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Synthesis and Characterization of New Linear π-Conjugated Molecules Containing Bis(ethynylpyridine) Units with a Benzothiadiazole Spacer

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Three novel 4,7-bis(n-pyridylethynyl)-2,1,3-benzothiadiazoles (n = 2, 3, and 4) were synthesized by using the Sonogashira cross-coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole with the corresponding ethynylpyridines in the presence of a Pd(II) catalyst. The viologen analogues were also prepared by methylation of pyridyl nitrogen atoms. X-ray structure analysis of these compounds revealed the linear molecular structures with unusual columnar crystal structures. Insertion of a benzothiadiazole moiety into the acetylene−pyridine skeleton brings about a large increase in electron affinity and the bispyridyl compounds obtained here show high fluorescence quantum yields.

Long π-conjugated molecules with rigid structures have attracted much attention due to their potential use as molecular wires.[1] Molecules with pyridyl substituents at the terminal positions are expected to be alligator clips for the synthesis of molecular devices.[2] They can also afford interesting supramolecular architectures by intermolecular interactions such as hydrogen bonding[3] and coordination with metals.[4] Supramolecular species formed by self-assembly exhibit interesting properties such as luminescence,[5] redox activity,[6] and magnetism.[7] In the dipyridyl compounds the structures and properties can be modified by changing the nitrogen positions and spacer groups. For example, we have found that dipyridyl acetylenes afford one-dimensional molecular tapes by hydrogen bonding complexation with chloranilic acid, whose structures and electronic states are strongly dependent on the nitrogen positions.[3a,8] The 1,4-dipyridylbutadiyne molecules have often been used to construct interesting supramolecular structures.[4,9] In this context, we have now introduced a benzothiadiazole ring into the skeleton of 1,4-dipyridylbutadiyne. There are the following advantages of the introduction of this group: First, this heterocycle is electron withdrawing and the compounds bearing this ring are possible candidates for electron carriers. The electron accepting conjugated molecules are also of interest from the viewpoint of the NDR (negative differential resistance) behavior since recent studies have shown that oligo (phenyleneethyl-

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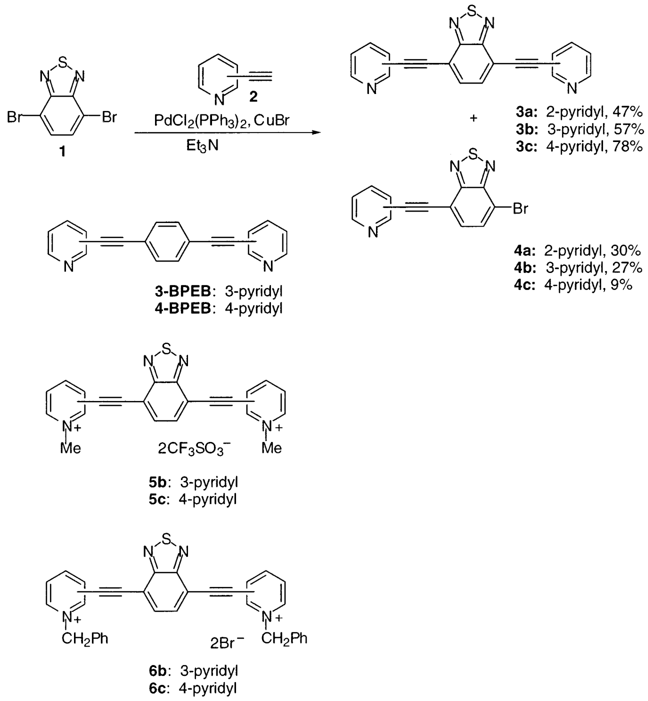
ene)s containing an electron-withdrawing nitro group can be used as active redox centers responsible for the NDR behavior in semiconductor devices.[10] Second, thiadiazole-containing compounds are expected to afford well-ordered crystal structures due to the highly polarized properties leading to intermolecular interactions such as heteroatom contacts or $\pi\cdots\pi$ interactions.[11] Third, the compounds containing thiadiazole rings are well-known as strong fluorescent materials.[12] Highly fluorescent π-conjugated molecules are of interest for application purposes such as EL (electroluminescence) devices[13] and single molecular detection.[14] We report here the synthesis, structures, and properties of a new linear π-conjugated system with a benzothiadiazole spacer between the ethynylpyridines. In addition, their dimethylated compounds and related dications have been prepared as viologen analogues. Viologens have been widely used in the basic study of electrochemical,[15] photoelectrochemical,[16] and electrochromic materials[17] and solar energy conversion,[18] and their π-extended analogues have been of much interest.[19]

