarity, the cyclic voltammetries of only **1a** and C_{60} are shown in Fig. 1 (see ESI†). Those of the phenylethynyl analogue **7** are similar. The redox potentials of **1a**–**c**, **6**, **7** and C_{60} are summarized in Table 1. Only $E_1^{\text{red}}/E_2^{\text{ox}}$ values are shown for simplicity, although three quasireversible reduction–oxidation peaks were observed. The one-electron reduction of the non-charged molecules **1** (E_1^{red}) and the one-electron oxidation to **1** (E_1^{ox}) are more important than the further reductions of the charged molecules (E_2^{red} and E_3^{red}) and the oxidations to the charged molecules (E_2^{ox} and E_3^{ox}), when we discuss the electrochemical property of the C_{60} end group. The three quasireversible reduction peaks of **1a** are similar to those found for C_{60}, **6** and **7** under the same experimental conditions. One additional irreversible oxidation wave at -187 mV (E^{ox}) most probably corresponds to the oxidation peak of the conjugated spacer fragment, since authentic samples of **6** and **7** also exhibited similar peaks at -122.5 and -286 mV, respectively. The three reduction potentials of **1a** were remarkably shifted to more negative values in comparison with those of the parent C_{60}, presumably due both to the saturation of a double bond of C_{60} and the electron donating character of the ethynylphenyl group. Consequently, it is clear that the C_{60} framework of **1a** behaves as an A group.

Similar observations were made for the *meta*- and *para*-derivatives **1b** and **1c**. An important question was whether the



Scheme 1

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† See http://www.rsc.org/suppdata/cc/b0/b003931o/ for electronic supplementary information (ESI): a detailed procedure of Scheme 1, Fig. 1 and 2, absorption spectra of **1**, **5**, **6**, **7** and C_{60}, and fluorescence spectrum of **1a**.

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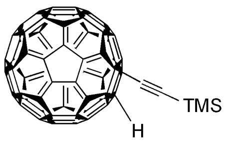
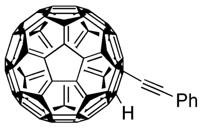
Table 1 Results of cyclic voltammetries and β values

Compd.	E_1^{red}/E_1^{ox} (mV)[a,b]	E^{ox} (mV)[a,c]	β (× 10^{-30} esu)
1a	−1242/−552	−187	346
1b	−1210/−581	−79	483
1c	−1193/−615	−170	1189
C_{60}	−1103/−631	—	0
6	−1262/−590	−123	87
7	−1086/−752	−286	139
5a	—[d]	—[d]	7
5b	—[d]	—[d]	28
5c	—[d]	—[d]	48

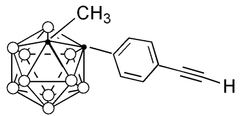
[a] Potentials in mV *vs.* ferrocene/ferrocenium measured in *o*-dichlorobenzene (see Fig. 1) (see ESI†). [b] Among three quasireversible redox peaks, only the first peaks E_1^{red}/E_1^{ox} are shown and the other peaks are shown in the ESI†. [c] Irreversible oxidation peak most probably due to the ethynyl spacer units. [d] The compound did not exhibit electroactivities within the potential range we investigated.



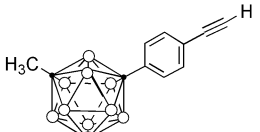
6



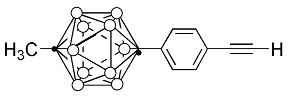
7



5a



5b



5c

carborane framework acted as a donor or (as usual) an attractor. We synthesized the reference compounds **5a–c** in order to help clarify this point, but those compounds did not exhibit electroactivities within the potential range we investigated. The E^{ox} value of **7** was −286 mV, which was the most negative value among those observed in Table 1, indicating that the electron density of the ethynyl group of **7** was higher than that of **1a–c**. Accordingly, we assume at present that the carborane end group acts as an attractor, as well established previously.[8]

Absorption spectra of **1a–c**/$CHCl_3$ in the UV-vis range showed two large absorption bands at 258 and 328 nm; **1a**, λ_{max} 258 (log ε 5.10), 328 (4.77); **1b**, 258 (5.05), 328 (4.58); **1c**, 258 (5.32), 328 nm (4.71). Absorption spectra of **5a–c** in $CHCl_3$ showed absorption bands at 260 (log $\varepsilon \approx$ 4.66–4.49) and 283 nm (3.83–4.36), and those of C_{60} in $CHCl_3$ showed two strong bands at 259 (4.85) and 329 nm (4.28). These data in addition to those for **6** and **7**[9] clearly indicate that the two strong bands of **1a–c** are due to the phenylethynyl–C_{60} chromophore and the influence of the carborane groups to the UV absorption is very small (see ESI†). Very weak absorption bands between 400–440 nm (log $e \approx$ 4.00–3.50) were observed for **1b** and **1c**, which were presumably due to a forbidden transition (see ESI†). In $CHCl_3$ solution of **1a–c**, no absorption was observed after 450 nm, although C_{60} itself, **6** and **7** in cyclohexane exhibited very weak absorption bands between 470–700 nm with log ε 2.3–3.2.[9]

The fluorescence spectra of **1a–c** in $CHCl_3$ following excitation at 258 and 328 nm showed broad band emission in the range 350–390 nm, which was attributed to Raman scattering of the $CHCl_3$ (see ESI†). Fullerene fluorescence is usually observed around 700 nm; this was in general measured in cyclohexane.[10] We attempted to dissolve **1a–c** in cyclohexane, THF and CH_3CN, but they were soluble only in $CHCl_3$. The emission spectra of **6** and **7** in $CHCl_3$ also exhibited Raman scattering of $CHCl_3$. In conclusion, no significant spectroscopic absorption or/and emission was observed for the $CHCl_3$ solution of **1a–c** (10^{-6} M) in the range of the double frequency value 532 nm, allowing us to get the necessary measurements to deduce the β coefficients of **1a–c**.[11]

The quadratic dependence of the second-harmonic signal intensity to the harmonic intensity for **1a**, for example, is demonstrated in Fig. 2 (see ESI†). The laser wavelength of 1064 nm was used. The molar absorption coefficients (ε) of **1a–c** at 532 nm were below *ca.* 1000 dm^3 mol^{-1} cm^{-1}, so that the influence of resonance effects were very small.[12] The β values of **1a–c** were 346, 483 and 1189 × 10^{-30} esu, respectively (Table 1). It should be noted especially that *the para-derivative **1c** exhibited a large β value*. As expected, the β value of C_{60} itself was zero under the same experimental conditions owing to its centrosymmetric structure. For comparison, the β values of **6** and **7**, which are typical D–A systems, were measured: the β of **6** was 87 × 10^{-30} and that of **7** 139 × 10^{-30} esu. The β-values of **5a–c** were 7, 28 and 48 × 10^{-30} esu, respectively. It is clear that the reference compounds exhibit ordinary level of β-values, although the values of **6** and **7** (~100 × 10^{-30} esu) are still higher than that for a standard *para*-nitroaniline, which showed 23 × 10^{-30} esu under the same experimental conditions. By attaching the carboranes, the β value increased up to 1189 × 10^{-30} esu confirming the strong electronic polarizable influence of the boron clusters.

Very high hyperpolarizability of **1c**, which constitutes the first example of its kind, is quite fascinating since it has often been surmised[13] that, by forming charge-transfer complexes with appropriate donors, the center of symmetry of C_{60} is broken. In our case the hybride **1** do not form any charged complex but present high β values. Further investigation on boron–carbon cluster hybrids is being pursued actively in our laboratories.

Notes and references

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