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Stereoselective Hydroboration of Diynes and Triyne to Give Products Containing Multiple Vinylene Bridges: A Versatile Application to Fluorescent Dyes and Light-Emitting Copolymers

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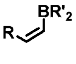
The Rh(I)-catalyzed hydroboration of a variety of aromatic diynes and a triyne afforded bis(boryl)- and tris(boryl)vinyl products. The hydroboration products underwent Suzuki cross-coupling reactions with a variety of substrates containing chromophore units to give fluorescent dye-substituted products. The hydroboration product also reacted with dibromoarenes to afford an oligomer with a vinylene unit along the oligomer backbone.

Introduction

Organic molecules bearing extended π-conjugated systems have received considerable attention due to their applications in molecular electronics[1] and photonics.[2] In particular, oligophenylenevinylene derivatives have been investigated extensively for applications in the fields of photo- and electroluminescence,[3] photovoltaics,[4] or nonlinear optics.[5] Although 1-alkenylboron derivatives are useful intermediates in organic synthesis on the basis of their applications in the Pd-catalyzed cross-coupling reaction with a variety of organic electrophiles,[6] little is known about the synthetic applications of such boron derivatives to the preparation of polymers or oligomers containing alternate vinylene units.[7] Although various polymerization methods for the synthesis of such polymers have been developed that include the Wittig reaction,[8] Heck reaction,[9] Gilch polymerization,[10] and Suzuki coupling reaction,[11] starting boranes such as **4** and **5** should be useful in the synthesis of fluorescent dyes and light-emitting copolymers using this methodology.



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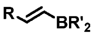

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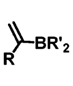

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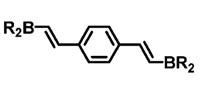

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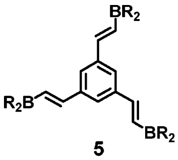

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Hydroboration provides a useful entry for the synthesis of vinylic boron compounds.[12] Although there has been significant progress using a variety of metal-catalyzed reactions to provide vinylboron derivatives of type **1**, **2**, or **3**,[13] aromatic compounds containing two[14] or three vinylborane substituents have received only little attention. We report here the preparation of a number of such compounds and their use in Suzuki cross-coupling reactions to prepare fluorescent dyes and light-emitting polymers.

Results and Discussion

Our initial experiment on the hydroboration of 1,3,5-triethynylbenzene with pinacolborane in the presence of Wilkinson's catalyst resulted in (*E*)-1,3,5-tris(borylvinyl)benzene **6** in very low yield (Table 1). Significant improvement in yield was achieved using Rh(CO)-

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(1) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

(2) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175.

(3) (a) Van Hutten, P. F.; Krasnikov, V. V.; Hadziioannou, G. *Acc. Chem. Res.* **1999**, *32*, 257. (b) Wong, M. S.; Li, Z. H.; Shek, M. F.; Chow, K. H.; Tao, Y.; D'Iorio, M. *J. Mater. Chem.* **2000**, *10*, 1805.

(4) (a) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467. (b) Gu, T.; Ceroni, P.; Marconi, G.; Armaroli, N.; Nierengarten, J.-F. *J. Org. Chem.* **2001**, *66*, 6432.

(5) (a) Cho, B. R.; Lee, S. J.; Lee, S. H.; Son, K. H.; Kim, Y. H.; Doo, J.-Y.; Lee, G. J.; Kang, T. I.; Lee, Y. K.; Cho, M.; Jeon, S.-J. *Chem. Mater.* **2001**, *13*, 1438. (b) Cho, B. R.; Park, S. B.; Lee, S. J.; Son, K. H.; Lee, S. H.; Lee, M.-J.; Yoo, J.; Lee, Y. K.; Lee, G. J.; Kang, T. I.; Cho, M.; Jeon, S.-J. *J. Am. Chem. Soc.* **2001**, *123*, 6421. (c) Brunel, J.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M. *Chem. Commun.* **2001**, 923.

(6) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219. (c) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314. (d) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018.

(7) Terao, T.; Tang, A.; Michels, J. J.; Krivokapic, A.; Anderson, H. L. *Chem. Commun.* **2004**, 56.

(8) Yang, Z.; Hu, B.; Karasz, F. E. *Macromolecules* **1995**, *28*, 6151.

(9) Jung, S.-H.; Kim, H. K.; Kim, S.-H.; Kim, Y. H.; Jeoung, S. C.; Kim, D. *Macromolecules* **2000**, *33*, 9277.

(10) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci. Part A: Polym. Chem.* **1966**, *4*, 1337.

(11) (a) Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531. (b) Schlüter, A. D. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1533.

(12) (a) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001. (b) Juliette, J. J. J.; Rutherford, D.; Horváth, I. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 2696. (c) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696. (d) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198.

(13) (a) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127. (b) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283. (c) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.

(14) (a) Chen, Y. K.; Lurain, A. E.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 12225. (b) Corriu, R. J.-P.; Deforth, T.; Douglas, W. E.; Guerrero, G.; Siebert, W. S. *Chem. Commun.* **1998**, 963.