Results and Discussion

Preparation. A convenient one-pot consecutive Sonogashira cross-coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole (**1**)[20] with 2-, 3-, and 4-ethynylpyridines (**2**)[21] in the presence of $PdCl_2(PPh_3)_2$ and CuBr catalyst in Et_3N at 90 °C produced biscoupling products **3a**−**c** along with monocoupling products **4a**−**c**. The products were isolated and purified by column chromatography on silica gel with chloroform−ethyl acetate as eluent. Monobrominated compounds **4a**−**c** obtained as byproducts are expected to be key starting materials to afford longer conjugated oligomers. The pyridinium compounds of **3b** and **3c** were obtained as trifluoromethanesulfonate (TfO) salts **5b** and **5c** in high yields by mixing **3b** and **3c** with MeOTf (1:3 stoichiometry) in dichloromethane, respectively. The benzylated compounds **6b** and **6c** were also obtained in good yields by mixing **3b** and **3c** with $PhCH_2Br$ (1:3 stoichiometry) in dichloromethane, respectively. The methyaltion reaction of the 2,2′-dipyridyl derivative has not been successful probably due to its weak basicity.

SCHEME 1



Crystal Structures. Although the crystal structures of rigid long molecules are of interest,[1] there are limited numbers of reports on X-ray structure analysis of long π-conjugated molecules probably due to the difficulties of obtaining single crystals. The single crystals of **3** suitable for X-ray analysis were obtained from recrystallization from a mixed solvent of acetonitrile−ethyl acetate. The molecules **3a**−**c** are linear with 16.6−18.3 Å lengths and a little twisted with 1.5−15.2° of the angles between the pyridine and benzothiadiazole planes. The crystal structure of **3a** with the space group of the orthorhombic *Pbcn* is shown in Figure 1, where half of a molecule is independent. The molecules are stacked to afford unusual two-dimensional columns where the distance between the molecular planes is 3.79 Å. The columns run in two directions at 45°. No short heteroatom contacts such as S···N are observed. The crystal structures of **3b** and **3c** are similar to that of **3a**, although the space groups are different. Molecule **3b** crystallizes in the monoclinic *Cc* space group with two independent molecules. The noncentrosymmetric space group is interesting from the standpoint of nonlinear optical properties. Molecule **3c** crystallizes in the monoclinic $P2_1/a$ space group with one independent molecule. This result indicates that interheteroatom interactions are not involved in the crystallization and the nitrogen positions do not affect the crystal structures, suggesting that $\pi\cdots\pi$ intermolecular interactions are important for the crystallization of rigid long π-conjugated molecules.

