Nickel-2,2′-Bipyridyl and Palladium-Triphenylphosphine Complex Promoted Synthesis of New π-Conjugated Poly(2-hexylbenzotriazole)s and Characterization of the Polymers

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Abstract: A nickel(0) complex (Ni-bpy) promoted dehalogenative polycondensation of 4,7-dibromo-2-hexylbenzotriazole gives the new π-conjugated polymer, polybenzotriazole [P(BTz)]. Palladium-triphenylphosphine [Pd(PPh$_3$)$_4$] catalyzed the copolymerization between 4,7-dibromo-2-hexylbenzotriazole with 2,5-diethynyl-1,4-dihexyloxybenzene and 9,9′-dihexylfluorene-2,7-bis(trimethylene borate) to give the corresponding polymers P(BTz-AE) and P(BTz-F), respectively. The number average molecular weights, M_n, of the polymers ranged from 3000 to 7400. P(BTz-AE) showed a photoluminescence (PL) peak at 500 nm in CHCl$_3$ with a high quantum yield of PL (87%).

Keywords: benzotriazole; π-conjugated polymers; cross-coupling; nickel; palladium; polymerization

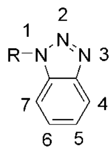
Introduction

π-Conjugated polymers are attracting much attention due to their interesting electronic and optical properties.[1–3] The utilization of π-conjugated polymers in flat panel displays is especially attracting attention. Poly(9,9′-dialkylfluorene)s are considered to be promising electroluminescent polymers for light-emitting diodes (LED) because of their thermal and chemical high stability, good solubility in common organic solvents, and a high photoluminescence quantum yield in the solid state. However, the development of new π-conjugated polymers is still desired. In addition, in order to achieve high quantum efficiency in the light-emitting diode, it is important to balance the electron and hole currents, which are carried through n-type and p-type π-conjugated polymers, respectively.

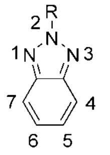
Recently, an n-type π-conjugated polypyridine (**PPy**) and a pyridine-fluorene copolymer have been employed successfully within the polymer light-emitting diode (PLED), affording improved device efficiencies.[4,5] The n-type conducting properties of the polymers are considered to originate from the π-electron-deficient nature of the pyridine unit due to the presence of an electron-withdrawing imine (−C=N−) nitrogen.[6]

Other n-type π-conjugated polymers such as the polyquinolines, polyquinoxalines, and polybenzobisazoles have also been demonstrated to be effective as electron transport (ET) layers in PLEDs.[7–9] However, the synthesis of new and better ET polymers with n-type electron-accepting properties is still needed for further improvement of the performance of such devices.

Benzotriazoles, **BTz**s, are considered to act as an electron transporting material[10] because they contain electron-withdrawing −N=N−or −C=N−groups.[6] The 2R-triazole unit in 2R-BTz is known as an electron-accepting unit.[11]



1R-BTz



2R-BTz

Previously, Ahn and co-workers introduced the 1R-BTz unit into a side chain of polythiophene.[10] They concluded that introduction of the unit to polythiophene made the polymer accept electrons more efficiently. However, the synthesis of a π-conjugated polymer containing the benzotriazole unit in the polymer main chain has not been reported.

π-Conjugated heteroaromatic polymers can be prepared by (1) oxidative polymerization of heteroaromatic compounds and (2) dehalogenative organometallic C−C coupling polycondensation of dihaloheteroaromatic monomers. The first oxidative method is suited to the polymerization of electron-excessive heteroaromatic compounds such as pyrroles and thiophenes. However, for synthesis of n-type π-conjugated polymers, the latter organometallic method is more effective.[2,3]

In this paper, we report the synthesis of **P(BTz)**, **P(BTz-AE)**, and **P(BTz-F)** using the organometallic polycondensation route.

