Novel Blue Light Emitting Poly(*N*-arylcarbazol-2,7-ylene) Homopolymers: Syntheses and Properties

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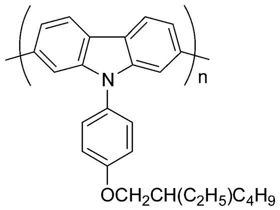
ABSTRACT: In this paper, we synthesized a new type of poly(*N*-phenyl-2,7-carbazole)s with alkoxy groups or a diphenylamino group at *o*-, *m*-, or *p*- position of the *N*-phenyl group using the Ni(0)-catalyzed Yamamoto polymerization in high yields. The series of structural isomers were synthesized in order to optimize the inter- and intramolecular interactions. The electron-rich triethylene oxide groups or the triphenylamino groups were introduced to tune the HOMO energy levels. These polymers were characterized by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis, GPC, TGA, UV−vis, fluorescence spectroscopy, and electrochemical analysis. All the polymers had enough high molecular weights to show a good solubility in common organic solvents and a good processability for making thin films. Deiodination of the terminal residual iodide of the polymers enhanced the fluorescent quantum yields in $CHCl_3$ (ϕ_f (sol) = 0.8). In the form of thin films, all the polymers displayed the fluorescence charts with emission bands around 430, 455, and 475 nm. Among the polymers, **P*m*DPAC**, **P*mp*EHOC**, **P*o*DPAC**, **P*op*EHOC** remarkably fluoresced blue (ϕ_f (film) > 0.2). The strong fluorescence band around 430 nm for **P*mp*EHOC** and **P*o*DPAC** suggested a poor visibility, and 475 nm for **P*op*EHOC** resulted in an impure blue color emission, while the strong emission band around 455 nm for **P*m*DPAC** was appropriate for pure blue emission. Furthermore, the series of **PDPAC** polymers possessed higher HOMO energy levels than the other carbazole homopolymers.

Introduction

Since the discovery of the first efficient polymeric electroluminescent device fabricated with poly(*p*-phenylenevinylene) (PPV) in 1990,[1] the field of polymeric light-emitting diodes (PLEDs) had attracted large interests from both academic communities and industrial laboratories especially for the development of full-color displays,[2] which required polymers emitting three basic colors of blue, green, and red. Among the three primary colors, a large number of blue-emitting materials for PLEDs have been investigated, because the high energy emission serves many uses.[3] Although bright and pure-blue electroluminescent polymers have been the top target[4] since then, the high stability and efficient performance of the polymers give inexhaustable opportunities.

Among the vast kinds of conjugated polymers, fluorene-based and carbazole-based conjugated polymers are a promising class of blue-emitting materials for PLEDs because of their good processability and high fluorescent performances in the solid state.[5] When polyfluorenes, the most widely investigated materials, are used as the active materials in PLEDs, they frequently emit impure blue colors because of formations of excimers and keto-defects.[6] On the other hand, polycarbazoles linked at 3,6- and 2,7-positions[7] have advantages of little formation of excimers and free of the keto-defects. Since the latter polymers should allow extension of conjugation through polymer main chain due to having a poly(*p*-phenylene)-like backbone, which can be expected to improve the luminescent properties. Some 2,7-linked carbazole homopolymers and copolymers have been synthesized from *N*-benzoyl,[8] *N*-octyl or ethylhexyl,[9] and a variety of *N*-alkyl carbazoles.[10] Despite the persistent researches, there have been few reports investigating poly(*N*-aryl-2,7-carbazole)s.

Chart 1



In our previous report,[11] poly[*N*-(*p*-(2-ethylhexyloxy)phenyl)-carbazol-2,7-ylene] (Chart 1) had the key properties for the blue-light emitting material in PLED devices, i.e., a good solubility, quantitative fluorescence quantum efficiency in $CHCl_3$, and a good thermal stability (T_g > 150 °C, T_s > 210 °C, T_d = 430 °C). The device composed of ITO/PEDOT(PSS)/polymer/Ca−Al realized the pure blue emission with the maximum luminance about 2000 cd/m^2 and the efficiency of >0.2 cd/A at 10 V, whose EL spectrum was same to that of PL in the solid state. However, this polymer needs some improvements for the PLED applications. First, the number-average molecular weight (M_n = 7.7 kDa) was not enough high to make thin polymer films with little defect by spin-coating. Second, intensity of fluorescence in the film state (ϕ_f (film) < 0.15) was modest. Third, emission λ_{max} at 433 nm suggested a poor visibility for the human eye,[12] where the ideal wavelength maximum was around 450 nm. Last, the HOMO energy level at −5.4 eV was basically satisfactory, but fine-tuning of the energy level is frequently required for an efficient emission of PLED.

In this paper, we synthesized some novel poly(*N*-aryl-2,7-carbazole)s with alkoxy groups or a diphenylamino group at *o*-, *m*- or *p*-position of the *N*-phenyl group by the Ni^0-catalyzed Yamamoto dehalogenative coupling[13] of 2,7-dihalogenocarbazole monomers in order to improve the molecular weights, intensity of fluorescence in the film state, visibility, and the

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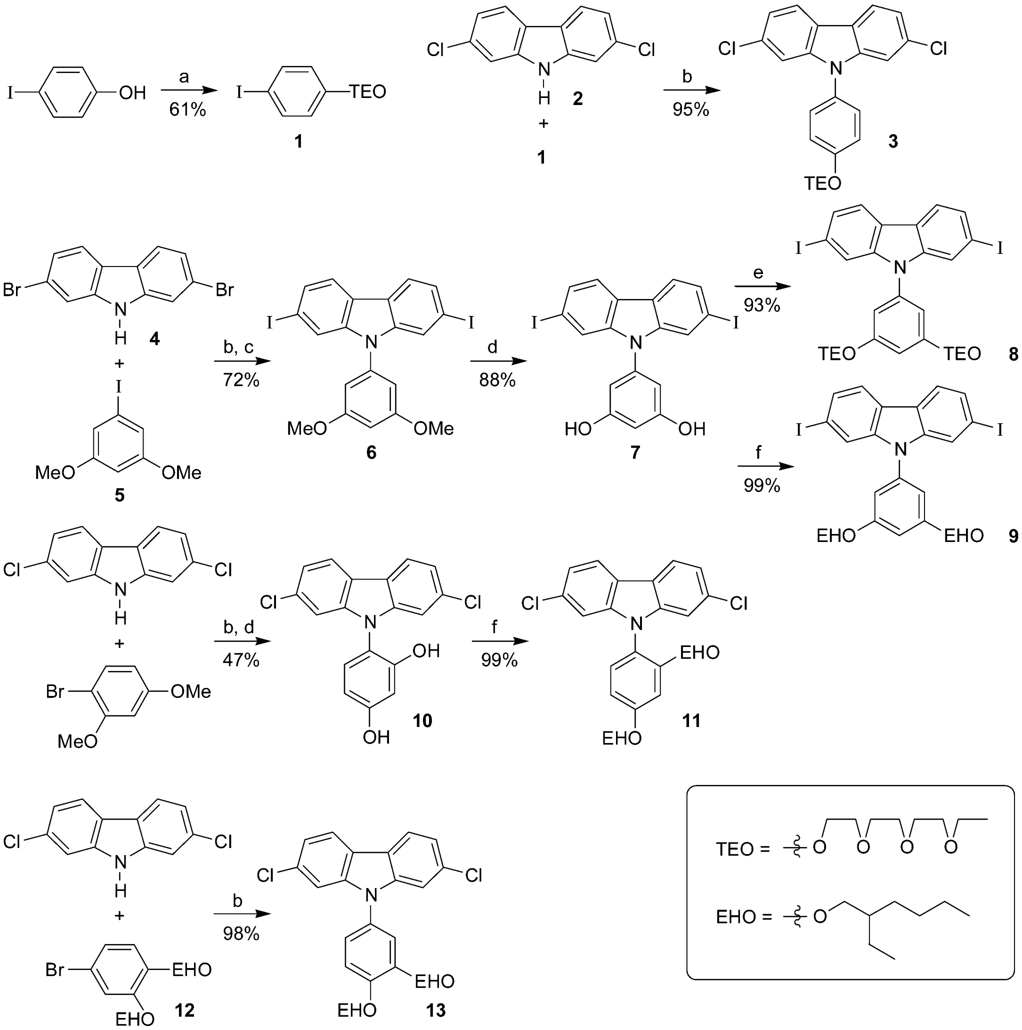
Scheme 1. Syntheses of Monomers with TEO or EHO Groups[a]



[a] Reagents and conditions: (a) triethylene glycol monoethyl ether *p*-tosylate, K_2CO_3, DMF, 130 °C; (b) CuI, K_3PO_4, CHDA, 1,4-dioxane, 100 °C; (c) CuI, NaI, CHDA, 1,4-dioxane, 105 °C; (d) BBr_3, CH_2Cl_2, −20 °C to room temperature; (e) triethylene glycol monoethyl ether *p*-tosylate, KOH, DMF, 60 °C; (f) 1-bromo-2-ethylhexane, K_2CO_3, DMF, 70 °C.

energy levels of HOMO as well as other electronic and optical properties of poly(2,7-carbazole)s.

