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Syntheses and Quadratic Nonlinear Optical Properties of 2,7-Fluorenylene- and 1,4-Phenylene-Functionalized *o*-Carboranes

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o-Carboranes *C*-functionalized by (4-substituted-phen-1-yl)ethynyl-1,4-phenyl groups or (2-substituted-fluoren-7-yl)ethynyl-2,7-fluorenyl groups, in which the pendant functionalization is electron-withdrawing nitro or electron-donating diphenylamino groups, have been synthesized and in many cases structurally characterized. Diphenylamino-containing examples coupled via the two π-delocalizable bridges to the electron-accepting *o*-carborane unit exhibit the greater quadratic optical nonlinearities at 1064 nm (hyper-Rayleigh scattering, ns pulses), the nonlinearities also increasing on proceeding from 1,4-phenylene- to 2,7-fluorenylene-containing bridge. The most NLO-efficient example 2-(*n*-butyl)-1-(2-((9,9-di(*n*-butyl)-2-(*N*,*N*-diphenylamino)-9*H*-fluoren-7-yl)ethynyl)-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane, consisting of diphenylamino donor, fluorenyl-containing bridge, *o*-carborane acceptor, and solubilizing *n*-butyl units, exhibits large $\langle\beta\rangle_{HRS}$ (230 x 10^{-30} esu) and frequency-independent (two-level model) $\langle\beta_0\rangle$ (96 x 10^{-30} esu) values. Coupling two 2-((9,9-di(*n*-butyl)-2-(*N*,*N*-diphenylamino)-9*H*-fluoren-7-yl)ethynyl)-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl) units to the 1,2-*ortho*-carborane core affords a di-*C*-functionalized compound with enhanced nonlinearities (309 x 10^{-30} esu and 129 x 10^{-30} esu, respectively).

Introduction

Icosahedral *closo*-carboranes have attracted considerable attention as emitting[1-8] and electronic materials,[9-13] as well as for applications in two-photon absorption,[14-16] due to their electron-withdrawing properties and their three-dimensional electron delocalization. *ortho*-Carborane (*o*-Cb) is an efficient electron-acceptor comparable in strength to the tetrafluorophenyl group,[17, 18] and therefore has potential in donor-π-bridge-acceptor (D-B-A) assemblies of interest in nonlinear optics, but the quadratic nonlinear optical (NLO) performance of Cb dyads has thus far remained modest, and few efficient examples are extant.[19-21]

In contrast to the dearth of studies with *o*-Cb-based compounds, there has been considerable success in synthesizing quadratic NLO-active D-B-A compounds with organic and inorganic donor and acceptor groups and phenyleneethynylene-based,[22-29] phenylenevinylene-based,[5, 30-34] and other π-bridges,[24, 35-38] which has afforded a large number of NLO-efficient examples, and thereby facilitated the development of design rules for the optimization of NLO performance. One observation is that the quadratic NLO coefficient β generally increases with π-bridge lengthening in such compounds,[30, 31, 36, 39-41] but the solubilities of the compounds usually decrease upon increasing the length of the bridge. Bridge substitution with alkyl groups has been employed to mitigate this problem,[28, 31, 41-44] but these solubilizing groups are usually located in the π-bridge plane, and are therefore inefficient at suppressing the aggregation that results in decreasing solubility.

In the present work, we have pursued possible improvement in the NLO performance of D-B-A compounds by employing *o*-Cb as acceptor and exploring π-bridge modifications to permit incorporation of out-of-plane solubilizing groups. Carboranes possess two active CH sites rendering derivatization (and therefore access to the targets) a facile process. We have targeted π-bridge elongation with fluorenyl units because the plane of the alkyl chain substituents is perpendicular to that of the π-system in such bridges.[45-51] For comparative purposes, we have also examined phenyl-based analogues of the fluorenyl-based *o*-carboranes, and report comprehensive structural and spectroscopic characterization of the new compounds, and an assessment of the impact of the structural modifications on second-order NLO properties using the hyper-Rayleigh scattering (HRS) technique.

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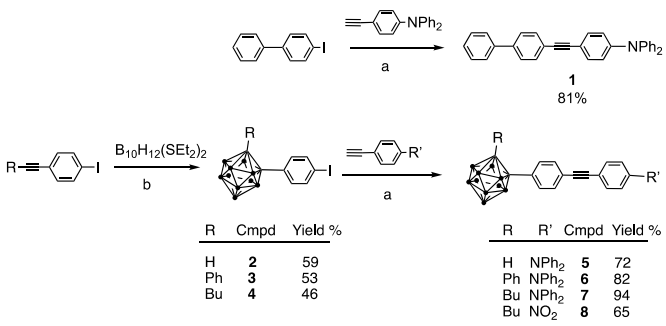
Electronic Supplementary Information (ESI) available: NMR spectra, single-crystal X-ray diffraction studies details and thermal ellipsoid plots, and overlays of optical absorption spectra. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/x0xx00000x.

Scheme 1. Preparation of compounds **1**, **5** - **8**.



The carborane skeletons are drawn as wireframes with the BH vertices as black balls. a) $Pd(PPh_3)_4$, CuI, NEt_3, THF (**1** and **8**: reflux, overnight; **5**-**7**: 70 °C, overnight); b) toluene, reflux 2 days.

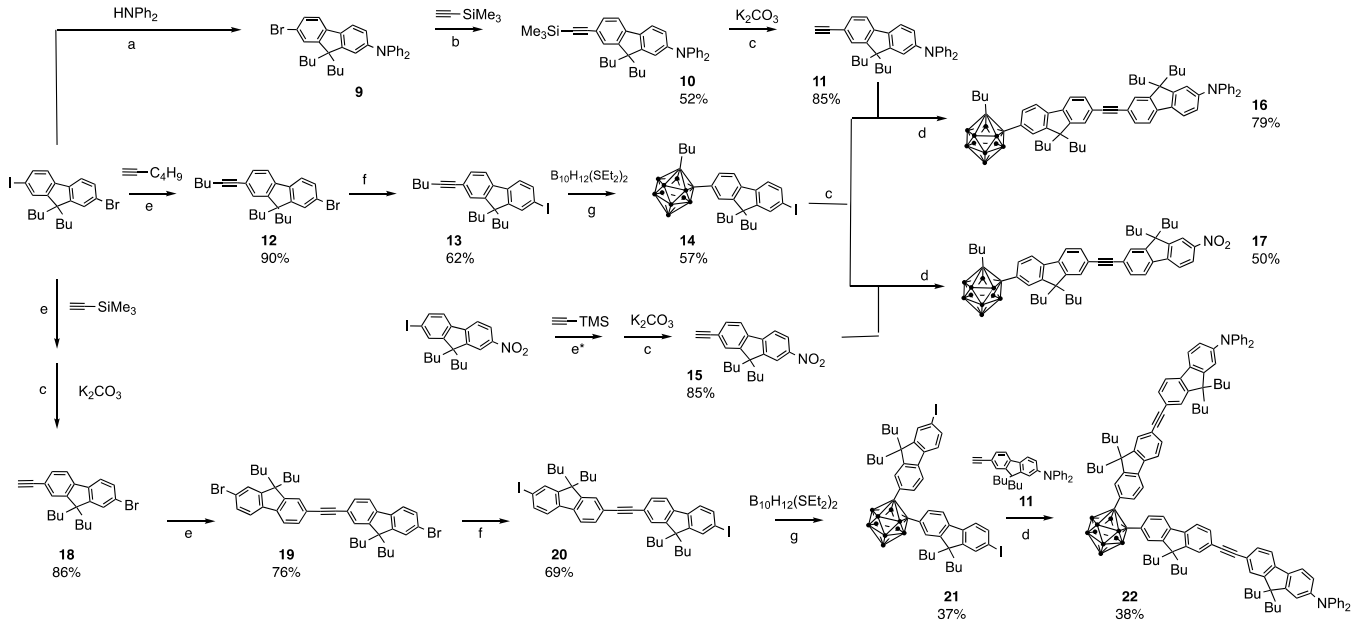
Results and discussion

Preparation and characterization of *C*-functionalized carboranes.

The target compounds consist of o-carboranes with one core C connected to 1,4-phenyleneethynylene-1,4-phenyl or 2,7-fluorenyleneethynylene-2,7-fluorenyl backbones functionalized by electron donating diphenylamino (**5**-**7**, **16**) or electron withdrawing nitro groups (**8**, **17**), and the other core C attached to H (**2**, **5**), Ph (**3**, **6**), *n*-Bu (**4**, **7**, **8**, **16**, **17**), or a second 7-diphenylaminofluorenyleneethynylenefluorenyl unit (**22**). The syntheses of the target compounds **5**-**8**, **16**, **17**, and **22** are depicted in Schemes 1-2 and extend the well-known displacement of the Lewis bases from decaborane(12)-Lewis base adducts with alkynes[52] to a series of new designed alkynes. The new alkynes **1**, **11**, **13**, **15**, and **20** were prepared as depicted in Schemes 1-2 and as described in the Experimental section; we note that the synthesis of ethyl[53] and hexyl[54] analogues of **11** have been reported previously, while the syntheses of **15** and **18** were based on those of their previously-reported hexyl analogues.[55, 56] The new functionalized *o*-carborane targets were isolated in fair to good yields and characterized by the usual spectroscopic and analytical techniques (Experimental section and ESI Figures S1-S50).