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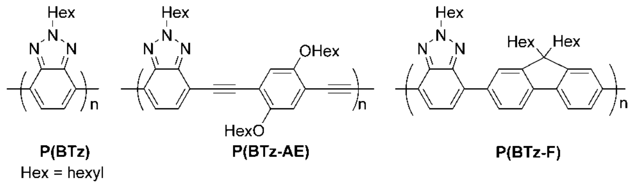
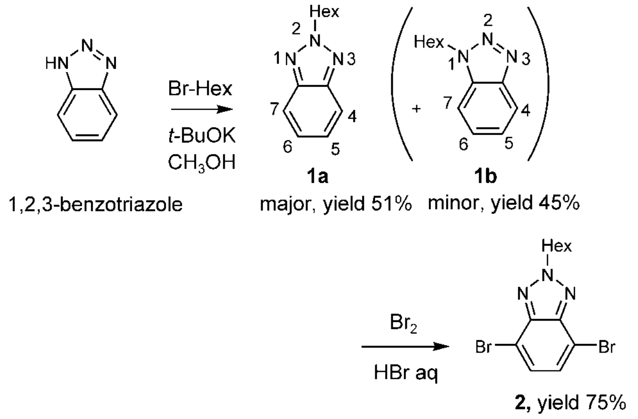




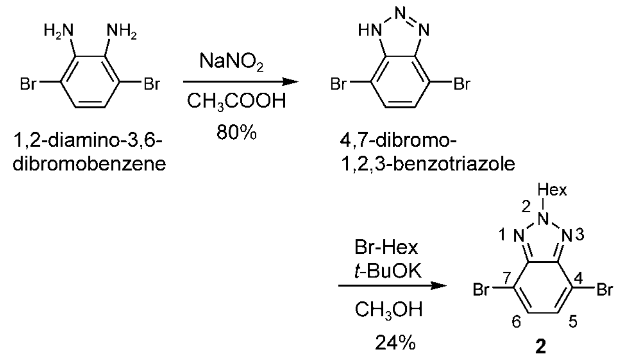
Scheme 1. Preparation of monomer **2**.

Results and Discussion

Scheme 1 gives the synthetic route for the monomer **2**. Monomer **2** was prepared by a 2-step reaction procedure starting from 1,2,3-benzotriazole.

Alkylation of 1,2,3-benzotriazole was carried out by modification of a previously reported method.[12] The reaction of 1,2,3-benzotriazole, 1-bromohexane, and potassium *tert*-butoxide in methanol gave 2-hexylbenzotriazole (**1a**) and 1-hexylbenzotriazole (**1b**), and **1a** and **1b** were easily separated by column chromatography. The positions of the alkyl group in **1a** and **1b** was confirmed by comparison of ^{1}H NMR spectra of **1a** and **1b** with those of the reported 1R- and 2R-BTzs (R = hexyl), although the reported ^{1}H NMR spectra[13] did not give a higher order of coupling patterns for the aromatic signals which are shown in Figures 1a and 1b. It is known that the amine proton of 1,2,3-benzotriazole can move among the N-1 and N-2, and N-3 positions,[14] however, from the ^{1}H NMR spectra, transfer of the alkyl group in chloroform did not seem to occur for **1a** and **1b** for 3 months. Bromination of **1a** was carried out by a modification of a previously reported method, applied to the bromination of benzothiadiazole,[15] and 4,7-dibromo-2-hexylbenzotriazole (**2**) was obtained.

Monomer **2** was also prepared *via* the following independent route (Scheme 2), and the positions of the two bromines in **2** was confirmed by comparison of the ^{1}H NMR spectra of the two samples prepared by the different two methods (*cf.* Schemes 1 and 2).



Scheme 2. Synthesis of 4,7-dibromo-2-hexylbenzotriazole (**2**) *via* a different route.

