Synthesis of Oligo(het)arylene Building Blocks with Bi- and Terpyridine Units

Govindaswamy Manickam[a] and A. Dieter Schlüter*[a]

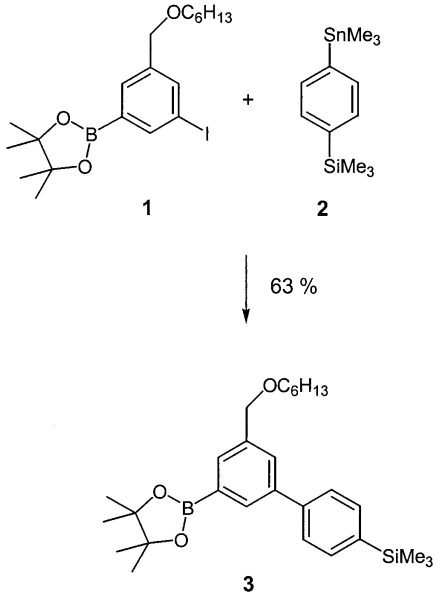
Keywords: Suzuki cross coupling / Stille cross coupling / Bipyridines / Terpyridines / Supramolecular chemistry / Nitrogen heterocycles / Macrocycles

The 330 mg to 12 g scale synthesis of a variety of arylene (**3**,**5**–**8**) and hetarylene building blocks with bipyridine (**16**,**17**,**19**) and terpyridine units (**21**–**23**,**25**) by and for transition metal-mediated cross-coupling reactions is reported. All these compounds carry hexyloxymethyl substituents, mainly for solubility reasons.

Introduction

Now that first ring-closing reactions of bi- (bipy) and terpyridine (tpy) containing oligo(het)arylene building blocks to hexagonal, shape-persistent macrocycles, using building blocks from a construction set[1,2] have been successful,[3,4] we have intensified our program to develop a versatile construction set for such building blocks, and make a variety of macrocycles available. The macrocycles should not only vary in size and number and orientation of bipy and tpy units, but also in their substitution pattern. With a number of cycles at hand, interesting aspects such as their metal complexation, adsorption on surfaces, aggregation into columnar stacks, and liquid crystallinity could be studied in detail. The present contribution describes the synthesis of a number of novel arylenic and bipy- and tpy-containing hetarylenic building blocks that carry bromo, iodo, trimethylstannyl (in situ), and boronic ester functions at positions appropriate for Suzuki-type[5] and related cross-coupling reactions.

The synthetic routes that rely heavily on the Stille cross-coupling reaction[6] are organized according to the targeted building blocks: biphenyl **3** (Scheme 1), *m*-terphenyls **7** and **8** (Scheme 2), pyridine precursors (Scheme 3) **12**–**15** for bipy′s **16**, **17**, and **19** (Scheme 4 and Scheme 5), and "half-cycles" **23** and **25** (Scheme 6). All building blocks carry hexyloxymethyl chains for two reasons: to provide sufficient solubility and the potential opportunity for chain exchange through ether cleavage. The synthesis of the functionalized arylene **3** was recently reported to proceed with 20% yield.[1c] Here, an improved synthesis is presented that provides this compound in a yield of 63%. Although the total number of steps of this modified route is higher, the availability of starting materials is much better and the yields per step are higher. As a consequence of this improvement, compound **3**, synthesized by Stille coupling of the iodobenzene derivative **1** with the stannyl component **2**, is now easily accessible on the 10 g scale. Compound **1** was obtained by iododesilylation of the corresponding trimethylsilyl analogue (not shown).[1c] Compound **8** was obtained from the bromide **4**,[1c] which was converted into its boronic ester analog **5**, and then iododesilylated to **6** with iodochloride at ambient temperature in excellent yield. Subsequent conversion of **6** into **7** was accomplished by coupling it with **2** according to the Stille protocol. Finally, iododesilylation of **7** into **8** with iodochloride again proceeded with excellent yield. All the steps involved in the conversion of **5** into **8** went smoothly without affecting the boronic ester function.