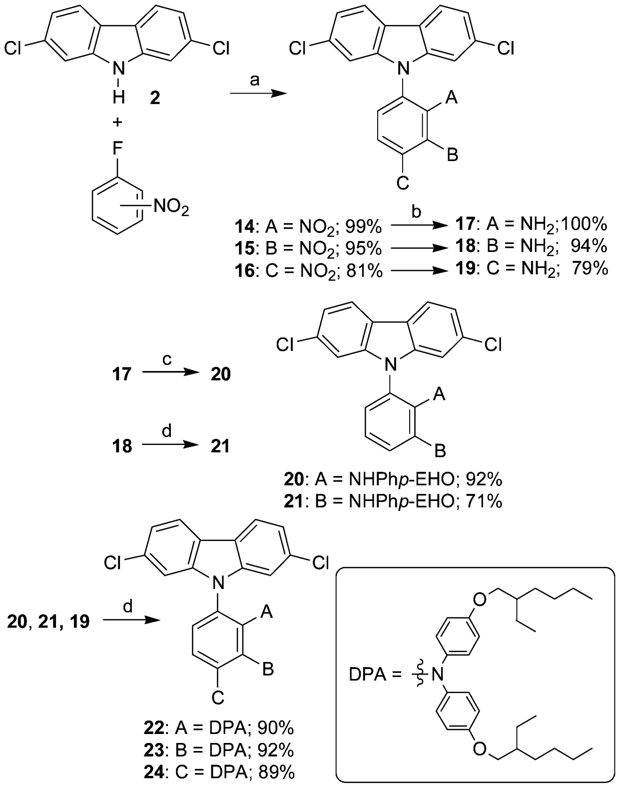
Results and Discussion

Syntheses of Monomers. Scheme 1 illustrates the synthetic route of the monomers with triethylene oxide (TEO) chains or 2-ethylhexyloxy (EHO) groups at *o*-, *m*-, or *p*- position of the *N*-phenyl group. 4-(3,6,9-Oxaundecyloxy)iodobenzene (**1**) was prepared from 4-iodophenol with triethylene glycol monoethyl ether *p*-tosylate[14] according to the literature procedure.[15] N-arylation of 2,7-dichlorocarbazole **2**[9f] with halogenobenzene **1** was carried out by the CuI−*trans*-1,2-cyclohexanediamine (CHDA) catalyzed method,[16] affording the monomer **3** in a good yield (95%). However, in the case of N-arylation of 2,7-dibromocarbazole **4**[17] with 3,5-dimethoxyiodobenzene **5**,[18] a halogen exchange reaction occurred during the N-arylation, forming a minor amount of iodocarbazoles. Thus, iodination of the halogenocarbazoles were successively carried out under the similar conditions but using NaI in stead of K_3PO_4,[9] giving **6**. After cleavage of the methoxy group of **6** with BBr_3 at room temperature, *N*-(3,5-dihydroxyphenyl)-2,7-diiodocarbazole **7** was treated with triethylene glycol monoethyl ether *p*-tosylate or 1-bromo-2-ethylhexane in DMF, quantitatively producing *N*-[3,5-bis(3,6,9-oxaundecyloxy)phenyl]-2,7-diiodocarbazole **8** or N-[3,5-bis(2-ethylhexyloxy)phenyl]-2,7-diiodocarbazole **9**, respectively. Geometrical isomers **11** and **13** were similarly prepared by the synthetic procedure for **9**.

The synthetic route of the monomers with diphenylamino (DPA) group is shown in Scheme 2. Since the synthesis of *N*-(*p*-aminophenyl)-2,7-dibromocarbazole has been reported by Jian et al.,[20] the substitution reaction of **2** with *o*-, *m*,- or *p*-fluoronitrobenzene was carried out according to the reported procedure, affording **14-16** that were reduced to amino compounds **17-19**, respectively. Mono N-arylation of aniline derivatives, 9-anilinocarbazoles, with 1-bromo-4-(2-ethylhexyloxy)-benzene,[21] or 1-(2-ethylhexyloxy)-4-iodobenzene[22] was carried out by the Pd-catalyzed reaction, selectively giving **20** and **21**. The mono-arylation step was not only important to produce the diaryl compounds, **22** and **23**, in high yields, but also useful to introduce another aryl group.[23] On the other hand, the *p*-amino compound **19** was reactive enough to obtain the diaryl monomer **24** in a high yield (89%).

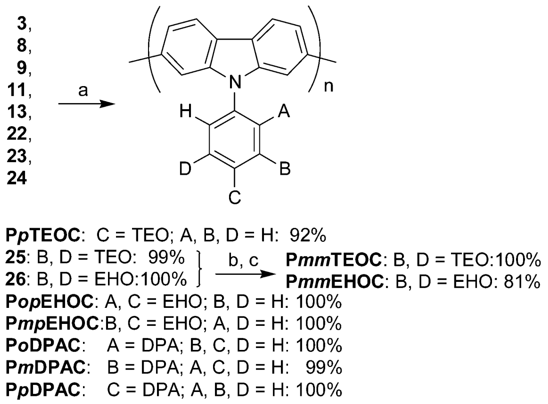
Synthesis and Characterizations of Homopolymers. All homopolymers were prepared by the Ni^0-catalyzed Yamamoto polymerization under slightly modified conditions as shown in Scheme 3.[13] To a mixture of 2,2′-bipyridine (bpy), bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$), and 1,5-cyclooctadiene (COD) in DMF was added the monomer in THF at 50 °C, and then stirred at 70 °C. The polymerization reaction proceeded almost quantitatively (92−100%). The polymers **25** and **26** which have

Scheme 2. Syntheses of Monomers with DPA Group[a]



[a] Reagents and conditions: (a) K_2CO_3, DMF, 150 °C; (b) $SnCl_2 \cdot 2H_2O$, EtOH, reflux; (c) 1-bromo-4-(2-ethylhexyloxy)benzene, $Pd(OAc)_2$, P(*t*-Bu)$_3$, K_2CO_3, toluene, 110 °C; (d) 1-(2-ethylhexyloxy)-4-iodobenzene, $Pd(OAc)_2$, P(*t*-Bu)$_3$, NaO-*t*-Bu, toluene, 110 °C.

Scheme 3. Syntheses of Polymers[a]



[a] Reagents and conditions: (a) $Ni(COD)_2$, COD, bpy, DMF-THF, 70 °C; (b) *n*-BuLi, THF, −10 °C; (c) NH_4Cl aq, 0 °C.

a terminal residue of iodide in some degree were subjected to treatment of *n*-BuLi to convert to **P*mm*TEOC** and **P*mm*EHOC** having terminal H. All resulting polymers are soluble in general organic solvents such as $CHCl_3$ and THF, and could be purified by reprecipitation from hexane or methanol. They showed a good processability to make a cast film on some substrates.

The chemical structures of the polymers were confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopies. The results of elemental analysis are summarized in Table 1. The found values of carbon content of the polymers were somewhat smaller than the calculated ones, which might be due to a flame resistivity of conjugated polyarylenes and remaining of the residual terminal Cl. Judging from the iodine content of **25** and **26** (I = 0.42 and 1.81%), the amount of the terminal-I residue is not negligible for the polymers to undego the heavy atom effect that significantly influences the luminescent performance of the polymers. After the treatment of **25** and **26** by *n*-BuLi, the residual I was no longer detected from **P*mm*TEOC** and **P*mm*EHOC**.

Table 1. Elemental Analysis Data of Polymers

polymer	formula (mol wt)		C	H	N	I
P*p*TEOC	$(C_{26}H_{27}NO_4)_n$	calcd	74.80	6.52	3.35	
	$(417.50)_n$	found	72.44	6.39	3.12	
25	$(C_{34}H_{43}NO_8)_n$	calcd	68.78	7.30	2.36	0.00
	$(593.71)_n$	found	68.96	6.88	2.64	0.42
P*mm*TEOC		found	66.79	7.13	2.51	0.00
26	$H(C_{34}H_{43}NO_2)_{20}I$	calcd	81.01	8.61	2.78	1.26
	(10082)	found	81.25	8.28	3.14	1.81
P*mm*EHOC	$(C_{34}H_{43}NO_2)_n$	calcd	82.05	8.71	2.81	0.00
	$(497.71)_n$	found	82.11	8.43	3.11	0.00
P*op*EHOC		found	77.60	8.33	2.68	
P*mp*EHOC		found	80.50	8.45	2.69	
P*o*DPAC	$(C_{46}H_{52}N_2O_2)_n$	calcd	83.09	7.88	4.21	
	$(664.92)_n$	found	82.02	7.72	3.95	
P*m*DPAC		found	80.13	7.75	3.85	
P*p*DPAC		found	82.13	7.81	4.05	

Table 2. GPC and Thermal Analysis Results of Polymers

polymer	M_n (kDa)[a]	M_w (kDa)[a]	PDI	DP	T_d (°C)[b]
P*p*TEOC	9.1	17.1	1.9	22	359
P*mm*TEOC	5.5	13.7	2.5	9	354
P*mm*EHOC	13.1	22.0	1.7	26	350
P*op*EHOC	14.3	31.8	2.2	29	402
P*mp*EHOC	29.0	79.9	2.8	58	386
P*o*DPAC	26.3	157	6.0	39	381
P*m*DPAC	62.0	1430	23	93	380
P*p*DPAC	51.5	3110	60	77	379

[a] Determined by GPC vs polystyrene standards in THF. [b] Defined as the temperature at the 5 wt % loss in the TGA process at a heating rate of 5 °C min^{-1} under Ar.

The results of number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers determined by gel permeation chromatography (GPC) and a thermal property evaluated by thermogravimetric analysis (TGA) are summarized in Table 2. The obtained polymers showed a good degree of polymerization (DP) due to having the flexible and solubilizing side chains. Exceptionally, a series of **PTEOC** polymers (**P*p*TEOC** and **P*mm*TEOC**) was found to have the low M_n of 9100 and 5500, whose DP is corresponding to 22 and 9, respectively. The low M_n might be due to a trapping effect of the Ni catalyst by the 3,6,9-oxaundecyloxy side chain. A series of **PEHOC** polymers showed satisfactory results of DP (ca. 30) and a small polydispersity index (PDI) (ca. 2.2). On the contrary, **P*m*DPAC** and **P*p*DPAC** showed the larger DP (93 and 77) and PDI (23 and 60). This is due to a low solubility of the polymers which caused partial gelation and inefficient stirring of the reaction mixture during the polymerization. The thermal stability of the polymers is evaluated by the temperature (T_d) at which temperature 5% of mass is reduced from the starting material in the TGA process. All of them showed a good thermal stability having the high T_d over 350 °C.