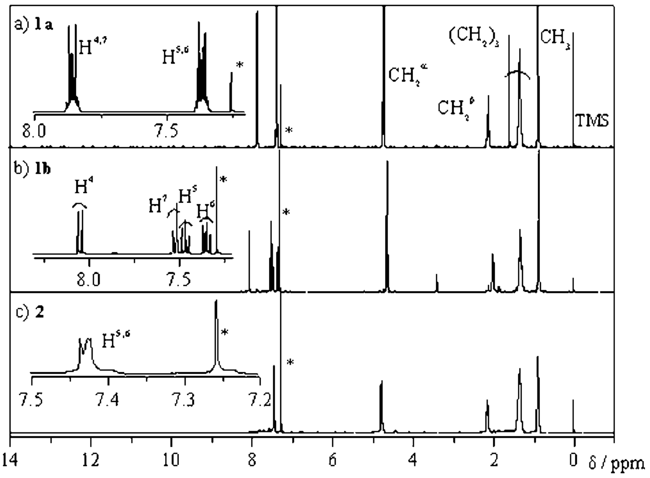
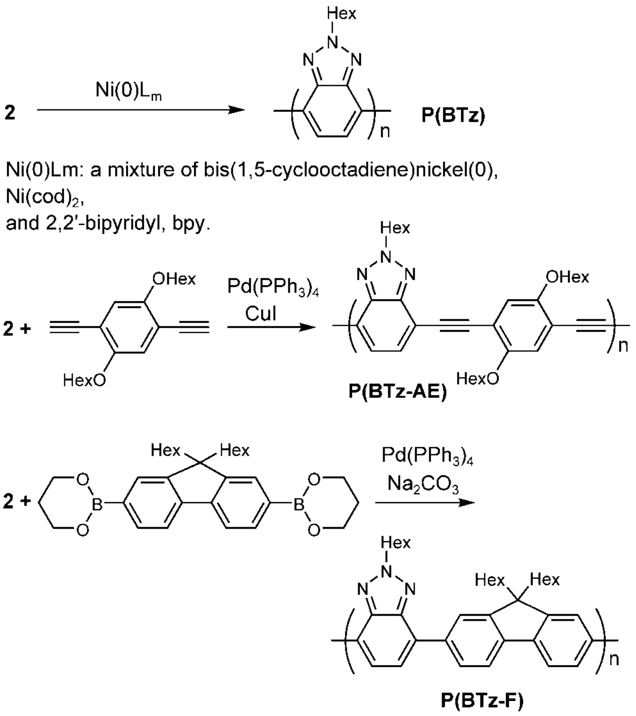


Figure 1. ^{1}H NMR spectra of monomer **2** in $CDCl_3$. The peak with an * mark is due to the solvent impurity.

The synthesis of **2** according to Scheme 2 was carried out by modification of the reported method, which was applied for the preparation of 4,6-dibromobenzotriazole from 1,2-diamino-3,5-dibromobenzene and $NaNO_2$.[16] As can be seen from Schemes 1 and 2, the method shown by Scheme 1 gave **2** in higher yield. As described above, the two ^{1}H NMR spectra of **2**, one obtained from 1,2,3-benzotriazole and the other obtained from 1,2-diamino-3,6-dibromobenzene, were identical, supporting that **2** had bromines at the 4- and 7-positions.

Figure 1 shows the ^{1}H NMR spectra of the compounds **1a**, **1b**, and **2**. The H-4,7 and H-5,6 peaks[13] of **1a** are observed at $\delta = 7.85$ and 7.38, respectively. It was reported that the H-5,6 signals appeared at a higher magnetic field than the H-4,7 signals in benzotriazoles.[17,18] In the contrast, the ^{1}H NMR spectra of **1b** exhibited multiple peaks. The chemical shifts agreed with reported ^{1}H NMR data of 1- and 2-hexylbenzotriazoles.[13] The aromatic peaks of **2** were observed at around $\delta = 7.43$ as an overlapping broad signal; tilting of the *N*-hexyl group



Ni(0)Lm: a mixture of bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, and 2,2'-bipyridyl, bpy.

Scheme 3. Preparation of poly(benzotriazole)s.

Table 1. Synthesis of the π-conjugated polymers.

Polymer	Yield [%]	M_n	M_w	M_w/M_n
P(BTz)	96	3.0×10^3[a]	–	–
P(BTz-AE)	89	3.1×10^3[b]	3.1×10^3[b]	1.02[b]
P(BTz-F)	88	7.4×10^3[b]	8.6×10^3[b]	1.16[b]

[a] Estimated from the ^{1}H NMR spectra (*cf.* the text).

[b] Determined by GPC (gel permeation chromatography), (*vs.* polystyrene standards; eluent = DMF). M_n = number average molecular weight. M_w = weight average molecular weight.

and possible partial coagulation of **2** in CDCl$_3$ may explain the complex peak pattern, however, a detailed analysis seems to be necessary for a full understanding of the peak pattern.

The dehalogenative polymerization[2,3] of **2** gives the corresponding polymers in good yields, and the results of this polymerization are collected in Table 1.

P(BTz) was prepared by using an Ni(0)-bpy complex,[2,3] as shown in Scheme 3. **P(BTz)** contained no bromine, which indicated that the polymer had two polymer-Ni terminal groups which were converted into polymer-H ends during the work-up procedure, similar to the case of polypyridine analogues.[3] **P(BTz)** showed low solubility in the usual organic solvents, but was soluble in CF$_3$COOH.