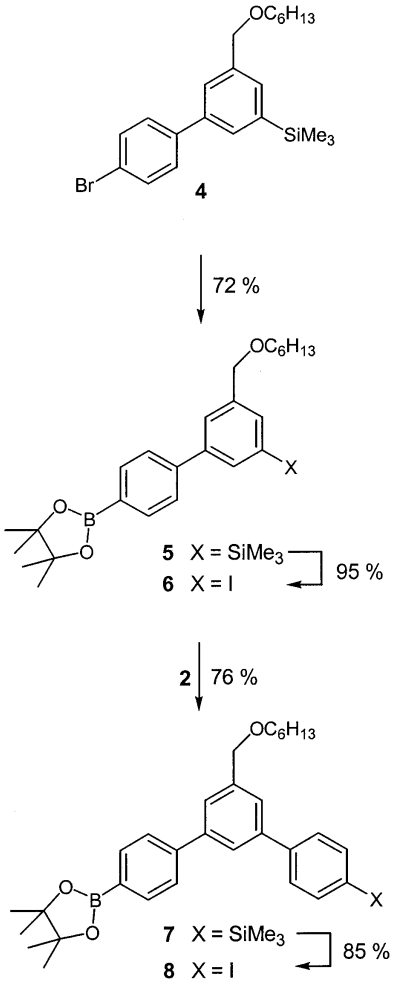


Scheme 1

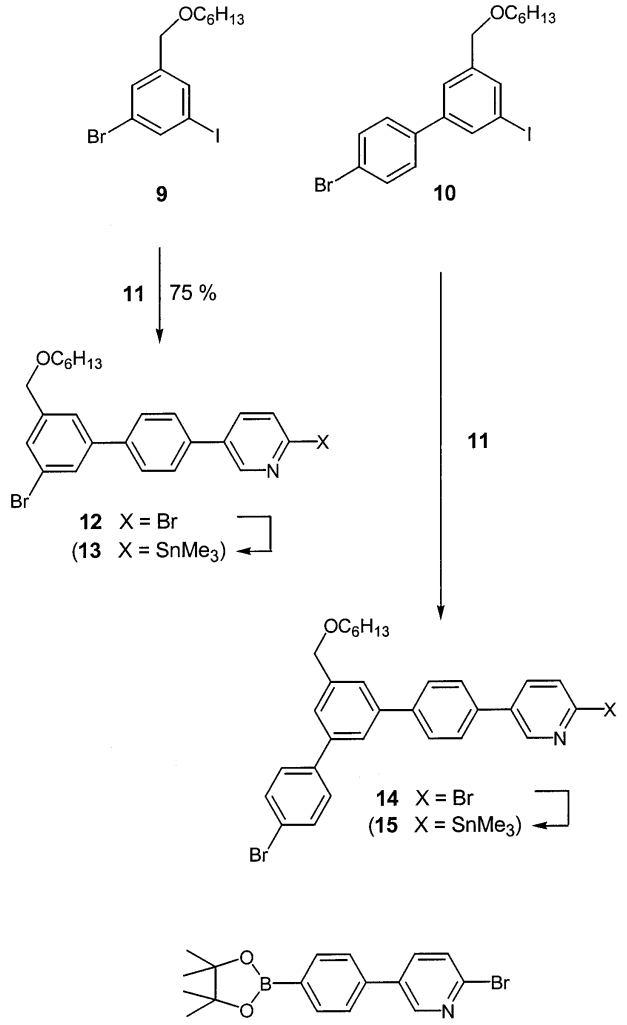
The stannylated building blocks **13** and **15** were obtained by first applying Suzuki cross-coupling of **9**[4b] and **10**[1c] with the pyridine derivative **11**[1c] to give the dibromo compounds **12** and **14**,[7] respectively. Treatment of these dibromides with butyllithium, and subsequent addition of trimethylstannyl chloride, gave compounds **13** and **15** (Scheme 3), which served as coupling counterparts for the dibromides from which they were generated in the subsequent bipy synthesis (Scheme 4 and Scheme 5). Stille cross-coupling of bromide **12** with the stannyl compound **13** (prepared in situ) gave bipy **16**. Similarly, **14** gave bipy

[a] Freie Universität Berlin,
Institut für Chemie/Organische Chemie,
Takustr. 3, 14195 Berlin, Germany
Fax (internat.) + 49-30/838-53357
E-mail: adschlue@chemie.fu-berlin.de

  1434–193X/00/1020–3475 $ 17.50+.50/0



Scheme 2



Scheme 3

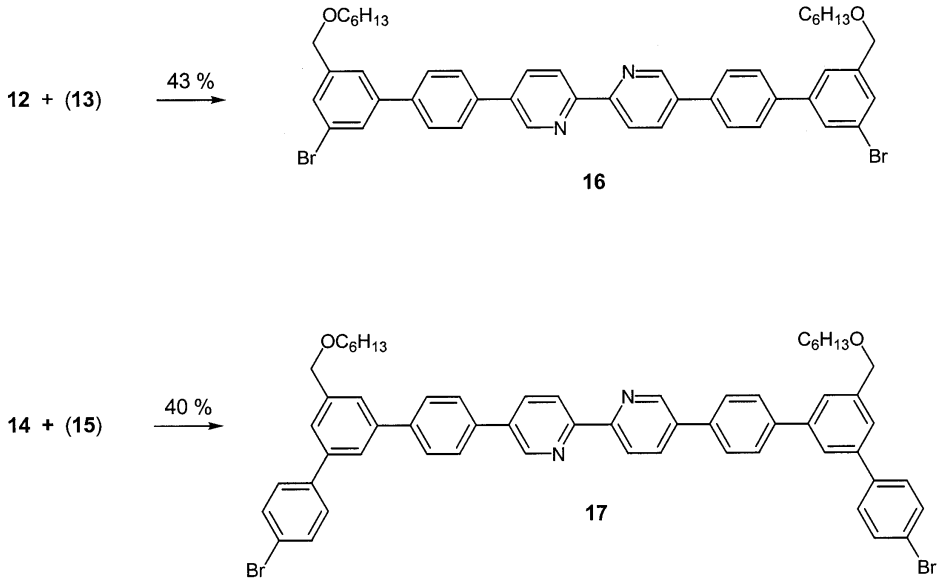
17 with **15** which was also prepared in situ. Both bipy′s were obtained in yields of 40−43%. The stannyls **13** and **15** were not isolated because their decomposition upon attempted purification by silica gel column chromatography could not be prevented. Bipy **19** was synthesized by reacting iodoterphenyl **8** with the known compound **18**[3] under standard Stille conditions. The purification of the resulting "half-cycle" **19** turned out to be tedious. Compound **19** decomposed under normal silica gel column chromatography conditions, resulting in the loss of the boronic ester functionality. Attempts to do a faster purification by preparative gel permeation chromatography also failed. ^{1}H and ^{13}C NMR spectroscopic evidence suggested loss of the boronic functions and their oxidative replacement by hydroxy groups. The best solution, which finally gave the product in 44% isolated yield, was to use a very short column (5 cm) and to elute as quickly as possible with hexane/EtOAc (3:2) as the eluent. Despite the limitations encountered in the purification of compound **19**, it could be obtained on a one gram scale.

Scheme 6 describes the synthesis of the tpy "half-cycles" **23** and **25**. The distannylated pyridine **20** serves as the linker for two equivalents of either **14** or **24**,[1c] and ends up as the central pyridine ring of the tpy units in **23** and **25**. Stille coupling of **14** with **20**[1a] gave **21**, which was converted into the iodo compound **23** via the distannyl **22**, which was in turn obtained from **21** by nucleophilic stannylation with $NaSnMe_3$ in moderate yield. Subsequent reaction with iodine gave **23**. Stille coupling between **20** and **24** gave **25** without affecting the boronic ester function. The purification of **25** was done analogously to the one described for **19**.

