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Red Light-Emitting Carborane-BODIPY Dyes: Synthesis and Properties of Visible-Light Tuned Fluorophores with Enhanced Boron Content

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Abstract. A small library of 2,6- and 3,5-distyrenyl-substituted carborane-BODIPY dyes was efficiently synthesized by means of a Pd-catalyzed Heck coupling reaction. Styrenyl-carborane derivatives were exploited as molecular tools to insert two carborane clusters into the fluorophore core and to extend the π-conjugation of the final molecule in a single synthetic step. The synthetic approach allows to increase the molecular diversity of this class of fluorescent dyes by the synthesis of symmetric or asymmetric units with enhanced boron content. The structural characterization and photoluminescence (PL) properties of synthesized dyes were evaluated. The developed compounds exhibit a significant bathochromic shift compared to their parent fluorophore scaffolds, and absorption and emission patterns were practically unaffected by the different substituents (Me or Ph) on the $C_{cluster}$ atom (C_c) of the carborane cage or the cluster isomer (*ortho*- or *meta*-carborane). Remarkably, the presence of carborane units at 2,6-positions of the fluorophore produced a significant increase of the emission fluorescent quantum yields, which could be slightly tuned by changing the C_c-substituent and the carborane isomer, as well as introducing ethylene glycol groups at the *meso*-position of

the BODIPY. All these features make these dyes promising candidates for further investigations in live-cell imaging and bio-supramolecular assays.

Keywords: carborane • BODIPY • dyads • photoluminescent material • Heck coupling

1. Introduction

The fascinating chemistry of polyhedral boron-carbon clusters has experienced an exponential and overwhelming growth since their discovery in the 1960s.[1] Icosahedral carborane derivatives have been the subject of an intense research owing to their unique properties such as high chemical and thermal stability,[2] delocalized three-dimensional aromaticity,[3] high hydrophobicity and enriched boron content,[4] electron-withdrawing character[5] and high biocompatibility.[6] The remarkable physico-chemical features of carboranes and their versatility toward functionalization[7] have been widely exploited in several areas including medicine (as anticancer agents for boron neutron capture therapy (BNCT) and pharmacophores),[7b, 8] catalysis,[9] optoelectronic (as non-linear optical materials and liquid crystals),[10] and nanomaterials.[11] Additionally, the development of fluorescent materials incorporating carboranes has significantly increased in the last decade,[2a, 12] and their photoluminescent (PL) behavior has been deeply investigated. As a result, the carborane cage linked to certain species (e.g. small fluorophores) directly influences both the PL properties and the thermal stability of the final material,[13] offering new outstanding opportunities toward the development of luminescent materials, organic field-effect transistors (OFETs), phosphorescent organic light emitting diodes (PHOLEDs), and biomedical tools (mainly bioimaging for diagnosis).[14] Owing to their unique spectroscopic features BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene)[15] represent a very interesting class of fluorophores for carborane functionalization. Moreover, the countless pre- and post-functionalization synthetic pathways of the BODIPY core allows its easy linkage to the carborane cluster using common synthetic procedures. Several carboranyl-BODIPY dyads with remarkable PL properties for luminescent devices and BNCT purposes have been thus synthesized in the last few years by means of Pd-catalyzed cross coupling reactions or alkyne insertion into decaborane.[16] In the course of our studies aimed at exploiting the

photophysical properties of BODIPY dyes for biological applications,[17] we recently reported the first synthesis of a small family of carborane-(aza)BODIPY dyads by means of a convergent Heck coupling approach, starting from a styrenyl-containing carborane and a brominated (aza)dipyrromethene fluorophore.[18] Although these styrenyl carborane-BODIPY derivatives preserved the photophysical features of the fluorophore, the design of new dyes with optical properties shifted toward the near-infrared region and into the therapeutic window in biological tissues still remains a urgency in view of biomedical applications of these compounds.[19] Moreover, the need to perform efficient boron rich carriers to find novel potential candidates for BNCT is still on the rise.

To this purpose, we planned to synthesize a new family of styrenyl carborane-BODIPY dyes exhibiting a whole π-conjugate system through the entire backbone of the molecule. In view of the development of bright and stable fluorophores emitting in the red spectral region, the extension of π-conjugation is essential for obtaining a bathochromic shift of both absorbance and emission maxima. The introduction of styrenyl groups on the BODIPY core at the 3,5- and 1,7-positions is one of the most efficient strategies toward a significant redshift of the spectral bands,[20] while to the best of our knowledge only one example of 2,6-distyrenyl substituted BODIPY dyes has been reported so far.[21]

On the basis of these considerations and motivated by our ongoing interest in the design of new fluorescent and high boron content carborane-based scaffolds, we herein report the Pd-catalyzed synthesis of a small library of red-light emitting carborane-BODIPY dyads linked at the 2,6-positions and 3,5-positions with a π-conjugated styrene moiety spacer (Figure 1). The rationale of this work focuses on the following key points: a) exploit styrenyl carborane derivatives as molecular tools to insert two boron-carbon cages into the fluorophore and extend the π-conjugation of the final molecule in a single synthetic step, b) enlarge the molecular diversity of the fluorescent dyads by the synthesis of symmetric or asymmetric units and c) enhance the boron content of the dyads. To this purpose, a series of *ortho*- and *meta*- (*o*- and *m*-) substituted styrenyl-carboranes were linked to suitable BODIPY dyes halogenated at the 2,6- and 3,5-positions by means of a Heck coupling approach. The spectroscopic and photophysical properties of these new dyes are also discussed.

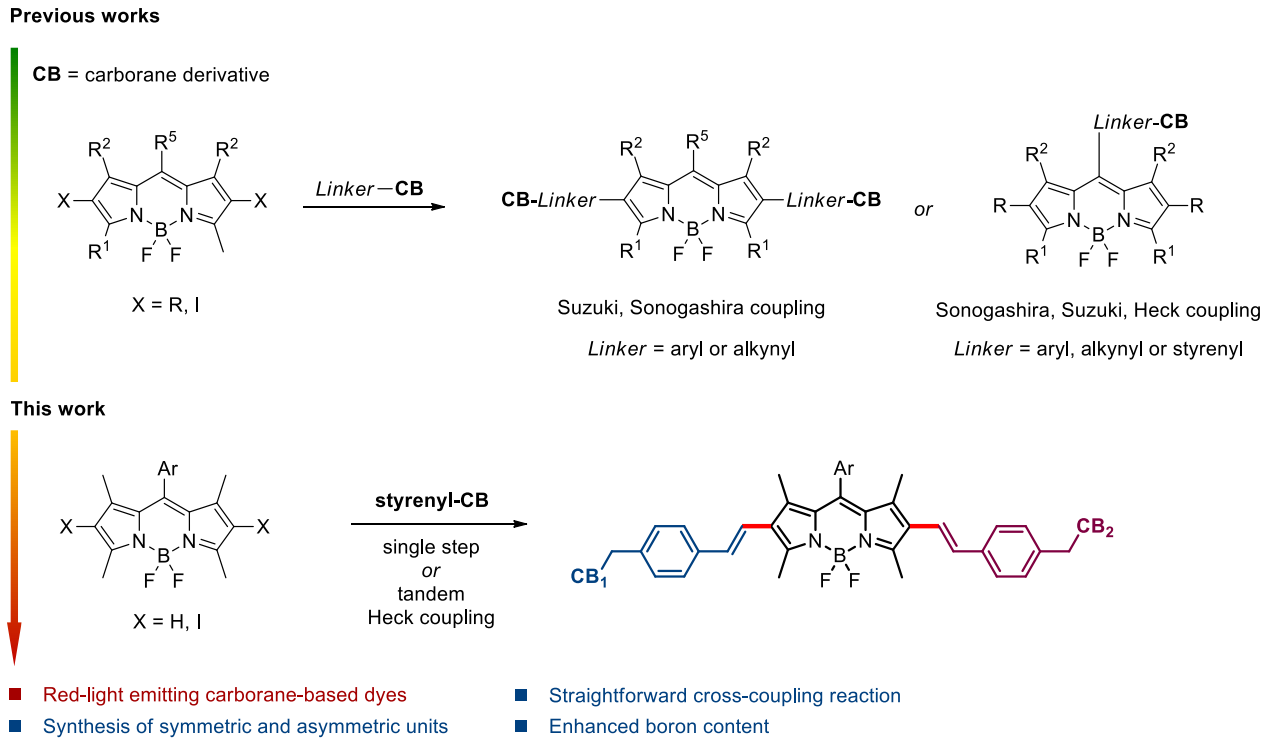


Figure 1. Aim of the work.