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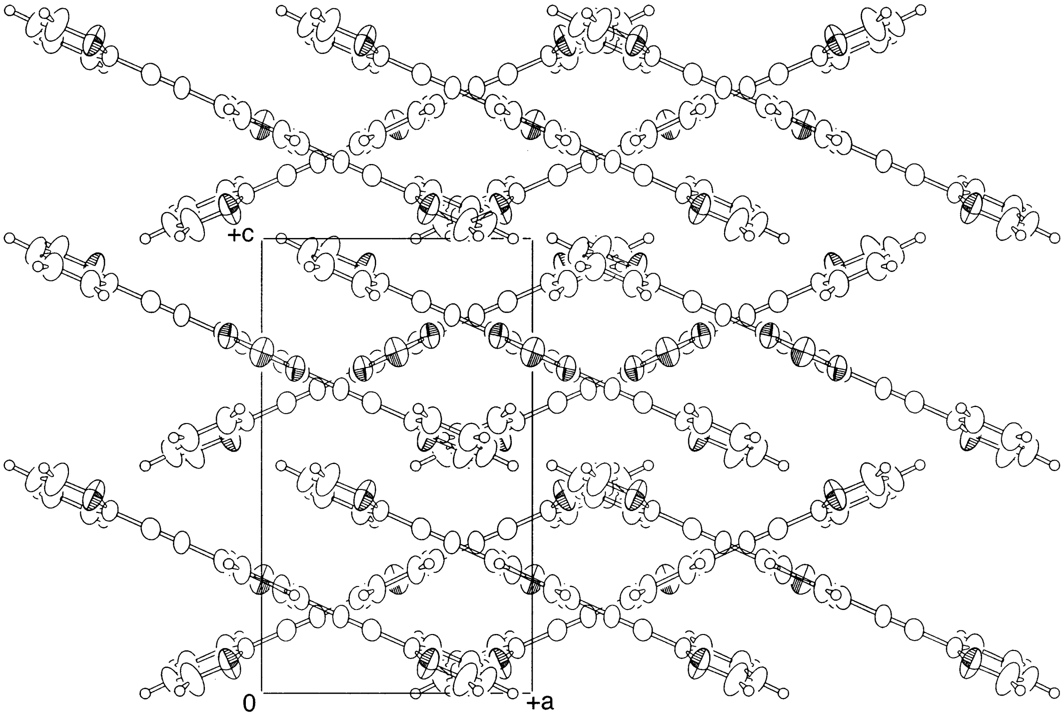

FIGURE 1. Crystal structure of **3a** viewed along the *b* axis.

