

Carborane-Bodipy Scaffolds for Through Space Energy Transfer

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Supporting Information (3 pages)

Experimental Section for the synthesis

1) *General Methods.*

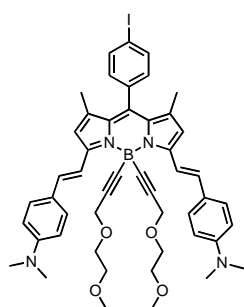
The 300 and 400 (^1H), 75.5 (^{13}C) MHz NMR spectra were recorded at room temperature with perdeuterated solvents with residual protiated solvent signals providing internal references. Column chromatographic purification was conducted using 40-63 μm silica gel. Thin layer chromatography (TLC) was performed on silica gel plates coated with fluorescent indicator.

2) *Synthesis and characterization.*

Compound 2: In round bottom Schlenk flask *p*-carborane **1** (0.520 g, 3.605 mmol) was dissolved in anhydrous THF (50 mL) and cooled at -78°C using a dryice /acetone bath. $^n\text{BuLi}$ titrated at 1.59 N (4.99 mL, 7.93 mmol) was dropwise added over a one hour period. During the addition the solution turned deep-yellow. After one hour at low temperature, anhydrous CuBr (0.520 g, 3.62 mmol) were added portion wise as a solid over 30 min. During this period the solution turned mauve. After 45 min the second portion of CuBr was added using the same procedure and the solution turned than purple red. After an additional period of 45 min anhydrous 4-(bromoethynyl)-iodobenzene was added in a single portion under argon. After progressive decoloration of the solution and in situ formation of a white precipitate the reaction mixture is quenched instantaneously by addition of HCl (1M, 20 mL). The organic product is extracted with dichloromethane (3 times 150 mL) and dried over magnesium sulfate. Careful column chromatography over flash silica using petroleum ether as eluant afforded 760 mg of the target compound **2** (35%, isolated yield).

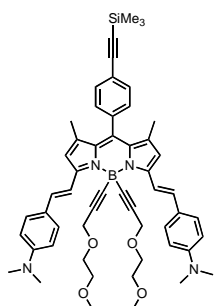
^1H NMR (400 MHz, CDCl_3); δ (ppm) 7.61 (d, $^3J = 8.4$ Hz, 4H), 7.02 (d, $^3J = 8.4$ Hz, 4H), 3.15-1.63 (broad B-H absorption, 10H). ^{13}C NMR (100.61 MHz, CDCl_3) 137.5 (CH), 133.4 (CH), 120.8 (phenylC \equiv -), 95.2 (C-I), 86.8 (C \equiv C), 78.5 (C \equiv C), 69.4 (C carborane). ^{11}B (128.4 MHz, CDCl_3); δ (ppm) -13.3 (d, B-H 165 Hz). EI-MS neat m/z 598.0 (100%). Anal Calc for $\text{C}_{18}\text{H}_{18}\text{B}_{10}\text{I}_2$ ($M_r = 596.25$): C, 36.26; H, 3.04. Found; C, 36.09; H, 2.85.

Compound G-I: In a Schlenk flask, ethylmagnesiumbromide (1 mL, 1.02 mmol) was added to a stirred solution of 2,5-dioxaoct-7-yne (135 mg, 1.18 mmol) in anhydrous THF. The mixture was stirred at 60 °C for 2 h. The resulting Grignard was then transferred via cannula to a solution of the difluoroBoron equivalent of G-I (330 mg, 0.46 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the solution was extracted with CH_2Cl_2 . After evaporation, the organic layer was purified by column chromatography on silica (CH_2Cl_2 /ethyl acetate