2. Experimental section

2.1 Materials and methods

Unless specified, all reagents were used as received without further purifications. $[Pd_2(dba)_3]$, $[Pd(tBu_3P)_2]$ and Cy_2NMe were purchased from Aldrich. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using the syringe septum cap technique. Anhydrous CH_2Cl_2 was obtained by distillation over CaH_2. Anhydrous THF was obtained by distillation over $LiAlH_4$, followed by distillation over Na-benzophenone. Et_3N was distilled over CaH_2 and dry 1,4-dioxane was purchased from Merck-SigmaAldrich and used as received. Reactions were monitored using thin layer chromatography on silica gel coated aluminium plates. Chromatographic separations were performed under pressure on silica gel (40-63 μm, 230-400 mesh). R_f values refer to TLC carried out on silica gel plates with UV light (254 nm and/or 366 nm) as visualizing agent.

2.2 Instrumentation

^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ (150 MHz) NMR spectra were recorded in $CDCl_3$ on a Jeol ECZR600 spectrometer at RT using residual solvent peak as an internal standard. $^{11}B\{^{1}H\}$ (128.38 MHz) NMR spectra were recorded on a Bruker ARX 400 spectrometer in $CDCl_3$. Chemical shift values for $^{11}B\{^{1}H\}$ NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, those for ^{1}H and $^{13}C\{^{1}H\}$ NMR were referenced to $[Si(CH_3)_4]$ (TMS). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). Multiplicities are reported as follows: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet). Low-resolution mass spectra were recorded on a Micromass Quattro microTM API (Waters Corporation, Milford, MA, USA) or at an ionizing voltage of 70 eV on a HP 5989B mass selective detector connected to an HP 5890 GC with a methyl silicone capillary column (EI). The MS flow-injection analyses were run on a high resolving power hybrid mass spectrometer (HRMS) Orbitrap Fusion (Thermo Scientific, Rodano, Italy), equipped with an ESI ion source. The samples were analyzed in acetonitrile solution using a syringe pump at a flow rate of 5 μL/min. The tuning parameters adopted for the ESI source were: source voltage 4.0 kV. The heated capillary temperature was maintained at 275 °C. The mass accuracy of the recorded ions (vs. the calculated ones) was ± 2.5 mmu (milli-mass units). Analyses were run using both full MS (150-2000 m/z range) and MS/MS acquisition, at 500000 resolutions (200 m/z).

2.3 Photophysical measurements

The optical properties were evaluated in anhydrous grade THF, MeOH, CH_3CN, $CHCl_3$, toluene, dioxane, DMSO purchased from Sigma Aldrich and used without further purifications. Stock solutions in the selected solvent with a concentration between $2.87*10^{-4}$ M and $3.73*10^{-4}$ M were prepared for all the compounds tested. UV-Vis spectra were recorded on VARIANT Cary 5 UV-Vis-NIR spectrophotometer. Molar extinction coefficients were determined with solutions of THF with concentrations in the range $0.20*10^{-5}$ M to $1.5*10^{-5}$ M. Emission spectra have been recorded with a VARIANT Cary Eclipse Fluorescence spectrophotometer. The excitation wavelengths were set just before the respective absorption maxima in each solvent tested to provide adequate excitation energy and maximize the detected signal, excitation and the emission slits are set at 2.5 nm. The samples concentration was adjusted to have an absorbance between 0.1 and 1 at the Abs_{max} to evaluate the general photophysical properties in THF (Abs_{max}, Em_{max}, Φ_F and Stokes Shift) and the possible solvatochromic features in MeOH, CH_3CN, $CHCl_3$, toluene, dioxane, DMSO. All the measurements were

carried out in a 1 cm four-sided quartz cuvette from Hellma Analitics. The absorption and steady state emission spectra were corrected for their respective blank. No fluorescent contaminants were detected on excitation in the wavelength region of experimental interest.

The Fluorescence quantum yield evaluation was carried out on samples with concentrations adapted to have an absorbance lower than 0.1 in THF at the excitation wavelength (λ_{ex}) using the above-mentioned DMSO stock solutions. The fluorescence quantum yield (φ) were evaluated compared on an external standard, Rhodamine 101 (φ :1 in MeOH, λ_{ex} 576 nm)[22] by applying the following equation:

$$\phi = \phi_{STD} \frac{I}{I_{STD}} \frac{Abs_{STD}}{Abs} \frac{n^2}{n_{STD}^2} \quad (1)$$

where φ_{STD} is the fluorescence quantum yield of the standard, I and I_{STD} are the integrated area of the emission band of the sample and the standard respectively. Abs and Abs_{STD} are the absorbance at the excitation wavelength for the sample and the standard, respectively. n and n_{STD} are the solvent refractive index of the sample and the standard solutions, respectively.

2.3 Syntheses and characterizations

Iodinated BODIPY dyes **1a**,[23] **1c**,[24] **1d**[25] and styrenyl-containing carboranes[12l] ***m*-Me-CB**, ***o*-Ph-CB** and ***m*-Ph-CB** were synthesized according to the procedures reported in literature. Mono-iodinated BODIPY dye **1b** was synthesized starting from the corresponding 4-alkoxy substituted benzaldehyde (see Supporting Information for full synthetic details). Full characterization data, including copies of ^{1}H and ^{13}C NMR spectra (see Supporting Information), have been reported for the newly synthesized compounds. The syntheses of 2,6-disubstituted styrenyl-carborane BODIPY dyes are depicted in Scheme 1 (**2**, **2a**) and Scheme 2 (**3-8**). The synthesis of 3,5-disubstituted styrenyl-carborane BODIPY dye **9** is illustrated in Scheme 3.

*General procedure (**A**) for the Heck coupling reactions*. A round-bottomed flask equipped with a condenser was charged with 3 mL of dry 1,4-dioxane, and the solvent was degassed with nitrogen for 15 minutes. The appropriate styrenyl-containing carborane (2.1 equiv.) and iodinated BODIPY derivatives **1a-b** or **1d** (1 equiv.) were added, followed by $Pd_2(dba)_3$ (3 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (6 mol%) and Cy_2NMe (4.8 equiv.). The reaction mixture was heated at reflux overnight. After complete conversion of the starting material (as monitored by

TLC analysis), the mixture was filtered over celite, washed with THF and concentrated to dryness. The crude residue was purified by flash column chromatography on silica gel.

*General procedure (**B**) for the Heck coupling reactions*. A round-bottomed flask equipped with a condenser was charged with 3 mL of dry 1,4-dioxane, and the solvent was degassed with nitrogen for 15 minutes. The appropriate styrenyl-containing carborane (1 equiv.) and the styrenyl-carborane BODIPY derivative **6** (1.1 equiv.) were added, followed by $Pd_2(dba)_3$ (5 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (5 mol%) and Cy_2NMe (1.34 equiv.). The reaction mixture was heated at reflux overnight. After complete conversion of the starting material (as monitored by TLC analysis), the mixture was filtered over celite, washed with THF and concentrated to dryness. The crude residue was purified by flash column chromatography on silica gel.

Synthesis and characterization of compound 2. General procedure (**A**) starting from **1a** and ***m*-Me-CB**. Purification by flash column chromatography on silica gel (PE/DCM 6/4 v/v) gave **2** as a bright blue solid. (43%, R_f = 0.5 PE/DCM 6/4 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54-7.52 (m, 3H), 7.37 (d, *J*= 8.2 Hz, 4H), 7.34-7.33 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 4H), 6.87 (d, *J* = 16.5 Hz, 2H), 6.63 (d, *J*= 16.5 Hz, 2H), 3.18 (s, 4H), 2.74 (s, 6H), 1.64 (s, 6H), 1.47 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 155.4, 141.6, 138.9, 137.1, 136.4, 135.4, 131.6, 131.0, 130.4, 129.4, 129.3, 129.0, 128.4, 128.2, 126.2, 120.0, 70.9, 42.8, 24.7, 14.2, 13.1. ^{11}B{^{1}H} NMR (128.38 MHz, $CDCl_3$) δ: 0.99 (s, 1B, BF_2) -6.17 (s, 2B), -7.88 (s, 2B), -10.50 (br s, 12B), -13.04 (s, 4B). ESI-HRMS $[M+Na]^+$: *m/z* 891.6674; $C_{43}H_{59}B_{21}F_2N_2Na^+$ requires 891.6638.