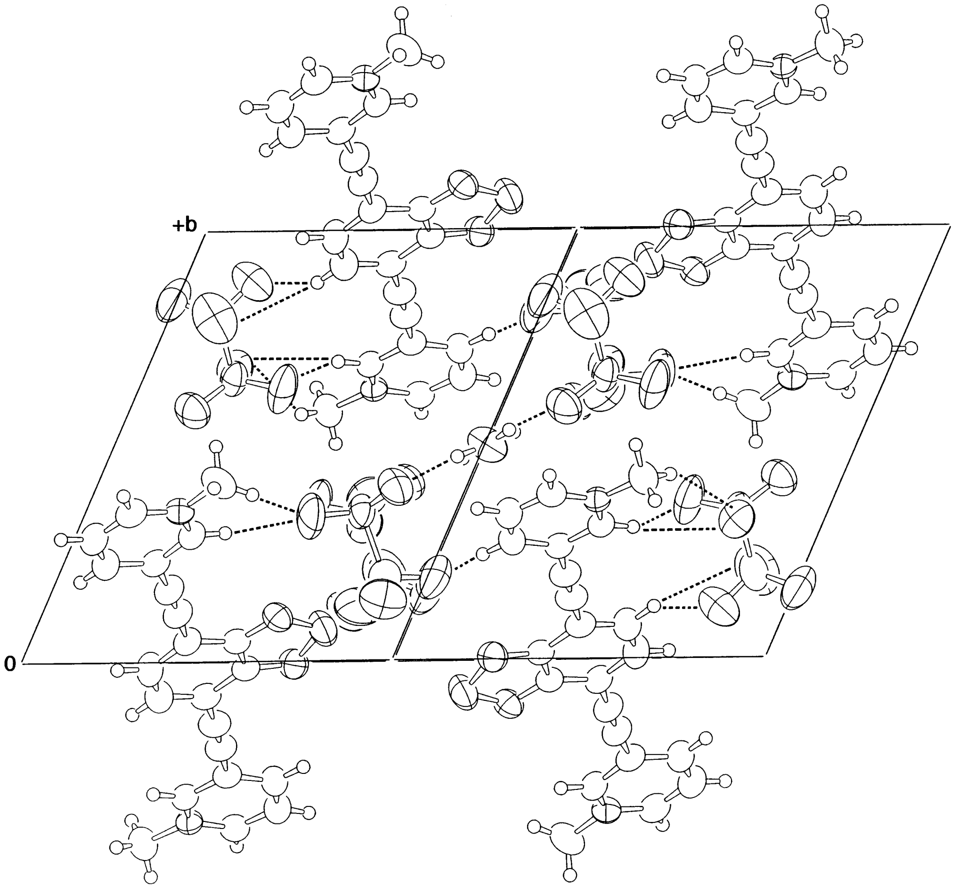

FIGURE 2. Crystal structure of **5b**·H_2O viewed along the [1 0 −1] direction. Dotted lines show the intermolecular O−H···O, C−H···O, and C−H···F interactions.

Single crystals of **5b** including water and **5c** were obtained from acetonitrile−ethanol and their crystal structures have been solved. The molecular structures of the methylated compounds are more planar than **3**.

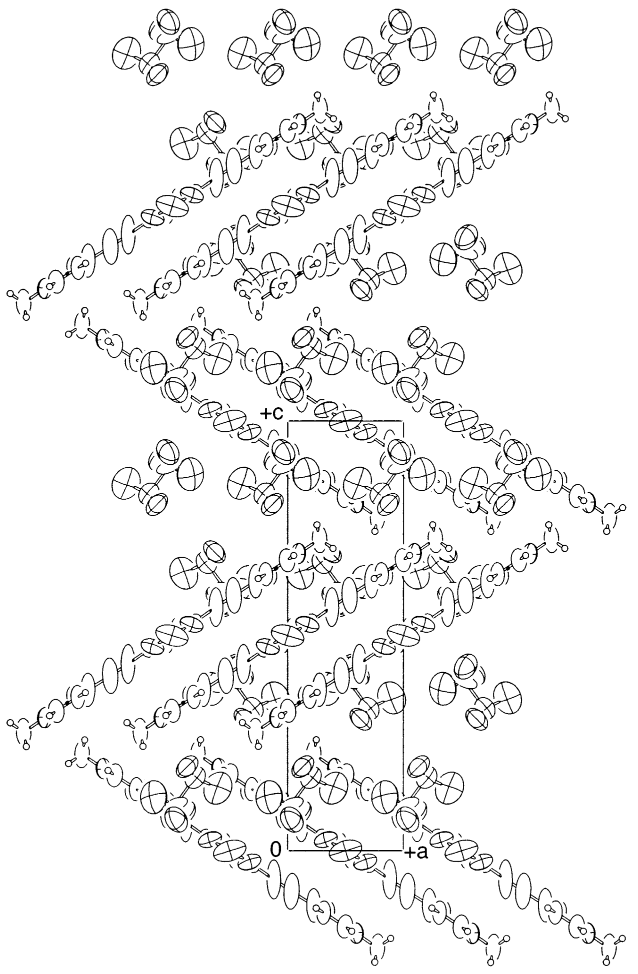

FIGURE 3. Crystal structure of **5c** viewed along the *b* axis.

Thus, the dihedral angles between the pyridines and the benzothiadiazole are 1.4 and 6.5° for **5b** and 5.3° for **5c**. Their crystal structures include $\pi\cdots\pi$ stacking of long molecules. The crystal structure of **5b**·H_2O is shown in Figure 2, where a uniform stacking with 3.41 Å distance is observed. A number of intermolecular O−H···O, C−H···O, and C−H···F interactions are also found in this structure. On the other hand, the herringbone structure with the interstack distances of 3.40 and 3.45 Å is observed in **5c** as shown in Figure 3. The different crystal structures of **5b** and **5c** can be attributed to the steric interactions of methyl groups.

