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Nonlinear optical properties of novel carborane–ferrocene conjugated dyads. Electron-withdrawing characteristics of carboranes†

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The novel carborane–ferrocene conjugated dyads **1–3** and **6–8** were synthesized and their NLO properties were investigated. *ortho*-, *meta*-, and *para*-carboranes act as electron-withdrawing groups, and the *para*-carborane dyads **3** and **8** exhibited higher β values (hyperpolarizability) than the *ortho*- and *meta*-carborane analogues **1**, **2**, **6**, **7**.

Introduction

Quadratic nonlinear optical (NLO) materials have great importance in their application to photonic devices.[1] Some organic compounds have been widely investigated as NLO materials because of their large hyperpolarizability. The typical organic NLO compounds include donor (D) and acceptor (A) moieties bridged by a π-conjugation system.[2] It is known that carboranes are chemically and thermally stable boron clusters. Previously some carborane derivatives containing suitable donor groups (D) were synthesized and their nonlinear optical properties were investigated,[3] but their NLO activities were quite low.[4] Recently, we found that a combination of seemingly attractive fullerenes and seemingly attractive carboranes through an ethynyl π-system gives unexpectedly high β values,[5] and suggested that in certain cases a seemingly AA system becomes a promising complementary combination for obtaining high hyperpolarizability. A question which occurred to us is whether carboranes really exhibit electron-withdrawing characteristics in *hyperpolarizability* or not, since there have been no systematic studies on the NLO properties of carboranes. Although it is well accepted that carboranes act as electron-withdrawing boron clusters in the *ground state*, NLO activities and HRS responses (hyper Rayleigh scattering) concern the properties of *the excited states* of carboranes. It is well known that ferrocene acts as a donor (D),[6] so we undertook the synthesis of carborane–ferrocene dyads bridged by either an ethenylphenyl π system (**1–3**) or by an iminylphenyl π system (**6–8**), and investigated their NLO properties to ascertain the characteristics of the carboranes.

Result and discussion

Synthesis of the carborane–ferrocene dyads 1–3, 6–8 and the simple ferrocene derivatives 4, 5, 9

The synthesis of the *ortho*-carborane–ferrocene dyads **1a**,**b** is summarized in Scheme 1. 4-Bromobenzaldehyde was protected with 1,2-ethanediol and the resulting bromophenyl derivative was converted into the iodophenyl derivative **10** (2 steps, 88%). The coupling reaction between *ortho*-carborane and **10** gave the phenylcarborane derivative **11**.[7] Deprotection by the standard procedure afforded 4-formylphenyl-*ortho*-carborane **12** (2 steps, 22%). Similarly, 4-formylphenyl-*meta*- and 4-formylphenyl-*para*-carborane were synthesized. The Wittig reaction of 4-formylphenyl-*ortho*-carborane **12** with (ferrocenylmethyl)triphenylphosphonium iodide **13** gave a stereoisomeric mixture of the *ortho*-carborane–ferrocene dyads **1** in 51% yield.[8] The Wittig reagent **13** was obtained in 75% yield from (ferrocenylmethyl)trimethylammonium iodide and triphenylphosphine.[9] In the case of the *meta*- and *para*-carborane derivatives, a similar procedure to that described above afforded the corresponding dyads **2, 3** in approximately 42–48% yields (Table 1). To investigate the electronic characteristics of the carboranes, non-substituted phenylethenyl ferrocene **4** and its *para*-nitro substituted analogue **5** were synthesized in the same way.

The synthesis of the *ortho*-carborane–ferrocene dyad **6**, bridged by an iminylphenyl π system, is summarized in Scheme 2. The Sonogashira coupling reaction of 4-nitroiodobenzene with trimethlsilylacetylene afforded **14** in 87% yield. The treatment of **14** with KF/KOH gave the acetylene derivative **15**. The reaction of **15** with decaborane gave 4-nitrophenylcarborane **16** and 4-aminophenylcarborane **17** in 18% and 26% yield, respectively. The condensation reaction of 4-aminophenylcarborane **17** with ferrocenecarboxyaldehyde gave the *ortho*-carborane–ferrocene dyad **6** in 59% yield.