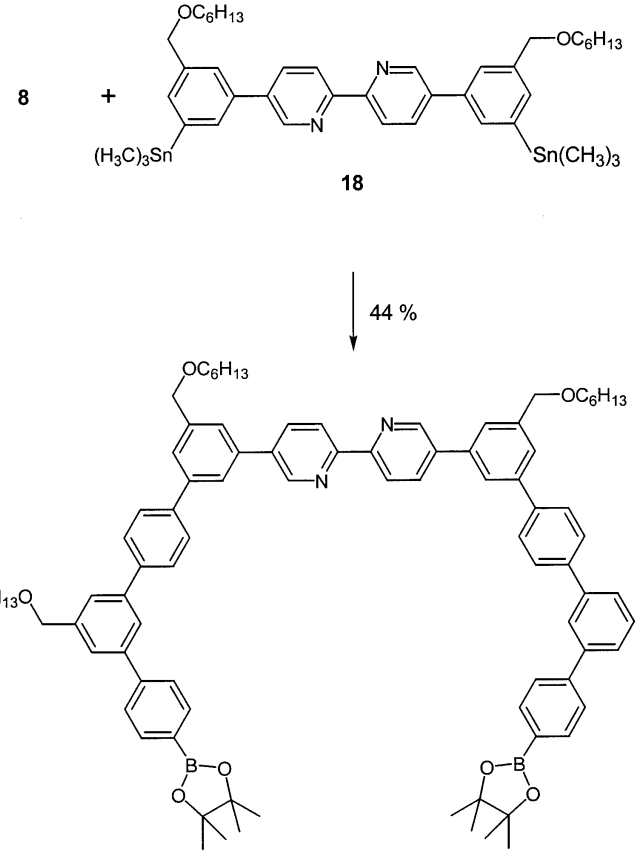
The bipy′s and tpy′s reported here will be used for cycle synthesis, but are reported at the present stage because they are of considerable interest for various supramolecular applications including catenane[8] and rotaxane[8] formation.

Experimental Section

General: Reagents were purchased from Fluka, Aldrich, or Acros, and used without further purification. Solvents were purchased from Fluka, Aldrich, or Acros and purified and dried by standard methods. Starting materials **4**,[1c] **9**,[4b] **10**,[1c] **11**,[1c] **18**,[3] **20**,[1a] and **24**[1c] were prepared according to literature procedures. Compounds **13** and **15** were prepared and used in situ and not further characterized. All the reactions were carried out under a nitrogen atmosphere. − ^{1}H (270 MHz) and ^{13}C NMR (67.9 MHz) spectra were recorded on a Bruker AM 270 spectrometer using $CDCl_3$ as solvent



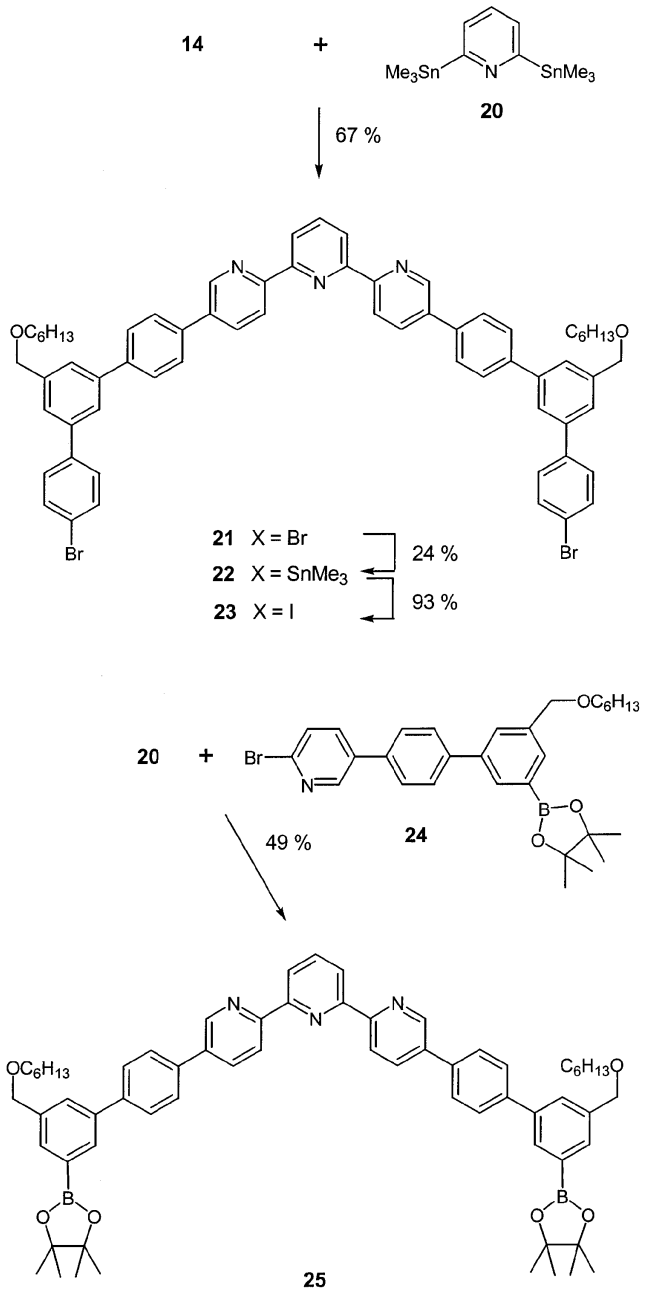
Scheme 4



Scheme 5

with TMS as internal standard unless otherwise stated. − Mass spectra were recorded with a Varian MAT 711 spectrometer. − Melting points were determined using Büchi 510 (open capillaries, uncorrected values). − Column chromatography was run with Merck flash silica gel (230−400 mesh) and Acros activated aluminum oxide basic (50−200 micron). − Analytical TLC was done with alumina sheets, silica gel Si 60 F_{254} (Merck), and UV detection. Elemental analyses were done using a Perkin−Elmer EA 240 instrument.

2-(3-Hexyloxymethyl-5-iodophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1): To a stirred solution of 2-(3-hexyloxymethyl-5-trimethylsilylphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (22.6 g, 57.9 mmol) in CH_2Cl_2 (200 mL), a solution of iodochloride (11.3 g, 69.5 mmol) in CH_2Cl_2 (100 mL) was added dropwise over a period of 30 min at −10 °C, and the resulting mixture stirred at this temperature for 30 min. Then a saturated solution of $Na_2S_2O_5$ (150 mL) was added. The layers were separated and the aqueous one was extracted twice with CH_2Cl_2 (100 mL). The combined or-



Scheme 6

ganic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **1** (24.2 g, 94.1%) as a colorless oil. − R_f = 0.81 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, J = 6.9 Hz, 3 H, CH_3), 1.20−1.38 (m, 6 H, γ-, δ-, ε-CH_2), 1.30 (s, 12 H), 1.58 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.41 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.39 (s, 2 H, benzyl-CH_2), 7.67(s, 1 H, phenyl-H), 7.78 (s, 1 H, phenyl-H), 8.02 (s, 1 H, phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = 13.94, 22.47, 24.69, 25.70, 31.51, 35.00, 70.59, 71.70, 94.47, 133.53, 133.80, 138.98, 142.34. − MS; *m*/*z* (%) for $C_{19}H_{30}BIO_3$: 444 (15) $[M]^+$, , 429 (9), 344 (100). − $C_{19}H_{30}BIO_3$ (444.16): calcd. C 51.38, H 6.81; found C 51.13, H 6.77.