Pyridyl groups work as proton acceptors and dipyridyl compounds are expected to form infinite hydrogen bonding networks with proton donors. Actually, the pyridyl compound **3c** afforded single crystals of the molecular complex with chloranilic acid, which is a strong proton donor.[22]

TABLE 1. Absorption Maxima,[a] Fluorescence Maxima,[b] Quantum Yields,[b] and Reduction Potentials[c] of Dipyridyl Compounds

compd	λ_{max}/nm (log ϵ)	$\lambda_{em,max}$/ nm	Φ_{em}	E_{red}/ V
3-BPEB[f]	317 (4.72), 335 (4.54)	342	0.95	<−1.8
4-BPEB[g]	315 (4.37), 334 (4.22)	344	0.71	−1.75[e]
3a	223 (4.47), 302 (4.61), 393 (4.48)	473	0.87	−1.18
3b	225 (4.46), 300 (4.58), 396 (4.45)	479	0.80	−1.08
3c	222 (4.46), 297 (4.53), 388 (4.43)	464	0.87	−1.00
5b	297 (4.37), 384 (4.50)	449	0.85	−0.85[e]
5c	225 (4.27), 324 (4.20), 398 (4.57)	437	0.82	−0.62
6b	230, 327, 387[d]	459	0.75	−0.84
6c	325, 401[d]	442	0.97	−0.57

[a] In MeCN. [b] In MeCN solution, $\lambda_{ex} = 299$ nm. The Φ_{em} values of 0.83 for 3-BPEB and 0.49 for 4-BPEB in toluene are reported.[25] [c] 0.1 mol dm^{-3} of Bu_4NPF_6 in MeCN, Pt electrode, scan rate 100 mV s^{-1}, V vs SCE. [d] Absorption coefficients could not be measured due to their low solubility in solvents. [e] Irreversible peak. [f] 3-BPEB: 1,4-bis(3-pyridylethynyl)benzene.[25] [g] 4-BPEB: 1,4-bis(4-pyridylethynyl)benzene.[26]

TABLE 2. Absorption and Emission Maxima and Fluorescence Quantum Yields of 3c in a Series of Solvents

solvent	λ_{max}/nm	$\lambda_{em,max}$/nm[a]	Φ_{em}
cyclohexane	395	441	0.61
chloroform	396	469	0.95
dioxane	392	458	1.0
acetonitrile	388	464	0.87
ethanol	390	474	0.92

[a] $\lambda_{ex} = 299$ nm.

Physical Properties. The physical properties of the linear molecules of **3a**−**c** and salts **5b**,**c** and **6b**,**c** are summarized in Table 1 along with those of 1,4-bis(3-pyridylethynyl)benzene (3-BPEB) and 1,4-bis(4-pyridylethynyl)benzene (4-BPEB). Their absorption maxima are significantly red-shifted compared with those of BPEBs. This can be explained by considering that the LUMO energy levels of **3a**−**c** are lower than those of BPEBs due to the electron-withdrawing thiadiazole ring, while the HOMO energies are not so different among them. This fact is supported by the PM3 calculations[23] [(HOMO, LUMO) 3-BPEB (−8.89, −1.12), 4-BPEB (−9.07, −1.20), **3a** (−8.80, −1.99), **3b** (−8.88, −2.17), **3c** (−9.04, −2.24)], indicating that the LUMO levels of **3** are lower than those of BPEBs. The calculations also show that the HOMO-LUMO differences are smaller in **3** than in BPEBs. The absorption spectra of **3a**−**c** are dependent on the solvent. In polar solvents blue shifts are observed as shown in Table 2. This result shows that the ground states of these molecules are more polar as compared to the excited states. All the heterocycles obtained here exhibit strong fluorescence. Interestingly, the emission maxima are prominently red-shifted compared to those of BPEBs due to the large Stokes shifts. They emit blue luminescence and the quantum yields are very high as exemplified by the 1.0 value of **3c** in dioxane.[24] There is no significant effect of the nitrogen positions on the quantum yields. It is also noteworthy that the salts **5b**,**c** and **6b**,**c** display high quantum yields. The reduction potentials listed in Table 1 show that the thiadiazole containing compounds **3** have stronger electron affinities compared with BPEBs due to the electron-withdrawing properties of thiadiazole rings. The salts **5b**,**c** and **6b**,**c** show higher reduction potentials than **3** because of the dication species. Since they have high fluorescence quantum yields, they are

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(22) The crystal structurs have not been solved yet probably due to the disorder of the thiadiazole ring.