The *meta*- and *para*-derivatives **7, 8** were synthesized in a similar way. For comparison, the non-substituted phenyl derivative **9** was also synthesized.

Photochemical and electrochemical studies of 1–5

The photochemical and electrochemical studies of the carborane–ferrocene dyads bridged by an ethenylphenyl π system **1–3** and the reference compounds **4, 5** were carried out and the results are summarized in Table 2. The UV-vis spectra of **1a** showed a strong high-energy absorption (λ_{max} = 272 nm), and one strong and one weak low-energy absorption (λ_{max} = 320 nm and λ_{max} = 463 nm). The low-energy absorptions of the *trans*-carborane derivatives **1a–3a** showed a bathochromic shift (red shift) in comparison with those of **4a** (309 nm and 458 nm, respectively). Furthermore, in the case of **5a**, the corresponding absorptions exhibited a much higher bathochromic shift (362 nm and 510 nm, respectively). The bathochromic shifts are presumably due to the extension of the conjugated π-electron system, which arises from the *para*-substituents of the phenyl ring. The low-energy UV absorptions of the *cis*-compounds **1b–3b** and **5b** were also shifted to a

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†Electronic supplementary information (ESI) available: a complete Experimental section containing HRS measurements, full NMR, IR, UV, mass spectrometry, and elemental analyses/HRMS data, as well as original NMR spectra and X-ray structural analysis of **1b**. See http://www.rsc.org/suppdata/jm/b2/b202236b/

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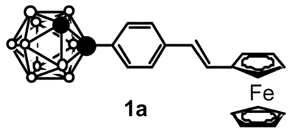
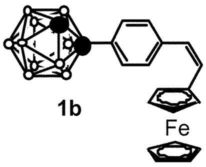
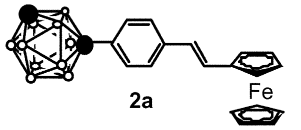


1a



1b



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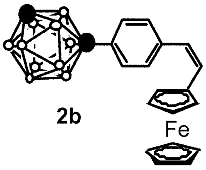

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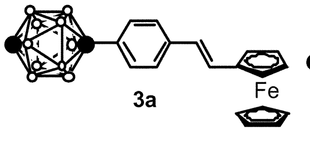
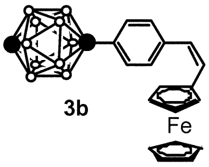
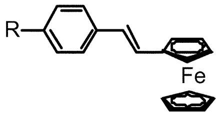
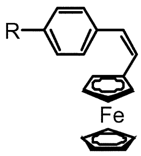


3a



3b

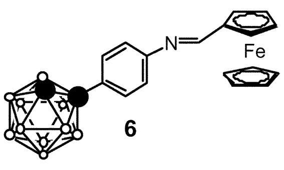




4a: R = H
5a: R = NO_2

4b: R = H
5b: R = NO_2

● : C or CH
o : BH



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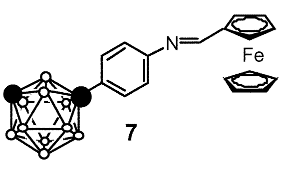

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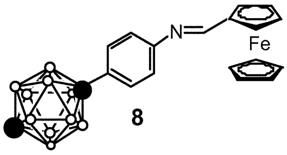

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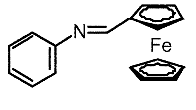