Synthesis and characterization of compound 2a. Isolated by flash column chromatography on silica gel (PE/DCM 6/4 v/v) from crude reaction mixture of **2** (6%, R_f = 0.6 PE/DCM 6:4 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.49 (m, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35-7.33 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 16.5 Hz, 1H), 6.63 (d, *J* = 16.5, 1H), 5.84 (s, 1H), 5.10 (s, 1H), 3.18 (s, 2H), 3.16 (s, 2H), 2.73 (s, 3H), 2.37 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.48 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.2, 155.0, 140.7, 140.5, 139.4, 138.8, 136.7, 136.3, 135.3, 131.5, 130.8, 130.3, 130.1, 129.3, 129.2, 128.7, 128.2, 126.5, 126.2, 120.1, 117.6, 80.4, 70.8, 42.7, 42.6, 29.8, 24.6,

14.1, 13.5, 13.0, 12.9. $^{11}B\{^1H\}$ NMR (128.38 MHz, $CDCl_3$) δ: 1.01 (s, 1B, BF_2), -6.24 (s, 2B), -7.91 (s, 2B), -10.50 (br s, 12B), -13.04 (s, 4B). ESI-HRMS $[M+Na]^+$: *m/z* 891.6618; $C_{43}H_{59}B_{21}F_2N_2Na^+$ requires 891.6638.

Synthesis and characterization of compound 3. General procedure (**A**) starting from **1a** and ***m*-Ph-CB**. Purification by flash column chromatography on silica gel (PE/DCM 6/4 v/v) gave **3** as a bright blue solid (57%, R_f = 0.4 PE/DCM 6/4 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.49-7.40 (m, 4H), 7.33-7.24 (m, 11H), 7.15 (d, *J* = 7.9 Hz, 4H), 7.02 (d, *J* = 7.9 Hz, 4H), 6.80 (d, *J* = 16.5 Hz, 2H), 6.55 (d, *J* = 16.5 Hz, 2H), 3.18 (s, 4H), 2.66 (s, 6H), 1.40 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 155.3, 141.5, 138.8, 137.0, 136.2, 135.3, 131.5, 130.8, 130.3, 129.3, 129.2, 128.9, 128.6, 128.3, 127.8, 126.2, 120.0, 78.2, 76.3, 42.9, 14.1, 13.0. $^{11}B\{^1H\}$ NMR (128.38 MHz, $CDCl_3$) δ: 0.95 (s, 1B, BF_2), -5,90 (s, 4B), -10.66 (br s, 12B), -13.51 (s, 4B). ESI-HRMS $[M+Na]^+$: *m/z* 1015.6956; $C_{53}H_{63}B_{21}F_2N_2Na^+$ requires 1015.6951.

Synthesis and characterization of compound 4. General procedure (**A**) starting from **1b** and ***m*-Ph-CB**. Purification by flash column chromatography on silica gel (DCM) gave **4** as a bright blue solid (52%, R_f = 0.55 DCM). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.6 Hz, 4H), 7.26-7.18 (m, 8H), 7.10 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 16.5 Hz, 2H), 6.62 (d, *J* = 16.5 Hz, 2H), 4.23-4.20 (m, 2H), 3.95-3.92 (m, 2H), 3.79-3.76 (m, 2H), 3.75-3.70 (m, 2H), 3.70-3.66 (m, 2H), 3.62-3.58 (m, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.26 (s, 4H), 2.72 (s, 6H), 1.58-1.54 (m, 2H), 1.52 (s, 6H), 1.40-1.33 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 155.2, 139.0, 137.2, 136.3, 135.4, 132.0, 130.9, 130.4, 129.6, 129.4, 128.9, 128.7, 128.4, 127.9, 127.6, 127.2, 126.3, 120.2, 115.5, 78.3, 76.4, 71.4, 71.1, 70.9, 70.8, 70.2, 69.9, 67.7, 43.0, 31.8, 29.8, 19.4, 14.1, 13.4. $^{11}B\{^1H\}$ NMR (128.38 MHz, $CDCl_3$) δ:0.93 (s, 1B, BF_2), -5.92 (s, 4B), -10.64 (br s, 12B), -13.48 (s, 4B). ESI-HRMS $[M+Na]^+$: *m/z* 1219.8335; $C_{63}H_{83}B_{21}F_2N_2O_4Na^+$ requires 1219.8318

Synthesis and characterization of compound 5. A round-bottomed flask equipped with a reflux condenser was charged with 3 mL of dry 1,4-dioxane, and the solvent was degassed with nitrogen for 15 minutes. The carborane ***m*-Me-CB** (1 equiv.) and mono- iodinated BODIPY derivative **1c** (1.1 equiv.) were added, followed by $Pd_2(dba)_3$ (1.2 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (1.6 mol%) and Cy_2NMe (1.34 equiv.). The reaction mixture was

heated at reflux overnight. After complete conversion of the starting material (as monitored by TLC analysis), the mixture was filtered over celite, washed with THF and concentrated to dryness. The crude residue was purified by flash column chromatography on silica gel (PE/DCM 7/3 v/v) to give **5** as a bright purple solid (72%, R_f = 0.4 PE/DCM 7/3 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53-7.46 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.31-7.27 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 16.5 Hz, 1H), 6.60 (d, *J* = 16.5 Hz, 1H), 6.00 (s, 1H), 3.16 (s, 2H), 2.71 (s, 3H), 2.57 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.1, 154.8, 143.6, 141.8, 138.7, 137.1, 136.4, 135.2, 131.9, 131.2, 130.7, 130.3, 129.3, 129.2, 128.6, 128.2, 126.2, 121.7, 120.1, 76.8, 70.8, 42.8, 24.6, 14.8, 14.6, 14.1, 13.0.

Synthesis and characterization of compound 6. To a stirred solution of **5** (0.13 mmol) in dry DCM (30 mL) under a positive N_2 atmosphere was added *N*-iodosuccinimide (NIS, 0.26 mmol, 2 eq.), and the reaction mixture was stirred at RT overnight. The mixture was then washed with water, dried over Na_2SO_4 and purified by flash column chromatography on silica gel (PE/DCM 75/25 v/v) to give **6** as purple solid (84%, R_f = 0.55 PE/DCM 75/25 v/v). ^{1}H NMR (600MHz, $CDCl_3$): δ 7.48-7.43 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.24-7.20 (m, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 16.5 Hz, 1H), 6.55 (d, *J* = 16.5 Hz, 1H), 3.10 (s, 2H), 2.65 (s, 3H), 2.58 (s, 3H), 1.56 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 157.2, 155.0, 143.6, 141.4, 140.3, 136.8, 136.6, 135.1, 131.5, 131.3, 130.3, 129.7, 129.4, 128.1, 126.2, 119.6, 84.8, 76.6, 70.8, 42.7, 29.8, 24.6, 16.9, 16.0, 14.3, 13.1.

Synthesis and characterization of compound 7. General procedure (**B**) starting from **6** and ***o*-Ph-CB**. Purification by flash column chromatography on silica gel (PE/DCM 6/4 v/v) gave **7** as a bright blue solid (55%, R_f = 0.35 PE/DCM 75/25 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.57-7.50 (m, 4H), 7.49-7.43 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.34-7.32 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.85 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 16.5 Hz, 1H), 6.58 (d, *J* = 16.5 Hz, 1H), 3.18 (s, 2H), 3.07 (s, 2H), 2.73 (s, 3H), 2.72 (s, 3H), 1.64 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.4, 155.3, 141.6, 138.9, 137.4, 137.1, 136.4, 135.4, 134.5, 131.6, 131.6, 131.0, 130.9, 130.7, 130.5, 130.4, 129.4, 129.3, 129.2, 129.0, 128.9, 128.4, 126.2, 126.1, 120.3, 120.0, 83.8, 82.1, 70.8, 42.8, 40.8, 32.1, 24.7, 22.8, 14.2, 13.1. ^{11}B{^{1}H} NMR (128.38 MHz, $CDCl_3$) δ: 1.08

(s, 1B, BF_2), -3.17 (s, 2B), -6.22 (s, 1B), -7.98 (s, 1B), -10.24 (br s, 14B), -12.93 (s, 2B). ESI-HRMS $[M+Na]^+$: *m/z* 953.6817; $C_{48}H_{61}B_{21}F_2N_2Na^+$ requires 953.6794 .