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expected to work as strong electron acceptors in photoinduced electron-transfer reactions.

Conclusion

In conclusion, we have explored novel dipyridyl compounds with electron-withdrawing properties and high fluorescence quantum yields. The bipyridinium compounds, viologens analogues, have been found to be easily obtained and show higher electron affinities. Further studies on construction of supramolecular systems composed of these compounds with use of hydrogen bonding and metal coordination are currently in progress.

Experimental Section

All reactions were performed under argon. Triethylamine was purified under argon by passing through aluminum oxide (neutral, activity I). All other reagents and solvents commercially available were used without further purification unless otherwise noted. 2-, 3-, and 4-ethynylpyridine[21] and 4,7-dibromo-2,1,3-benzothiadiazole[20] were prepared according to the literature methods.

Preparation of 4,7-Bis[(2-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3a). To a solution of 2-ethynylpyridine (0.302 g, 2.93 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.411 g, 1.4 mmol) in triethylamine (15 mL) were added bis(triphenylphosphine)palladium(II) dichloride (0.023 g, 0.033 mmol) and copper(I) bromide 0.01 g (0.070 mmol). After being stirred for 1 h at 60 °C, the reaction mixture was further stirred for 2 d at 90 °C under argon. Triethylamine was removed in vacuo and the residue was dissolved in $CHCl_3$. The solution was washed with aqueous K_2CO_3 and dried over Na_2SO_4. After filtration the solvent was removed to give brown solids. Chromatography on silica gel with chloroform−ethyl acetate as eluent afforded compound **3a**. Recrystalization from toluene gave a yellow solid (47% yield): mp 232−234 °C; IR (KBr) ν_{max} 2214, 1582, 1497, 1459, 1383, 1240, 1149, 988, 895, 860, 779, 547 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 242 (4.21), 306 (4.55), 399 (4.42) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.72 (br s, 2H), 7.9−7.93 (m, 2H), 7.70−7.80 (m, 4H), 7.30−7.34 (m, 2H); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 84.53, 96.46, 117.05, 123.47, 127.76, 133.10, 136.27, 142.79, 150.36, 154.36; MS (EI) *m/z* (%) 338 (M^+, 100). Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48. Found: C, 70.79; H, 3.20; N, 16.51; S, 9.11.

Preparation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3b). Following the same procedure as that for **3a**, compound **3b** was obtained. Recrystalization from toluene gave a yellow solid (57% yield): mp 189−191 °C; IR (KBr) ν_{max} 2356, 1564, 1538, 1470, 1182, 1022, 886, 807, 705, 547, 506 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 242 (4.35), 304 (4.54), 403 (4.39) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 8.91 (br s, 2H), 8.64 (br s, 2H), 7.96−7.98 (m, 2H), 7.87 (d, J = 3.9 Hz, 2H), 7.34−7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.18, 94.05, 117.02, 119.67, 123.11, 132.68, 138.80, 149.37, 152.52, 154.20; MS (EI) *m/z* (%) 338 (M^+, 100). Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48. Found: C, 71.24; H, 3.28; N, 16.43; S, 9.44.

Preparation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3c). Following the same procedure as that for **3a**, compound **3c** was obtained. Recrystalization from toluene gave a yellow solid (78% yield): mp 243−245 °C; IR (KBr) ν_{max} 2353, 2212, 1592, 1538, 1504, 806, 853, 816, 660, 543 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 243 (4.39), 301 (4.67), 396 (4.56) nm; ^1H NMR (270 MHz, $CDCl_3$) δ 7.55 (d, J = 5.9 Hz, 4H), 7.88 (s, 2H), 8.69 (d, J = 5.9 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 89.05, 94.64, 117.09, 125.71, 130.49, 133.04, 149.99, 154.21; MS (EI) *m/z* (%), 338 (M^+, 100). Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48. Found: C, 71.29; H, 3.12; N, 16.58; S, 9.37.