Optical Properties. The absorption and fluorescence spectral data of the synthesized poly(*N*-phenyl-2,7-carbazole) derivatives are summarized in Table 3.[24] When we pay attention the fluorescence quantum yields of **P*mm*TEOC** ($\phi_f = 0.78$) and **P*mm*EHOC** ($\phi_f = 0.81$) in $CHCl_3$, it is found that the quantum yields of **25** ($\phi_f = 0.46$) and **26** ($\phi_f = 0.65$) are unfailingly improved by the hydrogenation of terminal-I, respectively, which is due to cancellation of the heavy atom effect. Consequently, the quantum yield of the most poly(*N*-aryl-2,7-carbazole)s falls

Table 3. Absorption and Fluorescence Spectral Data of Polymers

	solution (in $CHCl_3$)[a]				thin film[b]				
polymer	abs λ_{max} (nm)	log ϵ[c]	em λ_{max} (nm)[d]	ϕ_f[e]	abs λ_{max} (nm)	E_g (eV)[f]	em λ_{max} (nm)[d]	ϕ_f[g]	CIE (*x*, *y*)[h]
P*p*TEOC	387	4.44	417	0.68	392	2.81	436, 463	0.06	0.161, 0.205
25	387	4.62	416	0.46	386	2.90	426		0.170, 0.141
P*mm*TEOC	386	4.56	415	0.78	386	2.89	426	0.08	0.178, 0.169
26	376	4.48	413	0.65	358	2.89	423		0.167, 0.151
P*mm*EHOC	377	4.50	413	0.81	365	3.03	422	0.07	0.173, 0.187
P*op*EHOC	379	4.45	414	0.82	375	2.92	425, 448, 474	0.28	0.160, 0.198
P*mp*EHOC	389	4.63	417	0.80	394	2.93	430	0.40	0.153, 0.096
P*o*DPAC	387	4.56	418	0.04	384	2.94	424, 447	0.20	0.159, 0.141
P*m*DPAC	391	4.56	418	0.19	397	2.90	430, 457	0.32	0.152, 0.139
P*p*DPAC	388	4.62	415	0.01	389	2.87	429, 455	0.13	0.156, 0.163

[a] Absorption and fluorescence spectra were measured at 1.0 × 10^{-5} M and 0.5 × 10^{-6} M per unit, respectively, at room temperature. [b] Cast film on a quartz glass plate from CH_2Cl_2 solutions. [c] Molar absorption coefficient calculated from per carbazole unit. [d] The excitation wavelength is almost the same as λ_{max}(abs) in each case because the excitation spectrum of each polymers almost matched the absorption spectrum. [e] Measured using 9,10-diphenylanthracene ($\phi_f = 0.97$ in cyclohexane) as the standard. [f] Band gap estimated from the onset of the absorption band edge. [g] Polymers were dissolved with chroloform and spin-coated onto a quartz substrate, and excited at 350 nm from Xe lamp. Photon measurement range of PL was 400−700 nm. [h] Tristimulus values were calculated from the fluorescence spectrum data in consideration of visibility factor.

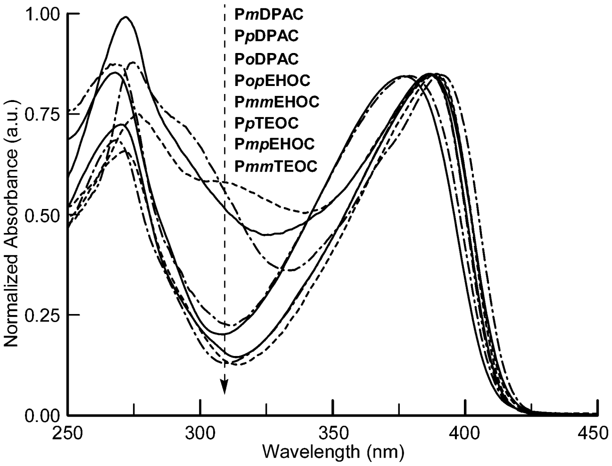


Figure 1. Absorption spectra of polymers in $CHCl_3$.

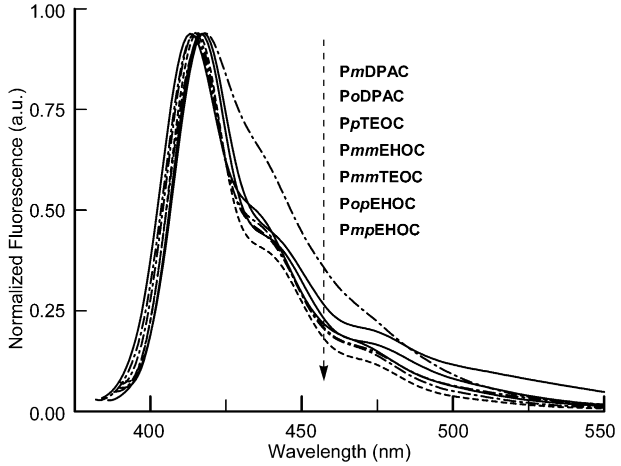


Figure 2. Fluorescence emission spectra of the polymers except for **P*p*DPAC** in $CHCl_3$.

in $\phi_f = 0.8$ except for **PDPACs**. In the case of **PDPACs**, an exciton quenching might occur between the directly linked triphenylamino group and the poly(2,7-carbazole) chains by resonance effect, judging from the descending order of fluorescent quantum yields of the regioisomers; **P*m*DPAC** (ϕ_f (sol) = 0.19) > **P*o*DPAC** (ϕ_f (sol) = 0.04) > **P*p*DPAC** (ϕ_f (sol) = 0.01). In the solid-film state, the similar tendency was observed for **PDPACs** (**P*m*DPAC** (ϕ_f (film) = 0.32) > **P*o*DPAC** (ϕ_f (film) = 0.20) > **P*p*DPAC** (ϕ_f (film) = 0.13)), but the quantum yields were apparently higher than those in solution. It is thought that the conformation of **PDPACs** in the solid state have a barrier to rotate the *N*-phenyl group, which might result in little conjugation between the carbazole unit and the triphenylamino group. Similarly in the case of **PEHOCs** and **PTEOCs**, the polymer having the bulkier substituent at the less conjugation position of the *N*-phenyl group is the more effective for efficient PL in the solid state (**P*mp*EHOC** (ϕ_f (film) = 0.40) > **P*op*EHOC** (ϕ_f (film) = 0.28), **P*mm*TEOC** (ϕ_f (film) = 0.08) > **P*p*TEOC** (ϕ_f (film) = 0.06)).

The UV−vis absorption and emission spectra of the polymers in $CHCl_3$ are depicted in Figure 1, and Figure 2, respectively. The absorption bands around 300 nm of **PDPACs** are attributed to the triphenylamino group. For all polymers, the absorption maximum (λ_{max}(abs)) and the emission maximum (λ_{max}(em)) in $CHCl_3$ are in the range from 377 to 391 nm and from 413 to 418 nm, respectively, depending on the nature of the functional groups and the molecular weight of the polymer. The λ_{max}(abs) in $CHCl_3$ for **PTEOCs** was about 386 nm which was longer in wavelength than those for **P*mm*EHOC** (λ_{max}(abs) = 377 nm) and **P*op*EHOC** (λ_{max}(abs) = 379 nm). The red-shift (ca. 8 nm) is probably due to difference of an electron-donating resonance effect of the flexible side substituent. Correspondingly, the λ_{max}(abs) values for **PDPACs** and **P*mp*EHOC** were 389 nm which was further longer in wavelength than those for **PTEOCs**. The additional red-shift (3 nm) is due to an effect of π-conjugation through the polymer main chain with the higher molecular weight. According to the shifts of λ_{max}(abs) values, the λ_{max}(em) values of poly(*N*-aryl-2,7-carbazole)s fall in an order; **PDPACs** and **P*mp*EHOC** (λ_{max}(em) ≈ 417 nm) > **PTEOCs** (λ_{max}(em) ≈ 416 nm) > **P*mm*EHOC** and **P*op*EHOC** (λ_{max}(em) ≈ 413 nm).

UV−vis absorption and PL spectra of **PTEOCs**, **PEHOCs**, and **PDPACs** in the thin solid-film state are depicted in Figure 3, Figure 4, and Figure 5, respectively. The absorption spectra of these polymers in solution and thin film states are similar, but the fluorescenece spectra in the solid state are considerably different from those in $CHCl_3$. The difference is due to a molecular arrangement of the polymers, induced by the functional groups at the *N*-phenyl position. All obtained polymers exhibit a strong fluorescence with the 0−0 emission band around 430 nm and additional emission bands in the longer wavelength region around 455 and 475 nm, probably because of their vibronic effects and π-aggregations. Since poly(*N*-alkylcarbazole)s such as poly(*N*-octyl-2,7-carbazole)[9f] and poly(*N*-octyl-2,7-carbazole)[25] have additional emission bands in the longer wavelength region around 490 and 500 nm, poly(*N*-phenyl-2,7-carbazole) derivatives in this work is superior to poly(*N*-

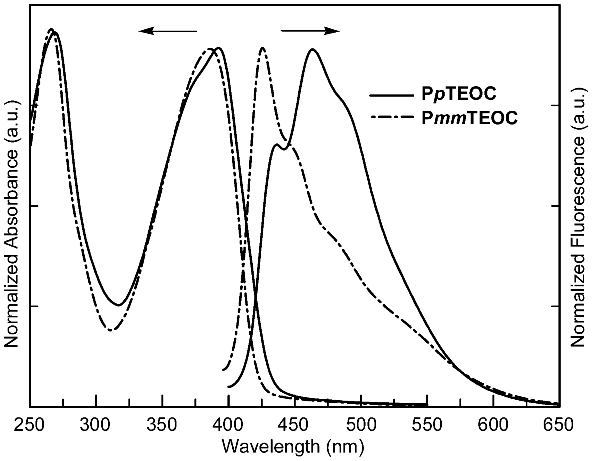


Figure 3. UV−vis absorption and photoluminescence (PL) spectra of **PTEOCs** in the thin film state.