Synthesis and characterization of compound 8. General procedure (**B**) starting from **6** and ***m*-Ph-CB**. Purification by flash column chromatography on silica gel (PE/DCM 7/3 v/v) gave **8** as a bright blue solid. (35%, R_f = 0.21 PE/DCM 7/3 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.38-7.33 (m, 9H), 7.23-7.21 (m, 2H), 7.10-7.06 (m, 4H), 6.87 (d, *J*= 16.5 Hz, 2H), 6.62 (d, *J*= 16.5 Hz, 2H), 3.26 (s, 2H), 3.18 (s, 2H), 2.74 (s, 6H), 1.64 (s, 3H), 1.47 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 155.4, 141.6, 138.9, 137.1, 137.1, 136.4, 136.3. 135.4, 132.0, 131.0, 130.9, 130.4, 129.4, 129.3, 129.0, 128.7, 128.4, 127.9, 126.3, 126.2, 121.0, 120.0, 78.3, 76.8, 76.3, 70.9, 43.0, 42.8, 24.7, 14.2, 13.1. $^{11}B\{^1H\}$ NMR (128.38 MHz, $CDCl_3$) δ: 1.01 (br s, 1B, BF_2), -6.05 (s, 3B), -7.85 (s, 1B), -10.46 (s, 12B), -13.01 (s, 4B). ESI-HRMS $[M+Na]^+$: *m/z* 953.6824; $C_{48}H_{61}B_{21}F_2N_2Na^+$ requires 953.6794 .

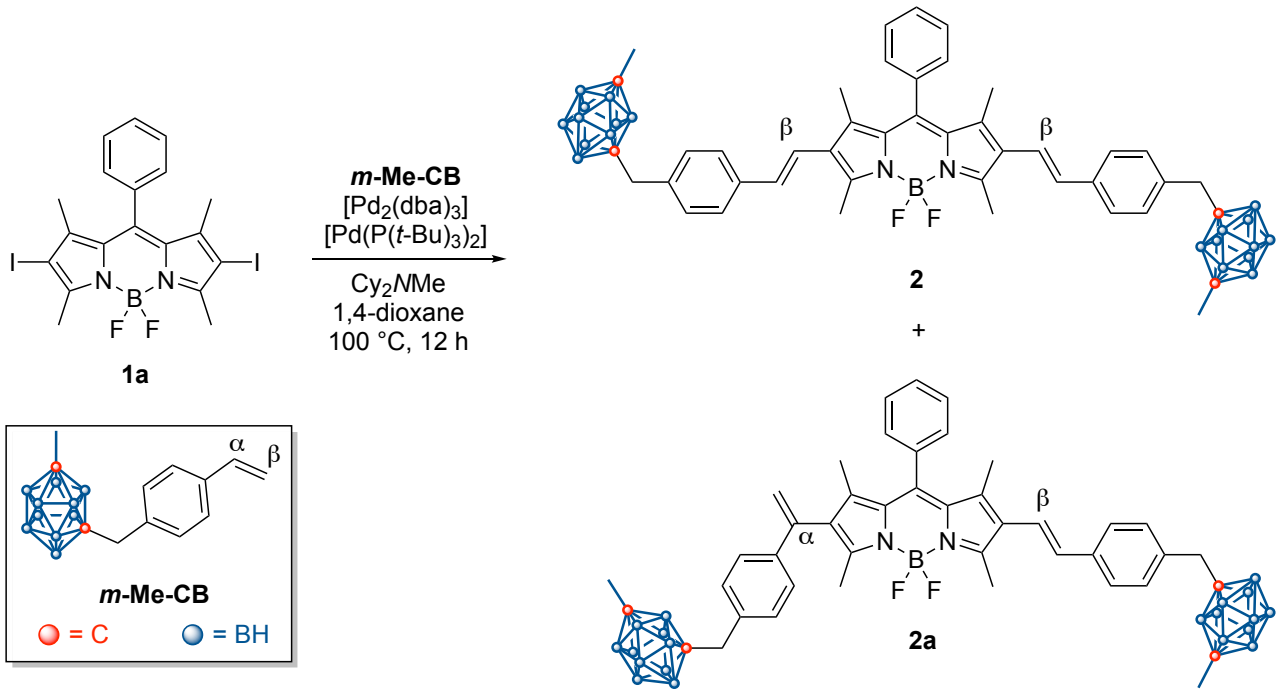
Synthesis and characterization of compound 9. General procedure (**A**) starting from **1d** and ***m*-Ph-CB**. Purification by flash column chromatography on silica gel (PE/DCM 7/3 v/v) gave **9** as a bright blue solid. (30%, R_f = 0.33 PE/DCM 7/3 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J*= 16.3 Hz, 2H), 7.62 (d, *J*= 8.1 Hz, 4H), 7.56-7.50 (m, 6H), 7.37-7.36 (m, 4H), 7.32 (d, *J*= 16.3 Hz, 2H), 7.25-7.21 (m, 5H), 7.19 (d, *J*= 8.1 Hz, 4H), 6.93 (d, *J*= 4.5 Hz, 2H), 6.82 (d, *J* = 4.4 Hz, 2H), 3.30 (s, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 154.8, 139.8, 138.0, 136.4, 136.2, 135.9, 135.3, 134.4, 130.6, 130.5, 130.0, 129.9, 128.7, 128.4, 127.9, 129.9, 119.7, 116.5, 78.4, 76.1, 43.1. ESI-MS $[M+H]^+$: *m/z* 939.16.

3. Results and discussion

3.1 Synthesis and characterization of dyes

The presence of halogen atoms, either directly on the BODIPY core or attached to an aryl ring, facilitates further extension of the π-conjugation and to build sophisticated structures by means of metal-catalyzed coupling reactions.[26] Based on our previously reported results on the functionalization of the (aza)BODIPY core with styrenyl-containing carborane derivatives,[18] we started our preliminary investigation by testing the

Heck coupling procedure on the 2,6-diiodo-BODIPY derivative **1a** and the methyl substituted styrenyl *m*-carborane ***m*-Me-CB** (Scheme 1). The 2,6-diiodo-1,3,5,7-tetramethylBODIPY dye **1a**, synthesized by condensation of 2,4-dimethylpyrrole with benzaldehyde followed by mild iodination with I_2/HIO_3,[27] exhibits an absorption maxima at 534 nm and a negligible fluorescence quantum yield due to the high heavy atom-induced intersystem crossing (ISC) at the excited state.[28] The styrenyl-carborane ***m*-Me-CB** has been easily synthesized by electrophilic trapping of the parent lithium-*closo*-carborane cluster with 4-vinylbenzyl chloride as previously reported.[12l]



Scheme 1. Model Heck coupling reaction for the synthesis of 2,6-bis(styrenylcarborane)-BODIPY dyes.

The 2,6-diiodoBODIPY **1a** was reacted with two equivalents of ***m*-Me-CB** in refluxing 1,4-dioxane using the $Pd_2(dba)_3$ (3 mol%) and $Pd(P(t\text{-}Bu)_3)_2$ (6 mol%) catalytic system,[29] in the presence of Cy_2NMe as a base. Under these conditions, the reaction proceeded smoothly in 12 h with full conversion of the starting materials affording the target compound **2** in 43% isolated yield (β,β-isomer). Successful incorporation of the carborane cage was easily confirmed by the presence of the BH broad band in the upfield region of the ^1H NMR (Figure 2, top). Additionally, protons from C_C-CH_3 are identified near 1.65 ppm, which was consistent with the *m*-Me substitution pathway of the carborane cage. The ^1H NMR spectrum confirmed the symmetric structure of the dye, showing the benzylic protons signal of the spacer at 3.18 ppm and the two equivalent methyl signals of

the fluorophore scaffold at 2.74 and 1.47 ppm. Moreover, analysis of the coupling constant for the olefinic proton doublets at 6.87 ppm and 6.63 ppm revealed the full *trans*-selectivity of the cross coupling reaction ($^3J_{HH}$ = 16.5 Hz). Although the formation of geminal substituted olefins in the cationic Heck reaction of 4-substituted styrenes should be suppressed by the presence of the strong electron-withdrawing carboranyl cage,[30] a small amount of α,β-isomer **2a** (6%) was also isolated from the reaction mixture, while no α,α-isomer was detected (Scheme 1).[21] The presence of both the terminal olefinic protons (5.84 ppm and 5.10 ppm respectively, $^2J_{HH}$ = 1.3 Hz) and the more deshielded *trans*-olefinic protons ($^3J_{HH}$ = 16.5 Hz) in the ^{1}H NMR spectrum of **2a** (Figure 2, bottom) revealed the asymmetric substitution pathway, alongside with the splitting of the four methyl groups of the BODIPY unit.