Methylation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3b). Tetrafluromethanesulfonic acid (0.080 g, 0.49 mmol) was added to a solution of **3b** (0.051 g, 0.15 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 2 h at room temperature. The resulting solid was filtered and washed with CH_2Cl_2 to give a yellow solid **5b** (82% yield): mp 289−291 °C; ^1H NMR (300 MHz, CD_3CN) δ 8.94 (s, 2H), 8.60−8.66 (m, 4H), 8.05−8.09 (m, 4H), 4.40 (s, 6H); ^{13}C NMR (75 MHz, CD_3CN) δ 49.69, 89.83, 93.05, 117.12, 117.32, 124.59, 129.25, 135.29, 146.02, 148.21, 148.63, 154.94. Anal. Calcd for $C_{24}H_{16}F_6N_4O_6S_3$: C, 43.25; H, 2.42; N, 8.41; S, 14.43. Found: C, 43.19; H, 2.84; N, 8.47; S, 14.41.

Methylation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3c). Following the same procedure as above, the dimethyalted compound **5c** was obtained as a yellow solid (86% yield): mp 229−232 °C; ^1H NMR (300 MHz, CD_3CN) δ 8.68 (d, J = 6.3 Hz, 4H), 8.14 (s, 2H), 8.11 (d, J = 6.6 Hz, 4H), 4.55 (s, 6H); ^{13}C NMR (67.8 MHz, CD_3CN) δ 49.25, 92.63, 98.18, 117.12, 117.48, 130.67, 135.88, 139.85, 146.43, 154.80. Anal. Calcd for $C_{24}H_{16}F_6N_4O_6S_3$: C, 43.25; H, 2.42; N, 8.41; S, 14.43. Found: C, 43.09; H, 2.84; N, 8.47; S, 14.41.

Benzylation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3b). Benzyl bromide (0.085 g, 0.50 mmol) was added to a solution of **3b** (0.05 g, 0.15 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 2 d at 40 °C. The resulting solid was filtered and washed with CH_2Cl_2 to give **6b** as a yellow solid (62% yield): mp 234−236 °C; ^1H NMR (75 MHz, DMSO-d_6) δ 9.76 (br s, 2H), 9.29 (dd, J = 6.3 Hz, 2H), 8.90 (dd, J = 6.9 Hz, 2H), 8.32 (dd, J = 8.1 Hz, 2H), 8.2 (s, 2H), 7.61−7.62 (m, 4H), 7.47−7.49 (m, 6H), 5.93 (br s, 4H); ^{13}C NMR (300 MHz, DMSO-d_6) δ 63.65, 89.79, 91.58, 115.63, 122.65, 128.73, 129.02, 129.22, 129.50, 133.86, 134.35, 144.76, 147.16, 147.64, 153.29. Anal. Calcd for $C_{34}H_{24}Br_2N_4S{\cdot}(H_2O)_{2.5}$: C, 56.29; H, 4.02; N, 7.72; S, 4.42. Found: C, 56.05; H, 3.94; N, 7.78; S, 4.3.

Benzylation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole (3c). Following the same procedure as above, **6c** was obtained as a yellow solid (86% yield): mp 374−376 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 9.29 (dd, J = 9 Hz, 4H), 8.41 (dd, J = 6.9 Hz, 4H), 8.29 (s, 2H), 7.45−7.55 (m, 10H), 5.89 (br s, 4H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ 63.31, 92.29, 96.89, 115.85, 128.90, 129.27, 129.47, 130.08, 134.00, 135.11, 138.03, 145.12, 153.24. Anal. Calcd for $C_{34}H_{24}Br_2N_4S{\cdot}(H_2O)_{1.5}$: C, 57.73; H, 3.84; N, 7.92; S, 4.53. Found: C, 57.53; H, 3.90; N, 8.17; S, 4.59.