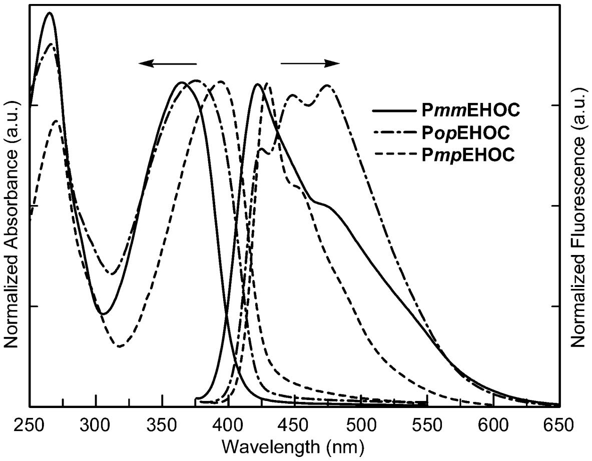


Figure 4. UV−vis absorption and photoluminescence (PL) spectra of **PEHOCs** in the thin film state.

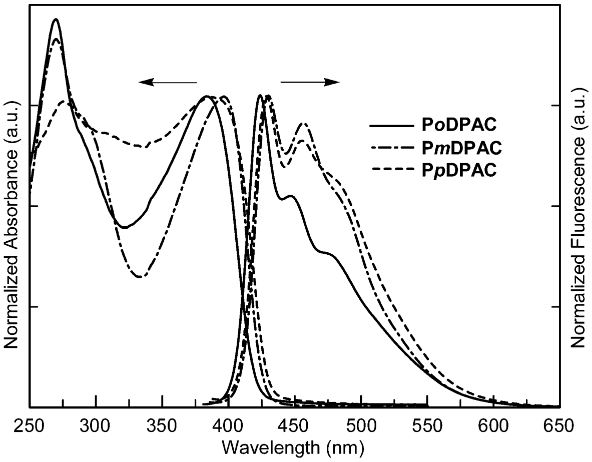


Figure 5. UV−vis absorption and photoluminescence (PL) spectra of **PDPACs** in the thin film state.

alkylcarbazole)s for pure blue PL emission. In Figure 3, a strong fluorescence band around 430 nm for **P*mm*TEOC** suggests a poor visibility to the human eye,[12] although the band is within a region for the pure blue emission. On the other hand, a strong emission band around 460 nm for **P*p*TEOC** suggests a good visibility, but the broad emission band decreases purity of blue color ($x = 0.161$, $y = 0.205$). In Figure 4, **P*mp*EHOC** had an intense sharp emission band (λ_{max}(em) = 430 nm; $x = 0.153$, $y = 0.096$), while broad bands were observed for **P*mm*EHOC** (λ_{max}(em) = 422 nm) and **P*op*EHOC** (λ_{max}(em) = 474 nm), respetively. A slight geometrical change at the *N*-phenyl portion influences large the intra- and intermolecular interactions of the polymers in the solid state, which might bring about the spectral change. Interestingly in Figure 5, **P*m*DPAC** having a strong emission band at λ_{max}(em) = 457 nm shows better visibility than **P*o*DPAC** (λ_{max}(em) = 427 nm). What is more, the emission band of **P*m*DPAC** that shows pure blue emission ($x = 0.152$, $y = 0.139$) is somewhat sharper than that of **P*p*DPAC**.

Electrochemical Properties. Electrochemical analysis of the thin-film sample of the polymers was employed to estimate the HOMO and LUMO energy levels.[26] Taking into consideration the electrochemical results and the optical band gap (Table 3), in general, the LUMO energy level was deduced from the optical band gap and the HOMO level determined by the electrochemical analysis. The energy levels of the polymers are summarized in Figure 6. According to this diagram, the HOMO energy level of the polymers changes from −5.17 eV to −5.70 eV in the following order: **P*p*DPAC** > **P*o*DPAC** > **P*m*DPAC** > **P*p*TEOC** > **P*mm*TEOC** > **P*op*EHOC** > **P*mp*EHOC** > **P*mm*EHOC**. The tendency might be determined by the following factors. Since electron donating ability of the functional goup at the *N*-phenyl portion lowers the ionization potential of poly(*N*-phenylcarbazole)s, a substantial permutation of HOMO level will be **PDPAC** > **PTEOC** > **PEHOC**. Second, resonance effect of the functional group to the polymer main chain will be controlled by the geometrical position (*para* > *ortho* > *meta*) at the N-phenyl portion. In effect, the HOMO energy levels could be largely changed by the functional group and mildly tuned by the geometrical effect. As a consequence, we succeeded to synthesize poly(*N*-phenylcarbazole)s with various HOMO levels; i.e., the average values of −5.21 eV for **P*p*DPAC**, **P*o*DPAC** and **P*m*DPAC** with the triphenylamino group, −5.36 eV for **P*p*TEOC** and **P*mm*TEOC** with the triethylene oxide group, and −5.62 eV for **P*op*EHOC**, **P*mp*EHOC** and **P*mm*EHOC** with the alkoxy group, respectively, and these polymers might have a low barrier for hole injection from ITO for PLED applications.

In addition, the band gap of the polymer in the thin film state is considered to be chiefly influenced by interchain π-interaction in association with excimer formation. The stronger the interchain interaction the polymer has, the lower the band gap of the polymer will be. In this case, the *p*-substituted poly(*N*-phenylcarbazole)s are less steric-hindered than *m*- and *o*-substituted ones. By the same token, the polymer having flexible, linear, and small substituents is less sterically hindered than those having rigid, branched, and large substituents. Consequently, the band gap of the polymer having less steric-hindered side chain is small as the case of **P*p*TEOC**.

Conclusions

In this paper, we presented the syntheses and characterizations of some novel poly(*N*-phenyl-2,7-carbazole)s with the alkoxy groups or the diphenylamino group at *o*-, *m*-, or *p*- position of the *N*-phenyl portion. These polymers were obtained in high yields, and they had a relatively high molecular weight, a good solubility in common organic solvents, and a good thermal stability. In the $CHCl_3$ solution, they showed similar electronic properties of absorption and emission, i.e., the values of λ_{max}(abs) and λ_{max}(em) of each polymer were almost steady, being about 385 and 415 nm, respectively. In the state of the thin films, all the polymers showed bright blue fluorescence with the emission bands around 430, 455, and 475 nm. Intensity of each band was strongly influenced by the molecular arrangement

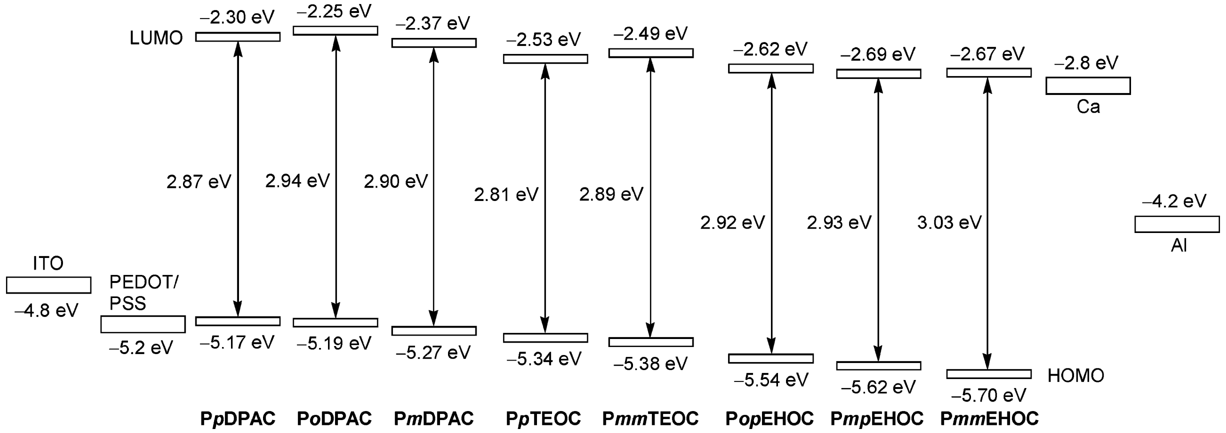


Figure 6. Energy band diagrams of the polymers.

of the polymers originating from the functional group of the *N*-phenyl portion. Fluorescence quantum yields of the polymers were high in both solution and thin solid states. The introduction of the triethylene oxide group or the triphenylamino group have lowered the ionization potential, and the HOMO energy levels could be changed up to −5.17 eV, almost same as the energy level of PEDOT/PSS. Since the poly(*N*-alkoxyphenylcarbozole) had shown the good performance of PLED, which was superior to poly(*N*-alkylcarbozole)s as described in the previous report,[11] our synthetic approach was started from this point to develop the ultimate blue-light emitting polymer. Actually, our preliminary manufacturing of PLED device composing of ITO/PEDOT-(PSS)/**P*mp*EHOC**/CsF/Al realized pure blue emission ($x = 0.165$, $y = 0.117$), comfortable efficiency and luminance ($\eta_c = 0.48$ cd/A, 2700 cd/m^2) at 7 V. The maximum luminance reached 18800 cd/m^2 ($\eta_c = 0.95$ cd/A) at 11V, although it was slowly greenish afterward. From these results, it is considered that this new class of polycarbazoles have a great potential to be applied in PLED as the blue-light emitting material in view of processability, quantum yield, color purity, and HOMO energy level.