P(BTz-AE) was obtained by using a standard Sonogashira reaction[19] which had been applied to synthesis of such poly(aryleneethynylene) (**PAE**) type polymers.[2,3] **P(BTz-AE)** was partially soluble in common organic solvents. Data from its elemental analysis indicated that **P(BTz-AE)** contained 4.3% bromine, which agreed with an assumption that **P(BTz-AE)** with M_n of 3100 (*cf*, Table 1) contained Br at the both polymer ends, similar to usual **PAE**-type polymers.[3,20] The M_n value indicates that **P(BTz-AE)** is an oligomeric product with a degree of polymerization (n in Scheme 3) of about 6.

The copolymer with fluorene, **P(BTz-F)**, was prepared by the Suzuki–Miyaura coupling reaction[21,22] using Pd(PPh$_3$)$_4$. **P(BTz-F)** was easily soluble in common organic solvents such as chloroform and DMF. GPC analysis indicated that **P(BTz-F)** had M_n of 7400 (*vs.* polystyrene standards), which corresponded to the n value of about 14 in Scheme 3. Because **P(BTz-F)** contained only a negligible amount (0.02%, *cf.* the Experimental section) of B and its Br content (0.84%) roughly agreed with one Br at **P(BTz-F)** having the molecular weight of 7400, another polymer end was considered to have a polymer-Pd terminal group which was converted into a polymer-H terminal group during work-up.

Figure 2 shows ^{1}H NMR spectra of **P(BTz)**, **P(BTz-AE)**, and **P(BTz-F)**. These ^{1}H NMR spectra are compatible with the chemical structures of the polymers and the ratio between the peak areas of the aromatic signals and the aliphatic signals agrees with the structure of the polymer. The ^{1}H NMR spectrum of **P(BTz)** shows a broad peak around $\delta = 3$ ppm suggesting that the polymer contains a small amount of water. Thermal analysis of **P(BTz)** showed a loss of weight in a temperature range of 100 through 200 °C, supporting the view that **P(BTz)** contained a small amount of water. If the isolated aromatic peak at $\delta = 7.92$ ppm of **P(BTz)** is assigned to the 4-H (or 7-H) proton of the terminal unit, the M_n value of **P(BTz)** is calculated to be 3.0×10^3. The UV-VIS data of **P(BTz)** described below revealed that the polymer had a long effective π-conjugation system.

Chloroform solutions of the polymers gave strong photoluminescence (PL) under irradiation with long UV light (336 nm). UV-VIS and PL spectra of the polymers are given in Figure 3. Solid curves and dotted curves were obtained with chloroform solutions and cast films, respectively.

P(BTz) exhibits a UV-VIS peak at 407 nm which is shifted from a π-π* transition peak of 2-hexylbenzotriazole **1a** at 279 nm, because of expansion of the π-conjugated system in **P(BTz)**.

P(BTz-AE) gives the π-π* absorption peak at 445 nm in chloroform, and its cast film shows an additional peak at about 500 nm. The appearance of the new peak at about 500 nm suggests formation of a π-stacked structure in the solid assisted by a donor (the dihexyloxybenzene unit, AE)-acceptor (the benzotriazole unit, BTz) interaction. Formation of such a π-stacked structure has been proposed for **PAE**-type polymers containing