X-ray Analysis. Reflection data for **3a** and **3b** were collected on a Rigaku AFC-7R diffractometer and Rigaku R-AXIS IV imaging plate area detector, respectively, using Mo Kα radiation (λ = 0.71070 Å) at 296 K. Reflection data for **5b**·H_2O and **5c** were collected on an Enraf-Nonius CAD4 diffractometer, using Cu Kα radiation (λ = 1.54178 Å) at 296 K. No absorption correction was applied except **5b**·H_2O. An absorption correction for **5b**·H_2O was applied by using empirical procedures based on azimuthal ψ scans of seven reflections having an Eulerian angle, χ, near 90°. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97.[28] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model.

Crystal data for 3a: $C_{20}H_{10}N_4S$, M = 338.38, yellow brown plate, orthorhombic, space group *Pbcn*, a = 8.980(5) Å, b = 12.163(5) Å, c = 14.926(4) Å, V = 1630(1) Å^3, Z = 4, D_c = 1.379

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g cm^{-3}, $F(000) = 696$, $\mu = 0.208$ mm^{-1}, crystal dimensions 0.55 × 0.20 × 0.05 mm^3, 2165 reflections collected, 1875 independent reflections, $R_1 = 0.0606$, $wR_2 = 0.1546$ for $I > 2\sigma(I)$, $R_1 = 0.2059$, $wR_2 = 0.2071$, $S = 0.972$ for all data.

Crystal data for 3b: $C_{20}H_{10}N_4S$, $M = 338.38$, yellow block, monoclinic, space group Cc, $a = 15.3862(1)$ Å, $b = 17.5790(7)$ Å, $c = 12.1370(4)$ Å, $\beta = 103.690(3)°$, $V = 3189.5(2)$ Å^3, $Z = 8$, $D_c = 1.409$ g cm^{-3}, $F(000) = 1392$, $\mu = 0.212$ mm^{-1}, crystal dimensions 0.30 × 0.20 × 0.15 mm^3, 3377 reflections collected, 3280 independent reflections, $R_1 = 0.0458$, $wR_2 = 0.1159$ for $I > 2\sigma(I)$, $R_1 = 0.0562$, $wR_2 = 0.1213$, $S = 0.892$ for all data.

Crystal data for 3c: these data have already been reported in ref 27.

Crystal data for 5b·H$_2$O: $C_{24}H_{16}F_6N_4O_6S_3{\cdot}H_2O$, $M = 684.60$, yellow plate, triclinic, space group $\bar{P}$, $a = 11.1998(8)$ Å, $b = 12.2723(8)$ Å, $c = 12.3784(9)$ Å, $\alpha = 67.740(6)°$, $\beta = 67.542(6)°$, $\gamma = 72.373(5)°$, $V = 1430.1(1)$ Å^3, $Z = 2$, $D_c = 1.590$ g cm^{-3}, $F(000) = 696$, $\mu = 3.201$ mm^{-1}, crystal dimensions 0.55 × 0.25 × 0.10 mm^3, 6146 reflections collected, 5832 independent reflections, $R_1 = 0.0528$, $wR_2 = 0.1442$ for $I > 2\sigma(I)$, $R_1 = 0.0802$, $wR_2 = 0.1636$, $S = 1.024$ for all data.

Crystal data for 5c: $C_{24}H_{16}F_6N_4O_6S_3$, $M = 666.59$, orange plate, orthorhombic, space group $Pn2n$, $a = 6.3555(4)$ Å, $b = 9.470(2)$ Å, $c = 23.335(3)$ Å, $V = 1404.5(4)$ Å^3, $Z = 2$, $D_c = 1.576$ g cm^{-3}, $F(000) = 676$, $\mu = 3.216$ mm^{-1}, crystal dimensions 0.40 × 0.25 × 0.05 mm^3, 1440 reflections collected, 1277 independent reflections, $R_1 = 0.1240$, $wR_2 = 0.3322$ for $I > 2\sigma(I)$, $R_1 = 0.2241$, $wR_2 = 0.3763$, $S = 2.305$ for all data.

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Supporting Information Available: The X-ray crystallography data (ORTEP drawings and tables of crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters) for **3a**, **3b**, **5b**·H$_2$O, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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