The identities of **1**, **4**-**8**, **10**, **11** and **14** were confirmed by single-crystal X-ray diffraction studies. Thermal ellipsoid plots and selected bond lengths for **7** and **8** are given in Figures 1 and 2, respectively, while crystal data for all structures (Tables S1 and S2) and thermal ellipsoid plots and selected bond lengths for the remaining structures (Figures S51-S57) are collected in the ESI file. The structural studies shed light on the extent and nature of the π-system in these compounds. They reveal that the N-bound phenyl groups are twisted away from co-planarity with the N-1,4-C_6H_4 unit in the diphenylamino appended compounds **1**, **5**, **6**, and **7** and rotated from coplanarity with the N-2,7-fluorenyl group in the diphenylamino substituted compounds **10** and **11**. As expected, the *n*-butyl groups are orthogonal to the fluorenyl plane in **10**, **11**, and **14**. The two phenylene groups in the 1,4-C_6H_4C≡C-1,4-C_6H_4 units subtend dihedral angles of 9.84° (**1**), 40.1(2)° (**5**), 50.09(8)° (**6**), 8.5(2)°, 6.3(2)° (**7**, two crystallographically distinct molecules), and 35.95(9)° (**8**), the broad range of values emphasizing the soft

Scheme 2. Preparation of compounds **16**, **17** and **22**.



The carborane skeletons are drawn as wireframes with the BH vertices as black balls. a) 1,10-phenanthroline, CuI, K_2CO_3, DMF; b) $Pd_2(dba)_3$, PPh_3, CuI, NEt_3, THF; c) $MeOH/CH_2Cl_2$; d) $Pd(PPh_3)_4$, CuI, NEt_3, THF; e) $PdCl_2(PPh_3)_2$, CuI, NEt_3, THF; f) 1. *n*-BuLi, -78°C; 2. I_2, 30 min; g) toluene.

potential energy surface for rotation at the C-C linkages, and the dominance of crystal packing forces in controlling this structural

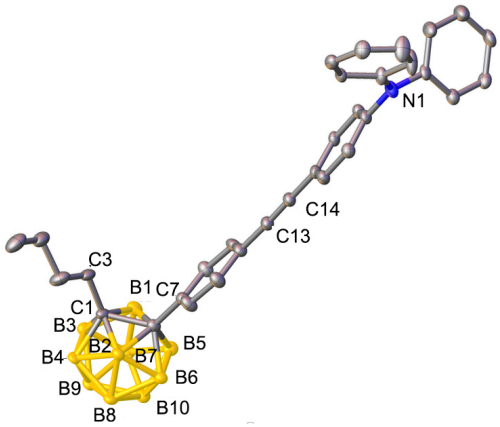


Figure 1. Molecular structure of **7**, with thermal ellipsoids set at the 40% probability level. Hydrogen atoms and the second crystallographically distinct molecule have been omitted for clarity. Selected bond lengths (Å): C1-C2 1.708(8), B(1)-B(3) 1.765(10), B(1)-B(5) 1.754(10), B(1)-B(7) 1.746(10), B(1)-C(1) 1.716(10), B(1)-C(2) 1.712(9), B(2)-B(4) 1.777(9), B(2)-B(6) 1.790(9), B(2)-B(8) 1.774(9), B(2)-C(1) 1.725(9), B(2)-C(2) 1.728(8), B(3)-B(4) 1.770(11), B(3)-B(7) 1.768(11), B(3)-B(9) 1.779(10), B(3)-C(1) 1.704(9), B(4)-B(8) 1.779(10), B(4)-B(9) 1.775(10), B(4)-C(1) 1.705(8), B(5)-B(6) 1.779(10), B(5)-B(7) 1.778(10), B(5)-B(10) 1.787(10), B(5)-C(2) 1.703(9), B(6)-B(8) 1.775(9), B(6)-B(10) 1.786(9), B(6)-C(2) 1.711(8), B(7)-B(9) 1.790(10), B(7)-B(10) 1.801(10), B(8)-B(9) 1.787(10), B(8)-B(10) 1.792(11), B(9)-B(10) 1.791(10).

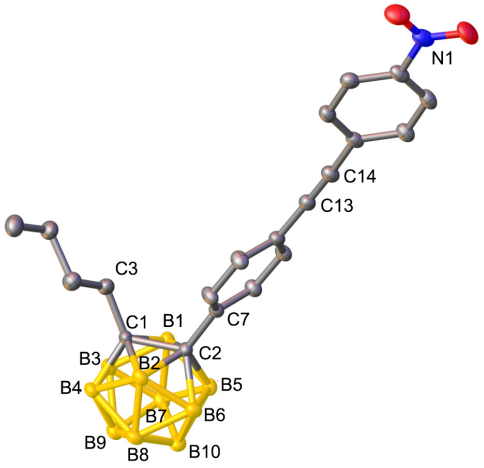


Figure 2. Molecular structure of **8**, with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): C1-C2 1.702(3), B(1)-B(3) 1.769(4), B(1)-B(5) 1.767(4), B(1)-B(7) 1.762(4), B(1)-C(1) 1.724(3), B(1)-C(2) 1.734(3), B(2)-B(4) 1.769(4), B(2)-B(6) 1.792(4), B(2)-B(8) 1.774(4), B(2)-C(1) 1.731(4), B(2)-C(2) 1.730(3), B(3)-B(4) 1.781(4), B(3)-B(7) 1.768(4), B(3)-B(9) 1.778(4), B(3)-C(1) 1.711(4), B(4)-B(8) 1.787(4), B(4)-B(9) 1.778(4), B(4)-C(1) 1.709(3), B(5)-B(6) 1.777(4), B(5)-B(7) 1.769(4), B(5)-B(10) 1.776(4), B(5)-C(2) 1.705(3), B(6)-B(8) 1.781(4), B(6)-B(10) 1.783(4), B(6)-C(2) 1.709(3), B(7)-B(9) 1.785(4), B(7)-B(10) 1.785(4), B(8)-B(9) 1.779(4), B(8)-B(10) 1.793(4), B(9)-B(10) 1.785(4).

parameter. These data also reinforce the benefit of progressing from phenyl-based bridges to **16**, **17**, and **22**, with fluorenyl bridging units and enforced bridge planarity.

Linear optical and quadratic NLO studies

UV-vis-NIR data were obtained for **1**, **5-8**, **16**, **17**, and **22** in CH_2Cl_2 solutions, the key parameters being collected in Table 1. Replacing the terminal phenyl unit in **1** with an *o*-carborane unit, in proceeding to **5-7**, results in a small red shift in optical absorption maximum, consistent with the carborane unit functioning as a weak-to-moderate strength acceptor group in the ground state. Proceeding from the D-B-A composition of **7** to an A-B-A composition in **8** leads to a blue shift in λ_{max}, as anticipated. Replacing the bridge 1,4-phenylene units in **7** and **8** with 2,7-fluorenylene units to afford **16** and **17**, respectively, leads to a significant red-shift in location of λ_{max} for the former and a dramatic red-shift in the location of this band for the latter, consistent with bridge extension and planarization. However, introduction of a second NPh_2-functionalized fluorenyl-containing unit, proceeding from **16** to **22**, leads to no change in λ_{max} and a doubling in the ε value, both observations being consistent with no extension of the effective π-system and independent fluorenyl-containing bridges.

The quadratic NLO properties were assessed by the hyper-Rayleigh scattering procedure, using an experimental set-up and data analysis that we have described in detail elsewhere.[57] A Nd-YAG laser was used to generate the fundamental light employed in the current studies (wavelength: 1064 nm, pulse width: ca. 20 ns, maximum pulse strength: 200 mJ) and the internal reference method was used to derive the $\langle\beta\rangle_{HRS}$ values. We note that the compounds are optically transparent at the fundamental and second-harmonic wavelengths. In the case of samples for which the signal observed was essentially HRS-only, and little to no scattering was seen at wavelengths around 532 nm (viz. **5-8**, **16**, **17**), the uncertainty in the measured $\langle\beta\rangle_{HRS}$ data was estimated to be ca. 10%, similar to that reported for most published HRS data. In contrast, **1** and **22** displayed strong non-HRS scattering at wavelengths near 532 nm (evidenced by strong scattering signals at 533 nm and 531 nm), and in these cases the estimated uncertainty in the measured $\langle\beta\rangle_{HRS}$ was ca. 25% (this increased error margin resulted from the (reasonable) assumption that the broad non-HRS scattering has the same strength at 532 nm as at 533 nm and 531 nm). No measurable HRS signals were observed for the 4-iodophenyl or 2-iodofluorenyl-functionalized carboranes **3**, **4**, and **14**, demonstrating the necessity of incorporating a polarizing diphenylamino or nitro substituent. The $\langle\beta\rangle_{HRS}$ values in Table 1 are the measured $\langle\beta\rangle$ values, and the $\langle\beta_0\rangle$ values were calculated from:[58]

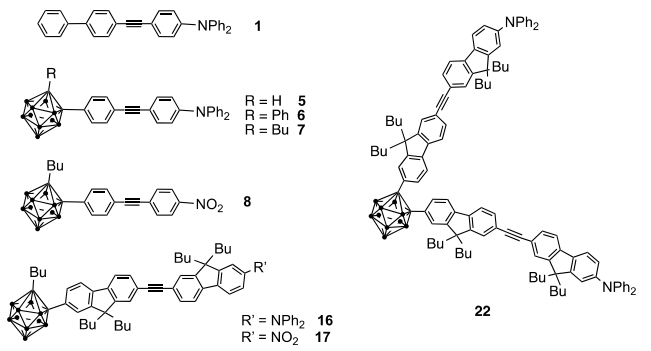
$$\langle\beta\rangle_{HRS} = \langle\beta_0\rangle D_0(\lambda) \text{ and } D_0(\lambda) = 1/ [(1-\lambda^2_{max}/\lambda^2) (1-4 \lambda^2_{max}/\lambda^2)]$$

where λ is the fundamental wavelength (1064 nm) and the optical absorption maxima λ_{max} values were obtained from the corresponding UV-Vis spectra.