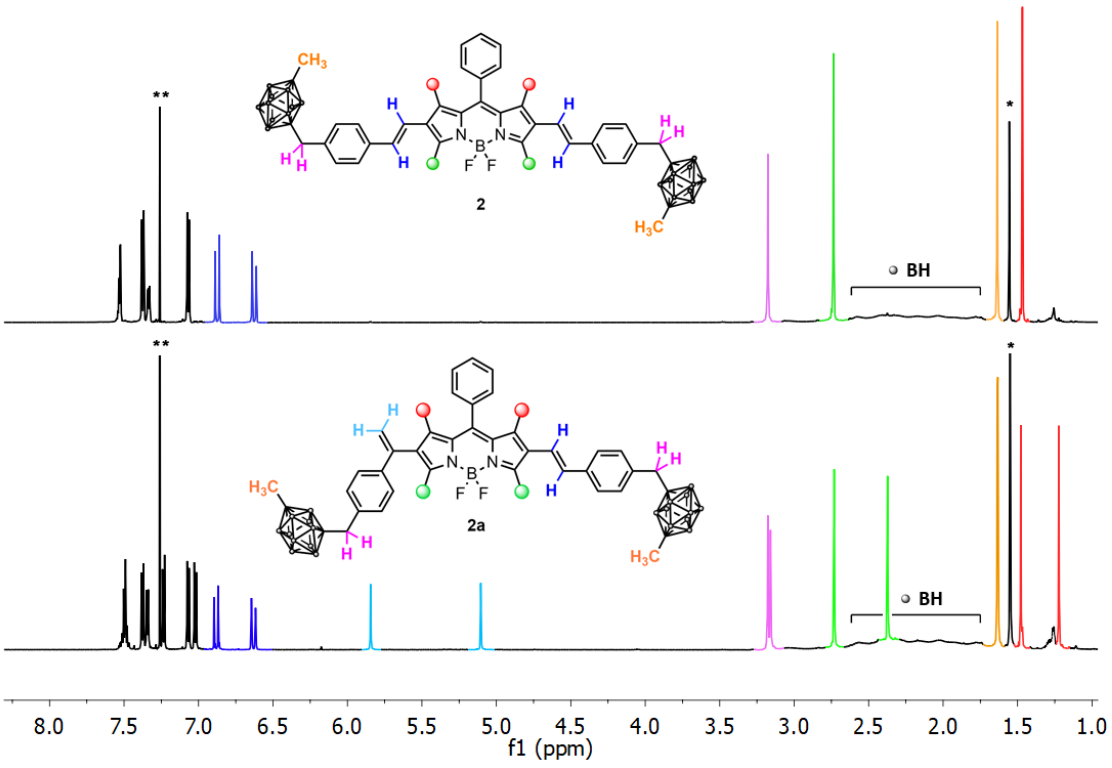
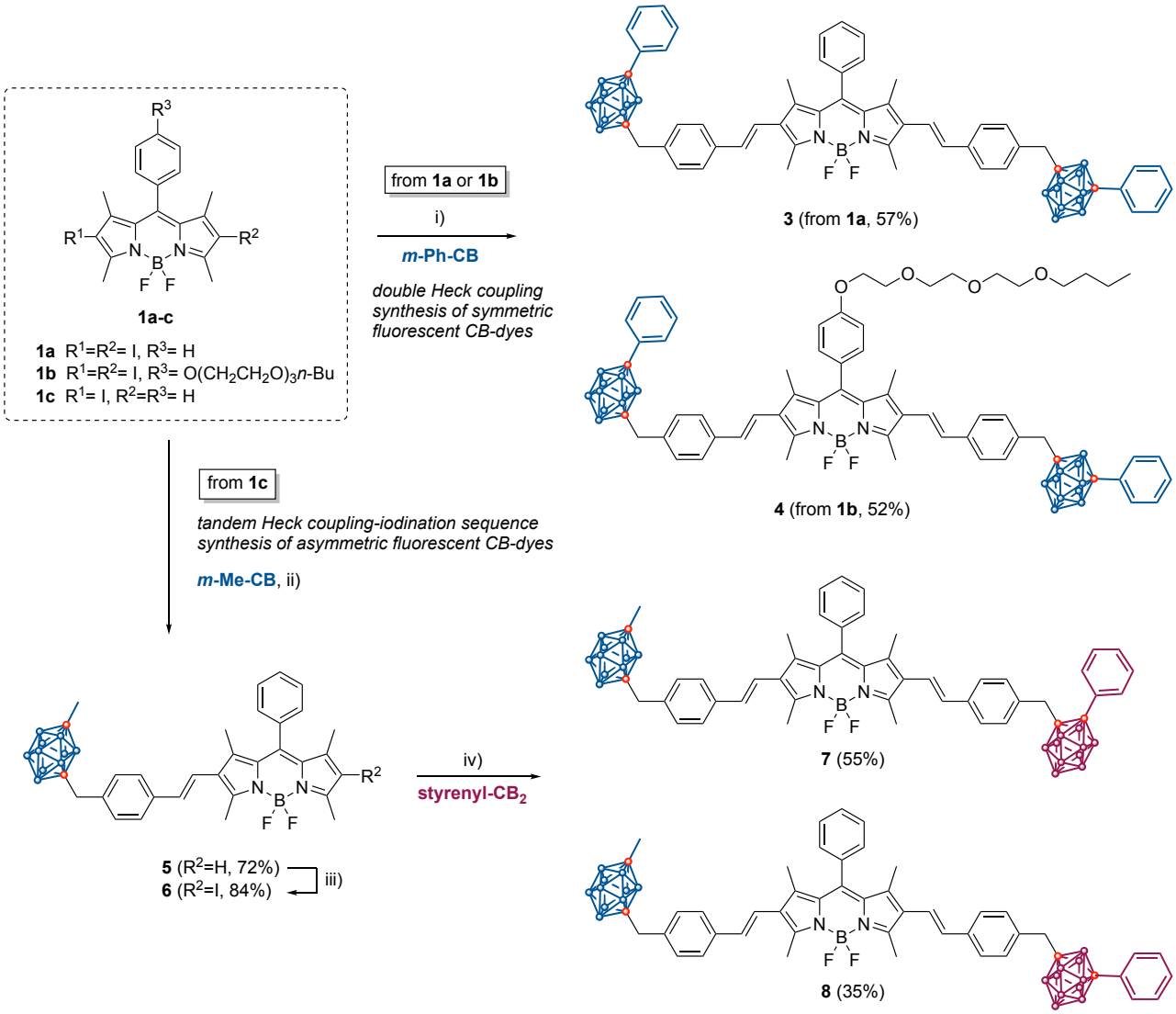


Figure 2. ^{1}H NMR spectra of bis-β,β-styrenyl carborane BODIPY derivative **2** (top) and its α,β-isomer **2a** (bottom) in $CDCl_3$. * H_2O signal; ** residual $CDCl_3$ peak.

Analysis of the $^{11}B\{^1H\}$ NMR spectra further confirmed the formation of the expected compounds, showing one resonance centered at 0.99 ppm for β,β-isomer **2** and at 1.01 ppm for α,β-isomer **2a** assigned to the -BF_2 unit. In addition to the -BF_2 resonance, these compounds show broad resonances in the region from -6.17 to -

13.04 ppm with the typical 1:1:6:2 pattern characteristic of *m*-carborane clusters.[12f] The $^{13}C\{^{1}H\}$ NMR spectrum of β,β-isomer **2** shows a resonance at 42.8 ppm assigned to the two equivalent benzylic carbon atoms (split into two different signals at 42.7 and 42.6 ppm for the asymmetric α,β-isomer **2a**), and the C_C-CH_3 can be identified from 24.0–25.0 ppm for both isomers.

The Heck coupling procedure was successfully applied to the styrenyl substituted *m*-carborane derivative ***m*-Ph-CB** bearing a phenyl ring at one C atom of the cluster (C_C) to achieve symmetric dyes **3** and **4** (Scheme 2). To our delight, the reaction of iodinated BODIPY **1a** using ***m*-Ph-CB** as coupling partner proceeded smoothly, affording the corresponding dye **3** in 57% isolated yield. Also halogenated BODIPY dyes **1b**, incorporating a nonionic amphiphile oligoethylene glycol alkyl chain at the *meso*-position,[31] was successfully reacted with ***m*-Ph-CB** derivative affording dye **4** in 52% isolated yield. The ^{1}H NMR spectra clearly confirmed the symmetric structure of the dyes and the incorporation of the carborane cage, showing the typical BH broad band of the *closo*-carborane cluster in the upfield region and the benzylic protons signal of the spacer at 3.18 (**3**) and 3.26 ppm (**4**). The $^{11}B\{^{1}H\}$ NMR spectra of these compounds exhibited a resonance at 0.93 ppm (**3**) and at 0.95 ppm (**4**) attributed to the -BF_2 unit, alongside with broad resonances in the region from -5.90 to -13.51 ppm with the typical 2:6:2 pattern of *m*-carborane clusters.