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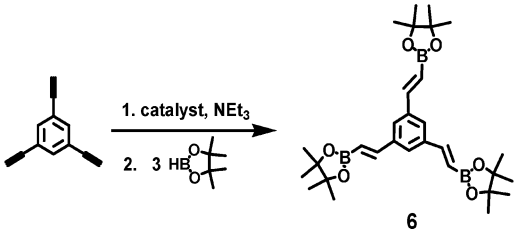
Table 1. Catalyzed Hydroboration of 1,3,5-Triethynylbenzene[a] and Catalyst Screening



6

entry	catalyst	solvent	yield (%)[b]
1	$Rh(PPh_3)_3Cl$	MC	5
2	$Rh(CO)(PPh_3)_2Cl$	MC	35
3	$[Rh(cod)Cl]_2$-4P^{i}Pr$_3$	cyclohexane	88
4	$[Rh(cod)Cl]_2$-4PCy$_3$	cyclohexane	8
5	$[Rh(cod)Cl]_2$-4P^{t}Bu$_3$	cyclohexane	5
6	$[Rh(cod)Cl]_2$-4PPh$_3$	cyclohexane	0
7	$[Rh(cod)Cl]_2$-(*t*)-BINAP	THF	0
8	$[Ir(cod)Cl]_2$-4P^{i}Pr$_3$	cyclohexane	45
9	$Pd(PPh_3)_4$	THF	15
10	Cp_2ZrHCl	MC	0

[a] To a solution of catalyst and 1,3,5-triethynylbenzene was added pinacolborane. The mixture was stirred at room temperature for 8 h. [b] Isolated yield.

$(PPh_3)_2Cl$ as the catalyst (entry 2). The catalyst generated in situ from $[Rh(cod)Cl]_2$ and P^{i}Pr$_3$ (4 equiv) gave **6** in excellent yield (entry 3). The use of Et_3N was found to be essential to achieve good yields and *trans*-selectivity in the case of some substrates. Use of different amines such as piperidine, pyrrolidine, Et_2NH, and ^{i}Pr$_2$NH resulted in unsatisfactory yields and gave a mixture of *E*- and *Z*-isomers. Screening a number of phosphine ligands during the hydroboration of 1,3,5-triethynylbenzene showed P^{i}Pr$_3$ to be superior in terms of yield and reaction rate (entries 4−7). An iridium catalyst, $[Ir(cod)Cl]_2$-4P^{i}Pr$_3$, was also effective, but led to a lower yield. The solvent is crucial in order to obtain a high yield and stereoselectivity, and cyclohexane was found to be the best solvent.

A variety of diynes and triynes were investigated. The data for the hydroboration in Table 2 were obtained with the Rh(I)-P^{i}Pr$_3$ catalyst under the optimum reaction conditions. The Rh-catalyzed hydroboration of 1,4-diethynylbenzene afforded (*E*)-bis(borylvinyl)benzene in high yield (entry 2). There is no great difference in *trans*-selectivity for the diynes and triyne studied (entries 1−4). Hydroboration of terminal alkynes using the same catalyst has been reported to give *cis*-1-alkenylboronates.[15] However, the hydroboration of 3,6-diethynyl-9-hexylcarbazole and 9,10-diethynylanthracene resulted in a mixture of products, *E*- and *Z*-isomers (entries 5, 6). Moreover, the 1,3-diethynylazulene underwent a hydroboration to form only the *Z*-isomer (entry 7). Although it has been well documented that the hydroboration of terminal or internal alkynes affords a variable product distribution depending on the nature of the catalyst and substrate,[16] it is quite remarkable that some of the diynes used in the present study reacted to give 100% *trans* product. The *trans* configuration was assigned on the basis of the characteristic large coupling constant of the vinylene unit ($^3J_{H-H}$ = 18.6−18.9 Hz).

To demonstrate the synthetic application of the obtained bis(borylvinyl) and tris(borylvinyl) products, compound **6** was chosen for a study of the Suzuki cross-coupling reaction with aryl bromides containing a chromophore unit. As expected, tris(borylvinyl)benzene is an efficient precursor for the cross-coupling reaction under mild conditions (Scheme 1). The Suzuki reaction of **6** with 9-bromoanthracene in the presence of $Pd(PPh_3)_4$ and aqueous K_2CO_3 afforded the trianthryl-substituted vinyl compound **13** in 55% yield. Compound **13** was obtained in 50% yield using a $PdCl_2(PPh_3)_2$-dppf, K_3PO_4 base, and DMF solvent system developed by Miyaura et al.[17] Compound **6** also reacted readily with 1-bromopyrene to afford **14**. The structures of compounds **13** and **14** were readily assigned by a combination of MS and ^{1}H and ^{13}C NMR spectroscopies and by comparison with analogous compounds.[18] A parent ion in the mass spectrum of **13** and **14** was observed at *m*/*z* 684 and 756, respectively. Two doublets and large coupling constants (16.8−17.4 Hz) in the ^{1}H NMR spectra of **13** and **14** are consistent with *trans*-vinylic hydrogens. The ^{13}C NMR spectra of **13** and **14** also exhibited the expected resonances. The amorphous *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline[19] underwent the Suzuki cross-coupling reaction with **6** to give **15**. The compound was purified by silica gel column chromatography and identified by NMR spectroscopy and elemental analysis. Furthermore, we found that **6** reacted with 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole[20] to provide the starburst product **16**, whose structure was confirmed by NMR spectroscopy and elemental analysis. Such π-electron starburst molecules have been extensively explored as either light-emitting materials or host materials in organic LEDs due to their good film-forming properties.[21] The absorption and emission spectra of **13**−**15** taken in methylene chloride, depicted in Figure 1, reveal the varying geometrical differences between the electronic ground state and the fluorescent singlet excited state (Table 3). The absorption spectra of **13** and **14** exhibit intense absorption bands at 390 and 384 nm, indicating that the electronic transitions are mostly $\pi\rightarrow\pi^*$, originating from the π-conjugation chain extending from the anthryl and pyrenyl units. Compounds **13** and **14** exhibit fluorescence emission in the blue (478 and 457 nm) wavelength region. Since the vinylene groups and the chromophore units are planar, their fluorescence spectra are characterized by a small Stokes shift (88 and 73 nm). The

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(15) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990.