1-Trimethylsilyl-(4-trimethylstannyl)benzene (2): To a stirred solution of 1-iodo-(4-trimethylsilanyl)benzene (26 g, 94.1 mmol) in dry ether (300 mL) BuLi (6.56 g, 102.4 mmol, 64 mL, 1.6 M) in hexane was added dropwise at −78 °C over a period of 30 min. The mixture was then stirred at this temp. for 30 min. and a solution of trimethyl stannyl chloride (20.2 g, 101.4 mmol) in ether (50 mL) added. The mixture was allowed to warm to room temp. over night. Then water was added, the layers were separated and the aqueous phase was extracted twice with ether (100 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The product was isolated as a white crystalline solid (27.2 g, 92.3%) and used in next step without further purification (purity, > 98% based on ^{1}H NMR). − M.p. 90−92 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.33 (s, 9 H, $SnMe_3$), 0.35 (s, 9 H, TMS), 7.62 (br. s, 4 H, phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = −9.64 ($SnMe_3$), −1.15 (TMS), 132.89, 133.05, 135.02, 135.66. − MS; *m*/*z* (%): 314 (1.6) $[M]^+$, 299 (100), 207 (10), 142 (7). − $C_{12}H_{22}SiSn$ (314.10): calcd. C 46.04, H 7.08; found C 45.92, H 7.13.

2-[5-(Hexyloxymethyl)-4′-(trimethylsilyl)biphenyl-3-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (3): Iodo compound **1** (15.3 g, 34.3 mmol) and compound **2** (11.8 g, 37.8 mmol) were dissolved in toluene (350 mL). The mixture was degassed, then $(PPh_3)_4Pd$ (1.58 g, 1.36 mmol) added and the system degassed again. This mixture was heated under reflux for 48 h then cooled to room temp. and extracted with a saturated aqueous solution of KF (300 mL). The crude product was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **3** (10.1 g, 63.0%) as a colorless viscous oil. − R_f = 0.77. For spectral and analytical data see ref.[1c]

2-[5′-Hexyloxymethyl-3′-(trimethylsilyl)biphenyl-4-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (5): To a stirred solution of **4** (14.8 g, 35.3 mmol) in dry ether/THF (1:1 v/v, 300 mL) butyllithium (2.5 g, 39.0 mmol, 24.4 mL, 1.6 M) in hexane was added dropwise at −78 °C over a period of 30 min. The mixture was then stirred at this temp. for 1 h and a solution of trimethyl borate (7.33 g, 70.5 mmol) in ether (50 mL) added. The mixture was allowed to warm to room temp. over night. Then water was added, the layers were separated and the aqueous phase extracted twice with ether (100 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography through silica gel, first with EtOAc/hexane (9:1) as eluent to remove the impurities and then with EtOAc/hexane (1:1) to wash the product off the column. This gave 10.1 g of crude boronic acid, which was isolated as a trimer and used for the esterification without further purification. − ^{1}H NMR ($CDCl_3$): δ = 0.41 (s, 9 H, TMS), 0.97 (t, J = 6.8 Hz, 3 H, CH_3), 1.35−1.50 (m, 6 H, γ-, δ-, ε-CH_2), 1.74 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.61 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.67 (s, 2 H, benzyl-CH_2), 7.60(s, 1 H, phenyl-H), 7.71 (s, 1 H, phenyl-H), 7.80−7.85 (m, 3 H, phenyl-H), 8.41 (d, 2 H, phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = −1.07, 14.03, 22.61, 25.93, 29.74, 31.69, 70.68, 72.94, 126.86, 127.73, 131.45, 132.02, 136.10, 138.44, 140.28, 141.26, 145.54. − MS; *m*/*z* (%) for trimer $C_{66}H_{93}B_3O_6Si_3$: 1099 (11) $[M]^+$, 999 (3), 678 (9), 632 (4), 356 (29), 340 (32), 325 (100), 239 (53). − HRMS ($C_{66}H_{93}B_3O_6Si_3$): calcd: 1098.65592; found 1098.65990. − $C_{66}H_{93}B_3O_6Si_3$ (1099.14): calcd. C 72.12, H 8.53; found C 71.35, H, 8.24.

The crude boronic acid (10.1 g, 26.2 mmol) and 2,3-dimethylbutane-2,3-diol (4.64 g, 39.3 mmol) were dissolved in 1,4-dioxane (200 mL), and the mixture warmed to 60 °C for 2 h. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **5** (11.9 g, 72.1% with reference to **4**) as a colorless oil. − R_f = 0.73 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 9 H, TMS), 0.92 (t, J = 6.8 Hz, 3 H, CH_3),

1.30−1.47 (m, 6 H, γ-, δ-, ε-CH_2), 1.39 [s, 12 H, $(CH_3)_2C-C(CH_3)_2$], 1.67 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.54 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.61 (s, 2 H, benzyl-H), 7.52 (s, 1 H, phenyl-H), 7.61 (s, 1 H, phenyl-H), 7.65 (d, J = 8.1 Hz, 2 H, phenyl-H), 7.69 (s, 1 H, phenyl-H), 7.94 (d, J = 8.1 Hz, 2 H, phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = −1.09, 14.02, 18.72, 22.59, 24.82, 25.91, 29.72, 31.67, 70.61, 72.93, 83.71, 126.57, 127.18, 131.36, 131.76, 135.19, 138.37, 140.46, 141.12, 144.17. − MS; *m*/*z* (%): 466 (100) $[M]^+$, 451 (80), 365 (49), 266 (71), 224 (66), 73 (16). − HRMS ($C_{28}H_{43}BO_3Si$): calcd. 466.30745; found 466.30722. − $C_{28}H_{43}BO_3Si$ (466.54): calcd. C 72.09, H 9.29; found C 71.00, H 9.20.