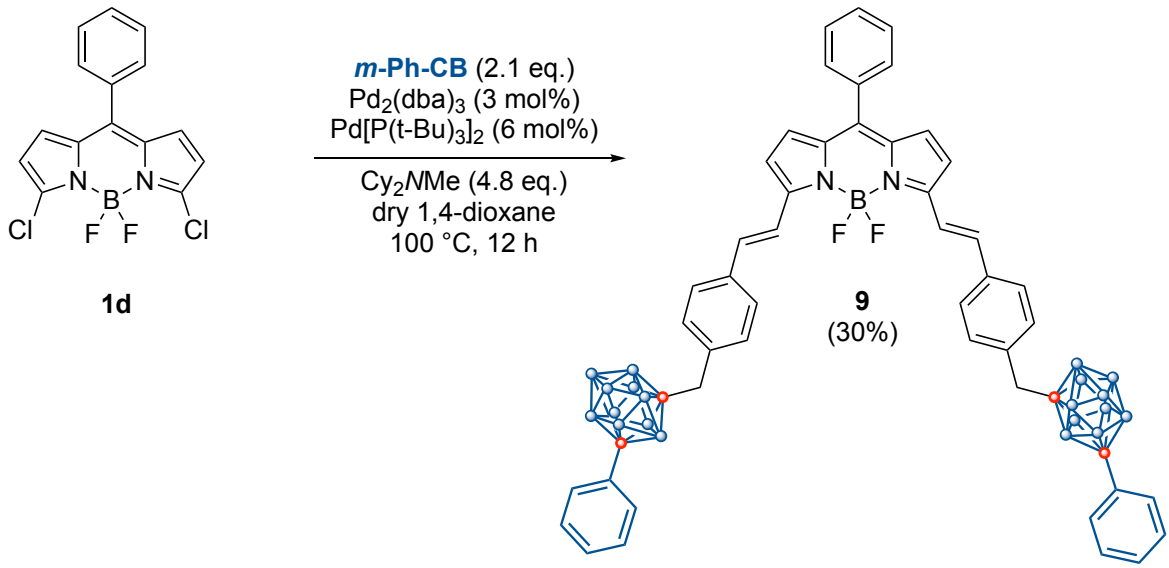


Scheme 2. Synthesis of symmetric and asymmetric carborane-BODIPY dyes **3-4** and **7-8**. Reaction conditions: i) substrate **1a-b** (1 eq.), ***m*-Ph-CB** (2 eq.), $Pd_2(dba)_3$ (3 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (6 mol%), Cy_2NMe (5 eq.). ii) **1c** (1.1 eq.), ***m*-Me-CB** (1 eq.), $Pd_2(dba)_3$ (1.2 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (1.6 mol%), Cy_2NMe (1.4 eq.), dry 1,4-dioxane, 100 °C, 12 h. iii) **5** (1 equiv.), *N*-iodosuccinimide (2 eq.), DCM, RT, 12 h. iv) **6** (1.1 eq.), **styrenyl-CB$_2$** (1 eq.), $Pd_2(dba)_3$ (5 mol%), $Pd(P(t\text{-}Bu)_3)_2$ (5 mol%), Cy_2NMe (1.4 eq.), dry 1,4-dioxane, 100 °C, 12 h.

As a further application of this methodology, we then envisaged the possibility to extend the feasibility of our approach to the synthesis of asymmetric compounds bearing two different C-substituted carborane units. We thus planned a tandem cross coupling/iodination/cross coupling approach starting from the mono-iodinated 1,3,5,7-tetramethylBODIPY dye **1c** (Scheme 2). Reaction of BODIPY **1c** with a stoichiometric amount of the

m-substituted styrenyl-carborane ***m*-Me-CB** afforded the corresponding mono-substituted derivative **5** in good yield (72%), which was easily converted into a new potential coupling partner **6** by mild iodination at the 6-position in the presence of *N*-iodosuccinimide (NIS). Although the final Heck coupling between substrate **6** and styrenyl-carboranes ***o*-Ph-CB** and ***m*-Ph-CB** required a higher catalyst loading, asymmetric dyes **7** and **8** were successfully isolated with moderate yields of 55% and 35%, respectively. Analysis of the ^{1}H NMR spectra revealed the asymmetric substitution pathway, showing two different benzylic signals of the spacers at 3.18 and 3.07 ppm (**7**) and at 3.26 and 3.18 (**8**). Moreover, the ^{1}H NMR of **7** exhibited two resolved *trans*-olefinic systems belonging to the different styrenyl carborane units ($^{3}J_{HH}$ = 16.3 Hz and $^{3}J_{HH}$ = 16.5 Hz), confirming the stereoselectivity of each Heck coupling reaction of the tandem sequence. The ^{11}B{^{1}H} NMR spectrum of **7**, bearing two different carborane isomers, one *m*- and one *o*-carborane, displayed the -BF_2 unit centered at 1.08 ppm and a set of broad resonances in the range from -3.17 to -12.93 ppm, with a 2:1:1:14:2 pattern reflecting the combined *m*- (1:1:6:2) and *o*- (2:8) typical distributions of *closo*-carboranes. Analysis of the ^{11}B{^{1}H} NMR spectrum of **8** showed a resonance of the -BF_2 unit at 1.01 ppm and the 1:1:6:2 pattern of broad resonances in the region from -6.05 to -13.01 ppm, ascribed to the two Me and Ph-substituted *m*-carborane clusters.

With the aim to compare the photophysical properties of this new class of red-shifted 2,6-disubstituted carborane-BODIPY dyes with other similar dyes with different substitution patterns, we finally envisaged the possibility to exploit our synthetic methodology for the introduction of two styrenyl-containing carboranes on the BODIPY core at the 3,5-positions. To this purpose, we planned a short one-step synthesis of the symmetric dye **9** bearing two ***m*-Ph-CB** units starting from the corresponding 3,5-dichloroBODIPY **1d** (Scheme 3). The 3,5-dichloro-*meso*-phenyl-BODIPY dye **1d** was synthesized by acidic condensation of pyrrole with benzaldehyde followed by chlorination/oxidation, and exhibits an absorption maxima centered at 517 nm (Φ_F = 0.13).[32] Pleasingly, the 3,5-dichloroBODIPY **1d** reacted smoothly in 12 h with two equivalents of ***m*-Ph-CB** in refluxing 1,4-dioxane under our Heck coupling conditions, affording the desired 3,5-disubstituted BODIPY **9** in 30% isolated yield. More details about the structural characterization of all the compounds can be found in the Supporting Information.

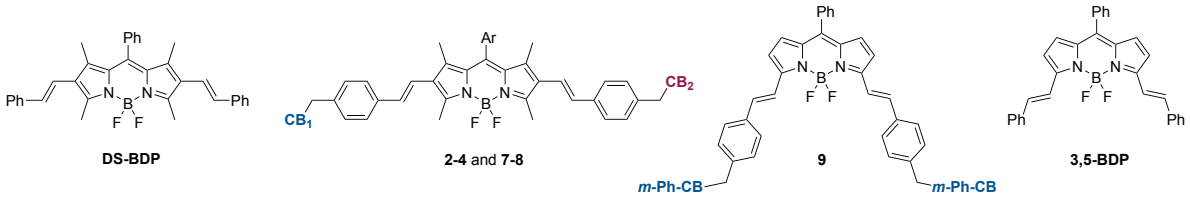


Scheme 3. Synthesis of symmetric 3,5-disubstituted BODIPY dye **9**.

3.2. Photophysical properties

The photophysical behavior of the final compounds was investigated, and the most significant spectroscopic properties are collected in Table 1. Figure 3 shows UV/Vis and fluorescence spectra of dyes in THF solution at 298 K. The optical properties of the new synthesized compounds were compared with the parent 2,6-styrenyl disubstituted BODIPY dye **DS-BDP** (*meso*-phenyl-2,6-distyrylBODIPY)[21] and the 3,5-styrenyl disubstituted BODIPY analogue **3,5-BDP** (*meso*-phenyl-3,5-distyrylBODIPY),[33] both lacking the carborane cages.

Table 1. Selected photophysical data for the reported compounds **2**, **2a**, **3**, **4** and **7-9**.[a] BODIPY dyes **DS-BDP** (entry 1)[b] and **3,5-BDP** (entry 9)[c] were added for comparison.