(16) (a) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220. (b) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *Organometallics* **1993**, *12*, 589. (c) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. (d) Pergament, I.; Srebnik, M. *Org. Lett.* **2001**, *3*, 217. (e) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909. (f) Doi, H.; Kinoshita, M.; Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 1080.

(17) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001.

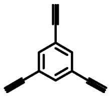
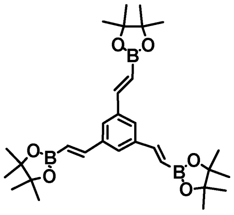
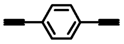
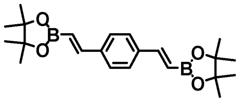
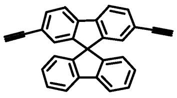
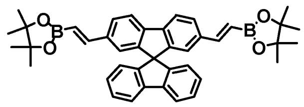
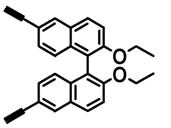
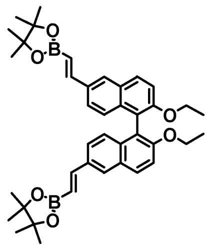
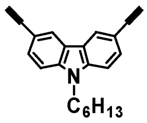
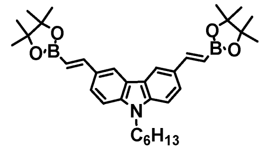
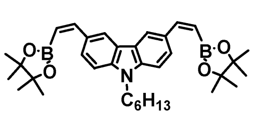
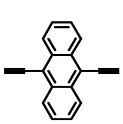
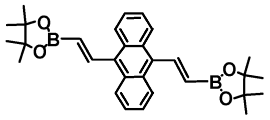
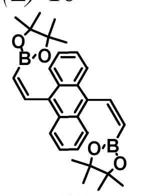
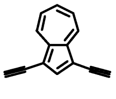
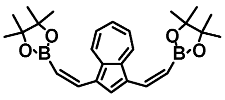
(18) (a) Hamaguchi, H.; Tasumi, M.; Karatsu, T.; Arai, T.; Tokumaru, K. *J. Am. Chem. Soc.* **1986**, *108*, 1698. (b) Gopal, V. R.; Rao, V. J.; Saroja, G.; Samanta, A. *Chem. Phys. Lett.* **1997**, *270*, 593.

(19) (a) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68. (b) Doi, H.; Kinoshita, M.; Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 1080. (c) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021.

(20) Lee, D. W.; Kwon, K.-Y.; Jin, J.-I.; Park, Y.; Kim, Y.-R.; Hwang I.-W. *Chem. Mater.* **2001**, *13*, 565.

(21) (a) Kuwabara, Y.; Ogawa, H.; Inada, N.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677. (b) Wu, I.-Y.; Lin, J. T.; Tao, Y.-T.; Balasubramaniam, E. *Adv. Mater.* **2000**, *12*, 668. (c) Gao, Z.; Lee, C. S.; Bello, I.; Lee, S. T.; Chen, R.-M.; Luh, T.-Y.; Shi, J.; Tang, C. W. *Appl, Phys. Lett.* **1999**, *74*, 865.

Table 2. Hydroboration of Diynes and a Triyne Catalyzed by Rh(I)

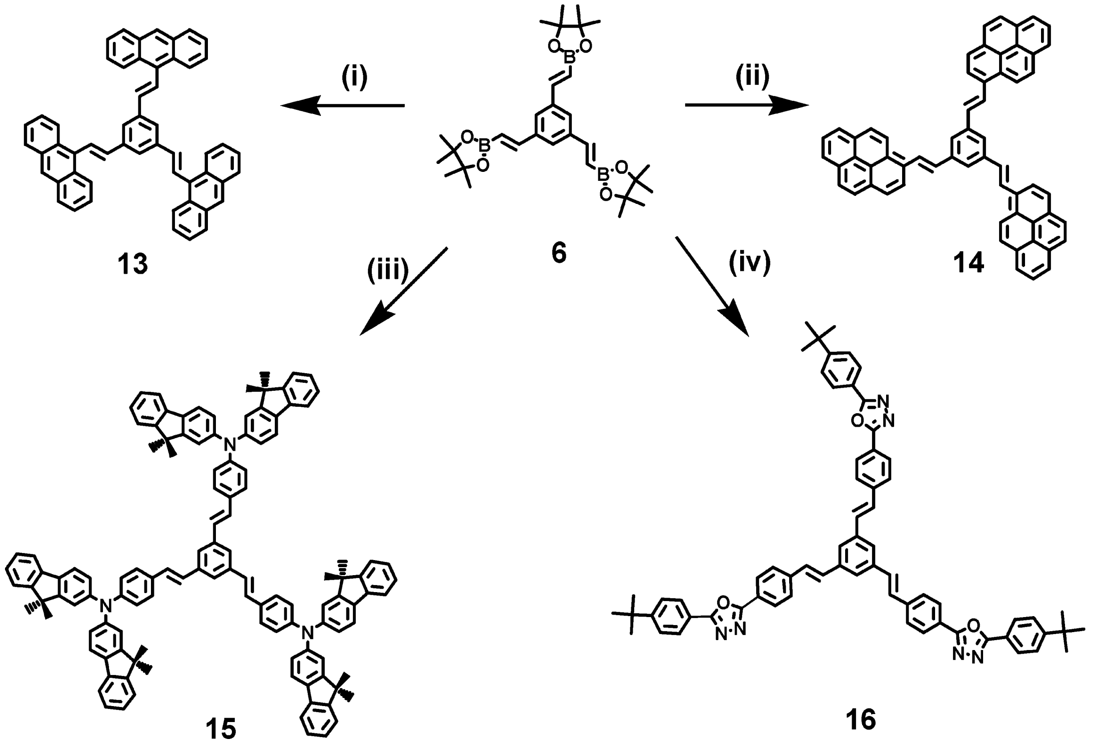
entry	alkyne	product	(hr, yield)[a]
1		 **6**	4 h, 85%
2		 **7**	4 h, 88%
3		 **8**	24 h, 45%
4		 **9**	6 h, 74%
5		 80% *(E)*-**10**  20% *(Z)*-**10**	8 h, 84%
6		 60% *(E)*-**11**  40% *(Z)*-**11**	8 h, 78%
7		 **12**	8 h, 38%