2-[5′-(Hexyloxymethyl)-3′-iodobiphenyl-4-yl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (6): Synthesis and workup were similar to that of compound **1**. Compound **5** (11.9 g, 25.4 mmol) in CH_2Cl_2 (200 mL), iodochloride (5.37 g, 33.1 mmol) in CH_2Cl_2 (100 mL). The crude product was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **6** (12.5 g, 94.6%) as a colorless oil. − R_f = 0.78 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3 H, CH_3), 1.27−1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.35 [s, 12 H, $(CH_3)_2C-C(CH_3)_2$], 1.62 (q, J = 6.7 Hz, 2 H, β-CH_2), 3.47 (t, J = 6.7 Hz, 2 H, α-CH_2), 4.48 (s, 2 H, benzyl-CH_2), 7.52 (s, 1 H, phenyl-H), 7.54 (d, J = 8.2 Hz, 2 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.85 (s, 1 H, phenyl-H), 7.86 (d, J = 8.2 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.00, 22.56, 24.82, 25.81, 29.62, 31.61, 70.78, 71.81, 83.79, 94.76, 125.56, 126.29, 135.10, 135.25, 135.35, 141.41, 142.04, 143.06. − MS; *m*/*z* (%): 520 (28) $[M]^+$, 420 (95), 395 (20), 293 (100), 208 (28), 193 (21), 83 (13). − HRMS ($C_{25}H_{34}BIO_3$): calcd. 520.16445; found 520.16423. − $C_{25}H_{34}BIO_3$ (520.25): calcd. C 57.72, H 6.59; found C 58.11, H 6.52.

2-[5′-(Hexyloxymethyl)-4-(trimethylsilyl)[1,1′;3′,1′′]terphenyl-4′′-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (7): Synthesis and workup are similar to that of compound **3**: Compound **6** (12.4 g, 23.8 mmol) and **2** (8.2 g, 26.1 mmol), $(PPh_3)_4Pd$ (820 mg, 0.71 mmol). The crude product was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **7** (9.8 g, 76%) as a colorless viscous oil. − R_f = 0.72 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 9 H, TMS), 0.91 (t, J = 6.3 Hz, 3 H, CH_3), 1.30−1.48 (m, 6 H, γ-, δ-, ε-CH_2), 1.39 [s, 12 H, $(CH_3)_2C-C(CH_3)_2$], 1.68 (qu, J = 6.3 Hz, 2 H, β-CH_2), 3.56 (t, J = 6.3 Hz, 2 H, α-CH_2), 4.65 (s, 2 H, benzyl-CH_2), 7.60−7.71 (m, 8 H, phenyl-H), 7.77 (s, 1 H, phenyl-H), 7.94 (d, 2 H, J = 7.7 Hz). − ^{13}C NMR ($CDCl_3$): δ = −1.15, 13.99, 24.82, 25.86, 29.73, 31.67, 70.67, 72.77, 83.73, 125.37, 125.64, 126.50, 133.75, 135.22, 139.39, 139.79, 141.39, 141.62, 141.85, 143.67. − MS; *m*/*z* (%): 542 (44) $[M]^+$, 527 (42), 442 (100), 427 (44), 394 (31), 294 (29), 193 (11). − HRMS ($C_{34}H_{47}BO_3Si$): calcd. 542.33875; found 542.33392. − $C_{34}H_{47}BO_3Si$ (542.65): calcd. C 75.26, H 8.73; found C 74.76, H 8.12.

2-[5′-(Hexyloxymethyl)-4-iodo-[1,1′;3′,1′′]terphenyl-4′′-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (8): Synthesis and workup was similar to that of compound **6**: Compound **7** (9.8 g, 18.1 mmol), CH_2Cl_2 (200 mL), and iodochloride (3.52 g, 21.7 mmol) in dichloromethane (50 mL). Yield: **8** (9.15 g, 85%), as a colorless viscous oil. − R_f = 0.69 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, J = 6.4 Hz, 3 H, CH_3), 1.27−1.44 (m, 6 H, γ-, δ-, ε-CH_2), 1.37 [s, 12 H, $(CH_3)_2C-C(CH_3)_2$], 1.65 (qu, J = 6.4 Hz, 2 H, β-CH_2), 3.53 (t, J = 6.4 Hz, 2 H, α-CH_2), 4.61 (s, 2 H, benzyl-CH_2), 7.38 (d, J = 8.1 Hz, 2 H, phenyl-H), 7.51 (s, 1 H, phenyl-H), 7.58 (s, 1 H, phenyl-H), 7.65 (d, J = 8.1 Hz, 2 H), 7.68 (s, 1 H, phenyl-H), 7.75 (d, J = 8.1 Hz, 2 H), 7.91 (d, J = 8.1 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.01, 22.58, 24.83, 25.88, 29.70, 31.65, 70.77, 72.67, 83.79, 93.18, 124.99, 125.29, 125.76, 126.49, 129.07, 135.26, 137.81, 140.04, 140.50, 140.73, 141.82, 143.43. − MS; *m*/*z* (%): 596 (14) $[M]^+$, 520 (19), 496 (100), 395 (77), 369 (70), 293 (52), 267 (67), 165 (41), 101 (43), 83 (49). − HRMS ($C_{31}H_{38}BIO_3$): calcd. 596.19587; found 596.19354. − $C_{31}H_{38}BO_3I$ (596.35): calcd. C 62.44, H 6.42; found C 62.92, H 6.36.

2-Bromo-5-[5′-bromo-3′-(hexyloxymethyl)biphenyl-4-yl]pyridine (12): Boronic ester **11** (9.40 g, 26.1 mmol) and **9** (11.4 g, 28.7 mmol) were dissolved in a mixture of toluene (260 mL) and an aqueous solution of 1 M Na_2CO_3 (260 mL). The mixture was degassed, then $(PPh_3)_4Pd$ (600 mg, 0.52 mmol) was added and the system was degassed again. After the mixture had been heated under reflux for 48 h, the layers were separated and the aqueous one was extracted twice with toluene (100 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography through silica gel with hexane/EtOAc (9:1) as eluent to give **12** (9.79 g, 75%) as a white solid. − M.p. 65−67 °C. − R_f = 0.58 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, J = 6.7 Hz, 3 H, CH_3), 1.24−1.40 (m, 6 H, γ-, δ-, ε-CH_2), 1.62 (qu, J = 6.7 Hz, 2 H, β-CH_2), 3.49 (t, J = 6.7 Hz, 2 H, α-CH_2), 4.50 (s, 2 H, benzyl-CH_2), 7.46−7.64 (m, 8 H, phenyl-H and pyrid-H), 7.72 (dd, J = 2.5 and 8.2 Hz, 1 H, pyrid-H), 8.58 (d, J = 2.5 Hz, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 13.99, 22.56, 25.81, 29.62, 31.60, 70.90, 71.90, 122.96, 124.06, 127.35, 127.84, 128.01, 128.96, 129.49, 135.20, 135.84, 136.68, 139.74, 141.03, 141.63, 142.13, 148.26. − MS; *m*/*z* (%): 503 (80) $[M]^+$, 403 (100), 322 (75), 240 (18), 201 (11), 121 (12). − $C_{24}H_{25}Br_2NO$ (503.27): calcd. C 57.28, H 5.01, N 2.78; found C 57.25, H 5.10, N 2.57.

