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Blue photoluminescence N-substituted poly(4*H*-benzo[*def*]carbazole)s

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ABSTRACT

N-Alkyl and N-phenyl substituted poly(carbazole)s having a 4,5-ethenylene bridge, poly(4*H*-benzo[*def*] carbazole)s, were newly synthesized. Poly(carbazole)s having a 4,5-ethylene bridge were also synthesized for comparison. They were prepared from corresponding dibromo monomers by Ni(0)-catalyzed Yamamoto polycondensation. All the polymers had good solubility in common organic solvents, enough high molecular weights to make thin films, and good thermal stability showing about 400 °C of temperature at 5 wt% loss in TGA. The band gaps of these polymers were in the range of 2.77–3.15 eV which were appropriate for bluish light emissions. The absorption and emission maxima of these polymers in $CHCl_3$ were in the ranges of 361–396 and 419–456 nm, respectively. These polymers showed good fluorescence quantum efficiencies in $CHCl_3$. The energy levels of highest occupied molecular orbital of the poly(benzocarbazole)s were shallower than those of corresponding 4,5-ethylene bridged poly(carbazole)s.

1. Introduction

The polymeric light-emitting diodes (PLEDs) have been investigated to be practically used as display devices, because they can be fabricated with simple coating techniques and show tolerable emitting efficiencies [1]. Among three basic colors of blue, green, and red for full-color displays, development of high-efficiency blue-light-emitting materials is important. Because the short-wavelength emission can serve as an excitation source for emissions over the whole visible range [2]. Since the first report on blue PLEDs device which was fabricated with poly(*p*-phenylene) (PPP) in 1992 [3], a large number of materials for blue-light-emitting have been developed [4–8]. Among the blue-light-emitting polymers, fluorene-based conjugated polymers have been recognized as a promising class, because they are good processable materials and show rarely high fluorescent performances in the solid state [9,10]. Unfortunately, polyfluorene-based PLEDs have usually emitted impure blue colors due to emissions from contaminates such as excimers and keto-defects in addition to principal emission from β-phase [11]. Since early in this century, poly(2,7-carbazole)s regarded as a strained planner poly(4,4′-biphenylylene) with an imino-bridge have been considered as a new candidate for blue light emitting materials comparable to the fluorene-based polymers, because they have wide band gaps appropriate for blue light emissions, sharp emission bands in the solid film state, and smaller ionization potentials compared to polyfluorenes [12–16].

In this paper, several new poly(carbazole)s for stable light emitting are attempted to synthesize by bridging a carbazole (**Cz**) unit with 4,5-ethenylene to construct the benzo[*def*]carbazole (**BCz**) structure as shown in Fig. 1. Dehalogenative polyconsensation of 2,6-dibrominated and 1,7-dibrominated **BCz** monomers gave corresponding poly(benzo[*def*]carbazole)s (**PBCz**). In parallel, 4,5-ethylene bridged polycarbazoles, poly(8,9-dihydro-2,6-benzo [*def*] carbazole)s (**PECz**), were also synthesized from the precursor derivatives of the ethylene bridged carbazoles (**ECz**) for comparison. Basic properties of these polymers were compared with those of poly(2,7-carbazole)s and poly(3,6-carbazole)s.

2. Experimental

2.1. Materials

1-Decylundecyl-4-methylbenzenesulfonate and 1-(1-decylundecyloxy)-4-iodobenzene were synthesized according to the procedures reported previously [17,18]. 2,6-Dibrominated **ECz** (**3**) was synthesized by reductive ring closure of **2** that was prepared by nitration of **1** according to the procedures reported