[a] hr = reaction time; yield = isolated yield.

absorption and emission spectroscopic properties of **15** and **16** are basically similar to those of **13** and **14**, suggesting that the loss of fine structures results from the conjugation of the phenyl groups with the vinylene chromophore units. The somewhat large Stokes shift (120 nm) of **15** most likely stems from the excited-state-induced coplanarity of the amorphous chromophore substituents.

Another synthetic utility of the hydroboration product was demonstrated by transformation of 2,2′-diethoxy-6,6′-bis(borylvinyl)-1,1′-binaphthalene **9** to chiral ditopic ligands. Compound **17** was prepared by Suzuki coupling

Scheme 1[a]



[a] Reaction conditions: (i) 9-bromoanthracene, 55% yield; (ii) 1-bromopyrene, 61% yield; (iii) *N*,*N*-bis(9,9-dimethylfluorene-2-yl)-4-bromoaniline, 47% yield; (iv) 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 48% yield. All the reactions were carried out in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in THF.

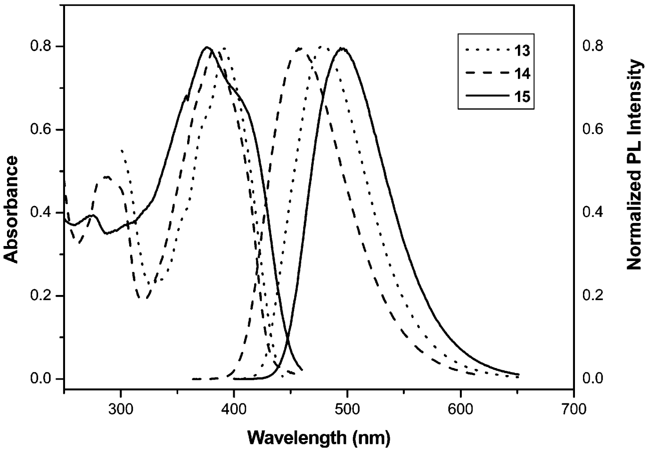


Figure 1. UV–visible spectra and PL spectra of **13**–**15**.

Table 3. Photophysical Data for 13–16 in CH_2Cl_2 at Room Temperature[a]

	UV–vis		emission	
compound	λ_{max} (nm)	ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)	E_{em} (nm)	Φ_{em}[b]
13	390	6240	478	0.12
14	384	12 420	457	0.22
15	376	19 240	496	0.26
16	349	18 840	406	0.34

[a] Concentration of compounds is in the range 10^{-4}–10^{-5} mol dm^{-3}. [b] Quinine sulfate in 1 M H_2SO_4 ($\Phi_{fl} = 0.55$) was used as quantum yield standard.

reaction between **9** and 4-bromopyridine hydrochloride in 32% yield. The compound had been synthesized earlier by Heck coupling reaction between 4-vinylpyridine and 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene by Lin.[22] Also the bis(borylvinyl)binaphthalene ligand **9** readily reacted with 5-bromo-2,2′-bipyridine to give **18** (Scheme 2). Many binuclear Ru(II) and Os(II) complexes containing two bipyridine units connected by various bridges have been reported.[23]

Preliminary results with the well-established synthesis of alternating copolymers using the Suzuki coupling reaction[24] encouraged us to extend the new synthetic methodology to copolymers containing vinylene units along the polymer backbone. Most remarkably, the Suzuki coupling reaction of 2,2′-diethoxy-6,6′-bis(borylvinyl)-1,1′-binaphthalene **9** with 9,10-dibromoanthracene afforded the fully conjugated oligomer **19** in 35% yield (Scheme 3). The molecular weight and the polydispersity of the oligomer, determined by gel-permeation chromatography using a polystyrene standard, were in the ranges 2450–2550 and 1.9, respectively. The oligomer was soluble in common solvents such as $CHCl_3$, CH_2Cl_2, and THF. The ^1H NMR spectrum of **19** shows a resonance at 6.18 ppm with a large coupling constant ($J_{H-H} = 18.6$ ppm) due to a vinylic hydrogen. The ^{13}C NMR spectrum of the oligomer shows the expected resonances in the aromatic region. Such multiple C–C bond formation by the stepwise Suzuki cross-coupling reaction, providing a route to PPV-based molecular wires, was recently reported by Anderson and coworkers.[25]

In summary, the first hydroboration of a variety of diynes and a triyne to afford bis- and trisboryl-substituted vinyl compounds with high stereoselectivity