5,5′-Bis {5′-bromo-3′-(hexyloxymethyl)biphenyl-4-yl]-[2,2′]bipyridinyl (16): To a stirred solution of **12** (1.5 g, 3.0 mmol) in dry ether (25 mL) was added at −78 °C, a 1.6 N solution of BuLi in hexane (210 mg, 3.3 mmol, 2.1 mL). After 2 h, to the resulting red solution was added a solution of Me_3SnCl (67 mg, 3.4 mmol) in ether (5 mL). The mixture was allowed to reach room temp. and then the solvent was removed. The remaining reddish oil **13** was added to a second portion of the same **12** (1.5 g, 3.0 mmol) dissolved in toluene (25 mL). After the addition of $(PPh_3)_4Pd$ (38 mg, 0.12 mmol), the mixture was heated under reflux for 24 h and then cool to room temp. Then aqueous saturated KF (20 mL) solution was added followed by aqueous 2 N Na_2CO_3 (30 mL). The organic phase was washed with water (50 mL) and dried over $MgSO_4$. After removal of the solvent the residue was purified by chromatography on silica gel (EtOAc/hexane, 1:3) to give **16** (1.08 g, 42.7%) as a white crystalline solid. − M.p. 73−74 °C. − R_f = 0.32 (hexane/EtOAc, 9:1). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3 H, CH_3), 1.28−1.43 (m, 6 H, γ-, δ-, ε-CH_2), 1.62 (qu, J = 6.7 Hz, 2 H, β-CH_2), 3.48 (t, J = 6.7 Hz, 2 H, α-CH_2), 4.49 (s, 2 H, benzyl-CH_2), 7.35 (br. s, 2 H, phenyl-H), 7.47−7.63 (m, 5 H, phenyl-H), 7.97 (d, J = 8.1 Hz, 1 H, pyrid-H), 8.46 (d, J = 2.5 Hz, 1 H, pyrid-H), 8.90 (br. s, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 14.00, 22.55, 25.80, 29.61, 31.59, 70.53, 71.86, 120.88, 122.93, 124.47, 127.25, 127.61, 128.83, 129.31, 134.80, 135.44, 136.76, 139.19, 141.51, 142.16, 147.33, 154.43. − MS; *m*/*z* (%): 846 (100) $[M]^+$, 760 (23), 746 (23), 667 (19), 282 (17), 243 (17). − HRMS ($C_{48}H_{50}Br_2N_2O_2$): calcd. 846.22185; found 846.22631. − $C_{48}H_{50}Br_2N_2O_2$ (846.74): calcd. C 68.09, H 5.95, N 3.31; found C 67.97, H 5.98, N 3.26.

5,5′-Bis-{4′′-bromo-5′-(hexyloxymethyl)-[1,1′;3′,1′′]terphenyl-4-yl}-[2,2′]bipyridinyl (17): Synthesis and workup are similar to compound **16**: First portion **14** (500 mg, 0.86 mmol), BuLi (66 mg,

1.03 mmol, 0.64 mL), Me_3SnCl (215 mg, 1.08 mmol), second portion **14** (500 mg, 0.86 mmol), $(PPh_3)_4Pd$ (40 mg, 0.035 mmol). The product was isolated as a white crystalline solid (337 mg, 40.2%). − M.p. 85−87 °C. − R_f = 0.26 (hexane/EtOAc, 4:1). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 1.29−1.43 (m, 6 H, γ-, δ-, ε-CH_2), 1.65 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.54 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.62 (s, 2 H, benzyl-CH_2), 7.41−7.79 (m, 11 H, phenyl-H), 8.03 (dd, J = 2.2 and 8.3 Hz, 1 H, pyrid-H), 8.52 (d, J = 8.3 Hz, 1 H, pyrid-H), 8.98 (br. s, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 14.02, 22.61, 25.91, 29.73, 31.67, 70.88, 72.68, 121.04, 121.76, 124.86, 125.39, 125.53, 127.39, 127.90, 128.80, 131.88, 135.03, 135.82, 136.62, 139.82, 140.18, 140.68, 140.77, 141.16, 147.51, 154.58. − MS; *m/z* (%): 998 (45) $[M]^+$, 920 (100), 840 (75), 820 (66), 720 (66), 640 (65). − $C_{60}H_{58}Br_2N_2O_2$ (998.93): calcd. C 72.14, H 5.85, N 2.80; found C 71.34, H 5.70, N 2.44.

Boronic Ester 19: Boronic ester **8** (1.45 g, 2.43 mmol) and **18** (950 mg, 1.10 mmol) were dissolved in toluene (80 mL). The mixture was degassed twice, then $(PPh_3)_4Pd$ (51 mg, 0.044 mmol) added and the system degassed again. The mixture was heated under reflux for 48 h, cooled to room temp. and extracted with a saturated aqueous solution of KF (50 mL). The solvent was removed under reduced pressure and the residue separated by silica gel column chromatography with hexane/EtOAc (3:2) as eluent. The product **19** was obtained as a white crystalline solid (790 mg, 44%). − M.p. 51−52 °C. − R_f = 0.17 (hexane/EtOAc = 4:1). − ^{1}H NMR ($CDCl_3$): δ = 0.89 (br. s, 6 H, CH_3), 1.28−1.44 (m, 12 H, γ-, δ-, ε-CH_2), 1.33 (s, 12 H, $(CH_3)_2C-C(CH_3)_2$), 1.62−1.67 (m, 4 H, β-CH_2), 3.53−3.61 (m, 4 H, α-CH_2), 4.65 (s, 2 H, benzyl-CH_2), 4.67 (s, 2 H, benzyl-CH_2), 7.51−7.93 (m, 14 H, phenyl-H), 8.12 (br. s, 1 H, pyrid-H), 8.56 (br. s, 1 H, pyrid-H), 9.01 (br. s, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 13.97, 22.54, 24.77, 25.86, 29.69, 31.62, 70.69, 70.82, 72.58, 72.71, 83.70, 120.91, 125.12, 125.45, 126.46, 127.15, 127.26, 127.63, 128.76, 135.23, 136.25, 138.27, 139.68, 139.91, 140.35, 141.20, 141.67, 142.21, 143.57, 147.68, 154.67. − FAB-MS; *m/z* $C_{98}H_{118}B_2N_2O_8$ (Xenon, CH_2Cl_2/MNBA)(%): 1475 (32), 1474(42), 1473 (39), 1472 (23), 1388 (26), 1081(43), 995 (25), 617 (29).