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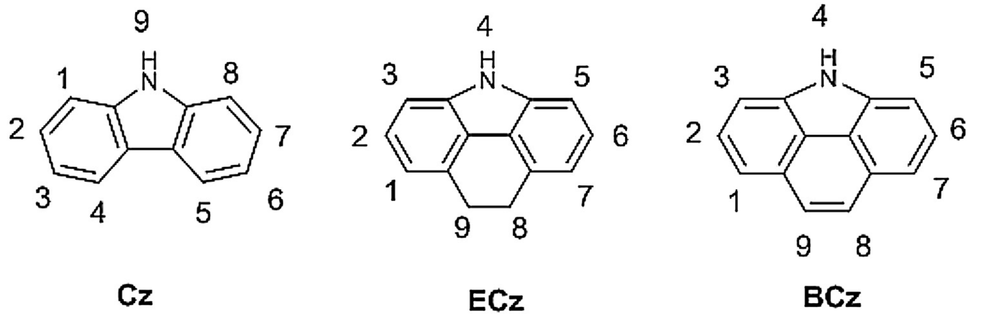


Fig. 1. The structures and numbering system of **Cz**,**ECz** and **BCz**.

previously (Scheme 1 see Supporting information) [19]. Reagents and solvents were purchased from Kanto Chemical, Tokyo Chemical Industry, Aldrich and Nacalai Tesque Inc., Dimethylformamide (DMF) and benzene distilled after drying with CaH_2 were stored under an argon atmosphere. Tetrahydrofuran (THF) distilled after drying with sodium was stored under an argon atmosphere. The other solvents and all commercially available reagents were used without further purification.

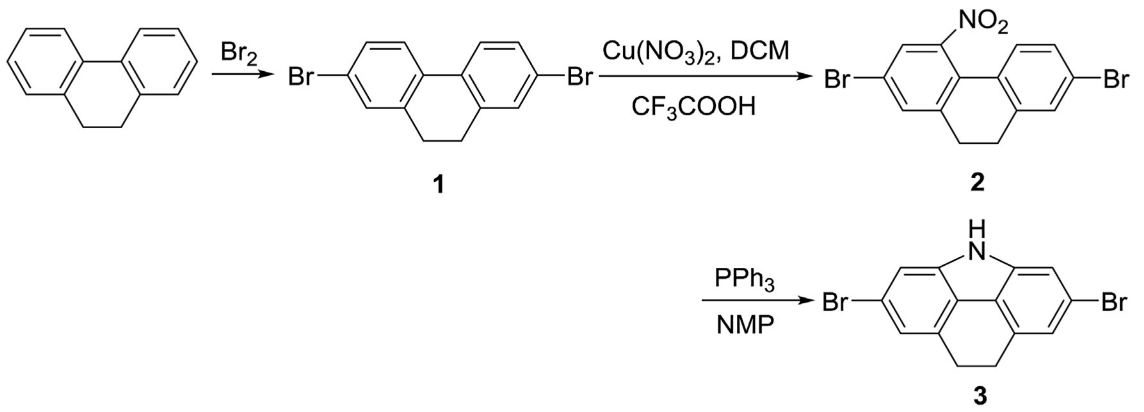
2,6-Dibromo-N-(1-decylundecyl)-8,9-dihydrobenzo[def]carbazole (**4a**). To suspension of **3** (2 g, 5.7 mmol) and potassium hydroxide (1.46 g, 26 mmol) in dimethyl sulfoxide (DMSO) (25 mL) was added dropwise solution of 1-decylundecyl-4-methylbenzenesulfonate (2.65 g, 5.7 mmol) in DMSO (14 mL) under argon. The mixture was stirred at room temperature for 6 h. Then the mixture was poured into water. After extraction with dichloromethane, drying over $MgSO_4$ and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, dichloromethane/hexane, 1:1, as an eluent), giving yellow oil (2.27 g, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.34 (s, 2H), 7.11 (s, 2H), 4.24 (m, 1H), 3.28 (s, 4H), 2.13–2.09 (m, 2H), 1.89–1.85 (m, 2H), 1.28–1.14 (m, 32H), 0.88–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 138.6, 131.4, 120.8, 119.9, 120.0, 111.4, 57.6, 34.0, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1. Calcd for $C_{35}H_{51}Br_2N$ (645.61): C, 65.11; H, 7.96; N, 2.17. Found: C, 65.42; H, 8.21; N, 2.20.