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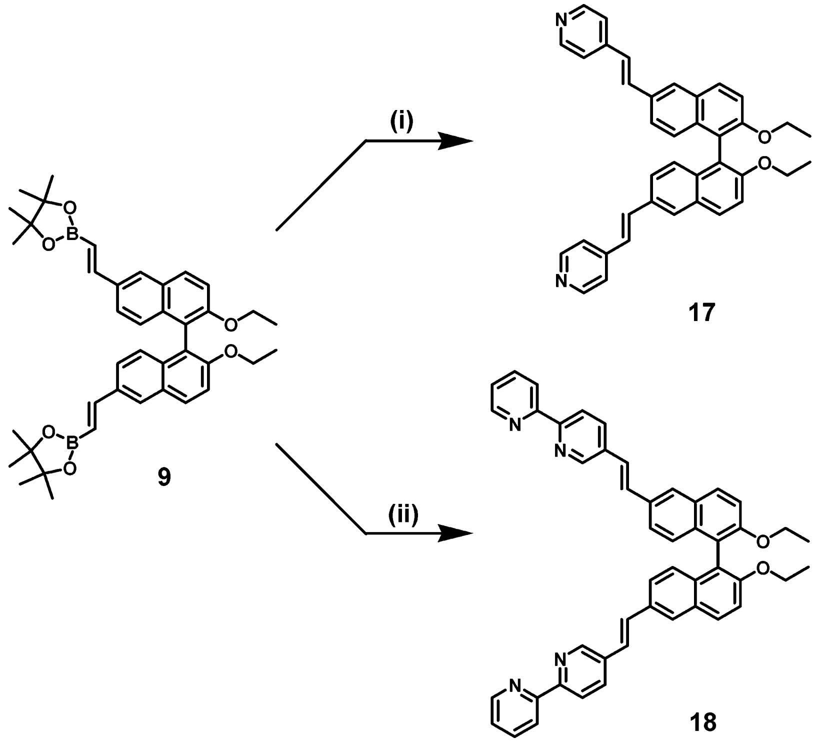
[22] Cui, Y.; Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 6014.

[23] Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553.

[24] (a) Morin, J.-F.; Leclerc, M. *Macromolecules* **2002**, *35*, 8413. (b) Lim, E.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 4288. (c) Miyaura, N.; Yanagi, T.; Suziki, A. *Synth. Commun.* **1981**, *11*, 513.

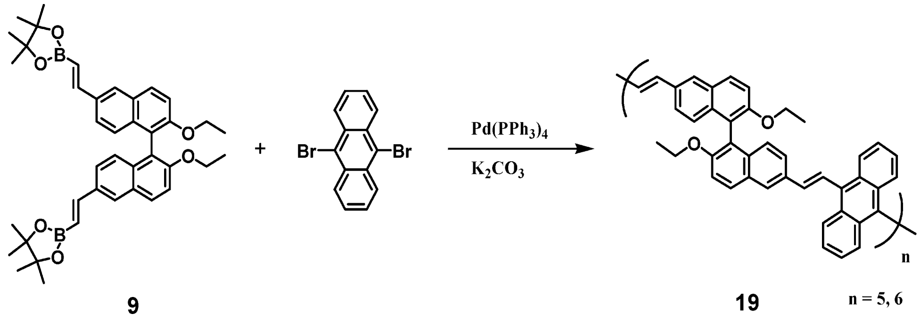
[25] Terao, J.; Tang, A.; Michels, J. J.; Krivokapic, A.; Anderson, H. L. *Chem. Commun.* **2004**, 56.

Scheme 2[a]



[a] Reaction conditions: (i) 4-bromopyridine, $Pd(PPh_3)_4$, K_2CO_3, toluene, reflux, 24 h, 32% yield; (ii) 5-bromo-2,2′-pyridine, $Pd(PPh_3)_4$, K_2CO_3, toluene, reflux, 24 h, 19% yield.

Scheme 3



is presented. The hydroboration products underwent the Suzuki cross-coupling reaction with a variety of substrates containing chromophore units to give tris-chromophore-substituted products. The mild and easy access of the isomerically distinct hydroboration protocol opens access to a host of potential subsequent transformations toward the construction of a large number of emitting copolymers. Additional investigations into the photophysical properties and novel synthesis of a variety of copolymers are now being undertaken in this laboratory.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene, THF, and cyclohexane were freshly distilled from sodium benzophenone. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 96.00 MHz, respectively. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 25 UV−visible spectrophotometer and a Perkin-Elmer LS fluorescence spectrometer, respectively. Pinacolborane, P^iPr_3, 1-bromopyrene, 9-bromoanthracene, 9,10-dibromoanthracene, and 4-bromopyridine hydrochloride were purchased from Aldrich Chemical Co. $[Rh(cod)Cl]_2$,[26] 1,4-diethynylbenzene,[27] 1,3,5-triethynylbenzene,[28] 2,7-diethynyl-9,9-dimethylfluorene,[29] 3,6-diethynyl-9-hexylcarbazole,[30] 2,2′-diethynyl-9,9′-spirobifluorene,[31] 1,3-diethynylazulene,[32] 9,10-diethynylanthracene,[33] 2,2′-diethoxy-6,6′-diethynyl-1,1′-binaphthalene,[34] *N*,*N*-bis(9,9-dimethylfluorene-2-yl)-4-bromoaniline,[19] 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-

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(26) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

(27) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(28) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981.

(29) Thomas, K. R. J.; Lin, J. T.; Lin, Y.-Y.; Tsai, C.; Sun, S.-S. *Organometallics* **2001**, *20*, 2262.

(30) Beginn, C.; Garžulevičius, J. V.; Strohriegl, P.; Simmerer, J.; Haarer, D. *Macromol. Chem. Phys.* **1994**, *195*, 2353.

(31) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924.

(32) Fabian, K. H. H.; Elwahy, A. H. M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2855.