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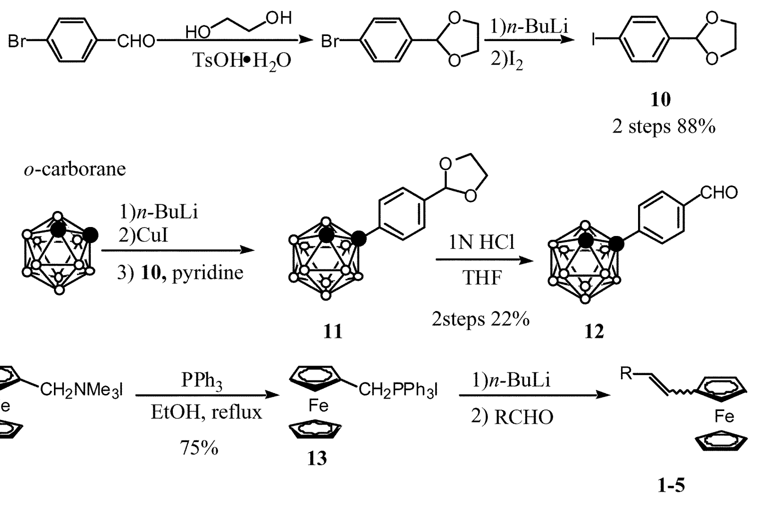
low-energy region when compared with **4b**. Excitation at 272 and 320 nm of **1a** did not produce any significant emission spectra around 532 nm. In conclusion, a $CHCl_3$ solution of **1–3**, **4**, and **5** (10^{-4} M) did not show any significant spectroscopic absorption and emission spectra around the double frequency value 532 nm, allowing us to carry out the hyper Rayleigh scattering (HRS) measurements necessary to deduce the β coefficients of **1–5**.

Cyclic voltammetric investigation for **1a–5a** showed an electrochemically quasi-reversible one-electron oxidation. The compound **4a** was oxidized at 406 mV. The $E_{1/2}$ values of the *trans*-carborane–ferrocene derivatives **1a–3a** showed cathodic shifts compared to **4a**, and **5a** was oxidized at the highest positive value ($E_{1/2}$ = 457 mV) among them. These results indicate that the order of electron densities of the π-system is **4a** > **1a** > **2a** ≈ **3a** > **5a**, and that the order of electron-withdrawing ability of the *para*-substituents is NO_2 > carboranes > H. A similar observation was also made for the *cis*-derivatives **1b–3b**, **4b**, and **5b**. Accordingly, the above order of the electron withdrawing ability of the substituents is valid not only for the *trans*-derivatives **1a–5a**, but also for their *cis*-analogues **1b–5b**.

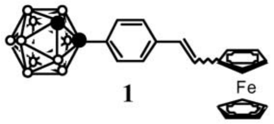
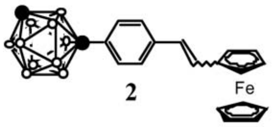
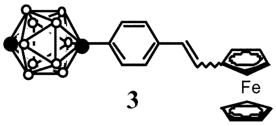
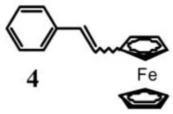
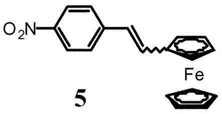
NLO activities of 1–5

The nonlinear response of **1–5** was studied by the hyper Rayleigh scattering method and the results are summarized in Table 2. We used *para*-nitroaniline (*p*-NA) as a reference compound. The β value of **4a** was 103 × 10^{-30} esu, whereas the *trans*-carborane derivatives **1a–3a** showed relatively larger β values in the range of 110–130 × 10^{-30} esu. In the case of **3a**, the β value was about 6 times larger than that for *p*-NA. On the other hand, the β value (152 × 10^{-30} esu) of **5a** was much larger than those of the other compounds **1a–4a**. The β value generally depends upon both the electron-withdrawing ability of an acceptor and the electron-donating ability of a donor. The donor in **1a–5a** is ferrocene, and only the acceptor part is variant in the current studies. Therefore, the order of the β values (**5a** > **1a–3a** > **4a**) is in good agreement with the order of the electron-withdrawing ability of the substituents obtained from the $E_{1/2}$ values. Very interestingly, the *para*-carborane derivative **3a** showed a larger β value than **1a** and **2a**, although



Scheme 1

Table 1 The Wittig reaction of the aldehydes with **13**

Product	Yield (%)[a]
 **1**	51 (*E* : *Z* = 35 : 65)
 **2**	42 (*E* : *Z* = 52 : 48)
 **3**	48 (*E* : *Z* = 31 : 69)
 **4**	49 (*E* : *Z* = 36 : 64)
 **5**	61 (*E* : *Z* = 52 : 48)

[a] Isolated yield.