80:20) to give 200mg of compound **G-I** (yield 87%): ^1H NMR (C_6D_6 200 MHz): 1.31 (s, 6H), 2.47 (s, 12H), 3.01 (s, 6H), 3.21-3.25 (m, 4H), 3.69-3.74 (m, 4H), 4.19 (s, 4H), 6.20 (d, 2H, $^3J=8.0$ Hz), 6.47-6.51 (m, 8H), 7.24-7.41 (m, 4H), 7.76 (d, 2H, $^3J=8.8$ Hz), 8.84 (d, 2H, $^3J=16.1$ Hz). ^{13}C NMR (C_6D_6 75 MHz): 15.13, 39.80, 58.47, 58.66, 58.80, 59.63, 68.83, 69.57, 71.99, 94.32, 112.80, 118.09, 126.47, 129.33, 131.24, 131.68, 135.12, 135.69, 136.06, 137.97, 139.31, 151.07, 152.90. ESI-MS 900.3 ($[\text{M}]$, 100). Anal. Calcd for $\text{C}_{49}\text{H}_{54}\text{BIN}_4\text{O}_4$ ($M_r = 900.69$): C, 65.34; H, 6.04; N, 6.22. Found: C, 65.59; H, 5.87; N, 6.55.

Compound G-TMS : To an argon-degassed solution of **G-I** (150 mg, 0.17 mmol) and ethynyltrimethylsilane (46 μL , 0.32 mmol) in benzene/triethylamine (10/2 mL) was added



[$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$] (7 mg, 0.009 mmol) and CuI (3 mg, 0.016 mmol). The reaction was then stirred at 25°C during 18 hours. The solution was poured into water (10mL) and extract with CH_2Cl_2 (3 x 10 ml). The organic phase was washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. After evaporation, the organic layer was purified by column chromatography on silica (CH_2Cl_2 /ethyl acetate 80:20) to give 117 mg of compound **G-TMS** (yield 84%): ^1H NMR (C_6D_6 200 MHz): 0.27 (s, 9H), 1.34 (s, 6H), 2.47 (s, 12H), 3.02 (s, 6H), 3.24 (t, 4H, $^3J = 5.3$

Hz), 3.73 (t, 4H, $^3J = 5.1$ Hz), 4.20 (s, 4H), 6.19 (d, 2H, $^3J=8.0$ Hz), 6.44-6.52 (m, 8H), 7.24-7.35 (m, 4H), 7.76 (d, 2H, $^3J=8.6$ Hz), 8.85 (d, 2H, $^3J= 16.1$ Hz). ^{13}C NMR (C_6D_6 50 MHz): 0.07, 15.06, 39.78, 58.44, 59.61, 68.81, 72.00, 92.50, 95.32, 105.63, 112.80, 118.13, 123.68, 127.47, 129.33, 132.40, 134.99, 136.87, 139.41, 151.04, 152.82. ESI-MS 870.2 ([M], 100). Anal. Calcd for $\text{C}_{54}\text{H}_{63}\text{N}_4\text{O}_4\text{BSi}$: C, 74.46; H, 7.29; N, 6.43. Found: C, 74.63; H, 7.12; N, 6.39.

Compound G: To a solution of **G-TMS** (80 mg, 0.09 mmol) in THF/MeOH (10/2 mL) was added K_2CO_3 (190 mg, 1.36 mmol) in one portion. The reaction was then stirred at 25°C during 2 hours. The solution was poured into water (200mL) and extract with CH_2Cl_2 (3 x 20 ml). The organic phase was washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. After evaporation, the organic layer was purified by column chromatography on silica (CH_2Cl_2 /ethyl acetate 80:20) to give 66 mg of compound **G** (yield 92%): ^1H NMR (C_6D_6 200 MHz) : δ 1.31 (s, 6H), 2.48 (s, 12H), 3.02 (s, 6H), 3.03 (s, 1H), 3.23 (t, 4H, $^3J = 5.1$ Hz), 3.72 (t, 4H, $^3J = 4.58$ Hz), 4.20 (s, 4H), 6.21 (d, 2H, $^3J=8.0$ Hz), 6.48-6.52 (m, 8H), 7.22-7.31 (m, 4H), 7.75 (d, 2H, $^3J= 8.6$ Hz), 8.85 (d, 2H, $^3J= 16.1$ Hz). ^{13}C NMR (C_6D_6 50 MHz): 15.06, 39.81, 58.44, 59.61, 68.81, 72.00, 78.61, 83.49, 92.51, 96.47, 112.80, 118.13, 122.74, 126.58, 127.47, 128.32, 129.29, 131.66, 132.52, 134.89, 136.87, 137, 10, 139.26, 151.04, 152.79. EI-MS 727.3 ([M], 100). Anal. Calcd for $\text{C}_{51}\text{H}_{55}\text{N}_4\text{O}_4\text{B}$: C, 76.68; H, 6.94; N, 7.01. Found: C, 76.46; H, 6.63; N, 6.87.