The λ_{max} values are 148-203 nm removed from the second-harmonic wavelength of 532 nm and span a comparatively narrow range of 55 nm. As a result, the $<\beta>_{HRS}$ values are ca. twice the size of the $<\beta_0>$ values and the broad trend in data is maintained on proceeding from $<\beta>_{HRS}$ to $<\beta_0>$ values. Several observations can be made. First, replacing the terminal phenyl group in 1 by an electron-withdrawing *o*-carborane unit (proceeding to **5**) results in a significant increase in quadratic nonlinearity. Second, introduction of weakly electron-donating phenyl or *n*-butyl groups (proceeding from **5** to **6** or **7**) results in a small decrease in nonlinearity, of the order of the error margins of these measurements. Third, replacement of the electron-donating diphenylamino group by an electron-withdrawing nitro group (proceeding from **7** to **8**, and thereby from a D-B-A assembly to an A-B-A construction) leads to a significant decrease in nonlinearity, as anticipated. Fourth, replacement of the 1,4-phenylene bridge unit by 9,9-di-*n*-butyl-2,7-fluorenylene groups (proceeding from **7** to **16** or **8** to **17**) results in a doubling or greater of the quadratic NLO coefficient. Fifth, introduction of a second 9,9-di-*n*-butyl-2,7-fluorenylene group in place of an *n*-butyl group at the *o*-carborane core (proceeding from **16** to **22**) results in a further 30-40% increase in the β coefficients.

While the present study was targeted at establishing the structure-NLO property outcomes in the preceding paragraph, we note that the absolute quadratic NLO values for the present compounds are large compared to extant data for *o*-Cb dyads. For example, *o*-carborane *C*-functionalized by (1,4-phenylene-*E*-vinylene)ferrocenyl groups exhibits a β value of 114 x 10^{-30} esu and a β_0 value of 66 x 10^{-30} esu (ns pulses, HRS, 1064 nm),[21] but this NLO-efficient compound (and related examples somewhat less efficient) are significantly less optically transparent (λ_{max} 463 nm) and may exhibit residual absorbance at the second-harmonic wavelength (532 nm). *o*-Carborane functionalized with a 1,4-phenylethynylfullerene[60] exhibited a resonance-enhanced β value of 346 x 10^{-30} esu (ns pulses, HRS, 1064 nm), but the authors noted residual absorptivity of up to 1000 M^{-1} cm^{-1} at 532 nm,[20] in contrast to the compounds in the present study which are transparent at the measurement wavelength (Figure S58). The transparency exhibited by the present series of compounds, coupled to the stability inherent in the carborane unit, the possibility of incorporating solubilizing substituents out of the plane of the π-system (*n*-butyl groups in the present work), and the increase in NLO performance to be anticipated on progressing from *o*-Cb to *m*- and *p*-functionalized carboranes, suggest that considerable opportunity exists in exploiting C-functionalized carboranes in NLO applications. Further studies addressing this potential are currently underway.

Table 1. Linear optical and quadratic NLO parameters.



Sample	λ_{max} [ε][a]	$<\beta>_{HRS}$[b]	$<\beta_0>$[b]
1	361 [1.7]	85 ± 20	41
5	367 [3.5]	131 ± 13	61
6	371 [3.8]	123 ± 12	56
7	370 [3.8]	105 ± 10	48
8	329 [3.0]	43 ± 4	24
16	384 [6.4]	230 ± 23	96
17	377 [4.5]	141 ± 14	61
22	384 [12.6]	309 ± 77	129

The carborane skeletons are drawn as wireframes with the BH vertices as black balls. a) CH_2Cl_2 solutions. λ_{max} in nm [ε in 10^4 M^{-1} cm^{-1}]. b) THF solutions. $<\beta>$ and $<\beta_0>$ in 10^{-30} esu (1064 nm, 20 ns). Errors in $<\beta_0>$ propagated from those of the $<\beta>_{HRS}$ values.

Experimental

General Procedures. All reactions were carried out under Schlenk conditions unless otherwise stated. Commercially available materials were used as received. Tetrahydrofuran and toluene were dried by distilling over sodium/benzophenone, and dichloromethane was dried by distilling over calcium hydride. Petrol refers to a fraction of petroleum spirits with a boiling range 60-80 °C. Chromatography was on silica gel (Aldrich, 200-300 mesh) or basic alumina (100-200 mesh). $B_{10}H_{12}(SEt_2)_2$,[59] 4-ethynyl-*N,N*-diphenylaniline,[60] 4-ethynyl-1-iodobenzene and 4-ethynyl-1-nitrobenzene,[61] 4-(hex-1-yn-1-yl)-1-iodobenzene,[62] 1-iodo-4-phenylethynylbenzene,[63] 7-bromo-9,9-di-*n*-butyl-2-iodo-9*H*-fluorene,[56] 9,9-di-*n*-butyl-7-ethynyl-2-nitro-9*H*-fluorene,[64] and 1-(4-iodophenyl)-1,2-*ortho*-carborane (**2**)[8] were prepared following literature procedures.

Instrumentation. Mass spectra were recorded at the Australian National University (ANU) using a Micromass/Waters LCT-ZMD single quadrupole liquid chromatograph-MS (ESI MS, both unit resolution and HR), a VG Quattro II triple quadrupole MS (EI MS, unit resolution) and a VG AutoSpec M series sector (EBE), or at Jiangnan University using a Micromass/Waters Quattro Micro API (ESI-MS) or a Bruker SCIONSQ-456-GC gas chromatograph (EI-MS). Microanalyses were carried out at the School of Human Sciences, Science Centre, London Metropolitan University, U.K. ^{1}H NMR spectra were recorded using Varian Mercury-300, Varian Gemini-300 or Bruker AVANCE III-400 FT-NMR spectrometers, and are referenced to residual chloroform (7.26 ppm). ^{13}C NMR spectra were recorded using Varian Inova-500 or Bruker AVANCE III-400 FT-NMR spectrometers and are referenced to *d*-chloroform (77.0 ppm). ^{11}B NMR spectra were recorded using Varian Mercury-300, Varian Gemini-300 or Bruker AVANCE III-400 FT-NMR spectrometers, and are referenced to external $BF_3.Et_2O$ (0.0 ppm). UV-vis-NIR spectra were recorded as CH_2Cl_2 solutions in 1 cm quartz cells

using Cary 5 or Lambda TU1901 spectrophotometers, and are reported as λ_{max} nm (ε 10^4 M^{-1} cm^{-1}). IR spectra were recorded using a Thermo Fisher Nicolet 6700 ATR FT-IR spectrometer.

Synthesis of Ph-1,4-C_6H_4C≡C-1,4-C_6H_4NPh_2 (1). A stirred solution of 4-ethynyl-*N,N*-diphenylaniline (155 mg, 0.58 mmol) and 4-iodobiphenyl (200 mg, 0.71 mmol) in NEt_3/THF (1:1, 30 mL) was deoxygenated via three freeze-pump-thaw cycles and then purged with N_2. $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) and CuI (8 mg, 0.042 mmol) were then added and the solution heated at reflux overnight. The solvent was removed under vacuum, and the residue purified by silica thin-layer chromatography eluting with petrol. Removal of solvent and recrystallization from petrol afforded compound **1** as a white solid (200 mg, 0.47 mmol, 81%). R_f - 0.4 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.59 (m, 6H), 7.56-7.38 (m, 5H), 7.28-7.33 (t, *J* = 8 Hz, 4H), 7.25-7.01 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 147.2, 140.6, 140.4, 132.5, 131.9, 129.4, 128.8, 127.5, 127.0, 125.0, 123.5, 122.5, 122.3, 116.1, 90.4, 88.6. FT-IR (KBr, cm^{-1}): 2214 (w, C≡C), 1270 (s, C-N). MS (EI): *m/z* (%): 421.2 (100, $[M]^+$). HRMS (EI): Calc. for $C_{32}H_{23}N$: 421.1830, found 421.1831. Anal. Calcd for $C_{32}H_{23}N$: C, 91.18; H, 5.50; N, 3.32. Found: C, 90.96; H, 5.58; N, 3.44.

Synthesis of 2-phenyl-1-(4-iodophenyl)-1,2-*ortho*-carborane (3). To a solution of $B_{10}H_{12}(SEt_2)_2$ (3.58 g, 11.9 mmol) in dry toluene (50 mL) was added 1-phenylethynyl-4-iodobenzene (3.04 g, 13.3 mmol). The reaction mixture was heated at reflux for 2 days, after which MeOH was added to quench the reaction. The solvent was removed in vacuum, and the residue was purified by silica column chromatography, eluting with petrol. The solvent was reduced in volume to give compound **3** as a white solid (2.95 g, 6.99 mmol, 53%). R_f -0.7 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 - 7.45 (m, 4H), 7.30 (t, *J* = 7 Hz, 1H), 7.18 (dd, *J* = 17, 8 Hz, 4H), 3.83 - 1.62 (br, 10H, BH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.5, 132.1, 130.6, 130.6, 130.4, 130.4, 128.5, 97.2, 85.3, 84.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ -1.70, -2.84, -8.47, -9.68, -10.83, -12.11. FT-IR (KBr, cm^{-1}): 2580 (s, B–H). HRMS (EI): Calc. Mass for $C_{14}H_{18}B_{10}I$ ($[M - H]^+$): 423.1384, found 423.1381. Anal. Calcd for $C_{14}H_{19}B_{10}I$: C, 39.82; H, 4.53. Found: C, 39.92; H, 4.69.