Entry	Compound	λ_{abs} (nm)	λ_{em}(nm)	$\varepsilon/10^6$ (M^{-1} cm^{-1})	Φ_F[d]	Stokes shift/ 10^3 (cm^{-1})	ε Φ_F (M^{-1} cm^{-1})
1	**DS-BDP**	575	633	0.031	0.01	1.59	310
2	**2**	584	640	0.056	0.14	1.50	7840
3	**2a**	548	627	0.030	0.05	2.30	1500
4	**3**	578	643	0.035	0.11	1.75	3850
5	**4**	580	640	0.029	0.14	1.62	4060
6	**7**	578	643	0.049	0.12	1.75	5880
7	**8**	582	641	0.058	0.12	1.58	6960
8	**9**	641	651	0.087	0.36	0.24	31320
9	**3,5-BDP**	633	646	0.104	0.83	0.32	86320

[a] Measured in THF at room temperature. [b] Data for **DS-BDP** are reported in the literature in CH_2Cl_2 (see ref. [21]). [c] Data for **3,5-BDP** are reported in the literature in THF (see ref. [33]) [d] Fluorescence quantum yields were determined using solutions of Rhodamine 101 in methanol (Φ_F=1) as standard.[22]

Generally, the absorption spectra of compounds **2-4** and **7-8** exhibited a significant bathochromic shift compared to their parent fluorophore scaffolds (*meso*-phenyl-1,3,5,7-tetramethyl BODIPY, λ_{abs} = 500 nm in THF),[34] but slightly red-shifted (3-9 nm) with respect to the **DS-BDP** (*meso*-phenyl-2,6-distyrylBODIPY),[21] showing a very small influence of the carborane cage and their respective C_C-substituents (Me or Ph). Remarkably, all the compounds showed an enhanced fluorescence emission efficiency compared to the reference compound **DS-BDP,** resulting in a ten-fold increase of the fluorescence quantum yield (Table 1). This result might be ascribed to the well-known influence of the carborane cage on the photoluminescent properties of CB-containing dyes,[12f] along with a lower degree of conformational flexibility in the S_1 excited state provided by the incorporation of the carborane clusters.[21] Moreover, compounds **2-4** and **7-8** showed large Stokes shifts (56-65 nm) compared to other BODIPY dyes, which suffer of some experimental limitations such as self-quenching.[35] The simplest symmetrical BODIPY derivative **2**, containing the ***m*-Me-CB** unit,

showed the highest fluorescence quantum yield (Φ_F = 14 %) of the series bearing a phenyl group at the *meso*-position (Table 1, entry 2). The photophysical features of **2** are easily distinguishable from the side product **2a** containing one α-styrenyl substituted unit. A remarkable hypsochromic shift in the absorption (548 nm) and emission (627 nm) spectra of **2a** in THF were observed (Table 1, entry 3), together with a larger Stokes shift and a significantly lower Φ_F, compared to the β,β-isomer **2**. These differences can be readily attributed to the lower degree of conjugation between the α-styrenyl substituent and the BODIPY scaffold, and to the increased HOMO-LUMO gap resulting from the stabilization effect of the α-styrenyl substituent exclusively on the HOMO.[21] The introduction of a phenyl ring on the same *m*-carborane isomer in **3** had minimal to no effect on the photophysical features of the compound (Table 1, entry 4), which were depicted by comparable λ_{abs}, λ_{em}, whereas a drop of the Φ_F was observed (Φ_F = 11 %). When Ph-substituted *m*-carborane derivatives were compared (**3** and **4**), a slight increase of the fluorescence efficiency (Φ_F = 14 %) was produced by introducing a short-terms oligoethylene glycol alkyl chain on the *meso*-phenyl ring (**4,** Table 1, entry 5). This latter was of particular synthetic value since it allowed the design of pre- or post-functionalization strategies for the introduction of amphiphilic solubilizing groups on the fluorophore core without affecting the PL properties. Regarding the asymmetric BODIPY dyes **7** and **8**, similar results were obtained for both compounds (Table 1, entries 6-7), exhibiting comparable photophysical features in the series, although slightly lower quantum efficiencies were obtained when compared to their symmetric analogues **2**-**4**. The replacement of one ***m*-Me-CB** in **2** with a different CB moiety (***o*-Ph-CB** or ***m*-Ph-CB**) in **7** had no significant impact neither on the BODIPY solubility in various solvents nor on the photophysical features as expected. Interestingly, shifting the substituents on the BODIPY core from the positions 2,6- in **3** to the positions 3,5- in **9** (Table 1, entry 8) caused a remarkable effect on the photophysical properties. The absorption spectrum of **9** (Figure 3, right) exhibited the typical narrow and intense structured $S_0 \rightarrow S_1$ transition with λ_{abs} = 641 nm, slightly red-shifted (8 nm) with respect to the reference compound **3,5-BDP** (*meso*-phenyl-3,5-distyrylBODIPY, λ_{abs} = 633 nm). The absorption maxima of **3** (578 nm) was largely blue-shifted in comparison to **9** suggesting a less planar conformation also characterized by a lower extinction coefficient. Noteworthy, compound **9** shows the highest molar extinction coefficient of the series which is comparable with the reference **3,5-BDP**. On the other hand, the fluorescence properties were similar in terms of quantum yields, while emission maximum of **9** was slightly

red-shifted (7 nm) compared to **3**. Compound **9** showed a smaller Stokes shift compared to reference **3,5-BDP** (13 nm) and **3** (65 nm) in THF, which can be rationalized on the basis of the dihedral angle between the two styrenyl substituents and the BODIPY moieties in the excited state.[21] Although 3,5-styrenyl disubstituted BODIPY dyes showed higher fluorescence quantum yields compared to their 2,6-analogues (e.g. entries 1 and 9) due to a lower nonradioactive decay, the presence of two carborane cages in **9** significantly lower the fluorescence quantum yields with respect to **3,5-BDP** (Table 1). We have also calculated the brightness of these dyes, which is the product of the molar extinction coefficient at the excitation wavelength and the fluorescence quantum yield [$\varepsilon(\lambda)\cdot\Phi_F$]. As expected, the 3,5-disubstituted compound **9** showed the highest brightness of the series (31320 M^{-1} cm^{-1}), while among the 2,6-substituted dyes the highest value of brightness was found for BODIPY derivative **2** (7840 M^{-1} cm^{-1}), followed by the asymmetric derivatives **8** (6960 M^{-1} cm^{-1}) and **7** (5880 M^{-1} cm^{-1}).

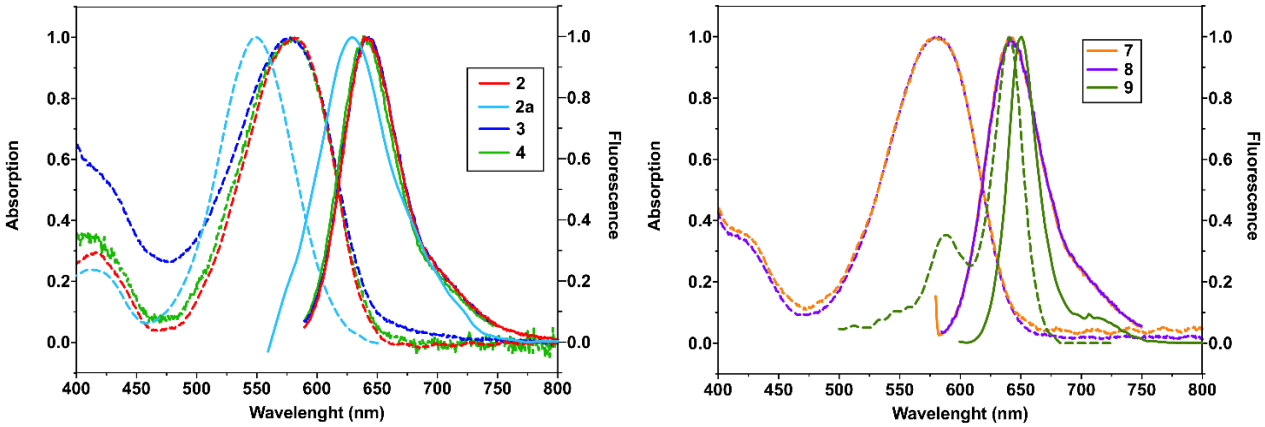
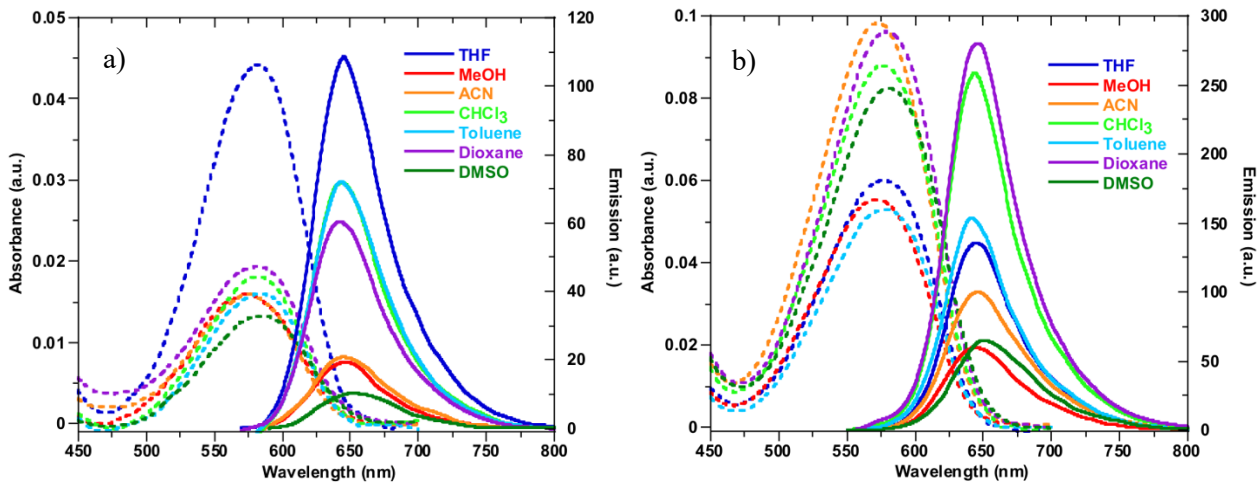