(33) Kobayashi, E.; Jiang, J.; Ohta, H.; Furukawa, J. *J. Polym. Sci. A: Polym. Chem.* **1990**, *28*, 2641.

(34) Onitsuka, K.; Harada, Y.; Takei, F.; Takahashi, S. *Chem. Commun.* **1998**, 643.

1,3,4-oxadi-azole,[20] and 5-bromo-2,2′-bipyridine[35] were prepared according to procedures reported in the literature.

General Procedure for Hydroboration of Diynes and a Triyne. To a stirred cyclohexane solution (10 mL) of $[Rh(cod)Cl]_2$ (0.022 g, 0.045 mmol), NEt_3 (0.7 mL, 5 mmol), P^iPr_3 (0.035 mL, 0.18 mmol), and pinacolborane (0.44 mL, 3 mmol) was added 1,3,5-triethynylbenzene (0.15 g, 1 mmol) dissolved in cyclohexane (10 mL) at room temperature. The solution was stirred for 8 h at that temperature. The solvent was removed in vacuo. The pure product **6** was obtained by silica gel column chromatography (eluent: methylene chloride/hexane, 2:1) as a white solid in 88% yield.

1,3,5-Tris[2-(pinacolboryl)vinyl]benzene (6). Mp: 225 °C. ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 3H, Ph-*H*), 7.37 (d, 3H, J = 18.9 Hz, C*H*=), 6.16 (d, 3H, J = 18.9 Hz, =C*H*-B), 1.32 (s, 36H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.7, 138.2, 126.1, 116.9, 83.5, 24.8. ^{11}B NMR ($CDCl_3$): δ 15.8. MS: m/z 534 [M$^+$]. Anal. Calcd for $C_{30}H_{45}O_6B_3$: C, 67.46; H, 8.49. Found: C, 67.18; H, 8.24.

1,4-Bis[2-(pinacolboryl)vinyl]benzene (7). Mp: 195 °C. ^{1}H NMR ($CDCl_3$): δ 7.45 (s, 4H, Ph-*H*), 7.36 (d, 2H, J = 18.6 Hz, C*H*=), 6.17 (d, 2H, J = 18.6 Hz, =C*H*-B), 1.31 (s, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4, 138.3, 128.4, 119.6, 83.6, 24.9. ^{11}B NMR ($CDCl_3$): δ 16.4. MS: m/z 382 [M$^+$]. Anal. Calcd for $C_{22}H_{32}O_4B_2$: C, 69.15; H, 8.44. Found: C, 68.97; H, 8.26.

2,7-Bis[2-(pinacolboryl)vinyl]-9,9′-spirobifluorene (8). Mp: 208 °C. ^{1}H NMR ($CDCl_3$): δ 7.83 (d, 2H, J = 7.8 Hz), 7.76 (d, 2H, J = 7.2 Hz), 7.50 (d, 2H, J = 7.8 Hz), 7.34 (t, 2H, J = 7.5 Hz), 7.24 (d, 2H, J = 18.9 Hz, C*H*=), 7.08 (t, 2H, J = 7.5 Hz), 6.86 (s, 2H), 6.71 (t, 2H, J = 7.2 Hz), 5.96 (d, 2H, J = 18.9 Hz, =C*H*-B), 1.22 (s, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.8, 149.2, 148.8, 142.0, 141.7, 137.4, 128.4, 128.1, 127.1, 125.0, 124.4, 123.4, 120.1, 119.8, 83.1, 26.8. ^{11}B NMR ($CDCl_3$): δ 16.0. MS: m/z 620 [M$^+$]. Anal. Calcd for $C_{41}H_{42}O_4B_2$: C, 79.38; H, 6.82. Found: C, 79.19; H, 6.65.

2,2′-Diethoxy-6,6′-bis[2-(pinacolboryl)vinyl]-1,1′-binaphthalene (9). Mp: 198 °C. ^{1}H NMR ($CDCl_3$): δ 7.91 (d, 2H, J = 9.0 Hz), 7.85 (s, 2H), 7.53 (d, 2H, J = 18.6 Hz, C*H*=), 7.48 (d, 2H, J = 9.0 Hz), 7.39 (s, 2H), 7.08 (d, 2H, J = 9.0 Hz), 6.15 (d, 2H, J = 18.6 Hz, =C*H*-B), 4.04 (m, 4H, OC*H*$_2$), 1.31 (s, 24H, C*H*$_3$), 1.05 (t, 6H, J = 6.9 Hz, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.7, 148.9, 137.8, 136.4, 134.0, 132.9, 129.4, 126.5, 126.2, 125.3, 123.8, 120.7, 83.2, 65.3, 25.3, 15.1. ^{11}B NMR ($CDCl_3$): δ 15.8. MS: m/z 646 [M$^+$]. Anal. Calcd for $C_{40}H_{48}B_2O_6$: C, 74.32; H, 7.48. Found: C, 74.12; H, 7.35.

3,6-Bis[2-(pinacolboryl)vinyl]-9-hexylcarbazole (10). Mp: 167 °C. ^{1}H NMR ($CDCl_3$): δ 8.12 (s, 2H, Ph-*H*), 7.60 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 18.9 Hz, C*H*=), 7.27 (d, 2H, J = 8.4 Hz), 6.14 (d, 2H, J = 18.9 Hz, =C*H*-B) {*cis*-**10**, 6.02 (d, J = 15.0 Hz, =C*H*-B)}, 4.18 (t, 2H, J = 6.6 Hz, NC*H*$_2$), 1.49−0.85 (m, 11H), 1.23 (s, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.5, 141.3, 140.8, 130.0, 129.1, 125.0, 123.0, 119.8, 82.8, 45.8, 31.4, 28.9, 24.6, 23.3, 22.4, 16.2. ^{11}B NMR ($CDCl_3$): δ 16.8. MS: m/z 555 [M$^+$]. Anal. Calcd for $C_{34}H_{47}O_4NB_2$: C, 73.53; H, 8.53. Found: C, 73.26; H, 8.40.