Synthesis of 2-*n*-butyl-1-(4-iodophenyl)-1,2-*ortho*-carborane (4). $B_{10}H_{12}(SEt_2)_2$ (2.33 g, 7.75 mmol) and 4-(hex-1-yn-1-yl)-1-iodobenzene (2.00 g, 7.04 mmol) were added to dry toluene (40 mL). The reaction mixture was heated at reflux for 2 days, after which MeOH was added to quench the reaction. The solvent was then removed and the residue was purified by basic alumina column chromatography, eluting with hexane. The solvent was reduced in volume to give compound **4** as a white solid (1.30 g, 3.23 mmol, 46%). R_f - 0.8 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9 Hz, 2H), 7.37 (d, *J* = 9 Hz, 2H), 3.29-1.55 (br, 10H, BH), 1.82-1.70 (m, 2H), 1.77 (m, 2H), 1.39 (m, 2H), 1.14 (dq, *J* = 15, 7 Hz, 2H), 0.79 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 132.7, 130.7, 97.5, 82.6, 82.5, 34.9, 31.5, 22.1, 13.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ -2.98, -4.18, -9.68, -10.68. FT-IR (KBr, cm^{-1}): 2627-2555 cm^{-1} (s, B-H). HRMS (EI): Calc. for $C_{12}H_{21}B_{10}I$ ($[M - 2H]^+$): 402.1619, found 402.1615. Anal. Calcd for $C_{12}H_{23}B_{10}I$: C, 35.82; H, 5.76. Found: C, 35.87; H, 5.64.

Synthesis of 1-(Ph_2N-1-C_6H_4-4-C≡C-4-C_6H_4-1)-1,2-*ortho*-carborane (5). Compound **2** (211 mg, 0.61 mmol) and 4-ethynyl-*N,N*-diphenylaniline (180 mg, 0.67 mmol) were added to deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) and CuI (12 mg, 0.063 mmol) were then added and the solution stirred at 70°C overnight. After the removal of solvent, the residue was purified through silica gel column chromatography, eluting with hexane/CH_2Cl_2 (v/v = 8/1). Recrystallization from hexane afforded the target compound as an off-white solid (213 mg, 0.44 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 4H), 7.37 (d, J = 8 Hz, 2H), 7.29 (t, J = 8 Hz, 4H), 7.17-7.05 (m, 6H), 7.01 (d, J = 9 Hz, 2H), 3.95 (s, 1H), 3.47-1.65 (br, 10H, BH). ^{13}C NMR (101 MHz, CDCl3): δ 148.4, 147.1, 132.7, 132.6, 131.6, 129.5, 127.6, 125.8, 125.2, 123.8, 122.0, 115.1, 92.5, 87.1, 76.2, 60.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ -1.37, -2.55, -8.27, -9.48, -10.13, -11.43. FT-IR (KBr, cm^{-1}): 2603 (br, B-H), 2201 (w, C≡C), 1279 (s, C-N). MS (EI) *m/z* (%): 487.3 ($[M^+]$, 100). HRMS (EI): Calc. for $C_{28}H_{28}B_{10}N$ ($[M - H]^+$): 488.3152, found 488.3159. Anal. Calcd for $C_{28}H_{29}B_{10}N$: C, 68.96; H, 5.99; N, 2.87 %. Found: C, 68.84; H, 6.00; N, 2.85%.

Synthesis of 2-phenyl-1-(Ph_2N-1-C_6H_4-4-C≡C-4-C_6H_4-1)-1,2-*ortho*-carborane (6). Compound **3** (845 mg, 2.00 mmol) and 4-ethynyl-*N,N*-diphenylaniline (539 mg, 2.00 mmol) were added to deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (46 mg, 0.040 mmol) and CuI (15 mg, 0.078 mmol) were added and the solution stirred at 70°C overnight. The solvent was removed under vacuum, and the residue purified by silica plate thin-layer chromatography, eluting with petrol /CH_2Cl_2 (2:1). The solvent was removed. Crystallization from petrol/CH_2Cl_2 afforded compound **6** as needle-like crystals. (921 mg, 1.63 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8 Hz, 2H), 7.39 (d, *J* = 9 Hz, 2H), 7.33-7.25 (m, 9H), 7.18-7.07 (m, 8H), 6.99 (d, *J* = 9 Hz, 2H), 3.65-1.68 (br, 10H, BH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.4, 147.0, 132.6, 131.1, 130.62, 130.55, 130.5, 130.3, 123.0, 129.5, 128.4, 125.8, 125.2, 123.8, 121.9, 115.1, 92.6, 87.3, 85.5, 84.8. ^{11}B NMR (128 MHz, $CDCl_3$): δ -1.78, -2.87, -9.73, -10.82. FT-IR (KBr, cm^{-1}): 2591 (s, B-H), 2217 (m, C≡C), 1275 (s, C-N). MS (EI) *m/z* (%): 564.3 ($[M - H]^+$, 100). HRMS (EI): Calcd for $C_{34}H_{33}B_{10}N$ 563.3632, found 563.3643. Anal. Calcd for $C_{34}H_{33}B_{10}N$: C, 72.44; H, 5.90; N, 2.48 %. Found: C, 72.43; H, 6.03; N, 2.54 %.

Synthesis of 2-(*n*-butyl)-1-(Ph_2N-1-C_6H_4-4-C≡C-4-C_6H_4-1)-1,2-*ortho*-carborane (7). Compound **4** (500 mg, 1.24 mmol) and 4-ethynyl-*N,N*-diphenylaniline (368 mg, 1.37 mmol) were added to deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (80 mg, 0.069 mmol) and CuI (30 mg, 0.16 mmol) were then added and the solution stirred at 70 °C overnight. The solvent was removed under vacuum, and the residue was purified by silica thin-layer chromatography, eluting with petrol. The solvent was removed to give a white solid. Recrystallization from methanol afforded compound **7** as a flaky white solid (630 mg, 1.16 mmol, 94%). R_f - 0.4 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 9 Hz, 2H), 7.48 (d, *J* = 9 Hz, 2H), 7.36 (d, *J* = 9 Hz, 2H), 7.30 - 7.26 (dd, *J* = 9, 7 Hz, 4H), 7.13-7.06 (m, 6H), 7.00 (d, *J* = 9 Hz, 2H), 2.51 (br, 10H, BH), 1.76 (m, 2H), 1.36 (dt, *J* = 16, 6 Hz, 2H), 1.10 (m, 2H), 0.76 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5, 147.0, 132.7, 131.6, 131.1, 130.0, 129.5, 125.2, 123.8, 121.9, 115.0, 92.8, 87.2, 83.2, 82.8, 34.8, 31.5, 22.1, 13.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ -3.14, -4.16, -9.72, -10.67. FT-IR (KBr, cm^{-1}): 2583 (br, B-H), 2211 (m, C≡C). MS (EI): *m/z* (%): 543.4 (100, $[M]^+$). HRMS

(EI): Calc. for $C_{32}H_{35}B_{10}N$ ([M – 2H]$^+$): 543.3700, found 543.3703. Anal. Calcd for $C_{32}H_{37}B_{10}N$: C, 70.68; H, 6.86; N, 2.58. Found C, 70.79; H, 6.93; N, 2.47.

Synthesis of 2-(*n*-butyl)-1-(O_2N-1-C_6H_4-4-C≡C-4-C_6H_4-1)-1,2-*ortho*-carborane (8). Compound **4** (300 mg, 0.75 mmol) and 4-ethynyl-1-nitrobenzene (121 mg, 0.82 mmol) were added to deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) and CuI (8.0 mg, 0.042 mmol) were then added and the solution heated at reflux overnight. The solvent was removed under vacuum, and the residue purified by silica thin-layer chromatography, eluting with a petrol/CH_2Cl_2 (2:1) mixture. Recrystallization afforded a flaky white solid (205 mg, 0.49 mmol, 65%). R_f - 0.5 (petrol/CH_2Cl_2 = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 9 Hz, 2H), 7.72 - 7.67 (dd, *J* = 11, 9 Hz, 4H), 7.59 (d, J = 8 Hz, 2H), 3.35 - 1.80 (br, 10H, BH), 1.82-1.77 (m, 2H), 1.44 - 1.36 (dt, J = 16, 8 Hz, 2H), 1.13 (dd, *J* = 15, 7 Hz, 2H), 0.78 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 132.5, 132.1, 131.5, 131.3, 129.4, 124.7, 123.7, 92.7, 90.0, 82.8, 82.7, 34.9, 31.5, 22.1, 13.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ -3.15, -4.22, -9.50, -10.69. FT-IR (KBr, cm^{-1}): 2613-2579 (s, B-H); 2217 cm^{-1} (w, C≡C); 1518, 1340 (NO_2). MS (EI): *m/z* (%): 421 (100, [M]$^+$). HRMS (EI): Calc. for $C_{20}H_{27}B_{10}NO_2$: 421.3056, found 421.3054. Anal. Calcd for $C_{20}H_{27}B_{10}NO_2$: C, 56.98; H, 6.46; N, 3.32. Found: C, 56.87; H, 6.36; N, 3.51.