Figure 3. Normalized absorption (dashed) and emission (solid) spectra of symmetric (**2-4**, left), asymmetric (**7-8**, right) and **9** (right) carborane-BODIPY derivatives in THF.

The most performing probes have been also investigated in different solvents to evaluate their solubility, spot potential aggregation issues and screen the photophysical properties related to various polar environments. Of these, the polarity-induced change in the optical properties, often denoted as fluorescence solvatochromism,[36] is of wide interest in order both to identify several polarity-dependent molecular events, and in advancing the design of novel functional dyes. Among the new compounds, one representative candidate for each class was

selected on the basis of the most promising optical features (Φ_F and brightness). The UV-Vis absorption and fluorescence spectra of carborane-BODIPY dyes **2** (*m*-Me symmetric), **3** (*m*-Ph symmetric), **7** (asymmetric) and 3,5-disubstituted analogue **9** were recorded in solvents with different dielectric constants (2.25–46.7) at 298 K (Figure 4). The scarce influence of solvent polarity observed on the absorption spectra of the new compounds reflected the typical photophysical behavior of BODIPY chromophores.[37] Compound **2** showed a weak dependence of the absorption (575-584 nm) and the emission (642-652 nm) maxima on the environmental polarity (Figure 5a), as expected in symmetrical scaffolds due to the lack of an intrinsic molecular dipole moment. As a consequence, a similar behavior was observed for compound **3** bearing the phenyl substituted *m*-carborane cage, showing very little solvent effects on the absorption maxima (572-581 nm) and fluorescence emission maxima slightly modulated in the 640-650 nm range (Figure 5b). The introduction of two different substituted *o*- and *m*-carborane units in the fluorophore core did not affect significantly the intrinsic molecular dipole moment of asymmetric carborane-BODIPY dyes, as a matter of fact the influence of solvent polarity on the PL properties of **7** (Figure 5c) remained very small (λ_{abs} = 572-584 nm and λ_{em} = 640-650 nm). A similar behavior was observed for the symmetric compound **9** (Figure 5d), as a consequence of the low molecular dipole moment. None of the investigated compounds had shown precipitation in different solutions or aggregation phenomena detectable by absorption or emission spectroscopies. Water AF

which make these dyes as promising candidates for further investigations in in live-cell imaging and bio-supramolecular assays.



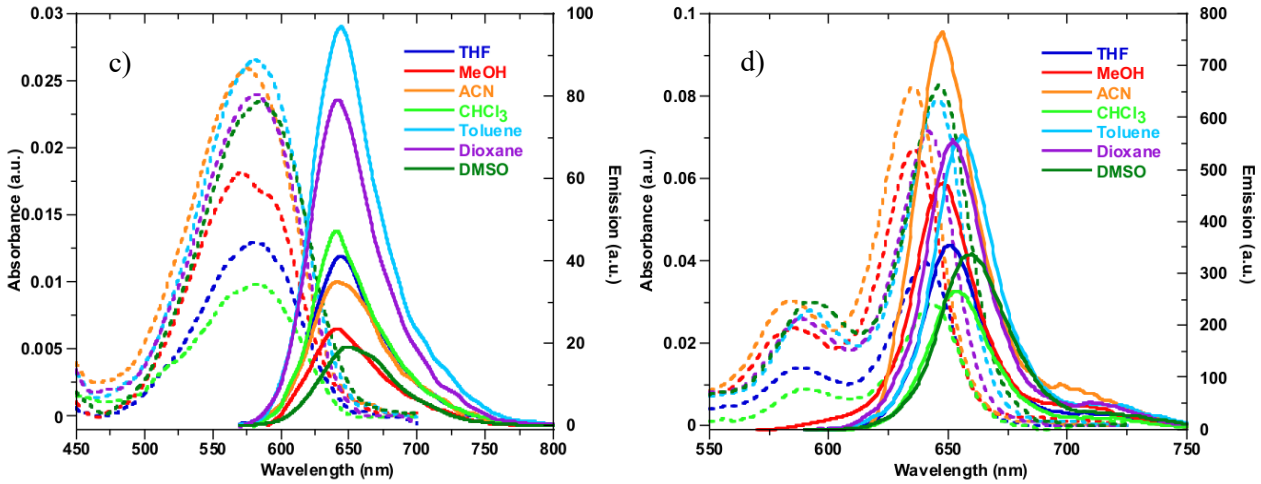


Figure 4. UV-Vis absorption and fluorescence spectra of BODIPY dyes (a) **2**, (b) **3**, (c) **7** and (d) **9** recorded in different solvents (ε) at 298 K: dioxane (2.25), toluene (2.38), $CHCl_3$ (4.81), THF (7.58), CH_3OH (32.7), CH_3CN (37.5), and DMSO (46.7). See Supporting Information for normalized spectra.

4. Conclusions

In summary, a set of new red-light emitting 2,6-distyrenyl-substituted carborane-BODIPY dyes with enhanced boron content was successfully synthesized by a versatile Pd-catalyzed Heck coupling reaction, starting from a styrenyl-containing carborane and a halogenated dipyrromethene fluorophore. The synthetic procedure was successfully applied to different types of carborane derivatives with moderate yields, allowing both the introduction of two identical carborane cages into the fluorophore core and the extension of the π-conjugation within a single synthetic step. Of particular synthetic value, this methodology allowed the preparation of asymmetric dyes, bearing two different substituted carborane cages, by means of a tandem cross coupling/iodination/cross coupling sequence. The final compounds were fully characterized and their photophysical behavior was investigated. Absorption and photoluminescence (PL) emission patterns of synthesized dyes were almost unaffected by the different substituents on the C_c of the carborane cage or the cluster isomer. The 2,6-disubstituted dyes exhibited a significant bathochromic shift compared to their parent fluorophore scaffold (without carborane clusters) with a significant increase of the emission fluorescent quantum yields, while the introduction of the two carborane units in 3,5-positions of the fluorophore led to a significant depletion of the fluorescence efficiency with regards to its homologous fluorophore. Remarkably, the introduction of a short-terms oligoethylene glycol alkyl chain on the *meso*-phenyl ring had no effect on the

PL properties of the dyes, allowing the design of pre- or post-functionalization strategies for the introduction of solubilizing groups on the fluorophore core. The scarce influence of solvent polarity observed on the absorption spectra of the new compounds, together with the absence of precipitation or aggregation phenomena, suggested high stability for all of them in solution and make these types of dyes promising candidates for further investigations in live-cell imaging and bio-supramolecular assays.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Chiara Bellomo: investigation, data curation, formal analysis. **Davide Zanetti**: investigation, data curation, formal analysis. **Francesca Cardano**: investigation, data curation, formal analysis. **Sohini Sinha**: investigation, data curation, formal analysis. **Mahdi Chaari**: investigation, data curation, formal analysis. **Andrea Fin**: validation, data curation, writing-review and editing, supervision. **Rosario Núñez**: conceptualization, methodology, validation, data curation, writing-original draft preparation, writing-review and editing, supervision. **Marco Blangetti**: conceptualization, methodology, validation, data curation, writing-original draft preparation, writing-review and editing, supervision. **Cristina Prandi**: conceptualization, methodology, validation, data curation, writing-review and editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at …..

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