2,6-Dibromo-N-(p-(1-decylundecyloxy)phenyl)-8,9-dihydrobenzo[def]carbazole (**4b**). Suspension of potassium phosphate (0.8 g, 3.7 mmol), **3** (0.66 g, 1.9 mmol), CuI (3.6 mg, 1.9 mmol), 1-(1-decylundecyloxy)-4-iodobenzene (4.37 g, 8.5 mmol) and trans-1,2-cyclohexanediamine (0.011 mL, 0.094 mmol) in THF (3 mL) was stirred at 65 °C for 3 days. After cooling to room temperature, the mixture was poured into water. After extraction with dichloromethane, drying over $MgSO_4$ and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (1.1 g, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.43 (d, J = 6.8 Hz 2H), 7.39 (s, 2H), 7.18 (s, 2H), 7.06 (d, J = 8.0 Hz 2H), 4.28 (m, 1H), 3.32 (s, 4H), 1.73–1.67 (m, 4H), 1.43–1.27 (m, 32H), 0.90-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 157.7, 139.0, 131.3, 130.0, 126.1, 126.0, 121.2, 121.1, 120.5, 116.9, 111.2, 78.5, 33.9, 31.9, 31.5, 29.7, 29.6, 29.3, 26.1, 25.4, 22.7, 22.6, 14.1. Calcd for $C_{41}H_{55}Br_2NO$ (737.71): C, 66.65; H, 7.52; N, 1.90. Found: C, 66.31; H, 7.68; N, 1.97.

2,6-Dibromo-4-(1-decylundecyl)-4H-benzo[*def*]*carbazole* (**5a**). A mixture of **4a** (0.5 g, 0.78 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.42 g, 1.8 mmol) in benzene (77 mL) was refluxed for 8 h under a N_2 atmosphere. After cooling to room temperature, the mixture was poured into water. After extraction with dichloromethane, drying over $MgSO_4$ and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (0.42 g, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.96 (s, 2H), 7.90 (s, 2H), 7.66 (s, 2H), 4.52 (m, 1H), 2.29–2.25 (m, 2H), 2.01–1.95 (m, 2H), 1.25–1.11 (m, 32H), 0.89–0.83(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 138.1, 127.7, 126.0, 120.7, 118.3, 118.2, 110.0, 58.1, 34.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 25.3, 22.6, 14.1. Calcd for $C_{35}H_{49}Br_2N$ (643.59): C, 65.32; H, 7.67; N, 2.18. Found: C, 65.57; H, 8.02; N, 2.05.

2,6-Dibromo-4-(p-(1-decylundecyloxy)phenyl)-4H-benzo[*def*] *carbazole* (**5b**). Dibromobenzocarbazole **5b** was similarly synthesized according to the procedure for **5a,** giving yellow oil (0.48 g, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.99 (s, 2H), 7.96 (s, 2H), 7.75 (s, 2H), 7.62 (d, J = 9.1 Hz 2H), 7.14 (d, J = 9.1 Hz 2H), 4.32 (m, 1H), 1.73–1.69 (m, 4H), 1.33–1.27 (m, 32H), 0.90–0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 157.8, 140.8, 130.3, 127.8, 126.2, 126.0, 121.2, 120.1, 119.3, 117.0, 109.9, 78.6, 33.9, 31.9, 31.5, 29.7, 29.6, 29.3, 25.4, 22.7, 22.6, 14.1. Calcd for $C_{41}H_{53}Br_2NO$ (735.69): C, 66.84; H, 7.26; N, 1.90. Found: C, 66.47; H, 7.50; N, 1.75.

4-(1-Decylundecyl)-4H-benzo[*def*]*carbazole* (**6a**). Dibromobenzocarbazole **5a** (0.8 g, 1.24 mmol) was dissolved in 12.5 mL of anhydrous THF and cooled to −78 °C under nitrogen atmosphere, in



Scheme 1. Synthetic route of 2,6-dibromo-8,9-dihydrobenzo[*def*] carbazole.