Synthesis of 9,9-di(*n*-butyl)-2-(*N,N*-diphenylamino)-7-((trimethylsilyl)ethynyl)-9*H*-fluorene (**10**). A mixture of 2-bromo-9,9-di(*n*-butyl)-7-iodo-9*H*-fluorene (9.66 g, 20.0 mmol), diphenylamine (2.20 g, 13.0 mmol), copper(I) iodide (248 mg, 1.30 mmol), 1,10-phenanthroline (468 mg, 2.60 mmol) and potassium carbonate (4.00 g, 24.6 mmol) was purged with nitrogen, and then 30 mL of anhydrous DMF was added. The mixture was heated to reflux for 24 h. After cooling to room temperature, the dark suspension was poured into ice-water. The precipitate was collected and purified by silica gel column chromatography, eluting with petrol to obtain 2-bromo-9,9-di(*n*-butyl)-*N,N*-diphenylamino-9*H*-fluorene (**9**) as a white solid (3.06 g, 45%). R_f - 0.50 (petrol). A stirred solution of **9** (1.05 g, 2.01 mmol) in NEt_3 (10 mL) and THF (20 mL) was then deoxygenated via three freeze-pump-thaw cycles and then purged with argon. To this mixture was added PPh_3 (21 mg, 0.080 mmol), $Pd_2(dba)_3$ (37 mg, 0.040 mmol) and CuI (8 mg, 0.042 mmol), followed by trimethylsilylacetylene (0.295 g, 3.00 mmol, 0.42 mL). This mixture was then sealed and stirred at 85 °C overnight. After cooling to room temperature, the mixture was reduced in volume, and flash-filtered through alumina (eluent: CCl_4). The solvent was removed in vacuo to afford a brown solid. Purification via TLC on silica gel (eluent: cyclohexane) gave compound **10** as a pale yellow solid (0.55 g, 1.01 mmol, 51 %). R_f -0.3 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.44-7.38 (m, 2H), 7.24 (t, *J* = 8 Hz, 4H), 7.12-7.09 (m, 5H), 7.03-6.99 (m, 3H), 1.84 (dd, *J* = 16, 8 Hz, 4H), 1.13-1.00 (m, 4H), 0.69 (dd, J = 8, 7 Hz, 6H), 0.63 (m, 4H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 150.49, 147.9, 147.7, 141.3, 135.5, 131.3, 129.2, 126.1, 124.0, 123.3, 122.7, 120.71, 119.0, 118.9, 106.5, 93.6, 55.0, 40.0, 26.0, 23.0, 13.9, 0.1. FT-IR (KBr, cm^{-1}): 2154 (m, C≡C. HRMS (EI): Calc. for $C_{38}H_{43}NSi$: 541.3165, found 541.3168.

Synthesis of 9,9-di(*n*-butyl)-2-(*N,N*-diphenylamino)-7-(ethynyl)-9*H*-fluorene (11). Compound **10** (0.45 g, 0.83 mmol) was added to a mixture of deoxygenated CH_2Cl_2/methanol (1:1, 20 mL). K_2CO_3 (0.230 g, 1.66 mmol) was added and the mixture stirred for 4 h. The solvent was removed under reduced pressure and flash-filtered through alumina (eluent: CCl_4) to give compound **11** as a pale yellow solid (332 mg, 0.71 mmol, 85%). R_f - 0.2 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.59-7.56 (dd, *J* = 8, 3 Hz, 2H), 7.50-7.46 (m, 2H), 7.31-7.27 (m, 4H), 7.17-7.13 (m, 5H), 7.07-7.04 (m, 3H), 3.15 (s, 1H), 1.91-1.85 (m, 4H), 1.12-1.10 (m, 4H), 0.76-0.24 (t, *J* = 7 Hz, 6H), 0.70-0.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 150.6, 147.9, 147.8, 141.8, 135.2, 131.2, 129.2, 126.4, 124.0, 123.3, 122.7, 120.8, 119.3, 118.94, 118.92, 84.9, 55.0, 39.9, 26.0, 23.0, 13.9. FT-IR (KBr, cm^{-1}): 2101 (w, C≡C), 3299 (m, ≡CH). HRMS (EI): Calc. for $C_{35}H_{35}N$: 469.2770, found 469.2778. Anal. Calcd for $C_{35}H_{35}N$: C, 89.51; H, 7.51; N, 2.98. Found: C, 89.51; H, 7.63; N, 2.87.

Synthesis of 2-bromo-9,9-di(*n*-butyl)-7-(hex-1-yn-1-yl)-9*H*-fluorene (12). 7-Bromo-9,9-di(*n*-butyl)-2-iodo-9*H*-fluorene (6.00 g, 12.42 mmol) in NEt_3/THF (20/20 mL) was deoxygenated via two freeze-pump-thaw cycles and then purged with N_2. To this solution was added $PdCl_2(PPh_3)_2$ (0.175 g, 0.25 mmol), CuI (0.095 g, 0.50 mmol), and 1-hexyne (1.60 mL, 14.0 mmol), and the mixture was stirred at RT for 10 h. The solvent was then removed under reduced pressure and the residue was purified by silica column chromatography using hexane as eluent. Compound **12** was obtained as a pale-yellow oil following removal of the solvent (4.91 g, 90 %). R_f - 0.7 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8 Hz, 1H), 7.51 (d, J = 9 Hz, 1H), 7.47-7.41 (m, 2H), 7.41-7.32 (m, 2H), 2.45 (t, J = 7 Hz, 2H), 1.97-1.86 (m, 4H), 1.69-1.58 (m, 2H), 1.56-1.46 (m, 2H), 1.07 (dd, J = 15, 7 Hz, 4H), 0.97 (t, J = 7 Hz, 3H), 0.67 (t, J = 7 Hz, 6H), 0.60-0.48 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 150.3, 139.6, 139.5, 130.7, 130.0, 126.1, 125.9, 122.9, 121.2, 121.2, 119.6, 90.7, 81.3, 55.3, 40.1, 30.9, 25.8, 23.0, 22.1, 19.3, 13.8, 13.7. FT-IR (KBr, cm^{-1}): 2227 cm^{-1} (C≡C). HRMS (EI): Calc. for $C_{27}H_{33}{}^{79}Br$: 436.1766, found 436.1764.

Synthesis of 9,9-di(*n*-butyl)-7-(hex-1-yn-1-yl)-2-iodo-9*H*-fluorene (13). Compound **12** (2.10 g, 4.80 mmol) was added to THF (30 mL) and cooled to -78 °C. n-BuLi (3.6 mL of a 1.6 M solution in hexane, 5.76 mmol) was slowly added via syringe and the mixture stirred for 2 h. Iodine (1.82 g, 7.17 mmol) in THF (25 mL) was added and the mixture warmed to RT. After 30 min stirring, aqueous $Na_2S_2O_3$ was added and the mixture extracted with CH_2Cl_2, washing well with water. The CH_2Cl_2 layer was dried with $MgSO_4$ and the solvent removed. The residue was purified by silica column chromatography, eluting with petrol. The solvent was removed to give compound **13** as a pale-yellow oil (1.44 g, 2.97 mmol, 43 %). R_f - 0.6 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.15 (m, 6H), 2.53-2.46 (m, 2H), 2.04-1.92 (m, 4H), 1.72-1.62 (m, 2H), 1.60-1.52 (m, 2H), 1.12 (dd, *J* = 15, 7 Hz, 4H), 1.05-0.97 (m, 3H), 0.71 (dd, *J* = 9, 6 Hz, 6H), 0.61 (dt, *J* = 10, 7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 150.1, 140.3, 139.6, 136.0, 132.1, 130.7, 130.6, 125.8, 123.1, 121.6, 119.6, 92.9, 90.8, 81.4, 55.3, 40.2, 25.9, 23.1, 22.2, 19.3, 13.8, 13.7. FT-IR (KBr, cm^{-1}): 2226 cm^{-1} (C≡C). HRMS (EI): Calc. for $C_{27}H_{33}I$: 484.1627, found 484.1628.

Synthesis of 2-(*n*-butyl)-1-(9,9-di(*n*-butyl)-2-iodo-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane (14). A solution of compound **13** (0.710 g, 1.47 mmol) and $B_{10}H_{12}(SEt_2)_2$ (0.530 g, 1.76 mmol) in dry toluene (50 mL) was heated at reflux for 3 days and then cooled to room temperature. MeOH was added to quench the reaction. The solvent was removed under vacuum. The residue was purified by silica column chromatography, eluting with petrol. The solvent was reduced in volume to give compound **14** as a white solid (0.505 g, 0.84 mmol, 57%). R_f - 0.5 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.38 (m, 6H), 3.7-1.7 (m, 16H, BH), 2.03-1.79 (m, 6H), 1.42-1.34 (m, 2H), 1.11-1.04 (m, 6H), 0.75-0.67 (m, 9H), 0.64-0.49 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 150.6, 142.5, 139.1, 136.3, 132.3, 130.6, 129.9, 125.5, 122.1, 119.9, 94.1, 84.3, 82.7, 55.5, 39.7, 34.8, 31.5, 26.0, 22.9, 22.2, 13.7, 13.4. ^{11}B NMR: (128 MHz, $CDCl_3$) δ -3.20, -4.17, -9.92, -10.79. FT-IR (KBr, cm^{-1}): 2596-2584 (s, B-H). MS (EI): *m/z* (%): 602.3 (100, $[M]^+$). HRMS (EI): Calc. for $C_{27}H_{41}B_{10}I$ ($[M - 2H]^+$): 602.3184, found 602.3192**.** Anal. Calcd for $C_{27}H_{43}B_{10}I$ (%): C, 54.73, H, 5.61. Found: C, 54.86, H, 5.80.