9,10-Bis[2-(pinacolboryl)vinyl]anthracene (11). Mp: 201 °C. ^{1}H NMR ($CDCl_3$): δ 8.35 (m, 4H, *anthryl*), 7.47 (m, 4H, *anthryl*), 7.45 (d, 2H, J = 18.6 Hz, C*H*=), 5.61 (d, 2H, J = 18.6 Hz, =C*H*-B) {*cis*-**11**, 6.02 (d, J = 14.1 Hz, =C*H*-B)}, 1.28 (s, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.7, 133.9, 131.7, 129.0, 126.3, 125.4, 83.7, 25.3. ^{11}B NMR ($CDCl_3$): δ 16.0. MS: m/z 482 [M$^+$]. Anal. Calcd for $C_{30}H_{36}O_4B_2$: C, 74.72; H, 7.52. Found: C, 74.53; H, 7.37.

1,3-Bis[2-(pinacolboryl)vinyl]azulene (12). Mp: 175 °C. ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 1H, Ph-*H*), 8.31 (d, 2H, J = 10.2 Hz), 7.77 (d, 2H, J = 15.0 Hz, C*H*=), 7.53 (t, 1H, J = 9.6 Hz), 7.11 (dd, 2H, J = 10.2 Hz, J = 9.6 Hz), 5.65 (d, 2H, J = 15.0 Hz, =C*H*-B), 1.23 (s, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.9, 139.2, 138.5, 135.1, 134.0, 133.7, 127.9, 124.5, 83.1, 24.7. ^{11}B NMR ($CDCl_3$): δ 18.4. MS: m/z 432 [M$^+$]. Anal. Calcd for $C_{26}H_{34}O_4B_2$: C, 72.26; H, 7.93. Found: C, 72.08; H, 7.80.

1,3,5-Tris[2-(anthryl)vinyl]benzene (13). To a stirred THF solution (25 mL) of **6** (0.15 g, 0.28 mmol), 9-bromoanthracene (0.24 g, 0.93 mmol), and $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol) was added degassed K_2CO_3(aq) (2 M, 2.1 mL, 4.2 mmol). The solution was heated at reflux for 24 h. After cooling the solution, H_2O (10 mL) was added. The organic layer was separated and dried with $MgSO_4$. The solvent was removed in vacuo. The pure product **13** was obtained by silica gel chromatography (eluent: methylene chloride/hexane, 1:5) as a white solid in 55% yield. Mp: 262 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.48−8.44 (m, 6H, *anthryl*), 8.13 (d, 3H, J = 17.4 Hz, C*H*=), 8.07−8.03 (m, 9H, *anthryl*), 7.98 (s, 3H, *Ph*), 7.54−7.50 (m, 12H, *anthryl*), 7.13 (d, 3H, J = 17.4 Hz, =C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.4, 134.2, 133.6, 132.6, 131.6, 129.8, 128.8, 127.5, 127.2, 125.9, 125.5. MS: m/z 684 [M$^+$]. Anal. Calcd for $C_{54}H_{36}$: C, 94.70; H, 5.30. Found: C, 94.46; H, 5.21.

1,3,5-Tris[2-(pyrenyl)vinyl]benzene (14). Compound **14** was prepared using the same procedure as that described for **13** except that 1-bromopyrene was used instead of 9-bromoanthracene. The pure product **14** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 1:1) as a white solid in 61% yield. Mp: 238 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.57 (d, 3H, J = 8.7 Hz, *pyrenyl*), 8.38 (d, 3H, J = 8.7 Hz, *pyrenyl*), 8.32 (d, 3H, J = 16.8 Hz, C*H*=), 8.22−8.02 (m, 21H, *pyrenyl*), 7.70 (s, 3H, *Ph*), 7.45 (d, 3H, J = 16.8 Hz, =C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.9, 157.1, 148.1, 138.6, 132.0, 131.8, 131.6, 131.2, 131.0, 128.6, 127.9, 127.6, 127.2, 126.5, 126.2, 125.3, 125.1, 124.4, 124.1, 122.3. MS: m/z 756 [M$^+$]. Anal. Calcd for $C_{60}H_{36}$: C, 95.21; H, 4.79. Found: C, 94.88; H, 4.67.

1,3,5,-Tris{2-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-anilinyl]vinyl}benzene (15). Compound **15** was prepared using the same procedure as that described for **13** except that *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline was used instead of 9-bromoanthracene. The pure product **15** was isolated by silica gel chromatography (eluent: methylene chloride/hexane, 1:3) as a pale yellow solid in 47% yield. Mp: 230 °C. ^{1}H NMR ($CDCl_3$): δ 7.65−7.16 (m, 60H), 7.14 (d, 3H, J = 16.8 Hz, =C*H*), 1.43 (s, 36H, C−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.2, 153.6, 147.7, 147.2, 139.0, 138.5, 138.1, 134.4, 131.5, 127.8, 127.4, 127.1, 126.7, 126.1, 123.8, 123.2, 122.9, 120.9, 120.6, 119.4, 46.9, 27.1. Anal. Calcd for $C_{120}H_{99}N_3$: C, 91.04; H, 6.30. Found: C, 90.83; H, 6.21.