Experimental Section

General Method and Instrumentations. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. Column chromatography was performed using a silica gel (Kanto Chem., 60 N, 63−120 μm). IR and NMR spectra were recorded on a JASCO FT/IR 550 spectrophotometer and a JEOL FT-NMR (270 MHz) spectrometer, respectively. ^{1}H and ^{13}C chemical shifts are given in units of δ (ppm) relative to δ (TMS) = 0.00 and δ (CDCl$_3$) = 77.0 ppm, respectively. Elemental analyses were carried out with a Perkin-Elmer type 2400. Molecular weights of the polymers were estimated by GPC equipped with a UV detector (Jasco) based on polystyrene standards (eluent = THF). Thermal analyses were carried out by an Extra 6000 TG/DTA (Seiko) thermogravimetric analyzer at a heating rate of 5 °C min^{-1} in argon atmosphere. UV−vis and PL measurements of the polymer samples in CHCl$_3$ and in a form of coating thin film on quartz glass were performed using a U-3500 spectrophotometer (Hitachi) and a FP-750 spectrofluometer (Jasco). The measurement of HOMO (or LUMO) energy level of the polymer films on a Pt disk was performed at a scan rate of 50 mV/s in an acetonitrile solution containing 0.1 M Et$_4$NBF$_4$ (Bu$_4$NBF$_4$ for LUMO) at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and platinum wire as the counter electrode. The electrochemical data (vs SCE) obtained by cyclic voltammetry was made a correction with the redox potential (4.8 eV) of ferrocene/ferrocenium$^+$.[5]

Materials. DMF, CH$_2$Cl$_2$, and toluene were distilled after drying with CaH$_2$ under an argon atmosphere. THF and 1,4-dioxane were distilled after drying with sodium under an argon atmosphere. The other solvents and all commercially available reagents were used without further purification. The triethylene glycol monoethyl ether *p*-tosylate,[14] 2,7-dichloro-9*H*-carbazole (**2**),[9f] 2,7-dibromo-9*H*-carbazole (**4**),[17] 3,5-dimethoxyiodobenzene (**5**),[18] 3,4-bis(2-ethylhexyloxy)bromobenzene (**12**),[27] 1-bromo-4-(2-ethylhexyloxy)benzene,[21] 1-(2-ethylhexyloxy)-4-iodobenzene[22] were prepared according to literature procedures.

4-[2-(Ethoxyethoxyethoxy)ethoxy]iodobenzene (1). A mixture of 4-iodophenol (2.20 g, 10.0 mmol), K$_2$CO$_3$ (2.07 g, 15.0 mmol), DMF (30 mL), and triethylene glycol monoethyl ether *p*-tosylate (3.32 g, 15.0 mmol) was stirred at 130 °C for 24 h. After the reaction was cooled to room temperature, Et$_2$O was added to the reaction mixture. The organic layer was washed with H$_2$O and brine and dried over Na$_2$SO$_4$. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with CH$_2$Cl$_2$ to give **1** (2.36 g, 61.0% yield) as a yellow oil. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.53 (d, $J = 9.0$ Hz, 2H), 6.96 (d, $J = 9.0$ Hz, 2H), 4.09 (t, $J = 4.9$ Hz, 2H), 3.84 (t, $J = 4.9$ Hz, 2H), 3.74−3.57 (m, 8H), 3.52 (q, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 158.5, 138.0, 117.0, 82.9, 70.8, 70.7, 70.6, 69.8, 69.6, 67.5, 66.6, 15.2. IR (KBr): 2972, 2869, 1678, 1572, 1486, 1283, 1246, 1176, 1134, 1057, 821 cm^{-1}. Anal. Calcd for C$_{14}$H$_{21}$IO$_4$: C, 44.22; H, 5.57; N, 0.00. Found: C, 44.04; H, 5.53; N, 0.05.

2,7-Dichloro-*N*-[4-(2-(ethoxyethoxyethoxy)ethoxy)phenyl]carbazole (3). A mixture of **2** (708 mg, 3.00 mmol), CuI (19.1 mg, 0.100 mmol), potassium phosphate (892 mg, 4.20 mmol), 1,4-dioxane (6 mL), and *trans*-1,2-cyclohexanediamine (CHDA) (45.7 mg, 0.400 mmol), **1** (760 mg, 2.00 mmol) was stirred at 100 °C for 7 h. After the reaction was cooled to room temperature, CH$_2$Cl$_2$ was added to the reaction mixture. The organic layer was washed with H$_2$O and dried over Na$_2$SO$_4$. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with CH$_2$Cl$_2$ to give **3** (946 mg, 95.0% yield) as a yellow oil. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.96 (d, $J = 8.9$ Hz, 2H), 7.37 (d, $J = 8.9$ Hz, 2H), 7.235 (dd, $J = 8.9$, 1.5 Hz, 2H), 7.225 (d, $J = 1.5$ Hz, 2H), 7.14 (d, $J = 8.9$ Hz, 2H), 4.26 (t, $J = 4.7$ Hz, 2H), 3.93 (t, $J = 4.7$ Hz, 2H), 3.80−3.60 (m, 8H), 3.54 (q, $J = 6.9$ Hz, 2H), 1.2 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 158.4, 142.0, 131.7, 128.9, 128.2, 120.9, 120.8, 120.4, 115.9, 109.8, 70.8, 70.63, 70.56, 69.7, 69.5, 67.4, 66.6, 15.1. IR (KBr): 2898, 1590, 1513, 1447, 1249, 1132, 1100, 1061, 792 cm^{-1}. Anal. Calcd for C$_{26}$H$_{27}$NCl$_2$O$_4$•0.25 H$_2$O: C, 63.35; H, 5.62; N, 2.84. Found: C, 63.08; H, 5.72; N, 2.89.

2,7-Diiodo-*N*-(3,5-dimethoxyphenyl)carbazole (6). A mixture of **4** (1.30 g, 4.00 mmol), **5** (6.33 g, 24.0 mmol), CuI (190.5 mg, 1.00 mmol), potassium phosphate (2.55 g, 12.0 mmol), 1,4-dioxane (5 mL), and *trans*-1,2-cyclohexanediamine (240 μL, 2.00 mmol) was stirred at 100 °C for 10 h. After the reaction was cooled to room temperature, CH$_2$Cl$_2$ was added to the reaction mixture. The organic layer was washed with H$_2$O and dried over Na$_2$SO$_4$. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (2:1) to give 2,7-dibromo-*N*-(3,5-dimethoxyphenyl)carbazole, but it was partially iodinated. Then we proceeded to following reaction in order to iodize perfectly. To this residue was added CuI (83.8 mg, 0.440 mmol), NaI (6.00 g, 40.0 mmol), 1,4-dioxane (8 mL), and *trans*-1,2-cyclohexanediamine (240 μL, 2.00 mmol). The resulting mixture was stirred at 100 °C for 50 h. After the reaction was cooled to room temperature, CH_2Cl_2 was added to the reaction mixture. The organic layer was washed with H_2O, and subjected to short path column chromatography on silica gel. After evaporation of solvent, the residue was recrystallized from $CHCl_3$−MeOH to give **6** (1.60 g, 71.9% yield) as a white solid. The excess **5** used in this reaction could be recovered in some degree (3.11 g). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 1.5 Hz, 2H), 7.58 (dd, *J* = 8.2, 1.5 Hz, 2H), 6.60 (brs, 3H), 3.86 (s, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 161.7, 141.5, 137.9, 129.1, 122.0, 121.6,119.0, 105.4, 100.3, 91.1, 55.7. IR (KBr): ν 1609, 1595, 1579, 1487, 1473, 1443, 1420, 1325, 1204, 1157, 784 cm^{-1}. Anal. Calcd for $C_{20}H_{15}NI_2O_2$: C, 43.27; H, 2.72; N, 2.52. Found: C, 43.28; H, 3.03; N, 2.59.

***N*-(3,5-Dihydroxyphenyl)-2,7-diiodocarbazole (7).** To a solution of 1 M BBr_3 in CH_2Cl_2 (6.72 mL, 6.72 mmol) was added **6** (1.24 g, 2.24 mmol) in a small potion at −20 °C. The resulting mixture was stirred for 4 h at −20 °C and then stirred for 4 h at room temperature. Water and EtOAc were added to the reaction mixture. The organic layer was washed with H_2O and brine. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with CH_2Cl_2−EtOAc (10:1). After evaporation of solvent, the residue was recrystallized from EtOAc−hexane to give **7** (1.04 g, 87.8% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 1.5 Hz, 2H), 7.58 (dd, *J* = 8.2, 1.5 Hz, 2H), 6.55 (d, *J* = 2.3 Hz, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 5.18 (s, 2H). ^{13}C NMR (CD_3-OD, 67.5 MHz): δ 161.8, 143.4, 139.7, 131.0, 124.1, 123.5, 120.9, 106.8, 104.4, 92.3. IR (KBr): ν 3449, 1607, 1509, 1422, 1228, 1145, 998, 936, 835, 783, 692 cm^{-1}. Anal. Calcd for $C_{18}H_{11}I_2NO_2$: C, 41.02; H, 2.10; N, 2.66. Found: C, 41.32; H, 2.29; N, 2.39.