Synthesis of 9,9-di(*n*-butyl)-7-ethynyl-2-nitro-9*H*-fluorene (15). A stirred solution of 9,9-di(*n*-butyl)-2-iodo-7-nitro-9*H*-fluorene (4.00 g, 8.90 mmol) in NEt_3 and THF (1:1, 40 mL) was deoxygenated via three freeze-pump-thaw cycles, and then purged with argon. To this mixture was added $PdCl_2(PPh_3)_2$ (180 mg, 0.26 mmol) and CuI (80 mg, 0.42 mmol), and then trimethylsilylacetylene (1.31 g, 13.3 mmol, 1.9 mL) was added via syringe. The mixture was stirred at 60 °C overnight. After cooling to room temperature, this mixture was reduced in volume, and then flash-filtered through alumina (eluent: CCl_4). The filtrate was again concentrated in vacuo to afford a yellow solid that was added to a mixture of deoxygenated CH_2Cl_2 and methanol (1:1, 30 mL), and then K_2CO_3 (1.85 g, 13.4 mmol) was added and the mixture stirred for 6 h. The solvent was removed under reduced pressure, and the residue flash-filtered through alumina (eluent: CCl_4). Removal of solvent and recrystallization from petrol afforded compound **15** as a yellow solid (2.62 g, 7.55 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (dd, *J* = 8, 2 Hz, 1H), 8.23 (d, *J* = 2 Hz, 1H), 7.85-7.72 (m, 2H), 7.56 (dd, *J* = 10, 2 Hz, 2H), 3.24 (s, 1H), 2.07-2.02 (m, 4H), 1.13-1.08 (dd, *J* = 15, 7 Hz, 4H), 0.71-0.67 (t, *J* = 7 Hz, 6H), 0.57-0.47 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.28, 152.27, 146.6, 139.3, 131.6, 126.8, 123.4, 122.7, 121.1, 120.2, 118.3, 84.0, 78.4, 55.7, 39.8, 25.9, 22.9, 13.7.

Synthesis of 2-(*n*-butyl)-1-(2-((9,9-di(*n*-butyl)-2-(*N,N*-diphenylamino)-9*H*-fluoren-7-yl)ethynyl)-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane (16). Compounds **14** (200 mg, 0.33 mmol) and **11** (155 mg, 0.33 mmol) were dissolved in deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) and CuI (4 mg, 0.021 mmol) were added and the solution heated at reflux overnight. The solvent was removed under vacuum, and the residue purified by silica thin-layer chromatography, eluting with petrol. Removal of solvent and recrystallization from MeOH/EtOAc afforded compound **16** as a yellow solid (250 mg, 0.26 mmol, 79%). R_f - 0.2 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.49 (m, 10H), 7.29 (dd, J = 11, 5 Hz, obscured by $CHCl_3$), 7.21 – 7.13 (m, 5H), 7.11 – 7.01 (m, 3H), 3.40 – 1.50 (br, 10H, B–H and 10H, CH_2), 1.46 – 1.32 (m, 2H), 1.20 – 1.01 (m, 10H), 0.81 – 0.42 (m, 23H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 151.5, 151.4, 150.7, 147.9, 147.7, 142.9, 141.5, 139.4, 135.4, 130.9, 130.8, 130.5, 129.6, 129.2, 126.0, 125.8, 125.6, 124.0, 123.3, 123.1, 122.7, 120.7, 120.44, 120.36, 120.0, 119.2, 118.9, 91.5, 89.9, 84.4, 82.8, 55.4, 55.1, 40.0, 39.9, 34.8, 31.5, 26.0, 23.0, 22.9, 22.2, 13.9, 13.8, 13.4. ^{11}B NMR (128 MHz, $CDCl_3$): δ -3.96, -10.51. FT-IR (KBr, cm^{-1}): 2585 (br, B-H), 2201 (w, C≡C). Anal. Calcd for $C_{62}H_{77}B_{10}N$: C, 78.85; H, 8.22; N, 1.48. Found: C, 78.94; H, 8.36; N, 1.57. HRMS (TOF-MS-ES): Calc. for $C_{62}H_{76}B_{10}N$ ($[M - H]^+$): 944.6908, found 944.6898. Anal. Calcd for $C_{62}H_{77}B_{10}N$: C, 78.85; H, 8.22; N, 1.48. Found: C, 78.94; H, 8.36; N, 1.57 %.

Synthesis of 2-(*n*-butyl)-1-(2-((9,9-di(*n*-butyl)-2-nitro-9*H*-fluoren-7-yl)ethynyl)-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane (17). Compounds **14** (240 mg, 0.40 mmol) and **15** (138 mg, 0.40 mmol) were dissolved in deoxygenated NEt_3/THF (1:1, 40 mL). $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) and CuI (5.0 mg, 0.026 mmol) were then added and the solution heated at reflux overnight. The solvent was removed under vacuum, and the residue purified by silica thin-layer chromatography, eluting with petrol/CH_2Cl_2 (3:1). The solvent was reduced in volume to give compound **17** as a yellow solid (166 mg, 0.20 mmol, 50%). R_f - 0.5 (petrol/CH_2Cl_2 = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 8.22 (d, *J* = 1.6 Hz, 1H), 7.81 (d, *J* = 5.6 Hz, 1H), 7.79 (d, *J* = 5.0 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.52 (m, 6H), 3.26 – 2.19 (br, m, 10H, BH), 2.20 – 1.95 (m, 8H), 1.93 – 1.68 (m, 2H), 1.36 (mm, 2H), 1.17 – 0.94 (m, 10H), 0.77 – 0.38 (m, 22H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 152.2, 151.50, 151.48, 147.4, 146.8, 142.8, 139.9, 138.9, 131.2, 131.0, 130.6, 129.8, 126.2, 126.1, 125.6, 123.9, 123.4, 122.6, 121.2, 120.5, 120.14, 120.12, 118.3, 91.5, 90.6, 84.3, 82.8, 55.8, 55.4, 39.94, 39.91, 34.8, 31.5, 26.0, 25.9, 22.9, 22.9, 22.2, 13.77, 13.75. ^{11}B NMR (128 MHz, $CDCl_3$): δ -4.31, -11.10. FT-IR (KBr, cm^{-1}): 2584 (br, B-H); 2200 cm^{-1} (w, C≡C); 1522, 1341 (s, NO_2). HRMS (TOF-MS-ES): Calc. for $C_{50}H_{66}B_{10}NO_2$ ($[M - H]^+$): 822.6024, found 822.6050. Anal. Calcd for $C_{50}H_{67}B_{10}NO_2$: C, 73.95, H7.07, N,1.72. Found: C, 73.74, H, 7.16, N, 1.89.

Synthesis of 2-bromo-7-ethynyl-9,9-di(*n*-butyl)-9*H*-fluorene (18). 7-bromo-9,9-di(*n*-butyl)-2-iodo-9*H*-fluorene (3.00 g, 6.21 mmol) in NEt_3 (30 mL) was deoxygenated via three freeze-pump-thaw cycles, and the flask purged with nitrogen. $PdCl_2(PPh_3)_2$ (130 mg, 0.19 mmol), CuI (70 mg, 0.37 mmol) and trimethylsilylacetylene (0.92 mL, 6.46 mmol) were added, and the mixture stirred at room temperature for 6 h. The solvent was removed under vacuum and the residue was flash-filtered through silica column chromatography, eluting with CCl_4. The solvent was removed to give a yellow solid that was added to a mixture of deoxygenated CH_2Cl_2 and methanol (1:1, 30 mL). K_2CO_3 (1.72 g, 12.42 mmol) was added and the mixture stirred for 5 h. The solvent was removed under vacuum, and the residue flash-filtered through alumina, eluting with petrol. Purification by silica gel column chromatography eluting with petrol/CH_2Cl_2 (3:1) gave compound **18** as a white solid after reduction in volume of the solvent (2.04 g, 86%). R_f - 0.50 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 4H), 3.15 (s, 1H), 2.03-1.86

(m, 4H), 1.17-1.02 (m, 4H), 0.68 (t, *J* = 7.2 Hz, 6H), 0.62-0.49 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 150.4, 140.8, 139.3, 131.3, 130.2, 126.6, 126.3, 121.7, 121.4, 120.8, 119.7, 84.5, 55.4, 40.0, 25.9, 23.0, 13.8. FT-IR (KBr, cm^{-1}): 3299 (s, ≡CH), 2102 (w, C≡C). HRMS (EI): Calcd. for $C_{23}H_{25}{}^{79}Br$: 380.1140, found 380.1142. Anal. Calcd for $C_{23}H_{25}Br$: C, 72.44; H, 6.61; Found: C, 72.56; H, 6.58 %.

Synthesis of 1,2-bis(2-bromo-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)ethyne (19). Compound **18** (1.14 g, 3.00 mmol) and 7-bromo-9,9-di(*n*-butyl)-2-iodo-9*H*-fluorene (1.45 g, 3.00 mmol) were added to deoxygenated NEt_3/THF (1:1, 40 mL). $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol) and CuI (60 mg, 0.3 mmol) were added and the solution heated at reflux overnight. The reaction was allowed to cool, and the solvent was then removed under vacuum, and the residue passed through a short pad of silica, eluting with petrol. The solvent was removed under vacuum, and the residue purified by silica column chromatography, eluting with petrol. The solvent was reduced in volume to give a white solid identified as compound **19** (1.67 g, 2.27 mmol, 76%). R_f -0.6 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.8 Hz, 2H), 7.58 (dd, J = 8.0, 6.0 Hz, 6H), 7.50 (d, J = 6.7 Hz, 4H), 2.00 (h, J = 13.5 Hz, 8H), 1.18-1.07 (m, 8H), 0.72 (t, J = 7.3 Hz, 12H), 0.67-0.54 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 150.5, 140.3, 139.5, 130.8, 130.2, 126.2, 125.9, 122.0, 121.6, 121.3, 119.8, 90.7, 55.4, 40.2, 25.9, 23.0, 13.8. FT-IR (KBr, cm^{-1}): 2162 (w, C≡C). HRMS (EI): Calcd. for $C_{44}H_{48}{}^{79}Br_2$: 734.2123, found 734.2122. Anal. Calcd for $C_{44}H_{48}Br_2$: C, 71.74; H, 6.57; Found: C, 71.64; H, 6.69 %.