Compound GC: A Schlenk flask was successively charged with the diphenyliodo-carborane **2** (50 mg, 0.084 mmol), benzene (10 mL), triethylamine (3 mL) and the green Bodipy **G** (27 mg, 0.035 mmol, 0.42 equiv.). The solution is vigorously degassed under argon during 30 min and than $[\text{Pd}(\text{PPh}_3)_4]$ (10 mg) was added as a solid and the mixture sealed with a tap and heated at 60°C overnight. After cooling to rt, the solvent was evaporated to dryness and the organic product extracted with dichloromethane and washed with water. The desired dye was purified by flash silica using a gradient of methanol (0 to 1% by portion of 0.25%) in dichloromethane. Final recrystallization by evaporation of dichloromethane from a mixture dichloromethane/ethanol afforded the pure dye **GC** (36 mg, 33%). ^1H NMR (400 MHz, d_6 -acetone); δ (ppm) 8.09 (d, $^3J = 16.2$ Hz, 2H), 7.75 (d, $^3J = 8.3$ Hz, 4H), 7.58-7.50 (m, 4H),

7.47 (d, $^3J = 8.1$ Hz, 2H), 7.41 (d, $^3J = 8.3$ Hz, 4H), 7.28 (d, $^3J = 16.2$ Hz, 2H), 7.14 (d, $^3J = 8.3$ Hz, 2H), 6.81 (d, $^3J = 8.1$ Hz, 4H), 6.78 (s, 2H), 4.06 (s, 4H), 3.53-3.50 (m, 4H), 3.21-3.18 (m, 4H), 3.16 (s, 6H), 3.03 (s, 12H), 1.47 (s, 6H), 3.45-2.35 (broad B-H absorption, 10H). ^{13}C NMR (100.61 MHz, CDCl_3) 152.7, 150.8, 139.1, 137.4, 136.8, 136.0, 135.5, 134.9, 133.2, 132.1, 131.8, 131.4, 126.3, 124.2, 123.0, 120.8, 120.2, 117.9, 112.6, 95.5 (C \equiv C), 92.3 (C \equiv C), 91.9 (C \equiv C), 90.0 (C \equiv C), 87.0 (C \equiv C), 86.6 (C \equiv C), 81.0 (C \equiv C), 80.4 (C \equiv C), 71.8, 68.6, 66.8, 59.4, 58.2, 53.0, 39.6, 30.0, 14.9. ^{11}B (128.4 MHz, CDCl_3); δ (ppm) -11.3 (bs), -15.8 (d, B-H 167 Hz). EI-MS neat m/z 1268.4 (100%). Anal Calc for $\text{C}_{69}\text{H}_{72}\text{B}_{11}\text{N}_4\text{O}_4$ ($M_r = 1267.16$): C, 65.40; H, 5.73; N, 4.42. Found; C, 65.22; H, 5.41; N, 4.17.