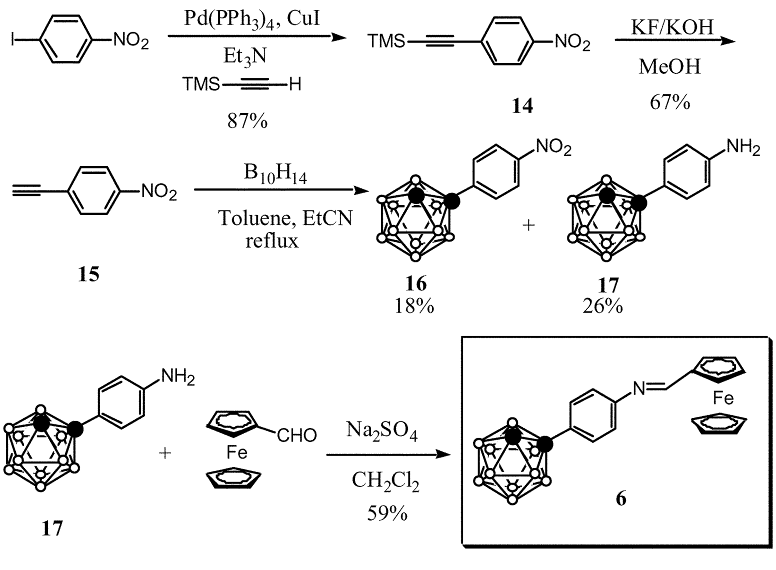
the order of the $E_{1/2}$ values is **1a** > **3a** > **2a**. In the *cis*-series, the β values increased in the following order; **4b** < **1b**–**3b** < **5b**. Again, interestingly, the *para*-carborane derivative **3b** showed a larger β value than **1b** and **2b**. These results clearly indicate that the order of electron-withdrawing ability of the *para*-substituents in NLO activities is NO_2 > carboranes > H. The intrinsic hyperpolarizability value $\beta(0)$ was calculated by the Oudar–Chemla equation.[10] The $\beta(0)$ values of **3a** and **5a** also indicated that *para*-carborane and the nitro group were better acceptors in comparison with *ortho*- and *meta*-carboranes. Compared to the *cis* isomers, the *trans* isomers showed much lower-energy absorptions and much lower $E_{1/2}$ values. Furthermore, the β values of the *trans* isomers were larger than those of the *cis* isomers, in agreement with the theory that the β value is dependent on the π-conjugation length and in general the longer the length, the higher the β value.

The carborane–ferrocene dyads having an imine spacer 6–8

We changed the olefinic (C=C) spacer of **1–3** to an imine group (C=N) in order to investigate the effect of a spacer on β-values. The photochemical and electrochemical studies of the carborane–ferrocene dyads having an imine spacer **6–8** and the reference compound **9** are summarized in Table 3. The UV-vis spectral data of **6–9** were similar to those of the corresponding olefin derivatives **1–3**. The *ortho*-carborane–ferrocene dyad **6** showed a strong high-energy absorption (λ_{max} = 250 nm) and one strong and one weak low-energy absorptions (λ_{max} = 303 nm and λ_{max} = 469 nm). The UV-vis spectra of **7**, **8** and **9** were significantly similar to those of **6**. As compared with **9**, the UV-vis absorptions of the carborane derivatives **6–8**, expect for an absorption at 303 nm of **6**, showed bathochromic shifts. There were no significant absorptions and emissions around 532 nm, and therefore the β-values of **6–9** can be deduced by HRS measurements. In the cyclic voltammetric investigation, **6–9** showed an electrochemically quasi-reversible one-electron oxidation. The half wave potential ($E_{1/2}$) of **6** was 613 mV. The $E_{1/2}$ values of **7** and **8** showed anodic shifts compared to that of **6**. The $E_{1/2}$ value of **9** was 519 mV and showed a large anodic shift compared to the carborane derivatives, indicating that **6–8** were more difficult to oxidize than **9** because of the electron-withdrawing ability of the carboranes. Here again, the order of electron withdrawing ability is *ortho*-carborane > *meta*- and *para*-carborane. HRS measurements were carried out in a similar way to that described above. The *para*-carborane derivative **8** showed a relatively large β value, 107 × 10^{-30} esu, although the β values of **6**, **7** and **9** were not so large and within the range of 53–60 × 10^{-30} esu. The exceptional behavior of the *para*-carborane–ferrocene dyad **8** having an imine spacer is in good agreement with that of the *para*-carborane dyads **3** having olefinic spacers.