Synthesis of 1,2-bis(2-iodo-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)ethyne (20). Compound **19** (1.00 g, 1.36 mmol) was added to THF (20 mL) and the solution was cooled to -78 °C. n-BuLi (3.6 mL, 1.6 M solution in hexane, 5.76 mmol) was slowly added via syringe, and the mixture stirred for 2 h. Iodine (414 mg, 3.26 mmol) in THF (20 mL) was added and the mixture warmed to RT and left to stir for 30 min. The mixture was washed with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum. The residue was then passed through a short pad of alumina, eluting with petrol, and the solvent reduced in volume to give a white solid identified as **20** (0.78 g, 0.94 mmol, 69%). R_f - 0.6 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 10.8 Hz, 4H), 7.60 (d, *J* = 7.8 Hz, 4H), 7.37 (d, *J* = 4.9 Hz, 4H), 2.03 (t, *J* = 8.2 Hz, 8H), 1.16-1.08 (m, 8H), 0.71 (t, *J* = 7.2 Hz, 12H), 0.68-0.55 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.0, 150.8, 141.4, 140.5, 130.6, 127.5, 126.9, 125.9, 122.9, 121.6, 120.0, 119.7, 90.5, 55.1, 40.3, 25.9, 23.1, 13.8. FT-IR (KBr, cm^{-1}): 2162(w, C≡C). HRMS (TOF-ES): Calcd. for $C_{44}H_{48}I_2$: 830.1846, found 830.1846.

Synthesis of 1,2-bis(2-iodo-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane (21). Compound **20** (0.50 g, 0.60 mmol) and $B_{10}H_{12}(SEt_2)_2$ (0.27g, 0.90 mmol) in dry toluene (20 mL) was heated at reflux for 3 days. The mixture was cooled to room temperature and MeOH (20 mL) was added to quench the reaction. The solvent was removed by evaporation under vacuum, and the residue was filtered through a short pad of alumina, eluting with toluene. Purification by silica plate chromatography, eluting with petrol, gave a white solid identified as **21** (0.21 g, 0.22 mmol, 37%). R_f -0.5 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 4H), 7.45 (dd, J = 11.8, 8.1 Hz, 4H), 7.35 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 4.88-1.61 (b, 18H, Cage-H and four CH_2 (1.83-1.77 (m, 8H)), 1.02-0.86 (m, 8H), 0.57 (t, J = 7.3 Hz, 12H), 0.36 (tt, J = 15.5, 7.6 Hz, 4H), 0.20 (tt, J = 15.3, 7.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 150.2, 142.1, 138.9, 136.1, 132.1, 130.0, 129.9, 125.1, 121.9, 119.2, 93.9, 86.4, 55.3, 39.6, 25.7, 22.8, 13.8. ^{11}B NMR: (128 MHz, $CDCl_3$): δ -2.83, -10.79. FT-IR (KBr, cm^{-1}): 2643-2592 (br, B-H). HRMS (TOF-ES): Calcd. for $C_{44}H_{57}B_{10}I_2$ ($[M - H]^+$): 949.3480, found 949.3481. Anal. Calcd for $C_{44}H_{58}B_{10}I_2$ (%): C, 55.70; H, 6.16. Found: C, 55.67; H, 6.19.

Synthesis of 1,2-bis(2-((9,9-di(*n*-butyl)-2-(*N*,*N*-diphenylamino)-9*H*-fluoren-7-yl)ethynyl)-9,9-di(*n*-butyl)-9*H*-fluoren-7-yl)-1,2-*ortho*-carborane (22). Compounds **21** (200 mg, 0.21 mmol) and **11** (200 mg, 0.42 mmol) were dissolved in a mixture of NEt_3 and THF (1:1, 30 mL). $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) were added and the solution heated at reflux overnight. The solvent was removed under vacuum and the residue purified by silica thin-layer chromatography, eluting with petrol. Removal of solvent and recrystallization from $MeOH/CH_2Cl_2$ afforded a yellow solid identified as **22** (267 mg, 0.162 mmol, 65%). R_f -0.3 (petrol). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.70-7.36 (m, 20H), 7.26 (t, *J* = 6.9 Hz, 9H), 7.13 (d, *J* = 8.1 Hz, 9H), 7.03 (d, *J* = 6.3 Hz, 6H), 4.11-1.61 (m, 26H, Cage-H and eight CH_2 (1.88, m, 16H)), 1.03 (dd, *J* = 38.8, 4.8 Hz, 16H), 0.82-0.50 (m, 32H), 0.40 (s, 4H), 0.24 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 151.3, 151.1, 150.7, 147.9, 147.7, 142.5, 141.4, 139.3, 135.4, 130.74, 130.69, 123.0, 129.7, 129.2, 125.9, 125.8, 125.2, 124.0, 123.3, 122.9, 122.7, 120.7, 120.4, 120.3, 119.3, 119.0, 119.0, 91.4, 90.0, 86.6, 55.2, 55.0, 40.0, 39.9, 26.0, 25.8, 23.0, 22.9, 13.9, 13.8. ^{11}B NMR (128 MHz, $CDCl_3$): δ -3.91, -10.91. FT-IR (KBr, cm^{-1}): 2589 (br, B-H), 2197 (w, C≡C). MS (MALDI-TOF): *m/z* calcd for $C_{114}H_{126}B_{10}N_2$: 1632.0948, found 1632.0927. Anal. Calcd for $C_{114}H_{126}B_{10}N_2$: C, 83.88; H, 7.78; N, 1.72. Found: C, 83.93; H, 7.75; N, 1.69.

Conclusions

Displacement of the Lewis bases from $B_{10}H_{12}(SEt_2)_2$ has afforded a range of *C*-functionalized *o*-carboranes in fair to good yields, the products being subjected to spectroscopic and in most cases single-crystal X-ray structural study. Quadratic optical nonlinearities were assessed by hyper-Rayleigh scattering using ns pulsed radiation at a measurement wavelength of 1064 nm, and therefore corresponding to a second-harmonic wavelength of 532 nm at which all compounds are optically transparent. The NLO studies confirmed that, as expected, replacing the terminal phenyl group by an electron-withdrawing o-carborane unit results in a significant increase in quadratic nonlinearity, introduction of weakly electron-donating phenyl or *n*-butyl groups results in a small decrease in nonlinearity, replacement of the electron-donating diphenylamino group by an electron-withdrawing nitro group (and thereby progressing from a D-B-A assembly to an A-B-A construction) leads to a significant decrease in nonlinearity, and replacement of the 1,4-phenylene bridge unit by 9,9-di-*n*-butyl-2,7-fluorenylene groups results in a doubling or greater of the quadratic NLO coefficient.

Introduction of a second fluorenylene group at the *o*-carborane results in a further 30-40% increase in the β coefficients, a significant increase given the unfavourable alignment of these substituents at the Cb core. The V-shaped **22** is reminiscent of Y-shaped alkynylruthenium complexes that we have recently explored, for which substantial off-diagonal first hyperpolarizability tensor components were observed.[65] It is likely that **22** has a similar 2D nonlinear character.

Conflicts of interest

There are no conflicts of interest to declare.