***N*-[3,5-Bis(2-(ethoxyethoxyethoxy)ethoxy)phenyl]-2,7-diiodocarbazole (8).** A mixture of **7** (500 mg, 0.949 mmol), K_2CO_3 (525 mg, 3.80 mmol), DMF (5 mL), and triethylene glycol monoethyl ether *p*-tosylate (946 mg, 2.85 mmol) was stirred at 60 °C for 26 h. The reaction mixture was subjected to column chromatography on silica gel eluted with CH_2Cl_2–EtOAc (7:1) and successively with CH_2Cl_2–EtOAc (1:1) to give **8** (750 mg, 93.4% yield) to give a colorless oil. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 1.5 Hz, 2H), 7.57 (dd, *J* = 8.2, 1.5 Hz, 2H), 6.65 (t, *J* = 2.1 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 2H), 4.16 (t, *J* = 4.9 Hz, 4H), 3.89 (t, *J* = 4.9 Hz, 4H), 3.77−3.56 (m, 16H), 3.51 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 160.8, 141.4, 137.6, 129.0, 121.9, 121.5, 118.9, 106.1, 101.4, 90.9, 70.8, 70.6, 70.5, 69.7, 69.4, 67.8, 66.5, 15.1. IR (KBr): ν 2871, 1611, 1587, 1446, 1323, 1241, 1175, 1107, 943, 847, 798, 691 cm^{-1}. Anal. Calcd for $C_{34}H_{43}I_2NO_8$: C, 48.18; H, 5.11; N, 1.65. Found: C, 48.25; H, 5.16; N, 1.77.

***N*-[3,5-Bis(2-ethylhexyloxy)phenyl]-2,7-diiodocarbazole (9).** A mixture of **7** (430 mg, 0.816 mmol), K_2CO_3 (1.35 g, 9.79 mmol), DMF (7 mL), and 1-bromo-2-ethylhexane (946 mg, 4.90 mmol) was stirred at 70 °C for 5 h. The reaction mixture was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (10:1) to give **9** (607 mg, 99.0% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 1.5 Hz, 2H), 7.57 (dd, *J* = 8.2, 1.5 Hz, 2H), 6.60 (t, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 2H), 3.87 (d, *J* = 5.6 Hz, 4H), 1.76 (m, 2H), 1.53−1.32 (m, 16H), 0.95 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 161.4, 141.5, 137.5, 128.9, 121.9, 121.5, 119.0, 105.6, 101.3, 90.9, 70.9, 39.3, 30.4, 29.0, 23.8, 23.0, 14.1, 11.1. IR (KBr): ν 2926, 1592, 1458, 1325, 1261, 1234, 1171, 1048, 942, 842, 793, 695 cm^{-1}. Anal. Calcd for $C_{34}H_{43}I_2NO_2$: C, 54.34; H, 5.77; N, 1.86. Found: C, 54.69; H, 5.82; N, 1.65.

2,7-Dichloro-*N*-(2,4-dihydroxyphenyl)carbazole (10). A mixture of **2** (544 mg, 2.30 mmol), CuI (24.8 mg, 0.130 mmol), potassium phosphate (1.10 g, 5.18 mmol), 1,4-dioxane (7 mL), 2,4-dimethoxybromobenzene (250 mg, 1.15 mmol), and *trans*-1,2-cyclohexanediamine (59.1 mg, 0.518 mmol) was stirred at 100 °C for 120 h. After the reaction was cooled to room temperature, the reaction mixture was subjected to column chromatography on silica gel eluted with CH_2Cl_2 (2:1). For further purification, to the residue was added a solution of 1 M BBr_3 in CH_2Cl_2 (4.6 mL, 4.6 mmol) at −20 °C. The resulting mixture was stirred for 12 h, and was allowed to warm to room temperature. Water and EtOAc were added to the reaction mixture. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexanes−EtOAc (4:1) to give **10** (185 mg, 46.5% yield) as a pale brown solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.11 (d, *J* = 1.8 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.67 (s, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 6.55 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.75 (s, 1H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 157.7, 153.5, 142.1, 132.1, 129.9, 121.3, 121.0, 120.9, 114.9, 110.2, 108.9, 104.1. IR (KBr): ν 3330, 1626, 1594, 1517, 1445, 1330, 1234, 1160, 1065, 1003, 797 cm^{-1}. Anal. Calcd for $C_{18}H_{11}NCl_2O_2 \cdot 0.25EtOAc$: C, 62.31; H, 3.58; N, 3.82. Found: C, 62.68; H, 3.95; N, 3.79.

***N*-[2,4-Bis(2-ethylhexyloxy)phenyl]-2,7-dichlorocarbazole (11).** The same procedure used for synthesis of **9** was used here to obtain a white solid (99.5% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.07 (brs, 2H), 6.67−6.61 (m, 2H), 3.94 (d, *J* = 5.6 Hz, 2H), 3.72 (d, *J* = 5.3 Hz, 2H), 1.79 (m, 1H), 1.65−1.32 (m, 10H), 1.26 (m, 1H), 1.01−0.77 (m, 16H), 0.67 (t, *J* = 7.1 Hz, 3H), 0.57 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 160.8, 156.3, 142.8, 131.5, 130.0, 120.9, 120.6, 120.1, 117.3, 110.4, 105.2, 101.0, 70.8, 70.4, 39.5, 39.0, 30.7, 30.3, 29.2, 28.9, 24.0, 23.5, 23.2, 22.8, 14.2, 14.0, 11.3, 10.9. IR (KBr): ν 2927, 1591, 1517, 1457, 1308, 1185, 1065, 965, 795 cm^{-1}. Anal. Calcd for $C_{34}H_{43}NCl_2O_2$: C, 71.82; H, 7.62; N, 2.46. Found: C, 71.43; H, 7.22; N, 2.50.

***N*-[3,4-Bis(2-ethylhexyloxy)phenyl]-2,7-dichlorocarbazole (13).** The same procedure was used as for the synthesis of **3**. Hexane−CH_2Cl_2 (6:1) was used as the eluent of the silica gel column chromatography and gave a colorless oil (97.9% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 2H), 7.23 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 3.97 (d, *J* = 5.7 Hz, 2H), 3.85 (d, *J* = 5.7 Hz, 2H), 1.88−1.71 (m, 2H), 1.62−1.29 (m, 16H), 1.02−0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 150.3, 149.5, 142.2, 131.8, 128.6, 120.93, 120.90, 120.5, 119.5, 113.6, 112.3, 110.1, 71.8, 71.6, 39.65, 39.60, 30.7, 30.6, 29.25, 29.19, 24.1, 24.0, 23.2, 23.1, 14.23, 14.17, 11.4, 11.3. IR (KBr): ν 2928, 1593, 1516, 1457, 1253, 1066, 963, 795, 700 cm^{-1}. Anal. Calcd for $C_{34}H_{43}NCl_2O_2 \cdot 0.2H_2O$: C, 71.36; H, 7.64; N, 2.45. Found: C, 71.32; H, 7.42; N, 2.78.

2,7-Dichloro-*N*-(2-nitrophenyl)carbazole (14). A mixture of **2** (500 mg, 2.12 mmol), K_2CO_3 (1.46 g, 10.6 mmol), DMF (10 mL), and *o*-fluoronitrobenzene (1.20 g, 8.47 mmol) was stirred at 150 °C for 12 h. After the reaction was cooled to room temperature, H_2O was added to the reaction mixture and filtered. The solid was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (2:1) to give **14** (747 mg, 98.8% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.23 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.89 (ddd, *J* = 7.8, 7.6, 1.7 Hz, 1H), 7.76 (ddd, *J* = 8.1, 7.6, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.27 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.03 (d, *J* = 1.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 147.0, 141.7, 134.6, 132.3, 131.4, 130.1, 129.8, 126.2, 121.6, 121.5, 121.3, 109.4. IR (KBr): ν 1594, 1525, 1497, 1454, 1425, 1344, 1329, 1231, 1068, 967, 797, 703 cm^{-1}. Anal. Calcd for $C_{18}H_{10}N_2Cl_2O_2$: C, 60.53; H, 2.82; N, 7.84. Found: C, 60.40; H, 3.00; N, 7.78.

2,7-Dichloro-*N*-(3-nitrophenyl)carbazole (15). The same procedure was used as for the synthesis of **14** to give a yellow solid (95.1% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.40 (d, J = 1.7 Hz, 1H), 8.40−8.36 (m, 1H), 7.99 (d, J = 8.7 Hz, 2H), 7.90−7.81 (m, 2H), 7.300 (d, J = 1.8 Hz, 2H), 7.299 (dd, J = 8.7, 1.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 149.4, 141.1, 137.8, 132.9, 132.4, 131.2, 122.9, 122.0, 121.7, 121.6, 121.3, 109.6. IR (KBr): ν 3094, 1596, 1537, 1493, 1421, 1346, 1331, 1225, 1070, 960, 795, 701 cm^{-1}. Anal. Calcd for $C_{18}H_{10}N_2Cl_2O_2$: C, 60.53; H, 2.82; N, 7.84. Found: C, 60.53; H, 3.18; N, 7.75.

2,7-Dichloro-*N*-(4-nitrophenyl)carbazole (16). The same procedure was used as for the synthesis of **14** to give a yellow solid (81.0% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.52 (d, J = 9.1 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 9.1 Hz, 2H), 7.41 (d, J = 1.8 Hz, 2H), 7.32 (dd, J = 8.4, 1.8 Hz, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 142.4, 140.7, 132.5, 126.9, 125.7, 122.0, 121.9, 121.3, 109.9, 109.3. IR (KBr): 1594, 1513, 1503, 1424, 1347, 1427, 1070 cm^{-1}. Anal. Calcd for $C_{18}H_{10}N_2Cl_2O_2$: C, 60.53; H, 2.82; N, 7.84. Found: C, 60.12; H, 2.98; N, 7.58.