5-{4′′-Bromo-5′-(hexyloxymethyl)-[1,1′;3′,1′′]terphenyl-3-yl)-4′′-(4′′-bromo-5′-hexyloxymethyl-[1,1′;3′,1′′]terphenyl-4-yl}-[2,2′;6′,2′′]terpyridine (21): Synthesis and workup are similar to compound **19**: Compound **14** (4.00 g, 6.90 mmol), stannyl **20** (1.40 g, 3.46 mmol), toluene (100 mL), $(PPh_3)_4Pd$ (319 mg, 0.28 mmol), reflux for 48 h, aqueous KF (100 mL). The residue was loaded on activated basic aluminum oxide and purified by chromatography using CH_2Cl_2 as eluent. The product was obtained as a white crystalline solid (2.50 g, 67.2%). − M.p. 158−160 °C. − R_f = 0.21 (hexane/CH_2Cl_2, 1:1). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6 H, CH_3), 1.23−1.42 (m, 12 H, γ-, δ-, ε-CH_2), 1.66 (q, J = 6.8 Hz, 4 H, β-CH_2), 3.55 (t, J = 6.8 Hz, 4 H, α-CH_2), 4.62 (s, 4 H, benzyl-CH_2), 7.46−7.64 (m, 12 H, phenyl-H), 7.71−7.79 (m, 10 H, phenyl-H), 7.99 (t, J = 7.8 Hz, 1 H), 8.12 (dd, J = 2.2 and 8.3 Hz, 2 H, pyrid-H), 8.52 (d, J = 7.8 Hz, 2 H, pyrid-H), 8.74 (d, J = 8.3 Hz, 2 H, pyrid-H), 9.01 (d, J = 2.2 Hz, 2 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 14.02, 22.62, 25.93, 29.75, 31.69, 70.91, 72.71, 119.36, 121.26, 121.79, 124.92, 125.43, 125.57, 127.46, 127.98, 128.84, 131.92, 135.21, 136.06, 136.66, 137.99, 139.88, 140.25, 140.83, 141.22, 147.29, 154.92. − FAB-MS; *m/z* $C_{65}H_{61}Br_2N_3O_2$ (Xenon, CH_2Cl_2/MNBA)(%): 1074 (8), 1075(11), 1076 (16), 1077 (12), 1078 (11). − $C_{65}H_{61}Br_2N_3O_2$ (1076.02): calcd. C 72.56, H 5.71, N 3.91; found C 72.92, H; 5.85, N 3.60.

5-{5′-(Hexyloxymethyl)-4′′-(trimethylstannyl)-[1,1′;3′,1′′]terphenyl-3-yl}-4′′-{5′-(hexyloxymethyl)-4′′-(trimethylstannyl)-[1,1′;3′,1′′]terphenyl-4-yl}-[2,2′;6′,2′′]terpyridine (22): To a stirred solution of $NaSnMe_3$ in dry dimethoxyethane, **21** (1.5 g, 1.4 mmol) was added at room temp. as a solid, in portions for the period of 10 min. The mixture was then stirred for another 5 h. The solvent was removed under reduced pressure and the residue was loaded on activated aluminum oxide column, with hexane/CH_2Cl_2 (1:3) as eluent. The product, **22** was obtained as a white solid (420 mg, 24.3%). − M.p. 55−57 °C. − R_f = 0.25 (hexane/CH_2Cl_2, 1:1). − ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 9 H, $SnMe_3$), 0.89 (t, J = 6.8 Hz, 3 H, CH_3), 1.25−1.38 (m, 6 H, γ-, δ-, ε-CH_2), 1.67 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.56 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.65 (s, 2 H, benzyl-CH_2), 7.46−7.69 (m, 6 H, phenyl-H), 7.75−7.82 (m, 5 H, phenyl-H), 8.00 (t, J = 7.8 Hz, 1 H), 8.13 (dd, J = 2.2 and 8.3 Hz, 1 H, pyrid-H), 8.52 (d, J = 7.8 Hz, 1 H, pyrid-H), 8.74 (d, J = 8.3 Hz, 1 H, pyrid-H), 9.01 (d, J = 2.2 Hz, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = −9.53, 14.04, 22.63, 25.95, 29.79, 31.72, 70.83, 72.84, 121.02, 121.13, 125.23, 125.69, 126.51, 126.87, 127.28, 127.44, 127.97, 128.80, 134.97, 136.01, 136.29, 136.68, 137.88, 140.03, 141.06, 142.11, 147.50, 155.17. − MS; *m/z* $C_{71}H_{79}N_3O_2Sn$ (%): 1228 (5) $[M^+ - CH_3]$, 1066 (15), 918 (83), 817 (100), 717 (68), 359 (34), 165 (87). − HRMS ($C_{67}H_{68}N_3O_2Sn$) [loss of $C_4H_{12}Sn$]: calcd. 1066.43330; found 1066.43290; ($C_{65}H_{63}N_3O_2$) [loss of $C_6H_{18}Sn_2$]: calcd. 917.492003; found 917.49222. − $C_{71}H_{79}N_3O_2Sn$ (1243.80): calcd. C 68.56, H 6.40, N 3.38; found C 68.22, H 5.97, N 3.21.