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References

1. H. J. Bae, J. Chung, H. Kim, J. Park, K. M. Lee, T.-W. Koh, Y. S. Lee, S. Yoo, Y. Do and M. H. Lee, *Inorg. Chem.*, 2014, **53**, 128.
2. H. J. Bae, H. Kim, K. M. Lee, T. Kim, Y. S. Lee, Y. Do and M. H. Lee, *Dalton Trans.*, 2014, **43**, 4978.
3. K.-R. Wee, W.-S. Han, D. W. Cho, S. Kwon, C. Pac and S. O. Kang, *Angew. Chem. Int. Ed.*, 2012, **51**, 2677.
4. K.-R. Wee, Y.-J. Cho, S. Jeong, S. Kwon, J.-D. Lee, I.-H. Suh and S. O. Kang, *J. Am. Chem. Soc.*, 2012, **134**, 17982.
5. L. Weber, J. Kahlert, R. Brockhinke, L. Boehling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder and M. A. Fox, *Chem. Eur. J.*, 2012, **18**, 8347.
6. C. Shi, D. Tu, Q. Yu, H. Liang, Y. Liu, Z. Li, H. Yan, Q. Zhao and W. Huang, *Chem. Eur. J.*, 2014, **20**, 16550.
7. S.-Y. Kim, A.-R. Lee, G. F. Jin, Y.-J. Cho, H.-J. Son, W.-S. Han and S. O. Kang, *J. Org. Chem.*, 2015, **80**, 4573.
8. Z. Wang, P. Jiang, T. Wang, G. J. Moxey, M. P. Cifuentes, C. Zhang and M. G. Humphrey, *Phys. Chem. Chem. Phys.*, 2016, **18**, 15719.
9. V. Stengl, S. Bakardjieva, M. Bakardjiev, B. Stibr and M. Kormunda, *Carbon*, 2014, **67**, 336.
10. A. Harriman, M. A. H. Alamiry, J. P. Hagon, D. Hablot and R. Ziessel, *Angew. Chem. Int. Ed.*, 2013, **52**, 6611.
11. R. N. Grimes, *Dalton Trans.*, 2015, **44**, 5939.
12. M. Eo, H. J. Bae, M. Hong, Y. Do, S. Cho and M. H. Lee, *Dalton Trans.*, 2013, **42**, 8104.
13. F. Barriere, B. Fabre, E. Hao, Z. M. LeJeune, E. Hwang, J. C. Garno, E. E. Nesterov and M. G. H. Vicente, *Macromolecules*, 2009, **42**, 2981.
14. L. Zhu, W. Lv, S. Liu, H. Yan, Q. Zhao and W. Huang, *Chem. Commun.*, 2013, **49**, 10638.
15. J.-F. Nicoud, F. Bolze, X.-H. Sun, A. Hayek and P. Baldeck, *Inorg. Chem.*, 2011, **50**, 4272.
16. F. Bolze, A. Hayek, X. H. Sun, P. L. Baldeck, C. Bourgogne and J. F. Nicoud, *Opt. Mater.*, 2011, **33**, 1453.
17. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
18. A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant and C. A. Mirkin, *Nature Chem.*, 2011, **3**, 590.
19. R. Hamasaki, M. Ito, M. Lamrani, M. Mitsuishi, T. Miyashita and Y. Yamamoto, *J. Mater. Chem.*, 2003, **13**, 21.
20. M. Lamrani, R. Hamasaki, M. Mitsuishi, T. Miyashita and Y. Yamamoto, *Chem. Commun.*, 2000, 1595.
21. N. Tsuboya, M. Lamrani, R. Hamasaki, M. Ito, M. Mitsuishi, T. Miyashita and Y. Yamamoto, *J. Mater. Chem.*, 2002, **12**, 2701.
22. B. R. Cho, K. H. Son, S. H. Lee, Y. S. Song, Y. K. Lee, S. J. Jeon, J. H. Choi, H. Lee and M. H. Cho, *J. Am. Chem. Soc.*, 2001, **123**, 10039.
23. M. H. Garcia, M. P. Rabalo, A. R. Dias, M. T. Duarte, W. Wenseleers, G. Aerts, E. Goovaerts, M. P. Cifuentes, S. Hurst, M. G. Humphrey, M. Samoc and B. Luther-Davies, *Organometallics*, 2002, **21**, 2107.
24. V. M. Geskin, C. Lambert and J. L. Bredas, *J. Am. Chem. Soc.*, 2003, **125**, 15651-15658.
25. C. Katan, F. Terenziani, O. Mongin, M. H. V. Werts, L. Porres, T. Pons, J. Mertz, S. Tretiak and M. Blanchard-Desce, *J.Phys. Chem. A*, 2005, **109**, 3024-3037.
26. O. Maury and H. Le Bozec, *Acc. Chem. Res.*, 2005, **38**, 691-704.
27. O. Mongin, J. Brunel, L. Porres and M. Blanchard-Desce, *Tet. Lett.*, 2003, **44**, 2813-2816.
28. B. N. Norris, S. Zhang, C. M. Campbell, J. T. Auletta, P. Calvo-Marzal, G. R. Hutchison and T. Y. Meyer, *Macromol.*, 2013, **46**, 1384-1392.
29. G. Grelaud, M. P. Cifuentes, F. Paul and M. G. Humphrey, *J. Organomet. Chem.*, 2014, **751**, 181.
30. L. Rigamonti, B. Babgi, M. P. Cifuentes, R. L. Roberts, S. Petrie, R. Stranger, S. Righetto, A. Teshome, I. Asselberghs, K. Clays and M. G. Humphrey, *Inorg. Chem.*, 2009, **48**, 3562.
31. G. T. Dalton, M. P. Cifuentes, L. A. Watson, S. Petrie, R. Stranger, M. Samoc and M. G. Humphrey, *Inorg. Chem.*, 2009, **48**, 6534.
32. C. K. M. Chan, C.-H. Tao, K.-F. Li, K. M.-C. Wong, N. Zhu, K.-W. Cheah and V. W.-W. Yam, *Dalton Trans.*, 2011, **40**, 10670.
33. A. Merhi, G. Grelaud, K. A. Green, N. H. Minh, M. Reynolds, I. Ledoux, A. Barlow, G. Wang, M. P. Cifuentes, M. G. Humphrey, F. Paul and C. O. Paul-Roth, *Dalton Trans.*, 2015, **44**, 7748.
34. P. Nguyen, G. Lesley, T. B. Marder, I. Ledoux and J. Zyss, *Chem. Mater.*, 1997, **9**, 406.
35. L.-T. Cheng, W. Tam, S. R. Marder, A. E. Steigman, G. Rikken and C. W. Spangler, *J. Phys. Chem.*, 1991, **95**, 10643.
36. B. J. Coe, J. Fielden, S. P. Foxon, J. A. Harris, M. Helliwell, B. S. Brunschwig, I. Asselberghs, K. Clays, J. Garin and J. Orduna, *J. Am. Chem. Soc.*, 2010, **132**, 10498.
37. B. J. Coe, J. L. Harries, J. A. Harris, B. S. Brunschwig, S. J. Coles, M. E. Light and M. B. Hursthouse, *Dalton Trans.*, 2004, 2935.
38. T. J. J. Muller, A. Netz, M. Ansorge, E. Schmalzlin, C. Brauchle and K. Meerholz, *Organometallics*, 1999, **18**, 5066.
39. D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.
40. Y. Liao, B. E. Eichinger, K. A. Firestone, M. Haller, J. D. Luo, W. Kaminsky, J. B. Benedict, P. J. Reid, A. K. Y. Jen, L. R. Dalton and B. H. Robinson, *J. Am. Chem. Soc.*, 2005, **127**, 2758.
41. B. Babgi, L. Rigamonti, M. P. Cifuentes, T. C. Corkery, M. D. Randles, T. Schwich, S. Petrie, R. Stranger, A. Teshome, I. Asselberghs, K. Clays, M. Samoc and M. G. Humphrey, *J. Am. Chem. Soc.*, 2009, **131**, 10293.
42. G. Brizius, N. G. Pschirer, W. Steffen, K. Stitzer, H.-C. zur Loye and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2000, **50**, 12435.
43. S. Hurst, M. P. Cifuentes, J. P. L. Morrall, N. T. Lucas, I. R. Whittall, M. G. Humphrey, I. Asselberghs, A. Persoons, M. Samoc, B. Luther-Davies and A. C. Willis, *Organometallics*, 2001, **20**, 4664.
44. X. Zhu, M. C. Traub, D. A. Vanden Bout and K. N. Plunkett, *Macromolecules*, 2012, **45**, 5051.
45. P. L. Wu, X. J. Feng, H. L. Tam, M. S. Wong and K. W. Cheah, *J. Am. Chem. Soc.*, 2009, **131**, 886.
46. Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin and Y. Cao, *Adv. Funct. Mater.*, 2013, **23**, 1781.
47. R. Yang, Y. Xu, X.-D. Dang, T.-Q. Nguyen, Y. Cao and G. C. Bazan, *J. Am. Chem. Soc.*, 2008, **130**, 3282.
48. M. Ranger, D. Rondeau and M. Leclerc, *Macromolecules*, 1997, **30**, 7686.
49. M. Ranger and M. Leclerc, *Macromolecules*, 1999, **32**, 3306.
50. D. Marsitzky, R. Vestberg, P. Blainey, B. T. Tang, C. J. Hawker and K. R. Carter, *J. Am. Chem. Soc.*, 2001, **123**, 6965.
51. K. T. Kamtekar, A. P. Monkman and M. R. Bryce, *Adv. Mater.*, 2010, **22**, 572.
52. R. N. Grimes, *Carboranes*, Academic Press, London, U. K., 3rd ed., 2016.
53. J. E. Rogers, J. E. Slagle, D. M. Krein, A. R. Burke, B. C. Hall, A. Fratini, D. G. McLean, P. A. Fleitz, T. M. Cooper, M. Drobizhev, N. S. Makarov, A. Rebane, K.-Y. Kim, R. Farley and K. S. Schanze, *Inorg. Chem.*, 2007, **46**, 6483.
54. T.-C. Lin, W. Chien, C.-Y. Liu, M.-Y. Tsai and Y.-J. Huang, *Eur. J. Org. Chem.*, 2013, 4262.
55. Q. Bellier, S. P. Pégaz, C. Aronica, B. Le Guennic, C. Andraud and O. Maury, *Org. Lett.*, 2011, **13**, 22.
56. J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin and K. R. Carter, *Macromolecules*, 2009, **42**, 8594.
57. J. Du, M. S. Kodikara, G. J. Moxey, M. Morshedi, A. Barlow, C. Quintana, G. Wang, R. Stranger, C. Zhang, M. P. Cifuentes and M. G. Humphrey, *Dalton Trans.*, 2018, **47**, 4560.
58. J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.
59. T. E. Paxson, K. P. Callahan and M. F. Hawthorne, *Inorg. Chem.*, 1973, **12**, 708.
60. L. Wang, L. Yin, C. Ji, Y. Zhang, H. Gao and Y. Li, *Org. Electron.*, 2014, **15**, 1138.
61. O. Lavastre, S. Cabioch, P. H. Dixneuf and J. Vohlidal, *Tetrahedron*, 1997, **53**, 7595.
62. N. T. Lucas, E. G. A. Notaras, S. Petrie, R. Stranger and M. G. Humphrey, *Organometallics*, 2003, **22**, 708.
63. J. Yang, M. Chen, J. Ma, W. Huang, H. Zhu, Y. Huang and W. Wang, *J. Mater. Chem. C*, 2015, **3**, 10074.
64. A. Picot, C. Feuvrie, C. Barsu, F. Malvoti, B. Le Guennic, H. Le Bozec, C. Andraud, L. Toupet and O. Maury, *Tetrahedron*, 2008, **64**, 399.
65. M. Morshedi, M. S. Kodikara, T. C. Corkery, S. K. Hurst, S. S. Chavan, E. Kulasekera, R. Stranger, M. Samoc, S. van Cleuvenbergen, I. Asselberghs, K. Clays, M. P. Cifuentes and M. G. Humphrey, *Chem. Eur. J.*, 2018, **24**, 16332.