Compound RCG: A Schlenk flask was successively charged with the carborane derivative **GC** (31 mg, 0.024 mmol), benzene (5 mL), triethylamine (2 mL) and the red Bodipy **R** (16 mg, 0.040 mmol, 1.6 equiv.). The solution is vigorously degassed under argon during 25 min and then $[\text{Pd}(\text{PPh}_3)_4]$ (10 mg) was added as a solid and the mixture sealed with a tap and heated at 60°C during 36 h. After cooling to rt, the solvent was evaporated to dryness and the organic product extracted with dichloromethane and washed with water. The desired dye was purified by flash silica using a gradient of methanol (0 to 0.5% by portion of 0.10%) in dichloromethane. Final recrystallization by evaporation of dichloromethane from a mixture dichloromethane/ethanol/methanol afforded the pure dye **RCG** (26 mg, 70%). ^1H NMR (400 MHz, d_6 -acetone); δ (ppm) 8.10 (d, $^3J = 16.1$ Hz, 2H), 7.77-7.74 (m, 4H), 7.51-7.45 (m, 8H), 7.38-7.18 (m, 6H), 7.28 (d, $^3J = 16.1$ Hz, 2H), 6.81 (d, $^3J = 8.9$ Hz, 6H), 6.78 (s, 2H), 4.06 (s, 4H), 3.53-3.50 (m, 4H), 3.21-3.12 (m, 4H), 3.03 (s, 6H), 2.77 (s, 12H), 2.47 (s, 6H), 2.32 (q, $^3J = 7.5$ Hz, 4H), 1.47 (s, 6H), 1.36 (s, 6H), 0.96 (t, $^3J = 7.5$ Hz, 6H), 3.37-2.21 (broad B-H absorption, 10H). ^{13}C NMR (100.61 MHz, CDCl_3) 150.7, 150.3, 139.6, 138.0, 137.6, 135.9, 136.4, 134.5, 133.9, 132.7, 132.6, 131.6, 131.4, 131.3, 126.8, 126.3, 124.5, 123.5, 123.4,

121.6, 120.9, 118.2, 116.4, 114.6, 95.7 (C≡C), 94.3 (C≡C), 91.7 (C≡C), 91.0 (C≡C), 88.6 (C≡C), 85.9 (C≡C), 82.4 (C≡C), 81.4 (C≡C), 80.9 (C≡C), 71.9, 67.9, 65.8, 59.7, 58.6, 53.6, 39.9, 31.0, 15.4. ^{11}B (128.4 MHz, CDCl_3); δ (ppm) -11.7 (bs), -14.4 (d, B-H 166 Hz). EI-MS neat m/z 1545.0 (100%). Anal Calc for $\text{C}_{94}\text{H}_{98}\text{B}_{12}\text{F}_2\text{N}_6\text{O}_4$ ($M_r = 1543.55$): C, 73.14; H, 6.40, N, 5.44. Found; C, 72.94; H, 6.36; N, 5.20.

3) *Spectroscopic Measurements.*

UV-vis spectra were recorded using a Shimadzu UV-3600 dual-beam grating spectrophotometer with a 1 cm quartz cell. Fluorescence spectra were recorded on a HORIBA Jobin-Yvon fluoromax 4P spectrofluorimeter. All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{exp}) was calculated from eq (1).

$$\Phi_{\text{exp}} = \Phi_{\text{ref}} \frac{F \{1 - \exp(-A_{\text{ref}} \ln 10)\} n^2}{F_{\text{ref}} \{1 - \exp(-A \ln 10)\} n_{\text{ref}}^2} \quad (1)$$

Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium. The reference system used were rhodamine 6G in methanol ($\Phi_{\text{ref}} = 0.78$, $\lambda_{\text{exc}} = 488$ nm) and cresyl violet in ethanol ($\Phi_{\text{ref}} = 0.50$, $\lambda_{\text{exc}} = 546$ nm) in air equilibrated water and deaerated solutions.

Luminescence lifetimes were measured on an Edinburgh Instruments spectrofluorimeter equipped with a R928 photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a G^wInstect GFG-8015G delay generator. No filter was used for the excitation. Emission wavelengths were selected by a monochromator. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution (LUDOX) for instrument response.