Conclusion

It is now clear that carboranes act as an acceptor in the photochemical, electrochemical, and hyperpolarizable activities. The order of electron withdrawing ability is NO_2 > carboranes > H. Among *ortho*-, *meta*-, and *para*-carboranes, the *para*-derivatives exhibit the highest β values, although the electrochemical data ($E_{1/2}$) indicate that the order of electron withdrawing ability is *ortho*- > *meta*- and *para*-carborane.



Scheme 2

Table 2 UV-vis spectra, cyclic voltammetry, β and $\beta(0)$ values of **1–5**

Compound	isomer	$\lambda_{max(1)}$/nm (ε^a /M^{-1} cm^{-1})	$\lambda_{max(2)}$/nm (ε/(M^{-1} cm^{-1})	$\lambda_{max(3)}$/nm (ε/M^{-1} cm^{-1})	$E_{1/2}{}^b$ /mV	β^c /10^{-30} esu	$\beta(0)^d$ /10^{-30} esu
1a	*E*	463(1900)	320(27400)	272(15500)	436	114	66
2a	*E*	460(1600)	317(26800)	271(15400)	413	111	65
3a	*E*	460(1700)	316(29000)	271(17000)	419	131	77
4a	*E*	458(1100)	309(23700)	265(16300)	406	103	62
5a	*E*	510(5700)	362(21500)	243(17000)	457	152	72
1b	*Z*	448(900)	302(14900)	276(12800)	451	81	50
2b	*Z*	449(800)	301(15200)	269(15600)	447	84	53
3b	*Z*	448(800)	301(15300)	270(15700)	444	98	61
4b	*Z*	448(500)	292(12200)	254(12800)	430	64	41
5b	*Z*	490(2200)	334(10800)	243(16700)	473	110	60

[a]All spectra were recorded in chloroform (10^{-4} M) at ambient temperature. [b]All potentials are relative to SCE in dry acetonitrile using a platinum-bead working electrode; 0.1 mol cm^{-3} NBu_4ClO_4 as suporting electrolyte; scan rate: 100 mV s^{-1}. [c]Measured in chloroform by the HRS method at 1.06 μm. [d]Determined by the Oudar–Chemla equation.

Table 3 UV-vis spectra, cyclic voltammetry, β and $\beta(0)$ values of **6–9**

Compound	$\lambda_{max(1)}$/nm (ε^a /M^{-1} cm^{-1})	$\lambda_{max(2)}$/nm (ε/M^{-1} cm^{-1})	$\lambda_{max(3)}$/nm (ε/M^{-1} cm^{-1})	$E_{1/2}{}^b$ /mV	β^c /10^{-30} esu	$\beta(0)^d$ /10^{-30} esu
6	469(1600)	303(13800)	250(18900)	613	59	37
7	467(1700)	312(15800)	248(21800)	579	60	36
8	467(1700)	313(16200)	249(22400)	578	107	64
9	462(1200)	307(10700)	243(17000)	519	53	32

[a]All spectra were recorded in chloroform (10^{-4} M) at ambient temperature. [b]All potentials are relative to SCE in dry acetonitrile using a platinum-bead working electrode; 0.1 mol cm^{-3} NBu_4ClO_4 as suporting electrolyte; scan rate: 100 mV s^{-1}. [c]Measured in chloroform by the HRS method at 1.06 μm. [d]Determined by the Oudar–Chemla equation.