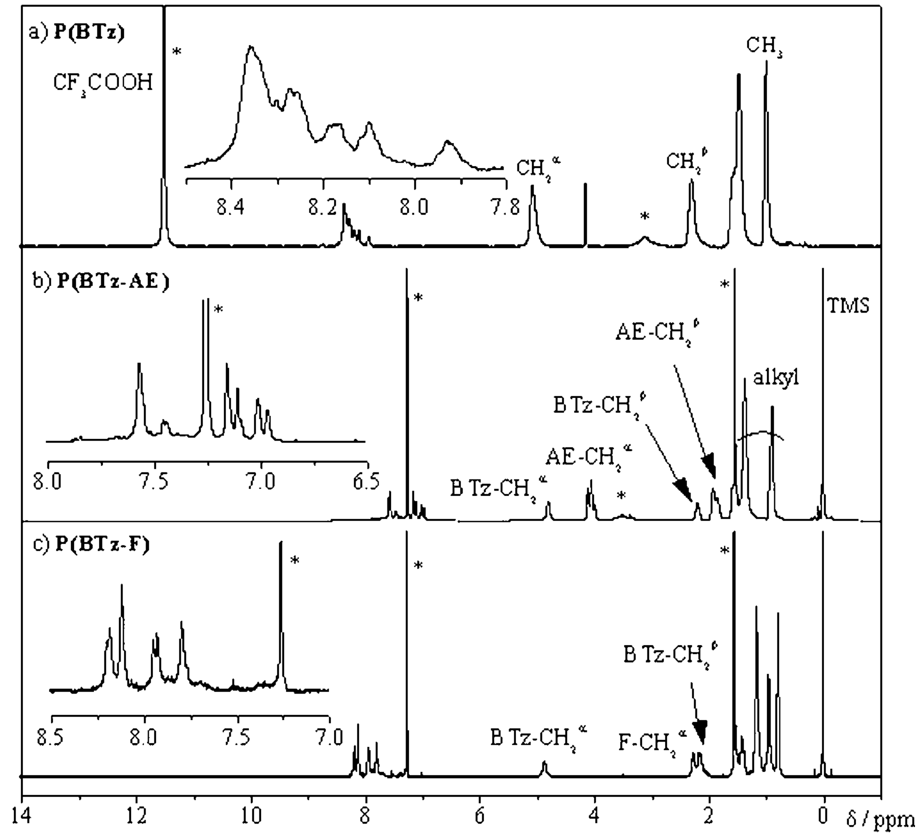


Figure 2. ^{1}H NMR spectra of a) **P(BTz)** in CF_3COOD, b) **P(BTz-AE)**, and c) **P(BTz-F)** in $CDCl_3$. Peaks with the * mark are due to impurities (CF_3COOH, $CHCl_3$, and H_2O). In Figure 2b, "BTz" and "AE" represent the benzotriazole and aryleneethynylene units, respectively. In Figure 2c, "F" represents the fluorene unit.

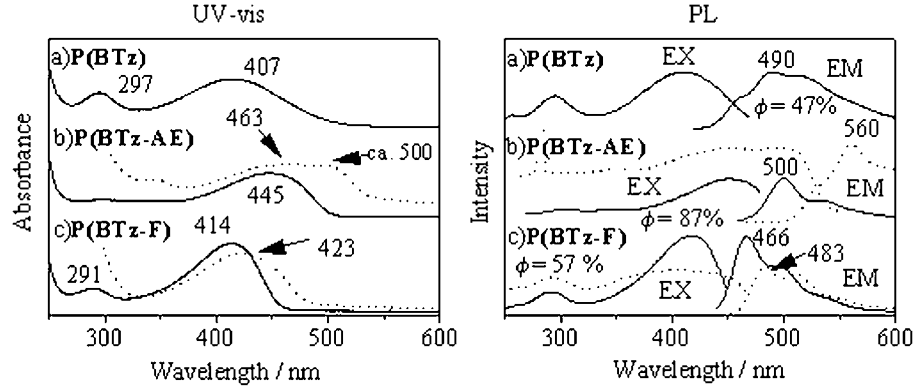


Figure 3. UV-VIS and PL spectra of a) **P(BTz)** ($CHCl_3$ soluble part), b) **P(BTz-AE)** ($CHCl_3$ soluble part), and c) **P(BTz-F)**. Solid line: data in the $CHCl_3$ solution. Dotted line: data of a cast film obtained from the $CHCl_3$ solution. In the PL spectra, EX and EM represent the excitation spectrum and emission spectrum, respectively.

both donor and acceptor units.[23,24] **P(BTz-F)** shows λ_{max} at 414 nm in chloroform and 423 nm in its cast film.

The PL data indicate that **P(BTz)** emits green light with λ_{max} (EM) at 490 nm in chloroform and a quantum yield ϕ of 47%. **P(BTz-AE)** and **P(BTz-F)** also show strong emissions with high quantum yields of 87% and 57%, respectively, in chloroform.

Conclusion

As described above, organometallic polycondensations are useful to prepare new π-conjugated polymers containing the benzotriazole unit. The obtained polymers show highly luminescent properties.