***N*-(2-Aminophenyl)-2,7-dichlorocarbazole (17).** A mixture of **14** (720 mg, 2.02 mmol), $SnCl_2{\cdot}2H_2O$ (2.27 g, 10.1 mmol), and EtOH (30 mL) saturated with Ar was stirred at refluxing temperature for 10 h. About 20 mL of EtOH was evaporated off, and 2 M NaOH was added to the reaction mixture, which was filtered. The solid was dissolved in $CHCl_3$. The organic layer was washed with H_2O and brine and dried over $MgSO_4$ to give **17** (660 mg, 100% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.98 (d, J = 8.2, Hz, 2H), 7.38−7.32 (m, 1H), 7.25 (dd, J = 8.2, 1.8 Hz, 2H), 7.20 (ddd, J = 7.7, 1.5 Hz, 1H), 7.14 (d, J = 1.8 Hz, 2H), 6.98−6.95 (m, 1H), 6.95−6.89 (m, 1H), 3,53 (s, 2H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 143.5, 141.3, 132.0, 130.1, 129.1, 121.1, 120.9, 120.74, 120.68, 118.9, 116.6, 110.3. IR (KBr): ν 3487, 3392, 1617, 1592, 1505, 1442, 1426, 1332, 1232, 1064, 962, 806, 741 cm^{-1}. Anal. Calcd for $C_{18}H_{12}N_2Cl_2{\cdot}0.4H_2O$: C, 64.55; H, 3.86; N, 8.38. Found: C, 64.44; H, 3.82; N, 8.26.

***N*-(3-Aminophenyl)-2,7-dichlorocarbazole (18).** The same procedure was used as for the synthesis of **17** to give a white solid (94.0% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.94 (d, J = 8.2, Hz, 2H), 7.37 (d, J = 1.8, Hz, 2H), 7.36 (t, J = 7.9, Hz, 1H), 7.22 (dd, J = 8.2, 1.8 Hz, 2H), 6.85−6.74 (m, 3H), 3,88 (s, 2H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 148.0, 141.6, 137.3, 131.8, 130.8, 121.1, 120.9, 120.6, 116.7, 114.7, 112.9, 110.3. IR (KBr): ν 3411, 3319, 3043, 1593, 1502, 1445, 1424, 1333, 1230, 1066, 959, 787, 704 cm^{-1}. Anal. Calcd for $C_{18}H_{12}N_2Cl_2$: C, 66.07; H, 3.70; N, 8.56. Found: C, 65.89; H, 3.94; N, 8.53.

***N*-(4-Aminophenyl)-2,7-dichlorocarbazole (19).** The same procedure was used as for the synthesis of **17** to give a white solid (79.0% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 1.6 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 7.21 (dd, J = 8.2, 1.6 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 3.91 (s, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 146.5, 142.3, 131.7, 128.3, 126.5, 120.9, 120.3, 115.9, 110.0. IR (KBr): 3398, 1624, 1591, 1518, 1439, 1064 cm^{-1}. Anal. Calcd for $C_{18}H_{12}N_2Cl_2{\cdot}0.1\ H_2O$: C, 65.71; H, 3.74; N, 8.51. Found: C, 65.92; H, 4.11; N, 8.11.

2,7-Dichloro-*N*-[2-(*N*-(4-(2-ethylhexyloxy)phenyl)amino)phenyl]carbazole (20). A mixture of **17** (327 mg, 1.00 mmol), $Pd(OAc)_2$ (4.49 mg, 0.0200 mmol), K_2CO_3 (829 mg, 6.00 mmol), toluene (3 mL), P(t-Bu)$_3$ (10 wt % in hexane, 175 μL, 0.0600 mmol), and 1-bromo-4-(2-ethylhexyloxy)benzene (1.43 g, 5.00 mmol) was stirred at 110 °C for 40 h. After the reaction was cooled to room temperature, CH_2Cl_2 was added to the reaction mixture and subjected to short path column chromatography on silica gel. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (4:1) to give **20** (488 mg, 91.7% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.97 (d, J = 8.2 Hz, 2H), 7.33 (td, J = 8.4, 1.5 Hz, 1H), 7.25 (dd, J = 8.2, 1.8 Hz, 2H), 7.22 (td, J = 8.1, 1.5 Hz, 1H), 7.21 (d, J = 1.8 Hz, 2H), 7.16 (dd, J = 8.4, 1.3 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.92 (td, J = 8.1, 1.3 Hz, 1H), 6.80 (d, J = 8.9 Hz, 2H), 5.08 (s, 1H), 3.77 (d, J = 5.8 Hz, 2H), 1.69 (m, 1H), 1.51−1.27 (m, 8H), 0.93−0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 156.3, 143.3, 141.6, 133.0, 132.2, 130.0, 129.3, 125.0, 121.4, 121.1, 121.0, 119.0, 115.2, 114.5, 110.4, 70.8, 39.4, 30.6, 29.1, 23.9, 23.1, 14.2, 11.2. IR (KBr): ν 3406, 2925, 1593, 1508, 1457, 1425, 1330, 1235, 1065, 963, 797 cm^{-1}. Anal. Calcd for $C_{32}H_{32}N_2Cl_2O$: C, 72.31; H, 6.07; N, 5.27. Found: C, 72.46; H, 6.14; N, 5.16.

2,7-Dichloro-*N*-[3-(*N*-(4-(2-ethylhexyloxy)phenyl)amino)phenyl]carbazole (21). A mixture of **18** (450 mg, 1.38 mmol), $Pd(OAc)_2$ (15.4 mg, 0.0688 mmol), sodium t-butoxide (661 mg, 6.88 mmol), toluene (6 mL), P(t-Bu)$_3$ (10 wt % in hexane, 400 μL, 0.138 mmol), and 1-(2-ethylhexyloxy)-4-iodobenzene (2.28 g, 6.88 mmol) was stirred at 110 °C for 30 h. The purification procedure was same for synthesis of **20**, and 1.95 g of overloaded iodide was recovered. A white solid (521 mg, 71.2% yield) was obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.93 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 1.8 Hz, 2H), 7.21 (dd, J = 8.2, 1.8 Hz, 2H), 7.12 (d, J = 8.9 Hz, 2H), 6.94 (ddd, J = 7.8, 2.3, 1.0 Hz, 1H), 6.92−6.85 (m, 2H), 6.87 (d, J = 8.9 Hz, 2H), 5.63 (s, 1H), 3.80 (d, J = 5.8 Hz, 2H), 1.70 (m, 1H), 1.50−1.27 (m, 8H), 0.94−0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.9, 147.5, 141.6, 137.4, 133.9, 131.8, 130.8, 123.6, 121.1, 120.9, 120.6, 116.9, 115.4, 114.4, 112.7, 110.3, 70.9, 39.5, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. IR (KBr): ν 3396, 2927, 1602, 1508, 1441, 1426, 1234, 1066, 961, 795, 706 cm^{-1}. Anal. Calcd for $C_{32}H_{32}N_2Cl_2O$: C, 72.31; H, 6.07; N, 5.27. Found: C, 72.22; H, 6.09; N, 5.30.

***N*-[2-(*N*,*N*-Bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl]-2,7-dichlorocarbazole (22).** The same procedure was used as for the synthesis of **21** to give a white solid (89.5% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.70 (d, J = 8.9 Hz, 2H), 7.39−7.33 (m, 3H), 7.21−7.15 (m, 1H), 7.08 (d, J = 1.8 Hz, 2H), 7.06 (dd, J = 7.7, 1.8 Hz, 2H), 6.45 (d, J = 9.2 Hz, 4H), 6.38 (d, J = 9.2 Hz, 4H), 3.58 (d, J = 5.6 Hz, 4H), 1.62 (m, 2H), 1.48−1.26 (m, 16H), 0.98−0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.2, 146.6, 140.9, 139.5, 130.9, 130.8, 129.4, 128.5, 125.7, 124.4, 123.1, 121.0, 120.3, 120.0, 114.4, 110.5, 70.5, 39.4, 30.6, 29.2, 24.0, 23.2, 14.2, 11.3. IR (KBr): ν 2927, 1592, 1505, 1457, 1239, 1065, 1038, 965, 828, 793 cm^{-1}. Anal. Calcd for $C_{46}H_{52}N_2Cl_2O_2$: C, 75.08; H, 7.12; N, 3.81. Found: C, 75.32; H, 7.08; N, 3.65.

***N*-[3-(*N*,*N*-Bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl]-2,7-dichlorocarbazole (23).** The same procedure was used as for the synthesis of **21** to give a white solid (92.2% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.92 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 1.8 Hz, 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.21 (dd, J = 8.4, 1.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 4H), 7.00−6.90 (m, 3H), 6.88 (d, J = 8.8 Hz, 4H), 3.81 (d, J = 5.8 Hz, 4H), 1.70 (m, 2H), 1.54−1.27 (m, 16H), 0.95−0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 156.1, 150.7, 141.3, 139.8, 136.9, 131.8, 130.2, 126.9, 121.2, 120.9, 120.6, 118.4, 117.3, 117.1, 115.5, 110.3, 70.7, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.2. IR (KBr): ν 2926, 1595, 1506, 1493, 1460, 1441, 1425, 1240, 1067, 761, 828, 796, 707 cm^{-1}. Anal. Calcd for $C_{46}H_{52}N_2Cl_2O_2$: C, 75.08; H, 7.12; N, 3.81. Found: C, 75.34; H, 7.05; N, 3.54.