Experimental

The coupling reaction of *ortho*-carborane with 2-(4-iodophenyl)-[1,3]dioxolane 10

To a solution of *ortho*-carborane (2.88 g, 20 mmol) in 80 ml of 1,2-dimethoxyethane was added dropwise a hexane solution of 1.60 M *n*-BuLi in hexane (13 ml, 20.8 mmol) at 0 °C under dry Ar. The mixture was stirred at room temperature for 30 min and copper(I) iodide (5.6 g, 29 mmol) was added in one portion. The mixture was stirred at room temperature for 30 min. Pyridine (12 ml) and then **10** (5.8 g, 21 mmol) were added. The resulting mixture was refluxed until **10** was mostly consumed, and the mixture was extracted twice with ether. The combined organic layer was washed with brine and dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1). A mixture of **11** and **10** was obtained (total 3.85 g). The mixture of **11** and **10** was used for the next reaction without further purification. To a mixture of **10** and **11** in 60 ml of THF was added an aqueous solution (6 ml) of 1 N HCl. The resulting mixture was stirred overnight and extracted twice with ether. The combined organic layer was washed with brine and dried over Na_2SO_4, and then the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane : ethyl acetate = 20 : 1), and **12** was obtained in 22% yield (1.18 g, 4.8 mmol).

The Wittig reaction of 4-formylphenyl-*ortho*-carborane 12 with (ferrocenylmethyl)triphenylphosphonium iodide 13

A solution of **13** (1.29 g, 2.2 mmol) in 12 ml of THF was cooled to −78 °C. A hexane solution of *n*-BuLi (1.53 M, 1.3 ml, 2.0 mmol) was added and the resulting mixture was stirred for 2 h at 0 °C. A solution of **12** (496 mg, 2.0 mmol) in 6 ml of THF was added at 0 °C, and the resulting mixture was stirred for 4 h at 0 °C and then for 16 h at room temperature. The reaction was quenched by addition of H_2O, and the mixture was extracted twice with ether. The combined organic layer was washed with brine and dried over Na_2SO_4, and then the solvents were evaporated. The residue was passed through a short column (aluminium oxide, hexane : ethyl acetate = 20 : 1), and **1** was obtained in 51% yield (438 mg, 1.0 mmol) as a mixture of stereoisomers (*E* : *Z* = 35 : 65). The stereoisomers, **1a** and **1b**, were separated by column chromatography (aluminium oxide, hexane : ethyl acetate = 50 : 1).

Preparation of 1-(4-nitrophenyl)-2-dicarbodecaborane 16 and 1-(4-aminophenyl)-2-dicarbodecaborane 17

To a solution of decaborane (743 mg, 6.1 mmol) in 25 ml of propionitrile was added a solution of *para*-nitrophenylacetylene **15** (854 mg, 5.8 mmol) in 50 ml of toluene. The resulting mixture was refluxed overnight. The solvent was evaporated and the residue was purified by column chromatography (silica gel, hexane : ether = 1 : 3) to give **16** (273 mg, 1.0 mmol) as a yellow solid and **17** (350 mg, 1.5 mmol) as a yellow solid.

Preparation of ferrocenylmethylidene-4-(*ortho*-carboranyl)-phenylamine 6

A mixture of **17** (43.5 mg, 0.2 mmol), ferrocenecarboxyaldehyde (42.8 mg, 0.2 mmol), and excess Na_2SO_4 in CH_2Cl_2 was stirred for 3 days. The mixture was filtered through a Celite pad and the solvent was evaporated. The residue was purified by GPC to give an orange solid (50.7 mg, 0.12 mmol).

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