Experimental Section

Measurements

^{1}H NMR spectra were recorded on JEOL JNM-EX-400 and JEOL Lambda 300 spectrometers. Chemical shifts are referred to TMS or CF_3COOH ($\delta = 11.50$). Element analyses of C, H, N and O were carried out with a Leco CHNS-932 or a Yanaco CHN CORDER MT-5 apparatus. Analyses of halogen were carried out with a Yanaco YS-10 system. ICP (inductively coupled plasma) emission spectrometry was applied for the analysis of B in **P(BTz-F)** with a Shimadzu ICPS-8100 system. GPC data were obtained with a Toso HLC-8020 gel permeation chromatograph (polystyrene standards; eluent = DMF containing 0.006 M of LiBr). UV-VIS spectra were recorded on a Shimadzu UV-3100 PC spectrometer. Photoluminescence was measured with a Hitachi F-4500 fluorescence spectrophotometer.

Materials

1,2,3-Benzotriazole, 9,9′-dihexylfluorene-2,7-bis(trimethylene borate), and solvents were used as purchased. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$)[25] and 1,2-diamino-3,6-dibromobenzene[15] were prepared according to literature methods.

Synthesis of the Monomer 2

To a methanol solution of 1,2,3-benzotriazole (5.0 g, 42 mmol) and potassium *tert*-butoxide (5.0 g, 44 mmol) was added 1-bromohexane (8.2 g, 49 mmol), and the reaction mixture was stirred for 96 h at room temperature. After removing the solvent by evaporation, the residue was washed with H_2O and extracted with $CHCl_3$. The organic solution was condensed by evaporation and the product was purified by column chromatography on SiO_2 (eluent = $CHCl_3$) to obtain **1a** as a colorless oil; yield: 51%. Separation of **1a** and **1b** was reported to be a difficult procedure,[13] however, use of the column chromatography conditions made the separation easy. Elemental analysis: predicted for $C_{12}H_{17}N_3$: C 70.90, H 8.43, N 20.67%; found: C 71.10, H 8.34, N 20.36%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.85 (m, 2H, aromatic), 7.38 (m, 2H, aromatic), 4.72 (m, 2H, CH_2^{α}), 2.11 (m, 2H, CH_2^{β}), 1.33 (br, 6H, $(CH_2)_3$), 0.87 (m, 3H, CH_3).

Compound **1a** (4.8 g, 22 mmol) and an aqueous HBr (5.8 M) solution (20 mL) were added to a flask and the mixture was stirred for 1 h at 100 °C. Bromine (7.8 g, 48 mmol) was added and the mixture was stirred for 4 h at 135 °C. After cooling to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic solution was condensed by evaporation and purified by column chromatography on SiO_2 (eluent = $CHCl_3$) to afford **2** as a yellow oil; yield: 75%. Elemental analysis: predicted for $C_{12}H_{15}Br_2N_3$: C 39.92, H 4.19, N 11.64%; found: C 39.71, H 4.19, N 12.00%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (br, 2H, aromatic), 4.75 (m, 2H, CH_2^{α}), 2.14 (br, 2H, CH_2^{β}), 1.33 (br, 6H, $(CH_2)_3$), 0.86 (m, 3H, CH_3).

Alternative Route to 2

To a solution of 1,2-diamino-3,6-dibromobenzene (0.80 g, 3.0 mmol) in 12 mL of AcOH, was added a solution of $NaNO_2$ (0.30 g, 3.3 mmol) in 6 mL of H_2O. After 20 min stirring at room temperature, the precipitate was collected by filtration and washed with water to afford 4,7-dibromo-1,2,3-benzotriazole as a pink powder; yield: 80%. Elemental analysis: predicted for $C_6H_3Br_2N_3$: C 26.02, H 1.09, N 15.17%; found: C 25.84, H 0.88, N 15.17%. ^{1}H NMR (400 MHz, CD_3OD): $\delta =$ 7.56 (s, 2H, aromatic).

Treatment of 4,7-dibromo-1,2,3-benzotriazole with 1-bromohexane and potassium *tert*-butoxide gave **2**; yield: 24%.