5-{5′-(Hexyloxymethyl)-4′′-iodo-[1,1′;3′,1′′]terphenyl-3-yl}-4′′-{5′-(hexyloxymethyl)-4′′-iodo-[1,1′;3′,1′′]terphenyl-4-yl}-[2,2′;6′,2′′]-terpyridine (23): To a stirred solution of **22** (400 mg, 0.32 mmol) in dry CH_2Cl_2 (25 mL), I_2 (250 mg, 985 mmol) in CH_2Cl_2 (5 mL) was added for the period of 10 min at room temp., and the mixture was stirred for another 4 h. Then, saturated aqueous solution of KF (20 mL) was added followed by the addition of 2M aqueous solution of K_2CO_3. The phases were separated, the aqueous phase was washed twice with 50 mL of CH_2Cl_2 and finally the combined organic phase was washed successively by 25 mL KF solution and 25 mL saturated $Na_2S_2O_5$ solution. The solvent was removed under reduced pressure and the residue was loaded on activated aluminum oxide column, using CH_2Cl_2 as eluent. The product **23** was obtained as a white solid (351 mg, 93.4%). − M.p. 175−178 °C. − R_f = 0.18 (hexane/CH_2Cl_2, 1:1). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 1.25−1.43 (m, 6 H, γ-, δ-, ε-CH_2), 1.66 (q, J = 6.8 Hz, 2 H, β-CH_2), 3.55 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.62 (s, 2 H, benzyl-CH_2), 7.37−7.64 (m, 6 H, phenyl-H), 7.68−7.79 (m, 5 H, phenyl-H), 8.00 (t, J = 7.8 Hz, 1 H), 8.09 (dd, J = 2.2 and 8.3 Hz, 1 H, pyrid-H), 8.50 (d, J = 7.8 Hz, 1 H, pyrid-H), 8.72 (d, J = 8.3 Hz, 1 H, pyrid-H), 8.99 (d, J = 2.2 Hz, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 14.04, 22.63, 25.93, 29.76, 31.69, 70.90, 72.71, 93.29, 121.09, 124.83, 125.33, 125.59, 127.27, 127.44, 127.94, 128.79, 129.07, 134.92, 135.88, 136.78, 137.88, 140.24, 140.69, 140.86, 141.22, 147.49, 155.12. − MS; *m/z* $C_{65}H_{61}I_2N_3O_2$ (%): 1169 (30) $[M]^+$, 1043 (100), 943 (60), 918 (59), 817 (41), 731 (51), 212 (15), 128 (40). − HRMS ($C_{65}H_{61}I_2N_3O_2$): calcd. 1169.28510; found 1169.28520. − $C_{65}H_{61}I_2N_3O_2$ (1169.30): calcd. C 66.73, H 5.25, N 3.59; found C 67.19, H 5.23, N 3.56.

5-{3′-Hexyloxymethyl-5′-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2yl)-biphenyl-3yl}-4′′-{3′-{hexyloxymethyl}-5′-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2yl)-biphenyl-3yl}- [2,2′;6′,2′′]terpyridine (25): Synthesis and workup are similar to compound **19**: Compound **24** (1.3 g, 2.4 mmol), **20** (0.48 g, 1.2 mmol), toluene (50 mL), $(PPh_3)_4Pd$ (110 mg, 0.095 mmol), reflux for 48 h, aqueous KF (50 mL). The crude reaction mixture was loaded on column (silica gel) and with hexane/EtOAc (3:2) as eluent. The product **25** was obtained as white crystalline solid (590 mg, 49%). − M.p. 54−55

°C. − R_f = 0.14 (hexane/EtOAc, 4:1). − ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, J = 6.8 Hz, 3 H, CH_3), 1.13−1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.38 [s, 12 H, $(CH_3)_2C-C(CH_3)_2$], 1.65 (qu, J = 6.8 Hz, 2 H, β-CH_2), 3.46 (t, J = 6.8 Hz, 2 H, α-CH_2), 4.57 (s, 2 H, benzyl-CH_2), 7.72−7.78 (m, 6 H, phenyl-H), 7.99 (t, J = 7.8 Hz, 1 H, pyrid-H), 8.06 (s, 1 H, phenyl-H), 8.11 (dd, J = 1.9 and 8.2 Hz, 2 H, pyrid-H), 8.53 (d, J = 7.8 Hz, 1 H, pyrid-H), 8.74 (d, J = 8.2 Hz, 1 H, pyrid-H), 9.01 (d, J = 1.9 Hz, 1 H, pyrid-H). − ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.62, 24.88, 25.90, 29.74, 31.69, 70.71, 72.76, 83.93, 121.17, 127.01, 127.28, 127.98, 129.22, 132.65, 133.67, 135.06, 136.18, 137.97, 138.72, 139.86, 140.96, 147.41, 154.85, 155.08. − MS; *m/z* (%): 1017 (2) $[M]^+$, 941 (3), 864 (2), 394 (5), 277 (91), 262 (100), 183 (36). − FAB-MS (Xenon, CH_2Cl_2/MNBA); *m/z* (%): 1017 (53), 1018 (100) $[M + H]^+$, 1019 (67). − HRMS ($C_{65}H_{77}B_2N_3O_6$): calcd. 1017.599800; found 1017.5900. − $C_{65}H_{77}B_2N_3O$ (1017.96): calcd. C 76.69, H 7.62, N 4.13; found C 75.91, H 6.82, N 3.87.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Sfb 448, TP A1) and the Fonds der Chemischen Industrie, which are gratefully acknowledged.

[1] [1a] U. Lehmann, O. Henze, A. D. Schlüter, *Chem. Eur. J.* **1999**,*5*,854−859. − [1b] O. Henze, U. Lehmann, A. D. Schlüter, *Synthesis* **1999**, 683−687. − [1c] G. Manickam, A. D. Schlüter, *Synthesis* **2000**, 442−446.

[2] For related work with homoaromatic building blocks, for example, see: V. Hensel, A. D. Schlüter, *Chem. Eur. J.* **1999**, *5*, 421−429; V. Hensel, A. D. Schlüter, *Eur. J. Org. Chem*. **1999**, 451−458.

[3] O. Henze, D. Lentz, A. D. Schlüter, *Chem. Eur. J.* **2000**, *6*, 2362−2367.

[4] [4a] U. Lehmann, O. Henze, A. D. Schlüter, *Am. Chem. Soc. Polym. Mater. Sci. Eng.* **1999**, *80*, 165, 233. − [4b] O. Henze, U. Lehmann, A. D. Schlüter, *Am. Chem. Soc. Polym. Mater. Sci. Eng*. **1999**, 80, 231−232.

[5] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

[6] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504; *Angew. Chem. Int. Ed. Engl*. **1986**, *25*, 508.

[7] For an alternative route to compound **14** see reference 1c.

[8] N. V. Gerbeleu, V. B. Ari, J. Burgess, *Template Synthesis of Macrocyclic Compounds*, Wiley-VCH, Weinheim **1999**; *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**.

Received April 4, 2000
[O00170]