1,3,5-Tris{2-[phenyl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]vinyl}benzene (16). Compound **16** was prepared using the same procedure as that described for **13** except 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole was used instead of 9-bromoanthracene. The pure product **16** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 1:3) as a white solid in 48% yield. Mp: 195 °C. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, 6H, J = 8.1 Hz), 8.02 (d, 3H, J = 16.8 Hz, C*H*=), 7.96 (d, 6H, J = 8.1 Hz), 7.67 (d, 6H, J = 8.1 Hz), 7.59 (s, 3H, *Ph*), 7.52 (d, 6H, J = 7.5 Hz), 7.53 (d, 6H, J = 7.5 Hz), 7.12 (d, 3H, J = 16.8 Hz, =C*H*), 1.37 (s, 27H, ^{t}*Bu*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.7, 164.4, 155.5, 145.5, 140.7, 137.2, 134.5, 127.5, 127.0, 126.8, 126.3, 126.0, 122.9, 121.2. 31.3, 25.0. MS: m/z 985 [M$^+$]. Anal. Calcd for $C_{66}H_{60}N_6O_3$: C, 80.46; H, 6.14. Found: C, 80.22; H, 6.02.

2,2′-Diethoxy-1,1′-binaphthalene-6,6′-bis(4-vinylpyridine) (17). Compound **17** was prepared using the same procedure as that described for **13** except that compound **9** and 2 equiv of 4-bromopyridine hydrochloride were used instead of compound **6** and 3 equiv of 9-bromoanthracene. The pure product **17** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 2:1 (R_f = 0.1)) in 32% yield. The spectroscopic data of **17** were identical to those of Lin.[21]

2,2′-Diethoxy-1,1′-binaphthalene-6,6′-bis(5-vinyl-2,2′-bipyridine) (18). Compound **18** was prepared using the same procedure as that described for **17** except that 5-bromo-2,2′-

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(35) Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, *67*, 443.

bipyridine was used instead of 4-bromopyridine hydrochloride. The pure product **18** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 2:1 ($R_f = 0.1$)) as a pale yellow solid in 19% yield. Mp: 253 °C. ^{1}H NMR ($CDCl_3$): δ 8.78 (s, 2H), 8.68 (d, 2H, $J = 3.6$ Hz), 8.40 (d, 2H, $J = 8.4$ Hz), 8.39 (d, 2H, $J = 8.4$ Hz), 8.00 (d, 2H, $J = 8.4$ Hz), 7.86 (d, 2H, $J = 9.0$ Hz), 7.94 (s, 2H), 7.81 (dd, 2H, $J = 8.4$ Hz, $J = 1.8$ Hz), 7.50 (d, 2H, $J = 9.0$ Hz), 7.44 (d, 2H, $J = 9.0$ Hz), 7.38 (d, 2H, $J = 17.1$ Hz, *vinyl*), 7.32 (dd, 2H, $J = 3.6$ Hz, $J = 1.8$ Hz), 7.17 (d, 2H, $J = 9.0$ Hz), 7.15 (d, 2H, $J = 17.1$ Hz, *vinyl*), 4.08 (m, 4H, OCH_2), 1.09 (t, 6H, $J = 6.9$ Hz, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.1, 155.0, 154.9, 149.5, 148.1, 137.0, 134.2, 133.5, 132.08, 129.7, 129.43, 128.5, 127.5, 126.0, 124.0, 123.5, 122.4, 121.3, 121.0, 120.7, 116.3, 115.9, 65.3, 15.0. MS: m/z 702 [M^+]. Anal. Calcd for $C_{48}H_{38}N_4O_2$: C, 82.03; H, 5.45. Found: C, 81.87; H, 5.32.

Oligo(2,2′-diethoxy-6,6′-divinyl-1,1′-binaphthalenyl-9,10-anthracene) (19). 2,2′-Diethoxy-6,6′-bis(borylvinyl)-1,1′-binaphthalene (0.24 g, 0.37 mmol) and 9,10-dibromoanthracene (0.12 g, 0.37 mmol) were dissolved in THF (20 mL). The palladium complex $Pd(PPh_3)_4$ (0.03 g) and degassed K_2CO_3 (5.25 mL, 1 M) were added to the mixture. The reaction mixture was heated at reflux for 48 h. An excess of bromobenzene (0.040 g, 0.25 mmol) was added as an end-capper. After it was refluxed for 10 h, the reaction mixture was cooled to about 40 °C and added to a stirred mixture of MeOH (100 mL) and 6 mL of 1 N aqueous HCl. The oligomer was collected by filtration and reprecipitated from MeOH and acetone. The oligomer was extracted by a Soxhlet in acetone for 1 day. The extract was dried in vacuo. The final product **19** was obtained as a yellow solid in 35% yield. Mp: 277 °C. ^{1}H NMR ($CDCl_3$): δ 7.92−7.06 (m, 20H, *aromatic and vinyl*), 6.18 (d, 2H, $J = 18.6$ Hz, *vinyl*), 4.12 (m, 4H, OCH_2), 1.05 (m, 6H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.0, 137.3, 134.1, 132.7, 132.3, 131.6, 130.6, 129.5, 128.3, 127.4, 126.8, 126.4, 126.0, 125.2, 124.6, 122.7, 120.8, 117.2, 115.2, 65.2, 16.1. Anal. Calcd for $(C_{42}H_{32}O_2)_n$: C, 88.51; H, 5.71. Found: C, 88.17; H, 5.58. The number-average molecular weights (M_n) was determined by gel permeation chromatography (GPC) with an HPLC Waters 510 using a series of monodisperse polystyrenes as standard in THF. The number-average molecular weight (M_n) was 2500 ($M_w/M_n = 1.9$).

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