***N*-[4-(*N*,*N*-Bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl]-2,7-dichlorocarbazole (24).** The same procedure was used as for the synthesis of **21** to give a white solid (88.7% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.94 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 1.8 Hz, 2H), 7.21 (dd, J = 8.2, 1.8 Hz, 2H), 7.19−7.15 (m, 6H), 7.05 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.7 Hz, 4H), 3.84 (d, J = 5.7 Hz, 4H), 1.73 (m, 2H), 1.55−1.29 (m, 16H), 0.96−0.88 (m, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 156.2, 148.9, 142.2, 139.8, 131.8, 127.5, 127.3, 127.2, 121.0, 120.9, 120.4, 119.8, 115.4, 110.1, 70.7, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.3. IR (KBr): ν 2927, 1592, 1502, 1457, 1330, 1238, 1066, 964, 828, 795 cm^{-1}. Anal. Calcd for $C_{46}H_{52}N_2Cl_2O_2$: C, 75.08; H, 7.12; N, 3.81. Found: C, 75.18; H, 7.11; N, 3.71.

A General Procedure for Homopolymerization. Synthesis of P*m*DPAC. Yamamoto polymerization[13] was carried out under modified conditions to obtain the polymer in good yield with high molecular weight. The GPC and elemental analysis results are shown in Table 2 and Table 1, respectively. A mixture of bpy (291 mg, 1.86 mmol), Ni(COD)$_2$ (511 mg, 1.86 mmol), DMF (2.5 mL), and COD (209 μL, 1.70 mmol) was stirred at 50 °C for 10 min.

To the mixture was added a solution of monomer **23** (570 mg, 0.775 mmol) in THF (6 mL), and this was stirred at 70 °C for 30 h. $CHCl_3$ was added to the reaction mixture. The organic layer was washed with 5 M HCl, pH = 3.8 EDTA aq, pH = 9 EDTA aq, H_2O, and brine and dried over Na_2SO_4. Polymer was dried under vacuum at 100 °C to give **P*m*DPAC**.

Poly[*N*-(4-(2-(ethoxyethoxyethoxy)ethoxy)phenyl)carbazol-2,7-ylene] (P*p*TEOC). A yellow film (92.0% yield) was obtained. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.10 (br, 2H), 7.46 (br, 6H), 7.09 (br, 2H), 4.18 (br, 2H), 3.88 (br, 2H), 3.57 (brm, 10H), 1.14 (br, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.0, 142.3, 140.1, 130.2, 128.6, 122.0, 120.3, 120.0, 115.8, 108.5, 70.9, 70.72, 70.66, 69.8, 69.7, 67.8, 66.6, 15.3. IR (KBr): ν 2925, 2865, 1600, 1514, 1451, 1231, 1106, 1060, 799 cm^{-1}.

Poly[*N*-(3,5-bis(2-(ethoxyethoxyethoxy)ethoxy)phenyl)carbazol-2,7-ylene] (P*mm*TEOC). To a solution of **25** (280 mg) in THF (5 mL) was added *n*-BuLi 2.6 M in hexane (0.35 mL, 0.90 mmol) in a small portion at −10 °C. After the reaction was stirred for 15 min, NH_4Cl aq (5 mL) was added to the reaction mixture at 0 °C. $CHCl_3$ was added to the reaction mixture. The organic layer was washed with H_2O and brine and dried over Na_2SO_4 to give **P*mm*TEOC** (267 mg, 99% yield over 2 steps) as a yellow film. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.10 (br, 2H), 7.60 (br, 2H), 7.49 (br, 2H), 6.72 (br, 2H), 6.58 (br, 1H), 4.07 (br, 4H), 3.78−3.40 (brm, 24H), 1.08 (br, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 160.8, 141.8, 140.1, 138.9, 122.1, 120.2, 108.8, 106.3, 101.3, 70.8, 70.7, 70.6, 69.7, 69.6, 67.8, 66.6, 15.2. IR (KBr): ν 2866, 1604, 1452, 1331, 1232, 1110, 1066, 803, 694 cm^{-1}.

Poly[*N*-(3,5-bis(2-ethylhexyloxy)phenyl)carbazol-2,7-ylene] (P*mm*EHOC). The same procedure was used as for the synthesis of **P*mm*TEOC**. Reprecipitation from $CHCl_3$−hexane gave **P*mm*EHOC** (81% yield over two steps) as a yellow film. ^{1}H NMR ($CDCl_3$, 270 MHz $_3$): δ 8.21 (br, 2H), 7.78 (br, 2H), 7.63 (br, 2H), 6.81 (br, 2H), 6.65 (br, 1H), 3.91 (br, 4H), 1.77 (br, 2H), 1.56−1.30 (brm, 16H), 0.99−0.92 (brm, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 161.4, 141.9, 140.1, 138.9, 122.1, 120.3, 120.1, 109.0, 105.8, 101.1, 70.9, 39.4, 30.6, 29.1, 23.9, 23.1, 14.2, 11.2. IR (KBr): ν 2925, 1604, 1454, 1330, 1230, 1170, 1155, 800, 693 cm^{-1}.

Poly[*N*-(2,4-bis(2-ethylhexyloxy)phenyl)carbazol-2,7-ylene] (P*op*EHOC). A yellow film (100% yield) was obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.09 (br, 2H), 7.50−7.34 (br, 4H), 7.02 (br, 1H), 6.69 (br, 2H), 3.95 (br, 2H), 3.67 (br, 2H), 1.80 (br, 1H), 1.54−1.39 (brm, 10H), 1.23 br, 1H), 1.03−0.79 (brm, 16H), 0.51−0.44 (brm, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 160.2, 156.5, 142.7, 139.7, 130.2, 121.7, 119.6, 119.3, 118.6, 108.9, 105.0, 100.9, 70.6, 39.5, 38.8, 30.6, 30.1, 29.2, 28.7, 23.9, 23.3, 23.1, 22.5, 14.1, 13.8, 11.2, 10.8. IR (KBr): ν 2925, 1604, 1517, 1455, 1307, 1234, 1182, 1101, 1035, 798 cm^{-1}.

Poly[*N*-(3,4-bis(2-ethylhexyloxy)phenyl)carbazol-2,7-ylene] (P*mp*EHOC). A yellow film (99.7% yield) was obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.08 (br, 2H), 7.55 (br, 2H), 7.49 (br, 2H), 7.02 (br, 3H), 3.92 (br, 2H), 3.79 (br, 2H), 1.72 (br, 2H), 1.46−1.22 (brm, 16H), 0.95−0.78 (brm, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 150.2, 148.9, 142.4, 140.1, 129.9, 121.9, 120.3, 119.9, 113.8, 112.7, 108.7, 71.8, 71.7, 39.8, 39.6, 30.8, 30.6, 29.3, 29.2, 24.1, 24.0, 23.2, 23.1, 14.24, 14.16, 11.4, 11.3. IR (KBr): ν 2926, 1603, 1508, 1456, 1418, 1329, 1235, 1020, 798 cm^{-1}.

Poly[*N*-(2-(*N*,*N*-bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl)-carbazol-2,7-ylene] (P*o*DPAC). A yellow film (100% yield) was obbtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.88 (br, 2H), 7.47−7.24 (brm, 8H), 6.56 (br, 4H), 6.35 (br, 4H), 3.53 (br, 4H), 1.54 (br, 2H), 1.27 (br, 16H), 0.86 (br, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 154.8, 146.3, 141.1, 141.0, 139.8, 139.5, 139.1, 128.7, 125.6, 124.1, 123.0, 121.8, 119.8, 119.4, 114.3, 108.5, 70.4, 39.3, 30.5, 29.0, 23.8, 23.0, 14.1, 11.1. IR (KBr): ν 2927, 1604, 1504, 1452, 1236, 1036, 824, 798 cm^{-1}.

Poly[*N*-(3-(*N*,*N*-bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl)-carbazol-2,7-ylene] (P*m*DPAC). A yellow film (99% yield) was obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.80 (br, 2H), 7.63 (br, 2H), 7.37 (br, 1H), 7.19−6.99 (brm, 9H), 6.66 (br, 4H), 3.52 (br, 4H), 1.52 (br, 2H), 1.33−1.23 (brm, 16H), 0.96−0.78 (brm, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.8, 150.4, 141.5, 139.8, 139.7, 137.9, 129.9, 127.4, 126.8, 122.1, 120.1, 117.4, 115.2, 114.5, 108, 7, 70.2, 39.3, 30.4, 29.0, 23.7, 23.0, 14.1, 11.1. IR (KBr): ν 2925, 1595, 1505, 1452, 1328, 1239, 1105, 1033, 826, 799, 699 cm^{-1}.

Poly[*N*-(4-(*N*,*N*-bis(4-(2-ethylhexyloxy)phenyl)amino)phenyl)-carbazol-2,7-ylene] (P*p*DPAC). A yellow film (100% yield) was obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.69 (br, 2H), 7.38 (br, 2H), 7.17 (br, 8H), 6.86 (br, 6H), 3.81 (br, 4H), 1.71 (br, 2H), 1.50−1.32 (brm, 16H), 0.94−0.89 (brm, 12H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.9, 142.2, 139.9, 127.4, 126.9, 121.8, 119.9, 119.6, 115.2, 115.0, 70.6, 39.4, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1. IR (KBr): ν 2926, 1603, 1504, 1452, 1325, 1237, 1104, 826, 800 cm^{-1}.

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Supporting Information Available: Figures showing UV−vis and PL spectra, TGA, electrochemical analysis of the obtained polymers, and ^{1}H NMR and ^{13}C NMR spectra of **1**, **3**, **6**−**11**, **13**−**26**, and individual polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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