Polymerization

P(BTz): Under N_2, to a toluene solution containing $Ni(cod)_2$ (2.1 g, 7.6 mmol), 1,5-cyclooctadiene (0.95 mL, 7.6 mmol), and 2,2′-bipyridyl (1.2 g, 7.6 mmol), was added **2** (1.1 g, 2.9 mmol). The reaction mixture was stirred at 60 °C for 96 h to give a black precipitate. The precipitate was washed with a methanol, aqueous ammonia, an aqueous solution of disodium ethylenediaminetetraacetic acid (Na_2-EDTA), distilled water, a methanol solution of dimethylglyoxime, diluted hydrochloric acid, and methanol, and dried under vacuum at 100 °C for 3 days to give **P(BTz)** as a red solid; yield: 96%. Elemental analysis: predicted for $H[C_{12}H_{15}N_3(H_2O)_{0.22}]_{16}H$: C 70.17, H 7.64, N 20.47, O 1.71%; $M_n = 3220$; found: C 68.95, H 7.36, N 19.39, O 1.36, Br 0%; $M_n = 3000$ (by ^{1}H NMR). ^{1}H NMR (400 MHz, CF_3COOD): $\delta = 8.0–8.4$ (br, 2H, aromatic), 5.07 (s, 2H, CH_2^{α}), 2.29 (s, 2H, CH_2^{β}), 1.46 [br, 6H, $(CH_2)_3$], 0.99 (s, 3H, CH_3).

P(BTz-AE): Compound **2** (0.36 g, 1.0 mmol), 2,5-diethynyl-1,4-dihexyloxybenzene (0.32 g, 1.0 mmol), 20 mL of toluene, 8 mL of triethylamine, $Pd(PPh_3)_4$ (0.052 g, 4.5×10^{-2} mmol), and copper iodide (CuI) (1.2×10^{-2} g, 6.0×10^{-2} mmol) were added to a 50-mL Schlenk tube under nitrogen. After stirring for 30 min at 60 °C the reaction mixture was poured into methanol. The precipitate was collected by filtration and the obtained solid was washed with methanol. The product was dissolved in chloroform, reprecipitated into methanol, and collected by filtration. After reprecipitation, **P(BTz-AE)** became partly insoluble in chloroform. The product was dried under vacuum to obtain **P(BTz-AE)** as a yellow powder; yield: 89%. Elemental analysis: predicted for $Br(C_{34}H_{43}N_3O_2)_6Br$: C 73.93, H 7.85, N 7.61, Br 4.82%; $M_n = 3300$; found: C 74.71, H 7.54, N 5.59, Br 4.30%; $M_n = 3100$ (by GPC analysis). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.56$ (s, 2H, aromatic), 7.11 (m, 2H, aromatic), 4.79 (s, 2H, BTz-CH_2^{α}), 4.04 (m, 4H, AE-CH_2^{α}), 2.19 (s, 2H, BTz-CH_2^{β}), 1.90 (m, 4H, AE-CH_2^{β}), 1.40 (m, 18H, alkyl), 0.90 (m, 9H, $-CH_3$).

P(BTz-F): Compound **2** (0.36 g, 1.0 mmol), 9,9′-dihexylfluorene-2,7-bis(trimethylene borate) (0.47 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.047 g, 4.1×10^{-2} mmol), and 20 mL of toluene were added to a 50-mL Schlenk tube under nitrogen. Then 5 mL of aqueous Na_2CO_3 (2.0 M) and 5 mL of methanol were added. After stirring for 60 h at 80 °C, the reaction mixture was poured into methanol. The precipitate was collected by filtration and washed with methanol. The product was dissolved in chloroform, reprecipitated into methanol, and collected by filtration. The product was dried under vacuum to obtain **P(BTz-F) as** a yellow powder; yield: 88%. Elemental analysis: predicted for $H[C_{37}H_{47}N_3(H_2O)_{0.14}]_{14}Br$: C 81.97, H 8.81, N 7.76, O 0.41, Br 1.04%; $M_n = 7547$; found: C 81.64, H 8.87, N 7.34, O 0.43, Br 0.84%; $M_n = 7400$ (by GPC analysis). The ICP emission spectrometry showed that the B content was negligible (0.02%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.18-7.79$ (m, 8H, aromatic), 4.86 (s, 2H, BTz-CH_2^{α}), 2.25 (br, 4H, F-CH_2^{α}), 2.15 (br, 2H, BTz-CH_2^{α}), 1.52 (br, 4H, F-CH_2^{γ}), 1.41 [br, 6H, BTz-$(CH_2)_3$], 1.15 [s, 12H, F-$(CH_2)_3$], 0.95–0.79 (br, 13H, F-CH_2^{β} and CH_3).

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